CHEMREACTOR-21

XXI

International Conference on Chemical Reactors

ABSTRACTS

CR-21

Devoted
to the 100th
anniversary
of Professor
Mikhail
SLIN'KO

September 22-25, 2014, Delft, The Netherlands

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ABSTRACTS

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The proceedings include the abstracts of plenary lectures, keynote lectures, oral and poster presentations of the following scientific areas:

- **Section I.** Advances in Chemical Reactors Fundamentals;
- **Section II.** Chemical Reaction Engineering and Reactors Design – Novel Approaches, Modeling, Scale-Up, Optimization;
- **Section III.** Chemical Reactors and Technologies for Emerging Applications;
- **Section IV.** Advanced Processing of Fossil Hydrocarbon Feedstocks;
- **Section** on PHOTOCATALYTIC REACTORS.

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SCIENTIFIC TRENDS

Section I.

Advances in Chemical Reactors Fundamentals

Chemical Reactions Kinetics

Energy & Mass Transfer in Chemical Reactors

Fundamentals of Hydrodynamics and Fluid Flow in Chemical Reactors

Specialized Software for Development of Chemical Reactors and Flow-Sheeting of Reactive Processes

Section II.

Chemical Reaction Engineering and Reactors Design – Novel Approaches, Modeling, Scale-Up, Optimization

Mathematical Simulation and CFD Studies of Chemical Reactors

New Designs of Chemical Reactors (e.g. Structured Reactors, Membrane Reactors, Microreactors)

Novel Approaches in Chemical Reaction Processes Engineering (e.g. Microwave/Induction Heated Reactors, Ultrasonic Reactors, Unsteady-State Forcing and Sorption Enhancement in Chemical Reactors, Multifunctional Reactors)

Section III.

Chemical Reactors and Technologies for Emerging Applications

Environmental Protection and Utilization of Wastes

Processing of Biomass and Renewable Feedstocks

Production of Novel Nano-Structured Carbon Materials

Section IV.

Advanced Processing of Fossil Hydrocarbon Feedstocks

Modern Reactive Technologies for Natural Gas, Oil and Coal Processing

Chemical Processes for intensification of Oil Production

Natural Chemical Reactors for In-Situ Processing of Oil and Coal in Deposits

Chemical Reactors and Processes for Treatment of Heavy Hydrocarbon Feedstock and Shale Oil

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On the centenary of the Professor Mikhail Slin'ko birth

PROFESSOR MIKHAIL SLIN'KO – INSTITUTE OF CATALYSIS IN NOVOSIBIRSK AND MATHEMATICAL MODELING OF CHEMICAL PROCESSES AND REACTORS IN RUSSIA

Valentin Parmon

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

Professor Mikhail Slin’ko contributed much to the progress in catalytic technologies in Russia and, first of all, to the formation of its theoretical basis – Chemical Engineering Science. Prof. Slin’ko took a very active part in the foundation of the Institute of Catalysis in Novosibirsk in 1958; later, in 1958 through 1976, he was a real leader of the new, in those years, scientific area – mathematical modeling of catalytic processes and reactors.

Approaches to the mathematical modeling, which were developed by Prof. Slin’ko, allow the reliable transfer from new lab-scale processes to large-scale industrial processes with shortening and, sometimes, skipping pilot tests. Numerical studies based on mathematical models of catalytic reactors make it possible to find modes of reliable and safe operation of industrial reactors. The team headed by Mikhail Slin’ko in the Institute of Catalysis in the period of 1959 to 1975 accomplished the following works:

1. A strong scientific basis was developed for scaling laboratory studies up to industrial applications with the aim of mathematical modeling.
2. The methods for creating the mathematical models of catalytic systems via balanced combination of computational and real experimental results were developed and adopted.
3. Regular and chaotic autooscillations of the rates of heterogeneous catalytic reactions were discovered and studied; few principles of non-linear dynamics of catalytic reactions, processes and reactors were developed as a basis of the theory and practice of industrial catalysis. Dynamics of emerging and propagation of fluctuations in catalyst beds resulting in the formation of various dynamic structures was studied.
4. The spaciotemporal hierarchical approach was developed for creating mathematical models of catalytic systems at various scales, including molecular level.

5. Correct mathematical models were developed for a wide variety of catalytic processes and reactors, which allow identification of optimal and stable modes for their operation.
6. The developed approaches to mathematical modeling of chemical reactions, processes and reactors and their scaling-up were practiced in numerous research centers of chemical, petrochemical and refinery industries.
7. The approach based on balanced combination of computational and real experiments was used for designing automated research systems for rapid development of mathematical models.

Some results obtained by scientists of the Institute of Catalysis are also presented to demonstrate the current level and trends of the mathematical modeling of catalytic processes and reactors. At present, the methods of mathematical modeling allow the complex dynamics of catalytic reactions on the catalyst surface to be described, calculations of catalytic transformations in multicomponent reaction systems to be conducted, dynamic thermal regimes in catalytic reactors and processes with phase transformations of reactants to be predicted. Currently, one of the most actively progressing fields of mathematical modeling of catalytic reactors appears to be the application of computational 3D-hydrodynamic methods for reacting systems.

On the centenary of the Professor Mikhail Slin'ko birth

M.G. SLINKO – AS A PERSON, SOLDIER AND SCIENTIST

Slinko M.M.

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The main periods of the scientific and personal life of M.G. Slinko will be will be offered to your attention. M.G. Slinko was graduated from one of the best schools in Moscow and following to the regulations of that time began his active life working in Giprokhim (State Designing Institute of Chemistry) at the age of only 16 years. Simultaneously he managed to study at the Mendeleev Institute and Moscow State University. Being the student he created the reactor K-39 for the sulfuric acid production. This was the first time, when a reactor was developed on the basis of mathematical modelling. For this work M.G. Slinko was awarded Stalin's Prize in 1946. He was graduated with an honors diploma on theoretical physics from the physical department of Moscow State University on June 19, in 1941. In first days of the war, M.G. Slinko was enlisted as the commander of a platoon and he finished the war in the First Guards Tank Army, with which he reached Berlin. Being the head of the department of the gasoline provision for the first time he applied the mathematical modelling for the planning of war operations, during which hundreds of tanks were involved.

After the demobilization, he continued his scientific work at the Laboratory of Technical Catalysis at the Karpov Physicochemical Institute. There, he started to work on the problems of obtaining heavy water and protection of nuclear installations from a blast of the explosive mixture formed as a result of water radiolysis. In 1960, he became a laureate of Lenin's Prize for his works on the production of heavy water by way of rectifying liquefied hydrogen.

From 1956 to 1959, he worked as an instructor for the Novel Technology Sector of the Machine-Building Department of the Central Committee of the USSR Communist Party. Here he used all his opportunities and possibilities for the foundation of the Institute of Catalysis in Siberian Branch of the USSR Academy of Sciences. As the deputy director for scientific work, he organized the Institute on the basis of the unity of theory and practice. He began pioneering works in our country on mathematical simulation of catalytic processes using computers. M.G. Slinko developed the spatio-temporal hierarchical approach of large-scale transition from the research laboratory to industrial conditions. He supervised the studies on kinetics of heterogeneous catalytic reactions, on the optimal size, shape and porous structure of the grains in fixed bed reactors. At this time the mathematical modelling of many industry processes including ethylene oxidation to ethylene oxide, the producing of sulfuric acid by the contact process, production of acrylonitrile by ammoxidation of propylene, production of phthalic anhydride by catalytic oxidation of naphthalene, partial oxidation of hydrocarbons, methanol oxidation to formaldehyde, dehydration of butylene and polymerization of monomers were carried out.

By the early 1960s, there was no satisfactory qualitative theory of nonlinear systems of differential equations with distributed parameters. Together with Dr. T.I. Zelenyak M.G. Slinko studied the nonlinear phenomena in lumped and distributed systems of differential equations. For the first time the appearance of multiplicity of steady states during the catalytic processes over one pellet, in a fixed bed and fluidized catalyst bed reactors were analysed. A lot of discoveries in chemical kinetics and chemical engineering have been done during this period of time including the observation and mathematical modelling of self-sustained oscillations in heterogeneous catalytic systems and the development of the new concept of the “organized” fluidized catalyst bed reactor.

In 1976, on the initiative of L.A. Kastandov, the minister of the chemical industry, Prof. Slinko became the head of the Department of Theoretical Principles of Chemical Technology at the Karpov Physicochemical Research Institute. During this period of time M.G. Slinko established the principles of non-linear dynamics of catalytic reactions, processes and reactors, which are the basis of the theory and practice of industrial catalysis. One of the first scientists he began mathematical modeling at the atomic–molecular and nanolevels to describe the nonlinear dependence of the reaction rate on the composition of the surface layer at the meso- and macrolevels. Also at this time M.G. Slinko together with NPO Khimavtomatika created the automated research system for scientific studies (ASNI) to produce mathematical models in a short time based on the methodology of a balance between computing and physical experiments.

Finally M.G. Slinko was a man of high moral principles and had a great personal charm. His life is a bright example of a honest service to the domestic science, chemical industry and native land.

On the centenary of the Professor Mikhail Slin'ko birth

MULTI-LEVEL ENGINEERING OF CATALYTIC REACTIONS

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Catalysis plays an important role in Chemical Process technology. It is *the* enabling technology for good chemicals manufacturing processes. Catalysis as a discipline is not just a part of chemistry or physics but it also is an engineering discipline. Chemical and physical aspects are often scale-independent but in the engineering disciplines usually the scale of the operation plays a role. Thus, it is not surprising that in catalysis both scale-independent and scale-dependent phenomena play a role. Examples of scale-independent topics are (reaction) mechanistic and structure elucidation subjects. Reactor design studies belong to the realm of chemical reaction engineering and are clearly dependent on the scale. An integrated approach of catalysis research and development covering aspects of (bio) chemistry and physics and chemical reaction engineering, referred to as “Catalysis Engineering”, is rewarding.

In such an integrated approach it is appropriate to distinguish three levels, the *microlevel*, focusing on molecules and catalytic sites, the *mesolevel* focusing on the catalyst particle and the reactor, and the *macrolevel*, considering the total process.

On the microlevel the scale-independent information is collected. Thermodynamics defines the possible window of operation and heats of reaction. High-throughput-experimentation (HTE) is a crucial part of the toolkit of catalyst development. HTE is very valuable in developing optimal catalysts. On the mesolevel fascinating developments are visible in the field of structuring the space. On the one hand, at the scale of the particle optimal porosity (optimal hierarchal pore networks consisting of micro-, meso- and macropores) can be realized. On the other hand, structured reactors often outperform conventional reactors such as packed bed reactors. Pros of fixed bed reactors are high catalyst loading, convenience, low cost; cons are maldistribution, leading to non-uniform concentration profiles and even hot spots, internal diffusion limitations that might lead to reduced activity and selectivity. In packed bed reactor hydrodynamics, mass transfer rates are coupled to particle shape and size. In a structured reactor in this respect more degrees of freedom exist.

For instance, dependent on the design, particle sizes can be chosen to be much smaller than those in packed beds. Structured reactors allow a high efficiency, partly because they allow high mass transfer rate at relatively low energy dissipation. The low energy dissipation is mainly related with the hydrodynamics regime: laminar rather than turbulent. In addition, in multiphase flow under most practical conditions the flow pattern is that of segmented flow (called Taylor flow), resulting in large gas-liquid mass transfer. For these reasons structured reactors have large potential in Process Intensification. Structured reactors allow decoupling of hydrodynamics and chemical kinetics, implying an extra degree of design freedom. From a chemical engineering point of view the intrinsic scalability of these reactors is intriguing.

It is not wise to carry out the research aimed at developing a good catalyst separately from the reactor design. It does not make sense to develop the best possible catalyst and to use it in an unsatisfactory reactor. Both the catalyst and the reactor should be close to perfect.

Assuming that the conceptual process design is largely agreed upon, the major basic concerns for catalytic particle and reactors are:

- catalyst quality on a microscopic length scale (quality, number of active sites),
- catalyst quality on a mesoscopic length scale (diffusion length, loading, profiles),
- ease of catalyst separation and handling,
- heat supply and removal,
- hydrodynamics (regimes, controllability, predictability),
- transport resistances (rate and selectivity),
- safety and environmental aspects (run-aways, hazardous materials, selectivity),
- costs.

With respect to these aspects, structured reactors in nearly all respects, expect for costs, outperform random packed bed reactors.

The potential of structured reactors in chemicals production will be illustrated by two examples of selective hydrogenation. The results demonstrate the achievable excellent gas liquid mass transfer at low energy dissipation (caused by the favourable hydrodynamics) and the favourable internal diffusion properties (caused by the favourable dimension of the diffusion length).

A case study on nitrous oxide abatement for nitric acid plants exemplifies the integrated three-level catalysis engineering approach. On the macrolevel, retrofitting in existing plants has to be distinguished from designing new plants. In the latter case there is more room for nitrous oxide abatement by changing the design of the reactor for the selective oxidation of ammonia (giving nitrous oxide besides the main product NO), allowing minimizing the formation of nitrous oxide. In existing plants such a new design is in general not an option. Regarding existing plants, it is realistic to accept the formation of nitrous oxide and add equipment for decomposition of the formed nitrous oxide. It will be shown that in principle several places in the nitric acid production plant suggest themselves for location of a nitrous oxide decomposition unit. In fact, choosing the place in the process guides the studies at micro- and mesolevel, as the specific place is associated with the specific reaction conditions to be covered in the catalyst development and the reactor design. An evaluation of the various options will be presented.

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CATALYTIC REACTION ENGINEERING OF THE REDUCTION OF DIESEL AUTOMOBILE EMISSIONS

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The traditional emphasis of chemical reaction engineering has been the design, operation and control of chemical reactors operating mainly by the chemical processing and petroleum industries. However, at present significant catalytic and reaction engineering efforts are devoted to the development, operation and control of chemical reactors used for the reduction of pollutants emission from automobiles. The specification of the performance of these reactors is mandated by regulatory agencies and public pressures in both developed and developing countries. The scale of the associated scientific and engineering challenges and the significant economic impact can be appreciated noting that every year about 70 million new cars are produced and sold in the world, all equipped with catalytic after-treatment (CAT) reactors. The CAT of gasoline driven cars is a single reactor (TWC), while that of diesel driven cars uses a series of four reactors. My goal is to describe the usefulness of catalytic and reaction engineering tools and methodology to develop these reactors in an environment of continuous tightening emissions regulations. I shall concentrate on issues related mainly to the emission control of diesel driven cars, as most current research and development efforts are conducted in this area, while the gasoline CAT catalyst and engine technologies already approach near zero emission.

The two most challenging technological tasks are the reduction of the emission of particulate particles (PM), which is conducted by diesel particulate filters (DPF) and the reduction of the NOx emissions, which is conducted by either one or two catalytic reactors depending on the type of vehicle. The PM emissions are known carcinogens, adversely affect visibility in cities and contribute to global warming. To establish suitable health counter measures we need to know the responsible sources. Until recently most regulations limited the emitted mass of particles smaller than 2.5 μm (EURO6 < 10 mg/km). Recently it was discovered that very small insoluble metal oxides (10-500 nm) attached to the PM are the most likely toxic species. This led to establishing a Particle Number (PN) limit (EURO6 < $6*10^{11}$), which is equivalent to 0.2 mg/km, or 50 times stricter the allowed PM limit in the USA. Until 2007 PM and PN were not regulated in cars in which gasoline was injected by a carburetor to the engine due to their very low emission. Because of the current shift to Direct Injection (DI) of gasoline to the engine (to reduce CO_2 emissions) it emits PM and a novel engineering challenge is to limit the PN of these emissions. Thus, EURO6 set limits on PM and PN of diesel driven cars that are equal to those of diesel driven ones. Current research attempts to develop fuels that lead to lower combustion temperatures which will eliminate the need for a DPF.

Ceramic particulate filters (DPF) are used to remove l of the particulate matter. The filter consists of thousands of parallel square channels, with the opposite ends of adjacent inlet and outlet channels being plugged. The PM which accumulated in the inlet channels is periodically combusted. A surprising destructive transient temperature rise sometimes forms following a rapid shift to idle which can destruct the expensive DPF. This counter intuitive behavior can be explained by its similarity to the wrong-way behavior of packed bed reactors. Mathematical modelling enables prediction of which changes in the operating conditions and DPF structure can decrease the maximum temperature rise.

The NOx emitted by Heavy Duty Diesel (HDD) vehicles is usually removed by selective catalyst reduction (SCR), which is a well-established technology. Mathematical models predict how the temperature window over which a high conversion is obtained can be increased by use of a bilayer catalyst. The NOx emitted by Low Duty Diesel (LDD) vehicles is removed either by periodic operation of a Lean NOx Trap (LNT) or by a combinations of an expensive LNT and a less expensive SCR. The need to compromise between the cost of the catalyst and the NOx reduction efficiency require the application of novel reactor and catalysts configurations. Mathematical modelling predicts how the NOx conversion can be optimized either by use of a sequence of blocks of the two catalysts or of a bilayer catalyst. Moreover, it shows that use of a non-uniform catalyst deposition profile can increase the NOx conversion and reduce the required expensive precious metal catalyst. This enables a decrease of the price of the catalyst.

I shall conclude with comments about the current development of novel reactors that satisfy the stricter upcoming regulations.

PLENARY LECTURES

KINETICS OF CHEMICAL REACTIONS: DECODING COMPLEXITY

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The analysis of complex reaction networks can be performed in two complementary ways. Insight in the chemistry of the investigated process can be translated in so-called chemical rules. The latter can be implemented as algorithms in computer codes allowing to generate "automatically" reaction networks consisting of several thousands of elementary steps. Data bases, based either on experiments or on quantum chemical calculations of model reactions, provide the corresponding thermodynamic and kinetic parameters. Numerical integration techniques or kinetic MonteCarlo simulations allow, e.g. via a sensitivity analysis, to assess the significance of the considered elementary reaction families and the effects of reaction conditions on the latter. Alternatively, so-called minimal reactions networks or mechanisms can be the starting point (Marin and Yablonsky, 2010). This will be the topic of the lecture.

Applying graph theory a general, but thermodynamically consistent, rate equation can be constructed. For linear reaction mechanisms this rate equation consists of a driving force, the cycle characteristic for a single-route mechanism, ensuring thermodynamic consistency and a resistance, the inverse of the total weight of the node spanning trees of the graph corresponding to the reaction mechanism. This resistance can be measured as the ratio of the driving force and the reaction rate. The analysis of the concentration and temperature dependence of the resistance provides rather direct information on the nature of the elementary steps involved in a reaction mechanism. For non-linear reaction mechanisms an implicit equation for the reaction rate can be conveniently used to obtain insights. This so-called kinetic polynomial is a generalization of the well-known Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate equation for linear reactions mechanisms. Indeed, the thermodynamic branch of the solution of the kinetic polynomial, i.e. the branch which contains the point where the rate equals zero, can be expressed explicitly as a four-factor overall reaction rate equation. The first three being the same as for a LHHW rate equation: kinetic factor, adsorption term and driving force. The fourth factor can be expressed as a series expansion of the driving force and equals unity for linear mechanisms.

Transient response techniques are particularly effective for analyzing complex reaction networks because the rates of the elementary steps constituting the catalytic cycle are not equal during transient experiments. The Temporal Analysis of Products (TAP) reactor was designed to that purpose and allows to overcome the limitations of conventional steady-state kinetic testing devices such as continuously stirred, plug-flow, or recycle reactors (Gleaves et al., 2010).

The new generation TAP-3E apparatus is a fully automated transient and steady-state reactor set-up that allows experiments to be performed over a wide range of reaction conditions. It allows for Knudsen pulse response experiments, pump-probe experiments, vacuum and atmospheric pressure Temperature Programmed Desorption, vacuum pulsed Temperature Programmed Reaction, Steady-State Isotopic Transient Kinetic Analysis, continuous-flow experiments at atmospheric pressure, and pulse-transient experiments. TAP pulse-response data can be transformed in a kinetically “model-free” manner into net production rates by the so-called Y-procedure (Yablonsky et al., 2007). Such type of state-defining experiments can be considered as chemical calculus i.e. implementing of infinitesimal perturbations. Software developed at Ghent University can be used to estimate kinetic and other physico-chemical parameters by regressing these experimental TAP pulse responses (Roelant et al., 2007, 2008).

Finally, some non-trivial properties of classical chemical kinetic schemes will be highlighted.

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NATURE-INSPIRED ENGINEERING OF CATALYTIC PROCESSES – AVENUES TO SCALABILITY, EFFICIENCY AND ROBUSTNESS

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Process intensification is key to biology and life in general. Within the constraints posed by the environment, the following properties are needed: scalability (in organs and organisms), efficient transport across length scales, the emergence of robust and resilient operation by collective processes (in a cell, amongst cells, amongst organisms and their environment), and more. When resources are scarce, efficiency and sustainability are the only choices for survival.

It goes beyond saying that all these features apply equally to industrial catalytic processes. However, current processes and materials are often designed using bottom-up principles, matching constraints *a posteriori*, using empirical patching up, while applying rational design principles at individual length scales only. Thinking about processes as "systems" is inherent to chemical engineering, but dynamics (the dimension of time) are often treated as a complication that needs to be controlled rather than utilized, and *a priori* systems engineering is rare. There is also a significant divide between chemistry and nano-materials discovery on the one hand, and device, product and process engineering on the other hand.

Discovering and applying the principles behind desirable traits in natural systems, like scalability and efficiency, may serve as a guide to process intensification in chemical processing and the design of novel catalysts. We believe that there is tremendous potential in this "nature-inspired chemical engineering" (NICE) approach if it is applied in a non-dogmatic manner in which (1) fundamental mechanisms omnipresent in nature (hierarchical transport networks, force balancing, dynamic self-organization) are utilized rather than "biomimetic" imitation of a single feature and (2) these mechanisms are properly translated within a technological context, i.e., cognizant of the different degrees of freedom in technological versus natural systems (different time scales, and different ranges in temperature, pressure and materials).

My presentation will focus on how the NICE methodology can be concretely applied to chemical reaction engineering. At the nanoscale, I will talk about how we can harness the subtle balance between various forces (electrostatics, steric confinement) to obtain high performance in catalysis. I will also discuss the design and synthesis of hierarchically structured catalysts, which optimize the balance between catalytic kinetics and transport phenomena. The example of lung-inspired fuel cells directly demonstrates nature-inspired process intensification. This involves structuring the catalyst at multiple levels, as well as additive manufacturing of the flow distribution and collection system in the bipolar plates.

RECENT ADVANCES IN THE DIRECT NUMERICAL SIMULATION (DNS) OF MASS, MOMENTUM AND HEAT TRANSFER IN MULTIPHASE CHEMICAL REACTORS

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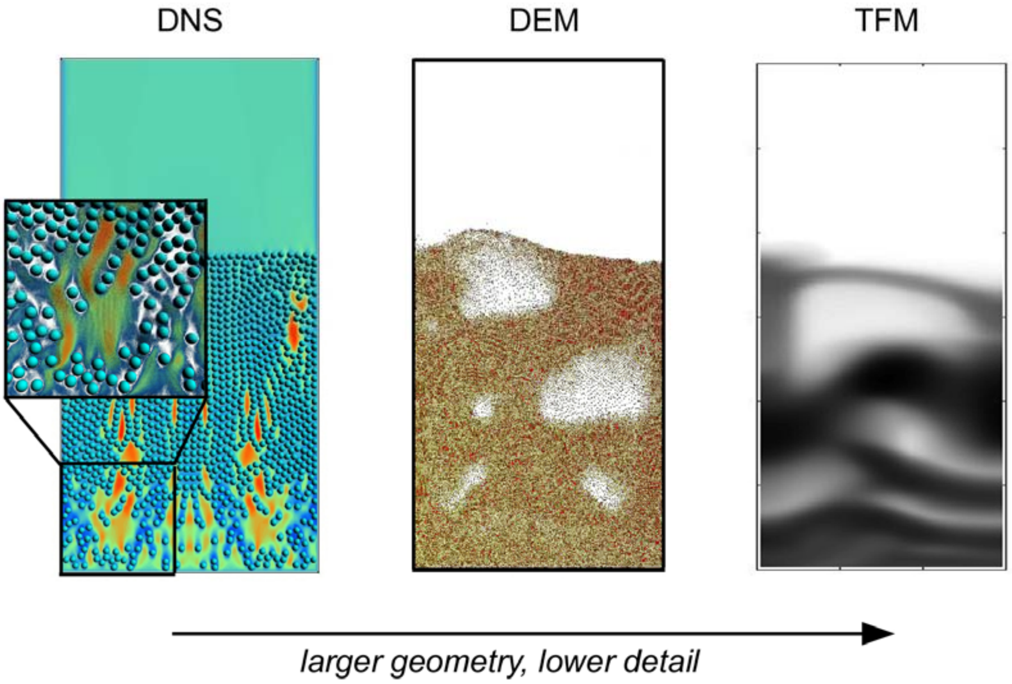
Dense gas-particle flows involving momentum, mass and heat transfer are frequently encountered in industrial processes involving granulation, coating and polymerization. In dense gas-particle flows both (effective) fluid-particle and (dissipative) particle-particle interactions need to be accounted for because (the competition between) these phenomena to a large extent govern the prevailing flow phenomena, i.e. the formation and evolution of heterogeneous structures. These structures have significant impact on the quality of the gas-solid contact and as a direct consequence thereof strongly affect the performance of the process. Additional complexities arise due to enhanced dissipation due to wet particle-particle collisions.

Due to the inherent complexity of these multiphase flows the authors have adopted a multi-scale modeling approach in which both fluid-particle and particle-particle interactions can be properly accounted. The idea is essentially that fundamental models, taking into account the relevant details of fluid-particle interaction (DNS) and particle-particle interaction (DEM), are used to develop closure laws to feed continuum models (TFM) which can be used to compute the flow structures on a much larger (industrial) scale. In this presentation recent advances in the DNS of dense gas-particle flows will be highlighted with emphasis on coupled mass, momentum and heat transfer. In addition, areas which need substantial further attention will be discussed.

PL-3



SORPTION ENHANCEMENT OF CATALYTIC REACTIONS

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The theme of this talk is Process Intensification by combining adsorption and reaction in a single unit in order to overcome thermodynamic limitations of conversión in reversible reactions. These processes are also called Sorption-Enhanced Reaction Processes (SERP). Two topics will be discussed: i) the synthesis of acetals (DEE, DBE…) in liquid phase using Simulated Moving Bed Reactors[1] (SMBR) where the acid ion exchange resin is the catalyst and also a selective adsorbent and ii) the production of hydrogen by methane or ethanol steam reforming coupled with CO_2 adsorption. Chromatographic reactors have been subject of research for a long time. In this framework, two interesting technologies can be spotted for the sustainable production of oxygenated compounds: the Simulated Moving Bed Reactor (SMBR) and the Simulated Moving Bed Membrane Reactor (PermSMBR).

The SMBR concept: The SMB concept was patented in 1961 by UOP and commercialized for p-xylene recovery as an example. It is a set of fixed beds arranged in a closed circuit and packed with adsorbent/catalyst. In the SMBR there are two inlet streams (feed and desorbent) and two outlet streams (extract and raffinate); these ports are shifted periodically one column in the direction of fluid flow, simulating the solid movement. If the feed contains reactants (A and B), in which, A, is also used as desorbent, and the reaction products are C and D (where D is the more adsorbed species) then a mixture of D+A is obtained in the extract and a mixture of C+A is obtained in the raffinate. The inlet/outlet streams divide the unit into four sections, each one with specific role.

The PermSMBR concept[2]: It is a hybrid technology that combines the SMBR with membranes; in the PermSMBR, each column contains a set of tubular membranes permeable to one of the reaction products – integrated PermSMBR or each SMBR column is followed by a membrane module – coupled PermSMBR. Depending on the configuration, the adsorbent/catalyst particles are packed in the membranes (integrated PermSMBR) or in the columns (coupled PermSMBR). The permeate is rich in the product for which the membranes are selective.

The process development[3] involves: i) batch runs to obtain the equilibrium composition, equilibrium constant and reaction enthalpy and the evolution of concentration of species to get a kinetic law; ii) fixed bed adsorption experiments with non-reactive pairs, from which adsorption parameters are obtained; iii) fixed-bed adsorptive reactor experiments to validate the model; iv) operation of the SMBR.

SERP for hydrogen production: It involves the use of hydrotalcites or modified HTLs (K-promoted) for CO_2 sorption in combination of a catalytic material in steam methane reforming[4] or ethanol steam reforming[5,6] (SE-SRE). For SE-SRE homemade hybrid materials with nickel and copper as active phases and hydrotalcite sorbent as support have been prepared and tested. The process study has been carried out to develop a continuous hydrogen production operation from SE-SRE. For this purpose, homogeneously packed columns with two sub-sections have been simulated, and a four-step pressure swing cyclic process has been used to achieve a continuous operation, where hydrogen with high purity can be produced continuously.

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CHEMICAL LOOPING TECHNOLOGY – METAL OXIDES, REACTORS AND PROCESSES

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The concept of chemical looping reactions has been widely applied in chemical industries. Fundamental research on chemical looping reactions has also been applied to energy systems. Fossil fuel chemical looping applications were used with the steam-iron process for coal processing from the 1900s to the1940s and were demonstrated at a pilot scale with the HYGAS process and Carbon Dioxide Acceptor process in the 1970s. There are presently no chemical looping processes using carbonaceous fuels in commercial operation. Key factors that hampered the continued use of these earlier processes were the inadequacy of the recyclability and economic viability of the looping particles and their associated reactor system operation. With the CO_2 emission control now of great concern and the need for the development of high efficiency operational processes, interest in chemical looping technology has resurfaced for its unique ability in generating a sequestration-ready CO_2 stream with efficient and versatile process applications.

Chemical looping technology is a manifestation of the interplay among all the key elements of particle science and technology including particle synthesis, reactivity and mechanical properties, flow stability and contact mechanics, gas-solid reaction engineering and particulates system engineering. This presentation will describe the fundamental and applied aspects of modern chemical looping technology that utilizes fossil and other carbonaceous feedstock. Specifically, it will discuss the reaction chemistry, ionic diffusion mechanisms, metal oxide synthesis and thermodynamics, reactor configurations, and system engineering along with energy conversion efficiency and economics. The Coal-Direct Chemical Looping Process and Syngas Chemical Looping Process being developed at Ohio State University at a pilot level will be illustrated. Further, the CO_2 emission control using the chemical looping technology will be compared with other CO_2 capture methods. Selective oxidation in the production of fuels and chemicals, solar based chemical looping technology and various process application options will also be discussed.

CHEMICAL REACTION ENGINEERING OF THE LOW-TEMPERATURE TRANSFORMATION OF BIOMASS

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Keywords: biomass, macromolecule, reaction, diffusion, reactor modelling, structured reactor

The use of molecules from biomass for the production of chemicals and fuel components is a big global research trend. We are shifting from relatively simple molecule structures appearing in crude oil and natural gas to the very complex ones in biomass. Molecules originating from biomass are, typically polyfunctional macromolecules, such as cellulose, starch, hemicelluloses and lignin fractions. On the other hand, a typical biomass, for instance woody biomass is a well-organized entity, consisting mainly of cellulose, hemicelluloses and lignin. Chemical reaction engineering plays a key role in this green transformation.

There are three principal ways of chemical treatment of biomass: gasification, pyrolysis and low-temperature treatment. Gasification leads to syngas formation, while the main product of pyrolysis is pyrolysis oil and gas. The low-temperature treatment, often called the sugar platform is based on bio-chemical conversion processes of biomass.

Several problems have to be solved to make the sugar platform working well in industrial practice. One of the key issues is the catalyst development. In order to obtain platform chemicals from cellulose and hemicellulose, the glycosidic bonds between the sugar units should be broken by hydrolysis. Several catalysts have been proposed, such as homogeneous mineral and organic acids, heterogenized acid catalysts on carbon support, cation exchange resins as well as enzymes. The hydrolysis kinetics in the presence of several catalysts will be presented, particularly a self-accelerating phenomenon in the hydrolysis of hemicelluloses on resin catalysts. A new kinetic model will be presented, based on the change of the reactivity along the macromolecule chain. The model is applied on the hydrolysis of wood hemicelluloses, such as O-acetylgalactoglucomannan.

