Baltic Supercritical 2015

Russian Academy of Sciences
Institute of Laser and Information Technologies of the Russian Academy of Sciences
M.V. Lomonosov Moscow State University
Immanuel Kant Baltic Federal University
Institute of Solution Chemistry of the Russian Academy of Sciences
Institute of General and Inorganic Chemistry of the Russian Academy of Sciences
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The Editorial Board "Supercritical Fluids: Theory and Practice"
ZAO “Schag”

VIII Scientific and Practical Conference with international participation "Supercritical Fluids (SCF): fundamentals, technology, innovation"

BOOK of ABSTRACTS

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Kaliningrad-2015

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SCIENTIFIC PROGRAM

The scientific program of the VIII Scientific-practical conference with international participation "Supercritical Fluids (SCF): Fundamentals, Technologies, Innovations" includes 7 plenary lectures (40 min), 9 key lectures (30 min), 33 oral reports (20 min), 19 oral reports by young scientists (10 minutes), 52 poster presentations and 17 correspondence reports, and addresses a wide range of fundamental and applied issues related to development and application of supercritical technology in the following directions:

- Physical and physicochemical bases of the processes in SCF media and SCF technologies;
- Analytical applications, analysis and diagnostics of SCF media;
- Chemical processes in SCF media;
- Synthesis, separation and purification materials (including natural);
- Creation of functional and composite materials. Aerogels;
- Processes involving water in sub- and supercritical state;
- Engineering and technological aspects.

The conference will host the VI Russian School-Conference of Young Scientists "Supercritical fluid technology – a way to solve environmental problems" as well as a one-day symposium with international participation "Supercritical fluid technologies for biomedicine and pharmacy".

The conference languages are English and Russian.

ПЛ-1

АДДИТИВНЫЕ ТЕХНОЛОГИИ

Панченко В.Я.

ФГБУН Институт проблем лазерных и информационных технологий РАН, Троицк

PL-2

NEW DIRECTIONS IN SUPERCRITICAL FLUIDS

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Our research group has been working in supercritical fluids for nearly 30 years and for 25 of those years we have been collaborating with scientists in Russia [1]. This talk will look at how that collaboration has led to new ideas, particularly in the measurement of high pressure phase behaviour [2, 3] and will also describe recent work in our group in reactions in supercritical CO_2 [4, 5] and near-critical water [6].

We thank the EPSRC, Lucite, CBMM, Sanofi and the University of Nottingham for supporting our research. We particularly grateful to Professor V.N. Bagratashvili and Dr. V.K. Popov for countless years of fruitful collaboration and scientific partnership in research. Finally, we thank all of our students, postdocs and collaborators who have contributed to the research described in the lecture, and all of our technicians whose skills have contributed so much to the success of the experiments.

[1] "Steric Effects in the kinetics of organometallic reactions: a time-resolved infrared study of (η^5-C_5R_5)$Mn(CO)_2$] (R = H, Me or Et] in n-heptane solution" (F. P. A. Johnson, M. W. George, V. N. Bagratashvili and L. N. Vereshchagina and M. Poliakoff) *Mendeleev Commun*, (1991) 26-28.

[2] "Determining phase boundaries and vapour/liquid critical points in supercritical fluids: a multi-technique approach" (R M. Oag, P. J. King, C. J. Mellor, M. W. George, J. Ke, M. Poliakoff, V. K. Popov and V. N. Bagratashvili) *J. Supercritical Fluids* (2004), *30*, 259-272.

[3] "Detecting Phase Transitions in Supercritical Mixtures: an Enabling Tool for Greener Chemical Reactions" (J. Ke, Y. Sanchez-Vicente, G. R. Akien, A. A. Novitskiy, G. Comak, V. N. Bagratashvili, M. W. George and M. Poliakoff) *Proc. Roy. Soc. A*, (2010) *466*, 2799-2818.

[4] "Remote-controlled experiments with cloud chemistry" (R. A. Skilton, R. A. Bourne, Z. Amara, R. Horvath, J. Jin, M. J. Scully, E. Streng, S. L. Y.

Tang, P. A. Summers, J. Wang, E. Perez, N. Asfaw, G. L. P. Aydos, J. Dupont, G. Comak, M. W. George and M. Poliakoff) *Nature Chemistry* (2015) *7*, 1-5.

[5] "Applying Green Chemistry to the Photochemical Route to Artemisinin" (Z. Amara, J. F. B. Bellamy, R. Horvath, S. J. Miller, A. Beeby, A. Burgard, K. Rossen, M. Poliakoff and M. W. George) *Nature Chemistry* (2015) *7*, 489-495.

[6] Unpublished work, (L. Schofield, T. Huddle and M. Poliakoff) 2015.

PL-3

GREEN PROCESSING USING ALTERNATIVE SUPERCRITICAL FLUIDS

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Separation processes and product formulation require the use of solvents or of high temperature in processing steps.

Conventional solvents are potential environmental pollutants, and the application of heat involves high energy consumption; therefore research is oriented towards the development of new processes with lower environmental impact. High pressure technologies involving sub and supercritical fluids offer the possibility to obtain new products with special characteristics or to design new processes, which are environmentally friendly and sustainable. By using high pressure as a processing tool one can also avoid the legal limitations for solvent residues and restrictions on use of conventional solvents in chemical processes.

Extraction of substances from plant materials and their “in situ” formulation in products with specific properties is at the moment one of the very promising applications of supercritical fluids. Other advanced processes are polymer processing in/with supercritical fluids, use of sub-and supercritical fluids as sustainable reaction media, etc…

There are several processes using sub- and supercritical fluids which are already developed to the commercial scale, like dry cleaning, high pressure sterilization, jet cutting, thin-film deposition for microelectronics, separations of value-added products from fermentation broths in biotechnology fields and as the solvent in a broad range of synthesis. All of these applications lead to sustainable manufacturing methods that are not only ecologically preferable but also give the products with very special properties.

Special attention will be given to thermodynamic fundamentals of these processes - phase equilibrium data for systems plant extracts or pure substance with different gasses like propane, argon, chlorinated hydrocarbons, sulfur hexafluoride and carbon dioxide.

The presentation will give also a limited overview of future perspectives in developments of processes and applications of sub-and supercritical fluids as green processing media.

PL-4

SPECTROSCOPY AND SUPERCRITICAL FLUIDS

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In situ FTIR spectroscopy has proven to be a powerful tool to study supercritical fluids and materials subjected to high-pressure or supercritical fluids. We have pioneered and developed a number of novel approaches and applications using in situ FTIR spectroscopy both in mid and near infrared regions as well as applications of confocal Raman microscopy to study materials processed with supercritical fluids. This talk will outline the research we are developing in this field, which includes studies of intermolecular interactions, polymer processing and CO_2-expanded liquids. Polymer processing has particularly benefited from the use of supercritical (sc) CO_2, where long term objectives for using $scCO_2$ to replace harmful organic solvents currently used in such applications. In situ FTIR spectroscopy probes interactions between $scCO_2$ and materials at a molecular level and provides a fundamental understanding of the origin of many effects of $scCO_2$ on polymeric materials (such as plasticisation, sorption, swelling, etc.). It has been demonstrated that effects of CO_2 on polymers are not purely physical phenomenon but include specific interactions with functional groups in polymers. This is the basis in plasticising effect of CO_2 on polymers, which is a key for polymer processing with $scCO_2$. Most recently, in collaboration with Boreskov Institute of Catalysis in Novosibirsk, we undertook a systematic study of interactions of high-pressure CO_2 with nine unsaturated polyketones each containing a different concentration of carbonyl groups to understand how intermolecular interactions affect swelling of polymers. FTIR spectroscopic imaging has emerged as a powerful tool for characterisation of materials. We combined FTIR spectroscopic imaging with in situ high-pressure approach to study polymeric materials subjected to high-pressure CO_2. The enhanced chemical visualisation allowed us to measure the effects of CO_2 on the morphology of polymer blend, and simultaneously measure sorption of CO_2 into different domains of heterogeneous polymer blend. FTIR spectroscopic imaging opens a window of opportunities that would facilitate the understanding of materials processes with supercritical fluids. The implications of this novel imaging technology range from pharmaceutical applications to the use of high-pressure CO_2 in crude oil processing, which will also be discussed.

PL-5

NEW ENERGY TECHNOLOGIES - POTENTIAL ROLE OF SUPERCRITICAL FLUIDS

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In presentation are discussed the following topics and application of supercritical fluids for creation and developments of new technologies:

- Trends of developments of modern energetics,
- New Russian technology of enhanced oil recovery,
- Biofuels,
- Conversation of solid wasts into fuels on the basis of flash pyrolisis,
- Container for electricity for solar, wind energetics and electrotransport.

PL-6

SYNTHESIS AND APPLICATION OF NEW TYPES OF ORGANIC AND HYBRID AEROGELS

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Aerogels are well known nanoporous materials, which are obtained from wet gels by supercritical drying process, in order to avoid the pore collapse and keep intact the porous texture of the wet material. Previous research was mostly focused on silica and carbon aerogel development with a wide range of applications in different fields, e.g., aeronautics, biomedicine, construction, environmental remediation or agriculture. However, among the broad range of possible applications, just few of them have been commercialized so far. Main application is the thermal insulation due do the extremely low thermal conductivity of aerogels. Even though the first reports on aerogels made by Kistler in 1930s dealt with aerogels from both inorganic oxides (silicon, aluminum and others) and biopolymers (gelatin, agar, cellulose), only recently biopolymers have been recognized as an abundant source of chemically diverse macromolecules for functional materials including aerogel production. Properties of biopolymers are strongly determined by their role in the living organisms offering a vast functionality. Moreover, biopolymer sources are well known, they are relatively cheap and accessible at industrial scale.

In this work, an overview about recent achievements in organic aerogel production, mainly based on the natural sources is discussed. Biopolymers from various sources such as alginate, cellulose, lignin, pectin, chitosan, proteins and others are presented. Resulting aerogels exhibit both specific inheritable functions of the starting biopolymer and distinctive features of aerogels (open porous structure with high specific surface and pore volume). This synergy of the properties has prompted to view biopolymer aerogels as promising candidates for a wide gamut of applications. Up-to-date reports on biopolymer aerogels describe their use for thermal insulation, tissue engineering and regenerative medicine, drug delivery systems, functional foods, as catalysts and sensors, adsorbents and as starting materials for carbon aerogels.

Generally, all materials that can be obtained as wet gels by the sol–gel process are potential candidates to be turned into aerogels after supercritical drying. Also a combination of the aerogels production with the biorefinery processes can be realized by using of biorefinery products as raw materials for gelation. This was for instance demonstrated by using lignin as a precursor.

On the way from the lab to the production the scale up of the supercritical extraction step is the main issue. Here the energy demand can be dramatically reduced by optimization of the extraction process, which is currently the main task for aerogel commercialization. The present situation in the field of commercialization of different aerogel types will be also discussed.

PL-7

COMPUTATIONAL MOLECULAR MODELING OF SUPERCRITICAL WATER AS A MEDIUM FOR CHEMICAL REACTIONS

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Due to the extremely high compressibility, thermal expansivity, and heat capacity of supercritical water (SCW), small changes in pressure (*P*) or temperature (*T*) generate very substantial changes in density and enthalpy. These, in turn, affect diffusivity, viscosity, thermal conductivity, dielectric, and solvation properties of water, thus dramatically influencing the kinetics and mechanisms of chemical reactions in the aqueous phase. Therefore, SCW has attracted rapidly growing attention as a promising medium having a wide range of environmentally friendly and energy-efficient technological applications from green chemical synthesis of new compounds and nanoparticles, to the production of synthetic fuels from biomass by catalytic conversion in SCW, and to the environmentally friendly disposal of toxic wastes by the process of supercritical water oxidation.

It is well known that the many unique and anomalous properties of water, including its unusually high critical parameters, are the results of strong hydrogen bonding between the H_2O molecules. The question of the *T*-*P* ranges where H-bonding can significantly affect the observable properties of water has long been considered very important for the construction of realistic structural models for this fluid, but a direct experimental investigations of the water structure at high temperatures and pressures is a very challenging task. Molecular computer simulation studies of SCW can greatly benefit the research in this field. The advantage of "computer experiments" is in their ability to generate and analyze in detail spatial and energetic environments of every individual molecule or multi-molecular configuration, thus providing extremely useful micro-thermodynamic and micro-structural information, not available from any real physical measurement.

This talk will provide an overview of the computational molecular modeling efforts made over the last 20-30 years to achieve accurate quantitative understanding of the anomalous properties of SCW on the fundamental molecular scale. Future potential of such methods, strongly stimulated by the continuing growth of the computing power, will also be briefly discussed from the perspective of their benefits for the SCW and SCF research.

KL-1

MODIFICATION OF AEROGELS PROPERTIES BY CHANGING THE SYNTHESIS CONDITIONS

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Aerogels (AG) are mesoporous solid materials possessing unique properties including very low bulk density, large specific surface area, low thermal conductivity, high thermal stability, etc.

Aerogels are usually prepared by a sol-gel technique which involves, in general, several stages. The first stage is the formation of sol through hydrolysis reactions of precursors. In the second stage a three-dimensional gel – liogel – is formed. The third stage of the AG synthesis is the so-called supercritical drying (SCD). This stage includes a solvent removal at a temperature exceeding its critical temperature. Ethanol (T_{cr}=243°C, P_{cr}=6.38 MPa) and carbon dioxide (CO_2) (T_{cr}=31°C, P_{cr}=7.38 MPa) are the most conventional types of SCD fluids for aerogels preparation.

The report discusses synthetic methods for the different chemical composition AGs - inorganic, organic, hybrid/mixed.

The influence of some factors on the AG properties has been shown:

- a solvent at the gel formation stage;
- a solvent used at the SCD stage;
- surface modification of AG by organic (mostly fluoroorganic) substituents.

It is shown that the changes in the synthesis conditions have significant influence on the texture (surface area, porosity, pore size) properties of the AG obtained and also on their hydrophobicity and thermophysical properties.

A financial support from the RSCF (Grant no. 14-13-01150) is greatly acknowledged.

KL-2

STRUCTURAL TRANSFORMATION AND FUNCTIONALIZATION OF POLYMERS IN SUPERCRITICAL FLUIDS

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The unique properties of supercritical fluids (SCF) allow to realize many of processes based on the use of SCF solvents. Nowadays, this possibility is already well understood in the world, and the development and implementation of processes in SCF is steady global trend in the preparation of a number of practically important products. Supercritical fluid technologies are increasingly used for the synthesis and directed modification of polymer materials and polymer composites. Such materials are obtained without the use of organic solvents, are particularly clean, not containing impurities often undesirable from the standpoint of future use, do not require additional purification steps in the preparation processes.

The characteristics of the resulting composite often unattainable using other methods of synthesis and modification. Functionalized polymers obtained by SCF technology required for a wide range of applications in medicine (e.g., implants and tissue engineering matrices), pharmacy (e.g., increased bioavailability of dosage forms, sustained-release and controlled release), optics (e.g., in the development of composites of polymers with quantum dots for the needs of optoelectronics or composites of polymers with carbon nanotubes for the needs of the photonics), catalysis (composites of nanoparticles of metal catalysts with highly porous polymers) and many other areas of science and practice. Despite of the diversity of polymer materials and polymer technology functionalization desired products via SCF has several common physical and chemical processes that determine the main steps of the process of functionalization of the polymer, and hence the properties of the desired product. It is, first of all: sorption of SCF macromolecules in the matrix polymer; swelling of the polymer in the SCF; irreversible transformation of the native structure of the polymer in SCF, solubility of low molecular weight compounds in SCF, the plasticization of polymers in SCF.

A number of new experimental (primarily spectroscopic) and theoretical approaches to the study of the dynamics and the results of structural transformation and functionalization of polymers in supercritical fluids will be discussed in the report.

KL-3

SUPERCRITICAL FLUIDIC TECHNOLOGIES – A NEW VERSATILE APPROACH FOR DEVELOPMENT OF ANTI-MICROBIAL DRUG DELIVERY SYSTEMS WITH PROLONGED RELEASE FEATURES

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Infectious diseases caused by pathogenic bacteria pose a serious global threat, being a major cause of death in some developing countries, and a substantial problem for developed countries. Broad and sometimes unjustified use of antibiotics leads to the appearance of diseases resistant to existing drugs. This is due primarily to the emergence and development of multi-drug-resistant strains of pathogens and infections that are resistant to multiple types of antibiotics. It is significant that the spread of nosocomial infections, often caused by resistant pathogens to antibiotics, primarily affects people with weakened immune systems: children, the elderly, and patients after surgery. The most acute this problem is manifested in the case of chronic infection and tuberculosis, which requires long-term medical therapy with high dose antibiotics, significantly increasing the risk of developing resistance. Tuberculosis is one of the most prevalent and the second most deadly infectious disease worldwide. Caused by M.tuberculosis, it requires prolonged treatment involving high systemic doses of 4-5 combined front-line antibiotics, administered daily by oral route for 6-12 months. Such treatment is often associated with adverse side effects and poor patient compliance.

It’s worth mentioning that most of anti-bacterial drugs have non-optimal pharmacological properties, such as pharmacokinetics, bioavailability and stability. Optimization of these properties would lead to more efficient treatment regimens with fewer side effects. So, the development of new efficient anti-bacterial drugs is strongly needed. However, the rapid development of strains of bacteria resistant to antibiotics, as well as the duration, complexity and high cost of developing restrict the creation of new antibacterial preparations. As a result, despite the ongoing world wide screening of antibiotics, the number of new drugs recommended for clinical use is limited and lags behind the needs.

An alternative approach to improving the effectiveness of antimicrobial drugs is the development of new dosage forms by encapsulation of drug components in various types of nanoparticles from biocompatible polymers, lipids, sometimes with the addition of pharmaceutically permitted synthetic emulsifiers like twin. This approach aims at improving the solubility and bioavailability of poorly soluble hydrophobic organic molecules, as well as to overcome the side effects developing in the application of antibacterial drugs. A serious problem in the development of new dosage forms and scale their production are the technological constraints. Existing technologies for industrial preparation of nano-drugs typically include emulsification using organic solvents and stabilizers (surfactants) with subsequent stages of removal of the solvent by evaporation, washing and drying the particles.

One of the most recent and perspective trends in the area of biomedical chemistry is the development of new advanced antimicrobial drug formulations using supercritical fluid (SCF) technologies, facilitating nanoformulation and encapsulation. SCF technologies offer the range of unique advantages compared to traditional approaches, including adjustable density, high solubilization capacity, low viscosity, high mass transfer velocity, extra-low surface tension. These features enable generation of particles with desired size distribution, and with precise control of composition, structure, porosity, and other features in a broad range. This is utterly important for creating drug formulations with improved bioavailability, sustained release and targeted delivery. Variation of process parameters allows creating the required dosage form of antibacterial preparations (oral, intravenous and inhalation forms) depending on medical indications. Plastification, swelling and solubilization in supercritical CO_2 as a solvent increase the solubility both for polymers and for other components, including active pharmaceutical ingredients. The SCF process is performed at room temperature, which allows for application of a wider range of thermo-labile substances. Also purification of end product is greatly facilitated. So, SCF technologies are much more ecologically benign, economically efficient and technologically feasible. This is mainly due to elimination of toxic organic solvents from the technological process, which greatly facilitates isolation/purification of the target product.

Thus, SCF technologies open up the possibility to create new dosage forms with prolonged action and targeted delivery features to the extent which has never been possible before. With using SCF, the pharmacologically optimized antibacterial drugs and their combinations would have a more favorable risk/benefit ratio, resulting in reduced time of treatment and lower frequency of side effects and significantly improve the situation with resistance. SCF is a platform technology for producing micronized and prolonged dosage forms and besides antibacterial drugs, SCF opens prospects in application to a wide range of drugs where optimization of pharmacological properties and technological processes is of high importance.

KL-4

POLYMER MATRICES IN THE PROCESSES OF IMPREGNATION AND CATALYSIS IN SC-CO_2 MEDIUM

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The features of the interaction of various polymer matrices and low molecular weight compounds with a SC-CO_2 medium in connection with the opportunities offered by the use of this medium for addressing catalysis and create functional composite materials. Presents the results of a comparative study of impregnation effectiveness in the environment of SC-CO_2 linear polymers and crosslinked polymer compositions conjugated aromatic heterocyclic compounds during the preparation of composite materials for medical purposes and photoactive polymer materials with different functional properties. As discussed thermoplastic polymer matrix polymers (polyolefins, polycarbonate, polyvinyl chloride, fluoropolymer), spatially-crosslinked oligoester acrylates having different degrees of swelling in SC-CO_2 and degradable polysaccharides, including, without swelling SC-CO_2. A model system – fluoropolymer impregnated of spiroantrooksazin (SAO) belonging to the class of indoline chromophore compounds was used for demonstration of the active role of the polymer matrix in the structural and conformational relaxation. Such rearrangements, in general, are subject to being introduced into the polymer molecules are spatially extended. This is revealed in this case, the relaxation dynamics by fixing consistently recorded by the three "color" isomeric forms of the SAO. Another class of problems under discussion relates to the possibility of an effective environment in SC-CO_2 of catalytic oxidation of organic substrates due to the abnormally high lifetime $\tau \sim 5$ ms in this environment of singlet oxygen $^1O_2$.

KL-5

ORGANIC AEROGELS BY SUPERCRITICAL DRYING

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From the very beginning in studies on aerogels, the main attention is devoted to gel drying processes. Evaporation of liquids from gels at normal conditions resulted in large capillary pressures within the pores by the receding liquid meniscus from surface tension of solvent. These materials are called xerogels. This is leading to shrinkage of the material with reduced porosity or cracking fragile solid skeleton. Preparation of low-density 5-methylresorcinol-formaldehyde (MR/FA) organic aerogels is one example of that. Double catalysed synthesis leads to quick gelling and homogeneous gels. In order to obtain aerogels with low density and high specific surface area, the solvent in the gel pores has to be removed without destruction of the solid gel structure. It has been found that under supercritical conditions of solvent the fluid can be removed from the material without surface tension, leaving the porous structure of the material unharmed resulting aerogels.

Water is common solvent to prepare gels, however because it's very high critical parameters (T_c=374.1°C, P_c =220.6 bar) and reactivity at these conditions this process is not used. There are two approaches: either forming the gel in the solvent that has lower critical parameters (acetone - T_c=235°C , P_c =48 bar [Liang, C, Sha, G., Guo, S. Resorcinol-formaldehyde aerogels prepared by supercritical acetone drying.– J Non-Cryst Solids 2000, 271, 167-170], methanol - T_c=240°C, P_c=81 bar [Liu, N., Zhang, S., Fu, R., Dresselhaus, M.S., Dresselhaus, G. Carbon aerogel spheres prepared via alcohol supercritical drying.– Carbon 2006, 44, 2430-2436]) to be dried directly via supercritical state, or after the gel being formed, the water in the pores is replaced with another solvent which is miscible with the fluid used (usually also acetone or alcohol) later for supercritical drying of the gel. Carbon dioxide is usually the fluid used for supercritical drying because of its low critical parameters (T_c=31.1°C;

P_c=73.7 bar). It is also readily available and inexpensive, non-flammable, non-toxic, reusable, environmentally friendly, no CO_2 residues are left in the treated medium, and the properties of the supercritical fluid can be finely tuned by varying the temperature and pressure [Wood, C.D., Tan, B., Zhang, H., Cooper, A.I. Supercritical carbon dioxide as a green solvent for polymer synthesis. Thermodynamics, Solubility and Environmental Issues 2007, 383-396]. However, CO_2 is not suitable for removing water and in order to use supercritical CO_2 drying, water in the gel pores is replaced with another solvent miscible with CO_2.

In our studies on 5-methylresorcinol-formaldehyde aquagel, the water is step-wise exchanged for acetone after followed by CO_2 extraction also step-wise at different extraction parameters. Supercritical extraction is very short (3-5 hours) and without significant shrinkage of gel. The slow changes of temperature and pressure are needed to avoid from thermal expansion or compression.

Optimal ratios for the lowest density and minimum shrinkage are MR/FA=0.5, MR/C=60 (C-catalyst) and W/MR=45 (W-water) [Concentrations of reagents are given in molar ratios]. Basic catalyst used in this work is sodium carbonate; acid catalyst, which is 5.7% acetic acid, is used after gelation in basic conditions.

Aquagels are opaque or transparent depending on catalyst amount used, but drying do not maintain the transparency of the gel.

Although in case of it was found that with only slightly lower specific surface areas of conventionally dried gels, compared to the gels dried using SFE, were only, the cracking, high density and apparent decrease in porosity make the supercritical drying preferable. In order to obtain high quality of drying, it is necessary to use the optimized regime of supercritical extraction that considers the parameters of the reactor and the specific sample.

At optimal molar ratios, the drying shorter than 4.5 h resulted in the MR-F aerogel with a radial shrinkage of 2%, density of 0.21 g cm^{-3} and specific surface area of 350 m^2g^{-1}.

There still occurs a small the shrinkage of the aerogel monolith. One reason may be related to incomplete solvent exchange from the small pores and capillary forces being present to some extent. Other explanation can be related to displacing acetone with carbon dioxide and complete removal of solvent causes destruction of hydrophilic interaction between acetone and polymer matrix and of hydrophobic interaction between CO_2 and hydrophobic groups in polymer matrix, respectively, which cause volume shrinking of gels. [Zhang, R. et al. Small angle X-ray scattering study of microstructure changes of organic hydrogels from supercritical carbon dioxide drying. J Supercrit Fluid 2004, 28, 263-276]

Because of hygroscopic nature of the resorcinol-formaldehyde organic aerogels they cannot be directly utilised because of their shrinkage in humid conditions.

KL-6

DESULFURIZATION OF HYDROCARBON FEEDSTOCKS IN SUPERCRITICAL WATER

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Interest in the study of low-grade hydrocarbon feedstocks (bitumen, oil shale, coal) conversion in supercritical water (SCW: T>374°C, P>22.1 MPa) is caused by uneven distribution and exhaustion of natural reserves of light oil and the development of new environmental friendly and efficient methods of their refining. As a rule, the low-grade hydrocarbon feedstocks (HCFs) are characterized by a low hydrogen content (H/C<2) and a high content of S, N, and O atoms. The report provides an overview of the data on kinetics and mechanism of HCFs S-containing components conversion in supercritical water fluids and the effect of catalysts on the degree of HCFs desulfurization.

Table. Degree of desulfurization (χ) of S-containing substances and hydrocarbon feedstocks at their conversion in supercritical water [1,3−9].

Substances	χ, %	Ref.	Hydrocarbon feedstocks (sulfur content, % wt.)	χ, %	T, °C	P, MPa	Ref.
dihexylsulfide	25	[1]*	brown coal (0.4)	52	430	30	[3]
tetrahydrothiophene	16	[1]	synthetic bitumen (1.3)	7	400	30	[4]
isopropylphenylsulfide	30	[1]	synthetic bitumen (1.7)	22	700	30	[5]
benzylphenylsulfide	22	[1]	liptobiolith coal (1.7)	42	470	30	[6]
dibenzylsulfide	60	[1]	heavy crude oil (3.0)	6−7	400	25	[7]
diphenylsulfide	<5	[1]	asphalt (7.4)	5	400	35	[8]
dibenzothiophene	3−5	[1]	asphaltite (8.1)	21	400	30	[9]

*Experimental conditions: 400°C, 23.5 MPa, mixture of H_2O and $C_{16}H_{34}$ at 25°C (1:1, v:v).

From the results [1] it follows that the rate of S-containing substances decomposition in SCW decreases in the following order: $C_{al}{-}S > C_{ar}{-}S > C{=}S$ (Table) and corresponds to the energy of bond cleavage (≈300, 355, and 580 kJ/mol [2], respectively). In the absence of oxidant, the end product of S-containing substances decomposition in SCW is hydrogen sulfide. When analyzing the data [3−9], it found that the degree of HCFs desulfurization (the proportion of sulfur atoms in the raw HCFs passed into H_2S) depends mainly on the content of aliphatic C_{al}–S bonds in HCFs and the temperature of SCW conversion (Table). Mechanisms of organic sulfides desulfurization are proposed in [1] and it is suggested that the process is consistent with a radical chain reaction pathway; transfer of proton from the CH-group in α-position to sulfur atom is the rate-limiting step. By means of the quantum chemistry methods it is shown [10] that the desulfurization of organic sulfides proceeds via the formation of thioaldehyde as an intermediate; water plays important role in thioaldehyde hydrolysis (as a reactant) and aldehyde decarbonylation (as a catalyst).

The results [7] of SCW conversion of model S-containing substances and heavy crude oil (Table) indicate that among ZnO, MoO_3 and MoS_2 the most efficient catalyst for desulfurization is ZnO, for dibenzothiophene in particular. At SCW conversion of bitumen, liptobiolith coal, and asphaltite with addition of zinc [4,6,9], a decrease in S/C atomic ratio in the liquid products and more than 1000-fold reduction in the amount of H_2S are determined. According to the data [4,6,9], when adding zinc, the degree of bitumen, coal, and asphaltite desulfurization (the proportion of sulfur atoms in ZnS) is equal to 13, 42 and 60%, respectively. It should be noted that the addition of zinc to HCFs at SCW conversion not only promotes *in situ* desulfurization of the conversion products owing to interaction between S-containing substances and ZnO formed by the reaction $Zn+H_2O=ZnO+H_2$ but also it provides for effective *in situ* hydrogenation of HCFs [4,6,9]. Kinetics and mechanism of zinc sulfidation by H_2S and catalytic effect of water on the process are described in [10].

In the presence of oxidant, the end product of S-containing substances decomposition in SCW is sulfuric acid. The results [12] of coal SCW conversion (sulfur – 0.31% wt., 380-420^{o}C, 25 MPa, oxidant – H_2O_2) indicate that the decomposition of S-containing substances proceeds via the thiosulfate and sulfite formation; a maximum degree of decomposition (99.6%) is detected at 420^{o}C. It is revealed [8] that partial oxidation of asphalt by oxygen at SCW conversion results in increase in the degree of desulfurization.

As a whole, the analysed results are evidenced for the possibility of using supercritical water for HCFs desulfurization and refining. An important advantage of SCW, as an internal source of hydrogen and a solvent of organic substances and gases, is a significant suppression of condensation reactions leading to the solid carbonaceous residue formation. Taking into account the need to use H_2 for the HCFs desulfurization in the conventional technologies, we can assume that in the future supercritical water will have an important role in reducing the amount of consumed H_2 and thereby provide for decreasing the costs of HCFs refining.

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KL-7

CELLULOSE NANOCRYSTAL DISSOLUTION IN SUPERCRITICAL MIXTURE OF CO_2 AND COSOLVENT: A VIBRATION SPECTROSCOPY AND MOLECULAR DYNAMICS ANALYSIS

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We combined in this work molecular dynamics simulation and vibration spectroscopy in order to analyze the dissolution of cellulose in supercritical fluids or in a mixture of supercritical fluids/solvent mixture.

In a first step, we studied using molecular dynamics simulation various nanocrystal polymorphs of cellulose in 1-methyl,3 ethylimidazolium chloride ionic liquid (EMIMCl). In the second step we studied the dissolution of theses nanocrystals in CO_2-ethanol and CO_2-acetone supercritical mixtures. Finally various co-solvents were considered. The choice of these co-solvents was based on previous studies mentioning these co-solvents as potential solvents to dissolve cellulose. The principal property of these co-solvents is their ability to form strong hydrogen bonding with the oxygen atoms of cellulose. The co-solvents considered in this work are the following: trimethylamine oxide (TMAO), triethylamine oxide (TEAO) and urea. Finally we prospect the dissolution of cellulose in supercritical ammonia.

The analysis of the results was made by means of common dynamical quantities of molecular dynamics: root mean square displacement and radius of gyration.

Based on these molecular dynamic simulations results, we analyzed the dissolution process of cellulose using vibration spectroscopy.

KL-8

HYDROGEN TRANSFER REACTIONS IN SUPERCRITICAL FLUIDS

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Hydrogen transfer reactions (or “Transfer hydrogenation”), briefly – HTR, are called such reduction reactions of organic compounds that result in the transfer of H_2 from the organic donor molecule to another organic recipient molecule, e.g. from the alcohol molecule (donor – a group CH–OH) to ketone or aldehyde molecule (acceptor – a group C=O). As a general rule, HTRs require a catalyst the lack of which makes the reaction difficult to implement. Over the last 15-20 years, the interest in HTRs which involve organic compounds containing multiple bonds C=O, C=N, C≡N, C=C and C≡C is greatly increased (Fig. 1, according to SciFinder data). As methods of organic synthesis are developed, this is due to HTRs become a real alternative to the conventional catalytic hydrogenation by gaseous H_2 or chemical reduction with using a complex metal hydride – environmentally and technologically safe, preparatively acceptable.

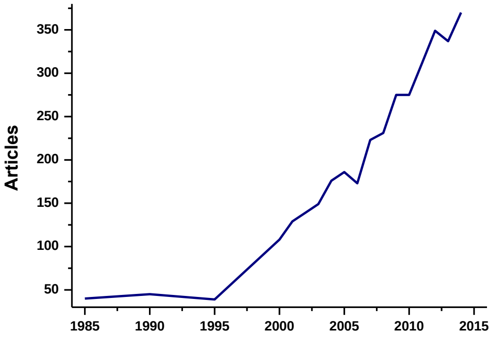

Fig.1.

For the first time, the HTR in supercritical fluids was published by Russian researchers in 1983 [S.P. Gubin, V.I. Men'shov, V.M. Kirilets, E.Ya. Plopskii, F. Tegai, Izv. Akad. Nauk SSSR, Ser. Khim., 1983, (12), 2835–2836 (Russ.)]. Experimental data accumulated over the past 30 years allow doing a detailed analysis of HTRs in SCFs, identifying the key features between the reaction in SCF and at conventional conditions, revealing the most promising reactions and trends of the further development of the chemistry in SCFs, predicting the likely practical use of HTRs in SCFs. These aspects will be presented in the presentation. Additionally, the results of the authors’ study on the HTR of monoterpene ketones in supercritical lower alcohols will be reported.

KL-9

TRENDS IN THE MODERN MATERIALS SCIENCE AND THE ROLE OF SUPERCRITICAL FLUIDS IN THEIR FORMING

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> “Materials are chemical compounds with properties,
> which define their application”.
>
> I.V. Tananaev

In the materialistic world of science, materials are of big importance, as any human activity eventually comes down to using materials. One might recall that breakthroughs in the currently popular information technology are closely related to the emergence of new materials, from clay tablets, paper and dyes, to materials for electronics (including computers). The importance of materials is reflected by the fact that several periods of human history are called after them (Stone Age, Bronze Age, Iron Age). The present time is also sometimes associated with some materials (polymers, nanomaterials).

As follows from the epigraph, chemistry and materials science, along with other sciences (physics, mechanics, etc.), are all different faces of the same knowledge, and the distinction between different sciences is often arbitrary in this respect. At the same time, the distinction is required, as it allows for better understanding of each aspect of a created or studied object. Each science has its own scope with specific mentality of researchers, theoretical and applied methods. The lecture mentions approaches of chemistry and materials science to creation and study of new materials, investigation of their potential application; complementarity and an optimum combination of the approaches are discussed. The lecture also mentions “green chemistry” methods, with the emphasis on the supercritical fluid technology, with respect to creating new materials and enhancing existing ones.

The big number of existing materials and their diversity require systematization and classification. The latter may be based on different criteria (such as chemical composition, material properties, application field, antropogenic, etc.) Classifications are required for a thorough and deeper view on all the listed materials. The lecture provides analysis of the existing classifications.

One peculiarity of the modern science development is the periodic emergence of “groundbreaking” lines of research. This also holds true for the materials science; the list of recent “hot” materials includes superionic conductors, high-temperature supercductors, carbon nanomaterials, etc. The aforementioned research lines have a specific feature: the public excitement about them. The excitement is often globally widespread, and it is commonly induced by media and the scientific community itself. Researchers should understand the peculiarities of the new research lines development and take them into account in their work. This is especially true for materials scientists, as the anticipations, and sometimes just speculations, are made about probable, stunning applications of materials.

A number of research trends have scientific and applied “popularity” which greatly affects the amount of funds allocated for the research by governments and societies, as well as interest in publications on the topic and ranking of scientists within the scientific community. The lecture covers the factors which make trends in materials science popular.

The modern materials science gets to creation of systems with complex and diverse chemical composition (which is sometimes self-conflicting), and it is important for the systems being created to have prospects for practical application. The lecture provides analysis of certain “popular” materials science subjects, which include: polymer composite materials, materials for additive technologies, aviation materials, arctic materials, smart materials, etc. The lecture also provides certain examples of possible supercritical fluid technologies applications for creation of new materials, polymer composites in particular.

Successful creation of new materials largely depends on effective cooperation of chemists and materials scientists. Its specific aspects are discussed in the lecture, based on the speaker's own work experience at academic and applied research institutions.

OR-1

FABRICATION OF METAL NANOCOMPOSITES ON GRAPHENE BY SUPERCRITICAL ISOPROPANOL

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The important discovery of graphene (G) (monolayer of carbon atoms arranged in a hexagonal lattice) with unique physical and electrical properties is difficult to overestimate. Many papers already showed manifold possibilities of graphene usage. In various significant number of works was shown extensive use of graphene in various fields of science and technology, such as energy storage, the development of chemical and biological sensors, polymer composites, catalysis, and so on [1]. The mutual influence of the metal-containing nanoparticles (NPs) and G leads to the fabrication of new hybrid advanced materials.

Previously it was shown, that the powders of metal oxides, in particular, Bi_2O_3, Ag_2O, CuO, easily reduced by supercritical isopropanol (SKI) to the metals [2]. The process of obtaining nanocomposites M/G was carried out in several stages. GO was obtained according to the method described in [3]. Next GO was dispersed under the action of ultrasound in the solvent, and then were added to the dispersion previously synthesized NPs of metal oxides. The last stage was the reduction of oxygen-containing functional groups of graphene oxide on which surface were, by SKI. The reduction of GO was carried out according to the method previously developed in the laboratory of nanomaterials chemistry of IGIC RAS in batch reactors [2]. SKI was used to reduce NPs of metal oxides (hydroxides) on the surface of graphene oxide (GO), whilst GO itself reduces in G (residence time τ in SKI was 18 hours). The obtained nanocomposites were characterized by complex methods of physicochemical analysis (XRD, AFM, TEM, XPS).

Thus:

1) SKI was media of reactions and reducing agent.

2) Series of experiments showed that the graphene oxide is reduced to graphene, while the

NPs retained on its surface.

3) There was a simultaneous reduction of the substrate (GO), containing on its surface metal oxides (hydroxides), and NPs of metals oxides (hydroxides) themselves.

4) For the first time the samples of nanocomposites Ag/G, Bi/G and Cu/G were obtained by SKI.

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OR-2

SYNTHESIS OF HIGH ACTIVE HYDROGENATION CATALYSTS BY IMPRAGNATION OF POLYMERIC MATRIX WITH METAL COMPEXES IN SUPERCRITICAL CARBON DIOXIDE

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In this report a new synthesis method of high active metal containing catalysts for hydrogenation of unsaturated compounds via impregnation of polymeric matrix with metal complexes in supercritical carbon dioxide followed by a reduction of complexes with molecular hydrogen was described. Polymeric carriers are the mesoporic materials: phenol-formaldehyde polymer as well as polypropylene imines and polyamide imines dendrymeres. In the two last events for producing of tight bonded polymer chains a cross linking reaction was performed with various agents such as: hexametylene diisocyanate, phenylene diisocyanate and dimetoxydi-phenyl diisocyanate. Acetylacetonato-rhodium-dicarbonyl, (acac)Rh$(CO)_2$, well soluble in organic medium, was used as the metal complex precursor. By varying of both polymer nature and cross linking agent as well as by changing of impregnation conditions the samples of polymer matrix with immobilized metal were produced. These samples were tested in hydrogenation reactions of model substrates – octane-1 and styrene. It was shown that synthesized catalysts revealed unique catalytic activity in hydrogenation of both substrates, in some cases specific activity (TOF) exceeded $1x10^6$ h^{-1}. Activity of catalysts strongly depends on both original polymer nature and cross linking agent type, as well as on its relation. Therefore activity is defined by tight degree of polymer networks.

OR-3

A FLEXIBLE POLYMER CHAIN IN A CRITICAL SOLVENT: COIL OR GLOBULE?

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As has been shown in experimental work [1] by Koga et al in the vicinity of a liquid-gas critical point of the solvent a dramatic expansion of a dissolved polymer chain takes place. Such anomalous conformational behavior of the polymer chain occurs due to strong solvent density fluctuations which arise in the neighborhood of the liquid-gas critical point. Up to now, only a few theoretical results [2-4] have been reported on a thermodynamically stable conformation of a single polymer chain in a supercritical solvent in the neighborhood of the critical point. Dua and Cherayil [2] have developed a first principles statistical theory of the isolated polymer chain in supercritical solvent and showed that on approaching the liquid-vapor critical point, a polymer chain first collapses and then returns to its initial dimensions. Simmons and Sanchez [3] published a scaled particle theory for the coil-globule transition of a chain of attractive hard spheres in an attractive hard sphere solvent. As was shown by the authors, in the vicinity of the solvent critical point only the collapse of the polymer chain takes place but not its expansion. In the framework of theory of Simmons and Sanchez the effect of solvent density renormalization near the polymer chain was taken into account but the effect of critical solvent density fluctuations was missing. The same result was obtained by Erukhimovich [4] in the framework of the field-theoretical approach at the level of Ginzburg-Landau theory within model of a compressible lattice gas.

Despite the evident success in rationalizing the conformational behavior of the polymer chain in the critical solvent, clear understanding of the different conformational regimes has still not been reached. How does the globular or coiled state conformation of the polymer depend on the microscopic polymer-solvent interaction parameters in a critical solvent?

Addressing this question we develop a simple analytical self-consistent field theory [5-7] of an isolated polymer chain immersed in a low-molecular weight solvent which on contrast on the all mentioned above models simultaneously takes into account two effects: (1) effect of solvent density renormalization near the polymer chain due to polymer-solvent interactions and (2) indirect solvent mediated monomer-monomer attractive interaction due to solvent density fluctuations near the critical point (so-called quasi-Casimir forces).

By means of the developed theoretical model we investigate the conformational behavior of the polymer chain approaching the critical point of the solvent along the critical isochore. In the case of a weak polymer-solvent attraction at the liquid-gas critical point the polymer chain is in a globular state. When the polymer-solvent attraction exceeds a threshold value the polymer undergoes a dramatic expansion at the critical point.

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OR-4

ENANTIOSELECTIVE SYNTHESIS OF NITRO DERIVATIVES OF TETRAHYDROQUINOLINE: FIRST EXAMPLE OF ASYMMETRIC DOMINO REACTION IN THE MEDIUM OF SUB- AND SUPERCRITICAL FLUIDS

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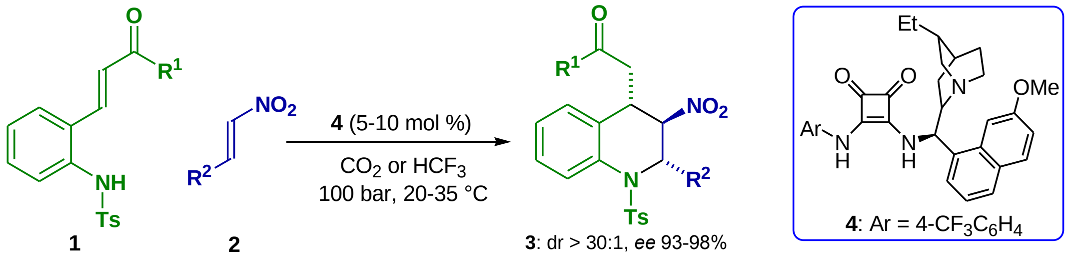
The most important task of “green chemistry” is a development of new cascade chemical processes involving two or more catalytic reactions carried out in a single reactor without the use of toxic organic solvents. Among them are particularly attractive processes with the use of highly selective chiral organocatalysts and environmentally friendly sub- or supercritical fluids. However, in the literature there is no information about cascade organocatalytic enantioselective reactions in sub- or supercritical fluids.

We first synthesized nitroderivatives of tetrahydroquinoline 3 - heterocycle, which is part of many biologically active substances, using bifunctional derivatives catalyzed dihydrochinin **4** containing a fragment of squaric acid, a “domino-reaction” of ortho tosylaminophenyl α,β-unsaturated ketones **1** with α-nitroalkenes **2** in media of sub- and supercritical CO_2 and HCF_3. The reaction involves sequential steps asymmetric Michael addition, diastereo- and enantioselectivity in which the proposed conditions comparable, and in some cases superior performance of the corresponding reactions in organic solvents, but it simplifies product isolation and purification. The results can be useful for creating new selective and environmentally friendly organocatalytic processes to obtain optically pure pharmaceuticals.



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OR-5

ASPIRIN DISSOLUTION IN SUPERCRITICAL CARBON DIOXIDE.