From the mild-temperature hydrolysis process, valuable monomeric sugars are obtained: besides glucose, i.e. polyfunctional molecules, such as arabinose, galactose, mannose and xylose are obtained. These molecules can be used as such, or refined further, e.g. by hydrogenation, oxidation, isomerization or esterification. A process intensification approach starts with catalyst selection and optimization, kinetic studies, investigation of physical properties as well as mass and heat transfer phenomena. The interaction of chemical kinetics and internal mass transfer effects in the pores of solid catalysts plays a crucial role in the transformation of molecules from biomass. In many cases, catalyst deactivation interferes with kinetic and mass transfer effects. Mathematical models for these phenomena will be presented and applications of continuous structured reactors in the transformation of sugars to value-added molecules are demonstrated. A general research strategy is presented: from reaction kinetics to reactor design.

KEYNOTE LECTURES

NEW CATALYSTS AND CATALYTIC PROCESSES FOR OXIDATIVE DESULFURIZATION OF DIESEL FUEL

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New requirements for ultra-low sulfur content (10 ppm) in liquid motor fuels demand novel approaches for ultra-deep desulfurization. The gas phase oxidative desulfurization (ODS) of motor fuels with air or oxygen, initially proposed for desulfurizing petroleum fractions, may become a new promising technology for removal of refractory sulfur compounds [1]. A number of oxide catalysts based on Cr, Fe, Mo, Cu, Ce, Zn and Al oxides or their mixtures have been prepared by precipitation or by incipient wetness impregnation with subsequent calcination at 500 °C. The catalysts were tested at 300-400 °C in ODS of thiophene, dibenzothiophene (DBT) and dimethyl dibenzothiophene (DMDBT) dissolved in octane or toluene, and the optimal catalysts were also studied in ODS of straight-run diesel fraction. The reactivity of different sulfur containing molecules in ODS over catalysts increased in the sequence: thiophene<DBT<DMDBT. The main sulfur containing product of oxidation of these compounds was SO_2. During the ODS reactions, carbon and sulfur accumulated in the catalyst. A method for catalyst regeneration at 300-500 °C was developed. Thus, the gas phase oxidative desulfurization of refractory sulfur compounds of motor fuels with air was shown to be feasible at atmospheric pressure and moderate temperatures: 350-400 °C, which can offer better economic solutions and incentives in fuel desulfurization [2-5].

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[3] International patent № WO2013015889 (A1) – 2013-01-31 Catalytic compositions useful in removal of sulfur compounds from gaseouhydrocarbons, processes for making these and uses thereof Bourane Abdennour; Koseoglu Omer Refa; Ismagilov Zinfer; Yashnik Svetlana; Kerzhentsev Mikhail; Parmon Valentin.

[4] International Patent № WO 2013116338 A1. Mild hydrodesulfurization integrating gas phase catalytic oxidation to produce fuels having an ultra-low level of organosulfur compounds: publication.patent.patent. WO / Bourane A., Koseoglu O.R., Ismagilov Z.R., Yashnik S.A., Kerzhentsev M.A., Parmon V.N.

[5] Korean Patent № KR20140079365 (A) Catalytic compositions useful in removal of sulfur compounds from gaseous hydrocarbons, processes for making these and uses thereof Bourane Abdennour; Koseoglu Omer Refa; Ismagilov Zinfer; Yashnik Svetlana; Kerzhentsev Mikhail; Parmon Valentin.

REACTION INTENSIFICATION BY INDUCTION HEATING AND ULTRASONIC CAVITATION

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Alternative energy forms and transfer mechanisms have dramatic intensification effects on chemical processes. The present lecture focuses on application of induction heating and ultrasonic cavitation in conventional and microstructured reactors. The combination of microstructures and sonication is a new and emerging area. Such a combination is technically feasible and often leads to synergistic results. Propagation of an ultrasonic wave in a medium generates the cavitation bubbles, which itself behaving like microreactors, are the centers of a high-energy phenomenon leading to intensified reaction conditions. The product yield in many (radical) reactions increases further at higher frequencies as compared to that obtained with the common 20-kHz probe. Novel applications of sonochemistry will be reviewed, paying attention to the latest developments and showing future directions.

Radiofrequency (RF) heating is used as yet another way of delivering thermal energy in a flow reactor which often allows to eliminate heat transfer limitations, temperature hot-spots, and to minimize energy losses [1-3]. Under radiofrequency field, composite magnetic catalysts (CMCs), containing a magnetic and a catalytic component, provide fast and efficient energy transfer to the active sites. For an RF-heated reactor bed, the rate of volumetric heat generation inside the packed bed reactor strongly depends on the magnetic properties of magnetic material. Therefore it is of importance that both catalytic and magnetic properties of the two components in CMCs can be optimised independently. The use of nickel ferrite nanoparticles embedded in a mesoporous framework provides a high degree of control over volumetric heating. Relatively uniform heating can be achieved with RF even for large packed bed reactors if an appropriate CMCs and geometry of the packed bed reactor are chosen.

Combined with the inherent advantages of high heat and mass transfer in microstructured chemical reactors, RF heating opens up new possibilities for transient operation under fast temperature excursions. This mode of operation allows to increase or decrease the surface coverages of reacting species as compared to their steady-stare values, which in turn could increase the product yield in many competitive reactions. On the other hand, cyclic RF irradiation allows to avoid excessive energy accumulation in the catalyst, which could lead to its overheating and unwanted changes in its morphology. To this end, the integral concept of RF-assisted microreactors will presented in this lecture.

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CONFINED SWIRLED FLOWS FOR PROCESS INTENSIFICATION

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Various chemical processes in multiphase reacting and nonreacting systems are widely presented in industries. The choice of the multiphase contactor depends on the field of application and being affected by specific process requirements such as residence time, required number of stages, desired throughput capabilities, ability to treat specific liquids or operate under high pressure, the necessity to handle with corrosive/flammable substances and etc.

There are many different thoroughly studied conventional multiphase contactors utilized for carrying out the multiphase processes: mechanically stirred vessels, centrifugal and jet mixing apparatuses, packed and sieve-tray columns, static or pipeline mixers, fluidized bed reactors and many others purposefully developed to meet the specific process requirements. Along with many advantages, all types of conventional contactors also have some well-known shortcomings. For different kinds of devices they derive from either maintaining the rotating machinery, or high cost, or slow mass-transfer and sufficient dimensions, or non-uniformity of multiphase medium or large residence time and so on. For instance the large dimensions of packed or sieve-tray column make it unsuitable for modularization and substantial efforts may be required to put up the column and to make the connections. Moreover, the capabilities of further intensification of interphase exchange processes quite often are limited by the stability loss problem arising at enhancing the physical impact on treated medium with subsequent multiphase chemical system structure disruption.

Although the substantial efforts continue to be applied in studying and improving existing technologies, the development of the new designs of multiphase contacting equipment is still welcome. The new approaches for process intensifications are very desirable to be studied and discussed with developing the new devices on their basis that may be compact and provide the high performance.

Turbulent confined swirled or vortex flows are widely encountered in chemical practices and being developed both for applications in nonreacting and reacting systems. The performance of these devices relies on exploitation of some advantages and peculiarities of swirled flows: regulable field of centrifugal forces excessing the gravity by many times, the turbulent and high shear stressed flow patterns facilitating the dispersing/mixing and interphase surface renovation with dramatic accelerating the exchange processes, elongation of particle trajectories with comparison with linear translation movement, achievement of high values of slip velocities for particles motion in fluid environment and high values of velocity difference at the gas-liquid interfaces leading to their efficient contacting, some another special features of vortex flows. The one of the main advantages consists in the possibility of over intensification of interphase exchange processes due to the stabilization of the multiphase system in the vortex flow field giving the chance to sufficiently enhance the value of energy introduced into and dissipated inside the system.

The following well-known applications of confined vortex flows and the variety of practical devices on their basis are being the subjects of only short mentioning in the current presentation and include the cyclones, high-gravity ultrasound and vortex tube separators, spraying and jet devices, various combustion systems, agitated flows used for mixing.

The main topic of present lecture is devoted to review and discuss the various approaches for making contact in multiphase chemical environment and intensifying the interphase exchange processes with utilizing the strained confined swirled flows produced in vortex chambers and in the rotating devices in various processes. Vortex chamber basically is a substantially cylindrical shell having the top and the bottom with fluid flow entering the body via a swirler located at the periphery. Swirler typically consists of a ring with multiple tangential speeding up slots or nozzles designed to convert the pressure energy to rotational motion.

Special attention will be paid to the survey of intensification approaches for gas-liquid processes including the using of the vortex contactors and vortex plates for packing columns, for carrying out of gas-solid processes including the drying devices and the discussion of the new data and ideas for industrial processes intensification in fluidized bed layers, for liquid-liquid contacting for extraction and another applications, for sophisticated liquid-solid-gas mixtures treatment including the bio-chemical applications and etc.

FLOW-THROUGH CATALYSIS FOR INTENSIFIED PRODUCTION

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The catalytic processes in flow represent an important alternative in comparison with batch processes in terms of efficiency, safety, waste processing, purification, energy consumption and provide a significant contribution to the sustainability of processes with long-term production of chemicals. A very interesting family of materials, unconventional monoliths with hierarchical porosity (macro-/mesoporosity) has been discovered in 1991 by Nakanishi [1] and have shown remarkable properties of mass transfer in high performance liquid chromatography. In the present study, the potential of these monoliths in liquid phase heterogeneous catalysis processes in flow is highlighted for several reactions: Knoevenagel condensation, Diels-Alder reaction, Friedländer reaction and selective hydrogenation reaction [4-11]. Silica, alumina and titania monoliths with hierarchical porosity were obtained by sol-gel process and spinodal decomposition between a oxide-PEO phase and water [1-5]. The monoliths were then functionalized by versatile catalytic phases: organic (NH_2), alumina deposition, *in-situ* synthesis of MOF (CuBTC) and Pd nanoparticles.

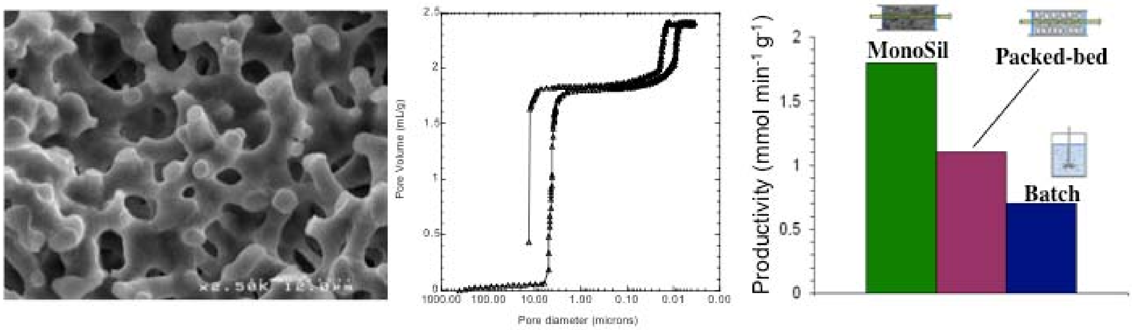

Fig. 1. SEM and Hg porosimetry of hierachical macro-/mesoporous silica monolith (MonoSil). Productivity of NH_2-MonoSil for the base catalysed Knoevenagel condensation in function of reactors types (batch and packed-bed experiments are performed with crushed and sieved monoliths)

A pseudomorphic transformation of the silica skeleton of the monolith into MCM-41 and zeolites (SOD, LTA) was also performed by adjusting the rate of silica dissolution to the rate of zeolites or MCM-41 formation. These monoliths used as microreactors increase importantly the efficiency and the productivity of reactions in comparison with more conventional systems such as particle beds (packed-bed) and batches (Fig. 1-2). These monoliths have demonstrated significant benefits by allowing the improvement of fluid dynamics with a higher mass transfer, low pressure drop, and higher control of contact time and open up the way to more process control and selectivity of reactions. Their stability and long-term productivity has been demonstrated. Their further development in catalysis but also in other flow-through processes as wastewater treatment (radioactive effluent) [12] or pollutants removal from oil [13] will contribute to process intensification for sustainable development.

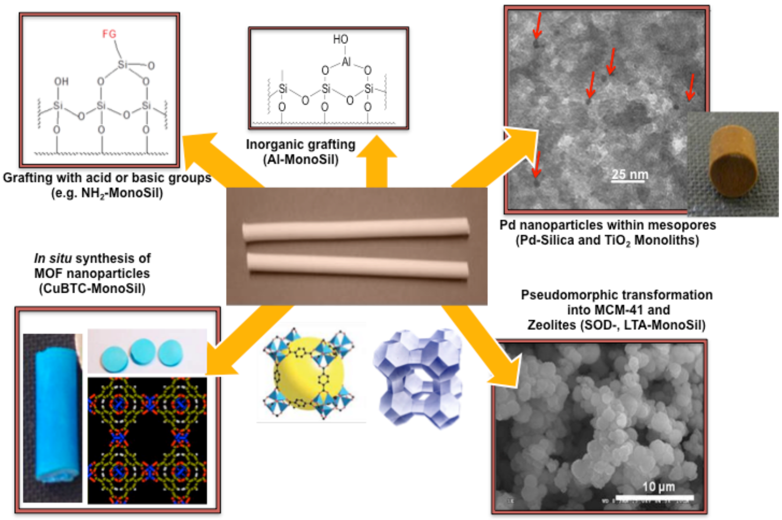

Fig. 2. Versatile functionalization techniques over hierarchical monoliths

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MICROWAVE-ASSISTED REACTION AND SEPARATION SYSTEMS

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Microwave fields have been investigated for some decades as an alternative form of energy for process activation. The main benefits attributed to microwave activation are fast and selective heating. In this presentation, some research highlights on microwave technology application to various reaction and separation processes including liquid-phase organic syntheses, gas-solid catalytic reactions, polymerizations, distillation, crystallization and adsorbents regeneration/dehydration will be presented.

Further, the research approach of development of specialized equipment that adequately integrates the application of electromagnetic fields with chemical processes will be discussed, as this approach can enable fundamental studies on microwave-chemistry/catalyst interactions under precisely defined electromagnetic and temperature conditions, process optimization and reliable scale-up.

KL-6

MICROREACTION TECHNOLOGY FOR CATALYTIC PROCESS DESIGN

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The pressure that the chemical industry is facing from new markets and increased environmental restrictions, places a demand for innovative and knowledge-based activities to enable more efficient catalytic processes and faster development times to plant commissioning. Catalyst and reactor design can be facilitated by continuous flow microfluidic technology that allows for rapid manipulation of reaction conditions, fast response times, precise control of the hydrodynamic environment, minimal consumption of reagent and catalyst. The transport intensification inherent to microstructured reactors makes them useful laboratory tools so that even fast, highly exothermic reactions can be performed isothermally and in the absence of mass transfer limitations. This allows not only the study of intrinsic reaction kinetics but also investigation of reactions under more extreme conditions (e.g. high temperature/pressure, solventless, flammable regime). Furthermore, microchannel reactors can be easily integrated with spectroscopic tools to gain insight into catalyst operation. Various examples will be presented that demonstrate the capability of microreactors to simplify kinetic data acquisition, expand the operational space and allow exploration of demanding reaction conditions to enable acquisition of the true intrinsic kinetics of reactions. Some processes can potentially be simplified by microreaction technology, through the use of undiluted feeds and single pass reactions without compromising yields and selectivities. Examples of integration of in-situ spectroscopy tools for gas/solid catalytic systems will be presented. The extension of such tools to gas/liquid/solid reaction systems is more demanding. Furthermore, there is increasing evidence that multiphase flow in small channels demonstrates different behaviour than in the macroscale due to the dominance of surface forces. Differences that need to be understood for successful microreactor design will be discussed.

CATALYTIC BIOMASS CONVERSIONS

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The search for novel conversion routes of biomass to biobased products like biofuels and biobased chemicals and materials is high on the global research agenda. The catalysis and chemical engineering disciplines are expected to play important roles in these development trajectories. In this presentation, our latest developments in this field will be highlighted.

The first part of the presentation will deal with the use of novel catalysts for the upgrading of fast pyrolysis oil and fractions derived thereof to products with improved stability and application potential. It will be shown that the use of advanced supported Ni-Cu catalysts allow the synthesis of stabilized pyrolysis oils that are suitable for co-feeding in FCC units. In addition, the use of novel Cu based catalysts for the upgrading of the sugar fraction of fast pyrolysis oil to a mixture of low molecular weight alcohols will be highlighted. Finally, the use of certain carbon supported catalysts for the upgrading of the pyrolytic lignin fraction to aromatics and alkylphenolics will be reported.

The second part of the presentation deals with the use of advanced catalyst for the synthesis of biobased chemicals, with an emphasis on hydrogenation strategies for 5-hydroxymethylfurfural (HMF) to high added value derivatives like diols (1,6-hexanediol and HMF-diol). The first is an already existing building blocks in the polymer industry, HMF-diol and derivatives have potential for the synthesis of novel biopolymers.

NEW TECHNOLOGIES FOR NATURAL GAS AND HEAVY OIL PROCESSING

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The processing of uncoventional hydrocarbon feedstocks is the key challenge for fuel and petrochemistry industry in the world. The conversion of such uncoventional resourse as natural gas to sinthetic oil, middle distilate or chemicals requires significant improvement in the term energy efficiency and use of carbon. The processes for transformation of heavy cride oils and residues to distillates are characterized not satisfactory yields, selectivity and catalysts stubility. The increasing of unconventional feedstocks production leads to the development of new approaches for design of processes and catalysts.

We will present the overview of new gas and heavy-oil processing technologies that have been developed in the last several years in Russia with the participation of A.V. Topchiev Insitute of Petrochemical Synthesis [1-4]:

- The process of the conversion of tars, heavy residues, bitum and heavy oils in blacking (slurry) reactor using nanoheterogeneous catalysts under pressure < 10 MPa and temperature <450 °C. The dramatic improvements have been achieved using nanoheterogeneous particles of the catalyst and upon the development of a simple and reproducible method for their synthesis. The fact that heavy oil fractions contain native surfactants, which prevent agglomeration and subsequent deposition of nanoparticles, also contributed to the success.
- The conversion of natural gas to syngas using metal oxide systems with a high lattice-oxygen content and a riser reactor. Optimal conditions for the manufacturing of synthesis gas have been determined, at which the methane conversion reaches 95–99 % and the H_2/CO ratio in the product is in the range of 2.0–2.2.
- The conversion of syngas to DME and DME using zeolite base catalyst into gasoline or the mixture of isoparafines and naphthenic hydrocarbons with high yield and selectivity.

- Process that combines the direct synthesis of DME with the olefins production.
- Fischer-Tropsch synthesis in a three-phase (gas-liquid-solid) system over iron and cobalt nanocatalys with production of light synthetic oil. This process can significantly improve system performance compared with the currently implemented in industry technology.

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ORAL PRESENTATIONS

Section I.

Advances in Chemical Reactors Fundamentals

Chemical Reactions Kinetics

Energy & Mass Transfer in Chemical Reactors

Fundamentals of Hydrodynamics and Fluid Flow in Chemical Reactors

Specialized Software for Development of Chemical Reactors and Flow-Sheeting of Reactive Processes

OP-I-1

KINETIC MODELING OF GALACTOSE HYDROGENATION OVER RUTHENIUM ON ALUMINA CATALYST

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Selective hydrogenation of monosaccharides is one of the important reactions for the synthesis and production of chemicals for pharmaceutical, agrochemical and food applications. Hydrogenation of sugars is typically done either using Raney nickel or carbon-supported ruthenium catalysts. In the current work hydrogenation of D-galactose to galactitol was investigated over a finely dispersed Ru/Al_2O_3 catalyst, which has several advantages with respect to industrial implementation compared to carbon supported counterparts. The catalyst prepared by impregnation was characterized by means of CO-chemisorption, ICP-OES and SEM-EDX. Experimental data were obtained in a semi-batch reactor at temperatures ranging from 105 to 135 °C and hydrogen pressures from 30 to 60 bar. Based on the experimental data, it can be concluded that at the lowest experimental temperature the effect of hydrogen pressure on the galactose conversion plays a key role. However, at higher temperatures the effect of hydrogen pressure was found to be less prominent. Several kinetic models were advanced and compared with experimental data (Figure 1). Numerical data fitting performed for all data sets simultaneously clearly demonstrated applicability of a model with first order dependence for both reactants.

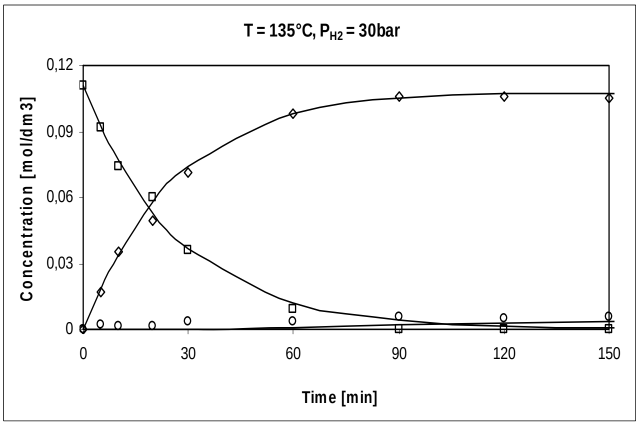

Figure 1. Hydrogenation of galactose to galactitol at 135 °C and 30 bar of hydrogen

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DISACCHARIDES HYDROGENATION KINETICS OVER Ru BASED NANOSTRUCTURED CATALYSTS

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Selective hydrogenation of disaccharides is one of the important reactions for the synthesis and production of chemicals for pharmaceutical, agrochemical and food applications. Moreover synthesized polyols can play a key role in the production of biofuels from renewable sources. Lactose and maltose is a low cost, large-scale product of dairy and agrecultur industry, annually several million tons of lactose and maltose is produced worldwide. Lactose and maltose is suitable for chemical synthesis and there hydrogenation to lactitol and maltitol is one of the best ways to obtain valuable products. The hydrogenation is commonly performed batchwise in stirred tank reactors at temperatures ranging from 60-150 °C, pressures of 30-80 bar with sponge nickel or transition metals supported on oxides. Hydrogenation is a complex chemical process characterized by formation of numerous side products along with lactitol formation. Typical side products are lactulose, lactulitol, lactobionic acid as well as sorbitol and galactitol. Therefore, investigation of lactose and maltose hydrogenation kinetics and preparation of efficient catalysts is important for increasing lactitol yield. Industrially used sponge Ni catalysts are very selective, with selectivity reaching up to 96-98 %. However, Ni leaching and fast catalyst deactivation is the main problem of this type of catalysts. Hydrogenation over ruthenium supported on MgO, silica, alumina and TiO_2 led to increased lactulose and to some extent lactobionic acid formation, therefore the process selectivity decrease to 20-80 % [1]. Commercial catalysts, Ru supported on different types of carbon, show good performance in lactose hydrogenation with selectivity up to 96-97 % [1]. However, Ru is more expensive compared to Ni therefore Ru based catalysts should have enhanced activity and stability.

Polymer-stabilized transition metals nanoparticles represent an attractive possibility for modification of catalytic properties and synthesis of efficient and stable catalysts. Stabilization of metal nanoparticles in rigid polymer matrices can be an alternative for commonly used oxides or carbon-supported catalysts, providing high target product yield along with improved catalyst stability. Hypercrosslinked polystyrene (HPS) is rigid polymer with superior mechanical and chemical stability that can provide a good matrix for catalytic active nanoparticles synthesis and stabilization. HPS is characterized by high surface area and volume containing both small and large mesopores [2-5], promoting substrate transport to active sites. The use of the catalysts based on Pd and RuO_2 NPs and HPS was reported in earlier work for D-glucose partial oxidation [2, 6]. These catalysts demonstrated high selectivity and activity in the formation of target products. Therefore in this report the focus is on synthesis of Ru-containing HPS catalysts and their behavior in lactose and maltose hydrogenation. The catalysts were characterized using X-ray fluorescence analysis (XRA), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), nitrogen physisorption and CO chemisorption methods. The influence of the Ru content and the various reaction conditions on the activity and selectivity of lactose and maltose hydrogenation. Lactitol and maltitol selectivity was found to be up to 97% at 99 % of conversion was observed for catalyst containing 4.9 wt. % of Ru. The developed kinetic model was used to compare it with experimental data through numerical data fitting. Identifiability of the developed parameters was checked with the Markov-Chain Monte Carlo method.

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SELECTIVITY OF SYNGAS FORMATION IN VOLUMETRIC MATRIX REFORMERS (RADIANT BURNERS): THERMODYNAMIC, KINETIC AND MACROKINETIC ASPECTS

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Introduction

Recently a new concept of syngas generator based on volumetric permeable matrix reformers (radiant burners – RB's) with efficient heat recovery was suggested [1,2]. In such burners it is possible to substantially widen the combustion limits, which allows one to convert fuel (e.g. gaseous hydrocarbons) to synthesis gas ($CO+H_2$ mixtures). In this paper we analyze thermodynamic, kinetic and macrokinetic factors which control the selectivity of syngas formation during methane oxidation in such devices.

Experimental

The details of the reformer (RB) construction are given elsewhere [2].

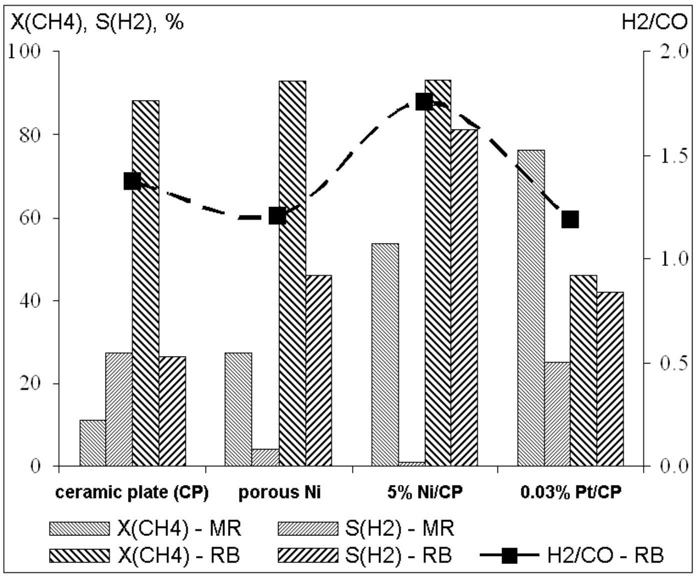
Several types of catalysts that allow one to stimulate the combustion and to vary product selectivities were tested. Among them, highly active Pt and moderate activity Ni supported on La-stabilized alumina ceramic plate (CP), porous nickel and nickel-based metal alloy plates of different morphology. The burner is equipped with a steel capillary for gas sampling and thermocouples for measurements of temperatures of external shell, matrix surfaces (inside and outside of the burner cavity), and gases (inlet and outlet). On-line GC and IR-analyzer are used to measure the outgoing gas composition (H_2, O_2, N_2, CH_4, CO, CO_2 concentrations).

The effect of thermodynamic factors onto product selectivities was analyzed using calculations of adiabatic temperature and equilibrium composition based on standard procedures and thermodynamic properties of reactants and products.

Results and Discussion

The main thermodynamic factors determining the final gas composition are the initial temperature of the gas mixture and O_2-to-methane ratio: selectivity to CO and H_2 increases at decreasing initial oxygen content and rising initial temperature. These two factors also determine the possibility to conduct the process in autothermal regime and, thereby, cause the limiting value of selectivity that provides the balance between the heat production at the expense of total oxidation and minimal temperature that is required to ignite the process. The latter can be considered as a kinetic factor that, withal, is strongly associated with the process thermodynamics.

One of the variables that control the kinetics of methane oxidation in RB's is the chemical nature of the matrix material. We have demonstrated, however, that the intrinsic catalytic activity of the matrix material in methane oxidation substantially differs from the overall performance of the RB charged with it. As can be seen from the Figure, whereas the activity tested in conventional microreactor (MR) increases from the bare CP to porous Ni plate and then to CP supported Ni and Pt, methane conversion is the highest in the BR equipped with Ni-doped CP. Also, the same material demonstrates the lowest selectivities to H_2 and CO in MR, but the highest in RB.



The obtained experimental results are interpreted in terms of the strong interaction between the combustion front (gas layer of <1 mm thickness) stabilized in an immediate proximity to the outer surface of the matrix material and this surface itself. Whereas the major conversion is taking place in the gas phase, the diffusion path of all gaseous particles exceeds by far the combustion front thickness and, as a result, their interaction with solid surfaces of different chemical activity leads to different product distributions. In the case of highly active Pt-doped CP, catalytic oxidation of methane to CO_2 and water strongly depletes the gaseous mixture with oxygen and reduces the efficiency of gaseous combustion (down to its complete extinction).

As a result, the overall efficiency of syngas formation is a product of strong reciprocal influence of thermodynamic, kinetic and mass-transfer (macrokinetic) factors.

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COMBUSTION OF LEAN METHANE-AIR MIXTURES IN MONOLITH BED: KINETIC STUDIES IN A LOW AND HIGH TEMPERATURE

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The paper summarizes results of [1] lean methane-air mixtures non-catalytic combustion kinetic studies, carried out in a low and high temperature, in monolith bed and compared with similar results for free space.

Homogeneous oxidation of methane is obviously free-radical process that may consist of several (to several hundreds) of elementary reactions. It is very important to find a suitable description of kinetic mechanism of homogeneous methane combustion which will be a compromise between simple one- or two- stage and multi- stage models based on large number of reactions to be convenient for complex numerical simulation. Computer thermal reversed flow reactor model simulations [2] with use of 4 various kinetic models revealed large differences in simulation results. Divergences concerned mainly ignition temperatures (i.e. difference of 290 °C in initial reactor preheating necessary to initiate run up to autothermal cyclic steady state) what caused significant (of about 360 °C) change of simulated maximum reactor temperature. The first kinetic experiments [3] on the monolith packing were carried out using ceramic samples with relatively narrow channel called in the paper as Monolith A. Neither experiments nor kinetic models used in these simulations included CO generation in products. As was shown in the further studies [4, 5] CO production depends on the temperature and environment in which combustion takes place, especially on the area of the surface in contact with the gas phase.

Own kinetic studies were undertaken to obtain simplified model for combustion in the monolith channels geometries forecasted for further industrial applications (called as Monolith B). The kinetic experiments in [1] were carried out using a setup, the same as shown in [6].The paper presents results of these studies on thermal methane combustion over monoliths, moreover comparing them with the earlier results carried out in the free space. The experiments revealed that reaction mechanism depends on temperature in combustion zone. Therefore it is not possible describe process by kinetic equation with the same kinetic parameters in a wide range of temperature. This is confirmed by totally different values of activation energy

E_j and pre-exponential factor $k_{0,j}$ obtained in experiments in low and high temperature. The problem with kinetic description in a wide range temperature was solved by combining kinetic parameters, obtained in low and high temperature experiments, in one algorithm presented in the paper.

The study revealed an influence of size, type of monolith's surface and temperature in combustion zone on the reaction mechanism and its kinetics. This has led to the conclusion that combustion in the monolith is not purely homogeneous, since it combines heterogeneous effects of the free radicals activation at the monolith surface with homogeneous combustion in the empty space of the monolith channels. Either the kinetic equations of the Arrhenius type parameters E_j, $k_{0,j}$ significantly vary with the combustion temperature. Moreover, these parameters and the light-off (i.e. ignition) temperature are strongly dependent on the specific surface area of the reactor packing (the monolith in the case discussed). Therefore a hypothesis that the share of combustion type: heterogeneous with surface effect (on the monolith's wall) and homogeneous (in the free space) depends on the temperature in the combustion zone was formulated.

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KINETIC STUDY OF N-BUTANE ISOMERIZATION ON Pd-SZ CATALYST

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Over the past few decades, low temperature skeletal isomerization of n-butane (n-C_4) on Pt-modified sulfated zirconia catalysts (Pt-SZ) was studied intensively. In some works advantages of Pd over Pt modifications of SZ resulting to the higher activity at low temperatures 130-170 °C [1, 2], and to the higher tolerance to sulfur impurities in a feed [3] were shown. Substantially lower production costs can be expected, as well. In the previous conference CR-20 (Luxemburg, 2012), we have reported that high activity and stability of the Pd-SZ catalyst [1] can significantly improve the process of n-C_4 isomerization [4]. The prospects for industrial implementation of the process require further in-depth kinetic studies; this is the main goal of the present work. Along with kinetic investigations, the contribution of mono- and bimolecular mechanisms in i-C_4 formation, as well as the parameters impact on the changes in isomerization mechanism were analyzed.

Kinetics of n-C_4 isomerization over Pd-SZ catalyst (Pd load was 0.35 wt. %) was studied within the range of 5-25 % n-C_4 conversion in a flow-type isothermal fixed-bed reactor with GC analysis of the reaction products. The influence of parameters on the reaction rates and selectivity was investigated by varying n-C_4 WHSV from 1.3 to 11.1 h^{-1}, temperature from 125 to 160 °C, molar ratio H_2/C_4 0.1-1.0 and pressure 6-25 bar. Normally, experiments have been carried out at a total pressure 24 bar, molar ratio H_2/C_4 0.2 and temperature 150 °C. Catalyst preparation procedure, its physical-chemical characteristics and details of the lab-scale setup have been described in [1]. For kinetic studies the catalyst granules were crushed and sieved as 0.25-0.5 mm fractures. No significant catalyst deactivation was observed during the long-time operation on-stream.

At the experimental conditions, the major reaction product was i-C_4, its selectivity was 74-86 %. By-products C_2 and n-C_3 were formed in appreciable amounts, other byproducts C_1 and C_5 were found as traces. Under C_5 we denote pentane, isopentane, and neopentane, totally. The rate of n-C_4 consumption and the rates of products accumulation (a) and its selectivity (b) were shown in Figure as a function of n-C_4 conversion at various temperatures. By extrapolating the products selectivity to a zero conversion value (See Fig.), one can estimate what fraction of the products was formed directly from n-C_4. Decrease in selectivity to i-C_4 while the selectivity to other products increased can indicate that some amount of by-products is formed due to the hydrogenolysis of i-C_4, or its surface intermediates.

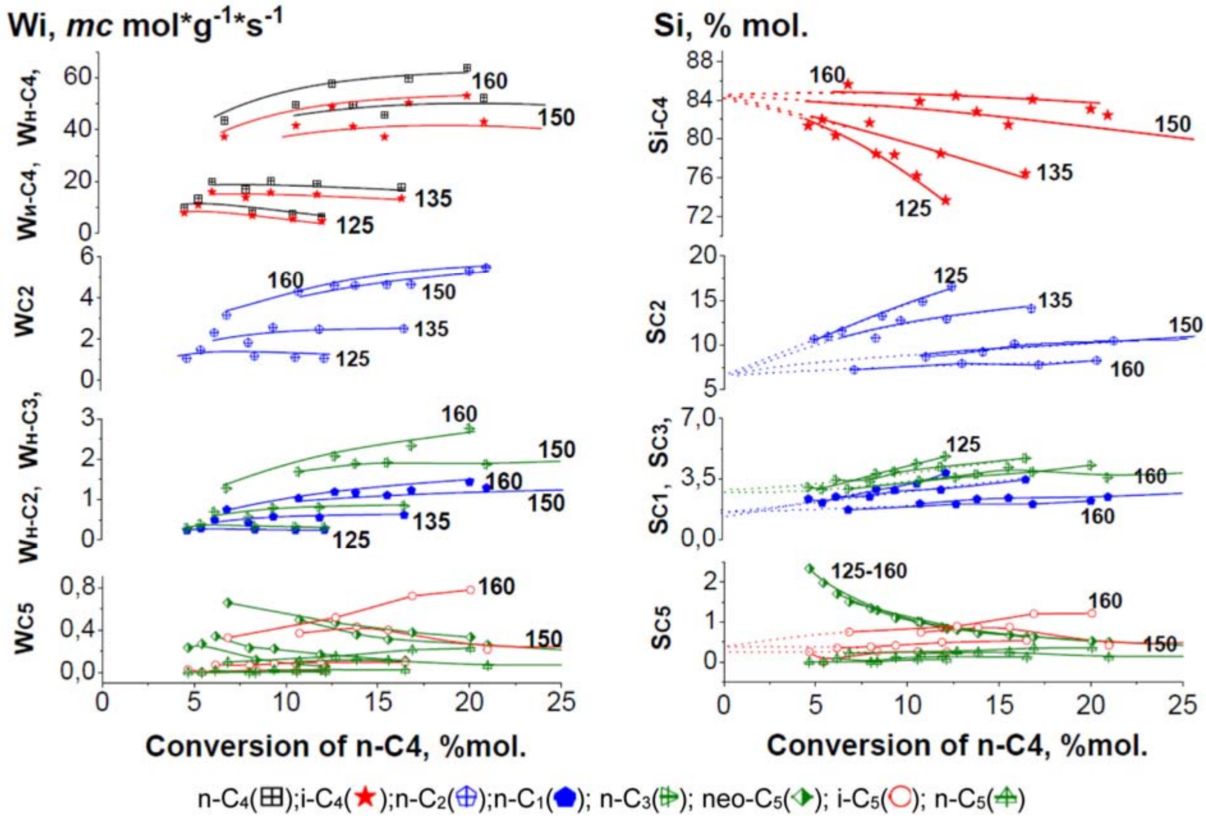

Fig. Rates (a) and selectivity (b) of n-C_4 isomerization *vs.* n-C_4 conversion over Pd-SZ catalyst at T = 125-160 °C. H_2/C_4 = 0,2, WHSV = 1.5-11.1 h^{-1}, P = 24 bar.

The apparent activation energy of n-C_4 consumption reaction rate was found to be ~100 kJ/mol; this is higher than that of the by-products formation rates.

The negative order in H_2 was defined for i-C_4 formation rate. For this reason, we can assume that the bimolecular mechanism of this reaction is predominant. Basing on the experimental kinetic studies, we elaborated a simplified kinetic model and evaluated a set of kinetic parameters by means of the standard computer procedure.

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SINGLE-EVENT MICROKINETIC (SEMK) ASSESSMENT OF THE CATALYTIC CRACKING OF CYCLOPARAFFINS ADMIXED WITH OLEFINS

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Introduction

It is of paramount importance to adequately understand the catalytic cracking behavior cyclic compounds as they can lead to aromatics as well as acyclics with significantly different octane numbers. In this respect, microKinetic modelling is a powful tool for tuning FCC gasoline quality and optimizing FCC reactor performance.

Single-Event MicroKinetic (SEMK) model is one of the most detailed microkinetic models, featuring feed independent rate coefficients[1].

In this work, we develop an enhanced SEMK model for the cracking of methylcyclohexane admixed with 1-octene in the absence of coke formation. The emphasis is put on differentiating between steps involving allylic carbenium ions and those involving conventional carbenium ions.

Methodology

Of particular importance for the enhancement of the SEMK model in this work are protonation (pro), deprotonation (dep) and hydride transfer (htr) reactions involving allylic as well as conventional carbenium ions. Hydride transfer reactions forming and consuming allylic carbenium ions are further differentiated due to the relatively stable structure of allylic carbenium ions as shown in Fig. 1.

SEMK activation energies have been determined by regression using a previously collected data set[2] in which methylcyclohexane admixed with 1-octene (17.65 mol %) was cracked over on a commercially availabble REUSY zeolite at 693 K – 753 K in the absence of coke formation and thermal cracking.

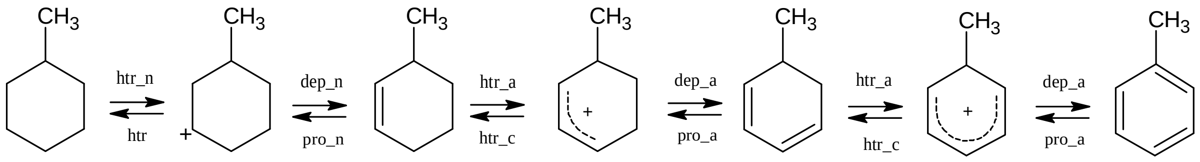

Fig. 1. Schematic representation of methylcyclohexane aromatization as a sequence of hydride transfer and deprotonation reactions. N, a and c mean involving normal carbenium ions, forming and consuming allylic carbenium ions

Results and discussion

Table 1. SEMK activation energies

reaction family	reaction type			
	p	*s*	*t*	
htr_n		122.0	127.8	
htr_a		89.4		
htr_c		177.0		
pro_n		121.8	122.3	
pro_a		110.6	95.0	
dep_n		178.5	228.2	
dep_a		200.3	179.0	
prsc_n	142.1	161.3	-	
disp		65.9		
	(s,s)	(s,t)	(t,s)	(t,t)
PCP_n	137.1	193.5	238.2	195.1
edβ	142.1	160.1	275.7	-

Table 1 shows the estimates for the activation energies of the various reaction families involved in cyclics cracking. These values are statistically significant and respect the trends expected according to free carbenium ion chemistry.

Using the enhanced SEMK model, a contribution analysis has been performed to assess relative reaction rates (arrow thickness) and percentages of a species converted via a reaction (the number above the arrow), see Fig. 2. It can be seen that PCP reaction rates are calculated to be the fastest among all reactions and significantly exceed endo β-scission. All cyclic diolefins are transformed to aromatics while the latter is hardly converted back to the former.

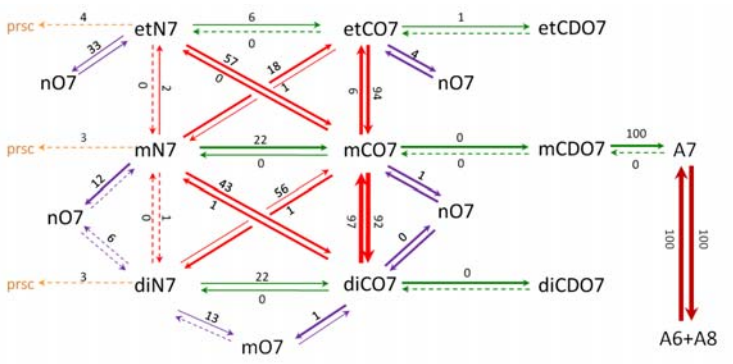

Fig. 2. Contribution analysis of the cracking of methylcyclohexane and 1-octene

Conclusion

The catalytic cracking SEMK model has been enhanced with respect to differentiating reactions involving allylic and normal carbenium ions and adequately describes data on a commercial RE USY. PCP reactions are the fastest reactions in the cracking system and the aromatization of cycloparaffins is almost reversible.

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OP-I-7

KINETIC MODEL OF NAPHTHA REFORMING PROCESS BASED ON THE USE OF THERMODYNAMIC POTENTIALS

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The prediction and application efficiency of kinetic models for the complicated reaction systems, such as petrochemical process, is defined by optimal relation between the level of reaction and reactants detailization and the number of kinetic parameters in the model. In this study we proposed the approach based on reasonable grouping of reactants and reactions into homologue groups with account of difference between individual reaction rates within the group accounting the influence of thermodynamic potentials (first of all, free Gibbs energy of corresponding reactions) values on the value of the apparent activation energy of the given reaction.

Application of such approach is demonstrated for the case study, dedicated to the modelling of the naphtha reforming process [1]. Particularly, it was shown that the rates of aromatization of all normal paraffins into corresponding alkylbenzenes may be described by one common equation: $W_j = k_0 \exp\left(-\frac{E+\beta\Delta G_j}{RT}\right)\left(P_{n/i-Pi} - \frac{P_{ARi}P_{H_2}^4}{K_{Pj}}\right)$,

where k_0 – pre-exponent, E – activation energy, ΔG_j – free Gibbs energy for j-th reaction, P – partial pressures of reactants, K_{pj} – equilibrium constant for j-th reaction, β – empiric coefficient. Therefore, we may describe the rates of 5 separate reactions (for C_6-C_{10} n-paraffins) using only 3 kinetic parameters to be defined from experiments (k_0, E and β) instead of 10 parameters (5 pairs of k_0 and E for each reaction). The similar approach may be applied to aromatization of iso-paraffins and hydrodecyclization of naphtenes, also providing the significant decrease of number of required kinetic parameters.

The rates of the irreversible paraffins hydrocracking reactions may be described by common kinetic equation with account of individual reactive ability by empiric power function from number of carbon atoms in paraffin or by empiric function from the bond energy of the initial paraffin.

The kinetic model of the naphtha reforming process, constructed on the base of such approach, includes description of 144 individual reactions with participation of 62 individual and group components, thus providing the qualitatively adequate and quantitatively accurate description of the experimental data, using only 22 kinetic parameters to be defined from experimental data. The model complexity level is quite appropriate for treatment of experimental data and for further model application in the process simulation purposes. The proposed model significantly exceeds all earlier known naphtha reforming kinetic models [2] in the ratio between the system detailization level and model complexity (fig.1).

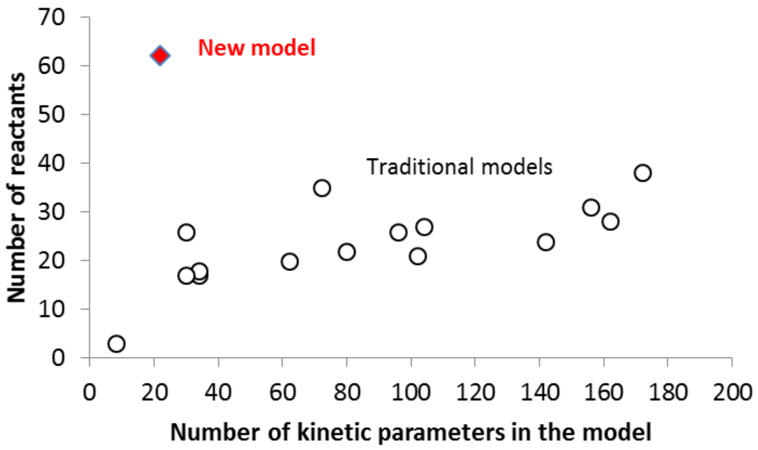

Fig. 1. Ratio between the reaction system detailization level and model complexity for proposed model and conventional naphtha reforming models (по данным [2])

Use of thermodynamic potentials and construction of the thermodynamically consistent kinetic models may provide the efficient simulation of the catalytic processes of oil refinery and petrochemistry in the wide range of their application conditions with quantitative prediction of the their key operation parameters. The proposed approach, except the naphtha reforming case, may be expanded to other petrochemical processes such as hydrotreatment, hydrocracking, isomerization etc.

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LIQUID TO PARTICLE MASS TRANSFER IN A STRUCTURED BED THREE PHASE MINI REACTOR

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The needs for reduction of experimentation cost, safer operation and minimization of experimental time have prompted many investigators to use small-scale reactors with total catalytic mass less than 10 g [1,2]. Small scale theree phase reactors appear to be a very promising and useful tool for applications like hydrotreatment of bio-oils, vegetable oils etc., but their successful use ultimately depends on their effective operation and simulation. Mass transfer effects and fluid dynamic characteristics are the most important parameters affecting the three phase reactor operation and their study allows the effective use and simulation of such reactors.

There are lots of liquid to paricle mass transfer investigations in literature for large scale packed beds, however respective studies for smal scale reactors are few. The main object of this study is the experimental determination of the liquid to particle mass transfer effects in a structured string-bed mini-reactor [1,2,3] for both spiral and vertical configuration in upflow mode and ambient conditions using the technique of the diffusion-controlled dissolution of copper particles in acidified dichromate solution.

Feed solution of 0.34 mM $K_2Cr_2O_7$ in 1 M H_2SO_4 was used as suggested by Gruber and Melin [4]. The reactors were PET tubes of 2.0 mm internal diameter. Three different structed bed reactors were studied, the one in spiral configuration and 32 cm long and the other two in vertical configuration being 32 cm and 6 cm long respectively. A 3 cm long active section filled with copper particles of 1.5 mm diameter was used for each reactor. Before and after the copper particles, inert particles of the same diameter were loaded. The liquid feed of dichromate solution was pumped by a peristaltic pump, while the flow rate of N_2 was controlled using a N_2 mass flow indicator/controller. Liquid-solid mass transfer effects were studied by conducting single phase and two phase flow experiments. The liquid superficial velocity varied within the range of $3.9\text{x}10^{-4} – 5.7\text{x}10^{-3}$ m/s. The impact of the gas flow rate on the liquid-solid mass transfer coefficient was studied by scanning the gas velocity within a range that corresponds to gas to liquid superficial velocity ratios, u_{gs}/u_{ls}, from 2.7 up to 23. Concerning the two phase flow experiments, the reactor was re-packed and the active copper particles renewed after each change of liquid flow rate, preventing the alteration of particles' shape and diameter. Samples were analyzed spectrophotometrically using a UV-VIS spectrometer. The two phase flow inside the reactor was also observed through the transparent reactor wall.

The vertical configuration indicated higher single phase liquid-solid mass transfer coefficients in comparison to the spiral configuration, for smaller liquid velocities. The liquid-solid mass transfer coefficient increases with increasing the liquid flow rate, for both the single and two phase flow. For the vertical configuration the introduction of the gas phase resulted in decrease of the liquid-solid mass transfer coefficient. For the lower gas to liquid velocity ratio, the volumetric liquid-solid mass transfer coefficient was calculated about two to three times smaller in comparison to the one phase operation at the same liquid velocity. Furthure increase of the gas velocity leads to small enhancement of the mass transfer coefficient. For the spiral configuration, gas flow marginally affects the mass transfer coefficient and the liquid-solid mass transfer coefficients deviate only ±30 % from the average value calculated at each liquid velocity.

Correlations of the volumetric liquid-solid mass transfer coefficient with liquid and gas superficial velocities were derived from the treatment of the single and two phase experimental results. CFD calculations were performed for the validation of the single phase flow experimental results. Profiles of the effective liquid-solid mass transfer coefficient with the reactor length were also calculated for different liquid velocities.

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GAS-LIQUID TWO-PHASE FLOWS IN SQUARE MINICHANNELS: DIMENSIONLESS ANALYSIS OF FLOW REGIMES AND TAYLOR FLOW PARAMETERS

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Research of the last two decades indicated that flow reactors consisting of hundreds or thousands of parallel channels with active sites at the channel wall show the potential to intensify reaction processes drastically. The high heat and mass transfer rates in such devices may open new process windows in terms of pressure, temperature, and concentration or may allow new chemical transformations as well as an operation in explosive regimes [1]. In order to provide high external mass transfer as well as low backmixing and pressure drop in gas-liquid applications, the reactor should be operated with a segmented flow regime, also known as Taylor flow. This regime occurs generally at superficial gas and liquid velocities below 1 m/s.

Naturally, the transitional velocities of the Taylor regime and its characteristics depend on fluids properties, such as surface tension, viscosity and the wetting characteristics as well as on channel properties, such as hydraulic channel diameter, shape of the channel cross section, and surface roughness. The nature of the gas-liquid feeding influences also the flow boundaries and characteristics of flow regimes. The conducted work in this field was recently reviewed by Shao et al. [2] and Rebrov [3]. The authors compared the attempts to predict the boundaries of the flow regimes of several researchers [4, 5, 6, 7] and concluded that flow maps using superficial gas and liquid velocities show the best agreement for most experimental data. It has to be noted that the most research focused on air/water or nitrogen/water systems, which differ from industrial relevant reaction systems especially in terms of surface tension. This hinders the development of dimensionless maps which are useful to predict flow transitions for a broad range of conditions.

Within this study, adiabatic gas-liquid downflow in a square channel with a hydraulic diameter of 1.0 mm was analyzed at pressures up to 2 MPa by using a high speed camera system. Liquids with surface tensions between 32 and 72 mN/m and dynamic viscosities between 1 and 20 mPa s were employed. Stainless steel needle injectors for the gas with different geometries acted as gas-liquid contactors. For each fluid pairing and injector geometry − in total more than 15 combinations, the impact of the liquid properties and the feeding system on flow regime boundaries as well as on gas bubble and liquid slug lengths was systematically investigated (see Fig. 1).

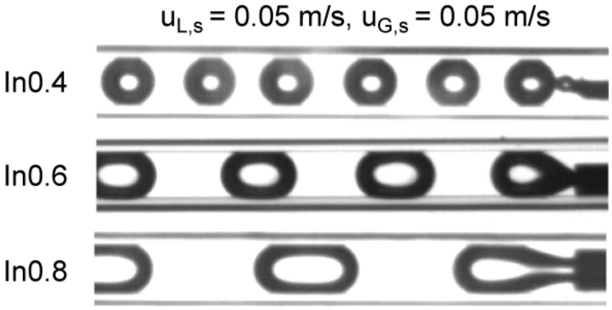

Fig. 1. Visualization of hydrogen-alpha-methyl styrene down flow by using different injectors at a pressure of 2.0 MPa (only photographs in horizontal orientation, flow direction: from right to left)

The enormous data base with more than 1500 entries was used to develop correlations to predict the flow regime boundaries as well as gas bubble and liquid slug length very precisely (coefficient of determination generally above 0.92). These equations contain 7 independent dimensionless groups: the liquid Reynolds number Re_L, the liquid Weber number We_L, the gas-to-liquid ratio u_G/u_L, the dynamic viscosity ratio between gas and liquid μ_G/μ_L, the ratio between the injector and the hydraulic channel diameter d_i/d_{Ch} as well as the dimensionless bubble and slug length (L_B/d_{Ch}, L_S/d_{Ch}) .

This contribution also addresses additional aspects such as bubble forming mechanisms, the impact of gas properties, and methods for feeding multiple channel systems among others.

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STRUCTURED REACTORS OPTIMISATION: ENTROPIC APPROACH

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Optimization of industrial structured catalytic reactors remains a complex problem. It includes prices of raw materials, energy, products and installations, which change rapidly and unpredictably often until a very negotiation stage. Therefore, although process optimisation is regarded usually as engineering domain, it is more connected with economics. The "technical" or "engineering" optimisation, which this work deals with, focus on reactor optimization in terms of fluid velocity, temperature, catalyst loading and reactor structure shape. Recommended fluid velocities or catalyst grains dimensions are given in many textbooks. In the literature, more sophisticated criteria are proposed to find multi-parameter optimisation [1, 4]. Another approach is comparison of reactor length (catalyst mass) and flow resistance [2]. New criteria for reactor evaluation based on the entropy production, formerly proposed by Bejan [3], are introduced and discussed in this paper.

Entropy production is an increase of the system entropy due to irreversible phenomena only (e.g. heat/mass transfer, irreversible reaction, fluid pumping). There is no entropy production at equilibrium. Since industrial processes run far from the equilibrium, they produce entropy. The entropy production can be referred to the process effect, e.g. to the product amount: the lower entropy is generated per kilogram of final product, the better is the process design. Such an approach to the process assessment was firstly developed in energetics (compact heat exchangers evaluation). The entropic approach seems convenient for structured reactors optimisation.

In this study, the entropic criterion is proposed to optimise structured catalytic reactors. The model process assumed is the catalytic combustion of an organic contaminant diluted in air. In the reaction model mass transfer to the catalyst surface is balanced by catalytic reaction. The entropy production is considered due to the following irreversible phenomena, namely mass transfer from bulk gas to catalyst surface and gas pumping through the reactor, i.e. work performed against flow resistance.

The entropy generated due to the irreversible reaction (combustion) is not included as this is almost the same for 1 kg of any contaminant regardless the process conditions, moreover, the combustion entropy is several orders of magnitude higher than that of transfer and friction. Entropic criterion ξ for the catalytic reactors is defined as the reciprocal of the entropy production per 1 kmol of burned contaminant.

The entropic criterion ξ was calculated for various reactor internals (Fig. 1) assuming propane combustion at the Pt catalyst. The optimisation results are shown in Fig. 1. Model equations are not presented due to complexity. The plots point the best solutions for particular process conditions, like monolithic reactor (low and the high Re range) or wire gauzes No. 3 and 4 or short-channels (moderate Re). Low temperature favours the monolith while the higher ones (faster kinetics) – the short-channel structures or wire gauzes No. 3 and 4. The results seem logical when compared with other criteria in [1, 2, 4].

The entropy-based methodology outlined above is able to optimise the reactor structure (pointing the best geometry, specific surface, etc.) as well as the process temperature and fluid velocity for considered reaction kinetics.

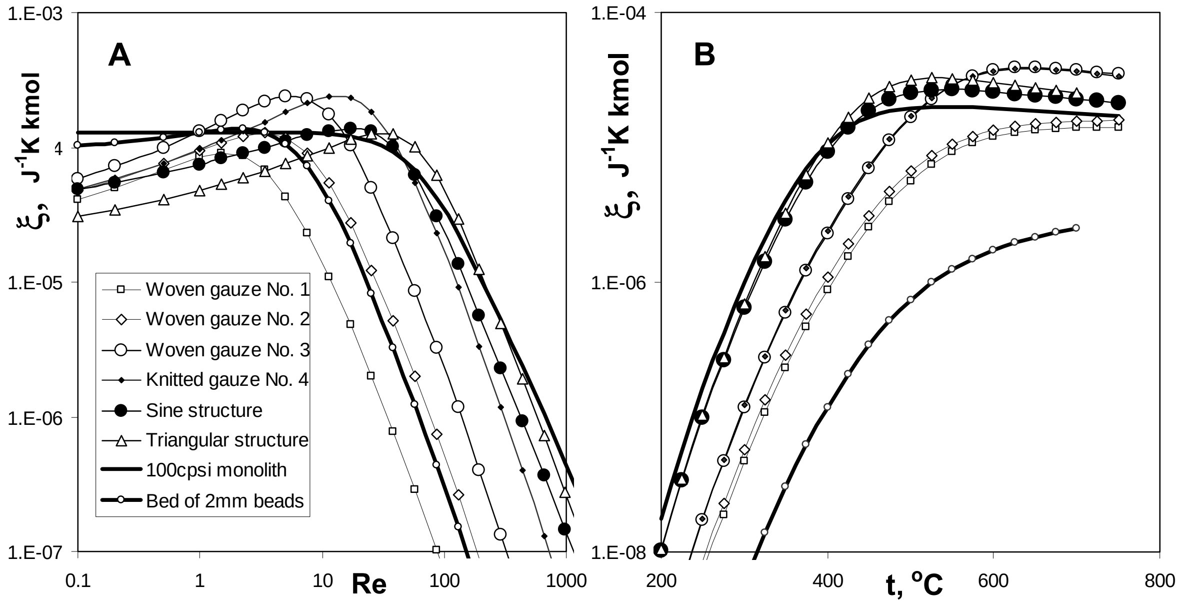

Fig. 1. Efficiency criterion ξ vs.: A – Reynolds number (t = 400 °C); B – process temperature (superficial gas velocity 5 m/s at process temperature, ambient pressure).
Structure description in [1, 2, 4, 5]

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FLOW RESISTANCE AND HEAT TRANSFER IN SHORT CHANNELS OF METALLIC MONOLITHS: EXPERIMENTS VERSUS CFD

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Growing interest in structured catalytic reactors is related to their environmental and industrial applications. Exact description of the mass, heat and momentum transfer is necessary to optimally design a reactor for given catalytic reaction kinetics. This question is of high importance for processes occurring at high temperatures and short contact times, such as fuel combustion and selective hydrocarbons oxidation.

Unique advantages of monolithic reactors determining their development are high specific surface area, low flow resistance and satisfactory transfer rate. Monoliths have long channels, which contribute to the formation of the fully developed laminar flow in the major part of channel. For this reason, the flow resistance is low, however, the heat/mass transfer intensity is low as well. Shortening the monolith channels by dividing them into several slices creates the so-called short-channel structures resulting in enhanced heat/mass transfer coefficients, however, increasing flow resistance per unit channel length.

The experimental procedure was the same as presented in [1-3]. The experimentally studied structures of triangular and sinusoidal channel cross-section had the channel lengths of 5, 10, 15 and 20 mm. Each structure was placed in test reactor perpendicularly to the flow direction. Strong electric current (up to 150 A) heated the structure surface. Several thermocouples measured the temperature of structure surface and flowing air. The Recknagel micromanometer was used to measure the pressure drop. The experimental results are described in [4] in details.

The computational fluid dynamics (CFD) applied ANSYS FLUENT 12 software. CFD was executed in three steps: pre-processing (geometry creation), model setup and post-processing (results examination). The single channels of triangular and sinusoidal cross-section shape, 5 and 15 mm long, were modeled. The continuity, momentum and energy equations were considered. Details are presented in [5].

The comparison of experimental and numerical results of heat transfer and flow resistance indicates that the CFD modeling is able to predict the transport and friction properties of the short-channel structures with a reasonable accuracy of around 30% (see Fig. 1). The main advantage of the short-channel structures is possibility to control the transport and friction properties by changing channel length.

It is worth noting that the drag force exerted by the frontal area of the short-channel structure results in much higher flow resistance component than that due to viscous friction inside the channel (see Fig. 2). Thus, the overall pressure drop of a reactor including numerous structures may be high. However, for fast reactions the short-channel structures may be profitable as the reactor length can be significantly shortened compared to classic, long-channel monolith [1].

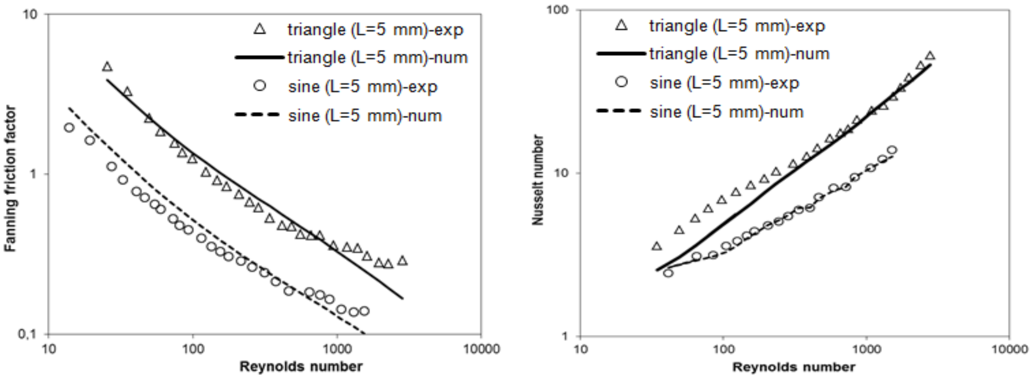

Fig. 1. Flow resistance and heat transfer for the structures: experiments (points) vs. CFD (lines)

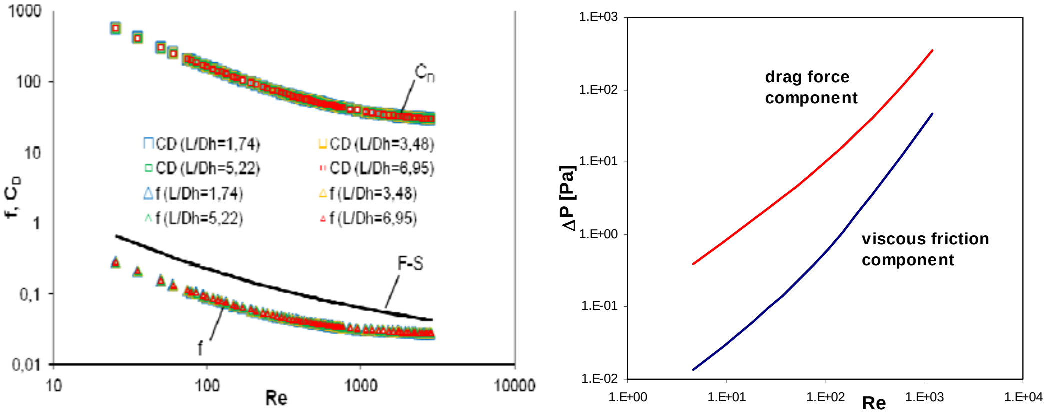

Fig. 2. Viscous friction and drag force comparison in terms of drag coefficient C_D and Fanning friction factor f or pressure drop vs. Reynolds number for the triangular short-channel structure

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OP-I-12

3D SIMULATION OF LAMINAR FLUID FLOW IN OPEN CELLULAR MONOLITHS FOR STRUCTURED CATALYTIC REACTORS

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In recent years, there has been an increasing focus on the use of consolidated structures (such as ceramic foams or monoliths) as novel catalyst supports, over conventional packed bed reactors filled with catalyst particles (unconsolidated structure). Open-cell foams offer several advantages such as enhanced heat and mass transfer and lower pressure drop as compared to conventional packed beds, due to their high porosity and specific surface area. Hence they are a promising alternative to achieve process intensification in chemical industries. However, as of today there is a lack of quantitative understanding of the structural influence of the local foam structure on the flow field and the heat and mass transport (and thus on the reactor performance). Therefore, further research in this direction is required, which forms the motivation for our work.

In this contribution the influence of foam structure on transport properties is investigated using a numerical simulation approach. The aim is to obtain a fundamental insight into the relationship between the local foam structure and the local and global transport characteristics.