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Introduction

Aspirin is nonsteroid anti-inflammatory, febrifugal and an anesthetic cure. Being strong acid, it can irritate and even to cause a burn of a mucous membrane. Encapsulation of aspirin in bioresorbable polymeric carriers by means of supercritical fluid (SCF) technologies allows to remove this problem and to provide the uniform prolonged action of a preparation. When we choice the method and parameters of SCF aspirin encapsulation it is necessary to know its solubility in supercritical fluid. In this work we investigated solubility of aspirin in supercritical carbon dioxide (sc-CO_2) by means of IR-Fourier spectroscopy.

Experiment

Aspirin substance (Shandong Xinhua Pharmaceutical Co., LTD, China) has been investigated. Optical high pressure stainless steel cell (to 30 MPa) was used for receiving IR absorption spectra of aspirin in sc-CO_2 it. Cell windows (10 thick and 15 mm diameter) were made from CaF_2. Distance between windows was 10 mm. The cell with the thermostat and sensors of pressure and temperature was located directly in IR-Fourier spectrometer (Impact 410, Nicolet, the USA)

Measurements of absorption spectra with various hinge plates of aspirin in the range of 0,5-15 mg were taken for determination of its solubility. The hinge plate of aspirin was placed in the cell before measurements. A cell with a hinge plate of aspirin it heated up and thermostabilized at a temperature 40 degrees C. Then the cell was filled by CO_2 up to the pressure of 10.0 MPa. Absorption IR spectra were registered through various periods after filling the cell by sc-CO_2 and the beginnings of process of aspirin dissolution. The analyzed spectral range made 1000-4000 cm^{-1}. Accumulation of spectra happened for 64 scans at spectral resolution of 4 cm^{-1}. Process of aspirin dissolution was controlled by measurement of integrated intensity of absorption on the chosen analytical line at 1199 cm^{-1}.

Stationary (maximum) values of integrated intensity were determined on the base of their temporary dependences. Then dependence of the received stationary integrated intensity on hinge plate size was obtained. The received graphic was approximated by two straight lines one of which corresponded to increase in the dissolved substance with increase in a hinge plate, and the second corresponded to concentration of saturation of solution of aspirin in a supercritical fluid (the increase in size of a hinge plate didn't increase integrated intensity of absorption line). The point of intersection of these straight lines determined the aspirin hinge plate amount at which the saturation concentration is reached.

Measured saturation concentration of aspirin in sc-CO_2 made $(8,8\pm1,6)\cdot10^{-4}$ molar shares at 40ºC temperature and 10,0 MPa pressure of CO_2.

The value of solubility of aspirin received in our experiments well correlates with its values received in work [1] by measurements in the dynamic mode with a constant stream (Solubilities with CO_2 pressure - 12 MPa and temperatures 35ºC and 45ºC were $8,9\cdot10^{-4}$ and $7,2\cdot10^{-4}$ molar shares, respectively).

Conclusions

Process of aspirin dissolution in sc-CO_2 was studied by IR-Fourier spectroscopy method in real time. Its solubility in sc-CO_2 defined at 40 degrees C temperature and 10,0 MPa pressure of CO_2 made $(8,8\pm1,6)\cdot10^{-4}$ molar shares.

Acknowledgements This work was performed with financial support of RFBR (grants No. 13-02-01256, No. 13-02-12215).

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OR-6

CONFORMATIONAL EQUILIBRIA OF IBUPROFEN DISSOLVED IN SUPERCRITICAL CO_2 IN A WIDE RANGE OF STATE PARAMETERS

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In this work we studied the influence of external parameters of the state on the conformational equilibrium of ibuprofen dissolved in supercritical carbon dioxide, basing on the results of the vibrational infrared spectroscopy, as well as the data of quantum-chemical calculations and molecular dynamics simulation.

Registration of IR spectra of ibuprofen was carried out under the isochoric heating conditions, in the temperature range 35-90°C ($\Delta T=5°C$) at constant fluid density corresponding $1,3\rho_{cr}(CO_2)$. An analysis of the experimental spectra, in particular, the assignment of spectral bands to vibrations in different conformers of ibuprofen was carried out on the basis of quantum-chemical calculations.

Based on these results, it was found that with increasing the temperature from 35 to 90°C, the solubility of ibuprofen in supercritical carbon dioxide increases by one order of magnitude. However, the probability of specific interactions between its molecules remains negligible. Thus, dissolved in $scCO_2$ ibuprofen molecules exist in monomeric form. Along with the increase of the equilibrium concentration of ibuprofen the redistribution of mole fraction of its conformers takes place. It was found that at temperatures close to 50°C, there is a qualitative change in their populations.

Additional investigation of the obtained results by matrix analysis (two-dimensional cross-correlation analysis and principal component analysis) allowed us to estimate the changes in the susceptibility of different conformer mole fractions to a change in the external parameters of the state. The thermal and concentrational changes of conformational equilibria of ibuprofen molecules dissolved in CO_2 phase are discussed in detail in the present study.

This work was supported by the Russian Foundation for Basic Research, Grant N 13-03-12041-офи_м.

OR-7

HYDROLYTIC HYDROGENATION OF CELLULOSE IN SUBCRITICAL WATER.

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Cellulose is one of the wide-spread organic structures in nature. It has been estimated that 10^{11}–10^{12} tons of cellulose are synthesized annually. It is mostly combined with hemicellulose and lignin in the plants cell walls [1]. A lot of scientists consider cellulose a prospective alternative to fossil fuels as its renewable resources can provide production of raw material for the chemical industry and second-generation biofuels on a large scale [2, 3]. Moreover, at present, chemicals obtained from cellulose biomass can be cheaper than those obtained from oil [4]. A large number of hydroxyl groups part of cellulose composition account for the optimum way of its conversion – hydrolytic hydrogenation to sorbitol (mostly) and other polyols. This process was first carried out by A.A. Balandin and his colleagues in the USSR. They conducted hydrolytic hydrogenation of cellulose in the presence of mineral acids and Ru, Pd and Pt-containing catalysts. Now great attention is paid to supercritical fluidic technologies in the chemistry of wood and its components [5]. One of the prospective media is sub- and supercritical water [6,7]. For example, there were studies discussing the possibilities of cellulose hydrolytic hydrogenation in a subcritical water medium [8]. It allowed excluding mineral acids from the process and solving the problems of their disposal and the corrosion of the equipment. Subcritical water (temperature <350ºC, pressure < 221 bar) is a universal medium for performing chemical reactions. It can serve as a non-toxic solvent with well variable physical chemical properties (due to the change in temperature and pressure). Subcritical water, in particular, contributes to the acceleration of acid- and base-catalyzed reactions by approximately 400 times higher ions H_3O^+ и OH^-

concentrations; the decrease of diffusion limitation, connected with low viscosity of subcritical water; the increase in gas solubility and, in consequence, the increase in hydrogen concentration on the catalyst surface.

In this paper a new type of Ru-containing catalysts on the basis of hypercrosslinked polystyrene (HPS) is suggested for the process of cellulose hydrolytic hydrogenation in a subcritical water medium. The use of rhutenium catalyst (1.0% Ru) on the basis of HPS allowed achieving the total sorbitol and mannitol yield about 50% on average that is comparable with the results obtained with more complex and therefore more expensive catalytic systems. Being reused this catalyst was stable.

So in prospect Ru-containing catalysts supported on HPS can form the basis of high-efficient catalytic systems for cellulosic biomass conversion into the raw material for chemical synthesis and industrial production of second-generation biofuel.

Acknowledgements

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OR-8

CONVERSION OF SODIUM LIGNOSULFONATE IN SUPERCRITICAL WATER

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Research in the field of processing of plant biomass is of considerable interest for developing technologies based on renewable raw materials. The main components of biomass are polysaccharides, such as cellulose, hemicellulose, and lignin. Lignocellulose materials are wastes of industry, agriculture, forestry, and household. Currently there are no technologies of complete processing of lignin-containing waste to produce useful products; instead, in some cases, extremely environmentally unfriendly processes, involving mineral acids and alkalis, are used. From this point of view, studies of the conversion of lignin in sub- and supercritical water, which could form the basis for developing energy effective and environmentally friendly processes of recycling of anthropogenic waste, in particular from the pulp and paper and hydrolysis industries, is of paramount importance.

Conversion of sodium lignosulphonate (LS) is studied in sub- and supercritical water (SCW) in the temperature range 200-750°C at 200-300 atm and the residence times 2.5-10 min. Gas products analyzed by GC.Soluble products of the LS depolymerization are analyzed using HPLC and GC-MS. Thermogravimetric, elemental, IR and NMR spectral analyses of insoluble products of LS conversion are carried out .

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OR-9

TUNGSTEN-PLATINUM NANOPARTICLES FOR HIGH EFFICIENCY ELECTROCATALISTS OBTAINED VIA SUPERCRITICAL CARBON DIOXIDE DEPOSITION.

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Abstract

We carried out comprehensive studies of preparation opportunities electrocatalytic nanomaterials in supercritical carbon dioxide (SC CO_2) using platinum and tungsten soluble compounds as precursors. We focused on finding the optimal scheme of synthesis of tungsten-containing nanoparticles. Best results were obtained in case of conversion of the precursor in a reactor containing, along with supercritical CO_2 (partial pressure of 10 MPa), also an admixture of oxygen (partial pressure of 1 MPa): formation of dispersed amorphous non-stoichiometric tungsten oxide showing reversible reloading in aqueous sulfuric acid solutions were obeserved. When using other synthetic schemes (deposition and subsequent thermal degradation in an inert atmosphere) W-containing materials were also dispersed but presented to be mixtures of various crystalline tungsten oxide, with a predominance of phase $W_{18}O_{49}$, and were electrochemically inert.

The electrochemically active material obtained via optimized procedure was subsequently used as a substrate for the formation of platinum nanoparticles by applying a supercritical solution of an organometallic precursor of platinum and subsequent conversion, allowing to form a platinum-tungsten (W-Pt) nanocomposites with high platinum specific surface area. The catalytic activity of these materials were tested in a three-electrode electrochemical cells (methanol

oxidation), and in the model oxygen-hydrogen fuel cells. Activity calculated per intrinsic platinum surface corresponds typical to platinum electrocatalysts despite partial poisoning of the platinum surface by the organic ligand precursor degradation. The possibility of the formation of the tungsten carbide phase during heating in the process of the tungsten oxides preparation. Simultaneously we investigated commercial tungsten carbide as a substrate for platinum nanoparticles formed form SC CO_2. So we derived materials with a narrow platinum particles size distribution for following electrocatalytic studies.

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OR-10

POLYMER COMPOSITES BASED ON NC-SI OBTAINED BY DIFFUSION DOPING IN SUPERCRITICAL CARBON DIOXYDE

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In recent years the attention of researchers obtaining fluorescent micro- and nanoparticles for use in the sensors and, in particular, for human tissue bio-imaging, attract particles of nanocrystalline silicon (NC-Si) [1,2].

This work includes experiments on the effects of continuous visible laser radiation on the luminescence of samples containing NC-Si at different temperatures exposure. These studies are also necessary for the development of models of formation and mechanism of radiative relaxation of centers with fluorescence bands in the region of 800-900 nm and wich received its name in [3] as NC-ODC, as well as to develop ways of managing their fluorescent characteristics.

Using the methods of fluorescent spectroscopy, we investigated microdisperced powder of polytetrafluoroethylene (PTFE) impregnated with silicon nanoparticles using SC-CO_2. For the comparative analysis was also used colloidal solution of nanoparticles of silicon (NC-Si) in toluene and DMSO, a composite material of NC-Si embedded in polybutylmethacrylate sorbed chemically on it by the mechanism of the hydrosilation. A track membrane based on polyethylene terephthalate (“Dacron”) with the tracks of 100 nm in diameter was also impregnated with silicon nanoparticles using SC-CO_2 technology and used at the study.

All samples demonstrate PL band with a maximum in the region of 800-900 nm characterized with non-linear intensity growth with increasing intensity of excitation (for the fluorescence excitation semiconductor laser 405 nm was used). The shape of the PL band is also changing due to the broadening and blue-shift of its maximum. These facts have got explained taking into account well-known increase of the luminescence decay time moving toward the fluorescence band from shorter wavelengths to the larger ones.

For all the synthesized samples the effects of “bleaching” PL intensity under the action of laser radiation and its subsequent thermal recovery at different temperatures were studied. It is established that in addition to the individual characteristics of these processes for each of the samples, there are common patterns that are associated with acceleration of the kinetics of the decay of the PL intensity and a slow recovery with increasing temperature of the sample above room temperature. The model taking into account the possibility of recharging NC-ODC with this band fluorescence during exposure of NC-Si and thermal recovery by tunneling recombination processes was proposed.

There are two mechanisms involved in recovery process: restoration involving charges located in the immediate environment from NC-ODC, (fast recombination of the formed defects) and a mechanism involving charges that can be delivered to a particular center due to tunneling processes in the matrix of the sample.

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OR-11

LIQUEFACTION, GASIFICATION AND COMBUSTION OF BROWN COALIN SUPERCRITICAL WATER FLUIDS

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Large and widespread reserves of low-grade fuels (LGF), such as brown coal, bitumen and oil shale provide the ability to create a system of distributed sources of heat and energy supply. In this regard, it becomes actual problem to develop economically and environmentally efficient processes for LGF conversion into high-calorific gas, liquid and solid fuels. The results of studies of the last decade [1,2] have shown that the LGF conversion can be very efficient in supercritical water (SCW: $T > 374$ ºC, $P > 22.1$ MPa). Due to the fact that at the temperature which is sufficient for the LGF organic matter thermolysis (from 400 to 600ºC) water still retains its high density, SCW is the universal solvent of the LGF organic matter and is actively involved in redox reactions. Under the SCW thermolysis of LGF, water molecules become donor of hydrogen and oxygen, providing a high yield of low-molecular hydrocarbons, and also gasification and oxidation of LGF. Combustion of LGE organic matter in SCW/O_2 fluid can be implemented at high rate without soot formation [3,4].

The paper presents the results of a study of brown coal (gross formula $CH_{0.97}N_{0.01}S_{0.002}O_{0.31}$) conversion in SCW and SCW/O_2 fluids during continuous feeding of coal as a part of coal-water slurry (CWS). The coal particles with the size of ≤ 350 μm were fed through the upper end of the tubular reactor (D_{in} = 30 mm, L = 1.5 m) and moved through SCW in a cylindrical channel (d_{in} = 26 mm, l = 0.5 m) located along the reactor axis. The channel occupies 1/3 of the length of the reactor’s central zone. The reactants flowed through the gap (1 mm thick) between the channel and the reactor walls through an orifice in the upper zone of the reactor into plug-in samplers. It was found that during the fall of particles in a cylindrical channel the coal organic matter (COM) is partially dissolved in SCW. COM discharge from coal at falling of particles is enhanced due to the increase in their temperature resulting in SCW excess pressure in the pores of the particles [5]. With increasing SCW temperature, the efficiency of organic matter removal from the coal particles, and also the rate of COM thermolysis and redox reactions involving water molecules increased.

The yields of SCW conversion products formed during the motion of coal particles inside the cylindrical channel in one of the tests are given in Table. The conversion pressure was $P = 30$ MPa, the temperature of the reactor walls increased uniformly from 100 to 550°C, the CWS flow was 10 cm^3/min, 90.91 g of dry COM was fed into the reactor. Based on the elemental balance it was determined that the residue of SCW conversion of coal corresponds to the gross-formula $CH_{0.87}N_{0.01}S_{0.002}O_{0.14}$.

Table – The product yield (in percentage of COM), formed during the fall of particles of brown coal in SCW with temperature increasing along the reactor axis.

H_2	H_2S	CO	CO_2	CH_4	C_2–C_{10}	Maltenes	Asphaltenes	Residue
0.09	0.01	1.62	18.59	1.29	2.76	9.5	16.8	49.3

After sedimentation of the coal particles on the reactor bottom their further conversion was carried out by pumping SCW/O_2 fluid upward through a layer of particles. At the COM partial oxidation by adding oxygen to SCW, the conversion and decomposition of water molecules forming H_2, CO, CO_2, and CH_4 have increased dramatically due to the rise in reactant temperature. Mechanisms of these processes are discussed in the report.

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OR-12

THE EFFECT OF STATIC ELECTRIC FIELD ON THE STRUCTURE OF OXIDIZED LAYER OF METAL AND THE COMPOSITION OF COMBUSTIBLE GASES FORMED BY OXIDATION OF METAL BULK SAMPLES BY H_2O, CO_2 AND H_2O/CO_2 SUPERCRITICAL FLUIDS

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Earlier, we have revealed the formation of oxide nanoparticles at the oxidation of bulk samples of metals by H_2O, CO_2 and H_2O/CO_2 supercritical fluids (SCF) (see, for example [1]), studied the kinetics of oxidation, proposed cluster mechanism of nanoparticle formation, showed the process condition influences on the morphology of ZnO nanoparticles. This report presents the results of an experimental study on the effect of static electric field (E=0–300 kV/m) on the oxidation rate of Zn, Zr, Cu bulk samples in the SCF based on H_2O and CO_2, the structure of the oxidized layer of ZnO and the composition of gas products. Experiments were carried out in an electrically insulated reactor on the set-up for the study of physical and chemical processes in the SCF. The procedure for the experiments and the simulations is described in [2]. Electrodes were prepared in the form of plates, the sample being anode, and the cathode being made from copper. The value of E depends on the distance between the electrodes and on the applied voltage U. The modelling in ANSYS package confirmed the uniformity of electric field spatial distribution between the electrodes. In all experiments the samples after interaction with SCF retains their shape. The oxidized samples were tested by X-ray diffractometer Bruker D8 ADVANCE and scanning electron microscope Hitachi S-3400N.

Oxidation of Zn in H_2O SCF at T=673 K, P=23 MPa inder electric field shows that the reaction rate constant k is a linear function of E:

k(mol/(m^2·s))=3,85·10^{-5}·E(kV/m)+3,70·10^{-2}. Reducing the pressure down to 17.5 MPa of H_2O at 673 K leads to a sharp drop in the ionic product of water Kw and the effect of E on k. The same dependence on Kw was observed in the reaction of Zn with H_2O/CO_2 SCF at 673 K. Effect of E on ZnO layer structure leads to the formation of alternate areas of different density and different spatial distribution therein equiaxial nanoparticles with an average size of about 50 nm. The impact of E to nanoparticle morphology was manifested most strongly in the surface layer of ZnO, wherein the prolate crystals with average cross-sectional size of ~50 nm and a length of 4 μm were found. In conditions of H_2O/CO_2 SCF the electric field increases the CO yield by about 10% and the relative amount of products of reactions between CO and H_2, promoting to catalytically activated reactions on a ZnO surface [1]. The residual amount of ZnC_2O_4 and $ZnCO_3$ increases with the increase of CO_2 in the initial SCF. Thermal destruction of Zn oxatale and carbonate at ~400°C and ~300°C, respectively, leads to the formation of a spongy layer structure of ZnO.

Oxidation of Zr in SCF CO_2 was carried out for 4 hours at a temperature of 823 K, and the following conditions: 1) P_{CO2}=20.2 MPa (0,126 g/cm^3) при E=0 (6.6·10^{-3} % Zr was oxidized) и 2) P_{CO2}=14.1 MPa (0,089 g/cm^3) при E=293 kV/m (0.12 % Zr was oxidized). In both cases, the formation of monoclinic and tetragonal ZrO_2 phases and amorphous carbon was found. Deposition of carbon on the surface of the experimental cell leads to an increase of the leakage current I through the quartz separators of electrode from 0.016 to 2.37 mA. At electrochemical nature of current transferred charge corresponds to the oxidation of 14% Zr from formed ZrO_2 layer. Electrical field promotes to growth of ZrO_2 layer thickness, thick layer cracks (due to differences in densities of the metal and oxide) which results in a periodic increase of CO_2 access to Zr surface and manifest itself in the wavy character of the $I(t)$ dependence.

At higher H_2O SCF densities (673 K, 34.17 MPa, 0.463 g/cm^3) and higher voltage (900 V) electrolysis resulted in a significant oxidation of the copper anode. Analysis of the anode surface with a scanning electron microscope and X-ray diffractometer revealed the presence of equiaxial Cu_2O agglomerates with size of 200–500 nm consisting of lamellar nanostructures with thickness <50 nm. It follows that the production of metal oxide nanoparticles in H_2O SCF can be accelerated by the electric field. This is especially important for metals with a high positive value of the standard electrode potential.

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OR-13

SUPERCRITICAL FLUIDS FOR THE PREPARATION OF NANOPOROUS POLYMERS

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The preparation of the nanoporous polymeric materials with controlled size, shape and location pores is an actual problem. To solve these tasks, supercritical (SC) fluids are suggested to use, because of they have unique properties, combining features of the gases (high diffusion rate, low surface tension) and liquids (relatively high density, ability to dissolve).

Foaming is the most studied mechanism of pore formation in SC fluids (mainly SC-CO_2). Using this method allows us, as a rule, to obtain the honeycomb type pores with sizes from 0.1 to 10 microns. In this paper, we propose other approach to the formation of the porous structure in SC fluids, using the mechanism of crazing that occurs under the simultaneous action of the uniaxial tensile stress and the adsorption-active medium on a polymer. As a result, the polymer gets specific oriented fibrillar porous structure with a nanometer level of dispersion.

The investigation of uniaxial tensile strain of the commercial films of glassy poly(ethylene terephtalate) (PET), and partially crystalline isotactic polypropylene (PP) and high density polyethylene (HDPE) at the presence of xenon (SC-Xe) at 6.8 MPa and 23^{o}C, carbon dioxide (SC-CO_2) at 5-30 MPa and 35-75^{o}C, air (SC-air) at 30 MPa and 23^{o}C was performed.

The PET film volume increased during its stretching in the SC-Xe [1], and a formation of crazes was observed (Fig.1a). Crazes are microcracks, in which the walls are bridged to the oriented fibrils with diameter about 10 nm, and there are the pores of the same size between those fibrils. The formation of similar nanoporous structure previously observed for polymers stretched in liquids via the mechanism of classical crazing. Feature of a crazed structure obtained in SC-Xe was that it kept permeable to liquids (e.g., ethanol) after the removal of medium from the pores.

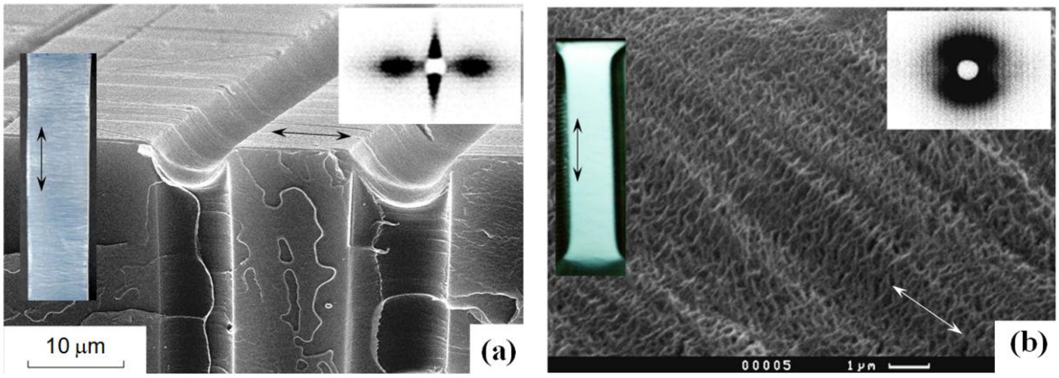

Fig.1. Micrographs of the brittle cleavage of PET after stretching at SC-Xe (a) and the surface of HDPE after stretching at SC-CO_2 (b). Images of samples after stretching and SAXS pattern show in the insets. The arrows show the direction of deformation.

Uniaxial deformation at SC-CO_2 and SC-air was studied for the films of partially crystalline polymers. It was found that stretching of HDPE and PP films at the presence of SC fluids carried out uniformly, without the neck formation, and accompanied by intensive cavitations [2]. The maximal value of effective volume porosity for the investigated polyolefins was 35-40 vol.%. The average effective diameter of pores determined using the data of the liquid permeability was 4-10 nm. Structural and morphological studies were allowed to conclude that the development of the polymer deformation proceeded via the mechanism of delocalized crazing, when the process of pore formation was accompanied by the extension and fragmentation of lamellae (Fig.1b). According to the SAXS data, crazes characterized by highly dispersed structure, namely, the diameter of fibrils was 8-12 nm and the specific surface fibrils reached the value of 100-150 m^2/g [3].

It is important to note that the maximum efficiency of SC fluids as the crazed media achieves at the supercritical temperature and pressure, where the density of a gas is near the density of liquids.

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OR-14

DEVELOPMENT OF METHODS OF DEEP CLEANING HETEROLOGOUS BIOMATERIALS FOR NEED RECONSTRUCTIVE SURGERY IN SUPERCRITICAL CARBON DIOXIDE EXAMPLE XENOPERICARDIALE TISSUE

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Proposed combined method of chemical-enzymatic processing and deep cleaning with supercritical carbon dioxide xenopericardial tissue with the aim of obtaining implants with enhanced biocompatible properties. The main problems associated with the use of xenopericardial held chemical-enzymatic processing and stabilization of the cross-linking agent, are possible residual amounts of phospholipids intercellular substance and glutaraldehyde. In turn, supercritical carbon dioxide can diffuse into the micropores of the matrices is much better than any other liquid and has a good ability to dissolve lipids and perform a deep cleaning of the matrix. Assessment of the impact of the proposed processing method showed that kenopanishad preserves the native structure without losing its physical and mechanical properties. The results of the study of local effects after implantation prototypes on models in vivo show that kenopanishad processed by the proposed method, does not cause an active inflammatory reaction observed active biointegrated biomaterial in tissue of an animal and almost complete bioresource, in the connective tissue around the material visible to newly formed blood vessels, calcium salts is not revealed. In accordance with GOST R ISO 10993-6 samples do not have an active irritant effect on the body. The present study is the first part of a larger work on the material for reconstructive vosstanovitelnoi surgery with desired physical, mechanical and biological properties.

OR-15

HEAT TRANSFER AND CHARACTERISTIC TIME OF CONVECTION DEVELOPMENT IN SUPERCRITICAL FLUIDS UNDER FAST ISOBARIC HEATING

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The peculiarities of heat transfer in SCF in the course of rapid transition from the initially stable state of compressed fluid (initial temperature – 300 K, pressure – which serves as a parameter – varied from 1p_c to 5p_c) to supercritical state along the isobar has been studied experimentally. We have revealed that in the course of this transition the passage through the critical temperature vicinity is accompanied by a threshold decrease in the heat transfer intensity. The interval of pressure values characteristic for this effect was from 1p_c to 3p_c. The closer is the pressure to critical value (p_c), the stronger does the observed effect manifest itself [1-4]. Experiments were carried out by the method of controlled pulse heating of a wire probe – resistance thermometer [1-6]. Probe diameter was 20 μm. The range of pulse lengths was chosen from considerations on the one hand, of the sufficiency of the thickness of the heated layer (which requires an increase in pulse length) and on the other hand, of minimizing the impact of macroscopic convection (which requires a decrease in pulse length). A compromise solution satisfying both conditions was the pulse length range of the order of one to ten milliseconds which corresponds to the heating rates from 10^4 to 10^5 K/s.

In discussing the results a question of the time scale of convection development under our experimental conditions has proved to be crucial. Basic data were obtained using a constant heating power mode [5]. To find the characteristic time scale of convection, which appeared to be of the order of tens of milliseconds, the heating power mode of temperature plateau [6] was applied. The comparison of data on the thermal resistance of pulse heated fluid at the stage before the convection development for the both heating modes (namely, [5] and [6]) is shown in Figure 1. Isopropanol served as a reference substance. The reduced pressure served as a parameter of experiment. The possible causes of the phenomena of threshold reduce in the heat transfer intensity in the course of passage through the critical temperature vicinity and sharp changes in the characteristic time of convection development in the near supercritical region will be discussed in the report.

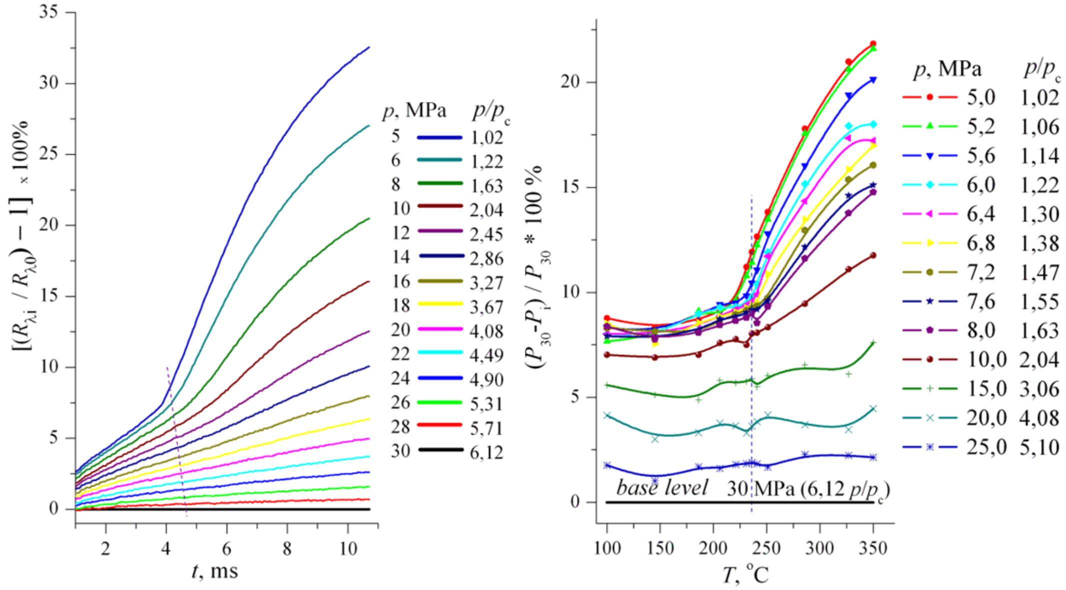

Fig.1. The change in isopropanol thermal resistance in the course of pulse heating by a constant heating power mode at different pressures ($R_{\lambda i}$) reduced to thermal resistance at the most high pressure ($R_{\lambda 0}$), left figure; the change in heating power released in the probe in the course of its thermostabilization (P, temperature plateau mode) in isopropanol at different temperatures (P_i) reduced to the power at the most high pressure (P_{30}) versus the plateau temperature, right figure.

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OR-16

INFLUENCE OF CONDITIONS ON THE PROPERTIES OF MODIFIED SIO_2-BASED AEROGELS

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Aerogels are mesoporous solid materials with very high surface area, a very low density, high porosity, and as a result, a low thermal conductivity [1]. Aerogels can be used as a thermal- and sound insulators, heterogeneous catalysts and bases for catalysts, sorbents et al. [2-4].

Aerogels are prepared by sol-gel method, followed by supercritical drying (SCD).

Our work is dedicated to find new ways to modify the properties of aerogels. We have developed two basic approaches to vary the properties of aerogels:

1. The influence of the solvent on the supercritical drying stage.
2. Two ways to modify the surface of the aerogels:

- Modification of the surface of the hydrogel;
- Modification of the initial monomer to its gelation and subsequent drying.

The influence of the solvent on the supercritical drying stage was studied for trifluoroacetate, lactate and trifluorolactate derivatives of aerogels containing aminopropyl group. We have found that the specific surface area of aerogels obtained by SCD in alcohols is 1.5-2 times higher than that for samples prepared in ethers. It was also shown that the type of supercritical fluid can affect the degree of hydrophobicity of aerogels.

A financial support from the RSCF (Grant no. 14-13-01150) is greatly acknowledged.

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OR-17

CREATION OF HYBRID AEROGELS BASED ON SODIUM ALGINATE

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Materials based on aerogels have a great potential in the pharmaceutical and biomedical fields. Structural combination and outstanding properties with physiological compatibility of aerogel results in a high potential for using them as modern drug delivery systems. The stability and release kinetics of the active substance could be significantly increased by loading of the drug into the aerogel matrix. It is perspective to use aerogels in the medical purposes in quality of sorbents.

During this work, aerogels based on sodium alginate with added polymers (Carbopol 974, Carbopol 940, Pluronic p123, Poloxamer 188, Eudragit L100) were obtained. The mass ratio of the added polymers to the alginate varied from 1:10 to 1:1. The particles were obtained as follows: sodium alginate in the form of powder was added to the solution of the polymer and the resulting mixture was stirred and then dropped through the needle into a solution containing calcium cations under constant stirring. Under the influence of the cross-linking agent (calcium cations) a polymerization process took place as a result of which particles with a diameter from 2.1 to 2.6 mm were formed. The next stage is a step by step solvent exchange. Then the particles were dried in supercritical carbon dioxide media. As a result of drying insignificant shrinkage of particles was observed. The obtained aerogels were white spherical particles with a diameter from 2 to 2.5 mm, collapsing at their compression, high-porous. The measurement results of the surface area and the porosity are as follows: the specific surface area (BET) from 320 to 480 m^2/g, total specific pore volume of 3.37 to 3.53 cm^3/g, the mesopore volume (method BJH) from 3.25 to 3.43 cm^3/g, the volume of micropores (Dubinin - Radushkevich method) from 0.17 to 0.20 cm^3/g.

Obtained particles further could be used as the matrix carriers of active pharmaceutical ingredients (API). Particular attention will be paid to the API with low bioavailability and solubility. Impregnation of the active substances in the aerogel matrix will be produced by the supercritical adsorption. Furthermore, the obtained aerogel particles will be examined for the possibility of their use as embolizing (swellable) materials for medical applications.

The research is supported by the Ministry of Higher Education and Science of The Russian Federation within the framework of project component or the State Assignment.

OR-18

THE PROCESS OF IMPLANTATION CARBON NANOTUBES IN INORGANIC AEROGELS DIFFERENT WAYS

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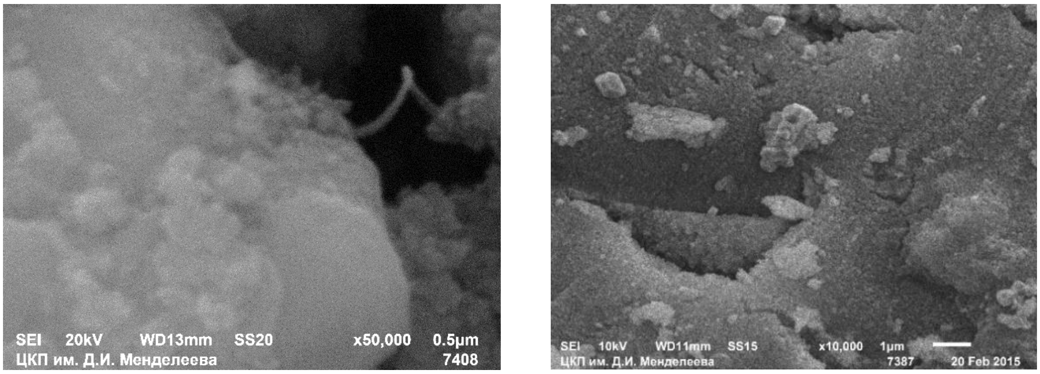
Nowadays the urgent task is to create new types of energy storage devices, which have a large capacitance. The main problem of modern energy storage devices is the poor value of the ratio of electrical capacitance to the weight of the device. In this article the process of implantation carbon nanotubes into inorganic aerogels for further use as supercapacitors will be considered.

Carbon nanotubes have a high specific surface area (up to 1500 m^2/g) and they can be used for energy storage. The problem of using carbon nanotubes in this field is the relative complexity of the structuring the nanotubes so that all of them should be closed to each other and they could be a single capacitor electrode.

The authors propose two approaches using an inorganic airgel of silica which can be used to solve the problem of structuration and fixing in a certain position carbon nanotubes. Inorganic aerogels serve as dielectric between the conductive nanotubes, as it is a "rigid" structure, which keeps the nanotubes in a certain position. In addition, due to the high porosity and low density aerogel, a new material is ultralight, which increases the ratio of electrical capacitance to the weight of the material. We used the method of preparation inorganic aerogels, which is described by Katalevich A.M.

The first approach is to implantation the carbon nanotubes to a sol. This is achieved by adding a suspension of carbon nanotubes and isopropanol in a sol. Thereafter, a sol is placed in a magnetic field generated by a solenoid (for direct magnetic field lines). The process of gelation occurs by the action of a magnetic field, which allows fixing the carbon nanotubes in a certain position. At the moment, work is carried out to determine the optimum ratio of the mass of nanotubes and mass aerogel. Nanotubes are densely incorporated in the aerogel, this provide good fixation. The image obtained with a scanning electron microscope is presented in figure 1a.

The second approach is to introduce the ions of molybdenum and cobalt (catalysts of growth of carbon nanotubes) to the gel and subsequent germination of carbon nanotubes in the pores of the aerogel. The molybdenum ions are introduced at the stage of gel because molybdenum forms a soluble compound with ammonium hydroxide (gelling agent). The cobalt ions are introduced after the gelation process. The gel was in a solution of cobalt nitrate in isopropanol 96 hours. The introduction of an organic polymer in the gel structure allows for better feed of the synthesis gas for growing nanotubes. Then organic polymer is removed by burning. Figure 1b is represented by a scanning electron microscope photograph at which visible crystals of a cobalt salt.



a b

Fig.1. a. A carbon nanotube introduced in the aerogel; b. Of cobalt nitrate crystals on the surface of the aerogel.

At the further researches will be found dependence of the properties of the new material (airgel with implantation nanotubes) from the amount of nanotubes and method of implementation.

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OR-19

TO THE QUESTION OF CLEANING OF THE COLLECTOR OF THE GAS-TURBINE ENGINE OF THE COKED DEPOSITS WITH MIX OF SUBSTANCES IN SUPERCRITICAL CONDITION

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At operation of gas-turbine engines of a nozzle of a fuel collector, working at liquid hydrocarbonic fuel, are subject to coking and as a result of it, the set technical characteristics of work of nozzles change. This phenomenon reduces reliability of operation of the engine and worsens starting characteristics.

The available industrial technologies of cleaning of nozzles of the coked deposits provide dismantle of the engine from object of placement and dismantling of a collector with the subsequent washing of details in ultrasonic bathrooms in the environment of hot solvents. The technology expensive, ecologically unsafe also doesn't give 100% of cleaning. Technologies of cleaning of a collector without dismantling of the engine are absent.

For the solution of a problem of effective ecologically safe cleaning of nozzles of a fuel collector of the gas-turbine engine pilot studies on the equipment of KNITU by basic possibility of removal of the coked deposits from elements of nozzles by mixes of various substances in supercritical condition were conducted.

As a result of the carried-out chemical analysis of the coked deposits from nozzles of different degree and conditions of an operating time, and also researches on cleaning of samples of nozzles of a real collector, possibility of creation of industrial technology of cleaning of nozzles of a fuel collector of the gas-turbine engine without dismantle from object of placement is proved.

OR-20

POLYFUNCTIONALITY OF SC CO_2 IN SYNTHESIS AND MODIFICATION OF POLYMERS AND SUPRAMOLECULAR STRUCTURES

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The task of the report is to show a great variety f roles or polyfunctionality of SC CO_2 in synthesis and modification of polymers and supramolecular structures (structures with non covalent bonds). A polyfunctionality of SC CO_2 will be demonstrated on the concrete examples: synthesis of polyarylates (SC CO_2 as a solvent and plasticizer), polyimides (as a solvent and a catalyst), aliphatic polycarbonates and their copolymers (as a monomer and a plasticizer), reactionary precipitation in synthesis of heterogeneous catalysts and processes of fractionation and purification of polymers (a solvent), impregnation of metal-organic complexes, dyes, BAS and monomers into polymer matrices (a solvent and transport medium), a development of porous materials for implants, airgels and materials with ultra low dielectric constant (porogen). It seemed that so rich spectrum of developed methodics and reglaments has to promote an effective commertialization, but it is not noticed. What are the reasons? The main of them (besides of visual ones for Russia) are weak development o technological and economical aspects of scaling, not full ecological purity of the processes and unsufficient their advance as compared with routine technologies, large initial investment, not clear perspectives of scailing.

The actual field – performance of functional materials – molecular and supramolecular structures (metal-polymer composites, heterogeneous catalysts at inorganic supports, gradient systems, materials for “drug-delivery” and “drug-release”have developed unsufficiently for realization as industry technologies, because strong correlations between values of variables in the synthesis and end results and economical aspects are so far not obtained. It is ought to note that in last years the fields airgels and “drug-delivery” – “drug-release where SC CO_2 plays a role of a porogen, a solvent, a plasticizer and a transport medium.” has been developed some faster than another ones. But an extraction in SC CO_2 remains all the same the most assimilating issue of fluids in industry.

The report is devoted to discussion and demonstration on concrete examples of polyfunctional properties of SC CO_2.

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OR-21

DIFFUSE SCATTERING SPECTROSCOPY OF RANDOM POROUS MEDIA WITH NEAR-CRITICAL COMPONENTS

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Analysis of parameters of diffuse scattered coherent or non-coherent light is the promising approach to study of the structure features and physical-chemical properties of multi-phase systems with near-critical components. Presently known optical probes of supercritical fluidic systems such as the fiber-optic reflectometry [1] and CARS spectroscopy require very specific conditions for their applications (in particular, the existence of a homogeneous probed medium in the first case and application of a nanoporous matrix medium with low extinction in the latter case). The diffuse scattering spectroscopy is free of these disadvantages and allows one to study the structure and physical-chemical properties of random media with supercritical components, which are characterized by the strong scattering of probe light, in the wide range of thermodynamic parameters. Analysis of the temporal correlations of scattered light fluctuations in the course of transition between the equilibrium states of multi-phase systems with near-critical components gives the possibility to characterize peculiarities of the structural changes and local mass transfer in such systems [3]. Simultaneously the analysis of the diffuse transmittance for a probed near-critical system in the dependence on its thermodynamic parameters (for example, the pressure) gives the information about the system structure and peculiarities of phase transitions under the condition of spatial confinement [4].

This work presents the results of theoretical and experimental studies of optical properties of random media with near-critical components using diffuse scattering spectroscopy. Mesoporous systems (such as the polymer layers with fibrillar structure and aerogels) saturated by subcritical liquids and supercritical fluids were chosen as the probed samples. The special attention was paid to the study of the optical immersion effect in random media, which is caused by variations of the refractive index of saturating media when its thermodynamic parameters (the pressure and the temperature) are changed. Above the critical point the refractive index of fluid can be obtained from the fluid density by using the modified Clausius-Mossotti relation. Below the critical point the influence of capillary condensation on the effective refractive index of saturating medium can be taken into account using the Maxwell Garnet model (in the case of nanoporous media) or the effective medium model in the framework of coherent potential approximation (in the case if the average pore size is comparable with the wavelength of probe light). Figure 1 illustrates the optical immersion effect for mesoporous polymer matrices saturated by supercritical carbon dioxide. In this case the effect is manifested as the increase in the transport mean free path of probe light propagation in the medium with the increasing pressure (and, correspondingly, the refractive index of the fluid).

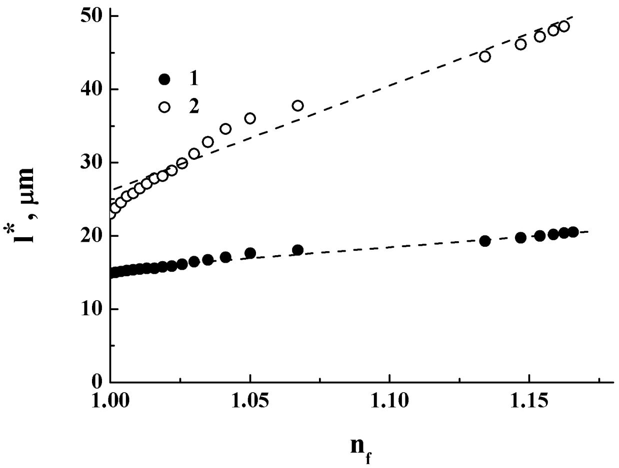

Fig.1. The dependencies of the transport mean free path of light propagation (633 nm) in mesoporous layers (on the base of: 1 – cellulose fibrils; 2 – Teflon fibrils) saturated by supercritical carbon dioxide (306.16 K) on the fluid refractive index. The solution of the inverse problem of diffuse scattering spectroscopy.

Future prospects of the application of diffuse scattering spectroscopy with coherent and non-coherent probe light as the diagnostic approach to dispersive systems with supercritical components are discussed.

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OR-22

DISTINCTIVE FEATURES OF LIGHT SCATTERING SPECTRA IN THE NEAR-CRITICAL FLUIDS IN THE PRESENCE OF TIME HIERARCHY

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This report provides the line-width theoretical calculation for vibrational Raman scattering spectra in the critical region of fluid.

We get the case as the time of change in neighbor environment of each oscillator is much less than the lifetime of critical density fluctuations and the lifetime of critical density fluctuations is much less than the time of spectral measurement.

We suppose spectral correlation function to be the Voigt function. Also we assume that the critical fluctuations do not affect the shape of spectral correlation function but cause a change in its homogeneous and inhomogeneous width. The last assumption is that the inhomogeneous part of Voigt function is not much sensitive to local density.