In this contribution the influence of foam structure on transport properties is investigated using a numerical simulation approach. The aim is to obtain a fundamental insight into the relationship between the local foam structure and the local and global transport characteristics. For this purpose, the complex foam structure is at first simplified to a regular geometry composed of cylinder struts in 3D Cartesian space (also called as cubic model). In the geometries with same porosity and specific surface area, the strut orientation is varied by tilting the cylinders around an axis in the Cartesian space. A laminar incompressible steady-state flow is simulated in these geometries using finite volume analysis. In addition, the effect of a confining wall is also investigated.

The results obtained showed that the global pressure drop and local velocity and pressure fields as well as the flow tortuosity are highly influenced by the strut orientation. The pressure drop increased with the rotation until a particular tilting angle and then decreased slightly. The flow field shows channeling at smaller tilt angles while becoming more homogeneous at larger angles. This clearly illustrates the need to systematically vary the structural parameters of the foam geometry to understand their influence on the local pore-scale processes and global characteristics. This fundamental understanding can further be extended to complex foam structures in order to obtain generalized correlations for transport properties necessary for design of optimal reactors.

EXPERIMENTAL AND NUMERICAL STUDY ON GAS POCKETS SURROUNDING HORIZONTALLY IMMERSED MEMBRANES IN FLUIDIZED BEDS

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Membrane reactors are considered as one of the most interesting technologies among different process intensification strategies. In these systems, selective reactant feeding and/or selective product separation/purification and chemical reactions take place in the same unit, thereby maximizing both reactant conversion and/or product selectivity and the driving force for the separation. For example, in equilibrium limited reactions such as in fuel reforming or dehydrogenations, the selective hydrogen extraction from the bed shifts the thermodynamic equilibrium towards the products, with which an important improvement in the global efficiency can be accomplished in comparison to traditional processes.

The most studied configuration for membrane reactors are packed bed membrane reactors. However, when integrating state-of-the-art highly permeable membranes in packed bed reactors, the extent of bed-to-wall mass transfer limitations, referred to as concentration polarization, becomes considerable and results in a large increase of the required installed membrane area. Moreover, large temperature gradients may develop, which can be detrimental for the performance of the membrane (too low temperatures resulting in low permeance) or for its stability (hot spots). To circumvent these drawbacks, fluidized bed membrane reactors have been proposed [1].

In fluidized bed membrane reactors mass transfer limitations are strongly reduced due to the continuous movement of the catalyst, in combination with a very small pressure drop and virtually isothermal operation. The immersion of membrane bundles in the fluidized bed modifies its behavior due to compartmentalization of the bed and enhanced bubble breakage [1]. However, the hydrodynamics in these novel reactor concepts are still not fully understood. In this work, a non-invasive coupled PIV-DIA technique is used to study the porosity and solids mass flux profiles simultaneously in a cold-flow, pseudo-2D fluidized bed with horizontally immersed porous filters in the bed. In this set-up, the membrane diameter and its configuration can be varied, as well as the amount of gas added to or extracted from the fluidized bed. Experimental results have demonstrated that dynamic gas pockets are created surrounding the membranes. Gas pockets are free of solids and have a very short lifetime and appear with very high frequencies. The bubble size and bubble velocity distribution along the bed height is clearly modified by their presence. For the evaluation of the bubble-to-emulsion mass transfer rates, these gas pockets need to be selectively removed in the DIA analysis to avoid underestimation of the average bubble size (Figure 1). Moreover, gas pockets may imply an additional resistance to the permeation through the membranes and also for heat exchange (important for submerged heat exchange surfaces). In this work, different configurations have been tested and the extent of gas pockets has been quantified using PIV/DIA. In general, membranes would be preferably installed at the center of the bed. However, for gas extraction, it might induce stagnant zones near the walls. Simulations with a Discrete Particle Model (DPM) using an immersed boundary technique have confirmed numerically these findings. According to these results, future novel concepts should consider the importance of gas pockets on the reactor performance.

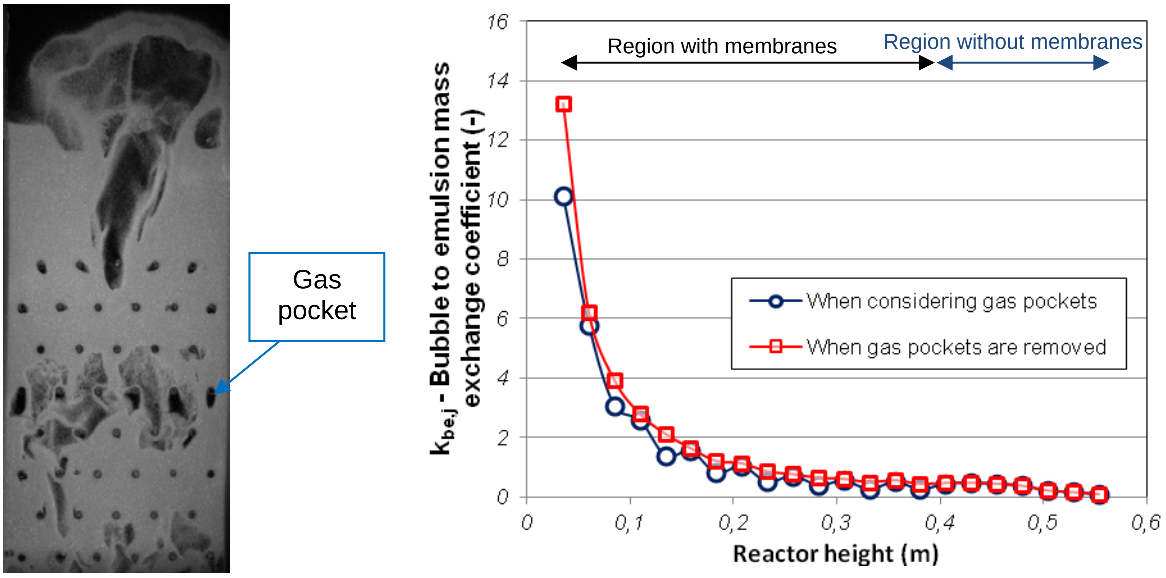

Figure 1. Left: Snapshot with bed configuration and gas pockets; Right: influence of gas pockets

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ORAL PRESENTATIONS

Section II.

Chemical Reaction Engineering and Reactors Design – Novel Approaches, Modeling, Scale-Up, Optimization

Mathematical Simulation and CFD Studies of Chemical Reactors

New Designs of Chemical Reactors (e.g. Structured Reactors,
Membrane Reactors, Microreactors)

Novel Approaches in Chemical Reaction Processes Engineering
(e.g. Microwave/Induction Heated Reactors, Ultrasonic Reactors,
Unsteady-State Forcing and Sorption Enhancement in Chemical Reactors,
Multifunctional Reactors)

BOOSTING THE FISCHER-TROPSCH REACTOR OPERATION BY STRUCTURING

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Introduction

Many catalytic processes, including new routes to process renewables, are multiphase operations, comprising mostly a solid catalyst and reactants and products in the gas and liquid phase. Intrinsic reaction kinetics, mass and heat transport processes in the catalyst, GL and LS phase equilibria, and reactor hydrodynamics are coupled and determine together the overall process.

Catalyst particle size, pore size and liquid phase determine the diffusion time for molecules to reach the active sites. Hydrodynamics in the reactor control the mass and heat transfer rates between gas and liquid and between liquid and solid catalyst and with the surroundings. In an optimal operation these characteristic transport times should be compatible with the intrinsic catalytic reaction time(s) for optimal productivity or selectivity. The increasing use of zeolites with strongly restricted diffusion creates even larger challenges.

Various multiphase reactor types are being used, with the slurry bubble column reactor and the trickle bed reactor as the two extremes of the most common operations. In these systems the reaction steps and transport phenomena are strongly coupled. Alteration of one step in a process to improve it affects the other. In an ideal situation one would like to optimize each step in the process independent of the other.

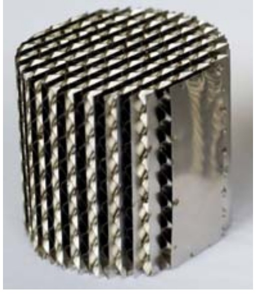

Figure 1. A Closed Cross Flow Structure (CCFS) packing element consists of a stack of corrugated and flat sheets. Channels can be packed with catalyst particles to increase catalyst hold-up

Structured reactors and catalysts

Structured catalysts and reactors offer high precision in catalysis at all relevant scales of the catalytic process, from that of the catalytic species up to that of the reactor [1,2]. As illustration and classical example the highly exothermal Fischer-Tropsch synthesis in a multitubular packed bed reactor is used. The application of cross-flow structures improves by convection the overall heat transfer of the reactor [3-6], allowing higher operating temperatures or larger reactor diameters (by a factor 2-3), considerably reducing the number of parallel reactor tubes.

Considering the mass transport in porous solid catalyst particles, while taking into account the local chain growth probability, the syngas H_2/CO feed ratio should be ~1 for particle sizes used in packed beds, much lower than the stoichiometric ratio. This compensates for the differences in diffusivities, while optimizing the space time yield of C5+ products [7]. This optimal feed ratio is more in-line with that is present in biomass derived syngas, while still being compatible with a high CO selectivity (minimizing CO_2 footprint).

Putting all elements together in a complete reactor model, an extensive optimization of the FTS reactor operation has been carried out, both for a random packed bed (RPB) and a closed-cross flow structure (CCFS) packed with catalyst particles to combine the excellent heat transport properties on the reactor level and the selectivity of smaller catalyst particles [8]. A considerable improvement of reactor performance (C5+ space time yield +95 %) compared to the RPB base case can be reached for highly active catalysts [9].

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HIGHLY CONDUCTIVE STRUCTURED CATALYSTS FOR THE METHANOL SYNTHESIS IN COMPACT MULTITUBULAR REACTORS

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Thanks to the prevailing conductive heat transfer mechanism, independent of gas flow velocities, highly conductive structured catalysts enable the operation of compact multitubular reactors for GTL or BTL applications, in view of the exploitation of any type of feedstock available in limited amounts (e.g. syngas from biomass or stranded/associated gas reservoirs), otherwise unfeasible with conventional packed-bed reactors (*PB*s) [1-3].

We present herein a modelling and experimental study of this concept applied to the methanol synthesis process. Mathematical models of compact (2-meter long) multitubular structured reactors (*SR*) loaded with washcoated copper open-cell foams (*OF*) and honeycomb monoliths (*HM*) for the methanol synthesis were developed using gPROMS® software. A simplified process loop model was also implemented, given the importance of quantifying the recycle stream. The performances of SRs were compared to those of an industrial PB reactor (8 m long tubes). Prototypes of washcoated copper open-cell foams were prepared by slurry-coating of a commercial $Cu/ZnO/Al_2O_3$ powder catalyst and tested in the methanol synthesis in a lab-scale tubular reactor (*ID*=11 mm) at relevant industrial conditions (P = 50 bar, T = 485, 505, 525 K, $GHSV$=15,000 Nl/h/kg$_{cat}$, $M = 6.5$ and $CO/CO_2 = 3.2$). For comparison purposes, original catalyst powder (*CC*) and slurried powder (*SP*, i.e. slurry dried and calcined) were also tested. An additional campaign was performed in the RWGS reaction at atmospheric pressure with a CO-free feed mixture ($H_2/CO_2 = 20$).

By exchanging heat mainly via a conductive mechanism, heat transfer in *SR*s is unaffected by reduction of the tube length at constant fresh feed flowrate to catalyst weight ratio. As a result, simulations demonstrate that the operation of compact multitubular reactors loaded with washcoated *HM* or *OF* is feasible and, contrary to *PB* reactor, hot-spot temperatures and recycle ratios can be kept limited [4] (Fig. 1a).

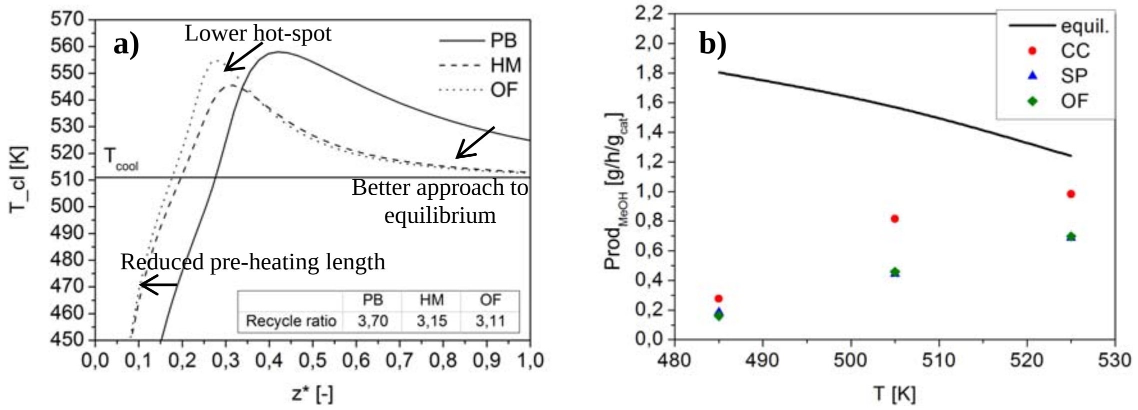

Figure 1. a) Simulated axial T-profiles at centerline and recycle ratio for 2-meter long reactor (ξ = 0.613); b) MeOH productivity as a function of temperature over different catalysts

Vol. catalyst fractions ξ typical of *PB* units (i.e. around 60 %) are not feasible on such structured substrates. However, a proper tuning of the coolant temperature and/or of the catalyst activity (in view of novel enhanced catalyst formulations) can compensate the lower catalyst load, making the operation of *SR*s at ξ down to 30 % still feasible. Increase of the reactor tube diameter is possible, too.

Concerning the experimental study, washcoated copper *OF* (ξ = 14 %) proved active in the MeOH synthesis, but showed a lower MeOH productivity than *CC* (Fig. 1b). *SP* exhibited very similar values to those of *OF*, therefore evidencing the absence of any effect related to the deposition step and identifying the slurry preparation and/or calcination step as responsible for a change in the catalytic performances.

Such a loss of activity was confirmed by a second campaign of RWGS runs at atmospheric pressure, which pointed out a CO_2 conversion decrease from 22 % in the case of *CC* to 15 % in the case of *SP*. The RWGS can therefore be regarded as a representative probe reaction for ranking the intrinsic activity of $Cu/ZnO/Al_2O_3$ methanol catalysts, without requiring operation under high pressures.

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ENHANCING THE HEAT TRANSFER WITHIN CATALYTIC REACTORS BY OPTIMIZATION OF NOVEL STRUCTURED SUPPORTS

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The heat transfer effectiveness within the catalytic reactor is a key factor in highly endothermic (e.g. steam reforming) and exothermic (e.g. phthalic anhydride synthesis) processes. In this regard, structured supports provide the possibility to adjust their properties in an optimal manner, achieving a more precise control over the transport and reaction phenomena taking place in the reactor. Among the family of structured packings, open-cell foams are a novel class of cellular materials attractive as structured catalyst support because of their high geometric surface area, high void-fraction, low pressure drop [1], and high gas/solid heat- and mass-transfer rates. Moreover, the interconnected solid matrix is expected to provide significant conduction inside the solid as additional mechanism for the heat transfer, particularly for supports made of highly conductive bulk materials. However, the knowledge about the influence of the local structure on the flow field and transport properties is still limited in literature. In this project, a detailed study of the fluid flow and the heat transfer on a local scale was performed by means of numerical simulation and lab-scale experiments. The aim is at first to develop a fundamental understanding of the relationship between the local support structure and the heat transfer characteristics. This knowledge was then used to derive correlations for the global transport characteristics of the support that can be applied in macroscopic "engineering" models. Experimental temperature profiles were collected in a lab-scale foam filled pipe and then used to estimate the effective radial and axial thermal conductivities of the foam bed, as well as the wall heat transfer coefficient. As result of the experimental activities, the solid fraction and the bulk conductivity of the solid material were identified as the controlling parameters for the determination of the bed effective conductivity [2]. Furthermore, the insight obtained from the simulations enables to identify optimization parameters for influencing the resulting thermal reactor performance. Starting from these evidences, the role of the solid distribution was investigated in the attempt not only to reproduce the results of the open-cell supports of irregular cell shape, but also to achieve higher thermal performances. On the other hand, experiments with gas-solid systems showed a high temperature gradient confined at the foam-tube wall interface [3] when highly conductive supports (i.e. Al) were used. The wall heat transfer coefficient was found to depend strongly on the fluid conductivity and the pore density. However, in the experimental setup it was not possible directly estimate the coupling between the foam and the reactor tube. For this reason, extensive simulations of conjugated heat transfer were performed to systematically investigate the role of different coupling tolerances between the support and the reactor wall, using a 3D scanned model geometry to validate the simulation results with experiments (see Figure 1). Moreover, to better understand the performance of these structures as novel catalyst supports in large-scale catalytic reactors, data were collected also at high Reynolds numbers and with different fluid phase thermal properties, overcoming the limitations of the experimental facilities. Further results will be reported concerning the correlation of the heat transfer parameters with foam properties and flow conditions and the related implications for the intensification of catalytic processes, as well as a comparison with the conventional random packing performance.

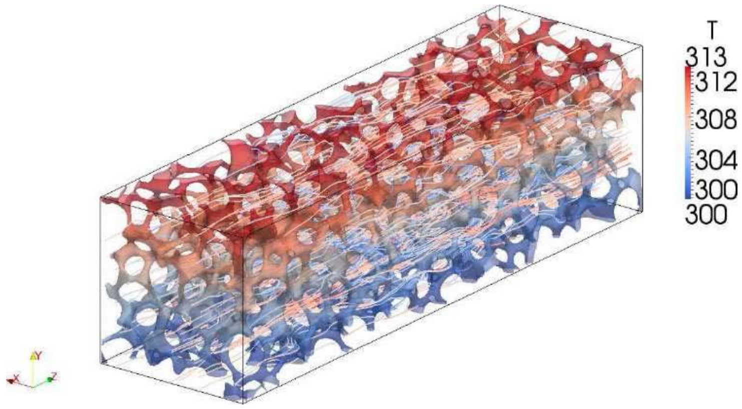

Figure 1: Simulated solid temperature (color scale) and fluid velocity (stream lines) field inside an open-cell solid foam

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SONOCHEMICAL REACTORS IN ENVIRONMENTAL APPLICATIONS

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Ultrasounds has a wide range of active applications spreading in solid, liquid and gaseous mediums, like: cleaning, degassing, quality control, sonochemistry disintegration, accelerate and optimize the machining, diffusion and electrochemical processes, embedded in new methods and technologies for preventing, reducing and removing of existing pollution.

This review covers summary classification, general aspects and main type of installations: gas bubbling and UV hybrid with specific configurations for chemical and electrochemical sonoreactors used with high impact of environmental protection: treatments of wastewater based on examples and enumerations and clean automotive industry using PEM fuel cells.

In order to introduce ultrasounds in a system is necessary to use instrumentation or installation with specific configurations named sonochemical reactors and usually for waste water treatment can have special and complex designs for ultrasonic bath and horn. A significant amount of work has been published concerning the sonochemical effects on both organic and inorganic chemical reactions. The ultrasound irradiation effects on the chemical reactions are: (a) ultrasound initiates the reaction, (b) ultrasound accelerates the rate of the reaction, (c) ultrasound changes the reaction pathway, and (d) ultrasound has little or no effect on the reaction. The majority of effects are included in (b) category.

The classification of sonoreactors depends on many elements of comparison such as functions, design, utilizations, etc. On basis of the application scale, they can be the laboratory chemical and electrochemical sonoreactors and industrial ones. The field of utilization includes water treatment, emulsions, washing, atomization, extraction, mixture or bonding processes, etc. Ultrasound bath can have one or multiple sources of ultrasound, which can produce the same or different frequencies. The wastewater treatment systems can work in continuous or discontinuous ways, and can be coupled with other processes such as electrochemical, UV irradiation, O_3, and Fenton reactions. The irradiation can be direct or indirect.

The sonoreactors used for bonding or welding composite materials were widely spread in recent years. This process is based on ultrasonic wave propagation effects in the joint area, acoustic cavitation related phenomena, the caloric effect of the movement of the two surfaces relative to the ultrasonic frequency and the effect of chemical polymerization in contact area and can be applied to obtain the bipolar fuel cell plates.

Today almost chemical and electrochemical sonoreactors use piezoelectric ultrasonic transducers that can convert electricity in sound with high frequency, but sometimes ultrasound can be emitted by mechanical devices (Galton's pipe and sirens) or by magnetostrictive transducers, also.

The approach of sonochemical installations and reactors can be generally classified as a technological rather than a scientific problem. Science and technology are like two steps closely related, not alternative. After being based on scientific stage, presented into the first paragraphs, technical progress of sonochemical reactors follow them. Now it is the time to treat these technical parts in the field of sonochemical reactions and installations with scientific tools in order to achieve new elements of progress. This consists of a summary classification and general aspects of the sonochemical reactors. There are presented main type of sonochemical installations and reactors applicable to environment systems in scientific literature: gas bubbling installation, UV hybrid or sono-electro-chemical systems, installation with specific configurations and large-scale sonochemical reactors.

Acknowledgements

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REACTOR DEVELOPMENT FOR UTILIZATION OF CO_2: CASE STUDY OF PRODUCING CYCLIC CARBONATES

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CyclicCO$_2$R is an EU FP7 project which aims to develop a continuous process that converts CO_2 and bio-based renewables into high value-added products in particular, cyclic carbonates. The goal of the project is to provide a showcase that inspires industry to further develop technologies utilising CO_2 as a sustainable raw material. Two routes are considered for the production of glycerol carbonate. The first route, the *direct route* [1], is the direct synthesis of glycerol carbonate from glycerol, while the second route, the *indirect route* [2], is the production of glycerol carbonate (and other cyclic carbonates) through the corresponding epoxides. The conventional and proposed reaction schemes are depicted in Figure 1.

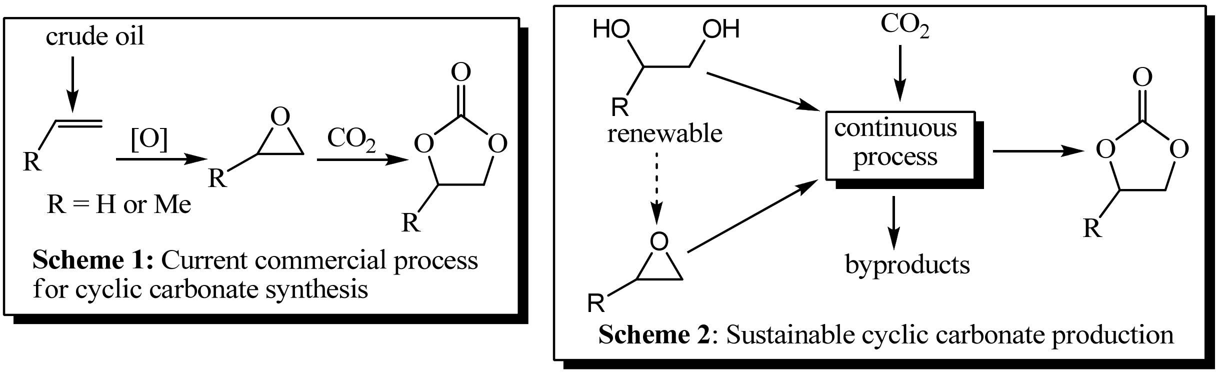

Figure 1. Schematic of cyclic carbonate production

One of the main tasks in the project is to design a process to ensure a net reduction in CO_2 emissions relative to the conventional route. In the first step, several reactor types, such as fixed bed (axial flow, trickle flow, *etc*.), slurry reactors (stirred tank, jet-loop, *etc*.), membrane reactors, *etc*., were identified. Subsequently, a reactor ranking exercise was carried out in order to select the best reactor type for both the direct and the indirect routes. Several important factors such as suitability for high pressure, mixing characteristics, operation mode (continuous), investment and operation costs, commercial availability, etc. were identified and divided into two main criteria: fundamental and applied criteria. Each sub-criteria was given a weighting factor considering the application i.e. (direct or the indirect route). The different reactor types were ranked based on this methodology and this resulted in the selection of a trickle bed reactor and a fixed bed reactor for the direct and indirect route, respectively. The methodology and results from this exercise will be further explained in the presentation.

A model is being developed for each reactor type in order to perform a preliminary design of the reactors. Subsequently, reactor prototypes will be tested at lab scale to validate the model and assess the performance of the catalysts. Process development efforts are aimed towards integrating the reaction with separation and downstream processing in order to obtain high purity cyclic carbonates. One of the key aspects for the direct route is the removal of water (reaction by-product) in order to achieve high conversion of the substrate and make the process viable. The results from the modeling, experimental activities and process design will presented at the conference.

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OP-II-6

HYDROGENATION OF α-METHYLSTYRENE IN AN INCLINED ROTATING FIXED BED REACTOR

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Trickle bed reactors are widespread in the chemical industry for the implementation of heterogeneous catalytic processes, especially for the production of bulk chemicals. Nevertheless, the reactor performance may be limited by liquid maldistribution as well as by poor mass and heat transfer rates. Furthermore, the rather simple reactor design and operation is accompanied by limited degrees of freedom for manipulation of local conditions to enhance the reactor performance.

Dynamic operation strategies, like the periodic inlet flow rate modulation, have been proposed for process intensification of trickle bed reactors [1]. These strategies have been proven to result in increased space-time-yields at lab-scale, however, their positive effects are strongly dampened with increasing reactor length. The inclined rotating fixed bed reactor is an alternative reactor concept, that aims to transform the temporal periodic operation into a spatial periodic one, which is maintained for the whole length of the reactor. The inclination of the reactor, with the catalyst fixed between retaining grates, results in a phase separation, whereas the superimposed slow rotation ensures a periodic wetting and draining of the catalyst and will therefore enhance the access of the gas phase to the active sites (see Figure 1).

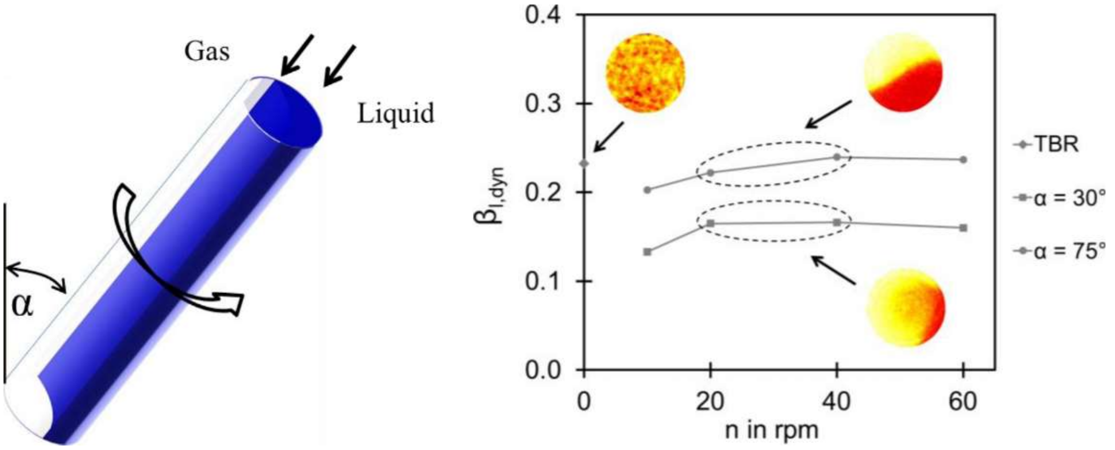

Figure 1: Left: Schematic drawing of the inclined rotating fixed bed reactor; **Right:** Dynamic liquid saturation $\beta_{L,dyn}$ and visualization of flow regimes at different inclination angles a and rotational speeds n at u_L = 0.01 m/s & u_G = 0.05 m/s (liquid: cumene, gas: air, packing: 4 mm γ-Al_2O_3 spheres)

By adjustment of the reactor inclination and rotation, the performance of the reactor can be adapted to a given reaction system and a specific process (e. g. fast or slow kinetics, high or low viscous liquid etc.) to optimize the local conditions with respect to flow regime and subsequently to mass and heat transfer performance. For the evaluation of the new reactor concept, the space-time-yield of the hydrogenation of α-methylstyrene to cumene ($C_9H_{10} + H_2 \rightarrow C_9H_{12}$) is investigated in the trickle bed reactor as well as in the inclined rotating fixed bed reactor. The reaction already exhibits mass transfer limititations of the gas phase at moderate conditions, which allows for attributing changes in the space-time-yield directly to the operational conditions [2].

The reactor (d_R = 0.1 m, L_R = 1.6 m) is operated like a differential loop reactor with a short layer of the palladium egg-shell catalyst (Pd/γ-Al_2O_3, d_P = 4 mm, w = 0,1 wt-% Pd) placed in the middle of the otherwise inert fixed bed. The reaction studies are performed at varying pressure (p = 1 and 6 bar) and temperature (θ = 25 °C and 40 °C) at isothermal conditions. The rotational speed and the inclination angle are adjusted to identify optimal hydrodynamic conditions regarding the space-time-yield. The results of the reaction studies are discussed with respect to the prevailing flow regimes obtained by additional tomographic imaging studies for the same setup and operating conditions.

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BIOCATALYTIC MEMBRANE REACTORS: STRATEGIES TO PRESERVE ENZYME LIFE TIME BY CONTROLLING MEMBRANE FOULING

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Biocatalytic membrane reactors are extremely selective and efficient systems. They can promote significant progress in terms of process intensification strategy. Nevertheless, their implementation at productive scale is far beyond their potentialities. The main bottleneck for this technology is represented by the enzyme stability during membrane cleaning procedures. In fact, fouling phenomena occur during operation and in order to keep high performing process cleaning strategies and maintenance procedures are needed. Usually, chemical cleaning methods are applied. These cleaning will also destroy the enzyme loaded to/within the membrane. Recently, we have promoted new strategies for implementing self-cleaning membrane properties and reversible immobilization of enzymes in order to prevent chemical cleaning or remove the enzyme when the membrane needs a severe cleaning process. For example, the self cleaning properties have been created by attaching enzymes on the membrane surface able to degrade the foulant molecules as they deposit on it. Reversible enzyme immobilization has been obtained by the use of magnetic nanoparticles that can be easily detached from the membrane by acting on magnetic intensities. Proof of concepts for the application of biocatalytic membrane reactors in the treatment of streams containing pectines will be illustrated. Furthermore, the unique feature of biocatalytic membrane reactors for the production and simultaneous separation and stabilization of intermediate reaction products will be presented.

CFD MODELING OF COMPACT METHANOL REFORMER

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Mini-scale reactors for hydrogen production found a wide application for various technologies and development of one is staying the focal problem for chemical engineering [1]. The one of advanced research is an applying of methanol as a primary product to produce the hydrogen and a fuel to provide temperature control.

This study presents the numerical simulation on the performance of compact hydrogen generator coupled with liquid methanol-water vaporizer, methanol-steam reformer, and methanol-air catalytic combustor.

The generator consists of two parallel reactors similar tubular ones. Both reactors have the mutual tube space like the honeycomb with channels of circular cross section. To provide the required heat transfer between the reactors tube space is made of brass. The first reactor plays the role of a methanol reformer and its channels filled with $Cu_kCe_nAl_m$ – catalyst. The second is the methanol-air combustor and its channels filled with Pt/Al_2O_3 – catalyst. Both reactors have separate input and output ducts and the opposite direction of reaction flow through their own channels.

Three overall reactions take place in the methanol reformer [2].

Steam reforming: $CH_3OH + H_2O \Leftrightarrow 3H_2 + CO_2$.

Decomposition: $CH_3OH \Leftrightarrow 2H_2 + CO$.

Water gas shift: $CO + H_2O \Leftrightarrow H_2 + CO_2$.

The parameters of semi-empirical kinetic models for the overall reactions were taken from [3, 4, 5]. In addition the evaporation of water and methanol takes place in input ducts. To simulate the heat balance were used nominal reactions of evaporation.

$$CH_3OH\ (liquid) \Leftrightarrow CH_3OH\ (vapor);$$

$$H_2O\ (liquid) \Leftrightarrow H_2O\ (vapor).$$

Methanol catalytic combustion on Pt/Al_2O_3 occurs in the second part of generator and is expressed by $CH_3OH + 1.5O_2 \Leftrightarrow 2H_20 + CO_2$.

The reaction parameters were taken from [6].

Using CFD simulation the basic properties of methanol reformer were determined, including the velocity, temperature and mass fraction of components, methanol conversion and output of hydrogen. The heat loss from the generator to the environment has also been defined.

Temperature distribution for cross-section of compact hydrogen generator is shown on Figure 1. The main parts of the hydrogen generator: methanol reformer, methanol-air combustor, methanol-water evaporator and inlet/outlet channels are also shown on figure.

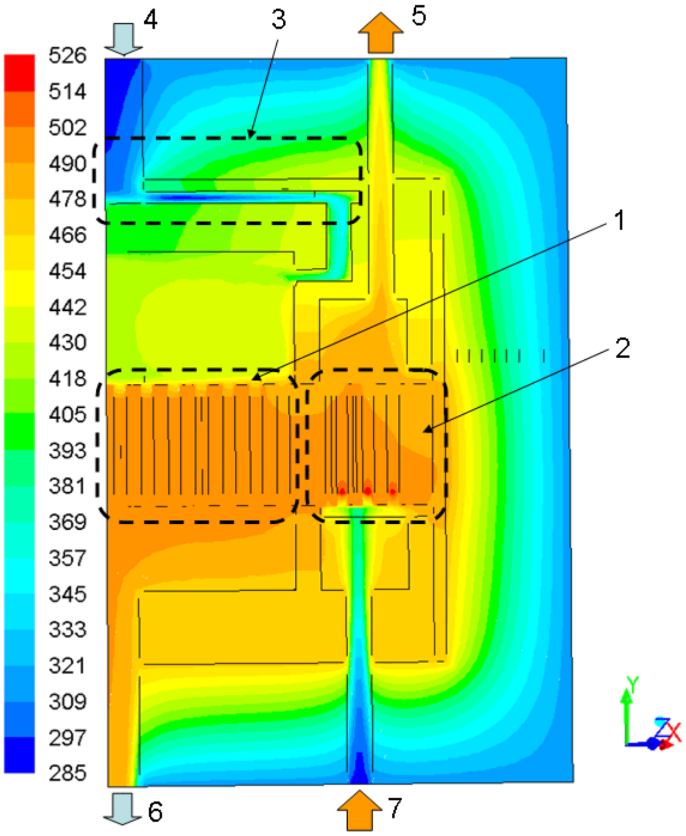

Fig. 1. Temperature distribution for cross-section of compact hydrogen generator. Value of temperature is shown by color in accordance with the scale on the left.
1 – methanol reformer,
2 – methanol-air combustor,
3 – methanol-water evaporator,
4,7 – inlets,
5,6 – outlets channels.

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CFD-BASED DESIGN OF 3D PYROLYSIS REACTORS: RANS vs. LES

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Pyrolysis is the main process for the production of many valuable organic building block chemicals such as ethylene, propylene and vinyl chloride. The gas phase reactions are accompanied by secondary reactions leading to the formation of a carbonaceous coke layer on the inner walls of the reactor tubes [1]. This layer leads to an increased pressure drop over the reactor causing a loss in selectivity. Additionally, the insulating effect of the layer forces a higher furnace firing rate and higher tube metal temperatures to maintain the same conversion. In industrial plants regular decoking procedures are hence inevitable, having a detrimental effect on the overall economics.

Hence, the design of novel reactor geometries exhibiting reduced metal temperatures with the aim of increasing run lengths has received quite some attention. A number of studies have already been performed in order to determine not only the hydrodynamic effects but also the influence on product distribution induced by these designs [2]. A main drawback of the classical Reynolds-Averaged Navier-Stokes (RANS) equations however, is the need for an a-priori understanding of the flow features and an extensive dataset for experimental validation of the simulation results.

The current contribution will discuss the use of wall-resolved large eddy simulation (WRLES) in a streamwise periodic pipe section. The concept of periodically fully developed flow was first introduced by Patankar et al. [3] and has since been widely used to investigate the thermal characteristics in a number of heat transfer applications. By reducing the computational domain to this periodic section, large eddy simulation becomes a viable alternative at Reynolds number approximating the values prevalent in industrial reactors. As all the large energy-containing turbulence scales are resolved, the applied methods can be considered insensitive to the geometry and hence offer an excellent tool for the evaluation of novel designs.

The methodology was validated by comparison with DNS results for turbulent heat transfer in pipes [4] and experimental results in ribbed channels and spirally corrugated pipes [5], see e.g. Fig.1. The results of the present study were obtained using the open-source CFD package OpenFOAM. Comparison with traditional RANS turbulence modeling shows a clear improvement in the ability to capture the flow features and a more accurate prediction of the global friction factors and Nusselt numbers. The contribution will also discuss the results obtained using this method for other state-of-the-art reactor designs, such as the x-MERT, Swirl Flow Tube and a variety of internally finned tubes.

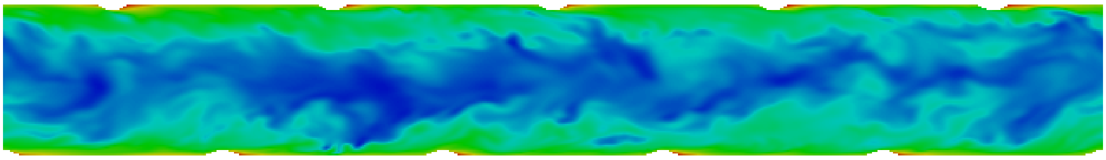

Figure 1: Streamwise periodic temperature field for a spirally corrugated pipe

Although the periodic domain does not allow an evaluation of the influence on product yields, radial concentration gradients were obtained by assuming local scale-similarity for the species. These radial concentration and temperature profiles are then used in the calculation of coking rates on the tube inner surface. The presented results confirm the potential of three-dimensional reactor designs for reduced coke formation although the influence on product yields induced by these designs also remains an important consideration for application in an industrial setting.

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Acknowledgements

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FIXED BED ADSORPTIVE REACTOR FOR BUTYL ACRYLATE SYNTHESIS

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Butyl Acrylate (BAc) is usually produced by an equilibrium limited reaction between acrylic acid and n-butanol, having water as a by-product. This reaction presents a very slow kinetics; many studies aim to improve the conventional production process in terms of cost and environmental issues, which is based on a homogeneous catalyzed multistage process using two reactors and three distillation columns for the recovery of the reactants and the purification of the desired product [1].

In the last years, process intensification is a topic that has been intensively explored in the chemical engineering field, because it leads to smaller, cleaner and more energy-efficient technologies than conventional ones [2]. Multifunctional reactors are an example of process intensification, where reaction and separation steps are combined into single equipment, which allows overtake the equilibrium conversion limitation by continuously removing one of the products. Among the multifunctional reactors, some of the most interesting are chromatographic reactors and reactive distillation. Reactive distillation was already assessed for the BAc production [3, 4]. However, the BAc synthesis involves a reaction with high risk of polymerization, which is further promoted by the high temperatures used in this technology. An actractive solution might be the use of reactive adsorptive technologies since they usually work at moderate temperatures, as is the case of the Simulated Moving Bed Reactor (SMBR), which was already successfully applied on the production of other esters, for instance, ethyl lactate [5].

The aim of this work is to study the synthesis of BAc in a fixed-bed adsorptive reactor packed with Amberlyst-15 resin in order to determine the feasibility of sorption enhanced reaction technologies for the sustainable BAc production.Thereby, an adsorption study was carried out in a fixed bed column with non-reactive pairs, ensuring the absence of reaction, at different temperatures, 323 K and 363 K. The multicomponent adsorption parameters were determined for the multicomponent Langmuir isotherm that was considered to describe the adsorption equilibrium.

Furthermore, a fixed bed adsorptive reactor experiment was performed at 363 K (see Figure 1) and it was compared with predicted values from a mathematical model which considers isothermal operation, axial dispersion, constant bed volume and packing (porosity), internal and external mass-transfer resistances, velocity variations due to changes in the bulk composition and the extended Langmuir Isotherm model. It was achieved 85 % of limiting reactant conversion, which is 29 % higher than the equilibrium conversion attained on batch conditions (60 %) at the same temperature and initial molar ratio of reactants. These results lead us to conclude that sorption enhanced reaction technologies, as the SMBR, are very promising for BAc synthesis.

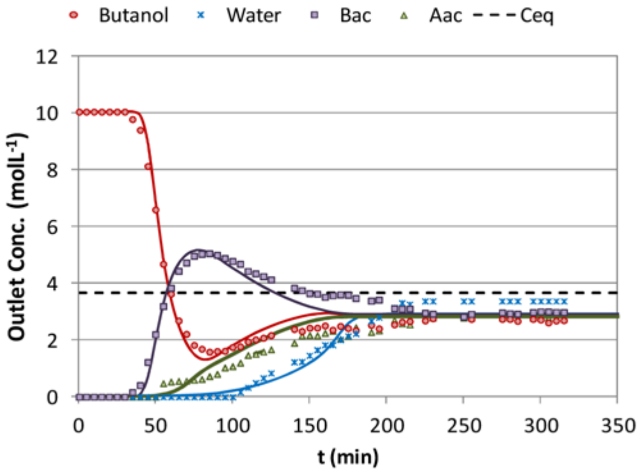

Figure 1. Concentration histories of the fixed bed adsorptive reactor
(T = 363 K; flow rate of 1 mL/min; C_{Feed} = 5.76 molL^{-1})
(Points represent the experimental values and the lines represent the simulated results, the dashed line represents the concentration of BAc at equilibrium on batch conditions)

Acknowledgements

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OP-II-11

COMPARISON OF ADVANCED PROCESSES BASED ON CHEMICAL LOOPING AND MEMBRANE SEPARATION FULLY INTEGRATED IN AN H_2 PRODUCTION PLANT WITH CO_2 CAPTURE

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Mitigation of anthropogenic greenhouse gases emissions is considered to be one of the main challenges of society for the mid-long term to combat climate change. H_2 production plants from natural gas are mainly based on steam methane reforming (SMR) or autothermal reforming (ATR) and water gas shift (WGS) reactors that convert the fuel into an H_2-rich syngas, which is subsequently separated in a pressure swing adsorption unit for H_2 recovery [1]. Novel processes have been recently proposed that lead to improved process efficiencies due to reduced separation energy penalties, as for example with membrane reactors with H_2 perm-selective membranes [2]. In recent years, ATR reactors have been proposed integrated with chemical looping [3,4] to avoid syngas dilution with N_2 in case air-based ATR, or cryogenic air separation units (ASU) for O_2-based ATR.

The present work addresses the thermodynamic analysis of a large scale hydrogen production plant with near zero CO_2 emissions that is based on membrane-assisted chemical looping reforming process (MA-CLR) introduced in our previous work [5]. The process is based on H_2-selective separation through Pd-based membranes directly immersed in the fuel reactor of a chemical looping reforming system (Fig. 1): the natural gas is converted in the fuel reactor where the hot oxygen carrier (i.e. Ni-based material) is first reduced transferring oxygen from the solid to the gas phase and then it acts as catalyst for the steam reforming reaction. The fuel conversion is almost complete because the H_2 extraction shifts the thermodynamic equilibrium towards the products and is thus not limited by the operating temperature. At the fuel reactor outlet a CO_2-rich stream is produced, that is compressed and sent for final treating and further sequestration (e.g. geological storage). The reduced oxygen carrier from the fuel reactor is then oxidized and heated up in the air reactor. The system is designed as two interconnected fluidized bed reactors operated at pressurized conditions and moderate temperature (600-700 °C).

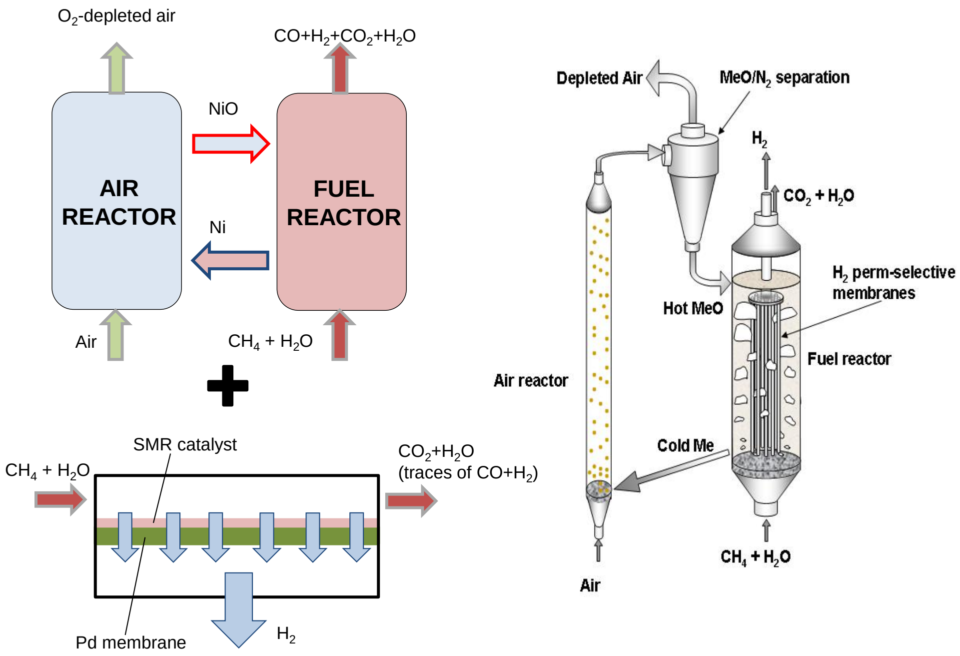

Figure 1: MA-CLR concept [5]

The system is designed to achieve a full integration with the steam cycle and the other units of the plant in order to improve the carbon and energy efficiency of the H_2 production process. A sensitivity analysis on operating pressure, solids circulation rate between the air and fuel reactors, the feed steam-to-carbon ratio, membrane surface area and the main parameters of the integrated units has been carried out in order to optimize the plant layout. The mass and energy balances of the plant are presented in detail and the plant performances are compared with reference technologies and the most promising process based on membrane reactors.

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OP-II-12

SORPTION-ENHANCED STEAM-METHANE REFORMING WITH SIMULTANEOUS SEQUESTRATION OF CO_2 ON FLY ASHES: MODELLING OF REACTORS OF DIFFERENT TYPE

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Integration of reversible chemical reactions with *in-situ* sorption of the one product helps to improve the reactant conversion. Simultaneously, due to products separation, a purity of the demanded product in the post-reaction mixture can be also augmented. In the steam-methane reforming (SMR) process, the *in-situ* sorption of produced CO_2 enables an almost total conversion of methane and high purity hydrogen can be also obtained, even in a single-step reactor. The main problem in practical application of this integrated process is a need of cyclic regeneration of the CO_2 sorbent. Our preliminary studies on the kinetics of CO_2 sorption on fly ashes originated from power plants indicate that fly ashes can be utilized as an efficient and cheap sorbent for the considered hydrogen production process [1]. Further, fly ashes fully or partially saturated with CO_2 can be utilized in a building industry or used directly in road construction or in mines. Therefore, by using fly ashes an economic efficiency of the hydrogen production can be significantly improved, due to elimination of the sorbent regeneration step. Additionally, all CO_2 emitted during the hydrogen production process is sequestrated. So, application of fly ashes helps to reduce emission of CO_2 and simplifies the process, so in consequence improves economical and ecological factors of the hydrogen production.

In this study, the mathematical models for three types of reactors: the gradient-less reactor (GLR), fixed bed tubular reactor (FBTR) and gas-solid-solid trickle bed reactor (GSSTBR) have been formulated. For a preliminary comparison of the performance of three chosen reactors types, the following simplifications have been introduced into all elaborated models:

- isothermal and isobaric operating conditions,
- temperature of gases at the reactor inlet equal to the operating temperature,
- negligible heat and mass transfer resistances.

For all reactor types the gradient-less and the tubular fixed bed reactors the active bed consists of the fixed catalyst and sorbent particles mixture. For the gas-solid-solid trickle bed reactor the fixed bed consists of the catalyst grains, while the stream of fine sorbent particles flows downwardly and co-currently with the gas stream.

A set of model equations have been formulated for each considered reactor type. Then solving these models an influence of the operating conditions on the performance of each considered reactor can be investigated, changing from run to run the following conditions: – the operating pressure, – the reactor temperature, – the excess of water vapor in the inlet gas stream, – the space time – i.e. the residence time of the reactants in the reactor.

Also an influence of the relative content of the catalyst and sorbent particles in the reactor bed (gradient-less and tubular fixed bed reactors) as well as an influence of the mutual flow-rates of the sorbent particles and the gas mixture (gas-solid-solid trickle bed reactor) can be investigated, respectively. To keep for both cases really the same operating conditions, the simulations of the conventional process have been carried out just “replacing” the sorbent by the inert particles of the same size and quantity.

For each reactor type, as a result of performed simulations, the molar compositions of gas stream at the reactor outlet have been obtained and analysed. Purity of the obtained hydrogen (estimated on the dry basis) as well as total hydrogen productivity can be also monitored to quantify a performance of each reactor type. To estimate quantitatively a degree of process improvement, resulted due to application of the CO_2 sorbent, the methane conversion enhancement factor has been defined. Additionally, to estimate an efficiency of fly ashes utilization, the CO_2 uptake coefficient and the efficiency parameter have been estimated.

On the basis of the obtained results a performance of different tape reactors has been compared and discussed.

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WET PEROXIDE OXIDATION OVER Cu-ZSM-5 AND Fe-ZSM-5 CATALYSTS. KINETICS STUDY IN BATCH AND FLOW REACTORS

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Catalytic wet peroxide oxidation (CWPO) is ecologically attractive catalytic process aimed to deep oxidation of toxic weakly biodegradable organics [1,2]. Fe-ZSM-5 zeolites are among most promising catalysts [2-5]. Much less information on the catalytic properties of Cu-containing zeolites is available [2,6]. In our previous works the most active and stable to leaching Fe-ZSM-5 and Cu-ZSM-5 catalysts were chosen owing to systematic study of the broad batch of zeolites in CWPO of organic pollutants [7,8]. This study is dedicated to CWPO kinetics of model organic substrates over the best Fe-ZSM-5 and Cu-ZSM-5 catalysts.

The catalyst samples were prepared by methods: ion exchange from the protonic form of ZSM-5 (Cu- ZSM-5) and template synthesis (Fe-ZSM-5). The kinetic studies were performed over powder catalysts using a batch reactor with variation of substrate type (formic acid and phenol), substrate initial concentration (0.050-0.5 M for formic acid and 0.007-0.03 M for phenol), H_2O_2 concentration (0.1-1 M), catalyst charge (0.38-6 g/L) and temperature (30-70 °C).

The observed reaction rate order in all cases was close to unit in respect to catalyst concentration and below unit in respect to H_2O_2 concentration. Reaction rate order for formic acid was also below 1, while the same order for phenol appeared to be negative, revealing the strong inhibition of the reaction by phenol and products of its partial oxidation. The best fit for formic acid oxidation was provided by kinetic equation $W_{FA} = k_0\left(-E/RT\right)C_{FA}C_{CAT}\Big/\left(1+k_2C_{FA}/C_{H_2O_2}\right)$. More complicated kinetic model, accounting for formation of intermediate oxidation products (e.g. hydroquinone and pyrocathehol) and strong reaction inhibition was proposed for CWPO of phenol:

$$W_{Ph} = k_1\exp\left(-\frac{E_1}{RT}\right)\frac{C_{Ph}C_{cat}C_{H_2O_2}}{1+k_2C_{H_2O_2}+k_3\left(C_{Ph}+C_{IP}\right)^2} \qquad W_{IP} = k_4\exp\left(-\frac{E_2}{RT}\right)\frac{C_{IP}C_{cat}C_{H_2O_2}}{1+k_5C_{H_2O_2}+k_6\left(C_{Ph}+C_{IP}\right)^2}$$

In both cases, the proposed model provided good description of the experimental data (average substrate concentration prediction error not exceeding 0.4 mmol/l).

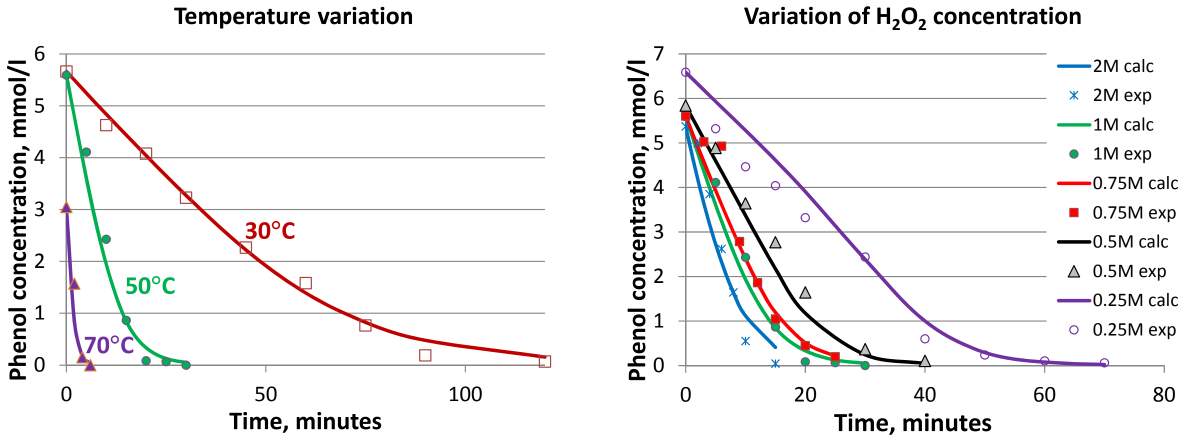

Fig. 1. Example of the comparison between experimental (points) and kinetic model (lines) data in phenol CWPO

The contribution of diffusion processes into overall kinetics was estimated from flow experiments for CWPO of phenol over Cu-containing catalysts of different shape (cylinders, spheres, trilobes and honeycombs) and size. The experiments were carried out in specially designed flow reactor at the constant concentration of substrate (0.007 M) and oxidant (1 M), amount of catalyst (20 g), temperature (50 °C) and pH = 3. Flow rate was varied from 5 to 20 ml/min. Reactor model was based on plug flow approximation. Account of the internal mass transfer limitation was performed on the base of Thiele modulus approach [10] while external mass transfer coefficients were calculated from known empiric equations [11]. Adequate description of experiments was achieved. The proposed approach can be used to scale up the CWPO process for abatement of organic pollutants in wastewater.

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OP-II-14

ATMOSPHERIC PLASMA JET FOR METHYLENE BLUE DEGRADATION

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Contamination of water bodies is one of the important issues and needs immediate attention. Dyes are chemical substances commonly used in textile, pharmaceutical, and food industries [1]. These compounds are toxic and may be carcinogenic and mutagenic [2]. Moreover, they are very persistent in the environment due to their resistance to biological degradation. An ideal waste treatment process should completely mineralize all the toxic species present in the waste water without leaving any hazardous rests [3]. Among the various physico-chemical technologies for waste water treatment, advanced oxidation processes (AOPs) like photocatalytic, sonolysis, electrolysis, etc have specific advantages, where mineralization of the pollutant is expected against mere removal by conventional treatments like adsorption, etc. In particular, nonthermal plasma (NTP) based AOPs is of particular interest due to the operation under ambient conditions [1-3]. Plasmas are partially ionized gases that contain chemically active species (e.g., free radicals, excited state atoms/molecules, ions, UV radiation, electrons and photons) [2].

During the present study, plasma was created by using homemade atmospheric pressure dielectric barrier plasma jet. The discharge reactor consists of a discharge chamber and vertically oriented cylindrical stainless steel rod acted as the high voltage electrode, whereas, a stainless steel mesh placed below the reaction vessel acts as the ground electrode (Fig. 1). Electrical parameters have been measured by a Tektronix, TDS 2014B

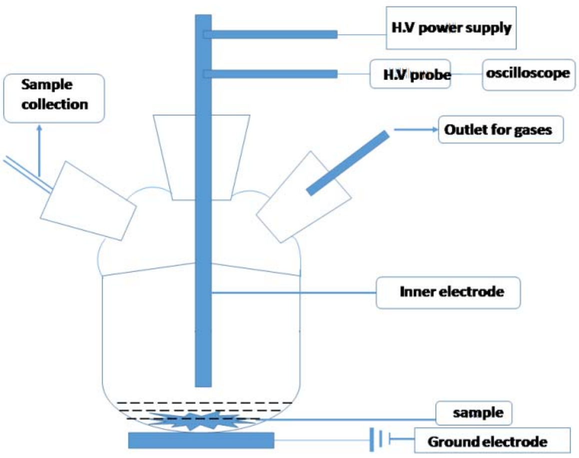

Fig. 1. Schematic picture of the experimental setup

oscilloscope using Agilent 34136A high voltage probe (1:1000). Mineralization of the dye was confirmed by a total organic carbon analyzer.

The decreasing concentration of MB was followed by measuring the absorption on a UV T90+ spectrophotometer operated from 800 nm to 300 nm corresponding spectra shown in Fig. 2. Effects of applied voltage, initial concentration, gas flow rate, kinetics and change in pH on bubbling various gases were studied. It has been observed that dye degradation followed first order kinetics. Typical results indicated that ozone formation and subsequent addition of suitable catalytic material (Al_2O_3, Fe_2O_3/CeO_2, $Fe_2O_3/$ Al_2O_3) improved the degradation and mineralization efficiency, possibly due to hydroxyl radical formation. Formation of hydrogen perodixde was confirmed and addition of ferrous salt also improved the performance.

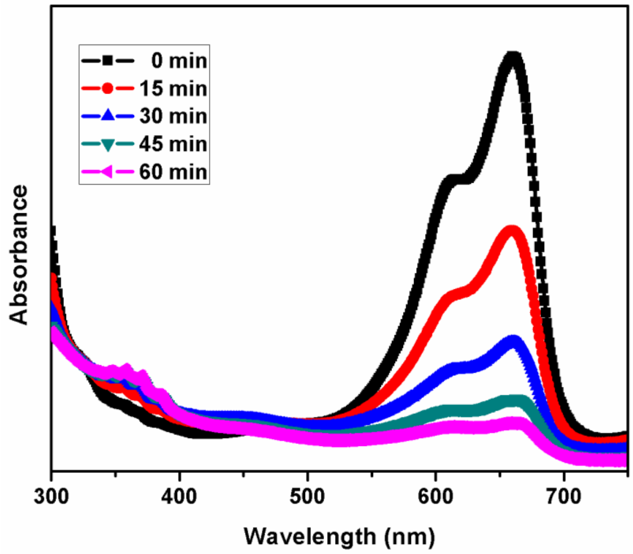

Fig. 2. Decrease in absorption maxima as a function of time for 20 ppm MB

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MATHEMATICAL MODELING OF THE FILTRATION PROCESS OF CATALYST SUSPENSIONS WITH KNOWN PARTICLE SIZE DISTRIBUTION: ACCOUNTING FOR DYNAMICS OF THE CAKE GROWTH AND FILTER PORE BLOCKAGE

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Hydrogenation of vegetable oils in slurry reactors is followed by the catalyst separation from the products on cartridge-type filters, to fit the strict limits on the heavy metals content in the foods. In the catalyst suspension particles vary in size from the very fine fractures to the coarse ones. If the particles are larger than the filter cloth pores or comparable with them, they deposit on its surface. This process is called *cake filtration*. If the particles are smaller than the filter cloth pores, they percolate through its medium or accumulate inside it causing the pores blockage. This process is called *depth filtration*. Even small amount of fine particles can significantly increase the hydraulic resistance of the filter cloth and reduce filtration rates, especially at the initial stage of filtration. However, depth filtration is not usually taken into account in mathematical models of the filtration processes of catalyst suspension [1,2]. This paper is devoted to mathematical modeling of the filtration processes of catalyst suspension with known log-normal particle size distribution accounting for both the cake growth and depth filtration.

The transient differential equations of the mathematical model are written for:

- The concentration of the catalyst particles of each size from a log-normal particle size distribution in suspension. These equations include convective particle mass transfer along the filter cloth and decrease of particles concentration due to their trapping in the filter cloth via inertial impaction and interception;
- The concentration of the catalyst particles of each size from a log-normal particle size distribution inside the filter cloth. These equations take into account increase of particles content by their trapping in the filter cloth through inertial impaction and interception, as well;
- The volume of filtrate collected. It depends on a driving force, that is, a pressure drop through the filter medium and the cake upon it; on the filtering

surface area, on the suspension viscosity, on the cake height, on the overall resistance of the cake and the filter medium. In turn, the filter medium resistance depends on the overall catalyst particles content inside it.

The time-dependent rate of filtration is expressed as the volume of filtrate collected per the filtering surface area and per time unit. In the mathematical model it is assumed that the particles do not penetrate into the filter cloth since the moment when the cake height becomes equal to 2-3 diameters of the largest particles.

Basing on the developed mathematical model we analyzed the effect of the catalyst particles size distribution, the porous structure of the filter medium, concentration of the catalyst particles in suspension on the rate of filtration and time duration needed for filtration of a fixed amount of suspension (T_n). The filtration patterns through both the initially clean filter cloth and that after discharge of particles are studied.

Some theoretical model predictions and experimental data are compared in Fig. 1. In both cases, sharp increase of T_n values at the beginning of the filtration process is explained by slowing-down the filtration rates due to significant increase of the filter cloth resistance. The filter pores are blocked because the particles are accumulated inside the filter cloth; this seems to be the main reason of it. Further, the total resistance grows only because of the increase of the cake height, and T_n values increase more slowly. The values of T_n in the filtration process after discharge are greater due to the incomplete cleaning of the filter cloth during discharge. Results of modeling fit experimental data with a good accuracy.

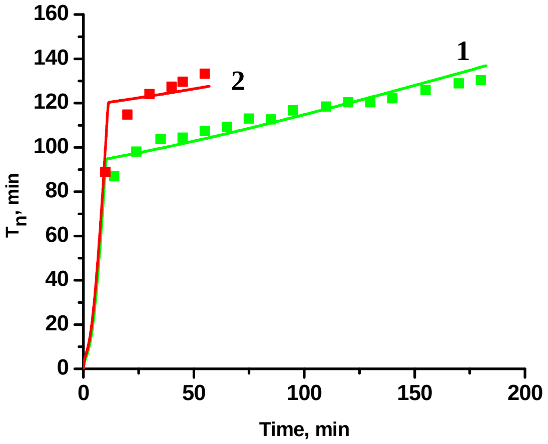

Figure1. The time duration needed for filtration of 40 kg of suspension *vs*. the time elapsed during the filtration process: *1* – filtration through the initially clean filter cloth, *2* – filtration through the filter cloth after discharge, lines – modeling results, symbols – experimental data

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PARAMETRIC ANALYSIS OF OXIDATIVE COUPLING OF METHANE IN A MICROCHANNEL REACTOR

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Oxidative coupling of methane (OCM) is a novel method that offers oil-independent production of ethylene. The main challenge in OCM is to get ethylene, an intermediate species, as a product before it is converted into steam and carbon dioxide. This challenge can potentially be overcome by running OCM, which is a strongly exothermic reaction, at well-controlled reaction temperatures and at short residence times with narrow distribution. Control of temperature, residence time and its distribution depends strongly on the structure and geometry of the catalytic reactor. Considering the strict requirements of OCM, the use of microchannel reactors that offer improved temperature and narrow residence time distributions [1] can be a novel approach to deliver high methane conversions together with improved ethylene selectivities. Microchannel reactors can also be configured to exchange heat between two separate streams in the same volume. Previous studies showed that temperature distribution in the reaction channels could be improved by fast heat exchange between the adjacent channels [2,3].

The aim of this study is to investigate OCM in a heat exchange integrated microchannel reactor involving solid wall separated, parallel reaction and cooling channels by means of detailed mathematical modeling techniques. Inner walls of the reaction channels are coated with layers of porous La_2O_3/CaO catalyst. The cooling channels carry the coolant (steam) flowing in the opposite direction of the reactive stream, whose inlet is composed of CH_4, O_2 and N_2. Simultaneous catalytic reaction and heat exchange within the reactor are modeled by 2D Navier-Stokes equations describing the steady state conservation of mass, momentum and energy. The kinetic model that is used to describe the OCM mechanism over La_2O_3/CaO catalyst is adapted from the literature [4]. The mathematical model, solved by finite volume method on ANSYS Fluent^{TM} 14.0 platform, is used to study the effects of operational parameters (inlet molar methane-to-oxygen ratio, inlet mass flow rates of the reactant mixture and coolant streams, inlet temperature of the coolant) and structural parameters (reactor wall material, thickness of the wall between the reaction and cooling channels) on reactant (methane and oxygen) conversions, and selectivity and yield of C_2-hydrocarbons and ethylene.