Under this approach we get two simple analytical expressions for changes in homogeneous and inhomogeneous width that cause by critical density fluctuations. These expressions show that the critical fluctuations are not always lead to the homogeneous line broadening and always lead to the inhomogeneous spectral line narrowing.

The assumptions we have considered are consistent with experimental conditions and results of CO_2 Fermi-dyad CARS measurements [1]. Thus we use our analytical results together with the experimental data [1] in order to formulate the optimization problem to get the upper bound for the critical density variance and lower bound for the lifetime of critical fluctuations. The optimization problem did not require any new assumptions.

We get [2] that CO_2 critical density variance may not exceed 0.4 and its realistic upper bound is 0.03-0.05. The lifetime of critical density fluctuations is bounded below by a value ~ 10 ns.

Such low values of CO_2 critical density variance supports the conclusion on nonthermodynamic nature of CO_2 critical fluctuations done in [3]. We get a question whether the density fluctuations of such a small variance can be the cause for critical opalescence. To clarify this, we calculated the near-critical CO_2 Rayleigh scattering spectrum taking into account the above time hierarchy. The preliminary joint analysis of theoretical results and experimental data on quasielastic small-angle scattering in CO_2 [4] also will be included in the report.

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OR-23

LUMINESCENCE PROPERTIES OF DIOXIDE SILICON AEROGELS WITH Β-EUROPIUM DIKETONATE MOLECULES INTRODUCED IN THE MATRIX BY SCF IMPREGNATION

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Porous materials based on silica aerogels such as attracting more and more attention due to the wide possibilities of their applications, including photonic, plasmonic and sensoric. One of the most important properties of aerogels is their ability to easily impregnate with various solutions. This allows materials to give new functional properties, while maintaining their high thermal and chemical resistance. In the case of low density SiO_2 aerogels (0.03-0.34g/cm^3) application of liquid organic solvents with high values of the surface tension is practically impossible due to the imminent destruction of the thin walls of the aerogel matrix. Therefore, the negligible surface tension characterisating the supercritical fluid (SCF), as well as the acceptable solvency of many compounds makes such impregnation a promising method of aerogels functionalization.

We used samples of silica aerogels with different densities. In the aerogel matrix were introduced europium β- diketonates, such as $Eu(tta)_3$ $2H_2O$ (tta=tenoil-4,4,4-trifluorobutan-1,3-dione), and $Eu(fod)_3$ (fod= 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octandione) which is well soluble in supercritical carbon dioxide (SC-CO_2) [1]. It is known that in the case of $Eu(tta)_3$ $2H_2O$ and $Eu(fod)_3$ occurs sensitized photoluminescence (PL) spectra of ions Eu^{3+} in the visible wavelength range due to the mechanism of effective excitation energy transfer from the ligand broad π*- levels on to the respective located close *f-f* levels of ions Eu^{3+} ("antenna effect").Therefore, as a excitating source of ions Eu^{3+} PL was used UV LED with a wavelength at the maximum of the radiation λ = 380 nm, half-width 0.1eV and power density on the sample 0,1 W/cm^2 (NSHU590, Nichia).

Figure 1 (see russian text) shows the PL spectra of the initial compound $Eu(tta)_3 \cdot 2H_2O$ (1), after dissolving it in the SC-CO_2 (2) and the aerogel (the density is 0.16g/cm^3) after impregnation in this solution (3). It can be seen that after the dissolution process of $Eu(tta)_3$ $2H_2O$ in SC-CO_2 and subsequent deposition on the filter paper no noticeable changes in the PL spectrum Stark component $^5D_0 \rightarrow {}^7F_j$ (j = 0,1,2) compared to the initial compound. This means that such treatment does not influence the $Eu(tta)_3 \cdot 2H_2O$ structure. At the same time in the PL spectrum there are significant changes in the system of these components for $Eu(tta)_3 \cdot 2H_2O$ molecules, immobilized in the airgel matrix after SCF impregnation. We believe that $Eu(tta)_3 \cdot 2H_2O$ molecule can conjugate to clusters of SiO_2 molecules , which constitute the basic skeleton of aerogel. This leads to a strong broadening of the Stark components in the PL spectrum. The intensive "red" PL doped aerogel is well observed when excited by UV nitrogen laser with a wavelength λ = 337 nm.

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OR-24

SUPERCRITICAL EQUILIBRIA IN TERNARY SYSTEMS WITH ONE VOLATILE COMPONENT AND BINARY SUBSYSTEMS WITH DIFFERENT TWO TYPES.

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There are two main types of binary systems with volatile and non-volatile components, particularly the water-salt systems. Binary systems of type 1 are characterized by continuous increasing of non-volatile (salt) component solubility up to melting temperature and by absence of critical phenomena (L=G) in solid saturated solutions. Binary systems of type 2 have the solubility curve (L-G-S) with a negative temperature coefficient of solid solubility in subcritical temperature range, the critical phenomena (L=G) occur both in not solid saturated and in saturated solutions. The supercritical fluid equilibria takes place above the temperature of critical phenomena (L=G-S). The liquid immiscibility phenomena sometimes appear both the systems of types 1 and 2, however usually the available experimental data indicate the immiscibility equilibria in the water-salt of type 2 such as $Na_2SO_4 – H_2O$, $K_2SO_4 – H_2O$, $Li_2SO_4 – H_2O$, $Na_2CO_3 – H_2O$, $BaCl_2 – H_2O$ etc.

A theoretical derivation [1] and experimental studies [2-9] of ternary water-salt systems with binary subsystems of types 1 and 2 show the main regularities of phase transformations taking place in ternary mixtures in a process of heterogenization of homogeneous supercritical fluid spreading from binary subsystems of type 2. Separation of supercritical fluid starts from the critical phenomena in solid saturated solutions and is accompanied (sometimes) with a transition of metastable immiscibility region into the stable equilibria.

Negative temperature coefficient of salt solubility (common in the binary subsystems of type 2) is changed to the positive one with increasing of salt 1 concentration in ternary solutions. Investigation of ternary critical equilibria (L=G-S) and (L_1=L_2-S) show that these monovariant critical curve can have temperature maximum as a result of continuous phase transformation (L_1=L_2-S⬄L=G-S) the double homogeneous point (DHP) or in the double critical end-point (DCE) when two critical end-points of the same nature (L_1=L_2-S), spreading from the binary subsystems of type 2, coincide.

The DCE can also be observed in ternary mixture when two monovariant critical curve of the same nature (L=G-S or L_1=L_2-S), originated in different nonvariant points, coincide at extreme concentration of a salt in ternary solution when gradually changing the nature of the solute from that of type 2 salt into that type 1 salt.

If the appearance of the double homogeneous point (DHP) is the first version of ternary phase diagram for binary subsystems of types 1 and 2, the second version of ternary phase diagram with the same types of binary subsystems is characterized by the emergence of four-phase equilibrium (G-L_1-L_2-S) with invariant critical points (G=L_1-L_2-S) and (G-L_1=L_2-S), from which the monovariant critical curves (G=L_1-L_2) and (G-L_1=L_2) originate, further going toward higher temperatures and ending at the tricritical invariant end-point (G=L_1=L_2).

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OR-25

THE CREATING OF PROLONGED FORMS OF ANTITUMOR DRUGS VIA THE IMPREGNATION OF BIODEGRADABLE POLYMERS BY TRIARYLIMIDAZOLES IN THE MEDIUM OF sc-CO_2.

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The possibility of using of supercritical carbon dioxide (sc-CO_2) in the process of impregnation of biodegradable polymers by medicinal substances (when creating long-acting drugs) eliminates the presence of impurities (including water) in the resulting medicinal forms, thereby the biological activity and selectivity of action of such drugs are increased.

The aims of this work are the creation of the prolonged forms of model compounds of triarylimidazole class (TAI) with high antitumor and neuroprotective activity when TAI is incorporated in biodegradable polymers based on chitosan in the medium of sc-CO_2.

It was shown that the content of TAI in biodegradable matrices depended on the sc-CO_2-impregnation conditions and the chemical nature of the polymer carriers. For the first time, the sc-impregnation of water-soluble unmodified chitosan (almost no swelling in the medium of sc-CO_2) by organic TAI was carried out due to the additional introduction of water as co-solvent in the system. It was found, that it is possible to impregnate in the system of sc-CO_2/water a higher amount of hydrophobic arylimidazoles into the unmodified chitosan, than that into chitosan modified with hydrophobic lactides and polylactides. The latter fact is probably due to a more intensive impregnation of polymer matrices at the interface of two efficiently mixing media – sc-CO_2 and water. The kinetics of TAI “wash-out” from impregnated chitosan films in a hydrochloric acid buffer solution was investigated and the rate constants of the TAI transition from chitosan films to the liquid phase were determined.

Thus, it is established that the use of biologically active TAI and the selection of appropriate conditions of sc-CO_2-impregnation and biodegradable polymers will allow creating in sc-CO_2 medium the prolonged forms of antitumor drugs with controlled release of TAI from polymer matrices.

This work is financed by RFBR (grant No. 15-02-06826).

OR-26

GENERALIZATION OF RESULTS OF RESEARCH OF PROCESS OF REPLACEMENT OF OIL WITH USE OF SUPERCRITICAL CO_2 AND FRINGES OF SUPERCRITICAL CO_2 AND WATER FROM UNIFORM AND NON-UNIFORM LAYERS

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The mathematical model of process of replacement of oil by supercritical CO_2 and fringes of supercritical CO_2 and water is created. The differential equations making mathematical model are processed by method of large-scale transformations. The system from similarity complexes three sizes in which have independent dimension is received. Complexes of similarity which equality is required for compliance of conditions of carrying out experiment on not hardpan sandstones to natural conditions are defined. On experimental installation researches of process of replacement model and real by nefty viscosity to 40 of uniform and non-uniform layer supercritical CO_2 are conducted with pressure up to 14 MPas, temperatures to 60ºC. The dimensionless generalizing equation of dependence of oil saturation of the porous environment on hydrodynamics of process of replacement of oil, superficial the phenomena on limit of the section of phases and the porometricheskikh of characteristics of layer is received.

OR-27

STRUCTURING SUBMICRON AND NANOSIZED COMPOSITE MATERIALS DURING IMPREGNATION AND EXPANSION SUPERCRITICAL FLUID AND GAS SATURATED SOLUTIONS

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An experimental setup to create porosity in polymers in supercritical carbon dioxide, allowing to carry out experimental studies of up to 40 MPa and 350ºC on the basis of Thar RESS-100 and certified methods for studying the kinetics of sorption and desorption of supercritical fluid solution in the amount of the polymer to form pores. It is also provided an apparatus for measuring the porosity of the polymer with water at high pressure. The results obtained in the temperature range of T = 120ºC-180ºC, the pressure P=25 MPa. The results of the experimental studies of the effect of operating parameters of the kinetics of sorption and desorption solution into the supercritical fluid volume sverhvysokomolekulyarngo polyethylene, polypropylene and polystyrene. An increase of the pore volume with increasing temperature and decreasing pressure of the pressure relief time.

In order to study the internal structure of the treated supercritical fluid polymers used microtome Rotmik-2P and optical microscope Livenhuk. It established the formation of a spatially oriented porous structures, due to the pressure gradient within the polymer sample.

For a theoretical description of the mathematical model numerically sorption and desorption kinetics of supercritical fluid solution based on Fick's second law in the amount of polymer. Calculations have allowed to find the coefficient of diffusion of carbon dioxide in a medium porous ultrahigh molecular weight polyethylene, polypropylene and polystyrene.

To enable the production of composite particles from gas saturated solutions (method PGSS) designed experimental stand allows to study the process in a wide range of temperatures and pressures. The results of experimental studies of the influence of operating parameters of PGSS on average size, dispersion, morphology, composition and structure of the obtained composite particles respiridon / polyethylene glycol, respiridon / polylactic acid. The technique for determining the quantitative composition and structure of composite nanostructured materials.

The results allow to control the properties of composite materials from UHMW polyethylene, polypropylene, polyethylene, polyethylene glycol, polylactic acid. Preparation of polymer composites of pharmaceutical substances can achieve purity, improved bioavailability, solubility, rate of absorption and elimination of a drug. The results can be used in materials, pharmaceuticals and medicine.

The work was performed as part of the RF President Grant MK-4440.2014.8

OR-28

THE DINAMIC OF ALTERATION OF THE SPYROANTROOXAZINE MOLECULES IN COLORED FORM AT INTRODUCING INTO FLUOROPLAST F-42 IN SUPERCRITICAL CARBON DIOXIDE MEDIUM

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It was shown before, that the «long-lived» (over year) stabilization of indolyne spirooxazines (ISO) by polymer matrix occurs when polymer is impregnated by ISO in supercritical carbon dioxide (sc-CO_2) under 90^{o}C. This stabilization is accompanied by formation of ISO colored forms, namely so-called B-form. It has maximal absorption on 600 nm in absorption spectrum. The stabilization of other ISO form was marked after the ISO has been introduced in halogenated polymers. More particularly, the absorption spectrum of fluoroplast F-42 impregnated by spiroantrooxazine (SAO) had maximum of wavelength on 535 nm.

The patterns of ISO stabilization in polymer matrix were investigated in this work for the case of impregnation of fluoroplast F-42 by SAO molecules in the medium of sc-CO_2. The impregnation modes (50^{o}C, 11 MPa) were established for this process. They allowed investigating of direct dynamic of forming and following relaxation alterations of colored SAO isomers.

The dynamic analysis enabled determine of rate constants for mentioned sequential transitions between colored forms leading to previously unknown B(475)-form of SAO.

The optical density alterations dynamic D(λ,t) was investigated on air (at 90, 85, 75, 70^{o}C) for absorption spectra of impregnated F-42 samples. It allowed determine of rate constants for mentioned variations of SAO isomers on air and estimate of activation energies for relaxation transformations. These values were approx. 60-80 kJ/mol. You can associate the founded high stability of colored ISO forms on air with just high values of given activation energies.

It was founded, that values of rate constants for relaxation alterations of colored SAO forms in F-42 matrix in the sc-CO_2 environment more than 10 times as compared with the same values for transitions in F-42 on air. Such differences characterize the plastific effect for F-42 matrix caused by introducing of carbon dioxide into polymer at sc-CO_2 conditions.

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OR-29

SYNTHESIS AND CHARACTERIZATION COMPOSITE MATERIAL, BASED ON METAL AND DIELECTRIC NANOPARTICLES, OBTAINED USES METHODS LASER ABLATION IN SC CO_2

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Using the method of laser ablation in supercritical carbon dioxide (SC CO_2) may receive a variety of metal and dielectric nanoparticles with a wide range of applications, ranging from sensory and ending with the medicine. Application of SC CO_2 environment allows you to smoothly change the density of the medium in a wide range for the implementation of various modes of ablation by controlling the parameters of nanoparticles. Using the transport properties of supercritical carbon dioxide medium may saturate resulting nanoparticles different materials with the free internal volume, for example polymeric films or powders, which allows to use this medium for one-step preparation of nanocomposite materials.

The report will present the results of the synthesis of film composite materials based on metal and dielectric nanoparticles stabilized in the volume and number of nanoporous polymer materials. For composites used method, based on the finished impregnated porous sample colloidal solution of nanoparticles in the SC CO_2 and gravitational deposition of the colloidal nanoparticle solution on the saturated material, followed by molding it into a film. The experimental data clearly demonstrate that it is possible one-step synthesis of nanocomposite film materials in the environment of SC using supercritical CO_2 colloidal solution obtained by laser ablation.

OR-30

THE FUNCTIONALITY INCREASE OF ROAD MATERIALS WITH THE USE OF SUPERCRITICAL FLUID IMPREGNATION OF BITUMINOUS COMPOSITIONS

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At present, there are already papers in which the authors suggest various versions of reinforcing the carbonated crushed stone. As a result of impregnating the carbonate crushed stone with the traditional technologies a gradient under-the-surface layer appears on the surface of the grains, having a more solid structure preventing the penetration of water in the porous space of the middle "nucleus" and its reliable capsulation is formed. This fact of the uneven impregnation – in this case of the crushed stone — is typical for all the approaches described above that use the liquid-phase solution as an impregnation material. It is due to this liquid condition such shortcoming features are typical from the point of view of the possibility of penetrating into the high-porosity matrixes including the high viscosity and low diffusion abilities, the presence of the surface tension and the capillary effect. This leads to the increased water absorption and the loss of physical-mechanical properties of the crushed stone thus minimizing the effect of the modification that was performed earlier. One of the solutions to this problem is a pass-through and uniform impregnation of crushed stone.

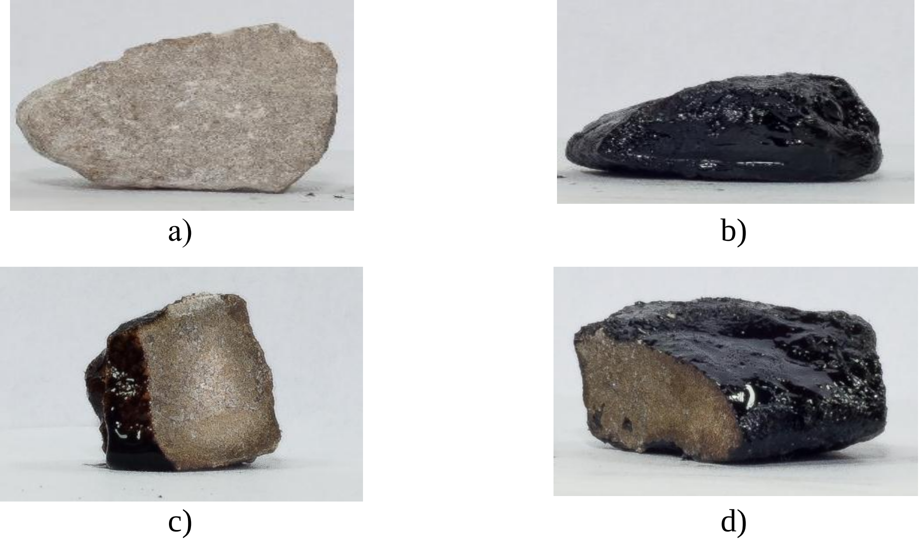
Therefore, an efficient technology of impregnation of carbonate crushed stone by oil-product based on SCF impregnation process usage with propane/butane solvent was developed.

At the heart of this technology is proposed use of supercritical fluid (SCF) impregnation process, by impregnating the crushed stone by the de-asphaltizer that is obtained in the process of the liquid propane/butane extraction from the crude oil residues.

Operating parameters of providing complex process are given in Table 1.

No. of working conditions	$P_{extraction,}$ Mpa	$T_{extraction}$, ˚C	$P_{impregnation}$, МПа	$T_{impregnation}$, ˚C	Mass ratio «extractant: oil residue»	Vent of deasphaltizate,%
1	4,5	85	4.5	85	2:1	66
2	4,5	85	4,5	138	1,5:1	54
3	6	85	7	138	2:1	65,4
4	7	85	7	138	1,5:1	52
5	7	85	7	138	1:1	42

The influence of SCF impregnation process conditions on quality of crushed stone impregnation is shown on photos given in Figure1.



a) b)

c) d)

Fig1. Photos of crushed stone samples: a) source sample; б) outer look of crushed stone sample after impregnation process; c) sample piece after impregnation in conditions No.1 (table1); d)sample piece after impregnation in conditions No.4 (table1).

Homogeneous deasphaltizate shell formed on the surface of the stone after the impregnation process (see Figure 1b, 1c, 1d), has good hydrophobic and adhesive properties. The latter has its force if applied to the asphalt coat material, which traditionally placed on the surface of crushed-stone layer during pavement forming up. Water absorption of the crushed stone sample is 0.24%.

However, during road construction process and during first years in service, crushed stone fractionizes intensively, whereby its inner part becomes bare. In case of impregnation with the traditional approach, this part usually stays untreated, it causes increasing of water uptake of the material and deterioration of its physical and mechanical properties.

Impregnation of crushed stone with liquid solution of deasphaltizate in propane-butane mixture (condition №1 in Table. 1) provides peripheral preferably the so-called "crusted" impregnation (see Figure 1c). In the case of transfer of propane - butane mixture in a supercritical fluid state (conditions in Table № 2-5. 2) impregnating of the crushed stone with deasphatizate is appears as uniform and "pass-through" (see Fig. 1d).

Table 2 shows the physical and mechanical properties of the original and impregnated samples of crushed stone, evaluated under GOST techniques.

Table 2. Physical and mechanical properties of the original and impregnated samples of crushed stone.

№ working conditions	fraction, mm	True density, g/cm^3	Average density, g/cm^3	sponginess, %	Water uptake, %	Crushability rate, %/ grade	
						In dry consistence	Hydro-saturated consistence
initial sample	20-40	2,7	2,36	12,6	3,6	16,4/600	17,1/600
1	20-40	-	-	-	3,6	-	-
2	20-40	-	-	-	0,95	-	-
4	20-40	2,69	2,29	14,9	0,54	16,4/600	16,9/600

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OR-31

ANOMALOUS PROPERTIES OF BINARY SOLUTIONS WITHIN LOW CONCENTRATION REGION

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In connection with the development of supercritical fluid extraction and chromatography technologies the structure and physico-chemical properties of binary solutions are intensively studied. A number of experimental data shows significant changes of the properties of binary solutions depending on their concentration. In particular, within low concentration region (up to 0.1 mole fraction) both the one and the other component we observed anomalous behavior of the physical properties (coefficients of Relay light scattering, sound velocity, the adiabatic compressibility, excess molar volume and excess adiabatic compressibility functions). Anomalies of physico-chemical properties in aqueous solutions within the low concentration region are known to exist, that are related to the existence of a 3D –network of hydrogen bonds. Abnormalities in a number of non-aqueous solutions [1-6] that we experimentally observed make possible to suggest the existence of intermolecular interactions that lead to similar effects in these solutions as well.

Analysis of experimental data on the physical and chemical properties of liquid binary solutions of organic substances, and computer simulation data show that molecular agglomerates (ensembles most tightly bound molecules) are formed in aqueous and non-aqueous solutions of organic compounds. We believe that the anomalous behavior of physical and chemical solutions properties within low concentrations region both one and the other component is explained by the formation of agglomerates, that are structurally different from the liquid phase in volume.

In the report, our experimental data and results of computer modeling will be presented, and that are the basis for creation of the model of supramolecular organization for some aqueous and non-aqueous binary solutions of organic substances. In particular, the properties of solutions depending on the concentration, the nature of the components and the nature of the interactions between them will be discussed.

The proposed approach to the consideration of the supramolecular organization of binary solvents may be used for the selection of effective eluents in supercritical fluid chromatography.

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OR-32

UNCERTAINTIES IN THE DEFINITION OF SUPERCRITICAL FLUID REGION ON THE PHASE DIAGRAM

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There is a constant problem in the field of supercritical fluid technologies (SCFT), a problem of defining an exact region of the phase diagram which can unequivocally be attributed to a true supercritical fluid (SCF) state. The only certain values which can be given for critical phenomena are the coordinates of a critical point for a two-phase liquid-gas medium where a second order phase transition takes place. To define a border between just a liquid and a SCF or just a gas and a SCF is much more cumbersome. And in the same time a lot of chemical processes which are traditionally seen as SCFTs in fact are conducted at such pressures and temperatures which cannot be unquestionably named supercritical. This raises a pack of questions, both of terminological and practical nature. If a certain SCFT is conducted at a pressure or a temperature below the critical value for a compound in use, then a) can said SCFT be truly called “supercritical”, b) if no – then how should it be called and c) do substances actually possess these special properties which are associated with SCF and which are being the ultimate goal for implementing this technology? In this discussion study we made an attempt to classify known approaches for tackling this problem. We did not aim for finding the final solution; there is a feeling that at a present state of minds it is hardly possible. Our goal was more to enlighten the advantages and limitations of every approach in order to underline the possible hampering effect to an overall field development in the case of a certain approach preference.

In our opinion existing approaches can be loosely divided into three groups: 1) a formal or a classical approach, 2) approaches based on deep investigation into microstructure of the matter in a supercritical state (a structural approach) and 3) approaches concentrating on investigation of those technologically attractive properties of SCF which become cornerstones of various SCFTs (a practical approach).

A formal approach states that a matter can only be named «supercritical» if it strictly complies to two conditions: $P>P_{crit}$ и $T>\max\{T_{crit},T_{melt}\}$. Its main advantages are simplicity and unambiguity. Its main limitations are the following: 1) neither critical isotherm nor critical isobar denote any stepwise structural change on the phase diagram 2) crossing these lines on the phase diagram doesn't lead to any key SCF quality appearance or disappearance. When using this formal criterion one has to exclude a lot of technologies traditionally perceived as supercrical from that pool. It mostly concerns those SCFTs in which a substance is used at temperatures below critical. Such technologies are often proposed to be name «subcritical». In our opinion this term doesn not solve but only increases the magnitude of a terminological problem since there no even remotely reasonable way to define the border between a liquid and a "subcritical" region on the phase diagram.

Structural approached are numerous. In this paper we particularly concentrate on the following two: 1) a family of Widom lines, 2) a Frenkel line. Their benefits come from thorough theoretical analysis of real microscopic structural changes that take place when a substance is being transferred into a SCF state. Knowledge accumulated in these researches represents a great value for SCFT practice since it allows a-priori assessment of many important physical parameters, experimental determination of which is very convoluted. Nevertheless to our knowledge all the approaches of that branch speak about the existence of a single line within a phase diagram which corresponds to a transition from a liquid-like to a gas-like fluid above the critical point. Whereas in order to define a SCF region on a phase diagram one needs two lines: a liquid - SCF transition line and a SCF - gas transition line. So these approaches are of little use in solving the terminological problem.

Practical approaches are arguably the most difficult in implementation. They tend to separate two terminological problems: what is SCF and what are SCFTs -

apart from each other and investigate them isolated. And the offered criteria of belonging to SCFTs are typically some numerical characteristics of those beneficial SCF properties which are the foundation of practical interest to SCFTs. The problem here is that for different SCFTs key properties of SCF are not the same, and they start to appear at different pressures and temperatures. Some of them do not even belong exclusively to SCFs. That makes it impossible to build up a universal way to look at SCFTs from practical point of view. This feature will be discussed in this paper on the following examples: 1) dense gas extraction, 2) dense gas chromatography, 3) «subcritical» water extraction and chromatography, 4) polymer plastification under compressed gases, 5) aerogel drying, 6) near-critical micellization, 7) Diels-Alder, hydrogenation and oxidation reactions in the SCF media.

OR-33

BASIC EDUCATIONAL GRADUATE PROGRAMS IN AREAS OF TRAINING 04.04.01 "CHEMISTRY" WITH THE DIRECTION OF "SUPERCRITICAL FLUID TECHNOLOGY TO PRODUCE PHARMACEUTICALS"

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A design and development of the variable part of the educational program (OPOP) towards the preparation of "Chemistry" with the direction (profile) "Supercritical fluid technologies for the production of pharmaceutical products" on the basis of competence-active approach. Design OPOP conducted with the "European" version of the module: the volume of structural elements OPOP (disciplines, practices) are multiples of 3, 6, and so on. N. This allows us to implement a network form of education and contributes to the mobility of students in the learning process.

The goals, objectives, learning outcomes that can be achieved in the preparation of this program, due to the content and objectives of the field of professional activity, as well as the structure of the general cultural, general professional, occupational and professional specialized competences set out in the maps of competences.

The BEP "Supercritical fluid technologies for the production of pharmaceuticals," offered three vertical module: M1, M2 and M3. The student, learning OPOP one of the modules:

– it protects the creative project as an interim assessment of the module-forming discipline ("SCF micronization in pharmacy: processes and devices", "supercritical fluid extraction in pharmacy: processes and devices", "supercritical fluid chromatography in pharmacy: processes and devices");

– maintenance practices (training practice, research, pre-qualification practice) combined single "red thread" - an object or a subject of study and research, which are formed of competence;

– the logical conclusion of practice, the final formation of competencies is to protect the master's thesis.

The module-forming subjects (and not only) of each module provide as a mandatory research students. The aim of this work is to identify and analyze the specific objectives, the rationale for the goals and objectives of the study, discussion of the results.

Formation of research competence of students based on their in-depth practical work that is provided by carrying out research work (semester), training and pre-qualification practices.

Master program modules, being independent integrative units are interconnected and form the basis for the development of professional competence in the chosen field.

Working curriculum OPOP drafted in such a way that allows you to develop an individual learning plan, depending on the target: the achievement of certain competencies in the depth or advanced level.

Specially designed OPOP is afforded the opportunity to study master of the variable elective courses (over 12 CU) as optional. Work programs of disciplines and practices (training practice, research, pre-qualification practice) developed in OPOP drawn up in accordance with the recommendations of the Ministry of Education and Science of the Russian Federation and the Association of Russian classical universities.

A high level of educational outcomes will be achieved through the establishment of research competencies, the relevant content of the employment actions under a professional standard.

Work is executed in accordance with the state contract number 05.R14.12.0013 for works (services) for the state needs from 07.11.2014, in the framework of the event 5.22 "Development of new educational programs and training modules for specialized higher and secondary special institutions" Federal Target Program "Development of the Pharmaceutical and Medical Industry of the Russian Federation for the period up to 2020 and beyond."

ORY-1

DETERMINATION OF BENZOIC AND CINNAMIC ACIDS BY SUPERCRITICAL FLUID CHROMATOGRAPHY

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Derivatives of benzoic and cinnamic acids are the secondary metabolites of plants, widespread in nature and possessing bioactivity. Nowadays, high performance liquid chromatography is widely used for their analysis, however, a significant problem of this method is the necessity to separate compounds with similar structure and polarity, requiring the use of highly effective sorbents and considerable analysis time. An alternative is supercritical fluid chromatography, which has several important advantages.

The aim of this study is a development of method for qualitative and quantitative determination of the most important representatives of benzoic and cinnamic acids by supercritical fluid chromatography.

Commercially available preparations of aromatic acids, which are widespread in the plant tissues, were selected as objects of study: benzoic (I), 4-hydroxybenzoic (II), vanillic (III), syringic (IV), veratric (V), cinnamic (VI), coumaric (VII), ferulic (VIII) and sinapic (IX).

Four different sorbents were used for separation: bare silica (BEH), silica with 2-ethylpyridinium linked groups (BEH 2-EP), silica with pentafluorophenyl (CSH Fluoro-Phenyl) linked groups, and zwitterionic sorbent Nucleodur HILIC, containing inner trialkylammonium cation and outer negatively charged sulfo group.

At the first stage of the study, selection of chromatographic separation conditions using selected stationary phases was carried out. It was found that back pressure and temperature have little effect on separation, so these parameters are the same for each stationary phase: 130 bar and 55°C respectively.

Gradient elution program that allows to achieve optimum separation was developed for each sorbent. The optimum separation was achieved using a sorbent with 2-ethylpyridinium linked groups BEH 2-EP, which showed maximum resolution between neighboring peaks and great efficiency. Analysis time is 2.5 minutes (Figure 1).

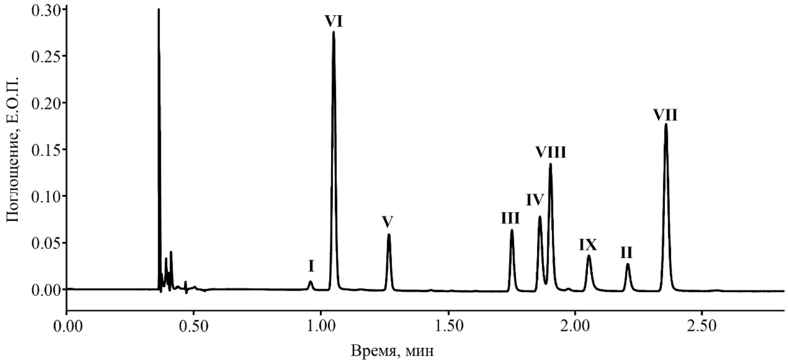

Fig.1. Chromatogram of standard mixture of benzoic and cinnamic acids. Column: BEH 2-EP, mobile phase: CO_2 (A) and 0.1% trifluoroacetic acid in CH_3OH (B). Chromatography conditions: oven temperature 55°C, back pressure 130 bar, flow 2 mL/min. Modifier program: 0 min – 5%B; 1.0-3.0 min – 15% B; 3.5 min – 5% B

Linearity was checked by constructing the calibration curves from peak area ratios of each analyte versus concentration using standard solutions with concentrations in the range 0.2-20.0 mg/L. It was found that all calibration curves are described by the equation “y = ax” with the correlation coefficient (r^2) more than 0.995. The calculations for limits of detection (LOD) and quantification (LOQ) were based on 3 sigma rule (signal-to-noise ratio equals to 3) and 10 sigma rule respectively. The detection limits obtained for the studied compounds are in the range of 13.0-51.3 μg/L.

The developed approaches were successfully tested on real objects - different wines. Aromatic acids were extracted with ethyl acetate. The resulting chromatograms show no significant interferences from the matrix with minimal sample preparation, as well as sufficient sensitivity.

The study was performed in Core Facility Center “Arktika” of Northern (Arctic) Federal University named after M.V. Lomonosov under the financial support of the Ministry of Education and Science of the Russian Federation (project № RFMEFI59414X0004) and Russian Foundation for Basic Research (project № 13-03-12238).

ORY-2

CALCULATION OF THE PHASE TRANSITION SURFACE NEAR CRITICAL POINT

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Information about the phase (vapor-liquid) equilibrium near the critical point is essential for development of technologies which involve critical condition of matter and condensed matter. If the research is technology-focused, it is reasonable to conduct the experiment under isochoric conditions, as in a chemical apparatus. In this case, for binary mixtures, the phase change temperature is a function of the density and composition (T_{dew}=f(ρ,x)). Therefore, a complete description of the critical area of a binary mixture can be achieved by calculating the surface of (vapor-liquid) phase change.

We analyzed the literary data on alkane binary mixtures, and constructed phase transition surface for these mixtures. Procession of literary data on the axes of "density" and "composition" was performed on the basis of information from [1,2]. As the result, the minimum of experimental data required for correct description of the function T_{dew}=f(ρ,x) was determined.

The experimental process was worked out on the binary mixtures of alkanes with aromatic hydrocarbons. The experiment was carried out in an ampoule mode, in an air bath oven. The phase change was recorded visually, by appearance of the phase division border. The approach to filling the ampoules is discussed in detail in [3].

On the basis of experimental data we calculated the surface of the phase transition for all studied binary mixtures and mixtures for which literary data is available. As a result, we found out, that for correct representation of the critical area which describes the maximum and critical temperatures of the system it is necessary to have the data for a wide range of compositions, reflecting all extreme states of the system.

Therefore, the conduction of an experiment for studying the critical properties of binary mixtures, which are followed by concurrent calculation of the phase transition surface, allows not only to obtain more complete information on the area of liquid and vapor phase coexistence, but also to substantially decrease the time required for the experiment.

Acknowledgments: This work was financially supported by The Ministry of Education and Science of Russian Federation within the framework of the basic part of governmental tasks of Samara State Technical University (project code 1708).

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ORY-3

NITRATION OF CYCLIC 1,3-DIACYLAMINES AND GLYCOLURYLS DERIVATIVES IN LIQUID AND SUPERCRITICAL FLUIDS

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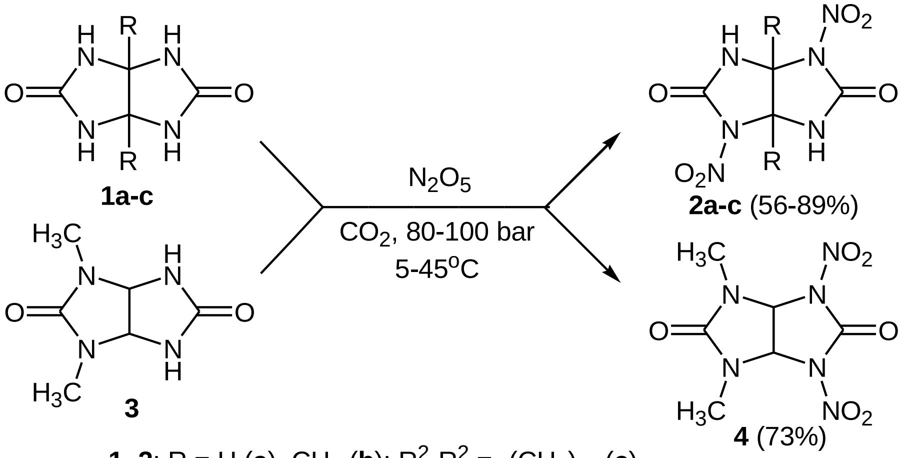
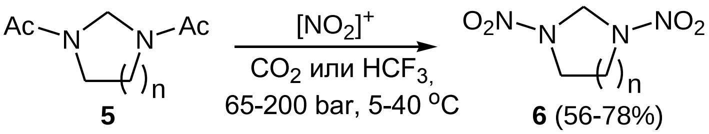
An effective and safe method of synthesis of bicyclic bis-ureas dinitroderivatives **2** and **4** by nitration of glycoluryl **1a** and its analogs **1b**, **1c** and **3** with nitro oxide (V) in liquid and supercritical carbon dioxide media has been developed. The yields of dinitroglycoluryls **2a-c** and **4** in the suggested conditions are 56-89% [1].



1, 2: R = H (**a**), CH_3 (**b**); R^2-R^2 = -$(CH_2)_4$- (**c**)

The nitration reaction of cyclic 1,3-diacetilamines **5** with different nitrating agents in liquid and supercritical CO_2 and fluoroform media has been investigated. Conditions (temperature, pressure, Lewis and Bronsted acids addition) allowing to obtain the dinitroproducts **6** with 56-78% yield are found.



5, **6**: n =1 (**a**); n=2 (**b**)
$[NO_2]^+ = N_2O_5$, N_2O_5/HNO_3; N_2O_5/SO_3

The work was financially supported by the Russian Foundation of Basic Research (project 13-03-12223) and the Presidium of Russian Academy of Sciences (Basic Research Program No. 8).

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ORY-4

INVESTIGATION OF SAS PARAMETER INFLUENCE ON MORPHOLOGY OF OBTAINED PARTICLES DURING PREPARATION OF PROLONGED-RELEASE AND ENHANCED BIOAVAILABILITY DRUGS

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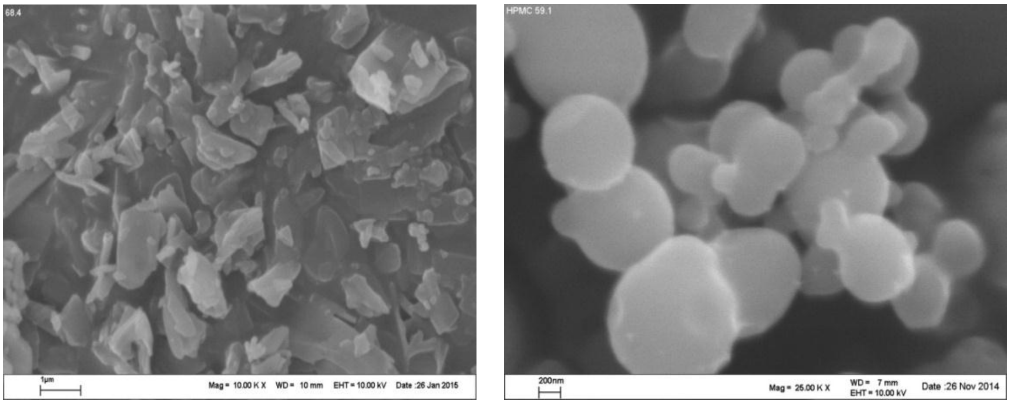
Development and preparation of new prolonged-release drugs and drugs with enhanced bioavailability is one of the most promising directions of modern pharmacology. This is caused by fact that their use allows to minimize the frequency of drug intake and also to optimize concentration of active pharmaceutical component in blood plasma.

One of the most common methods of increasing the bioavailability of pharmaceutical substances is micronization. Conventional methods of micronization, such as controlled crystallization, mechanical milling, etc. have a number of disadvantages associated with thermal and mechanical effects. In addition, the final product can have significant amount of undesirable toxic solvents.

Supercritical fluid approaches can be used as alternative methods of pharmaceutical substances micronization. Due to a number of advantages such as rapidity of the transition from liquid to solid phase and good controllability of the process, they provide an opportunity to avoid difficulties mentioned above. Moreover, it is not necessary to work at high temperatures. The most commonly used approach for micronization of insoluble in SC-CO_2 substances is supercritical antisolvent method (SAS).

SAS method also allows carrying out the co-precipitation of active pharmaceutical ingredient (API) and hydrophilic polymer to encapsulate the API in polymer matrix. Thus, in addition to increasing the bioavailability, SAS also open the possibility to achieve prolonged release or other types of controlled release. It is important to note that during preparation of drugs with increased bioavailability or controlled-release drugs there is a problem of obtaining particles (AFI or AFI in polymer particles-carriers) with narrow size distribution and specified morphology, which are very important for release kinetics of API. SAS method also has the advantage during solving this task, compared with conventional methods. It allows obtaining particles with a quite narrow size distribution. In addition, you can control morphology and particle size using variation of SAS parameters.

In this work the influence of SAS parameters, such as concentration of substance in the solution, pressure, temperature, flow rates ratio of the solution and SC-CO_2 on the morphology of obtained particles is studied. Moreover, special attention is paid to the influence of solvent on obtained results. A number of model AFI and polymers such as arbidol (fig. 1*a*) and hydroxypropylmethylcellulose (fig. 1*b*), were chosen to study in this work.



a *b*

Fig.1. SEM image of arbidol (*a*) and hydroxypropylmethylcellulose (*b*) particles after SAS micronization.

The work has been financed by RFBR grant № 13-03-12270 (micronization of low molecular weight compounds) and NSF grant №. 14-33-00017 (micronization of macromolecular compounds).

ORY-5

OLIGOMERIZATION OF ISOBUTYLENE IN SUBCRITICAL CONDITIONS

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At present time environmentally safe and non-waste technologies, which promote complete processing of feed in oil refining industry, become more and more important. In this production sector oligomerization processes have been implemented by leading global enterprises, aimed at processing of coking and FCC LPG as well as LCC gasoline. In licensed oligomerization process zeolitic catalysts are mainly used with operating temperature reaching and even exceeding 300^{o}C. In implemented process frequent regeneration of catalyst at high temperature is required, which negatively affects its activity and life.

Over recent years new process solutions have been developed, which was based on the use of substances in supercritical fluid (SCF) state. There are the possibilities of use of sub- and supercritical fluid mediums in organic synthesis, pharmaceutical industry to create new forms of medical agents, as well as for development of tight oils, and in other areas of the chemical industry.

At the moment supercritical technology is no doubt one of the most promising directions of development of modern catalytic science. Combining the properties of gases and liquids under high pressure, supercritical fluids intensify mass and heat transfer which consequently leads to increase of chemical reactions rate.

We have studied oligomerization of isobutylene in subcritical conditions with sulphocationites of different brands. At this stage it has been established that even at low temperatures of about 80-90^{o}C oligomerization is followed by destruction and isomerization of oligomers developed. Isomerization of butylenes dimers proceeds with formation of 14 basic isomers C_8, the major one (up to 40% wt.) is 2,3,4-trimethylpentyl. Coming close to subcritical conditions oligomers destruction and isomerization rate increases. These processes become dominant over sequential oligomerization of isobutylene.

This experiment has been performed with and without solvent in subcritical conditions. The experimental data are scheduled to be reported at the Conference.

Acknowledgments. This work was financially supported by The Ministry of Education and Science of Russian Federation within the framework of the basic part of governmental tasks of Samara State Technical University (project code 1708).

ORY-6

THE EXPERIMENTAL STUDY NON-CATALYTIC AND CATALYTIC REACTION IN SCF-CONDITIONS ON THE FLOW UNIT

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An experimental study of biodiesel production by transesterification of rapeseed oil in ethanol in supercritical fluid conditions using ultrasonic treatment on the reactive medium at a molar ratio of "ethanol - rapeseed oil" 6:1-18:1 in the temperature range 593-653 K, pressure 30 MPa at a flow-type installation. To reduce the state parameters and the acceleration of the reaction is realized using catalytic transesterification reaction using heterogeneous catalysts, carried out under the same regime parameters, as well as in non-catalytic method. As heterogeneous catalysts are used metal oxides (Al_2O_3, ZnO/Al_2O_3, MgO/Al_2O_3, SrO/Al_2O_3) in a granular form. For the preparation of the catalysts used method for impregnating carrier (Al_2O_3) by immersion in a concentrated aqueous solution of the appropriate nitrate salt of metal, followed by evaporation and calcination [1]. Optimum reaction conditions and molar ratio of the feedstock was identified. The most effective catalyst was selected [2] (Fig.1).