The results show that temperature control in the OCM channel can be improved by fast heat transfer rates offered by the microchannel architecture. Methane conversion and OCM temperature are found to decrease with the molar methane-to-oxygen ratio in the feed due to reduced release of exothermal heat, which also caused decrease in the yield of C_2 hydrocarbons. High coolant inlet temperatures hinder selective production of ethane and ethylene, whereas reduced reaction rates, low conversions and product yields are observed when coolant is fed at lower temperatures. Increasing the coolant mass flow rate decreases the OCM temperature and increases C_2 yield to a certain extent, whereas increasing the mass flow rate of the reactant mixture has an opposite effect on the evolution of the reaction temperature that favors the oxidation of C_2 hydrocarbons. Using reactor material with high thermal conductivity regulates temperature distribution along the reaction channel and improves the yield of C_2 hydrocarbons. Average reaction temperature increased but C_2 hydrocarbon yield dropped with the thickness of the wall between the reaction and cooling channels. This trend, however, is found to change after a certain wall thickness, which is found to favor better distribution of heat along the channel.

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SIMULATION OF THE CONVERSION OF OLEFINS TO DISTILLATES

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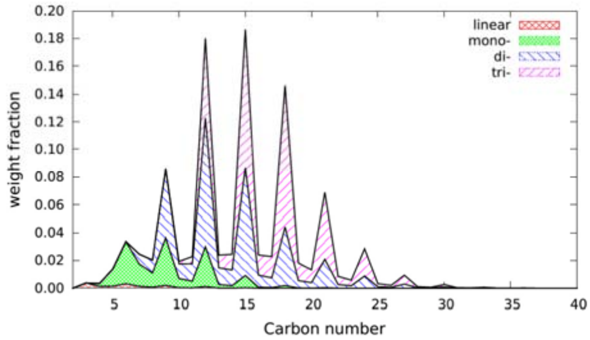
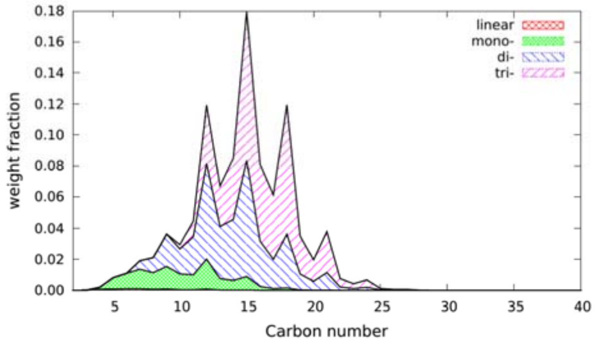
This paper presents the development and application of a reactor model that is able to describe the conversion of olefins to distillates. The model is capable of predicting the olefin isomer distribution as a function of conversion over a wide range of pressures and temperatures, using a mixture of olefin/paraffin feeds. The kinetic model is developed by considering all possible oligomerisation, cracking and structural isomerisation (methyl shift) reactions between the C2 to C40 olefins taking into account appropriate shape selective branching rules. The type-C carbenium ion intermediate mechanistic step is considered the dominant and only reaction step, which consequently allows all the reactions to be represented by two rate constants, one for oligomerisation and one for isomerisation [1]. The reversible reaction rate expressions are used in order to facilitate the cracking reactions and are formulated based on fluid phase activities in order to correctly predict chemical equilibrium and to be seamlessly applied in multiphase reactors [2]. Two kinetic models are developed, one based on carbon number lumps (CN) and the second based on 4 structurally distinct isomer lumps (4I), in which the mono-methyl branching follows that anticipated for olefin reactions over shape selective ZSM5 catalysts [3,4]. The thermochemical database describing the chemical equilibrium in the ideal gas phase is developed for isomer lumps using the methods of Alberty [4] and Benson [2]. Extrapolation is carried out up to C40 by deriving the structures and properties up to C12 olefins and paraffins (about 700 species) with restricted branching as observed for ZSM5 [3,4]. The Gibbs free energy and chemical equilibrium calculated from these thermochemical properties are able to predict the experimentally observed olefin properties and transformations over ZSM5 presented in [3].

The Peng-Robinson equation of state, with modifications proposed by Twu and co- workers [5] for use with heavy hydrocarbon mixtures, is used to predict the liquid phase and two phase reaction mixture in the reactor. The critical and reference properties for the chosen chemical structures needed by the EOS and the energy balance are predicted using the methods of Gani and Constantinou [6].





The figures above show the product distribution at "low conversion" (left) in which the degree of cracking is not significant and "high conversion" (right) in which the degree of cracking is significant which results in a flattening of the product distribution by adding intermediate carbon numbers and reducing oligomers. Comparing the products of the CN model and the 4I model for a pure propene feed, enables the quantification of the degree to which the CN model rate constant will have to depend on the carbon number in order to be equivalent to the 4I model, a consequence of lumping by carbon number. The liquid phase fugacity coefficients decrease strongly with increasing carbon number, which leads to a thermodynamically predicted carbon number dependence of the "effective" rate constants in all models. Consequently, the fugacity coefficient dependence of the "effective" isomerisation rate constant is first order in contrast to the second order dependence of the "effective" oligomerisation rate constant, yielding product distributions with increasing pressure, significantly different than those expected for ideal solutions. The effect of these phenomena on reactor predictions are systematically explored.

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DEMONSTRATION AND DESIGN PRINCIPLES OF AN EFFICIENT SCALED DOWN AUTOTHERMAL OR HEATED MEMBRANE REFORMER FOR PURE HYDROGEN PRODUCTION

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Hydrogen is expected to play an important role in the future of the energy sector, as an energy carrier to be converted in fuel cells. One of the main obstacles to the widespread use of fuel cells is the need for dispersion infrastructure of high purity H_2. Currently H_2 production involves steam reforming of methane (MSR) (natural gas) at high temperatures (>1000 °C), high and low temperature water gas shift (WGS), and final PSA purification. This process along with the need to compress, distribute and store the hydrogen greatly inhibits the use of FC's and lowers the well to electricity efficiency. The use of highly selective-Pd based membranes for pure H_2 separation will allow for on site and on demand production from natural gas at lower temperatures and with improved efficiency but a heat source is required to compensate for the endothermic MSR.

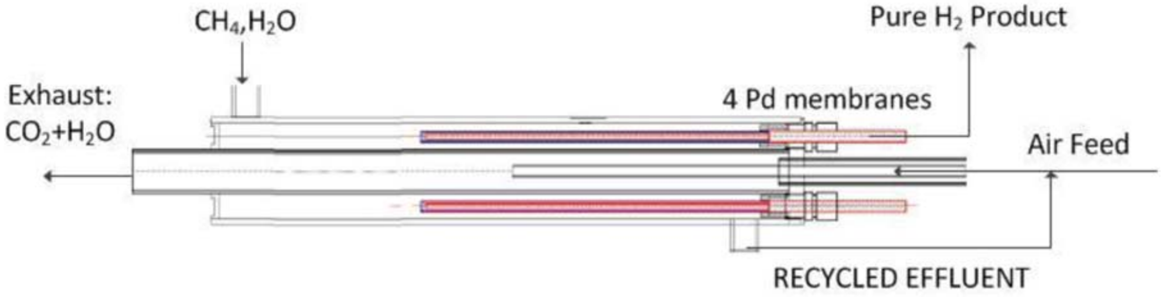

Figure 1: The auto thermal membrane reactor design.
The 3 mm in diameter membranes are colored red

In this work we portray the design process of a scaled down autothermal unit (Fig. 1) incorporating a tube-and-shell construction, with MSR taking place in the shell and oxidation of the recycled effluent from the reforming section (unconverted CH_4, H_2 not permeated, CO and CO_2) is carried out in the inner tube, after mixing with air or oxygen, in order to supply the required heat of reforming. Perm-selective Pd/Ag membranes located in the shell collect the H_2 stream shifting the equilibrium. The mathematical model analysis incorporates 3 levels: (i) Heat and mass balances assuming MSR equilibrium with hydrogen separation approximately defining the MSR reactor conversion; (ii) Approximate estimation of the membrane area required assuming a constant temperature reaction section; (iii) A 1-D model that incorporates heat and mass dispersion terms reveals the existence of hot-spots which should be avoided; these can be reduced by possible distribution of the recycle stream in several points (Fig. 2) leading to improved efficiencies. It also shows good heat transfer between the two streams except at the hot spot and the evolution of MSR conversion and hydrogen separation.

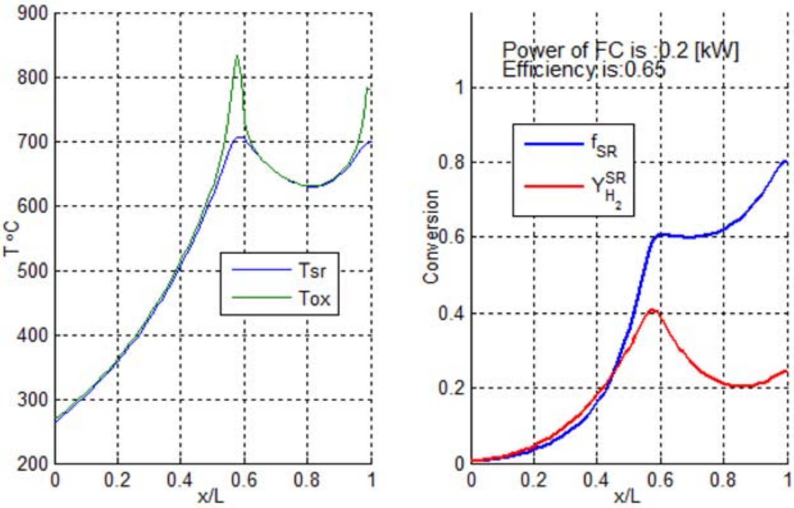

Figure 2: Temperature profiles in the autothermal design with feed to MSR to the left and the feed to the combustion chamber splitted to 2 locations. Notice the uniform temperature separation section and the heat recuperation section

Complete autothermal operation is simulated with hydrogen efficiencies (while accounting for heat loss) of up to 70 % obtained by the counter-current design. An experimental system was designed and constructed at a size of about 1.5 L based on this analysis, and is expected to produce H_2 stream equivalent to 0.25 kW (considering 60 % efficiency of PEM FC), enough to meet the electrical demands of a private house. We will present initial experimental results.

This concept is compared to a second design, of a wall-heated Membrane Reformer, now under experimental investigation in our lab, simulating solar energy use by circulated molten salts. The 1.5 L laboratory scaled membrane reformer, packed with a foam catalyst, demonstrated the concept feasibility with experimental hydrogen efficiency of 40 % (ratio of membrane H_2 flow to 4 times CH_4 feed flow) without sweep gas (Fig. 3). Higher results can be expected in optimized reactors, but there will be residual unconverted methane and hydrogen. The auto thermal design does not require full reforming conversion since some residual CH_4 is needed for heating, whereas in the (solar) wall heated reformer better reforming conversion implies better efficiency, and achieving high conversion is very challenging.

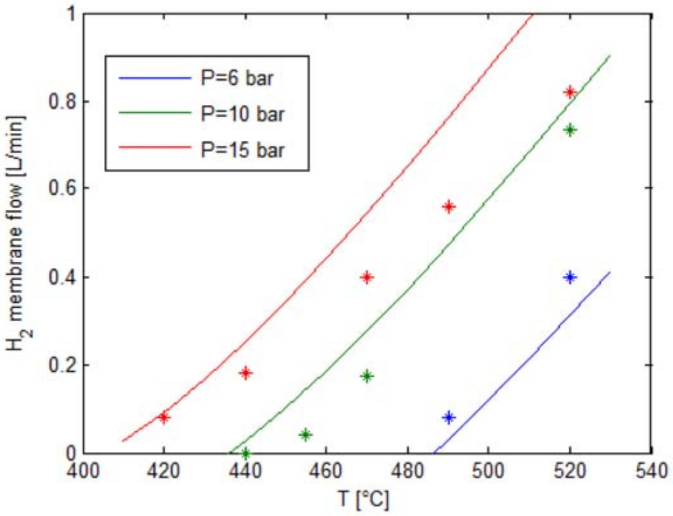

Figure 3: Experimental (stars) vs model (solid lines) H_2 flow through membrane of the wall heated reactor. Methane feed flow 0.5 L/min, S/C = 3, with no sweep

These designs pose several common challenges: Reaction rates are usually limited by the rates of hydrogen permeance or that of heat supply, and these parameters should be maximized. The reactor performance is presented vs the main design parameter, Pe_m, the ratio of methane feed flow to maximal membrane flow (Fig. 4). New catalysts that will operate at lower temperatures and be stable in H_2-lean environment are required. Sweeping gas increases H_2 flux through the membrane and improves conversion significantly, but H_2 has to be separated from the diluted stream and extra energy is required to heat the sweep.

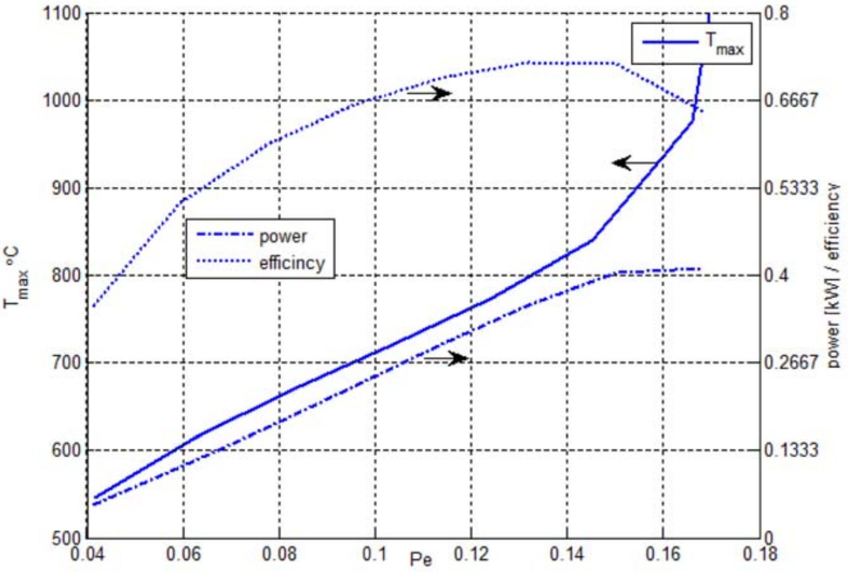

Figure 4: Autothermal reactor performance at full recycle vs Pe_m number (ratio of methane feed flow to maximal membrane flux). Maximum efficiency (~70 %) is achieved at a reactor operating at ~850 °C. Temperature asymptotically approaches that of simple exothermic reactor

OP-II-19

REACTOR DESIGN AND TESTING OF CATALYSTS USED FOR HYDROGEN PRODUCTION BY METHANOL STEAM REFORMING FOR POLYMERIC ELECTROLYTE MEMBRANE FUEL CELLS APPLICATIONS

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Hydrogen is foreseen to be one of the energy vectors of the future. Problems associated to transportation and storage of it could be overcome by the use of methanol as a hydrogen carrier. As a part of this concept, EU-project “BeingEnergy” aims to develop a fuel cell power supply prototype which combines high temperature PEMFC closely coupled with a methanol reformer. VTT is performing part of the work and has extensive knowledge both in various reformer technologies and in fuel cells.

The aim of this study was to design and test a methanol steam reformer, and to use the results of the experiments to develop kinetic models which simulate the behaviour of a new catalyst for methanol steam reforming at different conditions. These models were also used to simulate a microreactor which will generate the hydrogen necessary to feed a stack of HT-PEMFC of 350 W_e.

Experimental part

Both catalysts tested were Cu-based catalysts. The new catalyst was formulated by FEUP (Universidade do Porto) and the commercial catalyst was BASF RP-60. The experiments were performed at atmospheric pressure with a fixed-bed multichannel reactor (FBMR) made of aluminium with channel size of 1.2x3x60 mm (Figure 1). The experiments were performed at temperatures from 170 to 210°C, at 1.5 steam to carbon ratio (S/C ratio), and for different weigth of catalyst to initial feed of methanol ratios (W/F ratio).

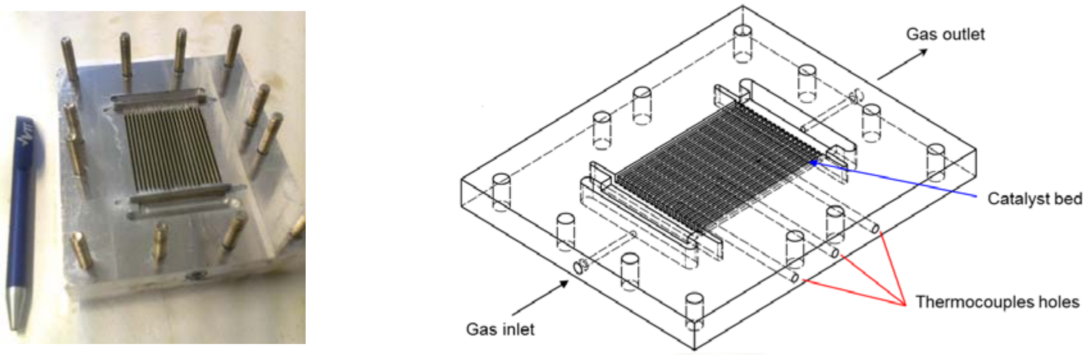
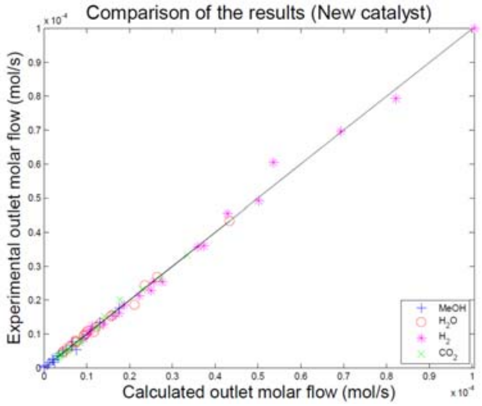


Figure 1: Fixed-bed multichannel reactor

The kinetic modelling was performed using Matlab. The CFD simulations were performed using COMSOL Multiphysics.

Results and Discussion

The results of the experiments were used to fit different kinetic models (power rate law and Langmuir-Hinselwood based models). The best fit was obtained with models presented by the Eq. 1 and Eq. 2. Figure 2 shows the comparison between the experimental and the calculated results with the model.



$$r_{MSR} = k(T)_{MSR}\, p_{CH_3OH}^{0.26}\, p_{H_2O}^{0.97} \qquad \text{Eq. 1}$$

$$k(T)_{MSR} = 2.04\cdot 10^{11}\, exp\left(-\frac{117000}{RT}\right) \qquad \text{Eq. 2}$$

Figure 2: Comparison of the results

Figure 3 shows the results of the experiments that were used for kinetic modelling of the new catalyst, and the lines of the model used to fit the data. This chart reveals the importance of the temperature control for an efficient catalyst performance. Figure 3 also shows a CFD simulation of the temperature distribution in one channel of the FBMR combined with oil heating.

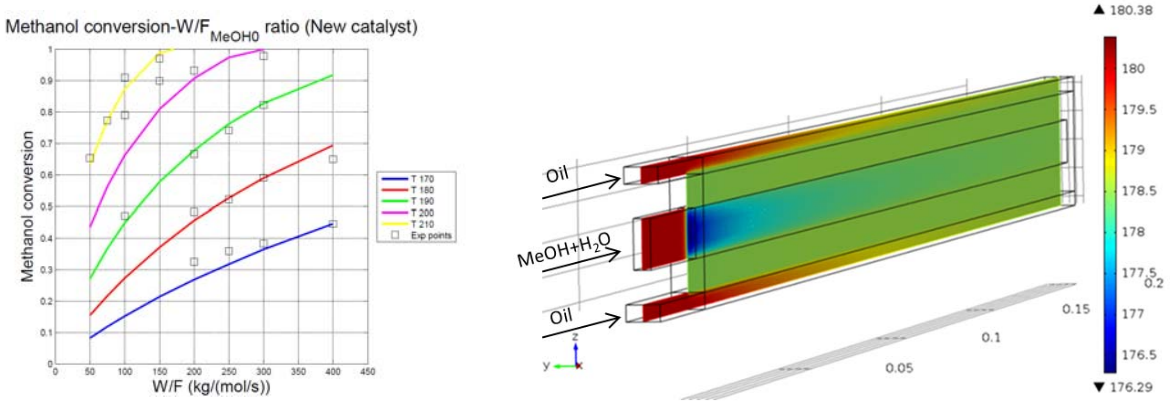


Figure 3: Results of the experiments of the new catalyst (left) and CFD simulation of the temperature distribution (right)

Conclusions

FBMR provides higher performace compared to tubular reactors due to better heat transfer and hence the reduction of the temperature gradients. This eventually results in reduced volume and weight of the reactor.

Acknowledgements

FEUP (Universidade do Porto) and ITQ (Universitat Politécnica de Valéncia) are acknolewledged and thank for developing and charaterizing the new formulation catalysts.

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement № 303476.

APPLICATION OF MULTI FUNCTIONAL REACTOR IN BIO OIL UP-GRADATION

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Multi functional reactor is a promising alternative to upgrade bio oil produced from vacuum pyrolysis of wood. Bio oil derived from biomass pyrolysis has some deleterious properties like high viscosity and acidity, low heating value. Bio oil contains heat sensitive as well as high boiling compounds. In the present work we studied the application of reactive chromatography which combines the reaction and separation in a single unit. This technique is especially useful for reversible, high boiling and temperature sensitive reactions. Synthetic bio oil was taken for this study which contains model compounds acetic acid, ethanol, phenol, o-cresol, furfural, cyclopentanone and guaiacol. Amberlyst-15 has been used as catalyst/adsorbent. The upgradation of bio oil involves in esterification and acetalization reactions as shown in figure 1.

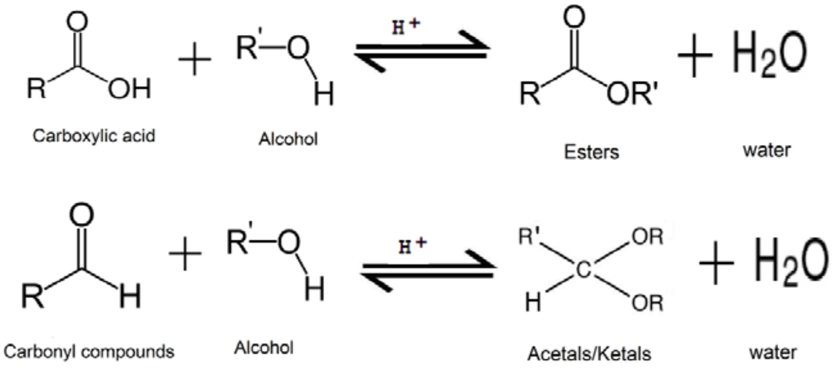

Fig. 1. (**a**) Esterification (**b**) Acetalization and ketalization

The reactive chromatography experiments were performed to obtain reactive break through curves which indicate a clear potential for the use of reactive chromatography. To evaluate the feasibility and design of the reactor in large scale kinetics of the reaction is necessary. Kinetics was experimentally investigated in a batch reactor with a cation exchange resin, Amberlyst-15. The effect of mole ratio, catalyst loading and temperature on a wide range was experimentally determined. Kinetic modelling was performed using different kinetic models.

Keywords: Reactive chromatography, Bio oil, Amberlyst-15.

MODELING THE DYNAMIC BEHAVIOR OF INDUSTRIAL-SCALE FIXED-BED REACTORS FOR THE SELECTIVE OXIDATION OF n-BUTANE

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Maleic anhydride (MA) is an important intermediate in the chemical industry. It is synthesized by the catalytic oxidation of n-butane with air. Mainly tubular fixed bed reactors are used for this strongly exothermal reaction, where the reaction heat is removed by molten salt. The catalysts consist of vanadium phosphorous oxides (VPO) and are employed as pelletized full-body shapes. The main side products of the reaction are CO and CO_2.

Even after many years of investigation, the reaction mechanism and the nature of the active sites are not fully understood. An important subject of discussion is the assumption that water interacts with the VPO surface forming separated phosphate groups. The slowly progressing loss of these phosphates from the catalyst shifts conversion and MA-selectivity to commercially unattractive regions. Therefore, it is industrial practice to add several ppm of an organic phosphorous compound to the reactor feed [1]. The distribution of the phosphorous within the catalyst bed is supported by further addition of steam.

The inlet concentrations of water and trimethyl phosphate (TMP) were dynamically varied in experiments in an industrial-scale pilot sample port reactor filled with commercial VPO catalysts from Clariant. Various, partially opposing effects were observed occurring at different time scales. Variations of these feed components caused e.g. slow changes in shape and height of the forming temperature profiles and in product composition, respectively.

As reported so far, kinetic models have been derived primarily from experiments in which significant changes in catalyst activity were not observed. Additionally, there are no studies reported with TMP feed under industrial reaction conditions. Thus, the scope of this work is developing a model which is able to describe all observed effects during complete test periods of several weeks.

According to findings in the literature [2], a novel kinetic model for MA formation was derived which accounts for all observed interactions between TMP and water on the VPO surface. The kinetic model was integrated into a two-dimensional, heterogeneous reactor model (gPROMS) that includes intra-particle heat and mass transfer resistances, pressure drop, and radial heat transport from the catalyst bed to the cooling medium. This reactor model could be successfully applied for parameter estimations. Kinetic and heat transport parameters were adapted to the experiments. The model is able to describe well up to 500 h time on stream including many variations of the operating conditions. The dynamically changing activity profiles reflect the evolution of temperature profiles and product compositions with only minor deviations.

Refereces

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ORAL PRESENTATIONS

Section III.

Chemical Reactors and Technologies for Emerging Applications

Environmental Protection and Utilization of Wastes
Processing of Biomass and Renewable Feedstocks
Production of Novel Nano-Structured Carbon Materials

STEAM REFORMING OF POLYALCOHOLS AS A HYDROGEN SOURCE FOR FUEL CELLS IN MICROCHANNEL REACTORS OF THE kW SCALE

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Hydrogen production from renewable sources and its utilization as fuel for fuel cells is a promising way to minimize the actual dependence on fossil fuels. In this context, the use of bio-renewable organic sources such as polyalcohols, in an intensified process through the use of a microstructured reactor seems to be a promising alternative [1].

The reforming of biomass-derived oxygenates such as ethanol or glycerol has been deeply studied [2-5]. However, the stability of catalyst formulations developed for glycerol reforming was not the main focus of this development work to date. In the case of ethylene glycol and propylene glycol, few studies have been addressed to date most of them focusing on aqueous phase reforming (APR) of ethylene glycol. Ethylene glycol (EG) can be produced directly and efficiently via catalytic hydrogenation of cellulose or cellulosic biomass derived oxygenated compounds [3]. Cellulose, as the most abundant component of biomass (accounting for 35-50 %), is currently considered a promising alternative to fossil resources [6]. In addition, EG is the most abundant molecule of compounds derived from the catalytic conversion of cellulose, accounting for more than 70 % of cellulose derivatives, thus making EG a renewable and available energy carrier [7]. Moreover, both ethylene and propylene glycol serve as coolants in many mobile applications nowadays and therefore a distribution grid already exists.

The practical processing of larger amounts of polyalcohols such as ethylene glycol and propylene glycol to synthesis gas for fuel cell applications in reactors larger than laboratory scale suited for distributed applications has not been adequately addressed to date. Microstructured reactors offer benefits concerning efficiency and size reduction owing to their potential of heat integration and improved heat and mass transfer.

The current work deals with (a) the development of stable catalyst formulations for ethylene glycol/propylene glycol reforming and (b) reactor development for the steam reforming of propylene glycol in the power range exceeding 17 $kW_{thermal}$ of the synthesis gas product.

Alumina supported rhodium catalysts containing large amounts of ceria additive showed best performance from an activity and stability point of view both for ethylene glycol and propylene glycol steam reforming. The addition of small amounts of air to the reactor feed (oxidative steam reforming) improved the performance of the catalyst further and allowed stable operation of the catalysts for several hundred hours duration at S/C ratios in the range between 2.5 and 3.5.

The medium-term stable catalyst formulation described above was then incorporated into a plate heat-exchanger reactor (see Fig. 1). The energy required to drive the endothermic steam reforming reaction was foreseen to originate from the combustion of fuel cell anode off-gas and additional propylene glycol in a future technical process. Therefore the demonstrator was composed of layers for energy supply carrying a micro-structured catalytic burner, which was fed with anode off-gas surrogate and reaction layers which carried catalyst for the oxidative steam reforming of propylene glycol.

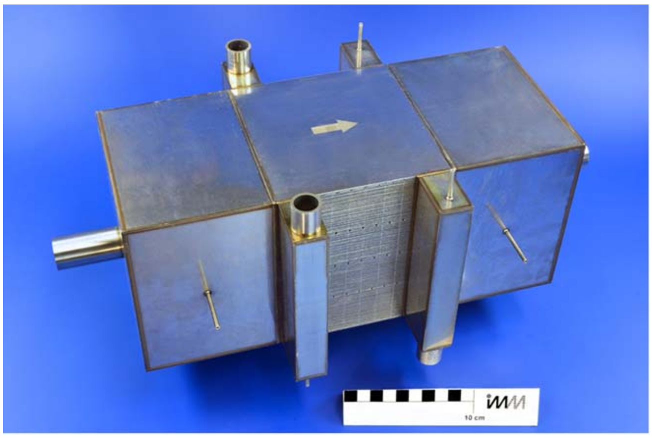

Fig. 1. Plate heat-exchanger reactor for steam reforming of polyalcohols with a thermal output of 17 kW_{th}

Up to 2.5 L/h propylene glycol were fed into the reactor.The resulting maximum flow rate of hydrogen produced exceeded 75 L/min. It is to the authors' knowledge the first prototype reactor for steam reforming of polyalcohols of that size presented in open literature.

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PLASMA GASIFICATION OF SANITATION BIOMASS

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Approximately 2.6 billion people on earth currently lack access to safe and affordable sanitation. The negative health impact of poor sanitation is enormous. To change this situation the toilet has to be reinvented. The Bill & Melinda Gates Foundation have posed a challenge to researchers worldwide to develop toilet solutions that do not require water, energy, or sewage infrastructure, and are affordable for people in developing countries.

The TU Delft approach is to employ a small-scale processing facility that gasifies the biomass in a microwave generated plasma. By applying energy in this form, lower residence times are required and heat losses can be compensated for, so that processing facilities can be scaled down considerably, enabling decentralized treatment. The gasification step is preceded by a pre-treatment stage to create optimal feed quality. In order to create a self-sustained process, the produced syngas is fed to a gas cleaning unit and then to a solid oxide fuel cell to recover the energy expended for microwave field generation.

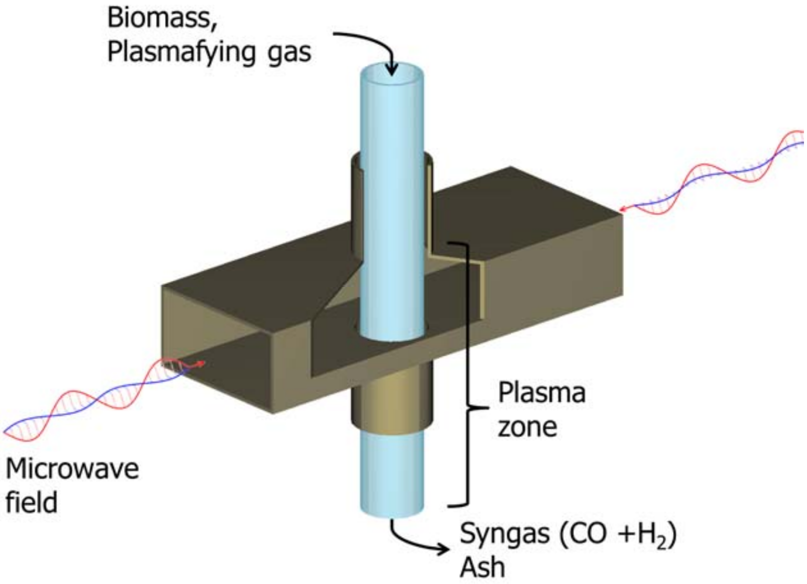

Figure 1. Schematic of plasma reactor

A series of short duration continuous flow experiments was performed to investigate the feasibility of the process. Figure 1 presents a schematic of the plasma reactor that was used. Biomass and gas are fed into a microwave energized plasma zone where a high temperature plasma gasifies the biomass, thereby generating a syngas rich gas mixture. The energy yield in terms of the lower heating value of the gas exceeds the net microwave energy transmission into the reactor, which indicates that this concept could potentially be developed into a self-sustained process.