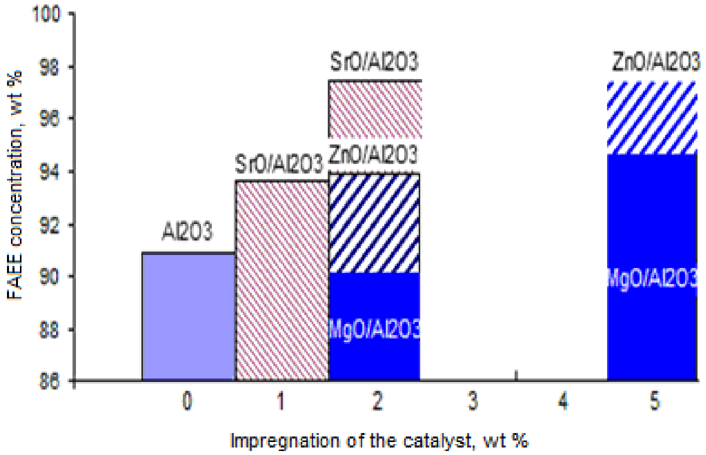

Fig.1. The concentration of FAEE in the reaction product using various catalysts. T = 623 K, P = 30 MPa. Molar ratio: 12: 1

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ORY-7

UNIVERSAL CORRELATIONS BETWEEN CHARACTERISTICS OF HYDROGEN BONDS IN LIQUIDS AND SUPERCRITICAL FLUIDS

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Supercritical fluid has been regarded as one of the promising solvents for industrial use in the coming decades and its special physical properties have caught worldwide attention for a long period of time. Understanding the nature of intermolecular forces in supercritical fluids is the breakthrough to further development of this technology. However, experimental and theoretical investigations on supercritical fluids are really scarce. Especially, for supercritical alcohols, although they are important co-solvents and excellent substitutes for supercritical water, there are many questions regarding their intermolecular forces, microscopic structure, dynamic property and hydrogen bond still remain unanswered. Thus, there has been increasing experimental and theoretical interest in this area of study recently. Since the properties of associating fluids are largely determined by the characteristics of their hydrogen bond network, this property is the main topic in current experimental investigations. [1]

This work is continuation of our previous investigation of supercritical methanol with respect of MD simulation model [2]. It was shown by MD simulations and Raman spectra proceeding that the correlation between average number of hydrogen bonds and molar fraction of non hydrogen bonded molecules seems to be a general feature of methanol, ethanol and 1-propanol and that these alcohols exhibit much stronger similarities in H-bonding in a very broad range of thermodynamic conditions. Common feature for molar fraction of different hydrogen bond degrees was found.

In present work we successfully used same approach for ethanol and propanol in wide range of state parameters. Suitable description of experimental

Raman spectra was shown. Experimental results have a good correspondence with our previous calculations and literature data. Deconvolution of spectra one more time validates used approach. This data has a big importance because one can easily obtain same results for different hydrogen bonded systems applying discussed correlations.

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ORY-8

SCF SYNTHESIS AND IN SITU DIAGNOSTICS OF SILVER NANOPARTICLES IN THE PORES OF BULK TRANSPARENT NANOPOROUS MATERIALS

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The report presents the results on synthesis and diagnostics of silver nanoparticles (NPs) in the pores of several nanoporous materials: aerogel, nanoporous glass, and oligo(urethane methacrylate). The method used is based on the impregnation of a porous sample by a silver precursor dissolved in supercritical carbon dioxide, following by the reduction of silver ions and clusterization into the NPs within the pores. The reduction of silver atoms was stimulated by laser irradiation at the wavelengths of 405 and 532 nm (fig.1a) or by heating (fig.1b) of the samples in SCF reactor. The extinction spectra of the composites were recorded during the synthesis process allowing the dynamics to be observed. The fitting of the extinction spectra using the nanoplasmonics model allowed us to characterize the size and shape of the NPs. The experimental data clearly demonstrates that different methods of sample treatment can be used to synthesize the NPs with different characteristics (fig.2).

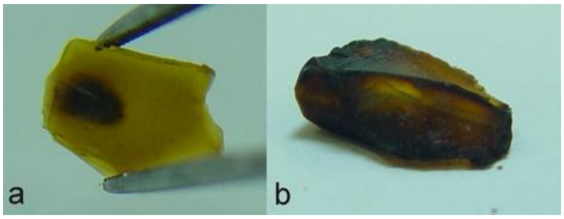

Fig. 1. Aerogel after radiation (a) and heating

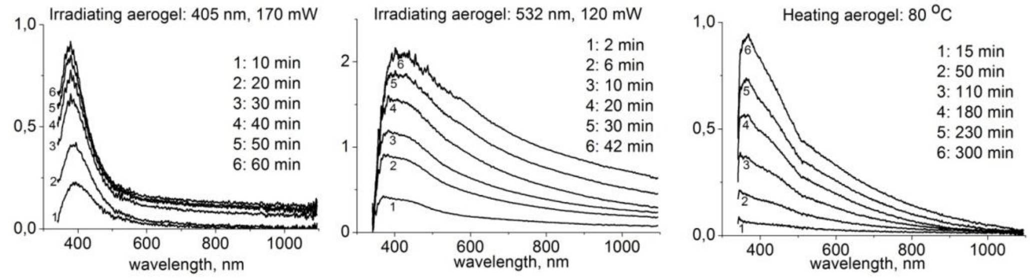

Fig. 2. Dynamics of extinction spectra of aerogel composites.

ORY-9

THE STRUCTURE AND MORPHOLOGY OF NI-, CU-, SI-CONTAINING CATALYTIC SYSTEMS SYNTHESIZED USING THE SUPERCRITICAL ANTI SOLVENT (SAS)

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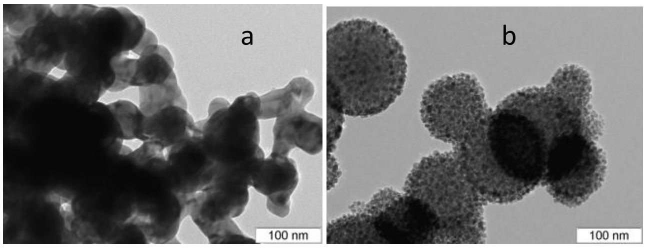
Heterogeneous catalysts are important functional materials which can be used in various industrial applications ranging from large refinery plants to the technologies of the fine organic synthesis. The one of the traditional methods for catalyst preparation is the precipitation using for example nitrates of different metals as the precursors. This method allows scientists to adjust the phase composition, dispersion and morphology of the catalysts. The main disadvantages of this approach are large amount of wastewater, as well as nitrogen oxides, which are formed during the annealing of the catalysts precursor.

The alternative approach based on the SAS (Supercritical Anti Solvent) method using supercritical carbon dioxide as anti-solvent allows overcoming the above difficulties. It's well-known that the supercritical carbon dioxide (SC CO_2) is an attractive media for various physicochemical processes due to its availability, low price, inertness, non-toxicity, safety, ease of recycling, and low critical parameters (T_c=303.9 K, P_c=7.38 MPa).

The rapid diffusion of SC CO_2 in SAS method leads to a supersaturating of the initial salt solution of a metal and the precipitation of X-ray amorphous fine powder. Previously it was shown that the SAS method can be used for the obtaining of amorphous vanadium phosphate catalyst for selective oxidation of butane to maleic anhydride [1], Cu- and Mn- oxide catalysts for CO oxidation [2], oxide catalysts (Fe_3O_4, NiO, CuO, Co_3O_4) for complete oxidation of propane [3].

Here we report the results of the synthesis of Ni-, Cu-containing catalysts obtained via SAS method for hydrogenation, steam hydrodeoxygenation, synthesis of carbon nanofibers and other processes. For the synthesis of these systems a new approach has been used based on the introduction of Si-containing compound into the metal salt solution, which is sprayed into a stream of SC CO_2. At every stage of the synthesis (including heat treatment, hydrogen reduction), the samples were investigated by scanning (SEM) and high-resolution transmission electron microscopy (HR TEM), X-ray diffraction (XRD) and ferromagnetic resonance (FMR) including *in-situ* regime.



TEM images Ni-, Cu-containing catalytic systems after reduction with different content of SiO_2: (a) 0%; 40% (b).

It was found that the introduction of SiO_2 can change the crystallinity and dispersion of the oxide and metal phases; at SiO_2 content more than 40 wt.% the formation of solid solutions of Cu in Ni is observed. Thus, the results indicate the possibility of using SiO_2 for the synthesis of catalysts via SAS method as a binder matrix, which prevents the sintering of the active component during the annealing and reduction steps. The proposed approach makes it possible to vary the size and phase composition of the catalyst systems prepared using SAS method. The work was supported by the foundation “Skolkovo” (grant agreement № 3 from 12.25.2014).

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ORY-10

AMMONIUM PALMITATE SOLUBILITY RESEARCH IN SUPERCRITICAL CARBON DIOXIDE

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For opportunity and supercritical condition use expediency in a materials properties modification problemstudying, and in particular giving of water repellency to them, there is a necessity for solubility data of the repellent agents in the supercritical fluids. In presentwork ammonium palmitate solubility as one of perspective repellent agents is investigated. Studies are carried out on the experimental unit presented in fig. 1, created on the supercritical fluid extraction R-401 system basis of ReactionEngineeringInk firmproduction (the Republic of Korea). Unit allows investigating substances solubility in supercritical carbon dioxide in the range of temperatures from 300.15 to 373.15 K and the range of pressure from 8.0 to 40.0 MPa.

Ammonium palmitatesolubility is investigated in the range of temperatures and pressure from 308.15 to 333.15 K and 10 to 32 MPa respectively, in the dynamic mode on the created experimental unit.

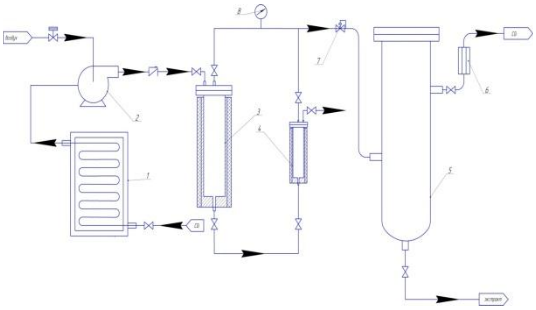

Fig. 1. Scheme of experimental installation 1 – the refrigerator, 2 – the pump for giving of CO_2 in system, 3 – a receiver, 4 – an extraction cell, 5 – a separator, 6 – a mass flowmeter –gasflow rate regulator,7 – pressure regulator "to itself", 8 – the model manometer.

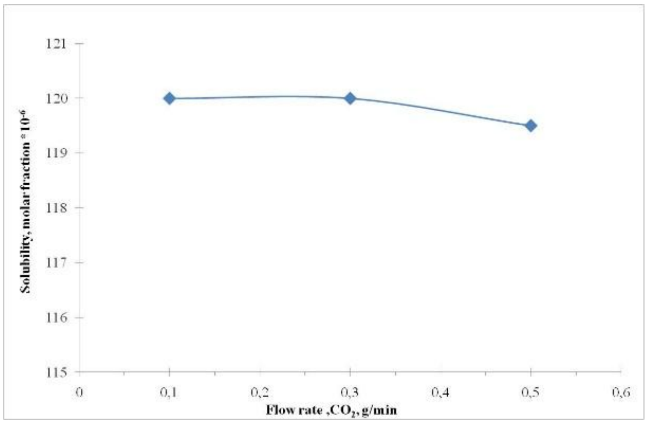

Fig. 2. Ammonium palmitate solubility dependence on a supercritical carbon dioxide flow rate at P=10 MPa and T=308.15 K.

During experiments ammonium palmitate solubility dependence in supercritical carbon dioxide from a fluid flow rate at P=10 MPaand T=308.15 K, and solubility on isotherms 308.15-333.15 K in the range of pressure from 10 to 32 MPa at a fluid mass flow rate about 0.3 g/min are investigated. Besides, the solubility description according to the Peng-Robinson equation of state [1] is carried out, thus as the adjustable parametresthe binary interaction parameter and ammonium palmitate saturated steam pressure are used. Ammonium palmitatecritical properties calculation is carried out according to Dorn's method [2]. Critical parameters are T_{cr}=1100 K, P_{cr} = 4.1 MPa. The CO_2critical parameters are taken from [3] Results are presented in fig. 2-4.

The binary interaction coefficients, saturated steam pressure and description results mean square deviation from experimental points received at the description are presented in table 2.

Table 2. "Supercritical carbon dioxide – ammonium palmitate" systembinary interaction coefficients

Temperature, K	308,15	318,15	328,15	328,15	333,15
Binary interaction coefficient, m_{ij}	1,92	1,94	1,86	2,15	1,76
Steam pressure, Pa	1,3	2,3	3,0	8,3	3,1
Thedescriptionerror, %	1,7167	7,1854	21,4461	4,8652	8,7253

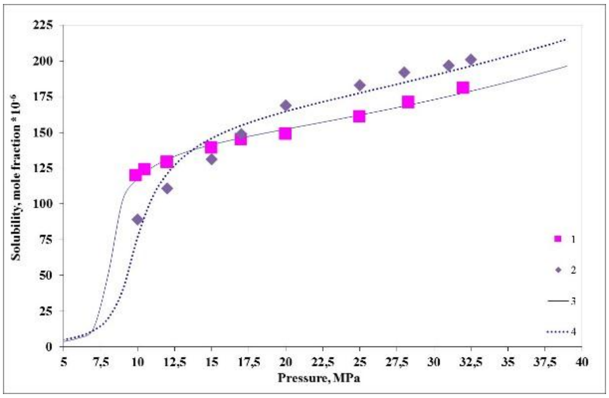

Fig.3. Ammonium palmitate solubility in SC-CO$_2$: *1* – experimental points at T=308.15 K; *2* – experimental points at T=318.15 K; *3* – the description at T=308.15 K; *4* – the description at T=318.15 K

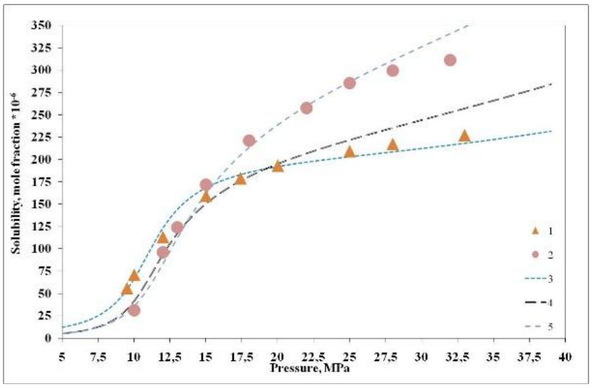

Fig. 4. Ammonium palmitatesolubility in SC-CO$_2$: *1* – experimental points at T=328.15K; *2* – experimental points at T=333.15 K; *3, 4* – the description atT=328.15 K;*5* – the description atT=333.15 K

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ORY-11

INVESTIGATION OF STRUCTURE AND PROPERTIES OF AEROGELS DEPENDING ON CONDITIONS THEIR SYNTHESIS

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Aerogels are mesoporous solids with unique properties such as high porosity and specific surface area, low density as well as outstanding thermo insulating properties. Due to the combination of these properties, aerogels are of interest to many fields of science.

Aerogel synthesis usually involves several sequential steps. The first step is a preparation of a precursors colloidal solution called sol. Next there is the step of hydrolysis and condensation (convertion sol into the gel). The obtained gel is then subjected to aging and washing. The result is a gel called a liogel. To transform the liogel into aerogel it is necessary to remove solvent from gel pores without damage of the fine gel structure. As a rule a supercritical drying (SCD) is used to remove the solvent. In our previous works we have shown that the nature of supercritical fluid (SCF, the solvent used for SCD) affects the parameters of the resulting samples.

Furthermore, it is obvious that the solvent of the starting sol affects the progress of hydrolysis and condensation processes occurring in solution. Thus we have supposed that solvent should also have an effect on the structure and properties of the obtained aerogels.

The purpose of this work was the study of the influence of solvents (such as SCF and solvent used for the sol preparation) on the structure and properties of the resulting aerogels samples.

The objects of the study were aerogels based on Al_2O_3, ZnO, NiO, Cr_2O_3, and aerogels based on mixed oxides Al_2O_3-ZnO with different components ratios.

We have investigated aerogels parameters such as specific surface area, phase composition, and studied by TEM morphology of the aerogels. For aerogels based on aluminum oxide the temperature dependence of the main characteristics was investigated.

A financial support from the RSCF (Grant no. 14-33-00017) is greatly acknowledged.

ORY-12

VISCOSITY MEASUREMENTS AS A SIMPLE CONTROL METHOD OF A FATTY ACID ETHYL ESTERS AMOUNT IN THE BIODIESEL FUEL SAMPLES

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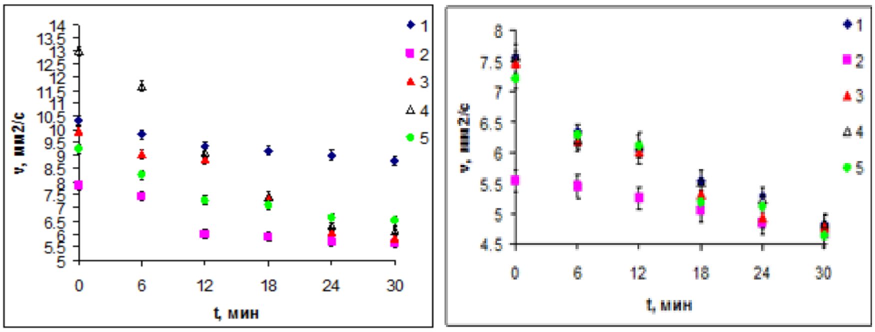
Knowing the biodiesel fuel viscosity is of a great importance for the design of equipment for synthesis processes of biofuels for diesel engines. In respect of an engine with high fuel viscosity usually forms larger drops after injection, which may lead to poor atomization of fuel, increase in engine deposits, high power consumption and wear of the pump and the fuel injector components. On the other hand, a low viscosity fuel can't provide sufficient lubrication for the fuel injection pumps, there are the result of leakage and increased wear [1,2]. Figures 1*a*) and 1*b*) shows the dependence of biodiesel kinematic viscosity on the transesterification reaction duration carried out under supercritical fluid conditions at temperatures of 623 K and 653 K and a molar ratio "Ethanol – rapeseed oil" 12: 1; 18: 1, both without a catalyst and in the presence of Al_2O_3, ZnO/Al_2O_3, MgO/Al_2O_3 and SrO/Al_2O_3 as the catalyst.



a) *b*)

Fig.1. Dependence of the kinematic viscosity on the transesterification reaction duration of the samples obtained 1) without catalysts and catalyst 2) Al_2O_3, 3) ZnO/Al_2O_3, 4) MgO/Al_2O_3, 5) SrO/Al_2O_3 on the timing of the process: *a* - at a molar ratio "ethanol - rapeseed oil' 12: 1 and the process temperature of 350°C; *b* - at a molar ratio 'ethanol - rapeseed oil' 18: 1 and the process temperature of 380°C.

According to data obtained by increasing the duration of the production process of biodiesel reaction product decreases the viscosity, as well as with increasing temperature, and the alcohol: oil molar ratio. Based on the kinematic viscosity values of the biodiesel samples using formula (1) were determined fatty acids ethyl esters (FAEE) content in the reaction product. De Fillipis et all. reported viscosity measurements as a potential analytical method for calculating the concentration of fatty acid methyl esters in the biodiesel fuel samples [3]. We have modified this method to calculate the content of fatty acid ethyl esters by a simple correlation with kinematic viscosity of the transesterification reaction products obtained from rapeseed oil with ethanol under supercritical fluid conditions [4]. Correlation parameters have been established on a large array of samples with different amount of fatty acid ethyl esters.

FAEE contents in the obtained samples were calculated using the formula:

$$C = A * \mathrm{Ln}\,(v) + B \quad (1)$$

where: C – FAEE concentration in a biodiesel sample %; v – kinematic viscosity mm^2/s, and A = -51.06; B =174.44 - coefficients.

The constants of the equation: A = -51.061 and B =174.44 for the approximation of the rapeseed oil are determined by a linear dependence of viscosity of two hypothetical samples of the reaction product, in which there was no alcohol component.

Correlation proposed by Fillipis and Sousa [3,5] were obtained for biodiesel samples produced by traditional catalytic method at a temperature of 60-70 ^{0}C. However, these correlations won’t previously described for biodiesel samples obtained under supercritical fluid conditions. In accordance with the results of chromatography, FAEE concentration for the sample obtained at a temperature of 653 K lower than that of the sample obtained at 623 K. This phenomenon is the result of thermal decomposition of esters of unsaturated fatty acids to form the ortho-esters of fatty acids. Thus, for the first time found that viscous correlations of Fillipis and Sousa is not universal and fully correct for the reaction product carried out in SCF-conditions.

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ORY-13

ACTIVITY OF IMMOBILIZED FLUORINE-SUBSTITUTED TETRAPHENYLPORPHYRINS IN THE PHOTOSENSITIZED OXIDATION OF OLEFINS IN SUPERCRITICAL CARBON DIOXIDE

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It is known that supercritical carbon dioxide (SC-CO_2), due to a long (~ 5ms) lifetime of singlet oxygen $^1O_2$ (in comparison with organic solvents), may be a promising medium for photosensitized oxidation of aromatic and steroid olefins in the presence of fluorine-substituted tetraphenylporphyrins (particularly, pentafluorotetraphenylporfirin TPPF20) with a sufficient solubility in the SC-CO_2 and activity in the $^1O_2$ photosensitization. It has been shown that, in the presence of porphyrins immobilized on low-molecular weight fraction of the MF-4SK copolymer (copolymer of tetrafluoroethylene and perfluorovinyl ether containing sulfogroups), photooxidation of cholesterol (a target substrate) proceeds with the formation of 6β-formyl-B-norholestan-3β,5β-diol – a substance with a potential antitumor activity. Our objective here is to obtain porphyrin-containing polymer catalysts via TPPF20 immobilization on fluorinated polymers in the SC-CO_2 medium and to study the catalytic properties of such systems in the photo-oxidation reactions of anthracene and cholesterol.

It has been shown that, by varying the conditions of immobilization in the SC-CO_2 medium – the MF-4SK film thickness (80-280 microns), process time (5-180 minutes), temperature (50-90 °C) and pressure (10-20 MPa) - the amount of immobilized TPPF20 can be controlled from $1 \cdot 10^{-9}$ to $4 \cdot 10^{-8}$ mol/cm^2. The increase of temperature and pressure increases the amount of TPPF20 in the polymeric matrix. We observed formation of the target 6-formyl-B-norholestan-

3,5-diol in cholesterol photooxidation in the SC-CO_2 medium in the presence of the prepared porphyrin-containing MF-4SK films. Thus, porphyrins immobilized on MF-4SK films are promising photosensitizers for cholesterol oxidation in the SC-CO_2 medium, with the purpose of obtaining products with antitumor activity.

This work was supported by RFBR (grant № 13-03-12029 ofi-m).

ORY-14

MODELING OF SOLUTES IN SUPERCRITICAL FLUIDS

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Nowadays the most perspective alternative to organic solvents are supercritical fluids (SCF), substances in the supercritical states. For example, supercritical carbon dioxide (SCCD). SCF are successfully used in the chemical industry, particularly, in the processes of extraction, sorption, chromatography, drying, etc. The main property in these processes is solubility of solutes in SCF. Therefore, there is a necessity in predicting the solubility of various substances in SCF.

The purpose of this work is to develop a software package to predict the solubility of various substances in SCCD.

This work explores the possibility of creating a universal technique of modeling the solubility of substances in SCCD. It is not possible to build a model that could accurately predict the solubility of compounds in a wide range of substances because of qualitative difference in the structural characteristics of the compounds. Therefore, to improve the predictive performance, in this paper the method of pre-classification was used.

The main purpose of the classification procedure is clusterization of substances by down into groups with similar characteristics.

The models used in this paper were created using the method of Quantitative Structure-Activity Relationship (QSAR). The results predict solubility values showed good correlation with experimental data.

There is a database (DB) which contains data about the solubility of six hundred substances in SCCD and software that allows working with this DB and model solubility of these substances with semi-empirical equations.

The research is supported by the Ministry of Higher Education and Science of The Russian Federation within the framework of basic component of the State Assignment.

ORY-15

FRACTIONAL COMPOSITION OF GROUND RAW MATERIAL AND SUPERCRITICAL FLUID EXTRACTION KINETICS

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In the present work, the results of ground raw material volume distribution measurements (with respect to particle size), made employing particle size analyzer Mastersizer 2000 (produced by Malvern), for typical batches of sizes 400-630 μm, 800-1000 μm, and 1000-1250 μm are discussed; pumpkin seeds are chosen as an example. Despite that every batch was produced via sieving, all measurements clearly indicate the existence of two characteristic modes for individual samples: the first one corresponds to the fraction of small, "dust", particles (~50-100 μm in diameter) with large specific surface area (SSA), and the second – to the fraction of ordinary particles (with sizes corresponding to the sieve mesh size). These results are also confirmed by microscopic observations of these batches. Therefore, it is demonstrated that sieving analysis cannot be always used as a reliable method for the packed bed structure investigation.

Obviously, supercritical fluid extraction kinetics is highly influenced by the particle size distribution in the batch [1], and in particular, by both the volume fraction of dust particles and the SSA of ordinary particles. Modeling approach based on the consideration of polydisperse packed beds containing a significant volume fraction of dust particles not only describes the prolonged duration of the initial (linear) extraction step, but closely reproduces the overall extraction curve (OEC) during the second (non-linear) extraction period. Simple asymptotic expansions for the duration of the linear extraction step and for the OEC at the second step are also derived for typical extraction conditions.

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ORY-16

SUPERCRITICAL FLUID EXTRACTION AS A METHOD OF THERMOCHEMICAL ACTIVATION OF WOOD CELL WALL

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Investigation of impact of thermochemical activation of lignocellulose matrix by method of supercritical fluid extraction (SCE) was carried out in this study. Changes of the chemical composition and morphological structure of the wood substance during this treatment were obtained. The experiments showed that wood substance had high structure heterogeneity. It appears as a presence of labile and stable regions of lignin-carbohydrate formations distributed in cell wall and middle lamellae.

The concept of thermodynamic incompatibility of lignin-carbohydrate matrix [1] allows considering of supercritical fluid technologies (SCFT) as a method for changing the structure and properties of biocomposite on the molecular level. The important aspect of SCFT application for the processing of plant raw materials is possibility of the use of SCFT for the deep delignification of wood and for the extraction of its components for the production of valuable high-quality by-products [2].

However, for a more in deep study of the ultrastructure of wood matrix we suggest the application of supercritical treatment as a method destroying the thermodynamical equilibrium of wood matrix and the physico-chemical model of structure and self-assembly of wood substance as a scientific approach for studying specific features of ultra-micro and submolecular structures of a coniferous wood matrix.

Juniper wood (*Juniperus Communis* L.) aged from 80 to 90 years was used as the representative experimental sample. Changes taking place in the cell wall during the SCE treatment were recorded by the methods of scanning electron microscopy (SEM), X-Ray analysis, FTIR- and UV-spectroscopy.

It is known that main components of the SCE impact are high temperature and pressure [3], and modifiers addition due to the absence of pure SC-CO_2 delignification impact [4]. Ethanol, isopropanol and acetic acid were chosen as modifiers. Acetic acid has the best delignification ability proven by FTIR-spectroscopy.

The analysis of SCE-treated wood samples showed significant differences taking place due to decrease of relative content of lignin (K value is 0.603 for acetic acid, 0.615 for ethanol, and 0.643 for isopropanol, 0.649 for the untreated wood). The analysis of the chemical composition confirms this data.

The investigations of the SEM-micrographs showed that lignin-carbohydrate complexes of intercellular substance (solid solution of hemicelluloses in lignin) had the highest lability while the helical structures of cellulose microfibrils in the secondary cell wall layer S_2 were the most stable.

Thus, the obtained experimental data confirm the statements about possibility of consideration of wood lignin-carbohydrate matrix as nanobiocomposite having high structure heterogeneity, while critical impacts on wood matrix lead to the increase of thermodynamic incompatibility of a system and a diffusion of lignin fragments and carbohydrate components away from wood substance.

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ORY-17

NEW SYNTHESIS AND PROPERTIES OF HYBRID NANOMATERIALS BASED ON ULTRA-POROUS CELLULOSE

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Nowadays, ultra-porous materials based on cellulose attract attention due to unique characteristics such as low density (0.004-0.2 $cm^{-3}g$), high porosity (up to 99.8%) and large surface area (up to 1000 m^2g^{-1}). Introduction the noble metal nanoparticles (Pt, Ag, Au) possessing catalytic and antibacterial activity, into the polymeric matrix allows to expand the application of these materials.

For the first time, the new technological approach, including two original methods - fluid technology and metal-vapor synthesis (MVS), for getting silver-carrying ultra-porous cellulose is developed.

The approach is based on the modification of microcrystalline cellulose with silver organosol, followed by obtaining the metal-carrying gel and drying under supercritical CO_2.The series of hybrid ultra-porous cellulose materials with a metal concentration of 0.1 - 1.8 wt. % and average particle size - 10 nm (TEM data) has been prepared and studied.

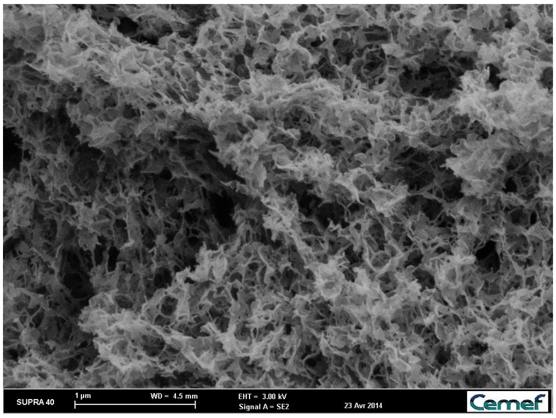

Fig.1. SEM image of ultra-porous cellulose loaded with silver NPs

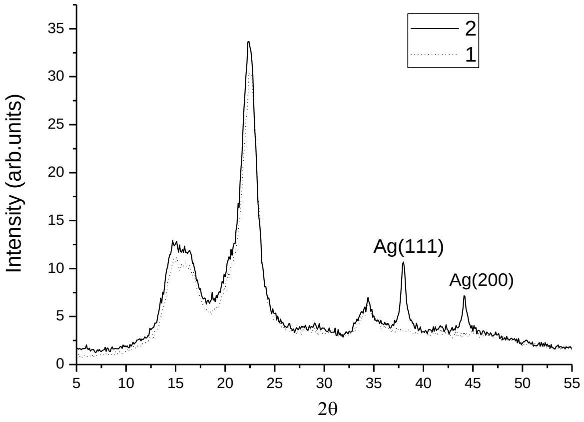

Fig. 2. XRD patterns of initial microcrystalline cellulose (1) and cellulose loaded with silver NPs (2)

The specific surface area and density of the obtained materials are about 250 m^2g^{-1} and 0.13 $cm^{-3}g$, respectively. The silver particles impregnated into cellulose with MVS have uniform distribution whereas the modification of porous polymer with organosol does not give similar result.

The XRD patterns of cellulose with silver nanoparticles (Fig.2) have peaks characteristic of native cellulose. These peaks are located at 15°, 16°, 12.5° and 34.8° which are correspond to (101), $(1\bar{1}0)$, (200) and (400) crystallographic plane reflections, respectively. Additional peaks at 38° and 44° correspond to (111) and (200) crystallographic plane reflections of silver. Comparison of the initial and metal-carrying cellulose (Fig.2) revealed that the modification of cellulose with silver nanoparticles does not alter its structure and crystallinity. The average size of silver particles was calculated using Selyakov-Scherrer equation and was 10 nm, which well agreed with TEM data.

The Ag 3d XPS spectrum exhibits two peaks with binding energies of 369.4 and 375.3 eV, corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ states, respectively. A positive shift of Ag $3d_{5/2}$ peak by 1.13 eV relative to that of pure silver foil is assigned to particle size effect. Comparison of the Ag 3d, C 1s and O 1s spectra, measured under various bias voltages applied to the sample, showed that the silver atoms in the nanocomposite are in a zero-valent state, and the metal surface is passivated by low- molecular weight hydrocarbon compounds.

This work was supported by Russian Foundation for Basic Research (grant 14-03-01074) and Russian Academy of Sciences (DCMS Programs 4 and 6).

ORY-18

MODELING SCF CHROMATOGRAPHY IN SUPERCRITICAL CARBON DIOXIDE WITH COSOLVENTS USING MARGOLUS CELLULAR AUTOMATA

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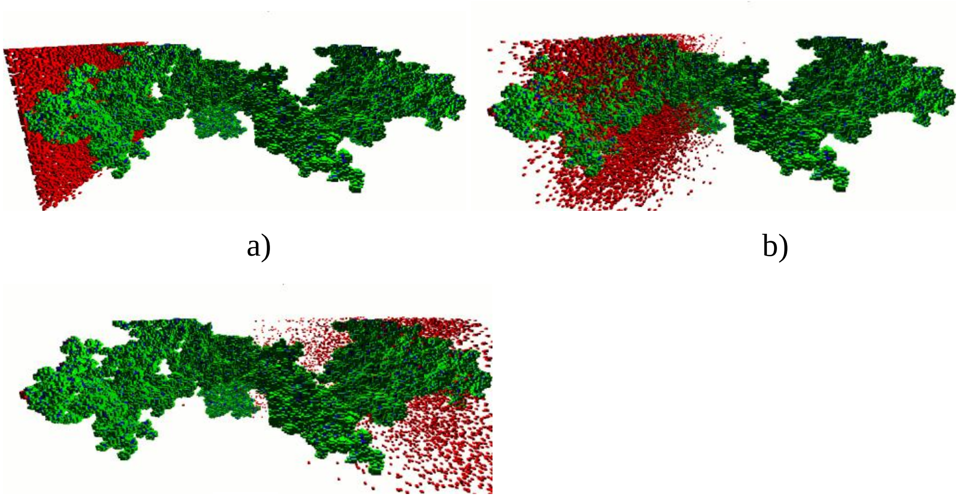
Currently in the world is widely developed a branch of supercritical fluid technology. Supercritical fluid chromatography (SFC) is used to separate a mixture of substances, as it has high speed and allows separating the enantiomers and higher hydrocarbons [1].

The most common supercritical fluid – carbon dioxide, which is a non-polar solvent. Therefore, the use of SFC with pure carbon dioxide as eluent limited due to its low capacity for dissolving polar substances. Most modern separation techniques using SFC is developed with the use of cosolvents often lower alcohols - methanol, ethanol (hydrogen bond donor) and acetonitrile (hydrogen bond acceptor).

The concentration of cosolvent in the mobile phase strongly influences the separation process. That is why for optimization the context of cosolvent should be scanned in a wide interval. That is the reason why SFC modeling using cosolvents in order to determine the optimum process conditions and the concentration of solvent in the mobile phase is an actual task.

In this paper we developed a model of supercritical fluid chromatography with a co-solvent based on cellular automata (CA) with Margolus neighborhood. It is based on a model of adsorption and diffusion in porous solids in supercritical carbon dioxide [2, 3]. Initially, there were three classes of substances - the solvent (fluid), dissolved active substance and solid (aerogel - column filler). Was added a new class of materials – “cosolvents”, which has a number of specific properties.

In modeling was used the three-dimensional cellular automata. As a model of a porous solid-aerogel was used a model of slightly overlapping spheres. For working with large structures an algorithm was implemented using technologies of parallel computing on graphics cards CUDA nVidia company. The aerogel structure was generated to correspond the structure which was obtained in the experiment. On the surface of the aerogel were disposed cosolvent particles. The proportion of surface coverage was calculated according to the Langmuir adsorption theory based on the adsorption energy obtained experimentally. In the initial state of the CA, the input of the column was filled with mobile cells (Figure 1) - the active substance.



a) b)

c)

Figure 1. The process of passing the substance through the column during the simulation:
a) at the initial time; b) at time τ; c) final stage of the process

Consider each movable cell, which reached the exit from the column, it is possible to obtain graphs similar to chromatograms and process them in the same way as experimental data.

The research is supported by Russian Foundation for Basic Research within the project № 14-08-91336 ННИО_a.

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ORY-19

STUDIES OF ANTHRACENE SOLUBILITY IN PURE AND MODIFIED SUPERCRITICAL CARBON DIOXIDE

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As part of the task of optimizing the regeneration process of nickel-molybdenum kerosene hydrotreating catalysts «Criterion514» and «DN 3531" produced by «Criterion Catalyst and technology», solubility of anthracene as a conditional model of coke on the catalyst surface in pure and modified supercritical carbon dioxide in the dynamic mode was studied in this work.

In this study, an experimental unit that allows implementing the solubility measurement and supercritical fluid extraction research process in order to regenerate the catalysts using pure and modified fluid extractant was created. Diagram of the apparatus, as well as research methodology is presented in work [1].

The necessity of investigating the solubility in pure anthracene SC CO_2 associated with many previously published works [2-6], the data which differ by more than three times. In this paper a study of solubility was performed according to the procedure described above. The results in comparison with the literature data presented in Fig. 1. It can be seen that the results obtained in the present study are within the range of previously obtained data, but do not repeat them.

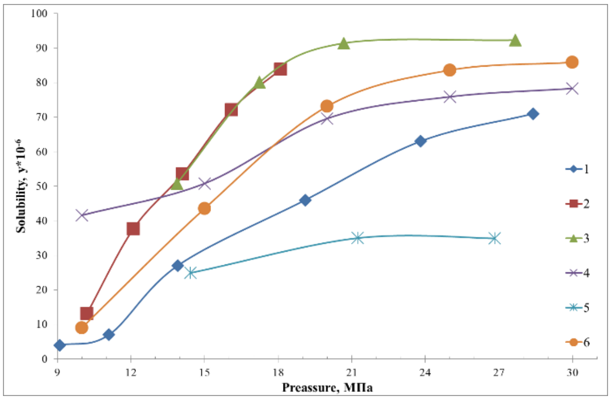

Fig.1. Solubility of anthracene in SC CO_2 at T=308,15 K, 1 – [2], 2 – [3], 3 – [4], 4 – [5], 5 – [6], 6 – present work.

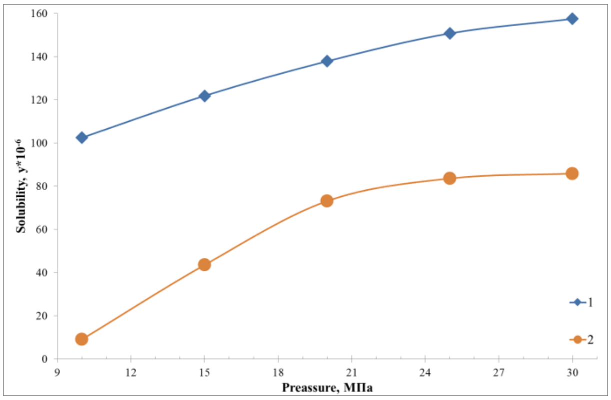

Рис. 2. Solubility of anthracene in pure (1) and modified (2) SC CO_2 at T=308,15 K

This is due to the fact that in works [2, 3] the solubility was studied in static mode, allowing obtaining the maximum equilibrium concentration of an analyte in the fluid. In the remaining works, dynamic measurement mode of solubility studies was implemented, but the flow rate of gas in all cases ranged from 0.5 to 1.5 g / min, which is significantly greater than the flow rate in the framework of the present work. Most likely, these flow rates did not allow to reach equilibrium concentration of solute in the fluid flow, which in turn gave lower values of solubility.

Study of the effects of different polar additives on solvent power of supercritical fluids is also very important. In previous studies [7], it was found that dimethyl sulfoxide (DMSO) in an amount of about 5% by weight of CO_2 can significantly improve the regeneration efficiency of various types of catalysts. However, no data on the effect of DMSO on the solubility of anthracene in supercritical carbon dioxide are present in the press. Therefore, the effect of 5%

by weight. DMSO on the ability of supercritical carbon dioxide to dissolve anthracene was investigated. Studies were also carried out at T = 308.15 K in the temperature range from 10 to 30 MPa. The results are given in Fig. 2.

Data shows that the use of dimethyl sulfoxide can significantly intensify the process of removing the contaminant from the surface of the catalyst.

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P-1

HETEROMETALLIC Au-Pt NANOCOMPOSITES OBTAINED WITH SUPERCRITICAL CARBON DIOXIDE AND METAL-VAPOR SYNTHESIS

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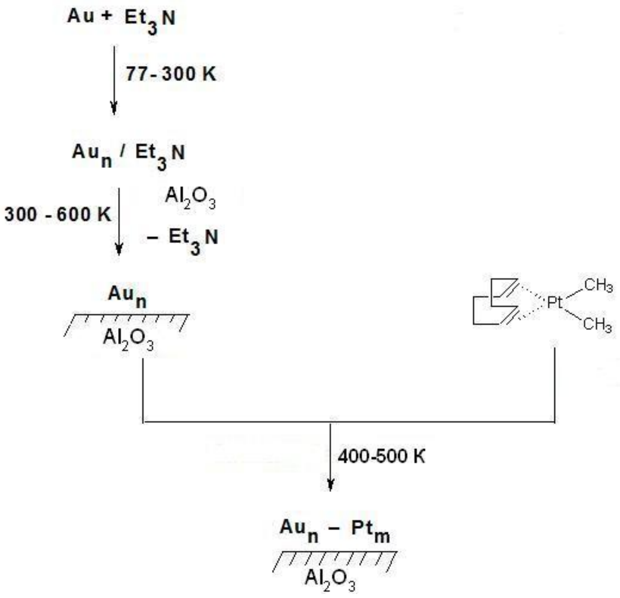
Bimetallic Au-Pt/Al_2O_3 nanocomposites were synthesized using supercritical carbon dioxide (SC CO_2) (fluid method) and metal-vapor synthesis (MVS). The nature of electronic properties of the nanocomposites was studied by X-ray photoelectron spectroscopy (XPS).

Catalytic activity of the nanocomposites was analyzed in the reaction of CO oxidation into CO_2.



Bimetal catalysts were synthesized by successive immobilization of metals on the support by combination of fluid and MVS techniques.

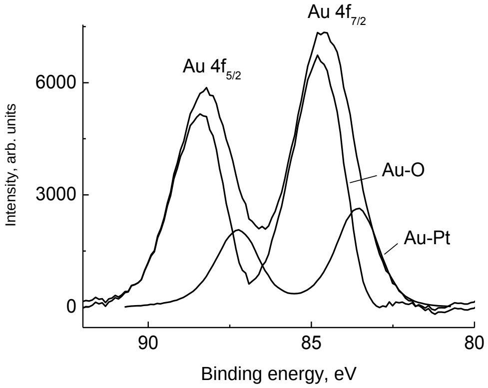


Fig. 1. Fitting the Au 4f spectrum of Au-Pt/γ-Al_2O_3 with Au-Pt and Au-O (Al_2O_3) states.

The Au 4f spectrum presented as a sum of two states related to the Au–Pt system, and the other to Au-O-Al one. The relative intensity of the first state is 26%.

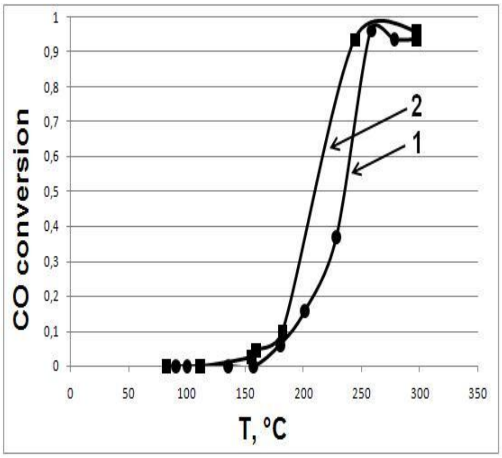


Fig. 2. The dependence of catalytic conversion CO into CO_2 on temperature for the Pt/Al_2O_3 sample: 1- heating, 2 -cooling.

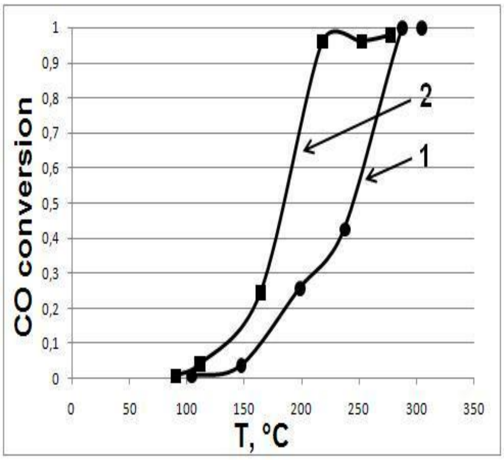


Fig.3. Pt-Au/Al_2O_3 (Au - MVS, Pt – SC CO_2): 1- heating, 2 -cooling.

For the Pt/Al_2O_3 and Pt-Au/Al_2O_3 samples, 97% conversion was observed at 260°C and 220°C, respectively. It indicates the strong activation. Therefore, an addition of gold enhances the activity of Pt/γ-Al_2O_3.

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P-2

PHASE EQUILIBRIA OF CO_2-NATURAL HYDROCARBON SYSTEMS AT SCF STATE

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This paper discusses options for phase equilibrium in binary CO_2-natural hydrocarbon mixtures in fluid condition. Systems consisting of components of different volatility under sub- and supercritical conditions have been studied.

Liquid hydrocarbon oil components (80-90% alkanes, naphthenes, aromatics) at SCF state [1] may form with CO_2 binary mixtures of type I, where both components have similar critical parameters.

In binary mixtures containing *n*-alkanes the phase equilibria in a fluid state are carried out at temperatures above the critical temperature of the high-melting and high boiling component.

In the *p*-*T* phase diagram of binary type I mixture, the critical curve generally has a maximum pressure (see figure 1).

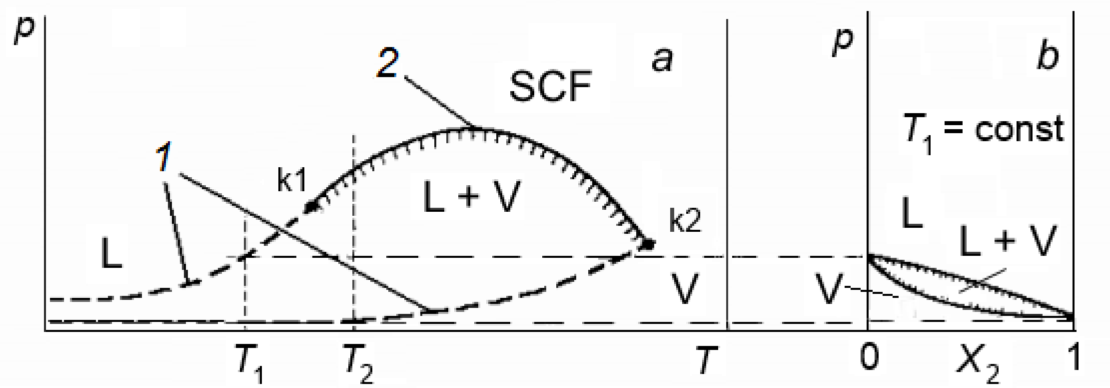

Fig.1. a) The *p*-*T* phase diagram of binary type I system. *1* – saturation curves for pure components, *2* – critical curve; b) The *p*-*x* phase diagram of binary type I system.

Index 1 corresponds to the volatile solvent in the figure and index 2 corresponds to the low-volatile solute. Here, the melting point (T_2) of low-volatile component is above the critical temperature of volatile component 1. Saturation curves for pure components 1 end at the critical points of pure components k1 and k2. Single phase regions for liquid (L) and for vapour (V) are below k1 and k2 and single phase region for SCF is above. The components mix in arbitrary proportions above the critical curve k1-k2 in single phase region of SCF.

The heterogeneous region for L+V binary system lies below the critical curve k1-k2. In the state parameters region, above the critical curve k1-k2, the low-volatile matter can be completely dissolved in the SCF. This behaviour of the critical curve is observed for the binary systems with different critical temperatures of components.

Increasing the number of components for the CO_2 – *n*-alkane systems leads to SCF heterogenization at temperatures above the critical parameters of the volatile component.

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P-3

AQUEOUS SOLUTIONS OF ELECTROLYTES AT HIGH TEMPERETURE AND HIGH PRESSURE: RAMAN SPECTROSCOPY

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System water - NaNO$_3$. The behavior aqueous solution of NaNO$_3$ (5 m %) was investigated by Raman spectroscopy in the temperature range from 25 up to 350ºC at a constant pressure 100 MPa. It appears that solution is suitable to study the phenomenon of ions "coupled". The symmetry of anion is violated in aqueous solution at low temperature and Raman band of bending vibration ν_4 is fissiled because there is the degeneration of vibration levels. The increase of temperature provides the renewal of symmetry, and Raman spectra of the solution and pure NaNO$_3$ coincide as temperature achieves 300ºC. The dielectric constant of water decreases as temperature increases and water cannot screen of charged Na$^+$ and NO$^-_3$.

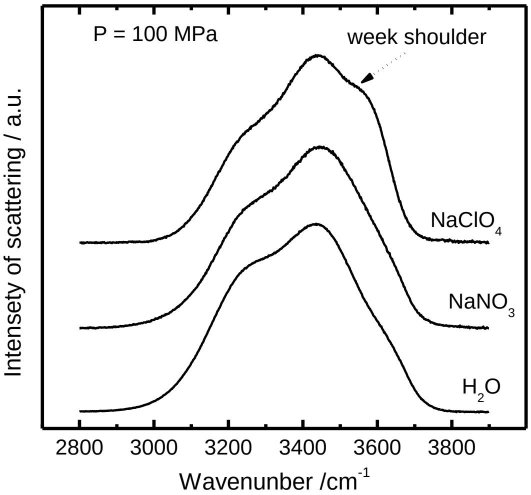

Fig.1. Raman spectra of water and aqueous solutions: NaNO$_3$ (5 m %), NaClO$_4$ (5 m %).

System water - H$_3$PO$_4$. Raman spectra of aqueous solution H$_3$PO$_4$ were obtained at constant pressure 100 MPa in the temperature range 25 - 400ºC. Spectra change poorly at temperatures from 25 up to 250^{o}C, although composition of the solution changes continually, having began from low temperatures. Sharp change of the spectrum and intensity of scattering begin at 300^{o}C only. Probably a new compositions appear and concentration of anion [PO$_4$]$^{3-}$ decreases strongly. The part of substances falls in sediment. The solution becomes opaque.

When aqueous solutions are investigated the most discussed question is effect of ions on hydrogen bonding network of water molecules. As a result, the conception of *kosmotropic* (*structure-strengthening)* and *chaotropic (structure-weakening)* ions became generally accepted [1,2]. Kosmotropic stabilize the structure of water while influence of chaotropic on network of hydrogen bonding is substantially. This conception is demonstrated in Fig.1, which shows the effect of some electrolytes on the Raman spectra of stretching vibration mode of H_2O. The important feature is a week high frequency shoulder in the band's contour of aqueous solution $NaClO_4$. This singularity is commonly assigned to the non-bond or week bond OH-groups.

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P-4

DEVELOPMENT OF METHOD FOR THE PREPARATION OF PHARMACEUTICAL SUBSTANCES FROM "SAPARAL" BY SUBCRITICAL WATER

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Triterpene glycosides are classical objects of study of modern medicinal chemistry due to their wide spectrum of biological activity. Aralosides A, B and C are the major biologically active substances in an extract from the roots of Aralia manchurian *Aralia mandshurica* Rupr. Aralosides A, B and C are glycosides of oleanolic acid (OA) [1] (Fig.1.)

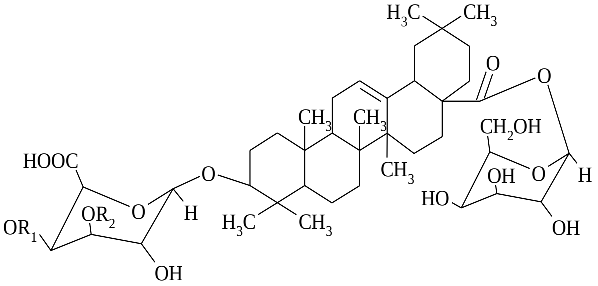

Fig. 1. Aralosides: **A** (R_1 = L - arabinose, R_2 = H), **B** (R_1 = R_2 = L - arabinose), **C** (R_1 = D- galactose, R_2 = D- xylose

The aim of this study is the development of the method to obtain the oleanolic acid from the triterpene saponin of pharmaceutical substance "Saparal" (FS 42-1924-82) by subcritical water.

Using water in the subcritical state allow us to change the selection of organic solvent on variation of temperature and pressure of water at which the properties of medium (density, ion product, dielectric constant, viscosity, etc.) are optimal for the particular organic reaction. Hydrolysis of aralosides by subcritical water was realized in according to methodology presented in [2]. The hydrolysis of triterpene saponin in SBW was studied in the temperature range from 120°C to 240°C, masses of raw plant material and process duration. Products hydrolysis of the triterpene saponin were identified by NMR, IR- spectroscopy and HPLC-MS. A maximal yield of OA is obtained at 210°C.

Thus a method to obtain oleanolic acid (OA) and its derivatives by hydrolysis in subcritical water from pharmaceutical substance «Saparal» is developed.

Acknowledgements.

This research was supported by the grant of the RFBR (project № 13-03-12271 OFI-M). The work was carried out with using the equipment center of collective using "Molecular Spectroscopy" of Institute of Physical and Organic Chemistry at Southern Federal University.

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P-5

DEVELOPMENT OF TECHNIQUE FOR OBTAINING A "DESIGNED" A MIXTURE BASED ON AMMONIUM GLYCYRRHIZINATE

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Glycyrrhizic acid (GA) (Fig. 1) is the major triterpene saponin of licorice (Glycyrrhyza glabra L.).The intense research indicates that glycyrrhizic acid and its derivates have wide range of pharmacological activities such as anti-viral, anti-inflammatory, anti-oxidant, anti-ulcer, anti-cancer, and anti-HIV.

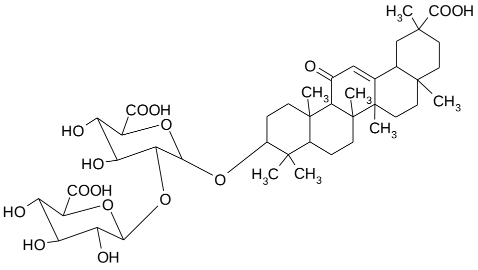
Fig. 1. Structural formula of GA

The products of metabolism of GA are glycyrrhetinic acid (GLA) and its mono-glycoside (mono-GLA). The glycyrrhetinic acid is one of the medicinal substances that already widely used in the market. It was shown that m-GLA has a number of advantages over the pharmaceutical GA [1]. However, the using of m-GLA is limited by difficulties associated with the methods of its production [2]. Stating their chemical importance and their pharmacological potentialities, the development of novel synthetic schemes for preparation of products the metabolism GA is an important and useful task in organic and medicinal chemistry and represents a field of current research and growing interest.

The aim of this study is the development of the method for transformations of the ammonium glycyrrhizinate in subcritical water (SBW) in order to obtaining a mixture of pharmaceutical substances. In this work, we investigated the transformation of GA in SBW at different temperatures from 100°C to 300°C. The experiment was performed in the SBW as described in [3, 4]. Products of transformations of GA were identified by HPLC and ESI MS. Figure 2 are shown the typical chromatograms of the hydrolysis products that were obtained in subcritical water at t= 160°C.

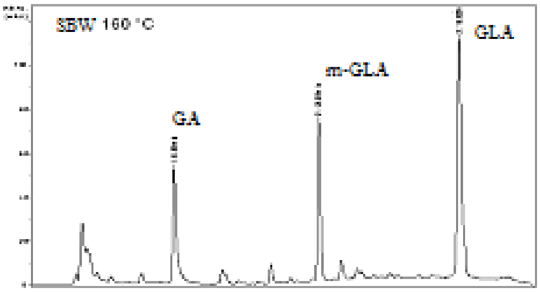

Fig. 2. The chromatogram of the reaction mixture at 160 °C.

From ESI-MS data the major substance of the hydrolysis at 160°C was identified as 3-monoglucuronyl-glycyrrhetinic acid (mono- GLA). Mass spectra of the products of hydrolytic transformation of GA obtained in SBW at 170° C contain peaks: *m/z* 821.31 of deprotonated ion $[M^{GA}\text{-}H]^-$, *m/z* 645.29 of deprotonated ion $[M^{m\text{-}GLA}\text{-}H]^-$ [5] and the *m/z* 469.28 of deprotonated ion $[M^{GLA}\text{-}H]^-$.

It was shown that variation of the only one parameter of the process (temperature) alters the composition of the hydrolysis products. For example, at 160°C the major substance in the obtained composition observed the mono-GLA, whereas at 190°C the major substance of the composition is the targeted product of hydrolysis – GLA.

Thus an ecologically clean procedure for obtaining a mixture of pharmaceutical substances by hydrolysis in subcritical water of glycyrrhizic acid was developed. The yield of GLA and its mono-glycoside (mono-GLA) in the product obtained in the medium of subcritical water is comparable with its yield obtained by the traditional method. However, the process is three times faster. Moreover, this method does not require use of expensive and toxic organic solvents.

Acknowledgements. This research was supported by the internal grant of the Southern Federal University (project № 213.01-2014/005ВГ). The work was carried out with using the equipment center of collective using "Molecular Spectroscopy" of Institute of Physical and Organic Chemistry at Southern Federal University.

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P-6

FEATURES OF THE ISOLATION OF BIOLOGICALLY ACTIVE SUBSTANCES OF VARIOUS TYPES OF LICHENS IN SUB- AND SUPERCRITICAL CONDITIONS

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Lichens are symbiotic organisms consisting of fungus and algae [1,2]. Currently identified more than 20000 species of lichens that inhabit diverse ecosystems from the Arctic tundra to desert [3]. Studies have shown that these slow-growing organisms contain different kinds of biologically active substances, in particular, usnic acid and lichen polysaccharides (chitin-glucan complex - CGC). Lichens are widespread in harsh climates in areas with arctic and subarctic climate, and in these conditions thalli is an active accumulation of valuable biologically active substances.

Thus, the aim of this study was the select the biologically active substances (BAS) from raw materials of lichens by the extraction by carbon dioxide in the sub- or supercritical (SKFE), and evaluation of the impact of extraction conditions on the yield and properties of biologically active substances.

The objects of the study were the thalli of lichen genera Cladonia and Peltigera, growing in the subarctic areas (Russky Kuzov Island, White Sea). A comparative analysis of the yield of extract of lichen acids, including usnic acid obtained by varying process parameters: pressure, temperature, duration of the extraction, the extractant feed rate, the introduction of co-solvents of different natures and polarities (acetone, ethanol and methylene chloride), as well as from lichen generic accessories was performed. Identification and quantification of usnic acid was performed by liquid chromatography-quadrupole mass spectrometer LCMS-2020 (Shimadzu, Japan) using DUIS ionization. The structure of the selected chitin-glucan complex was evaluated by IR spectroscopy with FTIR spectrometer Vertex 70 (Bruker, Germany).

It was established that the yield of extract of lichen acids increases with pressure and temperature. The introduction of co-solvents can increase the yield of the extract by 1.5-2 times. The maximum yield of usnic acid is observed at SKFE with the addition of a co-solvent of methylene chloride and was about 3% of absolute dry weight of materials. The yield of extract of lichen acids from lichen genus Peltigera higher than that of the lichen genus Cladonia. However, the content of the target component (usnic acid) in the extract obtained from genus lichen Peltigera, significantly lower than the extract of the genus lichen Cladonia.

IR spectroscopy shows that the structure of chitin-glucan complex, isolated from lichens, similar to the structure of crab chitin (chitosan). The estimation of the sorption capacity of the selected chitin-glucan complex with respect to a number of heavy metals and methylene blue. The sorptive capacity towards heavy metals decreases in the order Cu (II)> Hg (II)> Co (II)> Ni (II). It is shown that the CGC is highly selective with respect to cations of Cu (II) and allows to extract 100% of these cations from a solution.

Thus, as a result of the experiment, the optimal parameters for obtaining biologically active substances from the carbon dioxide extraction of lichens in sub- or supercritical state (SKFE) demonstrated that administration of cosolvents can dramatically increase the yield of usnic acid from lichens thallus.

This research was performed using the equipment of CCU SE “Arctic” (Northern (Arctic) Federal University named after Lomonosov), and by funding from the Ministry of Education and Science of the Russian Federation (the unique identifier of works RFMEFI59414X0004) and the equipment of CCU SE CT RF-Arctic (IEPN, IPNA of Ural Division of Russian Academy of Sciences).

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P-7

PETF RECYCLING IN SUBCRITICAL CONDITIONS

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Recycling of domestic and industrial waste is an important issue of energy conservation and environment protection. In [1] the methods of cellulose and polyethyleneterephthalate (PETF) waste recycling are discussed. However, all methods described in [1] are based only on partial thermal decomposition of polymers, while in case of PETF the most efficient method is complete chemical monomer recycling. Maximally complete monomer recycling methods make it possible to retrieve initial raw material for reuse without loss of quality. An example of this is recycling of aluminum cans, where production of new cans out of discarded old ones can continue infinitely. Recycling of petrochemical raw materials provides an opportunity not only to save energy and resources spent on manufacturing of monomers out of “crude oil”, but also to resolve the environmental problem of accumulation of non-biodegradable waste.

This paper suggests a method of recycling PETF bottles (a most common type of PETF product) chemically in subcritical environment.

There is literary data, both Russian and international, on hydrolyses and glycolysis of PETF bottles in presence of various catalysts. Russian research of PETF hydrolyses in subcritical environment is discussed only in one work [2]. There's no data in this work, however, on either the conditions of the process, or whether a catalyst was used.

The main characteristic feature of our research is that a special experiment, which made it possible to visualize every transformation of reaction mass in the process of PETF bottle recycling, was carried out. This information is essential for understanding the processes which run in the system. Based on the data obtained on this stage, possible technological solutions for extraction of dyes and whiteners out of retrieved monomers were developed.

The impact of temperature, contact time and proportion of reagents on the composition of the final reaction mass was studied.

The results of the research and a method of subcritical recycling of monomers from 'colorless' and colored PETF bottles, will be presented at the conference.

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P-8

QUANTUM CHEMICAL STUDY OF NON-CATALYTIC TRANSESTERIFICATION REACTION OF TRIGLYCERIDES AND THEIR ANALOGS IN SUPERCRITICAL FLUID CONDITIONS

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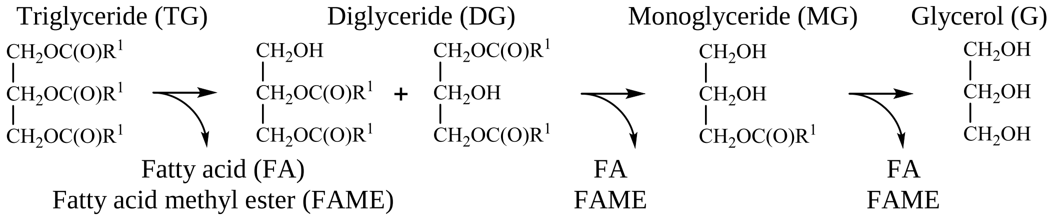
Quantum-chemical DFT method with density functional PBE in bazice 3z (comparable basis set cc-pVTZ) in the implementation of the program Priroda 4.11 and B3LYP / 6-311 ++ g (df, p) in the implementation of the program Gaussian09 investigated transesterification of triglycerides in methanol supercritical fluid conditions, i.e. at T = 623 K and P = 30 MPa [1,2]. We discuss the specifics of energy following reaction systems: 1) The simplified gas phase reaction systems involving triglyceride (or analogues thereof) and the monomeric form in which methanol flows in a one-step reaction mechanism involving communications alkoxycarbonyl or two-step mechanism involving the carbonyl group in the first stage and quaternary alkoxy a second intermediate stage; 2) Reaction System in which elementary event involving carbonyl, or alkoxycarbonyl group and triglyceride trimer or dimer form methanol and its substitution analogs.

The simplified gas phase reaction systems involving monomeric form of methanol are hypothetical and with dimeric and trimeric methanol forms are actual reaction proceeding direction, but do not have a pronounced potential traps for the desired products - the fatty acids methyl esters and their substitution analogs, which means the flow of equiprobable Most areas of the competitive transesterification of triglycerides, i.e., reaction systems described are in equilibrium with each other [3].

Under supercritical fluid conditions thermodynamic equilibrium has various reaction systems that implement elementary acts methanolysis and the hydrolysis of triglycerides to accumulation of catalytically significant amounts of fatty acids [4,5]. Thus carboxylic acid - methanol (or water) associates in the one-step methanolysis reaction (or hydrolysis) on the alkoxycarbonyl group triglyceride analogues in supercritical fluids provide a promoter effect, which in combination with the presence of potential pitfalls direction makes their reactions involving accumulation of target main channel products of the process of methanolysis of triglycerides, i.e. fatty acid methyl esters.

Thus, the overall reaction, chemistry reflecting transesterification and hydrolysis of triglycerides can be present by scheme 1.

Scheme 1. Transformation steps in triglyceride hydrolysis and methanolysis consistent with the intermediate formation of diglycerides (DG), the monoglyceride (MG) and the final form glycerol (G), fatty acids (FA), or fatty acid methyl esters (FAME).



R^1 – hydrocarbon residue of fatty acids and their analogues.

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P-9

EXPERIMENTAL AND THEORETICAL STUDY OF THE NUCLEATION AND GROWTH OF PARTICLES IN JETS WITH SHOCK WAVES IN THE OUTFLOW PROCESS OF SUPERCRITICAL FLUID SOLUTION FROM MICRON NOZZLE CHANNEL

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To determine the temperature distribution in an expanding free jet from the nozzle micron-sized carbon dioxide was used method of thermal imaging with a thermal imager and thermocouples on the modernized RESS-100-2 Base firms Thar Technologies Inc.

The data obtained by the thermal imager in a series of experiments with process parameters: P=10-35 MPa, T_{sat}=323 K, T_{nozzle}=343 K; P=25 MPa, T_{sat}=323 K, T_{nozzle}=313-353 K have provided profiles of temperature CO_2 flux in a free jet.

From these results it can be concluded that during the RESS temperature CO_2 free jet after exiting the nozzle device along the axis of expansion cools below -30ºC. Given the high flow rate (about 300 m/s) the carbon dioxide passes into the solid phase and the substance dissolved therein “freeze” in place of it, this results in a region of growth inhibition particles (Knudsen number tends to zero). Further expansion is accompanied by a flow mixing with the background gas, which is at room temperature. This leads to an increase in the flow temperature, whereby carbon dioxide passes into the gas phase and particle growth is restored. What was demonstrated in our study [1]. The flow of carbon dioxide after the field and inhibition of growth of the particles have a lower speed and a low density, so it is in this region coagulation particle growth become larger than homogeneous nucleation and condensation.

In this paper, the mathematical model of the nucleation and growth of particles from a supersaturated and supercooled fluid solution on the basis of the theory of an expanding drop in the channel and in the free stream of the supercritical fluid with the shock waves, molecular, convective heat transfer, and mass transfer with the background gas flow in the anomalous properties supercritical fluid. To find the fields of temperature, pressure, density and velocity of the flow is used the system of Navier-Stokes equations. Fluid flow is assumed dimensional, axially symmetric, stationary, viscous and compressible. The calculation is carried out in the capillary channel of the receptacle and an infinite volume in a free jet with a shock wave before and after the Mach disc. Physical conditions at the inlet to the channel conditions are identical to the saturation of the fluid substance. The capillary channel is considered tributaries heat due to friction against the walls of the fluid, and after exiting the channel is considered heat-mass exchange between the free jet and the background gas, which is at a normal physical conditions. The system of equations is solved numerically by finite element method. The boundary conditions are set: channel geometry, temperature and pressure at the entrance and exit of the channel. The adequacy of the developed mathematical model is verified by comparing the field of temperature and pressure, the calculated and experimental way. Solution of this model to describe processes giving hydrodynamic mass transfer equilibrium phase, nucleation and growth of particles from a supersaturated solution of the fluid which expands in the nozzle and the expansion device in a free jet in view of shock wave and the Mach disc.

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P-10

PERSPECTIVES ON THE CHEMICAL RECYCLING OF PET WASTES USING SUPERCRITICAL FLUIDS TECHNOLOGY

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World production of plastic reached now 300 million tons that makes actual the need for effective technologies of the recycling. On this issue the recycling of polyethylene terephtalate (PET) is of key importance. The annual global gain is estimated at the level of 1.1 million. According to Non-profit partnership on development of the industry of polyethyleneterephthalate (NP “ARPET”) Russia in the long term can enter in top-10 global manufacturers of PET at the accruing product range on the basis of primary and secondary polymer. An important advantage of PET is the possibility of the corresponding waste processing into the higher quality product (“Upcycling”). In this case the technologies of mechanical and chemical recycling compete. The restored PET at similar quality demands two thirds less energy, than primary. Also 80% reduction of CO_2 emissions in comparison with traditional production on an oil basis is provided. The saved energy and the prevented carbon emission at a closed cycles recycling per ton of the restored PET according to US EPA come respectively to 53 MBTUs and 0,42 MTCE (Metric Tons of Carbon Equivalent). Today large-scale plants of PET recycling are being built in many countries. In Russia there are some companies producing various PET brands. There are international multilateral agreements on creation of a number of new large capacities for production of PET as a part of the existing and new industrial agglomerations. Rapid growth of capacities of primary PET in Russia increases an imbalance with polymer recycling capacities. The increasing volumes of application and quantity of PET-waste allow to create their large-scale recycling. It predetermines the relevance of a choice, development or creation of advanced technologies for the waste recycling. At the present time the majority of secondary PET is used in the descending cycles to produce other products.

The chemical PET recycling started almost simultaneously with the production of polymer in the commercial scale confirmed by patents, starting with the 1950th. Originally the technology was used for the return of production wastes, later for PET consumption waste. The chemical recycling of plastic with the use of supercritical fluid technologies (SCFT) has been most consistently developed in Japan since 1995. Today South Korea and China also show the greatest activity and achievements in this area. In open sources there are no specified characteristics of technologies, however, they are likely based on SCFT.

The chemical PET recycling is reasonable in cooperation with the production of primary PET as a part of a chemical cluster. All technological stages of closed-loop recycling influence the economy of the whole loop. Efficiency of the closed contour depends on the limiting recycling component, i.e. the return logistic network capable to provide the return of waste streams from the distributed sources of the used products. In Russia an additional obstacle for development of this segment is the low level of collecting (less than 20%). Following the international experience, the accelerated development of PET recycling in Russia will demand additional legislative efforts.

The best world practice is multi-loop recycling. One of the most effective solutions is recycling within the chemical cluster. In other areas, remote from similar clusters, recycling networks will be developed without the use of depolymerization. Restrictions are logistic expenses and the presence of alternative consumers of secondary PET. The way to the accelerated development of opportunities of SCFT in the chemical PET recycling lies in the creation of the innovative partnership on all aspects of process chains of a straight and reverse logistics network for achievement of a common goal. First of all, it is an integration of fragmentary developments of the competence centers for SCF-technologies and the competence centers for production technologies and the use of PET. The alternative is the import of production technologies and PET recycling in the package contract (purchase of technologies for providing a whole cycle).

The review of the Russian and foreign centers of competence, industry leaders, and also results of scientific development on chemical PET recycling including the use of SCFT will be presented at the conference. The report will cover the competing developments of chemical PET recycling in connection with the risk of refusal of SCFT because of the hard process parameters. Different schemes of the competence centers integration for technological progress will be shown in the presentation.

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P-11

CALCULATION OF THE SOLUBILITY OF POORLY SOLUBLE SUBSTANCES IN SUPERCRITICAL MIXED SOLVENTS

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Solubility of non-electrolytes in supercritical systems is the object of a wide range of studies to provide data required for the design of processes of separation and extraction. Available in the literature experimental data [1] indicate that the solubility of a poorly soluble substance in the mixed solvent may increase considerably in relation to its solubility in an individual solvent. However, the number of such experimental studies is limited. Theoretical models in this area not enough developed. To describe the data on the solubility of non-electrolytes in mixed supercritical solvents mainly various modifications model Hildebrandt or semi-empirical approaches are used. But these models include several adjustable parameters. In this regard, there is a need to develop model approaches that not only describe, but also to predict the solubility of non-electrolytes in mixed supercritical solvents.

In this work a model based on the provisions of the theory of molecular association was used for the calculation of non-electrolytes solubility in supercritical systems. The expression for the logarithm of the activity coefficient of the solute (s) in the model containes three contributions: chemical (taking into account the molecular association) $(ln\,\gamma_S)_{chem}$, combinatorial (taking into account differences in the size of the particles of solution components) $(ln\,\gamma_S)_{comb}$ and residual (taking into account the universal intermolecular interactions) $(ln\,\gamma_S)_{res}$.

$$(ln\,\gamma_S) = (ln\,\gamma_S)_{chem} + (ln\,\gamma_S)_{comb} + (ln\,\gamma_S)_{res} \qquad (1).$$

Chemistry and combinatorial contributions are calculated on the basis of the theory of association equilibria as described previously [1]. To calculate the residual contribution used a simple lattice model. Parameters of the theory are: the equilibrium constants of reactions of association, the geometric characteristics of molecules components and binary interaction parameters.

The proposed model was tested on the example systems solute (caffeine, aspirin) – supercritical carbon dioxide – methanol, for which data on the solubility are available in the literature.

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P-12

CHEMICAL SYNTHESIS UNDER HIGH OXYGEN PRESSURE

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Oxidation under high oxygen pressure (several GPa) is an important approach of inorganic synthesis. It allows us to synthesize the substances which cannot be obtained now by others ways. To perform such an experiment a precursor and an oxygen-donor compound are placed into a capsule made of a noble metal. A capsule is hermetically sealed and hereafter pressurized and heated in a high-pressure cell such as a piston-cylinder, a belt or a multianvil apparatuses. The experiment is time-consuming and quite expensive, the quantity of a target substance being small. Therefore the method is difficult to be considered for application in industry. Moreover the product is usually contaminated by an oxygen-donor and products of its decomposition.

The alternative approach is a compression of aluminum capsules containing a precursor and filled with liquid oxygen which is performed in lentil-type high-pressure apparatus [1]. The method allows to conduct the synthesis in similar conditions but in a time-saving and inexpensive manner. This approach allowed us to synthesize $CaFeO_3$ and $LiLa_2FeO_6$ with the 100% and 25% yields respectively.

We have realized the compression of liquid oxygen at an industrial plant using industrial equipment. The approach is quite similar to the known one widely used for a production of synthetic diamonds. Thus, the production capacity and costs can be easily estimated.

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P-13

MODIFICATION OF POLYMETHYLMETHACRYLATE WITH SINGLE-WALLED CARBON NANOTUBES IN SUPERCRITICAL CARBON DIOXIDE

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Carbon nanotubes have unique electrical, optical and mechanical properties. Development of new structural materials based on carbon nanotubes with polymers is very interesting. Such composites significantly change the physicochemical properties of the polymers even with low concentrations of nanotubes.

For effective reinforcement of polymers by means of single-walled carbon nanotubes (SWCNTs) must be used stable suspension of nanotubes in solvents with low viscosity. An important aspect is also the solubility of the resulting stable suspensions of carbon nanotubes in supercritical carbon dioxide over a wide range of state parameters.

The aim of this work is the modification of polymethylmethacrylate (PMMA) with different molecular weight by impregnation of SWCNTs suspension in supercritical carbon dioxide, and study the effect of addition of fillers on the properties of the resulting composite material.

It is known that the interaction with $scCO_2$ PMMA swells, forming a ramified network of pore. This property was used to optimize the procedure for the composite.

For analysis of the nanocomposites were applied Raman spectroscopy, X-ray diffraction and thermal analysis methods (differential scanning calorimetry, thermogravimetry and differential thermogravimetry).

By Raman spectroscopy was carried out layer by layer scanning samples impregnated with carbon nanotubes to study of the penetration depth of SWCNTs. Investigation of the samples allows us to conclude the uniform distribution SWCNTs throughout the volume of the obtained nanocomposite. Tangential mode in the spectra of the samples are well resolved, allowing them to fix the shift toward shorter wavelengths in the case of the resulting composite with PMMA compared with the initial suspension of single-walled carbon nanotubes.

During the work it was revealed the influence of SWCNTs and molecular weight of the original PMMA on the characteristics of the nanocomposites.

The results of analyzes of these nanocomposites are presented in the report.

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P-14

SUPERCRITICAL DRYING OF OPAL MATRIX

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Currently one of the most actual problems is to find new materials for photonics with high mechanical resistance. Due to its high hardness and transparency opal-like structure are unique matrices for optical devices. The difficulty of obtaining such materials associated with difficulties in drying opal-like matrix nondestructive their structure.

In routine air-drying or vacuum having large stresses into the pores of the samples due to high surface tension at the the interface liquid-gas. The action of these forces during the drying process leads to deformation of the cavities, and sometimes destruction opal-like structures. Drying in supercritical fluids allows avoiding these problems.

The aim of the work was to optimize the process of supercritical drying opal-like matrices.

Submicron and nanometer spherical particles of amorphous silica were obtained by a multi-step sol-gel method Stober's [1]. This method allows you to receive opal-like structures consisting of equigranular spheres with a diameter of 40 nm to 2200 nm and a standard deviation of the average of 5%.

Gels obtained after repeatedly washing with liquid carbon dioxide had been dried by supercritical drying. Depending on the drying parameters is possible to obtain as defect-free opal matrix and micro-powder SiO_2. Optimized drying conditions are given in the report.

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P-15

THE EXPERIMENTAL STAND AND TECHNIQUE OF CARRYING OUT RESEARCH OF THE FILTRATION OF NEFT-VODA-SVERHKRITICHESKIY FLUID SYSTEM IN UNIFORM AND NON-UNIFORM MODEL OF OIL LAYER

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Authors created experimental installation for research of process of replacement of oil of various viscosity of oil layer with use of supercritical fluid systems and the technique of carrying out researches is developed. Experimental installation allows to conduct researches of processes of replacement real nefty of uniform, micro, layered and non-uniform, jointed поровых models of oil layer of various degree of water content supercritical CO_2 and fringes of supercritical CO_2 and water, and also from models of a carbonate collector. On experimental installation researches of process of replacement model and real by nefty viscosity to 40 of uniform and non-uniform layer supercritical CO_2 are conducted with pressure up to 14 MPas, temperatures to 60ºC. Results of researches showed that application of supercritical CO_2 in processes of replacement of oil leads to increase in oil recovery from not flooded layers, that is at the initial stage of operation of an oil field, and from layers which water content exceeds 60%, that is the layers which are in operation the long period. The main regularities of influence the termobaricheskikh of conditions, the porometricheskikh of characteristics of layer and viscosity of oil on oil replacement coefficient by supercritical CO_2 are revealed.

P-16

APPLICATON OF SUPERCRITICAL FLUIDS EXTRACTION METHOD FOR PROCESSING OF VEGETABLE RAW MATERIALS OF THE ARKHANGELSK REGION

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In work data on application of supercritical CO_2 in extraction processes of receiving valuable products of some perennial and annual plants growing in the territory of the Arkhangelsk region are provided. Ways of extraction of oils and biologic active substances (BAS) - carotinoids, chlorophylls – from cranberries, carrots, tomatoes are fulfilled.

For the last five years authors executed a number of works concerning application of super critical (SC) fluid technologies in processing of vegetable raw materials usual for the Arkhangelsk region. Approaches to processing of wood and not wood raw materials differ. The wood raw materials are basis of cellulose production while from not wood (and also needles) usually various BAS are allocated.

The most part of wood greens (needles of a pine and fir-tree) doesn't find application during wood processing and remains on preparation places. Application of SC carbon dioxide (60ºC and 300 atm) modified by ethyl alcohol (to 10%) allows to extract a chlorophyll and carotinoids completely within a reasonable time.

Important environmental and technological problem is utilization of the wood bark accumulating at the pulp and paper enterprises. The existing technologies of bark BAS extraction have shortcomings, among which high cost of the applied solvents; their combustibility and ecological danger take place. Replacement of the traditional solvents with SC carbon dioxide (100ºC and 400 atm) allowed to take to 80% of ether-soluble substances of fir-tree bark.

One of the traditional crops which are grown up in the Arkhangelsk region are carrots. Carrot can be raw material in production the karotin and carotinoids. The most widespread is the grade of Shantane. Use of toxic organic solvents creates difficulties at the subsequent purification of extract, and high temperatures promote the undesirable isomerization of carotinoids leading to loss of their activity. Application of SC CO_2 allows to allocate to 80% of carotinoids, and their ratio in extract corresponds to that in raw materials. Rather high temperature (80ºC) doesn't cause a noticeable isomerization of carotinoids, and processes of oxidation are impossible in view of lack of oxidizers. Similar results are received at extraction of production wastes and processings of tomatoes where lycopene is the main carotinoid (85%).

Processing of waste of food production is a significant problem. Alcoholic beverage production is a source of meal of the berries which are slightly pro-extracted by ethyl alcohol. We tested release of oils from meal of a cranberry and cowberry of the Arkhangelsk alcoholic beverage plant. Possibility of full release of oils during SC fluid extraction is shown. The received oils contain polynonsaturated carbonic acids, including ω3-nonsaturated, and possess high antioxidant ability. The received oils are characterized by the small content of free fatty acids. The oils received by SC fluid extraction method are a little enriched with a chlorophyll and carotinoids in comparison with the oils received in the traditional ways.

Colza is rather new culture for the Arkhangelsk regional cultivated in its southern areas (Kotlas, Velsk). Rape oil is valuable food and technical raw material. In literature there are many data on use of propane in supercritical condition for extraction of rape oil, however its high fire danger calls into question possibility of use of this solvent. There are some data about opportunity of use of supercritical CO_2; however it isn't enough data on release of rape oil in literature.

The SC fluid extraction method with application of CO_2 allows to receive rape oil with an yeild of 34%. The main difference of the oil received by the SC-CO_2 method from the oil received by extraction the geksany – the raised share of triglyceride, at reduction of free acids share. The chemical composition of oils is almost identical.

Thus, supercritical fluid technologies can play large role in processing of vegetable raw materials of northern subarctic territories.

P-17

COMPUTER SIMULATION OF CONFORMATIONAL MANIFOLD OF IBUPROFEN DISSOLVED IN SUPERCRITICAL CO$_2$

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A development of dosage forms with a high solubility and bioavailability is essential for pharmaceutical use. One of the characteristics that affect on these properties is the conformational manifold in the condensed phase. The conformational manifold of ibuprofen in supercritical CO$_2$ was studied in this work.

Molecular dynamics simulations of ibuprofen in supercritical CO$_2$ performed at temperatures of 40°C, 60°C and 80°C using a software package NAMD. The simulation box contained 216 molecules of CO$_2$ and 1 molecule of ibuprofen. Simulation time was 100 ns. Fluid density corresponded to 1.3 of critical density of CO$_2$. To create the initial box we applied the procedure “Packmol”. The calculation of the free energy surface carried out with the plugin PLUMED by scanning a pair of dihedral angles associated with internal rotation of different groups of the molecule. Then, from the resulting free energy surface the possible transitions in the molecule ibuprofen between states with minimal energy values and the values of the energy barriers were calculated. It was found that at temperatures close to 60°C, there is a qualitative change in the map of the populations of conformers. The peculiarities of such behavior discussed in detail in this work.

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P-18

OILS ISOLATION FROM SEEDS OF ASTRAKHAN REGION WILD FLORA BY SUPERCRITICAL FLUID EXTRACTION

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The plants chemical composition depends on the area of growing, climate change and many other factors. Astrakhan region is a unique climate zone of Russia. It is rich in wild oil plants such as mulberry, Xanthium strumarium, Elaeagnus angustifolia, Alhagi camelorum, Robinia pseudoacacia and others [1].

In the report will be presented data on the oil extraction from the wild plants seeds of the Astrakhan region by supercritical fluid extraction (extractor SFE-500 M1, "THAR Process Inc." company): the plant oil yield dependence on the degree of seeds fineness, the extraction time, pressure, temperature, the eluent flow rate, the influence of cosolvents [2].

The results analysis of the physico-chemical characteristics study of the obtained oils (refraction index, density, acid number, saponification number, ratio of saturated to unsaturated fatty acids and others). Fatty acid composition of obtained samples oils was studied by chromatography-mass spectrometry on an Agilent device with a library of 40 thousand chemical compounds. Quantitative determination of oil components was carried out after derivatization of fatty acids into corresponding fatty acid methyl esters by gas-liquid chromatography on Shimadzu Q12010 chromatograph with mass selective detector [3].

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P-19

ETHANOL AND PHENOL CONVERSION IN SUPERCRITICAL WATER

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Physical-chemical properties of water as well as characteristics of its interaction with organic compounds change substantially after passing the critical point. In the undercritical and transitional region the ionic product, dielectric permittivity, diffusion coefficient, kinetic and dynamic viscosity, dipole moment, volume density change significantly and the hydrogen bonding network disappears. This can be used for intensifying various transformations of organic compounds through hydrolysis, liquefaction, pyrolysis or gasification, and for regulating the selectivity of these processes.

We focus our attention on the kinetic parameters and channels of conversion of aliphatic and aromatic alcohols above the critical point. The investigations of ethanol and phenol conversion in supercritical water were carried out in continuous flow reactor at temperature 400-800°C, 300 bar pressure and residence time from 4 to 30 min.

We find that in supercritical water at temperatures 700-800°C there is complete or partial gasification of ethanol through formation of acetaldehyde to gas products: H_2, CH_4, CO_2, CO, C_2H_6, C_2H_4. Phenol conversion in supercritical conditions does not occur up to 700°C. At 700°C and above formation of both liquid products (benzene, toluene, diphenyl, benzofuran, dibenzofuran) and gaseous products – H_2, CO_2, CH_4 is observed.

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P-20

RELEASE OF METHYLURACIL FROM COMPOSITES ON THE BASE OF THE ALIPHATIC POLYETERS CREATED IN SUPERCRITICAL CARBON DIOXIDE.

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Introduction

Biologically active substances (BAS) included into biodegraded matrixes are one of the main components of tissue engineering. Among various methods of BAS encapsulation in polymeric matrixes, methods based on supercritical fluid (SCF) technologies have apparent advantages. They allow to refuse using of toxic solvents. All processes can be realized at a temperature of 35-40 °C. In this work one of the most known metabolic preparations Methyluracil which has the regenerative and immunostimulating properties was chosen as the model compound for carrying out SCF encapsulations into bioresorbable polymers of a homological series of aliphatic polyesters and for studying of kinetics of their release in buffer solutions *in vitro*.

Materials and methods

We used Methyluracil isomer - 6 Methyluracil (Nizhpharm, Russia) and bioresorbable, copolymer of lactic and glycolic acids – Polylactoglycolide (Purasorb PDLG 7507, Purac, the Netherlands) for formation of bioactive composite matrixes. Matrixes were formed by the SCF method of a monolitization of mix of initial components in supercritical carbon dioxide (sc-CO_2). Mix of powders of polymer (80th weight %) and Methyluracil (20th weight %) it was filled in Teflon compression molds which were located in the high pressure camera. SCF processing was carried out with the pressure of carbon dioxide 10 MPa and the temperature 40 degrees C within 1 hour. Then within 15 minutes dumping of pressure to atmospheric value was carried out.

The structure of the received matrixes was studied by method of the scanning electronic microscopy (SEM) on LEO 1450 microscope (Karl Zeis, Germany). Distribution of Methyluracil in composite matrixes was investigated by the Raman spectroscopy on dispersive Raman Almega XR spectrometer (Thermo Scientific, the USA) with high (~ in 1 micron) spatial resolution. The kinetics of release of Methyluracil from the created matrixes into PBS was also determined by Raman spectroscopy with the measuring in time integrated intensities of the chosen analytical line.

Results

Studying of structure of composite matrixes showed that the Methyluracil crystals, having a needle form from 20 to 100 microns long, are well integrated as into a surface, so into the internal volume of polyester matrixes. The maps of spatial distribution of Methyluracil received by means of Raman spectroscopy with a step of scanning of 10 microns showed its uniform inclusion into structure of matrixes. Experimental dependence of release of Methyluracil to PBS solution is presented in Fig. 1.

Concentration which would be received when all amount of the Methyluracil encapsulated in a polymeric sample will released into solution was accepted to 100%.

Measurements showed that for the first day matrixes leave less than 20% of Methyluracil. Then release speed smoothly decreased, and left, on the mode close to linear. By 60 days the exit of Methyluracil reaches about 85%.

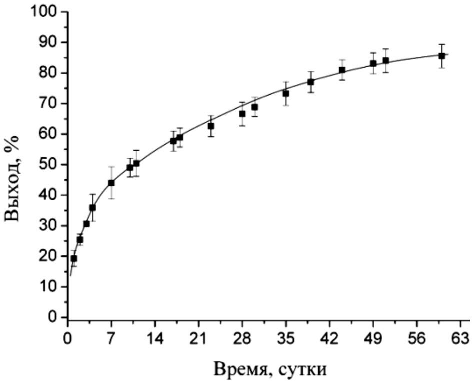

Fig. 1. Kinetics of release of Methyluracil from the polymeric matrixes into PBS solution.

Conclusions

Effective encapsulation of Methyluracil into bioresorbable polymeric matrix was carried out by SCF method of a monolitization of mix fine powders of a Polylactoglycolide and Methyluracil in sc-CO_2 at a temperature 40 degrees C. SEM and Raman spectroscopy methods were shown that crystals of Methyluracil are uniformly distributed on a surface of matrixes and in their volume. Research of kinetics of Methyluracil release into buffer solution showed absence of strong initial burst of bioactive agent. Thus, on model of Methyluracil it was shown that composite matrixes developed with use of supercritical carbon dioxide, provide rather smooth and prolonged (about two months) Methyluracil release into buffer solution, and they are perspective components for use as matrixes carriers for the address and prolonged delivery of medicines for stimulation of growth and regeneration of tissues of various types.