Figure 2. Plasma gasification setup

A continuous flow system that enables stable and long-duration continuous operation of the plasma (Figure 2) has been built and demonstrated. Using this system, research is currently ongoing to understand and optimize the process.

BATCH REACTOR COUPLED WITH WATER PERMSELECTIVE MEMBRANE: STUDY OF GLYCEROL ETHERIFICATION REACTION WITH BUTANOL

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In this study, a novel approach to obtain high yield to oxygenated additives by glycerol etherification reaction is proposed. Up today, several research papers deal with etherification of glycerol with isobutene or *tert*-butanol to obtain a mixture of glycerol *tert*-butyl ethers, in particular *di*- or *tri*- substituted which are considered as fuel additives due to their good miscibility with conventional diesel fuels [1]. However, the use of different alcohols such as bioethanol or biobutanol [2], could be an alternative way to valorize biodiesel-derived glycerol leading to the production of a biomass-derived product thus improving the environmental sustainability of the global process. Unfortunately, glycerol etherification reaction in presence of less-reactive alcohols than *tert*-butyl alcohol, is termodynamically more difficult.

Etherification with butanol is poorly studied and fews attempts of direct catalytic etherification of glycerol with long-alkyl chain alcohols are reported in the current literature [2-3].

According to the following reaction scheme, during the reaction in presence of butanol, water forms along with two *mono*-butylglycerol ethers (MBGs), two *di*-butylglycerol ethers (DBGs) and two *tri*-butylglycerol ethers (TBG):

$$\text{GLY} + \text{BUT} \leftrightarrows \text{MBGs} + H_2O \qquad (1)$$

$$\text{MBG} + \text{BUT} \leftrightarrows \text{DBG} + H_2O \qquad (2)$$

$$\text{DBG} + \text{BUT} \leftrightarrows \text{TBG} + H_2O \qquad (3)$$

Water negatively affects catalytic activity and selectivity, both for thermodynamic restrictions, the reaction being controlled by the equilibrium, and for problems reagrding the catalyst stability [4].

In the attempt of remove the water produced during the reaction and thus to overcome the equilibrium restrictions, a permselective membrane (*tubular membrane covered by polymer furnished by Pervatec)*, coupled with a batch reactor, was used (*permeation was ensured through the ricirculation of gas phase*). Preliminary tests have been performed in presence of A-15 resin which represents one of the main catalysts employed in glycerol etherification reaction [1,5]. In Table 1 are reported such results obtained at different reaction temperature. Without membrane, high glycerol conversion can be reached only at high temperature (160 °C). The main reaction products are the mono-substituted compounds (1-MBG, 72.1 % and 2-MBG, 14.0 %). The correspondent experiment performed with membrane, clearly reveals that the selective permeation of water through membrane significantly reflects both on glycerol conversion and products distribution. At 140 °C the conversion of glycerol is almost doubled (from 45.6 to 97.6 %) and the selectivity to MBG significantly decreases (from 74.2 to 47.5 %). The selectivity to poly-substituted ethers significantly increases, from 1.3 to 8.1 %, but many other compounds, currently unidentified, were formed (36.3 %). Experiments are in course to identify such compounds.

On the wall, the results obtained clearly demonstrate that the coupling of a water-permselective membrane with a batch reactor drastically affects the etherification of glycerol with butanol. Experiments are in progress to optimize the system with the goal of obtaining high yields to compounds suitable to be used as oxygenated additives for diesel.

Table 1. Glycerol etherification reaction with butanol: effect of temperature and use of a membrane reactor

Cat	T_R	X_{Gly}	Products Selectivity (%)					
			1-MBG	2-MBG	1,3-DBG	1,2-DBG	TBG	extra
A-15	70	-	-	-	-	-	-	-
A-15	90	2.6	71.0	10.3	7.0	-	-	11.7
A-15	120	26.1	79.6	12.4	2.5	-	-	5.5
A-15	140	45.6	74.2	12.2	0.8	0.5	-	12.4
A-15	160	89.3	72.1	14.0	1.8	2.6	0.1	9.4
***A-15**	140	97.6	47.5	7.4	4.5	3.6	0.7	36.3

* with Membrane

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PRIMARY CATALYSTS FOR FLUIDIZED BED GASIFICATION OF BIOMASS AND WASTES

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The production of chemicals, hydrogen, biofuels or power generation by conversion of syngas produced from biomass gasification is considered a very promising route, more efficient if compared to combustion. For the complete exploitation some technological barriers still need to be overcome. The main challenges of biomass gasification process are: a high conversion of the fuel into valuable syngas and a low content of tar, compatible with final use. Tar species produced during gasification can be efficiently removed via catalytic methods [1], that also have beneficial effects on syngas heating value.

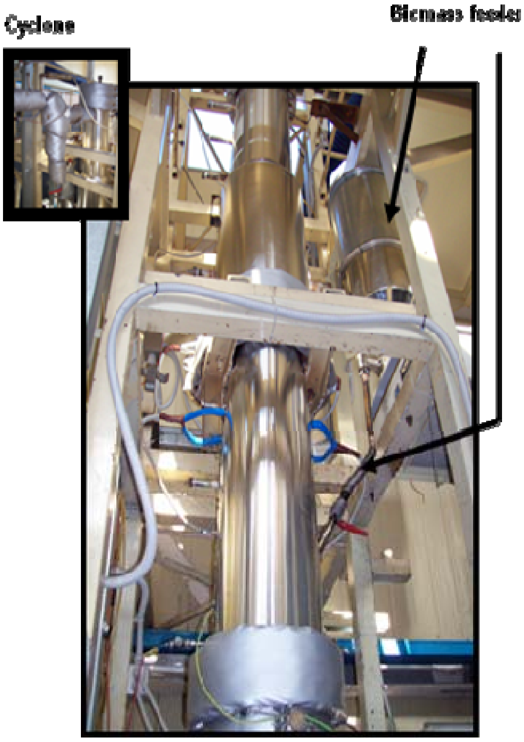

Fig. 1: Fludized bed gasifier

A gasification process carried out in fluidized bed reactors (FB) meets these requirements thanks to the internal mixing, the uniform temperature and to the high heating rate of the fed fuel particles (more than 100 °C·s^{-1}). Another advantage of FB gasifiers is the flexibility to process different types of fuels also mixed, e.g. biomass/waste feedstock. Thus, it is one of the preferred technologies for medium-scale biomass gasification plants [2].

In addition the use of a fluidized bed reactor allows to using a catalytic bed, promoting tar conversion, directly inside the gasifier. So far, Ni based catalysts have been largely employed for tar reduction [3] and hydrocarbon reforming. Application in fluidized bed reactor for Ni catalyst has been already investigated [4].

Metallic iron (Fe^0) is also considered an active catalytic phase for both tar conversion and WGS reactions [3]. Similar performances to those obtained with a Ni/olivine catalyst containing around 3.9 wt % of Ni have been reported for a Fe/olivine catalyst containing 20 wt % of Fe [3]. This offers the possibility of replacing nickel with a metal which is less toxic for the healt and the environment, particularly when used in fluidized beds, generating fine attrited particles [3]. Noble metal containing catalysts have been also proposed due to their higher efficient than conventional Ni based catalysts in terms of tar destruction, resistance to coking and H_2S poisoning [5,6]. However, the high cost of catalysts based on noble metals limits their industrial use.

The present article reports on a research activity carried out for in bed catalyst for FB gasification. The experimental facility is a 140 mm ID fluidized bed gasifier (figure 1), made of a stainless steel column, operated under bubbling conditions regime. Wood pellets and selected waste materials were used. The attention was also focused on the set up of a suitable (iron based and lanthanum cobalt perovskite systems) catalysts able to reduce TAR formation and characterized by adequate mechanical properties to be operated in fluidized bed conditions. The catalyst has been characterized as by means of BET, TPR/TPO, SEM, XRD, ICP experiments. In addition to the chemical physical characterization, the comminution behavior of the catalyst was investigated. The results of steady state gasification tests include the effect of changing the equivalence ratio and the catalyst dilution in the bed on syngas yield, syngas composition and tar production. The discussion of observed trends is presented in the paper along with the comparison with previous published results.

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FUELS FROM NATURAL TRYGLICERIDES

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The importance of fuels derived from alternative sources is more higher. The main reasons are the following: growing of quantity demands for good quality fuels all over the World, decrease in quality of crude oils causes more expensive refining operation, demand for satisfying the stricter quality requirements economically, sustainability, decrease in the harmful material emission during the whole life cycle etc. One of the sustainable raw materials of liquid alternative blending components is the natural triglycerides (and fatty-acids) (non-edible vegetable oils: eg. rapeseed oil of high euric acid content; jatropha oil; used cooking oil and fats, waste lards from slaughterhouses, protein processing plants, brown fat of sewage works, triglycerides of algaes, etc.) [1,2].– After suitable pretreatment fuels and fuel blending components of different chemical structures can be produced on different catalytical ways from the high triglyceride containing feedstocks, for example alkyl-esters of fatty acids with transesterification (mainly with methanol) and it followed by methathesis to be published recently, hydrocarbon fractions of high isoparaffin content (>60 %) with hydrogenation and isomerization of formed bioparaffins in one- or two steps [1-3]. Depending on the boiling point range these can be used as blending components of JET fuels or diesel fuels. Additionally, many papers discuss on studies of coprocessing of triglycerides with crude oil fractions applying different petroleum refining technologies (fluid catalytic cracking, hydrodesulphurization, etc.) [4].

However, relatively few information were presented about catalytic transformation of lards to fuels. The main aim of our research was to work to study the production of biofuels from vegetable oil containing waste lard as feedstocks using different catalytic systems (alkali-catalized transesterification, hydrodeoxygenation and isomarization in two-step). In this frame our aim was to determine the suitable process conditions [share of animal fat in the feedstock and process parameters (temperature, pressure, feedstock/catalyst ratio, etc.)].

Based on the obtained results, we found the vegetable oil feedstock containing 15-20 % waste lard should be suitable pretreated both for the catalytic transesterification, and for the hydrogenation (deoxygenation) and the following isomerization to produce good quality product with high yield (mixtures of methyl-esters or mixtures of n- and i-paraffins, respectively). With the latter technological solution vegetable oil feedstock of higher waste lard content can be transformed to valuable products than in case of transesterification. The reason is the better feed flexibility of hydrogenation technology caused by the differences existing in the catalytic systems and the reactions to be taken place on them. Yield of fatty-acid-methyl-esters was 94 % of the theoretical yield at the favourable parameters of transesterification, and its quality satisfied the main requirements of the EN 14214:2012 standard for biodiesel product, except the CFPP (Cold Filter Plugging Point) value which can be improved by suitable additivation. From the waste lard containing vegetable oil feedstock we obtained mixture of parafin hydrocarbons as intermediate product with almost 98.5% of the theoretical yield on a sulphided $NiMo/P/Al_2O_3$ catalyst at the favourable process parameters (T = 335 °C; P = 35 bar; LHSV = 1.1 m^3/m^3h; H_2/hydrocarbon ratio 560 Nm^3/m^3). The isomerization of this product (on an own-developed Pt/SAPO-11 catalyst) resulted 97% JET- and gas oil boilingpoint range product, and 2.8 % naphtha fraction rich in isoparaffins. The quality of the latter can be improved with the isomerisation of low octane number one-branch containing paraffins (ca. <74) and n-paraffins (ca. <62) in a light naphtha isomerization plant.

Gas oil fraction satisfies the quality requirements of EN 590:2012 standard for diesel fuel and the CWA 15940:2009 standard for paraffin fuel, except the density and lubricity. The obtained diesel fuel blending components have significantly better performance properties comparing to the product of transestericifation. For example, their cetane number is higher in 25-30 unit, and CFPP value is lower in 20-30 °C. However, their application requires higher amount of lubricity improver additive. To obtain the prescripted 10 % renewable fuel share in the EU until 2020 it is practical to use togerther the alkyl-esters and isoparaffinrich hydrocarbon fractions in a suitable ratio to set the density, lubricity, CFPP value based on compromise.

Fractionation of the whole gas oil fraction obtained from hydrogenation and isomerization resulted a kerosene and a narrow boiling range gas oil fraction, which are excellent blending compontents. On processing the waste lard – vegetable oil mixture the yield of JET fuel is higher comparing to the pure vegetable oil, because waste lard contains triglycerides of fatty acid constituens of lower carbon number, which increases the product flexibility of a crude oil refinery.

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BIOJET FUEL FROM KEROSENE/COCONUT OIL MIXTURES

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Recent demands for jet fuels has a significant grown in the last decades [1]. So, crude oil companies and different research groups began to study production possibilities of suitable kerosene fractions to drive jet engines not from crude oil, but other, not fossil source. At the same time, the question is how can be produced modern, environmental friendly, jet fuel with high energy content, that is according to the increasing quality requirements and what is able as fuel to drive the engine in the operating conditions of the engine in the working refinering technologies in system approach, because they are necessary conditions of mobility.

Nowadays reduced aromatic or non-aromatic hydrocarbon fractions are necessary for the production of jet fuels with good burning properties, which contribute to less harmful material emission. [2]. One of the production possibilities is using biocomponents from catalytic hydrogenation of triglycerides. Another possibility is coprocessing kerosene fraction and triglycerides with hydrogenation [2].

Present days there is only a few publications, what discuss the biocomponent containing jet fuel production possibilities.

The aim of our experimental work was to study catalytic transformation of different coconut oil containing (10, 30, 50 %) kerosene fractions at changing process parameters (temperature, pressure, liquid hourly space velocity, H_2/feedstock volume ratio). We carried out the experiments on a sulphided $NiMo/Al_2O_3$ catalyst (T = 280-360 °C, LHSV = 1.0-3.0 h^{-1}, P = 30 bar, H_2/feedstock volume ratio = 600 Nm^3/m^3).

Based on the experimental results, we determined, the yield of target product changed between 65-95 % depend on the applied process parameters. (Figure 1).

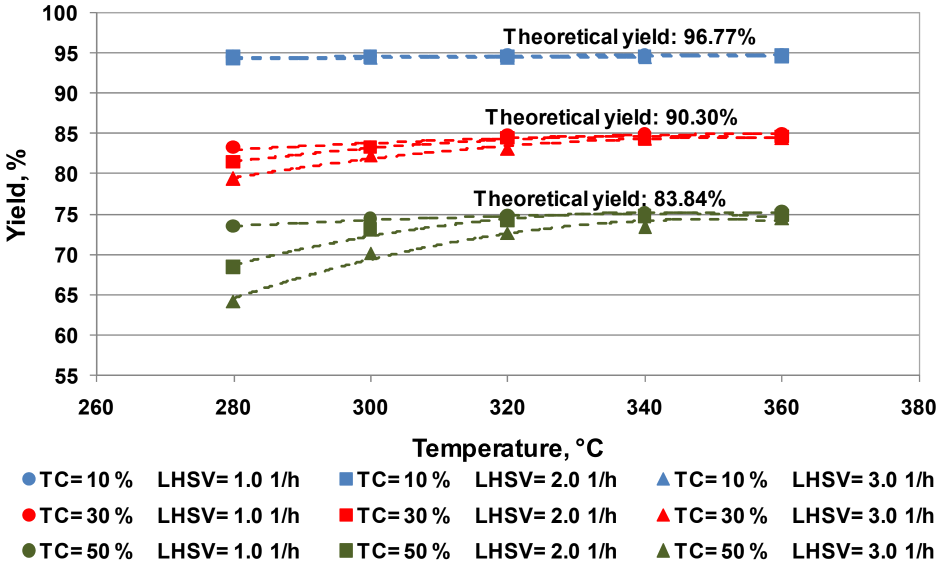

Figure 1. Changing of the target product yield as a function of the process parameters (P: 30 bar, H_2/ feedstock volume ratio: 600 Nm^3/m^3, TC: triglyceride content)

Based on the quality properties of the products, we obtained products with high yield at the favourable process parameters, which have excellent properties (sulphur content < 10 mg/kgs, aromatic content: 5 %) and they contain biocomponent. They are excellent jet fuel blending components, what are compatible the actual fuel supply systems and jet fuel blending components, and their burning product damage the environment less.

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OPTIMIZATION OF EXTRACTION AND BACTERIAL DEGRADATION OF BIOMASS IN A STIRRED TANK REACTOR

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Waste agricultural biomass has become an attractive feedstock material to produce useful chemicals from renewable abundant cheap source of non-petroleum origin. The structural complexity of biomass, composed of cellulose, hemicellulose and lignin, hampers the development of selective processes with traditional chemical catalysts, whereas biotechnological routes are highly adaptive and allow to save useful monomers functionality of the natural polymers. Being cheap in energy and costs and usually carried out in well studied commonly used batch reactors, biomass degradation with fungi, bacteria and enzymes have also become economically attractive and easy to set up.

Previously, we studied extraction of valuable compounds from wheat straw degraded by a mushroom, *Pleurotus ostreatus* [1] and verified the developed process on a pilot scale in a 300 L batch reactor [2]. The developed technology of *fungal* degradation of wheat straw followed by simple extraction in order to obtain semi-products for further processing can be easily adopted by farmers. Here, we present work on *bacterial* degradation of biomass which is more likely to be used in industry *due* to better understood methabolic engineering in bacteria compared to fungi.

A 1 L batch reactor was used for bacterial wheat straw degradation and degradation products extraction. This system equipped with a heating jacket, pH and oxygen meters, gas lines, condenser, and automatic pH controller supported by peristaltic pumps and stock solutions of base or acid allows to optimize fermentation parameters, such as pH, temperature, rotation speed and dissolved oxygen in order to obtain the highest production yield. We carried out two types of biomass degradation experiments. Firstly, we studied the extraction process in the reactor, using degraded in solid state fermentation biomass. For that, amended with 1 % of chicken manure wheat straw was fermented at 60 °C for several weeks and then total phenolics and sugars products were extracted into water. We optimized rotation speed, temperature and biomass pretreatment method in order to obtain the highest amount of extractives. The knowledge obtained in the first section was further used for wheat straw fermentation with *Sphingobacterium sp.*, a thermophile bacterium harvested in the reactor in M9 salt medium at 45 °C for several weeks. The biomass degradation products were analyzed with the help of HPLC, LC-MS and spectrophotometric methods. Here, again by optimizing pH, rotation speed and dissolved oxygen amount, maximum productivity was achieved.

To our knowledge, this is the first example of biomass degradation by thermophilic *Sphingobacterium sp.* bacterium carried out on a large scale.

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EFFECT OF BIOMASS ORIGINATED ASH IN CATALYTIC FAST PYROLYSIS OF BIOMASS

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Fast pyrolysis is an attractive single-step process for solid biomass conversion to an intermediate liquid energy carrier, suitable for further production of liquid fuels [1]. It includes the rapid thermal decomposition of lignocellulosic material in absence of oxygen, followed by quick condensation of the vapours produced initially. The condensed liquid is a mixture of numerous organic molecules with water, together often called pyrolysis oil or bio-oil. Crude bio-oil has a heating value roughly equal to that of the biomass, which is almost half the heating value of fossil fuel oil [2]. To improve the quality of crude bio-oil in relation to biofuel applications, and to reduce the upgrading costs, biomass fast pyrolysis can be carried out in the presence of suitable catalysts. Catalysis, either by adding catalyst particles to the reactor (in situ) or by secondary conversion in the vapour phase (ex situ), is applied for the removal of oxygen and the catalytic cracking of high molecular weight compounds in the pyrolysis vapours.

All biomass feedstocks contain various amounts (depending on their type) of inorganic ash-forming mineral nutrients in the form of cations which are bound onto the organic matrix of biomass. These indigenous and catalytically active minerals such as alkali and alkaline earth metals (AAEM species, e.g. Ca, K, Mg, Na) within biomass structure are known to catalyse cracking and several thermolysis reactions in gas phase which remould the chemical composition of resulting bio-oil and pyrolysis product distribution [3].

The primary goal of this work was to investigate the effect of alkali and alkaline earth metals in the form of pine wood ash on the fast pyrolysis product yields (e.g. organics, water, carbonaceous solids and non-condensable gases), non-condensable gas compositions, bio-oil compositions and the elemental distribution over various pyrolysis products and to gain an insight of the underlying mechanisms. A known amount of pine wood originated ash, ca. 3 wt. % relative to the amount of biomass fed and ca. 0.002 wt. % relative to the amount of bed material (pure sand in case of non-catalytic and a catalyst-sand blend in case of in situ catalytic fast pyrolysis experiments), was added within the process. Moreover, the in situ catalytic fast pyrolysis results obtained from the eight times reacted/regenerated catalyst (a commercial, spray dried heterogeneous ZSM-5 based FCC catalyst) were also compared with the ash-added in situ catalytic experiments in order to understand whether catalyst deactivation resulting from sequential reaction/regeneration cycles was due to thermo-mechanical, chemical and structural changes or because of the presence of the biomass originated ash. Experiments were performed in a newly designed laboratory scale mechanical agitated bed reactor at a fixed fast pyrolysis reaction temperature of 500 °C.

In case of non-catalytic experiments, biomass originated ash catalyzed the reactions that led to the formation of non-condensable gases, coke and acids (specifically acetic acid) while the yields of the organic phase of the bio-oil, sugars (specifically levoglucosan) ketones and phenols decreased. The presence of ash in in situ catalytic pyrolysis of pine wood favored the production of non-condensable gases (specifically CO, CO_2 and CH_4), sugars and acids while the yields of the organic and water phases of the bio-oil, coke, and phenols decreased. The results obtained revealed that even very small amount of biomass originated ash present in the pyrolysis process were sufficient to change the resulting pyrolysis speciation and the catalyst deactivation was not only related to the presence of ash but also to the thermo-mechanical, chemical and/or physical changes (e.g. poisoning, fouling, and attrition) occurring within the catalyst during the reaction/regeneration cycles.

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CATALYTIC STEAM REFORMING OF BIO-OIL AQUEOUS FRACTION WITH LABORATORY SCALE REACTOR

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Bio-oil aqueous fraction is a biomass pyrolysis sideproduct which contains approximately 80 wt % water and 20 wt % water soluble organic compounds [1]. This waste fraction can be utilized for hydrogen production by catalytic steam reforming. However, the high content of complex hydrocarbons in the bio-oil aqueous fraction leads easily to coke formation problems in the reactor and eventually to the deactivation of the catalyst. The coke formation can be avoided by adding more steam to the system but adding and heating excess water is not economically feasible.

In this study a atmospheric, fixed-bed reactor was used for steam reforming of bio-oil aqueous fraction on commercial nickel catalyst. The aqueous fraction was obtained from VTT's fast pyrolysis pilot plant and used in the experiments as such without any added water. The steam to carbon (S/C) molar ratio of the aqueous fraction was 3.8 which was lower than anywhere in the reviewed literature. The aqueous fraction was fed into the reactor through a nozzle while a flow of nitrogen from a second nozzle sprayed the liquid feed above the catalyst bed. The experiments were carried out at temperatures between 600 – 750 °C and with GHSV of 5 000 1/h. The analysis of the outlet gas was done with online GC and gas analyzer. The objective of the study was to test the functionality of the feeding system and the reactor, and to find the optimal reaction temperature.

In total eight experiments were carried out to at temperatures 600, 650, 700 and 750 °C with commercial nickel catalyst. The activity of the catalyst was measured by carbon to gas conversion which are presented for each experiment in Figure 1. The inlet carbon content was calculated from the total feed of bio-oil aqueous fraction and the outlet gaseous carbon from the gas analyzer and GC measurements. Almost all gaseous carbon was in CO and CO_2. Only small traces of CH_4, C_2H_4 and C_2H_6 was found. More than 60 mol % of the outlet gas was hydrogen. As can be seen in the Figure 1 carbon to gas conversion is highest at 750 °C as well as that there is less variance in the results as the temperature increases, which could be due to coke formation at lower temperatures. Coke was obtained in every experiment but it was partly due to technical problems with the feed nozzle. However, during the two hours run time there was no sign of catalyst deactivation or blockage formation despite the coke formation.

These experiments proved that the catalytic steam reforming of bio-oil aqueous fraction can be done even with relatively low S/C molar ratio of 3.8. The carbon to gas conversion was over 90 % above 650 °C and the hydrogen content of the outlet gas was high. The reactor and the feeding system was operated without major problems.

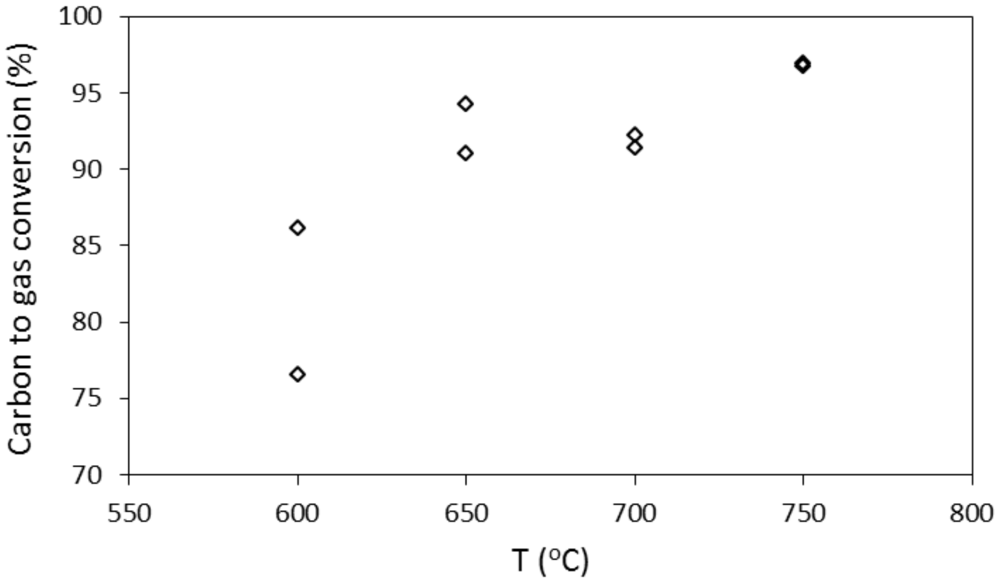

Figure 1. Inlet carbon conversion to gaseous carbon

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BEST OPERATING CONDITIONS FOR THE EPOXYDATION OF VEGETABLE OIL IN FED-BATCH REACTOR

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The epoxidation of vegetable oil has received a great interest from industry. One of the most important epoxidized vegetable oil is soybean oil. Typical process is based on epoxidation of unsaturated bonds of oil by peroxy-acids ($R\text{-}CO_3H$). The peroxy-acid is often generated in situ by reacting concentrated hydrogen peroxide with acetic or formic acid in the presence of a mineral acid as a catalyst in water phase, according to the following reaction:

$$H_2O_2 + RCOOH \leftrightarrows RCOOOH + H_2O \qquad (1)$$

Subsequently, the peroxy-acid migrates into the oil phase and reacts spontaneously to form the epoxide. This reaction is highly exothermic ($\Delta H = -55$ kcal/mol for each double bond) and an excessive increase of the temperature is prevented by adding a limited amount of a mixture of H_2O_2 and formic or acetic acid to the mixture of oil and acid catalyst [1]. However, the choice of operating conditions for the best yields should be balanced by safety considerations. In this light, the implementation of on-line and off-line prevention measures for the occurrence of runaway reaction is needed. To this aim, either "geometry-based criteria", or "sensitivity-based criteria" as defined in [2-4] have been developed for the specific reaction network, starting from the known kinetic model as defined in [1].

Main results have been tested on the experimental lab-scale reactor by varying the flow rate of reactive mixtures, the initial temperature of the bulk and that of the jacket. The best operating conditions, although in safe conditions, have been then checked with the aims of the maximum yield in epoxide.

Finally, a stability diagram for the definition of fair Conversion, smooth temperature profile plot as defined in [4] has been defined.

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ELECTROCATALYSIS FOR CARBON DIOXIDE RECYCLING

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CO_2 can be electrochemically valorised into different useful chemicals, such as CO[1] hydrocarbons (mostly mixtures of methane and ethylene), [2]formic acid or alcohols.[3] Nevertheless, converting CO_2 into alcohols is particularly interesting. Apart from the traditional industrial uses of alcohols, there is a growing demand for methanol as an energy vector. Methanol and its derivatives (ethers) is one of the most promising materials for hydrogen storage and has also been considered as fuel in direct methanol fuel cells.[4] It is widely accepted that hydrogen as an energy vector could be a solution for delivering energy from renewable sources, but the use of hydrogen is very difficult due to its extremely low critical point and very low density, and research on direct hydrogen storage and transportation has not revealed economically viable. This explains that attention has been focussed on alternative chemical hydrogen storage, where methanol is considered one of the most promising compounds, with a storage density of 1/7 g hydrogen per gram of methanol. However, methanol is currently produced by the oxidation of hydrocarbons or by thermo-chemical processes, which increase the negative environmental impacts and are relatively expensive production processes that mainly rely on fossil feedstock.

Therefore, the electroreduction of CO_2 to methanol has gained renewed and growing attention over the last decade. Different working conditions and cathodes of very different nature, using various types of electrochemical cells, have been investigated. Research efforts have been mainly focussed on studies with copper and copper alloys,[4] in which the catholyte and the anolyte flow through compartments that are separated by an ion exchange membrane (usually a Nafion cation exchange membrane). In this work a comparison of different electrocatalytic routes will be developed.

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SUPPORTED AND STRUCTURED CATALYSTS BASED ON CALCIUM AND CERIUM FOR THE PRODUCTION OF BIODIESEL

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INTRODUCTION

At present there is great interest in the intensification of the biodiesel production process (methanolysis) [1]. The conventional transesterification process is carried out using homogeneous catalysts, which are very active but pose significant problems [2]. Using heterogeneous catalysts would be preferable because they could be separated, regenerated if necessary and reutilized. From the practical point of view, structured catalytic reactors are even more interesting because they are hydrodynamically superior and avoid the necessity of catalyst separation. There are very few reports in the open literature on the use of structured methanolysis catalysts [3]. On the other hand, CaO is among the most investigated heterogeneous catalysts for the methanolysis reaction [4,5]. Within this context, this communication describes the use of different heteregeneous methanolysis catalysts based on calcium and cerium including catalysts structured on metallic monoliths.

EXPERIMENTAL

Several materials (Al_2O_3, SiO_2 and CeO_2) have been considered as supports of calcium (10 wt.% Ca) for preparing the catalysts. Commercial solids were used and the catalyts were prepared by incipient wetness impregnation. In the case of ceria, supports were also prepared by calcination of the solids obtained from a disolution of cerium nitrate using NH_4OH as precipitant agent as well as from the reaction of citric acid with cerium nitrate. In addition to the supported catalysts, Ca-Ce mixed oxides were also prepared from physical mixtures of the corresponding nitrates as well as by the citrate method. The structured catalysts were prepared by washcoating of Fecralloy monoliths (1.6 x 3 cm) with several suspensions that were prepared using additives such as fumed alumina. Catalysts were characterized by different techniques (SEM, XRD, S_{BET}, CO_2-TPD). Catalytic performance of the powder catalysts was assessed through the transesterification of refined sunflower oil with methanol at 60 °C in slurry reactors. For the structured catalysts, a monolithic stirrer tank reactor was used with two monolithic catalysts attached to the stirring bar.

RESULTS AND DISCUSSION

Among the supported catalysts, only those obtained with synthesized CeO_2 showed significant catalytic activity. Probably due to the acidic nature of Al_2O_3 and SiO_2, the corresponding catalysts achieved very low oil conversions (12 and 6 %, respectively, after 6 h of reaction). Figure 1 shows the results obtained with the supported CaO/CeO_2 catalysts (10 wt.% Ca) and mixed CaO-CeO_2 oxides with different CaO contents (5, 10 and 20 %). It can be seen that the supported catalysts gave similar results regardless of the ceria preparation method. The CeO_2 solids were tested and found to be inactive. The mixed oxides were more active than the supported catalysts and their catalytic activity increased significantly with the Ca content. Oil conversions well above 90 % can be obtained after 2 h of reaction at the low catalyst concentration used (2 wt.% referred to the oil) and methanol/oil initial molar ratio of 12:1. Figure 1 also includes the performance of metallic monoliths washcoated with a suspension of CaO containing alumina. Although the oil conversions obtained were higher than with the powdered supported catalysts the adherence of the catalytic layer was poor. In view of these results, the work is being continued with the structuration of catalysts based on mixed Ca-Ce compounds as catalytically active species with emphasis in the development of suitable preparation procedures that improve the adherence and catalyst stability.