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P-21

THE PROCESS OF ISOPROPYL-*p*-XYLENE PRODUCTION

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Isopropyl-p-xylene is used in obtaining 2.5-xylenol, an important intermediate product in the manufacturing of plasticizers, coatings, disinfectants, and even vitamin E. The main method of Isopropyl-p-xylene production is alkylation of p-xylene with propylene. The main difficulty here is to ensure maximum possible selectivity of the process, which is limited by volatility of methyl groups. For this reason, isothermal conditions are strictly regulated in any process, and energy efficiency of the technology becomes a secondary consideration. At the same time, for alkylation of benzene with propylene we have demonstrated [1] that performing this process in adiabatic mode with entrance into subcritical region allows not only to considerably reduce unnecessary energy consumption, but also to run the process in the special hydrodynamic mode peculiar to the critical region. Obviously, with p-xylene in place of benzene, the share of the energy consumption in the final cost of the product will not change - we obtain 100 kJ of high potential heat per 1 mol of transformed propylene, instead of non-recoverable and therefore problematic low potential heat. The problem, which appeared almost impossible to solve, was to carry out alkylation with entrance into subcritical region while retaining mutual orientation of methyl groups in the aromatic nucleus. Nevertheless, we managed to achieve this by liquid phase alkylation of p-xylene with contact time not exceeding 2 minutes. We propose to discuss the main issues of this and other technologies of alkylbenzene production at the present conference.

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P-22

SEARCHING FOR A NEW CRYSTAL FORMS OF ARBIDOL WITH IMPROVED SOLUBILITY PROPERTIES

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Drug molecules with limited aqueous solubility are becoming increasingly prevalent in the research and development portfolios of discovery focused pharmaceutical companies. About 40% of marketed drugs and more than 80% of drug candidates have low solubility. The solid state chemistry of active pharmaceutical ingredients (APIs) is a subject of fundamental, practical interest. Polymorphs, solvates, salts, molecular complexes and co-crystals of APIs represent extensions of chemical space wherein enhanced or new chemical and physical properties may lead to extended patent coverage and consequent legal protection of products.

The aim of our work is search of new crystal forms of arbidol with improved solubility parameters. The antiviral drug arbidol is very popular in Russia, nonetheless, arbidol practically insoluble in water, this limits its bioavailability. Researches devoted to the arbidol solubility improving have not been conducted, until recently. Therefore, obtaining of a new highly soluble form of arbidol is an important task.

Searching for new polymorphs of arbidol was carried out by crystallization from different solvents. Supercritical antisolvent technology (SAS) and supercritical fluid technique (SFT) were used for the arbidol polymorph searching, as well. Cocrystal screening of arbidol with more than 50 coformers were carried out using differential scanning calorimetry and solvent-drop grinding method. Two new cocrystals of arbidol have been discovered. Solubility experiments in water (pH 2.0, 5.5 and 7.4) were conducted for pure arbidol, its hydrochloride monohydrate and obtained in our work new crystal forms of arbidol.

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P-23

HYDROGENATION OF NITROBENZENE IN SUPERCRITICAL CARBON DIOXIDE WITH THE USE OF RU-CONTAINING CATALYST

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Catalytic hydrogenation of nitrobenzene is an important chemical and technological process of the production of aniline which is in turn used as an intermediate in the synthesis of polyurethanes, rubbers, pharmaceuticals, pesticides and herbicides. The process of gas-phase hydrogenation of nitrobenzene is usually carried out with the use of Ni-or Cu-containing catalysts, partial pressure of hydrogen is 1-5 atm and temperature 250-300ºC, while liquid-phase hydrogenation is performed with Pt-, Pd-, Ni-containing catalysts at a temperature of 50-220ºC and pressure of 10-50 atm. Both processes are carried out in the environment of various solvents, as well as in their absence, thus the selectivity to the main product makes 75-95%. [1]

The application of supercritical carbon dioxide ($CO_{2(sc)}$) in the selective hydrogenation of nitrobenzene is of considerable interest of researchers that is caused by the advantages of supercritical fluids application in the organic synthesis: the increase of high heat and mass transfer coefficients, the change in the processes direction due to the formation of new molecular complexes, the easiness of the product separation from the solvent and the decrease of the processes flammability. [2]

The magnetic-separated catalyst containing ruthenium (mass concentration of ruthenium is 17.5%) was used for catalytic hydrogenation of nitrobenzene in the environment of supercritical carbon dioxide. The accumulation of aniline in the reactionary environment is presented in Figure 1.

The maximal concentration of aniline is reached at the 180th minute, the product yield makes 54.6%, at 100% selectivity and the conversion of nitrobenzene of 54.6%. In the absence of the solvent under similar conditions the selectivity made 60-75%, the product yield was 32% at 45% conversion of nitrobenzene.

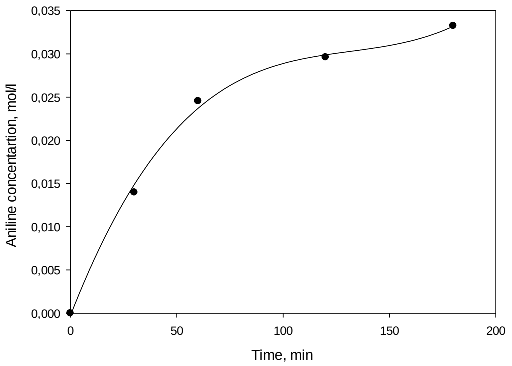

Fig. 1 Dependence of aniline concentration on time (Reaction temperature 150°C, nitrobenzene concentration 0.06 mol/l, mass of the catalyst 1.56 mg, hydrogen partial pressure 3 MPa, carbon dioxide partial pressure 20 MPa.)

Carbon dioxide is prospective solvent for carrying out organic syntheses, including hydrogenation of organic nitro compounds. In the environment of supercritical carbon dioxide the decrease of the carrier influence on the activity of heterogeneous catalysts is accounted for by the increase in the availability of the active Ru-centers for the reacting substrate.

ACKNOWLEDGEMENTS

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P-24

SYNTHESIS AND CHARACTERIZATION COMPOSITE FILM MATERIAL, BASED ON METAL AND DIELECTRIC NANOPARTICLES, OBTAINED USES METHODS LASER ABLATION IN SC CO_2.

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Development of methods for upconversion nanoparticles (UCNPs) based on crystals NaYF4, doped with lanthanide ions, is of interest in connection with the prospect of their application for solving problems of optical bioimaging to a depth of 3 cm. We first tested a method for producing upconversion nanoparticles in a wide range of sizes, using laser ablation of compressed microcrystals NAF target in the medium SC CO_2. The possibility of controlling the size of nanoparticles produced using the properties of the medium SC SO_2 that allows to smoothly change their density in a wide range, which is impossible when using liquid media.

The report results are presented which demonstrate the possibility of obtaining crystals with sizes less than 100nm. It is shown that the distribution of particle size obtained influence of gravitational deposition processes, which allows to separate particles by size in the bulk of the reactor pressure vessel.

P-25

INFLUENCE OF SUPERCRITICAL CONDITIONS ON REGULARITIES OF THE OXIDATIVE DEHYDROGENATION OF ETHANE ON Mo-V-Te-Nb-O CATALYST

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The oxidative dehydrogenation (ODH) of light paraffins is one feasible alternative to the current industrial productions of olefins. This method has several important advantages. Firstly, the ODH is an exothermic process which should serve as an incentive to implement it in a production of olefins. Secondly, oxygen, entered with the feedstock, reacts with carbon and prevents the formation of coke on the catalyst surface.

Mo-V-Te-Nb-O catalysts, prepared by hydrothermal synthesis, were found to be extremely active and highly selective in the ODH of ethane [1]. These catalysts provide high selectivity and conversion of ethane to ethylene above 90% at temperatures up to 400ºC. However, Mo-V-Te-Nb-O catalysts exhibit a high sensitivity to overheating. The use of supercritical conditions allows to decrease the reaction temperatures to 300ºC.

The purpose of this work was to study the effect of supercritical conditions on the structure, activity and selectivity of Mo-V-Te-Nb-O catalysts in the oxidative dehydrogenation of ethane.

Comparison of the data obtained in the ODH of ethane at atmospheric and supercritical pressures will be carried out in the report.

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P-26

THE ROLE OF CRITICAL STATE OF MATTER IN PETROCHEMISTRY AND INDUSTRIAL ORGANIC SYNTHESIS

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The contents of a previous scientific conference in any area of research and industry reflects, to this or that degree, the state of affairs in the area. We have performed an analysis of the questions stated in the titles of the papers, and obtained the following results:

- 23% of papers (on Baltic Supercritical 2013) were dedicated to fundamental issues of critical (liquid-vapor/gas) state of substances, adding experimental data to the database of the properties of various substances (mostly binary mixtures), characteristics of heat transfer in the critical region and environmental protection issues related to SCF use;
- 43% of papers focus on application of CO_2 as environment for physical processes as part of general technologies for manufacturing various products (aerogels, microdispersing compositions, micro capsules and medications - 17%), during extraction of substances (12%), for impregnation (10%), for cleaning and treatment of the polymer surfaces (3%) and finally (1%) as an environment for fine organic synthesis;
- 18% were distributed in the following descending order: supercritical fluid chromatography (6%), fine organic synthesis in various environments (5%), formation and extraction of oil (4%), production of nanocomposite materials (3%);
- 2% of papers deal with supercritical water. Only 2%! And that even though water in supercritical state has a unique combination of properties, and can act as oxidant, catalyst, or as a powerful agent of hydrolysis.

The remaining 14% are distributed across biodiesel fuel production (3%), hydration processes (3%), catalyst regeneration in heterogeneous catalytic processes (2%), aqueous runoff purification in industry (2%). **And only 4%** of papers are dedicated to the processes which can be classified as petrochemistry and industrial organic synthesis (with ≤ 0,8% devoted to each of the following topics: alkylation of isobutene with butenes, and benzene with propylene, oligomerization of isobuthilene, acilation, benzene oxidation to phenol, and nitrocellulose production).

P-27

SUBCRITICAL WATER EXTRACTION OF ANTHOCYANINS FROM *ARONIA MELANOCÁRPA*

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Black chokeberry fruits are a source of the valuable components for the human organism. It contain a rich complex flavonoids (rutin, quercetin, etc.), tannins, a large amount of ascorbic acid, organic acids [1]. Anthocyanins contained in the fruits of Black chokeberry are of particular interest because it has biological activity, primarily due to high antioxidant activity [2, 3].

This paper presents an effective, safe and the available method of extracting anthocyanins from fruits Black chokeberry (Aronia melanocarpa) in subcritical water in a dynamic mode in the temperature range from 110 to 150°C at a pressure of 12.5 MPa. Also this method compared with traditional methods of extraction.

The experiment carried out in dynamic modes using the apparatus which provides flow rate from 0.1 to 10 cm^3 / min, pressure of 40 MPa, the temperature in the extraction system from 35 to 250°C. [4]. Qualitative and quantitative analysis of the extracts carried out RP HPLC with spectrophotometric detection.

This work was supported by the Ministry of Education and Science of the Russian Federation within the project number 608.

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P-28

INFLUENCE OF THE POLAR COSOLVENTS ON THE SOLVATION PROCESSOF O-HYDROXYBENZOIC ACID DIMER IN SUPERCRITICAL CARBON DIOXIDE

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O-hydroxybenzoic acid (o-HBA) is widely used in the pharmaceutical industry, in particular in the synthesis of aspirin. Moreover, o-HBA is used as a precursor in the manufacture of many industrial compounds, and it is a key component in the means for skin care. Areas of o-HBA application imply a high demand for quality and purity of the product, which, in turn, is the motivation for the use of non-toxic solvents (for instance, supercritical (SC) carbon dioxide). However, solubility of the polar organic compounds (such as salicylic acid) is very low in the SC CO_2. Scientists propose to solve the problem by modifying the carbon dioxide with small additions of co-solvents. The increase in the solubility of polar organic substances in SC CO_2 with the addition of co-solvents was proved experimentally, but the reasons for this phenomenon remain controversial, although most researchers agree that intermolecular interactions solute – co-solvent is played the main role. In this context, the goal of this work was to study the solvation process of o-HBA dimer in pure and modified with the addition of water, methanol and ethanol (up to 0.035 m.f.) SC CO_2, and the identification of the nature of intermolecular interactions in the system.

To achieve this goal we used the method of classical molecular dynamics implemented in Gromacs-4.5.4 software package [1]. Simulation was performed in NVT-ensemble in a cubic box with periodic boundary conditions. The length of the box in each case was adjusted to maintain a constant density of 0.7 g/cm^3.

The analysis of the obtained data showed that the o-HBA dimer dissociation is faster in SC CO_2 modified with polar co-solvent. In pure SC CO_2 formation of solvation shells around salicylic acid molecules is due to the weak hydrogen bonds and electron donor-acceptor interactions with solvent molecules, in the binary solvent the modifier molecules are comprised in the solvation shell and form strong hydrogen bonds with the atoms of the carboxyl group of o-HBA. Furthermore, there have been enhancement of local mole fraction of co-solvent near salicylic acid to 0.12-0.17 m.f., while the mole fraction of co-solvent in the bulk not greater than 0.035 in the case of methanol and ethanol and 0.0079 - in case of water. These data are in good agreement with the experimental ones obtained for a molecule Phenol Blue dissolved in SC CO_2 with acetone as co-solvent [2]. The energy of formation of hydrogen-bonded complexes solute – co-solvent was calculated by means of Gamess and CPMD-3.13.2 [2] software packages. The calculated values were compared with the values of the enthalpy of hydrogen bond formation obtained according to ^{1}H NMR spectroscopy from temperature dependence of the heteroassociation constants.

The study was supported by the Russian Foundation for Basic Research (№ 14-03-00497a).

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P-29

SOLVATE OF SALICYLIC ACID AND ITS DERIVATIVES IN MODIFIED SUPERCRITICAL CARBON DIOXIDE

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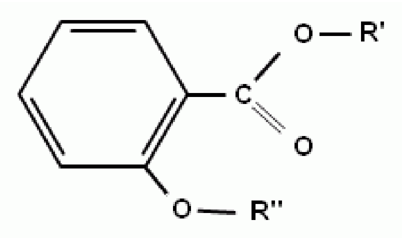
According to the contemporary terminology the salicylic acid and its derivatives are nonsteroidal anti-inflammatory drugs. The need to obtain high purity, soluble and bioavailable pharmaceutical compounds causes the interest in the development of supercritical (SC) fluid technologies for their separation and purification, and also to study the solubility of these substances in SC carbon dioxide and raising it by addition of a polar co-solvent.

Salicylic acid and its derivatives: acetylsalicylic acid (aspirin), sodium salicylate, salicylamide, methylsalicylate, are characterized by different nature and location of functional groups. This factor determines the character of formation of solvation structures solute - polar co-solvent. This phenomenon is studied in the present work.



Substance	R′	R″
Salicylic acid	H	H
Acetylsalicylic acid	H	$COCH_3$
Salicylamide	NH_2	H
Methylsalicylate	CH_3	H
Sodium salicylate	Na	H

Classical molecular dynamics method realized in Gromacs-4.5.4 software package [1] was used to investigate the structure of solvates o-hydroxybenzoic acid and its derivatives in supercritical carbon dioxide modified with polar co-solvent (T=318 K, ρ=0.7 g/cm^3, polar co-solvent – 0.03 molar fraction of methanol). Based on structural and dynamic characteristics obtained in the numerical simulation (radial distribution functions, averages numbers and lifetimes of hydrogen bonds, the distribution of local mole fraction of co-solvent around solute, self-diffusion coefficients) the ability of the compounds to form solvation complexes with the co-solvent, probability and way of their formation were analyzed.

The energy of formation of hydrogen-bonded complexes solute – co-solvent was calculated by means of Gamess and CPMD-3.13.2 [2] software packages. The calculated values were compared with the values of the enthalpy of hydrogen bond formation obtained according to 1H NMR spectroscopy from temperature dependence of the heteroassociation constants.

The study was supported by the Russian Foundation for Basic Research (№ 14-03-00497a).

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P-30

ROLE OF ENTROPY IN SEPARATION OF XYLENES ON GRAPHITE BY SUPERCRITICAL FLUID CHROMATOGRAPHY

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Preparative separation of xylene positional isomers is of importance in modern chemical industry. Para-xylene is a raw-material for the production of polyethyleneterephtalate, a wide-spread industrial polymer. Xylenes are synthesised by methylation of either toluene or benzene and a mixture of all three positional isomers plus ethylbenzene is always obtained in this process. Boiling temperatures as well as many other physico-chemical characteristics of xylenes are very much alike, so simple separation techniques such as distillation are impractical for their fractionation. It refers in particular to a pair of meta- an para-isomeres. The most effective modern method for xylene separation is SMB-chromatography. Two main keys for successful SMB-separation method development are 1) maximization of selectivity towards a critical pair and 2) minimization of expensive organic solvent use in mobile phase. In this regards supercritical fluid chromatography (SFC) offers significant advantages since 1) various stationary phases and elution regimes are available in SFC which makes it a versatile tool for highly selective separation of structurally close compounds and 2) its main mobile phase constituent is carbon dioxide which is remarkably cheap.

An initial goal of this work was an appraisal of applicability of SFC for preparative separation of xylene isomers and a choice of a proper sorbent. Column screening revealed only one stationary phase able to separate meta- and para-xylene - porous graphitic carbon (Hypercarb™, hereafter referred to as «graphite»). This separation is noticeable in several regards. First, all three xylenes can be eluted from graphite within a short time-frame with pure CO_2 as a mobile phase, there is no need for liquid cosolvents. This makes it particularly attractive for preparative chromatography both from economical and ecological points of view. Second, para-xylene is more retained on this sorbent than meta-. This is rather unexpected since most known meta-/para-xylene separation provide the opposite elution order. The presence of a dipole moment in meta-xylene and its absence in para-xylene typically leads to a longer retention of meta-isomer. Ortho-isomer is the most retained on graphite in SFC which is the same for other sorbents. Thirds and most peculiar, the selectivity coefficient between meta- and para-xylene doesn't depend on temperature. Whereas ortho-/para-xylene selectivity coefficient does depend on temperature as expected. According to Vant-Hoffs formalism selectivity coefficient (α) can be written as follows:

$$\log \alpha = - \Delta\Delta H/RT + \Delta\Delta S/R \quad (1),$$

where $\Delta\Delta H$ - sorption enthalpy difference for two compounds,

$\Delta\Delta S$ - sorption entropy difference for two compounds.

Normally selectivity coefficient is bound to be dependant on temperature due to the form of the first summand in equation (1). The discovered violation of this tendency can only be interpreted as follows: the sorption enthalpy for these two substances on this sorbent is practically equal while the separation is driven solely by the difference in entropy loss during sorption. The enthalpy equality was confirmed by quantum chemistry calculations in which coronene molecule served as graphite sorbent model. Calculations were performed within density functional theory using B97D functional and 6-311++G(d,p) basis set with counterpoise BSSE-correction. Calculated difference in dimerization energy of coronene with meta- and para-xylene was equal to several tens of calories per mole. In other words, it is absolutely negligible. So far we explain lesser entropy loss of para-xylene by its higher symmetry due to which it possesses lesser entropy in solution. Additional studies conducted showed that the described elution order is also registered for other sorbents on which retention is mainly governed by dispersion interactions and not exclusively on graphite. These are, for instance, all the silicas with long non-branched alkylic substituents, such as C_{18} or C_{30}. But the latter do not provide enough selectivity even for analytical xylene separations let alone preparative. We believe this is due to non-uniform 3D structure of these sorbents surface and conformational lability of their functional groups. This leads to much less sorption entropy losses on these sorbents in comparison with highly organised, symmetrical, 2D graphite surface.

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P-31

XPS- STUDY OF ZINC OXIDE AEROGEL

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The recently developed supercritical technology is applied to produce the aerogels of zinc oxide. ZnO aerogel is an attractive material being both semiconductor and weak ferromagnet. Ferromagnetic signal was detected for several oxides. It was shown that in order to demonstrate ferromagnetism, the ZnO should be in a nanocrystalline state. Some dopants can facilitate the ferromagnetism. Nevertheless, the reason for ferromagnetic behavior is not clearly understand.

There are some theoretical calculations, which show that structural defects like vacancies or interstitials can be the reason for the ferromagnetic properties of zinc oxide [1, 2]. The defects can be produced during the synthesis process. According to the data of X-ray photoelectron spectroscopy the, O1s oxygen line has one or more additional peaks, which is the witness for different states of oxygen atoms [3, 4]. In order to obtain reliable data, we study ZnO aerogels obtained under different synthesis conditions.This work was support by RFBR grant 15-03-04220 and by the program of Russian Academy of Sciences “New Materials”.

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P-32

RESEARCH OF PROCESS OF THE FILTRATION OF NEFT-VODA-SVERHKRITICHESKIY FLUID SYSTEM IN UNIFORM AND NON-UNIFORM MODEL OF OIL LAYER

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The mathematical model of process of a non-stationary one-dimensional multiphase multicomponent linear filtration of systems “oil - supercritical CO_2”, “oil-water-supercritical CO_2”, describing oil replacement process by supercritical fluid systems of homogeneous and non-uniform porous environment of various degree of water content is created. The model is created on the basis of the standard concepts of the theory of a filtration (the movement of a fluid submits to Darci's law, deformation of a skeleton of the porous environment is absent, concentration of hydrocarbonic components is equal in water to zero). As the equation of a state the equation of Soava-Redlikha-Kvonga is accepted. The model considers the capillary phenomena on limit of the section of the phases ”oil-supercritical CO_2”, “oil-water-supercritical CO_2” both heatphysical and physical and chemical properties of multicomponent multiphase systems. Numerical modeling of process of a non-stationary two-phase two-component filtration of “neft-CK CO_2” system in homogeneous porous environment and comparison of results with results of process of replacement of oil by pure supercritical CO_2 of model of a uniform terrigenous collector is carried out. The rejection of settlement data from the experimental doesn't exceed 13%.

P-33

REGENERATION OF THE HYDROGENATION CATALYSTS USING SUPERCRITICAL FLUID EXTRACTION

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Catalyst regeneration is one of the main problems in providing technical and economic efficiency of the vast majority of oil refining and petrochemical processes. One of promising method for regenerating catalysts is a supercritical fluid extraction (SCFE).

The aim of the present work is to explore the possibility of regeneration of spent catalyst from the enterprise of “Nizhnekamskneftekhim” (nickel-on-kieselguhr, palladium catalyst LD- 265) in a supercritical carbon dioxide medium.

In the first series of experiments, the regeneration of the catalyst was accomplished using pure SC-CO_2. For greater effect investigated the effect of concentration of different nature co-solvents of (chloroform, dimethylsulfoxide (DMSO), methanol and acetone) on the change in mass of the catalysts in the process of regeneration [1]. The extraction kinetics of catalyst LD – 265 at T=423 K using modified with various additives SC-CO_2 with an optimal concentration of co-solvents is presented in Fig.1.

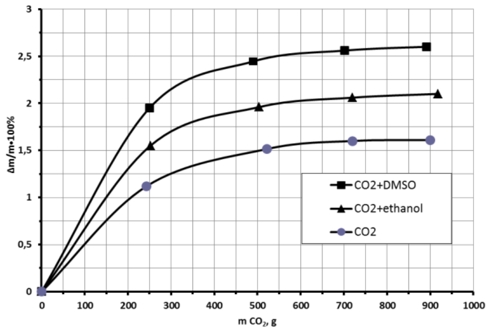

Fig. 1 Change of palladium catalyst LD-265 mass in the course of its regeneration at P=20 MPa

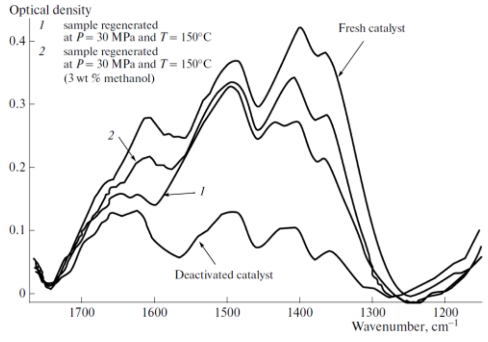

Fig. 2. The IR spectra of the samples of nickel-on-kieselguhr catalyst, regenerated using pure and modified SC-CO_2

The greatest degree of extraction decontamination compounds is provided when used as co-solvent DMSO, which has a high polarity, and allows the most complete extraction of polar compounds.

The IR spectra of the regenerated catalyst samples (Fig. 2) confirm the occurrence of changes, primarily a decrease in the amount of deactivating compounds.

The activity of the nickel-on-kieselguhr catalyst was estimated from the extent of hydrogenation of ethylene to ethane (table 1).

Evaluation of the activity of samples of the aluminum-palladium catalyst was carried out on the residual value of diene and bromine numbers in the hydrogenation product (table 2).

Table 1. Activity of the samples of nickel-on-kieselguhr catalyst subjected to various treatments in the hydrogenation of ethylene

Product	Sample			
	initial	worked out	regenerated (SC-CO_2+ 3% wt methanol)	regenerated (SC-CO_2)
Ethane, vol %	91,5	87,7	92,9	92,3
Ethylene, vol %	8,5	12,3	7,7	7,1

Table 2. Comparative analysis of hydrogenation results of the benzene-toluene-xylene-fractions, obtained on samples of the palladium catalyst LD-265

Activity index	Sample of catalyst, regenerated			
	steam-air treatment	pure SC-CO_2	SC-CO_2+ 6% wt DMSO	SC CO_2+ 6% wt ethanol
Diene number, gJ_2/100g	2,85	2,4	1,5	2,0
Bromine number, gBr_2/100g	20,5	19,0	16,2	17,0

Thus, the obtained values of the catalytic activity of the hydrogenation catalyst samples demonstrate the effectiveness of the extraction process, at the level of requirements imposed on the catalysts.

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P-34

ON THE APPLICABILITY OF THE QUASI-STATIONARY CONVECTIVE APPROXIMATION OF THE SOLVENT FLOW AT THE SUPERCRITICAL FLUID EXTRACTION PROCESS

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At supercritical fluid extraction the “liquid” solvent is pumped (with a constant superficial velocity v) through the porous packed bed of ground plant material. The general master equation, describing solvent flow in the pore phase, is usually derived on the basis of the unsteady-state convective approximation additionally accounting for the axial dispersion D_{ax} which in dimensionless form can be written as

$$\delta_t \frac{\partial x}{\partial \tau} + \frac{\partial x}{\partial \zeta} - \delta_D \frac{\partial^2 x}{\partial \zeta^2} = q, \quad \delta_t = \frac{e\theta_*}{(1-e)\theta_0}, \quad \delta_D = 6\frac{DD_{\mathrm{ax}}}{v^2 a^2},$$

where θ_* – saturation concentration of oil in the solvent, θ_0 – initial oil content in raw material, e – packed bed porosity, D (~10^{-12} $\mathrm{m^2 s^{-1}}$) – effective diffusion coefficient of solute in the solid phase, a (~$10^{[-4;-3]}$ m) – mean particle size, H (~10^{-2} m) – vessel height, q – the source term (solute flux from ground particles), and x, τ, and ζ

$$x = c/c_{\mathrm{sc}}, \quad \tau = t/t_{\mathrm{sc}}, \quad \zeta = z/z_{\mathrm{sc}}, \quad c_{\mathrm{sc}} = \theta_*, \quad t_{\mathrm{sc}} = \frac{\theta_0}{\theta_*}\frac{a^2}{6D}, \quad z_{\mathrm{sc}} = \frac{va^2}{6(1-e)D}.$$

are dimensionless variables (solute concentration in the fluid phase, time and spatial coordinate in the vessel) corresponding to their dimensional analogues c, t, and z, and normalized according to characteristic scales (subscript “sc”), deduces on the basis of scale analysis.

In this study on the basis of the shrinking core model and polydisperse approximation of packed beds (which specify the expression for q) the applicability of the quasi-stationary ($\delta_t \to 0$) convective approximation (with neglected axial dispersion, $\delta_{\mathrm{D}} \to 0$) of the fluid flow in the vessel is examined. The analysis of available correlations for the D_{ax} allowed, in particular, to determine extraction conditions when axial dispersion is negligible.

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P-35

EXTRACTION OF RARE EARTHS ELEMENTS FROM MONAZITE CONCENTRATE AND PHOSPHOGYPSUM AND THEIR SEPARATION FROM URANIUM, THORIUM AND RADIUM, USING SUPERCRITICAL CARBON DIOXIDE CONTAINING TBP, D2EHPA AND THEIR ADDUCTS WITH HNO_3

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Based on the application of supercritical fluid extraction (SKFE) and microwave (MW) radiation developed a scheme of complex processing of monazite concentrate (MC) and phosphogypsum (PhG) to extract rare earth elements (REE) and their separation from the Th, U and Ra. Conditions of quantitative extraction of REE, Th and U by using supercritical carbon dioxide (SC-CO_2) containing TBP or D2EHPA from PhG were determined. Removing the REE from the MC and their separation from Th and U using SKFE become possible after sintering MC with Na_2CO_3 in the presence of coal by MW radiation and converting phosphate REE, Th and U, contained in the MC, in their oxides. Obtained by sintering powder MK (MCS), consists of two phases, a mixture of pure oxides of REE and CeO_2 solid solution with oxides of Th, and U. Of the first phase of the MCS using SC-CO_2 containing adducts of TBP or D2EHPA with HNO_3 can extract up to 50% of REE. After dissolving the residue of MCS in a mixture 4 M HCl with 0,05 M HF, from the resulting solution using SC-CO_2 containing D2EHPA can be quantitatively extracted Th and U, and thus to separate them from the remainder REE remaining in solution. Skipping the resulting solution through a cell containing sorbent DGA with TODGA groups (N,N,N',N'-tetraoktildiglikolamida) can be isolated Ra-228 with the purpose and on the basis thereof producing isotopes generator 212Pb / 212Bi for use in radiotherapy studies.

P-36

ACCELERATED EXTRACTION OF 1,1-DIMETHYLHYDRAZINE TRANSFORMATION PRODUCTS FROM SOILS WITH SUBCRITICAL SOLVENTS

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1,1-Dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH) is widely used as a rocket fuel and is known as a highly reactive substance. When released into the environment it provides a wide range of transformation products which characterized by, as does the UDMH, the high toxicity. Control of such pollutants in environmental objects is an essential component of environmental support of space rocket activities. The problem of extraction of a broad range of target components to obtain extracts that are suitable for direct analysis is of special interest. The classical approaches described in the literature and based on the use of ultrasonic extraction and Soxhlet extraction are very laborious and time consuming, and in some cases ineffective. In this direction, the most promising approach is the use accelerated solvent extraction technology at elevated pressure and temperature (ASE, pressurized extraction) which allows to intensify the mass transfer processes and to reduce sample preparation time by orders of magnitude.

The automatic pressurized extraction system ASE 350 (Thermo, USA) was used to develop the approaches to extraction of formaldehyde 1,1-dimethylhydrazone (DMHF) acetaldehyde 1,1-dimethylhydrazone (DMHA), 2-furaldehyde 1,1-dimethylhydrazone (DMHFur), N-nitrosodimethylamine (NDMA), tetramethyl-2-tetrazene (TMT), dimethylformamide (DMF), 1-methyl-1,2,4-triazole (MT) and formic acid dimethylhydrazide (DMHFA) from soils.

The determination of transformation products was performed by gas chromatography with tandem mass spectrometric detection. Taking into account the possibility of direct injection of the extract into a gas chromatography system the acetonitrile chosen as an extractant.

It was found that the maximum recovery rate for all studied compounds from sandy soil is achieved at a process temperature of 100 °C (Figure 1). The increasing of number of extraction cycles above two does not affect the extraction effectiveness.

Figure 1 shows that in the transition through the boiling point of the solvent under normal conditions, there is a sharp increase in the efficiency of extraction, reaching 90-100% for all components except tetramethyl-2-tetrazene.

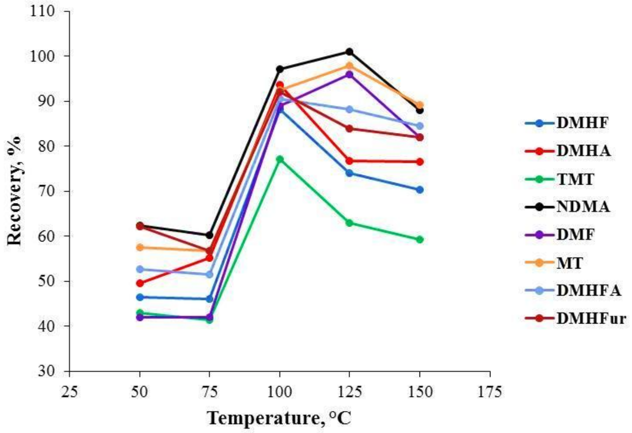

Fig.1 The dependence of the extraction efficiency of the UDMH transformation products from sandy soil on the extraction temperature.

This phenomenon is due to the achievement of the subcritical state of extractant. In such conditions, due to the destruction of the hydrogen bonds and, accordingly, the structure of the solvent, the decrease in viscosity, dielectric constant, and increasing of the diffusion coefficients and solubility of many organic compounds in the extractant occur.

It is shown that for the soils with high organic matter content (peat) extraction of hydrazones and tetramethyl-2-tetrazene is impossible under the conditions chosen for the sandy soil, the recoveries obtained does not exceed 10%. Low recoveries for hydrazones can be explained by the high acidity of peat, causing degradation of this class of compounds, and the high extraction temperature can intensify this process.

The increasing of recoveries for analytes can be achieved by the creation of alkaline medium in the peat sample. For this purpose the use of barium hydroxide was proposed. The addition of Ba $(OH)_2$ constituting 250% of the peaty soil sample (based on dry matter), allows to achieve the extraction efficiency above 75% for all target compounds. To approbate the approach developed the sample of a peat bog soil taken in the place of the impact of the "Cyclone" carrier rocket was analyzed. The example of obtained chromatogram is shown in Figure 2. In the sample extract the six of the eight analytes was determined.

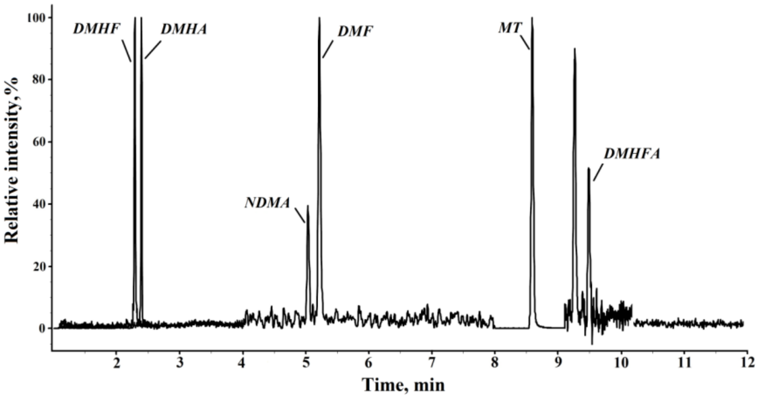

Fig.2 The chromatogram of the peat bog soil extract sampled at the epicenter of the impact site of the carrier rocket "Cyclone"

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P-37

SOME ASPECTS OF TEMPERATURE INFLUENCE ON RETENTION IN SUPERCRITICAL FLUID CHROMATOGRAPHY

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Among the factors having effect on retention in supercritical fluid chromatography (SFC) temperature takes a special place. On one hand it’s an important parameter controlling separation since it affect fluid’s density and solution strength. Temperature along with pressure is a parameter that provides the ability to fine-tune elution strength of a supercritical fluid which is traditionally considered as one of key benefits of SFC in comparison with liquid chromatography. On the other hand the effect of temperature on retention and selectivity is extremely complicated and virtually unpredictable. A change in temperature causes not only a change in fluid’s density and solution strength but also in sorption equilibrium, analytes’ volatility, mobile phase linear velocity, the amount of mobile phase adsorbed onto the stationary phase etc. All these factors affect retention in a cumbersome way and the overall result is often hard to predict. As a result nowadays temperature is only seldom used in SFC method development. The majority of SFC users prefer to work at so-called subcritical conditions ($T<T_{cr}$) in oder to avoid unexpected difficulties caused by high fluid compressibility. Unfortunately the possibilities to fine-tune SFC separations are significantly diminished at these conditions. In order to use temperature in SFC in a predictable manner it’s necessary to have a deep understanding of the influence of all these phenomena on retention. The goal of this work is the investigation of temperature influence on retention of model compounds in SFC.

Isobaric dependencies of retention coefficients (k) for ortho-, meta- and para-xylenes on temperature in the range from 10°C to 90°C were registered. The stationary phase was porous graphitic carbon, the mobile phase was pure CO_2 and different pressures and temperatures. At 10°C and pressures above 50 bar CO_2 is a liquid, at 90°C it's a gas-like fluid, thus a chosen temperature range allows making conclusions being representative for the whole supercritical fluid state. So-called crossover phenomena are observed during isobaric elution. At high pressures (>150 bar) k monotonously decreases with T increase. At low pressures (≤100 bar) the dependencies of k on T pass through a maximum: below 30-40 degrees k decreases, above that it increases. This could probably be explained by simultaneous influence of counter-facing factors: CO_2 density decrease caused by temperature increase leads to k increase whereas the increase of both analytes' volatility and mobile phase linear velocity while heating decrease retention. The first factor has a lesser influence at higher pressures since fluid's density stays high even at higher temperatures in this case.

Isochoric dependencies of k on T were also built in order to avoid complications caused by crossover phenomena. Densities from 0.3 to 0.8 g/ml were screened. The most noticeable feature of these data is a non-linear character of these dependencies at low CO_2 densities. At densities ≥ 0.5 g/ml k monotonously decreases with T increase. At lower densities dependencies of k on T have a shallow maximum. That can be interpreted as a symptom of the existence of some additional mechanisms of temperature influence on retention apart from the above-mentioned. Plotting the same data in a form on isothermal dependencies of k on ρ allowed revealing an interesting feature: the deviations from monotonous decline take place only in a narrow density range, 0.5 - 0.6 g/ml (see fig. 1). And the closer the temperature is to a critical point value - the more pronounced these deviations are.

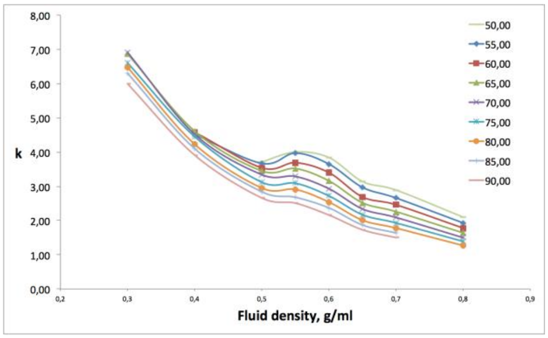

Fig. 1. Isothermal dependencies of k(p-xylene) on ρ

We believe that this phenomenon has some interconnection with residual critical phenomena, namely with high density fluctuations in the neighbourhood of Widom line. It’s been observed previously that high density fluctuations lead to high values of excessive Gibbs adsorption of mobile phase onto the stationary phase in SFC. We presume that it is high excessive adsorption of the fluid on the sorbent what causes the increase of xylenes retention coefficients.

This work was supported by Russian Scientific Foundation, grant 14-33-00017.

P-38

LINK OF THE SUPERCRITICAL FLUID STATE OF EUTECTIC MELTS AND THEIR HEIGHTENED PREDILECTION TO GLASS FORMATION

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The supercritical fluids arise both in case of singl-component, and in case of multicomponent systems. In one-component systems it there can be systems a gas - fluid, and at transition to two and more component systems the supercritical state can arise in liquid stratified systems. More often calotte of an unmixing corresponds to a maximum of temperature, by above which one the difference between fluid phases disappears. At the analysis of fundamental reasons of glass formation us was offered the eutectoidal model of glass formation, according to which one main motive for the formation of glasses is the presence in a melt low and of high molecular weight particles, between which one the interaction of an eutectic type is possible [1]. It concerns even of simple matters, for example, selenium, for which one at melts are present low and of high molecular weight clusters for the glass formation. At a glass transition during cooling of melts the freezing of equilibriums happens and also amount of metastable components entering eutectic interactions before a glass transition of melts increases sharply. The eutectic melts, as is known, are inhomogeneous, that is taped as diffraction methods, and at learning dependences of their structurally responsive properties from temperature and composition. In melts nanoclusters of atoms, appropriate to the initial components or solid solutions on their basis, find out. It confirms, for example, method of a centrifuging of melts. Outgoing from this, it is possible to state, that glass forming melts represent not only melted eutectics, but also lyophilic colloidal solutions. It is known, that on the eutectic phase diagrams in melts above eutectic area there is a calotte of an unmixing. Apparently, that thereof for glasses obtaining at cooling of melts from the different temperatures, different character of a microinhomogeneity can be exhibited. The cooling from temperature of below critical temperature on a calotte of an unmixing should result in to formation of glasses with an unmixing at any cooling rate. For example, for glasses of systems As-Se and Ge-Se with composition in the field of eutectics the microunmixing appears. If the melt is withstood at temperatures of above critical temperature, the glasses should be gained maximum homogeneous thanking slowly of flowing past relaxation viscid of the glass forming melts. The theoretical calculations are reduced, touching offered explanation.

Thus, the eutectoidal supercritical fluid theoretical concept is offered, according to which one for the everyone glass forming system in a melt there is a critical temperature, at cooling from temperatures is higher also than below which one the glasses with the different character of a microinhomogeneity will be formed.

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P-39

ENERGY AND METHOD FOR ECOLOGICAL SAVES NANOCOMPOSITE MATERIALS USING SUPERCRITICAL FLUID

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To implement the process of nanodispersion polymers and pharmaceuticals using supercritical anti-solvent method was developed experimental setup. This setting allows conducting dispersion polymers and pharmaceuticals in supercritical CO_2 at pressures up to 45 MPa and temperatures up to 473.15K, with a maximum speed of pumping carbon dioxide 50 g/min, the maximum pumping speed of the active substance of 50 g/min.

The experimental setup consists of a system of creation, management and measurement of pressure, measurement and control of temperature, feeding a mixture of "organic solvent-polymer" vessel of particle formation, cell trapping particles.

When you select a mode parameters of the process of dispersing polymers (polystyrene, polikarobonat) method SAS took place focus on relevant areas of the phase diagrams of binary systems “polymer solvent”, “polymer-carbon dioxide”, “solvent - carbon dioxide” [1.2, 3] and the ternary system “polymer dichloromethane - supercritical carbon dioxide.”

In one of the experiments the varied parameters, and the rest remained constant it possible to determine the particular influence of each parameter and the size of dispersed particles.

Results curves average particle size of the pressure at two different temperatures in the same manner are characterized by the presence of the maximum.

Particle distribution “polymer - CT CdSe / CdS” size indicates that the investigated pressure range with an increase in temperature increases the average particle size. The same behavior was typical for the case of pure polymer dispersion [1].

A very important indicator of the effectiveness of the applied approach encapsulating CT CdSe / CdS in the polymer of the SAS technology is the preservation of the optical properties of QDs in nanocapsules obtained, as evidenced by photoluminescence spectra. There is a bathochromic shift of the PL peak constituting 5 nm, indicating that the low degree of agglomeration of CT in the polymer matrix [4].

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P-40

SPATIAL STRUCTURE OF IBUPROFEN IN SUPERCRITICAL CO_2 STUDIED BY TWO-DIMENSIONAL NMR

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In this work, NMR studies were performed in order to obtain information on the molecular structure and conformation preference of ibuprofen in $scCO_2$ and chloroform. The influence of $scCO_2$ on a number of spectral parameters such as chemical shifts and nuclear Overhauser effect was studied. ^1H NMR spectra with high resolution were recorded for ibuprofen in $scCO_2$ and compared with ^1H NMR spectra obtained in chloroform. The results confirm the expected ibuprofen conformation reported earlier for the solution in chloroform.

This work was supported by the Russian Scientific Foundation (Project № 14-13-00232).

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P-41

PREDICTION OF CRITICAL POINTS OF THE MULTI-COMPONENT MIXTURES OF N-ALKANES

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The limited set of the experimental data on the critical state does not satisfy by the chemical or oil industry requirements. In this context it becomes relevant to estimate the critical parameters of mixtures reliably. For this purpose we use a set of complicated models based on various theories. But the shortage of reliable experimental base for multi-component mixtures forces to search the simple models.

It’s known that the concentration dependence of critical temperature of binary mixture, where only dispersion interactions are appeared becomes linearized when replacing of mole fraction to mass fraction is occurred. It allows an empty equation’s using to estimate T_{cm} of multi-component mixture of n-alkanes (1):

$$T_{cm} = \sum_{i=1}^{N} w_i \cdot T_{ci} \qquad (1)$$

where T_{ci} is critical temperature, w_i is mass fraction of component *i*.

Previously it has been shown [1] that the excessive critical pressure’s dependence of n-alkanes’ binary mixture to mass fraction is represented by the second degree polynomial that admits (with a lack of experimental data) to estimate the binary interaction parameters reliably and use it for calculation P_{cm} of multi-component systems.

$$P_{cm} = \sum_{i}\sum_{j} w_i\, w_j P_{cij} \qquad (2)$$

where $P_{cij} = k_{ij} \cdot (P_{ci} + P_{cj})/2$, and k_{ij} is binary interaction parameter, which is estimated by adapting of experimental dependence of the corresponding binary system, k_{ii} = 1,0.

Today the various models of different level are used to estimate critical parameters. The results of calculation of these models (Peng-Robinson equation of the state (PR); equation of the state based on the group model of the phase equilibrium – UNIFAC (PSRK); equation of the state based on simplified perturbed hard-chain theory (PC-SAFT); equation of the state based on modern renormalization-group theory (EOSCF+RG)) presented that more difficult models have no advantage in accuracy of prediction the critical parameters than method we used. Mean relative deviation (in percentage) of critical parameters of 17 mixtures (from three- to seven- components), which was calculated by various methods, regarding their experimental values is presented below:

Parameter\Model	PR	PSRK	SPHCT	PC-SAFT	Equations (1) and (2)
T_{cm}	0,87	1,11	3,48	1,23	0,85
P_{cm}	1,85	1,77	2,68	5,03	2,03

The comparison of calculation results of 23 (from three- to five-components) systems by offered method and EOSCF-RG method showed that the mean relative deviation by T_{cm} was 0.77% and 0.72% respectively, and by P_{cm} was 2.23% and 2.59%.

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Gratitude

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P-42

PRODUCTS OF BITUMEN CONVERSION IN A COUNTER-CURRENT SUPERCRITICAL WATER FLOW

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This work deals with a study of bitumen (vacuum residue) conversion in a supercritical water (SCW) flow at 30 MPa. Experiments were performed in the following modes: at continuous supply of bitumen into a counter-current SCW flow under isothermal conditions (400ºC), at SCW pumping through the layer of bitumen residue at uniform temperature increase from 400 up to 700ºC and subsequent holding at 700ºC [1], at continuous supply of bitumen into a counter-current SCW flow under temperature gradient along the reactor axis (at the top – 450ºC and at the bottom – 650ºC), and subsequent oxidation of bitumen residue in a flow of SCW/O_2 fluid [2].

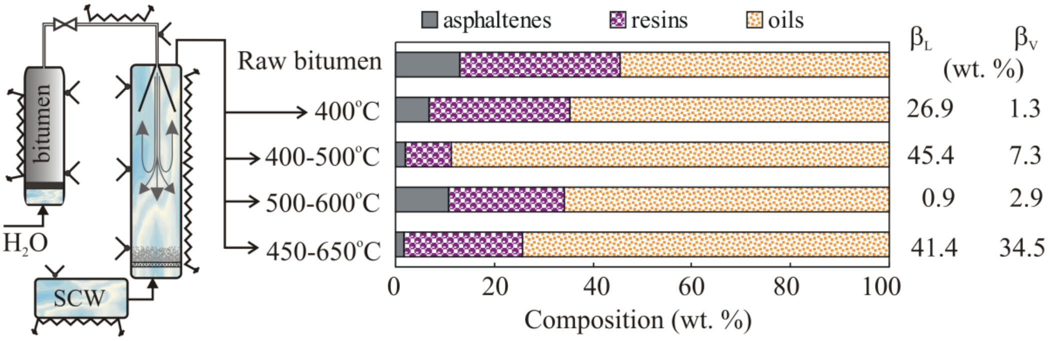

Fig. 1. Composition and yield of liquid (β_L) and volatile (β_V) products of bitumen SCW conversion.

The yield and composition of liquid and volatile products and carbonaceous conversion residue are measured. Participation of H_2O molecules in redox reactions with components of oxygen-free bitumen (gross-formula $CH_{1.47}N_{0.01}S_{0.007}$) became evident due to the formation of CO and CO_2 even at

400ºC. The maximum yield of liquid products, the maximum content of oils in them, and the maximum H/C atomic ratio in the liquid products are detected under SCW pumping through the bitumen residue at 400-500ºC (Fig. 1). According to the IR spectroscopy data, when increasing the temperature of SCW conversion, the content of aromatic and polyaromatic substances increases in the group components of liquid products. The maximum yield of C_1-C_9 hydrocarbons (28.4% relative to the weight of bitumen supplied into the reactor) is obtained at 450-650ºC temperature gradient (Fig. 1).

It is shown that gasification of the bitumen conversion residue at T>600ºC results mostly in the formation of combustible gases (H_2 and CH_4), whose total molar portions in the volatile products obtained at 600-700 and 700ºC are equal to 59.0 and 62.2%, respectively. This high yield of H_2 and CH_4 proceeds from the heterogeneous reactions between H_2O molecules and the bitumen carbonaceous residue with the high specific surface (224 m^2/g). Based on the temperature dependences of the amounts of CH_4, H_2, CO and CO_2 in the volatile products, it can be stated that the formation of CH_4 и CO_2 at T=700ºC results from the reaction $2\langle C\rangle+2H_2O=CO_2+CH_4$. The degree of bitumen desulfurization at 400–700°C and 450−650°C temperature gradient due to sulphur removal in form of H_2S accounts for ≈22% wt. The bulk of sulfur atoms (>50% wt.) is detected in the liquid products.

It is revealed that the compositions of bitumen carbonaceous conversion residues obtained at 400-700ºC and 450-650ºC temperature gradient, including the SCW/O_2 pumping through bitumen residue, are similar ($CH_{0.29}N_{0.01}S_{0.003}$ and $CH_{0.29}N_{0.01}S_{0.005}$, respectively). The presence of H_2, lower alkanes and arenes in the products of bitumen conversion in a SCW/O_2 flow indicates that the oxidation of bitumen by oxygen is accompanied by the reactions of thermolysis, reaction of steam reforming and water gas shift reaction.

It is shown that proposed schemes of bitumen conversion are efficient for practical use. The bitumen is not coked due to the low temperature of the top area of the reactor, but when it falls down it is partially converted into light hydrocarbons, which are removed by a SCW counter-current flow from the reactor. Having accumulated at the bottom of the reactor, heavy bitumen components are converted in SCW into lighter hydrocarbons with increasing the temperature. The obtained results clearly evince the important role of water in the bitumen conversion consisting in dissolving the bitumen components, preventing the recombination of radical fragments formed during thermolysis, and as an internal source of hydrogen.

This study was supported by the Russian Foundation for Basic Research (№14-03-00055) in the part of bitumen SCW conversion and by the Russian Science Foundation (№14-19-00801) in the part of bitumen residue oxidation by SCW/O_2 fluid.

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P-43

SYNTHESIS OF MANGANESE OXIDE PARTICLES FOR ELECTROCHEMICAL APPLICATIONS USING SUPERCRITICAL CARBON DIOXIDE

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Developing new approaches to synthesis of manganese oxides, including ones using supercritical carbon dioxide (SC CO_2) as a solvent with unique properties, is currently an important scientific task on the way to create effective and economically perspective alternative power sources, such as lithium-air batteries [1] and alkaline fuel cells [2]. It is known that catalytic activity of manganese oxides varies significantly with the phase and morphology of particle’s surface, which both depends greatly on the synthesis route.

In this work we have demonstrated that an effective method of manganese oxides particles synthesis can be developed using manganese organometallic precursor tris(2,2,6,6-tetramethyl-3,5-heptanedionato)manganese(III) dissolved in SC CO_2 in the presence of 10 partial atmospheres of O_2. It is the specific character of prolonged growth of manganese oxide particles dispersed in SC CO_2 that can provide MnO_x particles with highly porous hierarchical structure, that is known to be beneficial for catalytic applications.

Authors are grateful for RFBR grants 13-03-01096 and 14-29-04101

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P-44

STUDY OF RECOVERY OF VALUABLE COMPONENTS FROM VEGETABLE RAW MATERIALS USING SUPERCRITICAL FLUID TECHNOLOGY

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Supercritical fluid extraction of vegetable raw materials - modern and advanced technology of extraction of components of plant raw materials from biomass. Supercritical CO_2-extracts are brand new product on the Russian market, and not only in the market. For most researchers such extracts were and remain inaccessible for reasons different, mainly due to lack of funding, as both their production and processing requires different methods, different analytical approaches, finally, other equipment than conventional extracts.

One practical application is the SC extraction and the pharmaceutical manufacture of food extracts. Pharmacological studies conducted by a number of plant extracts obtained by the SFT, allow to predict the natural production of new pharmaceuticals.

As part of this work were obtained extracts of tea leaf, hawthorn, motherwort herb, valerian root, rhizome Siberian ginseng and licorice root.

Processing of samples was carried out using supercritical fluid extraction unit SFE -1000 production company THAR Instruments (Figure 1) and the cell phase equilibrium of high pressure, in which the shutter in the carbon dioxide atmosphere and subsequent decompression.

Fig.1. Supercritical fluid extraction unit SFE - 1000.

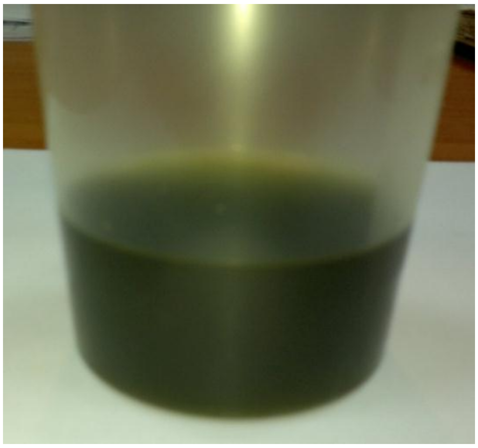

Fig.2. Tea extract

The samples were treated in a static mode (temperature of 35ºC, pressure of 10 MPa, treatment time 3 hours) and dynamic decompression mode (temperature of 35ºC, a pressure of 30 MPa, treatment time 3 hours decompression three times for 15 and 10 minutes).

In the vegetable raw material contains a large amount of extractives differ in chemical composition and extractive capacity.

It has been established that the mass fraction of soluble solids (extractives) for samples processed in supercritical carbon dioxide medium is 15-20% higher than the original sample.

Based on the analysis of laboratory studies on the extraction of vegetable raw materials and calculation of exergy extraction cycle, the optimal operating parameters of the process plant raw material processing with supercritical carbon dioxide.

P-45

DISPERSIVE POLYMERIZATION DINUCLEAR PIVALATE $(Hpiv)_6Tb_2(Piv)_6$ IN SUPERCRITICAL CARBON DIOXIDE MEDIA.

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Development and optimization of supercritical fluid (SKF) processes of highly effective synthesis and funktsionalization of essentially new materials for a wide range of scientific and technical applications and their use in innovative economy are extremely important directions of modern applied researches. In particular, use of SKF technologies alternative traditional, allows to receive effectively organic polymers of high chemical purity, the targeted morphology and dimension in quite soft temperature conditions, is one of intensively developing directions of modern synthetic chemistry. In the present work possibility of receiving known coordination magnetic and luminescent polymer {Tb(piv)3}n (piv = (CH3)3CCO2-) [1] by dispersive polymerization of a dinuclea complex $(Hpiv)_6Tb_2(piv)_6$ in the supercritical carbon dioxide (SKF-CO_2) media is investigated. It is known that metal-organic coordination compounds of lanthanides of a discrete and polymeric structure possess unique physical and chemical properties and cause considerable interest owing to high prospects of their practical use as innovative molecular materials in various areas of optics, magnetism, sorption, a sensorika, etc.

It is established that the modernized RESS-100 setup (Thar Technologies Inc., RESS, Rapid Expansion of Supercritical Solution), the developed approach which can be considered as a combination of the SAS method (Supercritical

AntiSolvent precipitation) and SAA (Supercritical Assisted Atomization), use of SKF-CO_2 as media, CH_2Cl_2 as organic solvent and $(Hpiv)_6Tb_2(piv)_6$ as a source of a monomeric unit allow to receive crystal coordination polymer $\{Tb(piv)_3\}_n$, which composition and structure correspond to known $\{Tb(piv)_3\}_n$ [1] whereas the sizes of particles and morphology depends on the parameters of process (Fig.1).

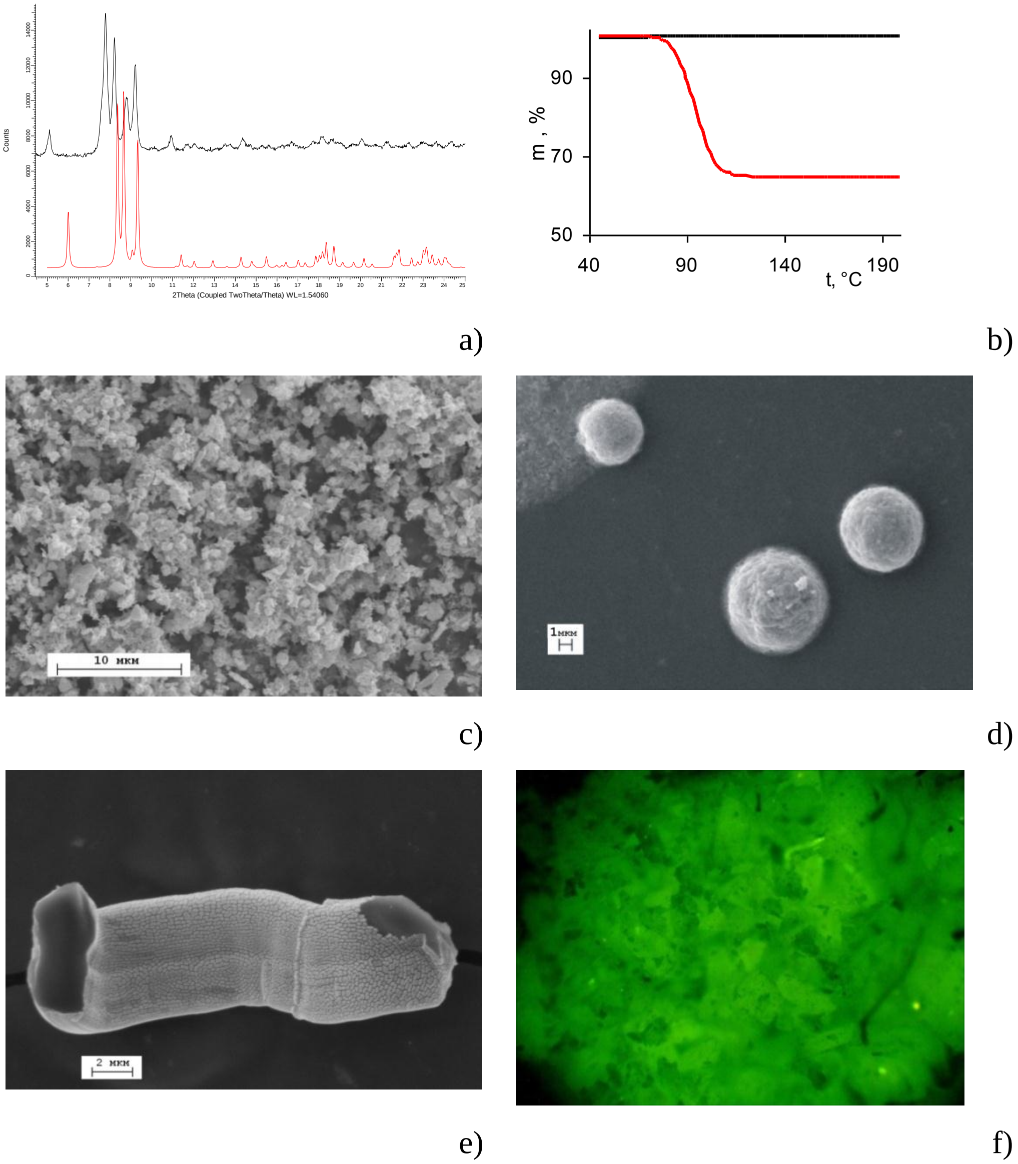

Fig.1. Theoretical roentgenogram $(Hpiv)_6Tb_2(piv)_6$ (red) [1] and experimental roentgenogram $\{Tb(piv)_3\}_n$ (black) (a); change of weight when heating $(Hpiv)_6Tb_2(piv)_6$ (red) [1] and $\{Tb(piv)_3\}_n$ (black) (b); SEM image of morphology $\{Tb(piv)_3\}_n$: polycristals, 90 bar (c), spheres, 20-100 bar (d), tubes, 100 bar (e); Image of PhotoLuminescence of polymer $\{Tb(piv)_3\}_n$ (Tb^{3+}, ${}^5D_4 \rightarrow {}^7F_J$, J = 3-6) in an optical luminescent microscope, λ excit = 450 nm (f).

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P-46

THE LUMINESCENT PROPERTIES OF POLYMER COMPOSITES OF NANOSILICON OBTAINED IN SUPERCRITICAL CO_2

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Introduction

Currently, important problm is the incorporation of the nanoparticles into polymer materials. For the impregnation of such nanoparticles as particles of nanosilicon (nc-Si) polymers with quite large pores are required. This paper is aimed at applying the effect of polymers crazing for embedding of nc-Si into polymer.

Crazing in polymers – is the formation of ordered fibrillar-porous structures in orientation drawing of amorphous polymers in adsorption-active liquid media [1].

A promising application of the technology is the formation of surface crazing of micro- and nano-relief in polymer films and fibers continuously to improve their optical characteristics.

Along with crazing of polymers, the polymeric membrane track polyethylene terephthalate (PET) with a pore diameter of 50 nm were used [2]. When polymers irradiation with high-energy ions occurs, a local modification of the structure of polymers takes place in which the intensity of damage varies radially from the axis of the track to the intact area.

Features synthesis nanokremniya

Silicon nanoparticles were obtained by the disproportionation reaction of SiO, the technique is described in [3].

The particle sizes of nanosilicon were determined by high resolution transmission electron microscopy (HRTEM).

The technique of SCF impregnation

Using supercritical carbon dioxide ($scCO_2$) the immobilization of polymer matrix (polyethylene terephthalate (PET), polypropylene (PP)) with photoluminescence silicon nanocrystals (nc-Si) was accomplished, which leads to the formation of photoluminescence nanocomposite.

The approach is based on the effect of swelling the polymer in $scCO_2$, efficient transport of nanoparticles into the internal free volume of the polymer using the $scCO_2$ and the shrinkage of the polymer introduced with its free volume of the nanoparticles after CO_2, release, that prevents their subsequent agglutination. More detailed procedure is given in [4].

Photoluminescence nanocomposites.

The PL spectra of the samples were recorded by spectrophotometer «Ocean optics QEPro» and were corrected for spectral functions of the device hardware. PL was excited by diode laser with a wavelength of 405 nm.

Photoluminescence in the resulting polymer composite with silicon nanoparticles demonstrates intense band with a maximum in the region of ~830 nm, in contrast to the initial pure film, which can be attributed to the luminescence of silicon nanoparticles. This fact confirms the occurrence ncSi inside the pores of the polymer. This conclusion follows from a comparison of the respective PL spectra of the obtained polymer nanocomposites and the dispersion of these same nanosilicon particles in hexane.

Conclusion

A new approach to immobilize photoluminescencent ncSi particles in the matrix of polymeric materials (PP subjected to crazing, powdered PTFE and track membranes based PET) was realized, using SCF as a transport medium for delivery of nanoparticles in the polymer matrix.

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P-47

RESEARCH AND POROUS POLYMER STRUKUTUR IN SUPERCRITICAL CARBON DIOXIDE

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The experimental setup for the preparation of porous polymeric structures in supercritical carbon dioxide, allowing to carry out experimental studies of up to 40 MPa and 350ºC. Also, a system for measuring the porosity of polymers using water at high pressure. A porous polymeric structure UHMW polypropylene and high density polyethylene in the temperature range of T = 60-180ºC, a pressure P of from 10 to 30 MPa. The dependence of the porosity of the polymer from the pressure and temperature.

For the research, an experimental setup (Fig.1) and the method of carrying out the sorption polymers supercritical carbon dioxide.

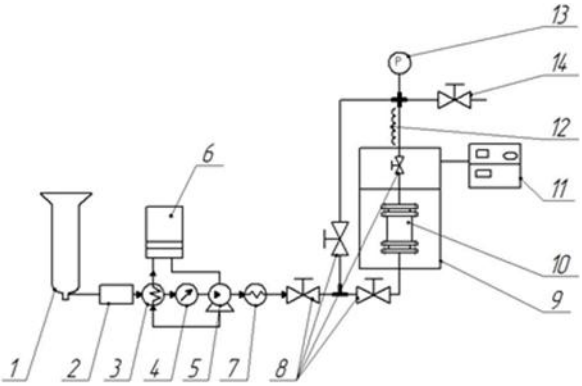

Fig.1 Schematic diagram of the experimental setup

1 – a cylinder with CO_2, 2 – the filter drier, 3 – cooling heat exchanger, 4 – flowmeter 5 – high pressure pump, 6 – thermostat, 7 – the electric heater, 8 – valve, 9 – band heater, 10 – experimental cell, 11 – control unit temperature and pressure, 12 – the heater, 13 – gauge, 14 – a throttle valve.

This setting allows you to carry out research in the pressure range of 6-40 MPa and temperatures 20-350ºC.

Before starting the experiment, the test substance produced in the loading cell (10). Further included thermostat (6), which is required for cooling the pump head (5) and a heat exchanger (3). The temperature control continues as long as the coolant temperature reaches -5ºC.

The cell temperature is set and maintained by the control unit (11). Further opened cylinder valve (1) from the carbon dioxide with the initial pressure of 5-6 MPa enters the cooling heat exchanger (3) through a filter drier (2). After the transition to the liquid phase through the flow-CO_2 (4) enters the pump (5) where it is compressed to a predetermined pressure, after which carbon dioxide is supplied to the cell (10). Because heating CO_2 passes into a supercritical state and begins to interact with the analyte. After soaking in supercritical carbon dioxide in the cell temperature was lowered to room temperature and slowly depressurised system. Valve (8) is in the open position and the throttle - valve (14) allows to control the flow CO_2, and thereby speed depressurization.

As of the objects are used:

- Ultra-high molecular weight polyethylene PE-1000 with a weight average molecular weight of M=1000000 g/mol in a cube with dimensions of (2.15x 2x2.1 cm)

The resulting porous polymer structures are geometrically measured on the basis of what has been revealed pore volume dependence on temperature, pressure and dwell time system, as well as temperature and holding time after depressurization system.

The same sections were examined received samples microtome Rotmik-2P microscope.

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P-48

MODELING AND SCALE-UP OF SUPERCRITICAL FLUID PROCESSES

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Special properties of supercritical fluids allow using it in various areas of the industry, for the extraction of different substances from plant material, micronization, chemical reactions, for producing of aerogels composites based on them.

To carry out the processes using supercritical fluids or processes which take place in supercritical fluid media it is required specialized equipment designed for use at high pressure. The creation process of such equipment results in significant capital expenditures. Using the methods of mathematical modeling it could be predicted the course of the process and it could be carried out its optimization to offer the most effective geometry of the equipment. A distinctive feature of the systems in a supercritical state is significant local changes of their properties when changing process parameters. Application of continuum mechanics and one of its methods - the method of computational fluid dynamics is suitable for the calculation of such systems. The most promising is the use of mathematical models for scaling-up. The use of such methods allows simplifying the scale transition, reduce the cost of creating a pilot plant and in some cases allow passing this stage.

In this paper it is suggested the mathematical model of the supercritical drying and supercritical adsorption processes. Mathematical models are based on the continuum mechanics, for calculation of model equations is used the program Ansys Fluent. It considers a two-component homogeneous system, which is a viscous compressible fluid and is described using the equation of state of Peng-Robinson. The system is divided into two computational spaces: the free volume of the reactor and the volume of the porous body (gel). In the porous body takes place only diffusive transport of the target component. The adsorption obeys the

Langmuir theory. As an example of using mathematical modeling to scale-up it is proposed 5 liter reactor geometry and was chosen the best options of conducting the supercritical drying process under this geometry.

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P-49

ROLE OF SUPERCRITICAL WATER IN SOLVENT LASER ETCHING PROCESS

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Optical materials microstructuring under pulsed laser irradiation is a promising technology for material processing for novel types of microelectronic devices (fiber and integrated optics, microfluidics, bio sensors) structuring. One of the most promising type of transparent dielectric materials treatment are laser-induced etching of the rear surface of the liquid in the transparent material (laser-induced backside wet etching - LIBWE) [1]. In this process, high-intensity laser light is focused on the back surface of the transparent sample cuvette which is filled with a strongly absorbing laser light liquid. In the laser focus, on solid-liquid interface many processes occur (nonlinear absorption, absorption by defects, and thermal, photochemical and hydrodynamic processes, the formation and collapse of the bubbles, melting, evaporation, etc.), leading to material etching. Recent studies have shown that a certain contribution to the process of laser etching may cause the formation and supercritical water at the boundary of the processed material and strongly absorbing fluid. The contribution of different mechanisms during laser etching, and their interaction is not fully understood and are the subject of numerous studies. This report provides a comprehensive approach for the development of methods of diagnostics of laser etching and their results with a view to understanding LIBWE-processes mechanism and examination of samples obtained by laser etching. To initiate LIBWE process the second harmonic of a solid-state diode-pumped lasers has been used with a wavelength of 527 nm. The processed sample is positioned three-axis controlled by a motion of the computer. As a strongly absorbing at the laser wavelength of the liquid used in the experiments, food color Amaranth, as models for etching - microscopic glass of silicate glass with a thickness of 1 mm. Process monitoring carried out by the video camera an image displayed on the computer screen. In order to diagnose and identify the processes occurring during laser etching, during the experiment conducted acoustic measurements using a needle hydrophone with a preamplifier (1 mm PVdF, Precision Acoustics, UK). For diagnostic specimens derived from LIBWE-etching developing a number of complementary techniques that include the study of the surface morphology of the etched patterns and structures etched surface using the methods of optical microscopy, atomic force microscopy and scanning electron microscopy; study of the chemical composition to be formed on different parts of the sample during etching by using Raman spectroscopy, and energy dispersive x-ray spectroscopy.

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P-50

PRINCIPLES OF FORMATION OF SOLID-PHASE COMPOSITE SYSTEMS IN SUPERCRITICAL CARBON DIOXIDE

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Technology using supercritical carbon dioxide (SC-CO_2) open a novel possibilities for the creation of solid-phase composite systems - metal, ceramic, polymer, used in various fields of science and technology - modern systems, optoelectronics, devices for information processing and transmission, to create medicines preparations, for regenerative medicine. Due to the wide variety of solid-phase systems produced using these technologies, there is a need to systematize (classification) of such opportunities through the establishment of the basic principles of the formation of solid-phase composite systems in supercritical carbon dioxide. The report is an attempt to identify these principles and show examples of their applications to the processes of formation of solid-phase systems in the medium SC-CO_2. Thus in each case should occur to the extent necessary properties of not only the environment (low viscosity, increased transfer rate of target components to impregniruemym matrices even at low equilibrium solubility of target components, low surface tension, the ease almost complete removal of CO_2 from the produced materials, high Activity in plasticizing polymer matrix), but also the original matrices, in particular their holding preliminary "training" before the finishing stage of processing in the medium SC-CO_2. Specific processes under consideration - impregnation target components and nanoporous polymer solid-phase systems, the initiation of processes of dispersion copolymerization monomers encapsulating target inorganic objects, and others.

P-51

VAN DER WAALS MODEL OF UNSTEADE EXPANSION OF SUPERCRITICAL CARBON DIOXIDE

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One of the key points of the study of the collapse of single polymer molecules in experiments with pulsed jets [1] supercritical polymer solutions is to build a model of expansion of the jet, which allows to calculate the temperature and density at the transition point "coil-globule" and optimize the strategy of the experiment. The basic objective of this model - the unsteady expansion of the gas cloud in a vacuum - is both fundamental and practical interest (explosion, laser physics) and as widely studied (analytically and numerically) for an ideal gas. For a real gas, this problem has not previously been considered.

Description expansion of supercritical CO_2 we traditionally began with the simplest model of a real gas - van der Waals gas. This allows, first, to outline the way to get analytical (self-similar) solutions of equations of gas dynamics; secondly, to identify the qualitative features of the expansion of a real gas and the possibility of using more rigorous equation of state of the Redlich-Kwong (mod.); third, to outline a strategy of numerical solution and its comparison with the self-similar.

Gas-dynamic system of equations representing conservation laws of mass and momentum, has the form

$$\frac{\partial \ln \rho}{\partial t} + u\frac{\partial \ln \rho}{\partial r} + \frac{\partial u}{\partial r} + 3\frac{u}{r} = 0$$

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial r} + \frac{1}{\rho}\frac{\partial \rho}{\partial r} = 0, \qquad p = \frac{\rho R_0 T}{1-b} - a\rho^2 \qquad \text{(equation of state)}$$

(ρ -the density, u- average speed and p -pressure of the gas, and r - the distance from the center of the sphere) and closes the isentropic equation for a van der Waals gas

$$p = c_0 R_0 \left(\frac{\rho}{1 - b\rho} \right)^{\frac{R_0}{c_v} + 1} - a\rho^2 ,$$

where c_v – isochoric heat capacity, R_0 – universal gas constant, a, and b – the parameters of the equation of state of the van der Waals constant c_0 is determined by conditions in the nozzle (p_0 and T_0 – stagnation pressure and temperature). Specific calculations are made for the expansion of supercritical CO_2 at p_0 = 100 atm and T_0 = 323 K from a nozzle diameter of 0.025 cm with a pulse duration of 200 μsec. Distance from the nozzle exit to the target plate – 10 cm. Diameter of target is 0.5 cm. The results of calculation of the distribution of density and temperature of the substrate along the target (a. u.) are shown in Figures 1a and 1b. The important detail behavioral is that the "plateau" on the calculated curves overlap the boundaries of the target (vertical line). This ensures uniform distribution of the parameters of the expanding gas within the target plate.

P-52

STUDING THE MICROCAPSULATION IN PULSED EXPANSION OF SUPERCRITICAL SOLUTION IN BACKGROUND GASES

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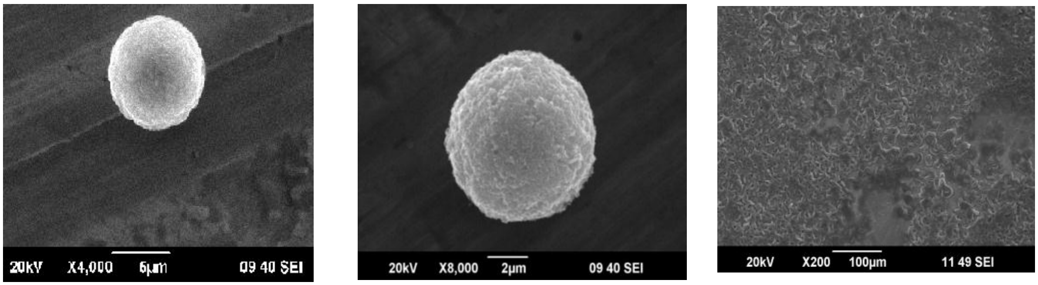
Research and development in the field of microencapsulation technology is largely devoted to the polymeric microcapsules prepared using supercritical carbon dioxide. Optimizing the conditions of such processes necessary for obtaining capsules with a predetermined content and properties of the active substance.

Basis of microencapsulation – the collapse of the polymer molecule in the transition "coil-globule" – is a convenient object of study by means of pulsed gasdynamics jets, as in this experiment can be implemented almost ideal conditions singles that do not interact with each other polymer molecules (high rarefaction in the process of jet expansion). Furthermore, the change in the experiment of source conditions (temperature, pressure, composition of suspension), the background gas pressure in the injection chamber and the distance "nozzle-target" allow to change the properties of the microcapsules (size, composition) and fix the instant of transition and "coil-globule". Changes same duration pulse and duty cycle allow you to vary the surface microcapsules density on the target and thus avoid their coagulation.

Experimental setup consists of a high pressure reactor in which the suspension TiO_2 in polyethylene glycol (PEG 8000) solution in supercritical CO_2 at predetermined pressure and temperature obtained, the nozzle with variable pulse duration and duty cycle to inject in chamber with background gas and the target.

Supercritical solution is composed (in weight %) of carbon dioxide (70.4%), ethanol (27.1%), polyethylene glycol PEG 8000 (2.2%) and titanium dioxide nanoparticles 21 nm in size (0.3 %). The injection produced through a nozzle diameter of 0.025 cm with a pulse duration τ = 400 μsec. The distance between the nozzle exit and the substrate is 10 cm.

The microcapsules were precipitated from jet to the copper target have been studied by the scanning electron microscope JEOLJSM-6490LV with 10 nm resolution. Method of energy dispersive X-ray microanalysis investigated quantitative elemental composition of the microcapsules (EDX). Images results at 1 atm in the deposition chamber for He(a), SF_6 (b) and CO_2 (c) are shown in Figure 1. It is interesting to note that in contrast to the typical globular structure for He and SF_6 at injection in CO_2 background at the surface target formed a distinct spatial structure - film composed probably from deposited coil.



a) b) c)

Fig. 1. Microcapsules images TiO_2 in PEG8000 (background gas: a)-He, b)-SF_6 и c)-CO_2).

P-53

THE EFFECT OF SALT ADDITION ON THE PROCESS OF SUPERCRITICAL HYDROLYSIS OF BIOMASS OF MICROALGAE

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Plant biomass is the main renewable raw material for industrial production and it is also considered as an energy source, particularly for the preparation of gas or liquid fuel. For such purposes biomass can be divided into 3 types of biological products: edible oils and sacchariferous plants (1); nonfood, cellulosic plants (2) and nonfood aquatic plants comprising polysaccharides and oil with a low content of lignin – algae (3). Social, economic and technical aspects hinder the development of energy products from the first two types of biomass (obviously, it is more profitable to make food products from plants of type 1, and the effectiveness of the processing of plants with high lignin content is low), so the 3rd type of biomass becomes more important [1].

The main components of microalgae biomass are polysaccharides and oil. Absence of a hard shell and the almost complete absence of lignin in algae makes processing of liquid fuel technologically simpler and more efficient in comparison with the processing of the biomass from any land plants. We used a water mixture of microcrystalline cellulose and oil as a model of microalgae biomass.

Hydrolysis reactions occur during the interaction of SC water with cellulose or other polysaccharides from algae biomass, and, depending on the conditions, they result in formation of glucose, sugar oligomers, oils, alcohols, aldehydes, liquid and solid complex hydrocarbons and also gas components [2-4].

The present study aims to clarify the composition of the gaseous components formed during hydrothermal treatment of microcellulose (MCC-101, degree of polymerization is 200 ÷ 250) in the SC water and aqueous solutions at temperatures 430 ÷ 550 °C. The current model [5] mainly describes decomposition to H_2, CH_4, CO and CO_2 in pure water, without considering the effects of salts on formation of gaseous hydrocarbons and on composition of solid and liquid residues.

Experiments were conducted using hydrothermal autoclaves equipped with a shut-off valve for taking samples of gas phase formed in the mixture. The autoclave was filled with a mixture of cellulose and aqueous salt solutions, as well as alkali (NaOH, pH = 11 ÷ 13) or acidic (HCl, pH = 1 ÷ 3) aqueous solutions. The autoclaves were kept at 430 ÷ 550 °C and at pressure of 30 ÷ 40 MPa for 30 ÷ 90 minutes and then cooled to a room temperature. Samples of gas phase were taken in the plastic sampler during the experiment and after the cooling. The weight of the sample was ~ 7 ÷ 10% of the loaded weight. Determination of the composition of the samples was carried out by GC spectrometry method on the Agilent HP 5973 MSD (IGIC RAS). The results of determination show that the composition of the gas phase changes slightly as composition of the solution changes. The main components of the gas mixtures are H_2, CH_4, CO, CO_2, ethane, ethylene, propane, propylene, and a significantly smaller amounts of heavier hydrocarbons (C4, C5).

The studies were conducted with the financial support of the Russian Federation represented by the Ministry of Education and Science of the Russian Federation in the framework of the federal target program "Research and development on priority directions of scientific-technological complex of Russia for 2014-2020", a unique identifier applied research RFMEFI57514X0052.

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P-54

KINETICS OF DIFFUSION OF PARAMAGNETIC PROBES INTO POLYMER MARICES IN SUPERCRITICAL CO_2

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Estimation of optimal time needed for impregnation of polymer materials in supercritical CO_2 ($scCO_2$) and sufficient for obtaining of uniform distribution of embedded compounds in a sample is much simplified if kinetic parameters of their diffusion in polymers in $scCO_2$ are known. Electron paramagnetic resonance spectroscopy of spin probes is a convenient method to study diffusion as it allows to quantitatively estimate spin probe content diffused into polymer, whereas polymer matrix itself is completely transparent for EPR [1].

In this work kinetics of diffusion of spin probe 4-oxo-2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPONE) in polymer matrices (PMMA, PTFE, etc.) in $scCO_2$ is measured. For various times in $scCO_2$ concentration profiles are constructed and kinetic parameters of diffusion are extracted.

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P-55

SUPERCRITICAL CO_2 HYDROGENATION BY RUTHENIUM CATALYST

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Over the past fifty years, the concentration of carbon dioxide in the atmosphere is significantly increased due to using of huge amounts of carbon-containing fuels (coal, oil, natural gas, etc.). As an economical, safe, and renewable carbon source, CO_2 turns out to be an attractive building block for making organic chemicals and materials. The utilization of CO_2 as a feedstock for producing chemicals contributes to alleviating global climate changes caused by the increasing CO_2 emissions. [1]

Catalytic hydrogenation of CO_2 to methane (Sabatie reaction) an important catalytic process, which is expected for the application in manned space colonization on Mars. [2] A large number of researches related to the study of this process catalyzed by VIII group metals (Ru, Rh, Ni, etc.) supported on various oxides (SiO_2, TiO_2, Al_2O_3, etc.). [3] Compared with a gas-phase process, the hydrogenation of supercritical CO_2 has several advantages, however, a number of works in this area is limited.

In this work we were studied the process of supercritical CO_2 hydrogenation conditions (80 bar, 200–350°C, GHSW = 4800 h^{-1}) on the model ruthenium catalyst Ru/C and the impact of these conditions on its physicochemical properties.

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CR-1

NONLINEAR PHYSICAL PROCESSES IN INHOMOGENEOUS CRITICAL FLUIDS IN THE EARTH'S GRAVITATIONAL FIELD

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Earlier studies [1] proposed a new mechanism for the physical processes responsible for the successful use of the unique properties of the critical fluid (CF) in modern industrial technologies [2]. This mechanism is based on the fluctuation theory of phase transitions (FTFP) [3], is directly related to the fluctuation of the dispersed structure CF: correlation radius R_c of such a system, the number of fluctuations of the order parameter $N_f \sim R_c^{-3}$ in the mole of substance, the high density of matter $\rho_f \approx 3\rho_c$ in these nanoscale fluctuation volume $v_f = 4/3\ \pi\ R_c^3$, large propagation velocities of the molecules of matter $u_f = 10^6 \div 10^7$ cm/s [1] in the decay of fluctuations of the order parameter. It can be argued that these structural features are the basis of CF nonlinear physical processes occurring in the system and are responsible for widespread practical use of the unique properties of CF in the latest industrial technologies [2].

First nonlinear physical processes in inhomogeneous critical fluid detected by optical methods of light scattering and refractometric [4,5]. In these works the first time it was shown that under the influence of Earth's gravity field $h = \rho_c zg/P_c$ in CF, an inhomogeneous internal electromagnetic field $\Delta U(h)$, altitude changes which significantly exceeds the change in hydrostatic pressure h $(U(z) \approx (10 \div 10^2)\ h >> h)$. On the nonlinear nature of this phenomenon is illustrated by the fact that the gradient of the internal electromagnetic field depends on the critical temperature of the material, the linear size of the sample, its geometric shape, medium density $\bar{\rho}$ system filling material.

On nonlinear physical processes in inhomogeneous CF also show a number of other physical phenomena. For example, self-focusing [6,7], low luminous flux from the mercury lamp DR-250, passing through an inhomogeneous critical fluid at a height of z=0 the critical density ρ_c of the material when $t\to 0$. Under these conditions, the refractive index gradient in a nonuniform CF reaches values ($dn/dz\to 0.1\div 1$) cm^{-1}. Said a new phenomenon in a nonuniform KF like self-focusing of high-power laser beams in an environment far from the critical point [8]. Under these conditions, the CF also occurs and the intensity of the light beam [6,7] for the energy scale of the order parameter fluctuations. This statement is consistent with similar findings of the authors of [9]. In these works, expressed the view that “the propagation of waves in nonlinear fluctuation-dynamical systems with dispersion near the critical point of bifurcation points and waves are able to increase their energy due to the potential energy of critical fluctuations of the order parameter”.

It can be argued that the above list of nonlinear physical processes in CF will certainly find its further widespread practical use of the latest industry technologies.

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CR-2

REGULAR AND FLUCTUATION COMPONENTS OF CRITICAL INDICES OF A CRITICAL FLUID

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At present, interest in studying various properties of the critical state of the substance – the critical fluid (CF) – has considerably increased due to its wide practical applications in the newest technologies [1]. In this connection, researchers critical state of matter are increasingly turning to a more careful definition of the critical parameters of the fluctuation theory of phase transitions (FTPT) [2, 3], which are some of the main parameters of the equation of state of matter near the critical point.

This work presents a new phenomenological approach to estimating values of critical exponents [4] of the critical fluid of two components, regular and fluctuation. The values of regular components were determined by Novikov based on the form of the thermodynamic Gibbs potential and its derivatives near the critical point [5]. Fluctuation components, which are small additives to the regular part of the critical exponents: $\nu_0=2/3-\nu$ и $\xi_0=\xi-2/5$, are responsible for fluctuation processes in the system near the critical point. These main small parameters are fluctuation components of critical exponents of the temperature and field dependences of the correlation radius: $\nu_0=0.03$, $\xi_0=0.005$.

A direct interconnection between small fluctuation components and critical exponents of the heat capacity and correlation function was established. The form of the two new equations connecting critical exponents of the field and the temperature dependences of the correlation radius has been found. Using these new equations, based on the phenomenological approach presented and FTPT equations [2, 3], the values of eight critical exponents of the critical fluid have been determined.

In this work, based on the proposed phenomenological approach, the value of the field dependence of heat capacity $\alpha_\mu=(0.058\pm0.001)$, has been found and the values of critical exponents of the temperature dependence of heat capacity $\alpha_t=(0.090\pm0.001)$, correlation function $\eta=(0.061 \pm 0.001)$, and critical exponent of the coexistence curve $\beta=(0.338 \pm 0.001) > 1/3$ have been refined.

The obtained values of the critical exponents ν, ξ, α_t, α_μ completely satisfy the fundamental FTPT relationships [2, 3]: $2\beta+\gamma+\alpha_t=\beta+\beta\delta+\alpha_t=\beta+\frac{\nu}{\xi}+\alpha_t=2\pm0.001$, and $\frac{\alpha_t}{\alpha_\mu}=\frac{\nu}{\xi}=\beta\delta=1.570\pm0.001$. This result indicates the fact that the presented estimates for values of critical exponents are close to their real values of the critical FTPT exponents [2,3].

Proceeding from the direct interconnection between values of small critical exponents α_t, α_μ, η and fluctuation components of critical exponents of the correlation radius ν_0 and ξ_0, it is necessary to conclude that the zero value of the critical exponent of the correlation function $\eta = 0$ which is rather often used in theoretical calculations leads to zero values of the critical exponents of heat capacity $\alpha_t = \alpha_\mu = 0$. This result corresponds to the average field approximation [6] and is an attribute of the absence of large-scale order parameter fluctuations in the system. In this case, proceeding from the FTPT [2, 3] and [5], one should use the following values of all other FTPT critical exponents [2, 3] for three-dimensional systems: $\delta=5$, $\gamma=4/3$, $\nu=2/3$, $\xi=2/5$, and $\beta=1/3$; these values were obtained based on Novikov's thermodynamic method [6].

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CR-3

EXPERIMENTAL VERIFICATION EQUATION FOR A CRITICAL VISCOSITY ON BASIS OF THE THEORY OF DYNAMIC SCALING AND ALLOWANCE FOR SPATIAL DISPERSION SYSTEM

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At this time, due to the wide practical use of the unique properties of the substance in critical condition: the critical fluid (CF) in the latest technologies [1] significantly increased interest in experimental and theoretical studies of the properties of different states of matter. This applies particularly to the kinetic properties of the substance: the diffusion coefficient and viscosity.

This paper presents the experimental data of the temperature and concentration dependences of the critical viscosity [2] dual solution isobutyric acid-water near the critical temperature stratification in a wide range of concentrations and temperatures x T, including their critical values x_c, T_c.

Using these data in the constructed three-dimensional surface of the critical viscosity $\eta_f(x,T)$ based on the modern dynamical theory of critical phenomena [3], as well as the critical viscosity equation [4], which takes into account the spatial dispersion of the system near the critical point (CP) [5]. On the basis of the results determined by the range of applicability of these qualitatively different equations critical viscosity and the following conclusions.

1. The results of the concentration and temperature dependences of the viscosity fluctuation confirm viscosity form of the equation, which takes into account the spatial dispersion of the system over the entire temperature $t \approx 10^{-4} \div 10^{-2}$ and concentration $x = 0 \div 0{,}5$. It is shown that at the critical temperature stratification than ($x = x_k$, $t \to 0$), viscosity of the solution tends to the finite value $\eta_f(t \to 0, x \to x_\kappa) = const$.

2. Dynamic viscosity of critical equation theory of critical phenomena [3] and viscosity equation taking into account the spatial dispersion of the system [4] are consistent with each other and with the experimental results only in a narrow range of concentrations near the thermodynamic critical areas izocontsentraty in the temperature range $t \approx 10^{-4} \div 10^{-3}$.

3. The results and conclusions are consistent with the results of many studies of the critical viscosity, presented in [6, 7] and others.

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CR-4

PALLADIUM CATALYST FOR SELECTIVE HYDROGENATION OF ACETYLENE, PREPARED BY IMPREGNATION IN SUPERCRITICAL CARBON DIOXIDE

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Six samples of palladium catalysts with 0,03-0,05% mass content of metal were prepared by supercritical impregnation method. γ-Al_2O_3 was used as a support [1]. Metal precipitation was carried out in reactor with magnetic stirrer.

Also six samples of palladium catalyst with the same metal content were prepared by impregnation of PdCl water solution. The same γ-Al_2O_3 was used as a support. Metal precipitation was carried under continuous stirring.

Prepared catalyst samples were tested in hydrogenation of acetylene in ethane-ethylene rich flow which consist of (% vol.): C_2H_2 – 0.55; H_2 –1.6; C_2H_6 – 23; C_2H_4 – 74; C_3 hydrocarbons – 0.85. Volume of loaded catalyst was 0.5 cm^3, gas hourly space velocity 2400-7200 h^{-1}. Reaction was carried out in a reactor with fixed bed of catalyst at atmospheric pressure in temperature range 40-90°C. Catalytic activity tests results are showed in Table 1.

Table 1. Catalytic activity tests results

№	**Sample**	**GHSV, h^{-1}**		**Temperature, °C**					
				40	**50**	**60**	**70**	**80**	**90**
1	0,03%Pd (H_2O)	2400	Acetylene conversion	4,4%	9,4%	20,2%	46,1%	87,7%	100,0%
2	0,03%Pd (Sc-CO_2)			9,7%	15,3%	30,2%	55,5%	96,6%	100,0%
3	0,05%Pd (H_2O)			5,0%	14,0%	31,1%	59,4%	98,6%	100,0%
4	0,05%Pd (Sc-CO_2)			8,3%	14,2%	34,4%	70,8%	100,0%	
5	0,07%Pd (H_2O)			12,0%	21,0%	49,0%	94,8%	100,0%	
6	0,07%Pd (Sc-CO_2)			13,1%	23,4%	54,8%	98,7%	100,0%	
7	0,1%Pd (H_2O)			18,8%	32,9%	74,6%	100,0%		
8	0,1%Pd (Sc-CO_2)			32,1%	52,5%	95,6%	100,0%		
9	0,1%Pd (H_2O)	7200		7,0%	12,0%	26,4%	53,8%	92,5%	100,0%
10	0,1%Pd (Sc-CO_2)			7,1%	13,3%	30,0%	60,8%	95,7%	100,0%
11	0,3%Pd (H_2O)			12,6%	24,3%	53,8%	94,4%	100,0%	
12	0,3%Pd (Sc-CO_2)			13,3%	31,4%	60,2%	98,7%	100,0%	
13	0,5%Pd (H_2O)			37,7%	65,6%	95,6%	100,0%		
14	0,5%Pd (Sc-CO_2)			21,3%	48,7%	93,1%	98,0%	100,0%	

Except of 0.5% Pd-catalyst, all the samples prepared by impregnation in supercritical CO_2 have higher activity than catalysts prepared by impregnation of PdCl water solution. 0.1% Pd-catalysts have the highest difference in acetylene conversion (19% at 60°C and GHSV 2400 h^{-1}).

For the all catalysts hydrogen temperature reduction curves were obtained and acidity by the ammonia temperature-programmed desorption was determined. The quantitative content of palladium confirmed by X-ray fluorescence analysis.

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CR-5

THE LIMITS OF THE SUPERCRITICAL REGION OF EQUILIBRIUM SISTEMS LIQUID-GAS

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The equilibrium state of chemical substances in the two phase system of liquid-gas can be described by the equation type

$\alpha = (P_m T_m/PT) \exp(1 - T_m/T)$,

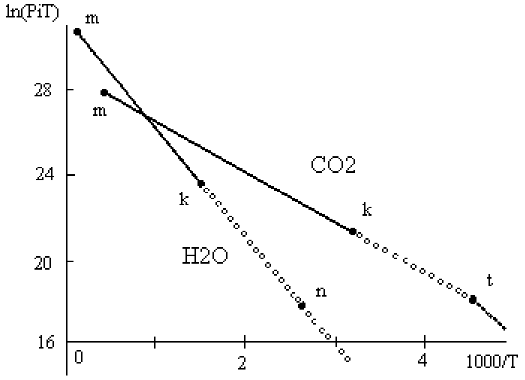
where α is volumetric, molecular or molar fraction of gaseous substances in the gas phase, $(P\ \alpha) = P_i$ is the saturated vapor pressure, P_m and T_m – personal limit parameters at which two-phase system becomes a single (gas).

Limit parameters P_m and T_m significantly exceed parameters of the critical point (T_k and P_k); they can be calculated using the equilibrium parameters of the two arbitrary points (P_{i1} at T_1 and P_{i2} at T_2) on the equations

$T_m = (1/T_1 – 1/T_2)^{-1} \ln[P_{i2}T_2/(P_{i1}T_1)]$,

$P_m = (P_{i1}T_1/T_m) \exp(T_m/T_1 - 1) = (P_{i2}T_2/T_m) \exp(T_m/T_2 - 1)$.

If experimentally-reference parameter equilibrium systems liquid-gas to represent graphically coordinate $\ln(P_i\ T) – 1/T$, then get straight dependencies. At this, the point with parameters T_m and P_m is on the same straight line (see figure). For H_2O – T_m=5318 K and P_m=3.775 10^9 Pa, for CO_2 – T_m=2249 K and P_m=5.93 10^8 Pa.



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CR-6

SELECTIVE PLANE ILLUMINATION MICROSCOPY (SPIM, MSPIM, MUVISPIM) AS A TOOL FOR SUPERCRITICAL FLUID VISUALIZATION & CHARACTERIZATION

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In this report, we propose a novel procedure for the supercritical fluid behavior visualization and measurements based on SPIM or similar microscopic techniques in the rotational micro-capillary tubes (such as micro-columns for the supercritical chromatography [1,2]) or using a rotating multi-objective turret on an spindle (relative to the capillary tube axis). Very little attention has been paid to the supercritical fluid structure microscopy until now, since the major focus is on the confocal studying of the chemical products of supercritical fluid effects on the organic [3,4] and inorganic matter [5] (but not *in situ*). The selective plane illumination microscopy method is intended for providing a realistic volume visualization of dynamical objects (such as living cells [6]) as well as standard CLSM techniques. The above microscopic procedure is applied for *in vitro* embryological studies in time-lapse regimes. We simply propose to replace a time-lapse registration by a superfast registration (using high-speed cameras) for *in situ* fixation of supercritical fluid dynamics and for slow-motion representations of physical states and transitions, distinguishable using mathematical morphology tools. An elegant version of this method for our purposes includes also a cross-correlation spectroscopy for supercritical fluid behavior analysis [7].

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CR-7

3D PIV & 3D LDV / LDA / LDF BASED ON SPIM AS THE NOVEL TOOLS FOR THE STUDIES ON CRYOGENIC SUPERCRITICAL TECHNOLOGIES

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Cryogenic technologies play a significant role in the development of physics of the supercritical states, and particularly, the supercritical fluids. The early works considered the cryophysical aspects of the supercritical pressures [1,2], while at the studies on the supercritical extraction the main attention was paid to the cryogenic cooling of the adsorbent [3] and related problems. From the early 2000-th the research focus was shifted to the cryogenic liquid injection technologies [4-6]. Later the strategy for simulating supercritical cryogenic jets using high-order schemes was proposed [7]. To date there is a clear boundary between the technologies of the cryogenic fluid injection into a supersonic flow field [8], supercritical pressure cryogenic injection [6], etc, and cryogenic spray-freezing technologies [9]. To date there are no methods for the hydrodynamic jet microstructure 3D visualization and measurements for most of the above methods. We propose to use SPIM-like (Selective Plane Illumination Microscopy) setups with 2-3-4-objective registration schemes for this purpose in order to perform PIV (Particle Image Velocimetry), LDV (Laser Doppler Velocimetry) / LDA (Laser Doppler Anemometry) / LDF (Laser Doppler Flowmetry) and similar measurements using the above configuration.

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CR-8

SUPERCRITICAL FLUID EXTRACTION OF URANIUM COMPLEXES WITH CARBON DIOXIDE IN GRADIENT TEMPERATURES FIELD

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It is known that incomplete extraction of uranium from raw material – up to 95-97% constitutes disadvantage of obtaining uranium by method of uranium ores processing. Therefore, for example, a large quantity of waste uranium is accumulated in Ukraine in the form of tailing dumps, forming anthropogenic deposits fields with total area ~2.5 mln. m^2 and mass about 40 mln. t. Waste piles of coal mines, containing heavy metals, uranium and thorium, with total volume of coal rocks ~1056.52 mln. m^2, can also be referred to as anthropogenic deposits.

That is why one of the main tasks of development of nuclear power engineering is search of alternative, low-waste technology of uranium ores treatment and anthropogenic deposits fields reclaiming.

One of such technologies, satisfying selective, deep and low-waste treatment of feed stock, can be the technology of supercritical fluid extraction with carbon dioxide (SFE-CO_2) of uranyl-nitrate complexes with organophosphorous compounds [1]. Within the frames of realization of this technology, supercritical fluid (SF) with dissolved uranium complex appears in the reactor under high-pressure (more than 7.38 MPa) and relatively low temperature (more than 31.06ºC). It was experimentally determined that under pressure 9 MPa and temperature 38ºC, up to 62% of uranium complexes is extracted, whereas theoretical model showed that maximal efficiency of uranium complexes extraction constitutes about 96% [1]. At it goes from the theoretical model, quantity of the added in supercritical fluid water influences the extraction effectiveness: it is maximal under quantity of added water equal to its solubility limit in SF.

The paper presents experimental research of SFE-CO_2 of natural uranium on condition of presence of spatial temperature gradient. Experiment was conducted on the upgraded laboratory facility for supercritical fluid extraction SFE-U [2]. Upgrade was carried out only for the reactor, constituting, in the original form, the cylinder with height 9 cm and diameter – 2.6 cm. After upgrade reactor height was increased to 21.8 cm, retaining the initial sizes. Upper and lower reactor flanges were kept under specified temperatures by means of regulated heaters, at this the lower flange temperature was assigned higher than the upper.

In the process of conducting of works, method of preparation of probes and order of extraction procedures form granite samples described in [1] was used. Granites, containing maximal quantity of natural uranium, were selected as samples. Before conducting the SFE-CO_2 extraction, for the purpose of verification, initial samples of solution were checked on gamma-spectrometers on the correspondence of ^{235}U content to the natural. Content of ^{235}U on gamma-spectrums depending on the selection point on the reactor height was determined in the obtained as result of SFE-CO_2 extraction samples of eluent, precipitated on filter paper. Detector based on high-purity germanium – coaxial germanium detector GC 1818 with relative efficiency of registration ε_{rel}=18%, energy resolution ΔE=180 keV under energy of gamma - quants E_γ=1.33 MeV, was used as detector for gamma rays.

As a result of conducted research, it is shown that under certain pressure and spatial temperature gradient, SF concentration of ^{235}U isotope is distributed irregularly over the reactor height: maximal concentration is observed close to the heated lower flange, and minimal – close to the cold flange. It was concluded that in gradient temperatures field, ^{235}U isotope distribution irregularity rate (relation of isotope concentration to the natural) in supercritical carbon dioxide can exceed one. In order to explain the observed phenomenon, physical model based on usage of developed earlier double two-level model [1] was offered.

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CR-9

PROBE PREPARATION AND SUPERCRITICAL FLUID EXTRACTION OF MOLIBDENUM COMPLEXES WITH CARBON DIOXIDE

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Radioisotope methods of diagnostics and treatments with ^{99m}Tc isotopes are widely used in present-day medicine. That is why it is important, for example, to solve the problem of Mo isotopes selective extraction [1].

The paper presents method of supercritical fluid extraction with carbon dioxide (SFE-CO_2), of well soluble in supercritical carbon dioxide (SC-CO_2) Mo complexes of molybdic acid with tributylphosphate (MA-TBF) [2].

The paper presents research of Mo solubility dependence (molybdenum, wire with weight 0.4763 g) in 4 ml diluted HNO_3 on time. Content of Mo in water solution of HNO_3 in the form of molybdenum acid (MA) of different composition was determined on X-ray analyzer КРАБ-3УМ. It is experimentally showed that in 1.14 mol/l water solution of HNO_3 entrance of Mo in to solution is characterizes with quasiperiodic dependence on time of solution, presented on Fig.1. Such dependence is explained with the fact, that when reaching the MA in solution in saturation condition, crystal precipitate appears, and the process of Mo getting into solution repeats again. Dependence of Mo wire weight decrease on time is presented on Fig.1. In order to conduct the SFE-CO_2 extraction of Mo, complexes MA-TBF should be formed [2]. For this, TBF with kerosine in relation 1:1 is added into 2 ml of Mo solution. Quantity of the obtained complex MA-TBF is inversely proportional to the multiplier on Fig.1 and constitutes the value about 5-7% from the Mo content in nitric acid solution. SFE-CO_2 extraction of complexes MK-TBP was investigated after their formation. In order to optimize the effectiveness of SFE-CO_2 extraction, different modifiers (see Table 1) were added in to the determined organic phase of the MA-TBF.

Thus, the HNO_3 solution has the solubility limit of Mo. Dependence of Mo content in the solution on time of solution has quasi-periodic character. When reaching the solubility limit MA is precipitating. Quantity of the appeared complex of MA-TBF constitutes about 5 - 7% of Mo content in solution. The biggest percentage of SFE-CO_2 extraction of the complex MA-TBF is equal to 90% and is achieved when adding 0.1 ml of acetylacetone and 0.05 ml of water.

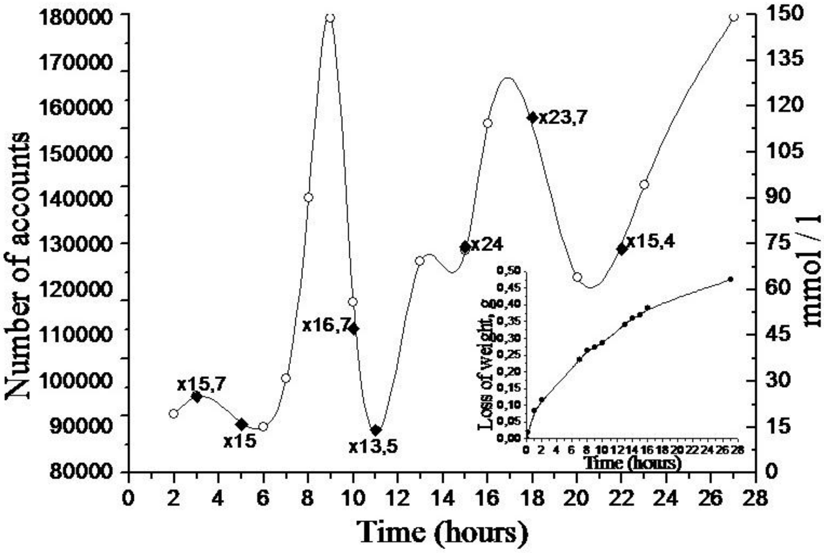

Fig.1. Dependence of Mo content in HNO_3 on the solubility time (○)
Dependence of MA-TBF complex in HNO_3 appearance on time (♦).

Table. 1. Efficiency of SFE-CO_2 complexes of MA-TBF in presence of modifiers(ISA - isopropyl alcohol; d.d. –double dumping)

№	TBF	Modifier			% Mo extraction
		acetylacetone	water	other	
1.	0,2 ml	–	–	0,6 ml ISA	18 %
2.	0,2 ml	0,4 ml	0,05 ml	–	19 %
3.	0,2 ml	0,6 ml	0,05 ml	–	22 %
4.	0,2 ml	0,7 ml	0,05 ml	–	24 %
5.	0,2 ml	–	0,05 ml	–	26 %
6.	0,2 ml	–	0,05 ml	0,1 ml hexane	27 %
7.	0,1 ml	0,1 ml	–	–	52 %
8.	0,2 ml	0,6 ml +0,3 ml + d.d.	0,05 ml	–	61 %
9.	0,2 ml	0,1 ml	0,05 ml	–	90 %

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CR-10

CONVERSION OF CARBOHYDRATES IN THE ENVIRONMENT OF SUPERCRITICAL ISOPROPANOL

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The paper presents results of a study of the conversion of glucose, as monomer plant polysaccharides - starch and cellulose, fructose and sucrose in the medium of supercritical isopropanol (SCI). Known technological advantages of supercritical fluids in combination with high restores the activity SCI, the ability to carry out the hydrogenation of the double bond and hydrogenolysis single [1]) can open new possibilities of realization of processes of processing of renewable vegetable raw materials with the aim of obtaining useful low molecular weight products, including compounds with high reactivity- 5-hydroxymethylfurfural (HMF) and its derivatives. These compounds are used for the synthesis of pharmaceuticals, drugs for agricultural purposes, various chemicals, additives for fuels, intermediates for polymer industry and so on.

The reaction of interaction SCI (critical parameters isopropanol: temperature – 235.3°C, a pressure of 5.3 MPa, a density of 0.27 g/cm^3) with carbohydrates was performed by the method of "sealed glass ampoule " in accordance with [1]. A portion of carbohydrate and isopropanol in a ratio of 1:10 and 1:20 were sealed inside a regular glass ampoules of 10-12 cm^3, a diameter of 10 mm and a wall thickness of 0.7-1 mm. The ampoules were placed in a heated solid metal container with a displacement of 680 cm^3 (container height - 100 mm, diameter - 90 mm), which was also filled with isopropanol so that at a given temperature, the pressure in the reactor was equal to the pressure in the ampoule. The container was sealed and was heated for 30 min to 290°C. At this temperature, the ampoule was kept for 30 minutes. After cooling container ampoule was opened. The liquid phase was collected and used for subsequent studies.

Analysis of the products of the liquid phase was performed by gas chromatography on the chromatograph Trace GC ULTRA with a mass spectrum detector DSQ II. The interpretation of the chromatograms was performed using the software NIST Mass Spectral Data Base. Identification of the GMF in the analyzed solutions was performed according to retention time of the standard sample GMF.

On the chromatograms of the products of the conversion of glucose, fructose and sucrose in SCI registered to 16 peaks of different intensity.

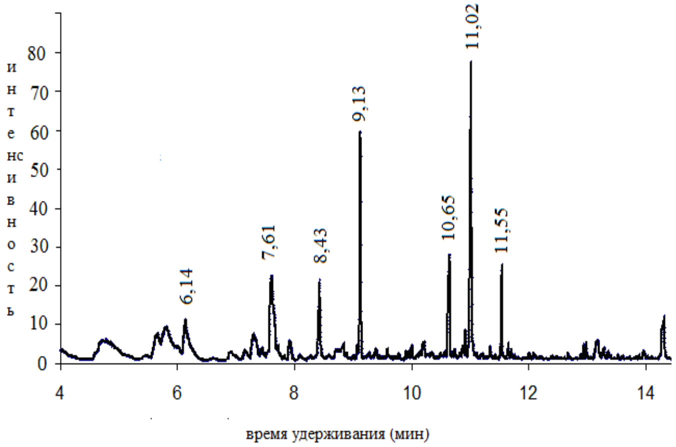

Fig. 1 Fragment chromatogram of the products of the conversion of glucose in SCI (ratio 1:10).

As an example, figure 1 shows fragment chromatograms of the products of the conversion of glucose. Among the components of all the analyzed compounds were identified: 5-hydroxymethylfurfural (10.65 min); 5-methylfurfural (7.61 min); 5-methyl-2-furanmethanol (7.45 min); 2.5-dimethylfuran (5.81 min); 2.5-hexandione; difurfurylether (7.31 min), levoglucosan (13.19 min) and isopropyllevulinate (9.13 min). To identify peaks with retention time 11.02; 11.55 and 14.32 minutes failed.

The nature of the conversion products of glucose in the SCI indicates the flow in the considered conditions, several types of reactions: dehydration of hexoses proceeding with the formation of levoglucosan, 5-hydroxymethylfurfural, levulinate acid, which in turn is subjected to alkylation with the formation of isopropyllevulinate; reaction of catalytic hydrogenation of 5-hydroxymethylfurfural with the formation of 2.5-dimethylfuran and others.

The obtained results are promising for the study of processes of conversion of carbohydrates in the SCI.

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CR-11

DETERMINATION OF REAGENTS RATIO IN THE PREPARATION OF SILICA AEROGEL BY RAPID SUPERCRITICAL DRYING

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Aerogel – a lightweight highly porous material that attracts the attention of researchers working in different fields of science and technology. Silica aerogel has a weblike microstructure and high surface area (over 1000 m^2/g), thereby causing interest as the catalyst supports, heat and sound insulation material, and as carrier of bioactive substances in the pharmaceutical industry. The aerogel microstructure comprised of interconnected spherical particles of quartz with diameters 0.004 microns, forming a three-dimensional network pores filled with air. Pore sizes of ten or more times the size of the clusters, which allow to obtains a very lightweight material. The first samples of the aerogels were made relatively long ago, however, for now, the method to process aerogels is quite time-consuming and cost-uneffective, limiting its field of application.

We have chosen the optimal conditions to obtain samples of silica aerogel by rapid supercritical drying (autoclave Parr Instrument, USA) with surface area more than 1000 m^2/g and bulk density in range of 0.05-0.12 g/cm^3. Synthesis was carried out as a two-step reaction: hydrolysis precursor carried in an acidic medium (citric acid), polycondensation - in alkaline (ammonia). Compared to the conventional method of producing silica aerogel using tetramethoxysilane (TMOS) and methanol, we used less toxic and more available reagents - tetraethoxysilane (TEOS) and ethanol. The proposed method avoids several stages - long initial gelation and washing alcogel from excess unreacted reactants, which significantly reduces the time of preparing aerogel.

CR-12

KINETIC LAWS OF THE TRANSESTERIFICATION REACTION, CARRIED OUT IN SbCF AND SCF CONDITIONS AND RESULTS OF THE EQUILIBRIUM PROPERTIES OF THERMODYNAMIC SYSTEMS PROCESS FOR PRODUCING BIODIESEL

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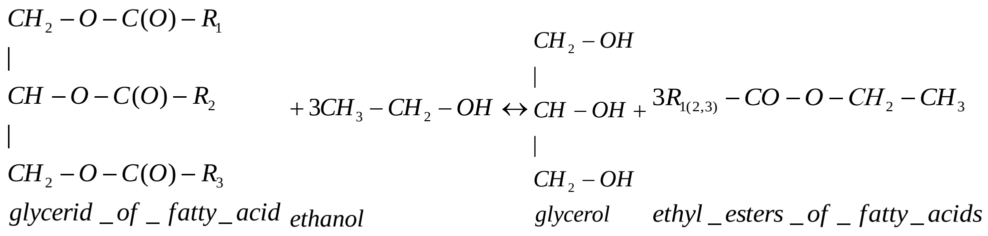
The advantages of biodiesel:

- more compared to traditional diesel fuel cetane number;
- high flash point;
- absence in the benzene and sulfur;
- easy microbiological and enzymatic degradation [1].

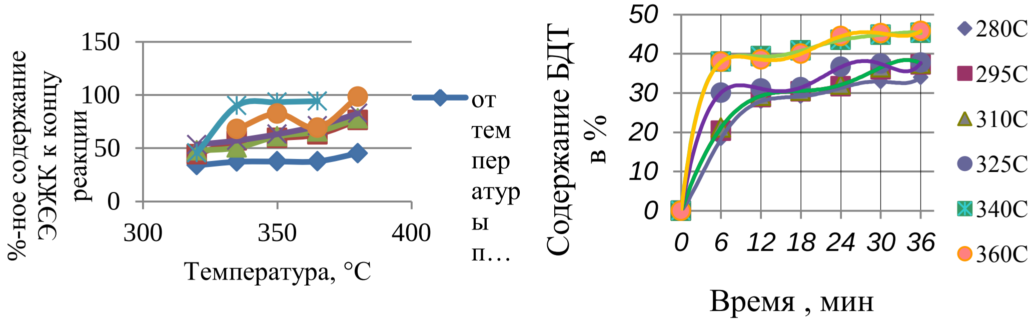
Traditional methods for producing biodiesel fuel does not provide solutions to such problems as the catalyst and removal of products after the saponification reaction, which plays an important role in the problem of purity of the product and process energy. In [2] the first esterification reaction carried out under supercritical fluid conditions with a large excess of the alcohol component (mole ratio for a system of “alcohol-oil” 42:1). In the range of 350÷400° C and 30-40MPa, 3÷5 minutes reached 95-97% degree of conversion. Problematic result is high values of thermodynamic parameters and an excess of the alcohol component, forming a fairly energy-intensive process economics.

The kinetics of the transesterification reaction of rapeseed oil in ethanol at a flow installation investigated in the temperature range of 320÷380°C under a pressure of 30 MPa and a molar ratio range of “alcohol-oil” of 6:1 to 20:1. The resulting samples were collected every 6 minutes during the 30 minutes of the process. Concentration obtained during the transesterification of ethyl esters of fatty acids (EEFA) evaluated by the correlation of viscosity-conversion (as measured by the coefficient of kinematic viscosity of the samples). In view of the substantial excess of the alcohol component of the reaction is regarded as pseudo first order reaction.



$$\begin{array}{l} CH_2-O-C(O)-R_1 \\ | \\ CH-O-C(O)-R_2 \\ | \\ CH_2-O-C(O)-R_3 \\ glycerid\_of\_fatty\_acid \end{array} \begin{array}{l} +3CH_3-CH_2-OH \\ ethanol \end{array} \leftrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \\ glycerol \end{array} + \begin{array}{l} 3R_{1(2,3)}-CO-O-CH_2-CH_3 \\ ethyl\_esters\_of\_fatty\_acids \end{array}$$

Results of studies on the influence of the characteristics of the process and the conversion rate of the reaction kinetics, shown in Fig. 1.



a) b)

Fig. 1 - Effect of the process on the conversion value (a) and the reaction kinetics for the ratio of 6:1 (b).

The kinetic equation is written in the form [1]:

$$\frac{dC_{ЭЭЖК}}{d\tau} = k \cdot C_{ЭЭЖК} \cdot$$

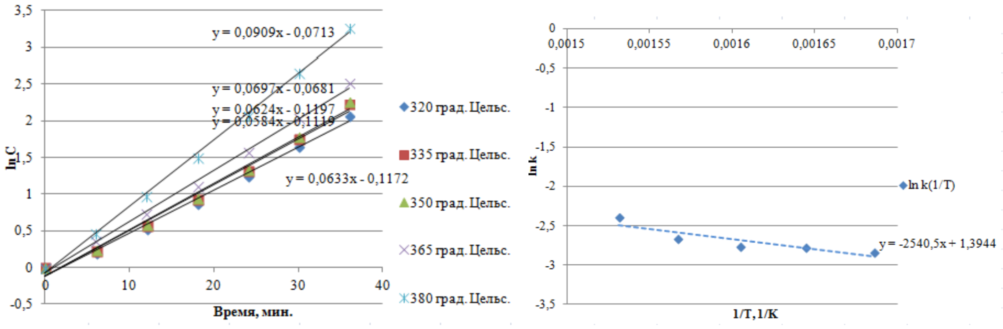
The reaction rate constant of the 1st order is determined by [1]:

$$k = \frac{1}{\tau} \ln \frac{C_0}{C} .$$

After determining the effective reaction rate constants determined by the dependence of these constants on the temperature in the form of the Arrhenius equation [4]:

$$k_r = A \cdot e^{-\frac{E_a}{RT}} .$$

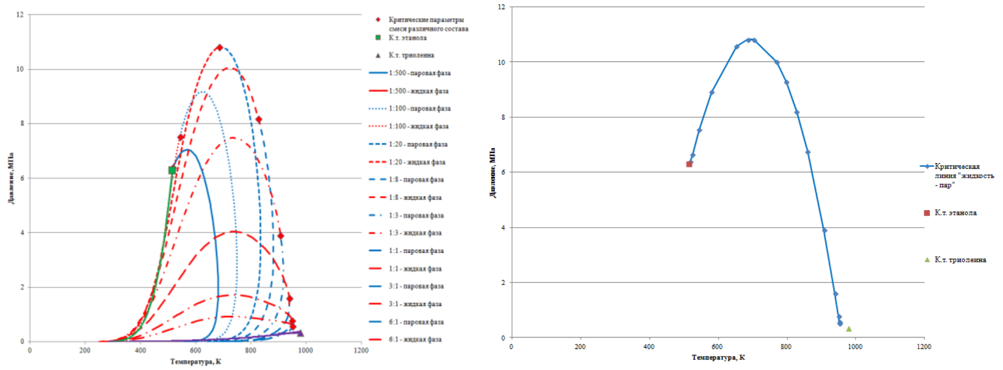
Some of the results of kinetic calculations is shown in Fig. 2.



a) b)

Fig. 2 Dependence of the natural logarithm of concentration against time (a) and the natural logarithm of the effective reaction velocity constants of 1/T (b) at a molar ratio of starting mixture 20:1

Below are the results of the modeling of the thermodynamic characteristics of binary systems. The upper branch of the curve of constant composition corresponds to the liquid phase, the bottom - steam (Figure 3). The critical point of the binary system is neither in the maximum temperature or maximum pressure at which the system can exist in two-phase state. This is the main peculiarity of the behavior of solutions in the near-critical conditions. The diagrams were obtained using the program VMGSim [www.virtualmaterialsgroup.com] under thermodynamic package “Peng-Robinson”.



a) b)

Fig. 3 Binodal for binary systems "triglyceride oleic acid - ethanol" different composition (a) and the critical line "liquid - vapor"

In the simulation of processes is important to consider and anomalous changes in the thermodynamic and thermophysical properties of thermodynamic systems involved in the process (reagents, components of the reaction product).

Figure 4 shows some simulation results isobaric heat capacity, carried out using the program VMGSim.

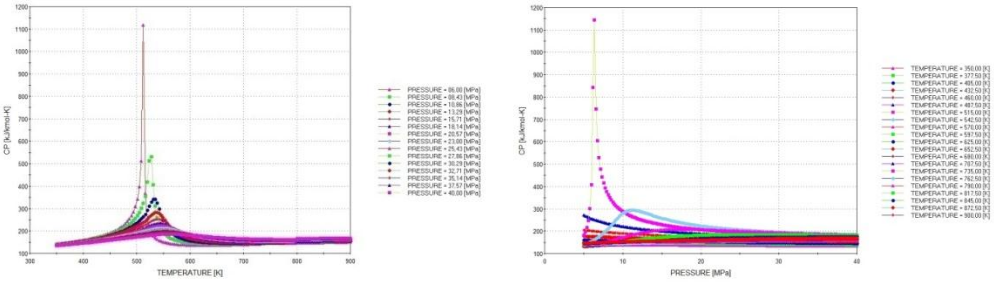


Fig. 4. Isobaric heat capacity of the mixture "triglyceride oleic acid - ethanol."

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CR-13

CHEMOMETRIC OZONOMETRIC MICROSCOPY FOR THE STUDIES OF OZONE SOLUBILITY IN SUPERCRITICAL FLUIDS

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It is well established that many gases, particularly ozone, which is known to be an unstable and poorly soluble agent, possess an increased solubility in supercritical fluids. It has long been shown that using of supercritical CO_2 allows to vary ozone concentration within a wide range and to change its partial pressure [1], wherein O_3 concentration can be controlled specrtophotometrically due to its intense absorption band near 200-300 nm. It was also mentioned in the above cited paper that supercritical CO_2 effectively inhibits ozone decomposition and the rate of ozone thermal decomposition decreases with the increasing CO_2 pressure. There are also special techniques for O_3 monitoring in narrow spectral regions including its spatial localization with time resolution for biomedical purposes [2]. We propose to use similar methods for ozone determination in supercritical systems.

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CR-14

SUPERCRITICAL SPECTROCHEMICAL LACTOCHEMISTRY ON A CHIP AS A NOVEL DIRECTION OF THE APPLIED RESEARCH FOR DIARY INDUSTRY

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Supercritical technologies are widely used in the analysis of milk and diary products in recent decadesв [1-10]. However, there are a number of microfluidic technologies and devices (lab-on-a-chip) dealing with supercritical fluids [11,12]. We have previously developed labs-on-a-chip with the CMOS / CCD sensors calibrated by the spectrophotometric temperature [13] and one of the authors has even introduced a term "spectrochemical lactochemistry" [14] later included into the DNB (Deutschen Nationalbibliothek), at group 540 (Chemie) [urn:nbn:de:101:1-2014030717651]. The existence of labs-on-a-chip for spectral studies and suprcritical applications allows us to introduce a novel approach to the development of microfluidic equipment for spectrochemical lactochemistry – "supercritical spectrochemical microfluidics" and supercritical chips for lactochemical analysis, which can be used in a large number of dairy product analysis applications [1-10].

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CR-15

STUDY OF THE BEHAVIOUR OF MACROMOLECULES WITH NITROGEN-CONTAINING GROUPS IN CARBONIC ACID SOLUTIONS

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When water is saturated with carbon dioxide at high pressure the medium becomes distinctly acidic due to formation of carbonic acid. Indeed, the formed carbonic acid molecules dissociate and generate protons, thus it becomes possible to reduce pH down to value of 3 and below in a high-pressure reactor. In the acidic medium nitrogen-containing groups of macromolecules may become protonated therefore certain nitrogen-containing polymers are soluble in this medium. Such method of dissolution of these polymers in carbonic acid solutions is promising taking into account certain benefits of the solvent used. Firstly, the acidity of the obtained water solution of carbonic acid is to be regulated by means of changing such parameters as pressure and temperature. Moreover, after completing of any reactions in carbonic acid solutions it is not required to perform any neutralisation and subsequent washing out of salts due to peculiar ability of carbonic acid to decompose spontaneously into H_2O and CO_2 at normal conditions after decompression. Secondly, along with absolute biocompatibility of its decomposition products carbonic acid demonstrates certain antimicrobial properties. Indeed, it is a fluid saturated with pressurised CO_2, antimicrobial properties of which are well known [1]. As a result, this solvent seems to be rather promising for different medical applications.

Previously, we developed an approach to dissolve biopolymer chitosan in carbonic acid solutions [2]. It was found out that chitosan macromolecules self-organize in such media into elongated nano-sized aggregates that consist of several macromolecules only [3]. Besides, a method of deposition of chitosan coating on biotissue from carbonic acid solutions preventing its calcification during the subsequent usage inside the human body was proposed [4].

Recently we found out that block-copolymers of polystyrene and poly(4-vinylpyridine) in carbonic acid form micelles with hydrophobic polystyrene core and swollen protonated corona of poly(4-vinylpyridine) block. Therefore, we proposed the scheme of encapsulating the palladium nanoparticles into the corona of such micelles in carbonic acid solutions. Such stabilised metal nanoparticles may be used as effective and renewable catalysts for different chemical transitions. The location of the nanoparticles in the corona of the micelles prevents them from coalescence because of steric repulsion of coronas of different micelles. Yet, the accessibility of the nanoparticles towards the reagent is not restricted significantly in the corona being swollen in a good solvent.

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CR-16

SYSTEMATIC ANALYSIS OF THERMODYNAMIC RESPONSES OF CRITICAL FLUID UNDER EXTERNAL FIELD ON THE BASE OF "COMPREHENSIVE SCALING"

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The unique properties of the supercritical fluid (SCF) [1] and of the critical fluid (CF) [2], are widely used in modern industrial technologies [1]. Unfortunately, the physical mechanism of the processes in the CF responsible for their successful practical use has not been elucidated. Earlier in [2] it was suggested that this mechanism is related to the fluctuation-structural characteristics of the substance under the critical condition [3]. Investigations of these characteristics under the Earth's gravitational field [4,5] discovered for the first time a number of nonlinear processes occurring in CF. With the help of scaling equation of state [3] and "comprehensive scaling" [6] a description of homogeneous and inhomogeneous CF under external field has been proposed on the basis of including all field and density variables, thermodynamic responses related to each other. In this approach, the Yang-Yang relation [7] has been used

$$\left(\frac{\partial \, S/V}{\partial T}\right)_{\frac{N}{V}} = \left(\frac{\partial^2 P}{\partial T^2}\right)_{\frac{N}{V}} - \frac{N}{V}\cdot\left(\frac{\partial^2 \mu}{\partial T^2}\right)_{\frac{N}{V}} \qquad (1)$$

Complete system of thermodynamic relations for 48-thermodynamic response [8] has been proposed. Analysis of the obtained exact relations

$$\left(\frac{\partial \, V/N}{\partial P}\right)_{S/N} = \frac{S}{N}\left(\frac{\partial^2 T}{\partial P^2}\right)_{S/N} + \left(\frac{\partial^2 \mu}{\partial P^2}\right)_{S/N}, \quad \left(\frac{\partial \, N/S}{\partial \mu}\right)_{V/S} = \frac{V}{S}\left(\frac{\partial^2 P}{\partial \mu^2}\right)_{V/S} - \left(\frac{\partial^2 T}{\partial \mu^2}\right)_{V/S} \qquad (2)$$

has been shown that the use of variables pressure P, temperature T and chemical potential μ for scaling equations of state are qualitatively similar (S is the entropy). All variables of "comprehensive scaling" have complete symmetry [8] on the number of density and field variables. At the same time, the third field of complete scaling [7], tittled "similar pressure", $(\mu/V)_f$ which vanish only at the critical point, it is not determine of the critical isobar [8], it does not replace the pressure in (2), it has no conjugate variable density. Therefore, the algebra of fluctuating quantities [7] is asymmetric with respect to the number of density and field variables.Obtained only possible one mathematical form [8], for which in the fluctuation region the relations of scaling are true for all thermodynamic parameters. Each field variable consists of two contributions $\sim R_c^{-\beta\delta/\nu}$ and $\sim R_c^{-1/\nu}$, and vanish at two critical lines of the critical value of the order field and the disorder field, respectively, and of the third "fluctuation" contribution $\sim R_c^{-(2-\alpha)/\nu}$ which vanish at the critical point. Each density variable consists of two contributions $\sim R_c^{-\beta/\nu}$ and $\sim R_c^{-(1-\alpha)/\nu}$, and vanish at two critical lines with the critical value of the order parameter and the disorder parameter, respectively, and of the third "fluctuation" contribution $\sim R_c^{-(2-\alpha)/\nu}$. For each of thermodynamic variable (including field and density variables) the existence of the fluctuation part of the thermodynamic potential has been shown. This allows you to complete many years of discussion on the role of two terms of equation (1) (as well as for other of 47 thermodynamic responses [8]): they are characterized by the same scaling dimension and are differ quantitatively. Choosing of coordinates P, V / N or μ, N / V [9] of inhomogeneous CF [4] under the external field is qualitatively similar.

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PHASE TRANSITIONS DURING THE ALKYLATION USING HETEROGENEOUS CATALYST

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The main problem hindering the implementation of a heterogeneous catalyst to obtain alkylbenzene instead of environmentally hazardous mineral acids – conventional alkylation catalysts is the short cycle length of work, which is caused by the reactions of conjugated olefinsoligomerization, by secondary alkylation of C_8 products, by cracking of the part of target products into saturated and unsaturated fragments [1]. The negative impact of alkylation products cannot be ruled out entirely, but there are prerequisites to minimize such impact when used for carrying out the process of alkylation in supercritical conditions when a forming supercritical hydrocarbon fluid removes precursors of coke formed on the catalyst surface.

As a raw material for the study of the alkylation of isobutane with olefins under supercritical conditions isobutane was used (isobutane fraction - IF) and butane-butylene fraction (BBF).

The authors investigated the effect of phase transitions in the system Ж-Г-СКФ on the performance of the process to produce alkylbenzeneusing zeolite catalysts (NH_4-Y; $LaNH_4Ca$-Y; H-USY; $LaNH_4$-USY) in flow-through mode. The alkylation process under supercritical conditions and in the gas phase was conducted at temperatures 110-150°C, a liquid phase process at 50-100°C.

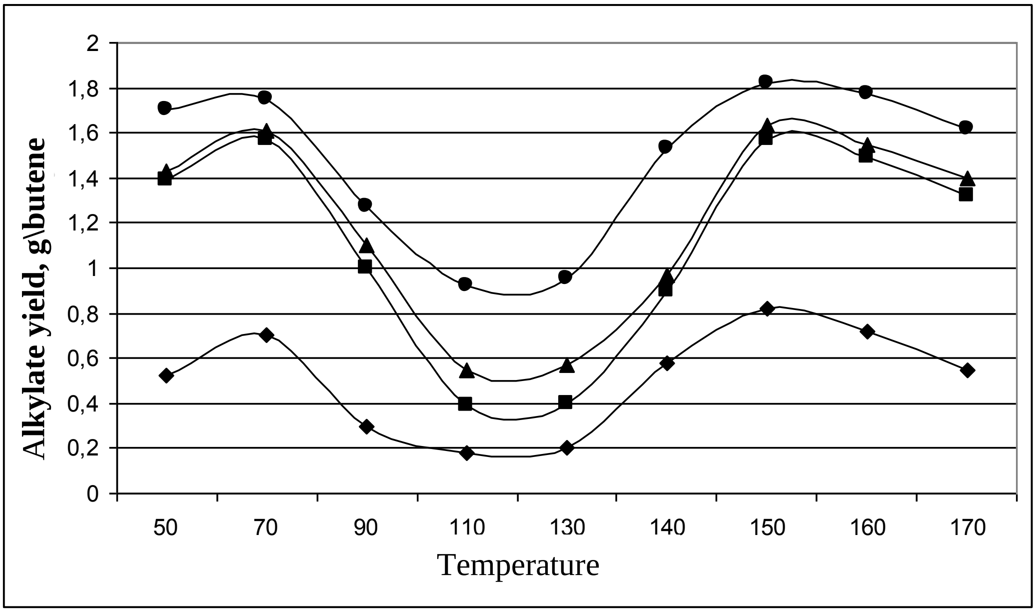

Fig. 1 Dependence of alkylate yield on the missed butylene (pressure 5.0 MPa) depending on the temperature of the catalyst sample in liquid phase and under supercritical conditions:♦ –NH_4-Y; ■ – $LaNH_4Ca$-Y; ▲– H-USY;● – $LaNH_4$-USY.

Further, the effect of increasing the pressure was investigated (process temperature - 150°C) and transfer of alkylation process to supercritical conditions on catalyzate hydrocarbon composition (Fig. 2).

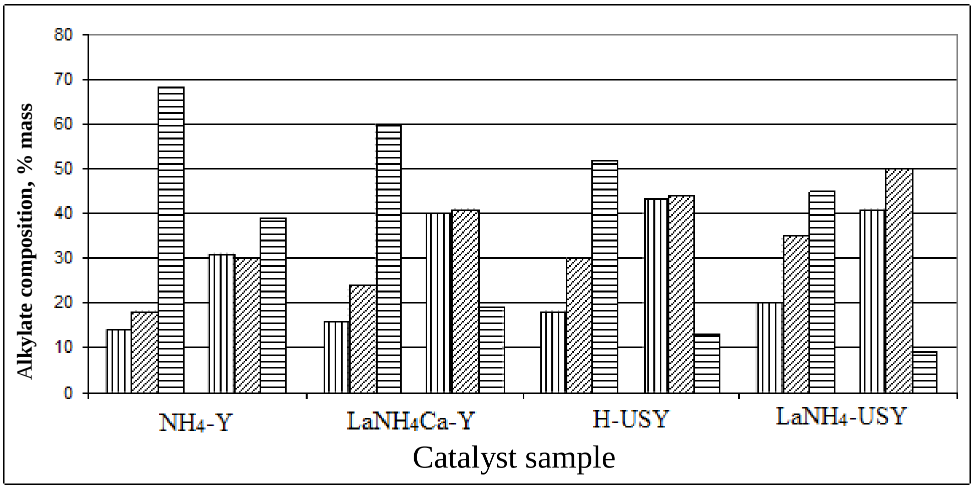

Fig. 2 Dependence of alkylate hydrocarbon composition (t = 150 ° C) from the process pressure (liquid phase – 2.0 MPa and supercritical conditions-5.0 MPa) on catalyst samples К-1 ÷ К-4: ▥ - hydrocarbons C_5-C_7; ▨hydrocarbons; C_8; ▤hydrocarbons C_{9+}.

As can be seen from Figure 2, the process at a pressure of 2.0 MPa the system is dominated by products C_{9+}:

NH_4-Y → 68 % wt., $LaNH_4Ca$-Y → 60 % wt., H-USY → 52 % wt., $LaNH_4$-USY → 45 % wt.

During the transition to the supercritical region, at a pressure of 5.0 MPa, the main products of the reaction are hydrocarbons C_8:

NH_4-Y → 30 % wt., $LaNH_4Ca$-Y → 41 % wt., H-USY→ 44 % wt., $LaNH_4$-USY→ 50 % wt.

and products of disproportionation and cracking - hydrocarbons C_5-C_7:

NH_4-Y → 31 % wt., $LaNH_4Ca$-Y → 40 % wt., H-USY → 43 % wt., $LaNH_4$-USY → 41 % wt.

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