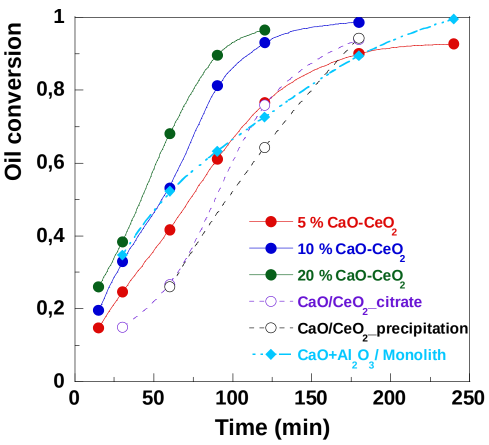
Figure 1

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Financial support by the Spanish Ministry of Economy and Competitiveness (ENE2012-37431-C03 grant) and by UPV/EHU (GIU11/13) is gratefully acknowledged.

ORAL PRESENTATIONS

Section IV.

Advanced Processing of Fossil Hydrocarbon Feedstocks

Modern Reactive Technologies for Natural Gas, Oil and Coal Processing

Chemical Processes for intensification of Oil Production

Natural Chemical Reactors for In-Situ Processing of Oil and Coal in Deposits

Chemical Reactors and Processes for Treatment of Heavy Hydrocarbon Feedstock and Shale Oil

CATALYTIC REACTOR FOR COMBUSTION OF LIQUID FUEL WITH CATALYST SUPPORTED ON METALLIC GAUZE

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Accumulation of unburned residues of fuel and formation of carbon on hot surfaces of reactors are the main problems at catalytic combustion of liquid hydrocarbons [1]. The combustion process is complicated by using mixed fuels, for instance, diesel fuel, which consists of hydrocarbons with different boiling temperatures (from 150 to 360 °C).

The reactor design was developed in such a way that an external heat supply is not required to evaporate liquid fuel. Heat transfer is carried out from the catalytic unit toward the evaporation one by radiation and heat conductivity through structural components. The temperature inside the evaporation unit is maintained in the range 450–500 °C in all operating regimes. On the one hand, this is a sufficient temperature to evaporate all diesel fractions, including fractions with the highest boiling temperature. On the other hand, there is no decomposition of hydrocarbons, which can lead to coke formation at this temperature.

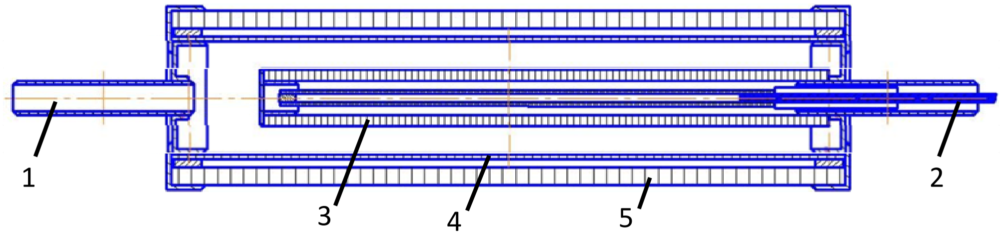

Fig. 1. Design of reactor. Main units: 1 – gas inlet; 2 – liquid fuel inlet; 3 – evaporation unit; 4 – gas distribution unit; 5 – four-layer catalyst unit

The reactor has a cylindrical shape and two different inputs: for gas fuel (1) and for liquid fuel (2). Feed of both fuels is provided by an excess pressure. The gas fuel is aimed only for initial heating of the catalyst unit to the operating temperature (above 300 °C). The evaporation unit (3) is made of a metal tube with slots that are spread along the entire length of the tube. The gas distribution unit (4) provides a uniform distribution of a gas flow in both radial and longitudinal directions. The catalytic unit (5) consists of four layers of gauze made of heat-resistant steel (wire diameter is 4 mm, grid size is 1 mm), which is coated with a layer of a Pt/Al_2O_3 catalyst having a thickness of 30-40 microns.

The reactor has demonstrated stable operating with n-decane and diesel fuel. A notable result is that the maximum capacity of the reactor was about 20 % higher with diesel fuel than with n-decane (15 and 18 kW/m^2, respectively, Fig. 2).

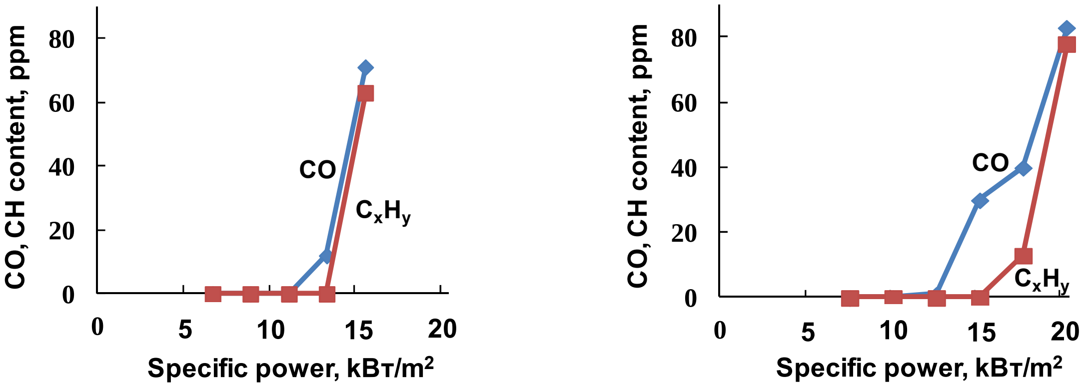

Fig. 2. Amounts of unburned CO and CxHy vs. specific power of catalytic reactor: n-decane (left), diesel fuel with sulfur content of 7 ppm (right). Maximum power of reactor was determined according to a following criterion: the content of CO or C_xH_y is equal to 50–60 ppm

Remarkably, no deterioration of the reactor effectiveness was observed throughout a 100-hour test with diesel fuels with the sulfur content of 7 and 50 ppm. Moreover, in both cases the operating range was extending. The lowest power below which the reaction fades out as a result of a temperature decrease shifted gradually toward lower temperatures during the testing process. The catalytic reactor faded out at the specific power below 7.5 kW/m^2 in the beginning of the test, whereas after 40–50 hours, the fading of reaction occurred at the specific power below 4 kW/m^2. Most likely, this effect is associated to the presence of SO_2 in the fuel. Interaction between SO_2 and alumina leads to the change of acid centers and to the formation of sulphate species on the alumina surface, which in turn interact with hydrocarbons. These phenomena beneficially affect the catalyst performance [2,3].

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NEW CONCEPTIONS FOR LOW-SCALE GTL

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Recent developments in unconventional gas production have shown that natural gas will be one of the world's main sources of energy and hydrocarbon feedstock, at any rate, up to the end of this century. Rapidly rising gas production has decreased its price in the USA fivefold relative to that of petroleum [1]. Abundant resources and low prices make natural gas very attractive as petrochemical feedstock. However, these new vast hydrocarbon resources are spread over large areas, and their sources usually have low debit and lifetime. Therefore, gas industry extremely needs new technologies, more flexible and low-scale, for gas processing and transportation.

Practically all traditional technologies for chemical processing of natural gas are based on its preliminary conversion in syngas. This complex, costly, and energy consuming stage consumes up to 60 % of the total capital and operating costs [2]. Its complexity restrains many practical applications of chemical processing of gaseous hydrocarbons, especially for low-scale production. The overcoming of these restrains is possible by two ways. The first one is the developing of more effective and less complex methods for syngas production. The second is the elaboration of principally other methods of direct natural gas conversion into chemicals without producing of syngas. We will consider the prospective possibilities for both of these routes.

The most attractive method for low-scale syngas production is the partial oxidation because of it is exothermic reaction with no need for external heating. From the thermodynamic point of view, the optimal conditions for the reaction

$$CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2$$

are attained at an oxygen-methane ratio 0.5. However, it is very difficult to maintain stable conversion of such rich mixtures in any non-catalytic process. Standard burners can rarely operate at this ratio less than 1.0. Although a number of alternative technologies for the partial oxidation of natural gas into syngas have been proposed [3], none of them proved to be technologically applicable.

Real possibility for economically effective small-scale syngas and hydrogen production not only for chemicals but as well for ecologically clean energy, transport and other applications opens recently developed method based on flameless low-temperature combustion of hydrocarbons in 3D matrix burners [3, 4].

As for direct methods of natural gas conversion, several possibilities can be discussed. Among them the most known and developed are direct oxidation of methane to methanol (DMTM) [5, 6] and oxidative coupling of methane (OCM) [5]. Some other technologies are trying to make use of the halogenation of natural gas or its oxidative conversion into acetylene with subsequent catalytic hydration to ethylene and oligomerisation of the later to liquid fuels (see, e.g. in [5]). But these routes are too complex and multi-stage to be really competitive.

Recently we have suggested an alternative way for the low-scale GTL which is based on different reactivity of light hydrocarbons C_1-C_5 (Fig. 1), the main components of natural gas [7]. At appropriate conditions selective oxidative cracking of complex gas mixtures of real natural or oil associated gas let to practically completely convert heavier C_3-C_5 hydrocarbons into olefins, mainly ethylene, hydrogen, methane and carbon monoxide without converting methane itself.

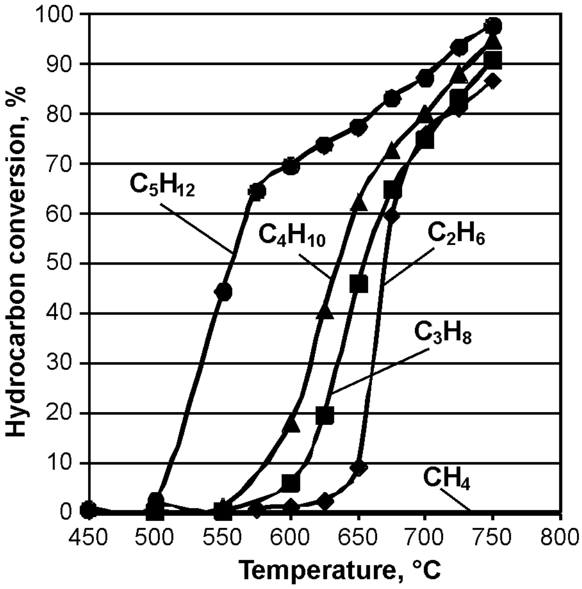

Fig. 1. Temperature dependences of the oxidative conversion of C_1-C_5 alkanes ($[C_nH_{2n+2}]$ = 5 mole %, $[O_2]$ = 2.5 mole %, balanced by N_2, t_r = 2 s)

The possibility to obtain ethylene-carbon monoxide or methanol- carbon monoxide mixtures with regulated ratio of these components by direct oxidation of hydrocarbon gases opens the possibility for production of some valuable chemicals and octane additives by subsequent catalytic carbonilation or oligomerisation of olefins and oxygenates (Fig. 2), and can be considered as an alternative more simple route for natural gas conversion to liquid products (GTL) and dry methane gas.

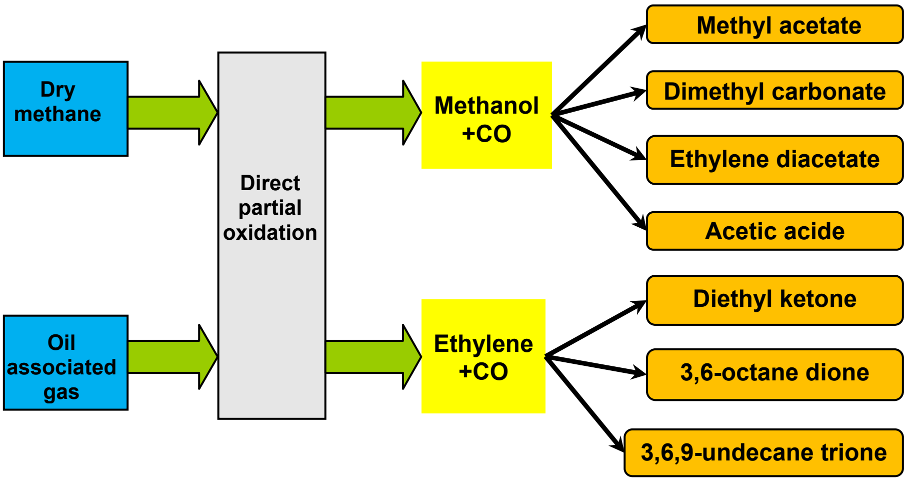

Fig. 2. Alternative GTL route for production of chemicals with high added value

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OP-IV-3

COMPLEX MODELING SYSTEM FOR OPTIMIZATION OF REACTION PROCESSES OF TRADE GASOLINE PRODUCTION

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The main challenge facing the modern oil industry is to improve the resource efficiency of oil refining and the quality of oil products. However, the processes of motor fuels production are extremely difficult to optimize due to several factors: the multistage technology; changing composition of raw materials and the activity of catalysts used during the preparation steps of motor fuel components, nonadditivity of trade gasoline physicochemical properties. The solution to such multi-factor and multi-criteria optimization problem can be the use of mathematical modeling method.

At the Department of Fuel Engineering and Chemical Cybernetics of Tomsk Polytechnic University has developed an complex approach for optimization of reaction processes of trade gasoline production and created modeling system, consisting of the following modules: module of automatic systematization of chromatography data, module of catalytic reforming reactor block modeling, module of catalytic isomerization of pentane-hexane fraction reactor block modeling; module of trade gasoline blending recipes calculation.

Reforming and isomerization modules are based on kinetic models of multi-component catalytic processes and take into account reactivity of substances, lifetime of the catalyst and non-additivity of hydrocarbon mixtures properties [1, 2].

$$G\cdot\frac{\partial C_i}{\partial z}+G\cdot\frac{\partial C_i}{\partial V}=\sum_{j=1}^{m}a_j\cdot r_j \qquad \text{at } z=0\ \ C_i=C_{i,0};\ T=T_{en}$$

$$\text{at } V=0\ \ C_i=C_{i,0};\ T=T_{en} \tag{1}$$

$$G\cdot\frac{\partial T}{\partial z}+G\cdot\frac{\partial T}{\partial V}=\frac{1}{\rho\cdot C_p^{\mathrm{m}}}\sum_{j=1}^{m}Q_j\cdot a_j\cdot r_j \qquad a_j=\frac{k_{j,current}}{k_{j,initial}}$$

where *z* – volume of raw material processed from the moment when the fresh catalyst was loaded, m^3; *G* – raw material flow rate, m^3/h; *z* = *G*·*t* (*t* – time of catalyst work from the new catalyst load, h); C_i – concentration of i-th component, mol/m^3; *V* – volume of the catalyst layer, m^3; *a* – catalyst activity; *ρ* – density of mixture, kg/m^3; C_{pm} – heat capacity of mixture, J/(kg·K); Q_j – j-th reaction heat, J/mol; *T* – temperature, K; r_j – j-th reaction rate, mol/(m^3·h); $k_{j,initial}$ – rate constant of j-th reaction on the fresh catalyst; $k_{j,current}$ – rate constant of j-th reaction on the catalyst at present time.

Calculation of trade gasoline blending recipes taking into account the reaction interaction between the hydrocarbons [3]. All this allows to develop recommendations for inclusion of different raw materials (reformate and isomerizate 1 and 2 in the table) in blending.

With the use of the developed complex modeling system gasoline blending recipes on Russian refinery «KINEF» was optimized.

Table – Recipes for EURO-5 gasoline blending, % wt.

FLOWS	Brand of gasoline					
	REGULAR-92		PREMIUM-95		SUPER-98	
	1	2	1	2	1	2
Reformate №1	44	–	44	–	44	–
Reformate №2	–	38	–	38	–	38
Isomerizate №1	44	–	38	–	30	–
Isomerizate №2	–	46	–	38	–	27
Isopentane	10	13	10	14	12	20
MTBE	2	3	8	10	14	15

As seen from the table, the gasoline blending recipes using reformates and isomerizates composition 1 and 2 are different.

Thus, accounting of the involved flows composition and non-additive of blending increases the yield of trade gasoline by an amount Δ, where Δ - addition due to the forecast of the product yield and the octane number of components of motor fuels obtained during the reforming and isomerization processes. Variability of technological mode of reforming and isomerization process caused by changing the composition of the feedstock and the catalyst activity and determines the value of Δ in the motor fuels production process.

Refinement of gasoline blending recipes depending on the composition of involved in blending flows, to avoid overspending of high quality and expensive components can improve resource efficiency of trade gasoline production process.

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A COMPARATIVE STUDY OF FIXED-BED AND DISPERSED CATALYTIC UPGRADING OF HEAVY CRUDE OILS USING-CAPRI

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ABSTRACT. In situ Catalytic upgrading Process (CAPRI) incorporated with Toe-to-Heel Air Injection (THAI) for oilsands recovery and upgrading was studied at the laboratory scale using fixed-bed and dispersed catalyst processes. Upgrading was evaluated in terms of API gravity, viscosity and yield of light distillates of the produced oil.

INTRODUCTION: As light oil reserves decline, attention has been shifted to large deposits of untapped heavy oil and bitumen energy resources which account for about 70 % of the world's total 9-13 trillion barrel oil resource [1]. Previous studies of fixed-bed process by Shah et al. [2] and Hart et al. [3] showed that asphaltenes, coke and metal deposition drastically deactivates the catalyst. In this study, a comparative study was carried between fixed-bed and dispersed catalyst.

EXPERIMENTAL: Heavy oil feedstock of viscosity (1091 mPa·s), API gravity (14^{o}API), Asphaltene 10.3 wt.% and sulphur 3.52 wt.% from the THAI process Kerrobert oilfield (Canada) was used. The procedure for the fixed-bed experiment is detailed in previous studies [2,3]. The dispersed catalyst experiments were conducted using a batch autoclave (100 mL) at temperature 425 °C, catalyst-to-oil ratio (CTO) 0.1, agitation 133 rpm and residence time 10 minutes. Pellets (0.14 x 0.571 ± 0.293 cm) and particles (35 ± 1.08 μm) of CoMo/alumina catalyst were used. The samples were analysed using density meter, rheometer, and ASTM-D2887 distillation. The conversion of high-boiling fractions (343 °C+) was calculated using Equation 1.

$$\% \text{ Conversion} = [(343°\text{C+ in Feed} - 343°\text{C+ in Product}) / 343°\text{C+ in Feed}] \times 100 \quad (1)$$

RESULTS AND DISCUSSION: The level of upgrading from fixed-bed, dispersed catalysts and thermal cracking alone are presented in Table 1 and Figure 1. The produced oil from dispersed catalyst showed the highest level of upgrading in API gravity (change of 8.7°), viscosity (7mPa.s) and conversion of high boiling fraction (59.7 %) compared to thermal and fixed-bed systems.

Table 1. Upgrading from fixed-bed, dispersed catalyst and thermal cracking at 425 °C, 20 bar, CTO 0.1, 133 rpm and 10 minutes residence time

Experimental Run	Change in API (°)	Viscosity (mPa·s)	Conversion (%)	Coke (wt.%)	Gas (wt.%)	Liquid (wt.%)
Thermal (No catalyst)	6.6	8	33.1	12.95	8.15	78.9
Dispersed micro catalyst	8.7	7	59.7	7.10	8.05	84.85
Fixed-bed catalyst	5.6	28	46.4	1.86	3.34	93.8

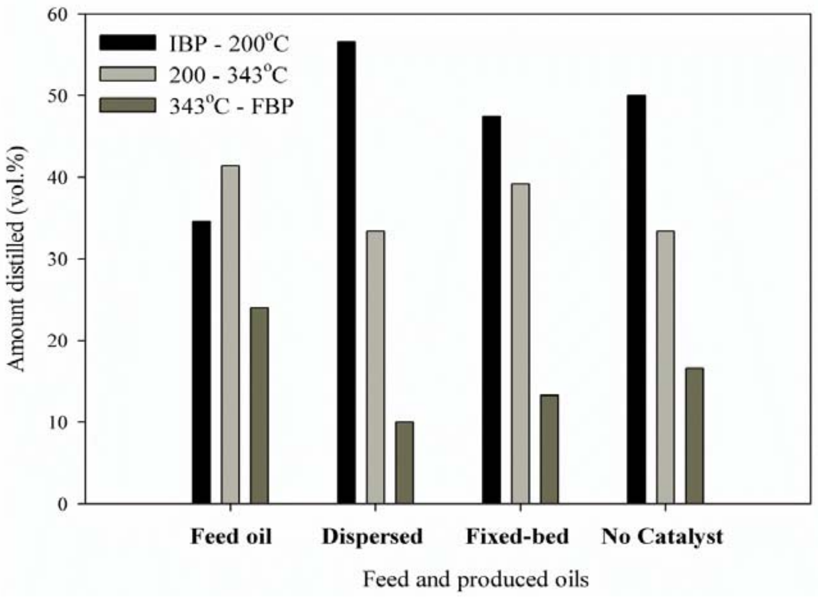

Figure 1. Simulated distillation of feed and produced oils from fixed-bed and dispersed catalyst systems at 425 °C, 20 bar, 0.1 CTO, 133 rpm and 10 minutes (where; IBP, FBP are initial and final boiling point)

Figure 1 also shows that the upgraded oils contain more low-boiling fractions and low residue compared to the feed oil. This is attributed to the dispersed catalyst promoting faster cracking reactions due to its reduced particle size, increased surface area, high heat and mass transfer in comparison to the fixed-bed catalyst.

CONCLUSION: CAPRI was investigated in fixed-bed and dispersed catalyst processes. It was found that the produced oil improved in API gravity, viscosity, as well as yield of distillates.

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Section on PHOTOCATALYTIC REACTORS

FAST DEGRADATION IN IMMOBILIZED PHOTOCATALYTIC MICROREACTORS

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Photocatalytic reactors form an interesting platform for environmental and chemical applications. Despite the attractive features of photocatalysis, true implementation remains limited. Fundamental understanding of the processes should include mass transport, light distribution and true reaction kinetics. Here we present a microreactor platform incorporating an immobilized photocatalytic layer in which mass transport and light distribution are accurately desribed. Experimental observations indicate very fast degradation kinetics for a variety of compounds, that are orders of magnitude faster compared to generally reported. The microreactor is modeled by implementing a flux boundary condition into the convection diffusion equation [1]. The flux boundary condition describes the complete mass transport, light distribution, and reaction inside the porous catalyst film. This approach is crucial as it allows one to obtain true reaction kinetics, instead of overall or apparent conversion kinetics. Only with true kinetics it will be possible to compare catalysts accurately. As such, a Thiele modulus can be defined that includes the light adsorption characteristics and an internal effectiveness factor is presented that elucidates the relative limitations of mass and light transport within the photocatalyst layer.

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OP-Ph-2

COUPLING RADIATION TRANSPORT WITH CFD MODELLING FOR THE SIMULATION OF PHOTOCATALYTIC REACTORS

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This work reports the development of a CFD-based model for the simulation of photocatalytic reactors that integrates hydrodynamics, species mass transport, chemical reaction kinetics, and irradiance distribution within the reactor. In addition to the resolution of the momentum, heat and mass conservation equations required for the simulation of conventional thermally activated chemical reactors, modelling of photocatalytic reactors requires the estimation of the radiation field by means the resolution of the radiation transfer equation (RTE). The reason is that photocatalytic reactions are initiated by the absorption of photons by the catalyst, and therefore the rigorous kinetic description of the process requires the inclusion in the model of the local volumetric rate of photon absorption.

Considering the catalyst suspension of a photocatalytic slurry reactor as a pseudo-homogeneous medium, and assuming that the emission of radiation can be neglected at the low operation temperatures of photocatalytic processes, the RTE takes the following form [1]:

$$\frac{dI_{\lambda,\underline{\Omega}}(\underline{x},t)}{ds} = -\underbrace{\kappa_\lambda(\underline{x},t)I_{\lambda,\underline{\Omega}}(\underline{x},t)}_{\text{ABSORPTION}} - \underbrace{\sigma_\lambda(\underline{x},t)I_{\lambda,\underline{\Omega}}(\underline{x},t)}_{\text{OUT-SCATTERING}} + \underbrace{\frac{\sigma_\lambda(\underline{x},t)}{4\pi}\int_{\Omega'=4\pi} p(\underline{\Omega}'\rightarrow\underline{\Omega})I_{\lambda,\underline{\Omega}'}(\underline{x},t)\,d\Omega'}_{\text{IN-SCATTERING}}$$

where $I_{\lambda,\Omega}$ is the intensity of photons with wavelength λ propagated along direction Ω, κ_λ is the volumetric absorption coefficient, σ_λ is the volumetric scattering coefficient and $p(\Omega'\rightarrow\Omega)$ is the phase function. The solution of this equation permits the evaluation of the radiation field at any point inside the reactor space. Once the intensities are known, the incident radiation can be readily obtained and the local volumetric rate of radiation absorption rate can be calculated multiplying this value by the absorption coefficient.

The CFD model has been developed using the commercial software Ansys Fluent 14.5. An annular photoreactor working in recirculation with a reservoir tank has been simulated, being the experimental system available in the laboratory for getting the validation data using the photocatalytic oxidation of methanol as model reaction.

Assuming that there is no coupling between the velocity and radiation fields, the model can be solved in three steps. First, the equations of conservation of mass and momentum were solved for getting the flow field across the computational domain. Then, the velocity values were kept and the radiation field was computed, being both calculations carried out assuming stationary state. Finally, the conservation of species equation was solved in a transient mode, allowing the simulation of the performance of the photocatalytic reactor as a function of the irradiation time. The reaction rate was assumed to follow a pseudo-first-order kinetics dependence on methanol concentration and the radiation absorption, being the rate constant estimated from experimental data at low optical thickness. Those conditions allow the reliable determination of the reaction rate through the assumption that the small gradients in the photon absorption rate do not affect the volume-averaged reaction rate [2].

Figure 1 shows the calculated radial profiles of irradiation are more pronounced as the catalyst concentration increases. Figure 1 also shows the mass fraction of formaldehyde formed in the reaction at a specific time. Predictions of the model show good agreement with experimental data, with errors below 10 % in certain cases.

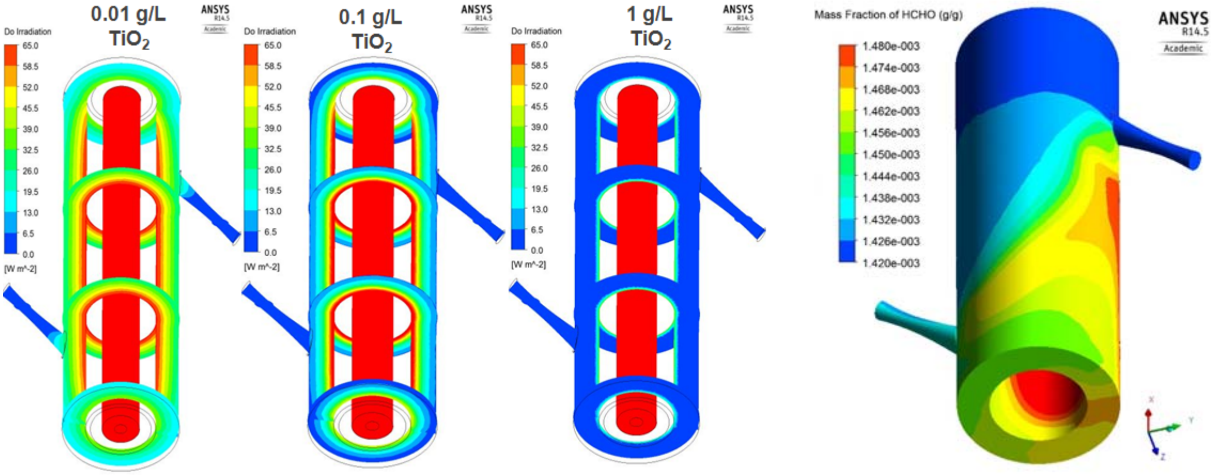

Figure 1. Contours of irradiance distribution for different TiO_2 concentration (left) and contour of mass fraction of HCHO after 30 min of irradiation time with 0.05 g/L TiO_2

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Acknowledgements

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OP-Ph-3

UV LED PROTOTYPE PHOTOREACTOR FOR STANDARDISED PHOTOCATALYTIC ACTIVITY TESTS

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ISO standards for the standardisation of photocatalytic activity present some controversial features [1] so that they are rarely used by researchers. Moreover, the standards do not provide correct experimental data for kinetic modelling and reactor design since they are only focused on the comparison of the activity of materials for evaluation. This work describes a simple reactor to test the efficiency of different photocatalytic materials in a comparable way while also providing suitable results for the determination of intrinsic kinetic parameters that are independent of light intensity and reactor geometry; such information is of benefit for modelling and eventually scale-up to a pilot scale reactor. The reactor (Figure 1) is a constant volume batch system equipped with a cooling jacket to allow temperature control. The catalytic materials to be tested are immobilized on disks of 40 mm in diameter that will be located at a fixed distance of 50 mm from the light source by the use of a PTFE frame. The use of a frame facilitates the possibility of oxygen bubbling, withdrawal of samples, and to measure pH, temperature, oxygen or any other parameters required to follow the reaction. Stirring ensures well-mixed conditions for isothermal operation and prevention of mass transport limitations.

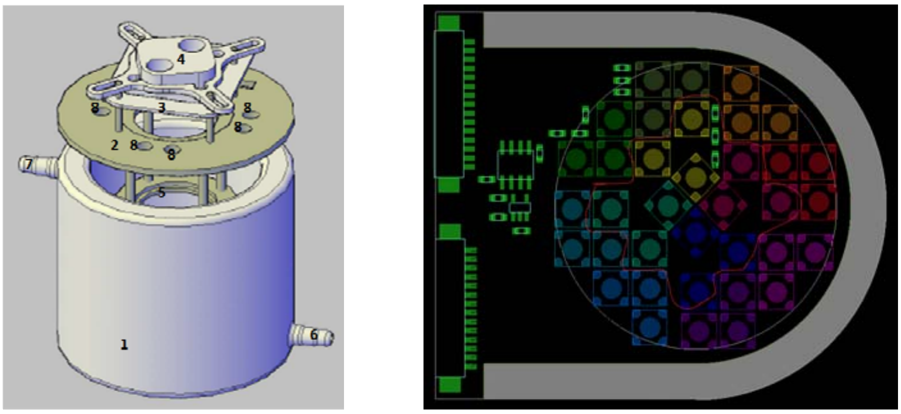

Figure 1. Scheme of the reactor (left). (1) Reactor vessel, (2) frame to hold catalyst, LED unit and cooler, (3) LED board, (4) cooler, (5) catalyst holder, (6) inlet coolant, (7) outlet coolant, (8) sample ports. Diagram of the UV LED board (right)

Intrinsic kinetic modelling with explicit radiation absorption effects requires precise control of irradiation conditions, achieved by the use of a computer-controlled UV LED light engine coupled to a cooling unit bolted to the upper part of the frame. The light engine contains 36 UV-A LEDs (Figure 1) distributed to deliver an almost uniform optical power density over the photocatalytic disk. The system provides an interface with a personal computer for user-control of the output power both by pulse width modulation (PWM) or direct current control.

Resolution of the radiative transfer equation has been carried out by means of the discrete ordinate method implemented in Fluent v14.5 software (Ansys Inc.), showing that a reasonably homogenous irradiation flux is achieved at the catalytic surface (Figure 2). Estimation of radiation absorption by the catalyst requires knowledge of the optical properties of the materials, especially the absorption coefficient. Absorbed radiation would obviously increase with the thickness of the catalyst layer, reaching a maximum that also depends on the irradiation power. As an example, Figure 2 shows the dependence of the absorbed radiation for a semiconductor film of P25 TiO_2 (Evonik Industries AG) immobilised on glass. The optimal thickness that captures almost all the available radiation at the catalyst surface can be easily derived from this plot.

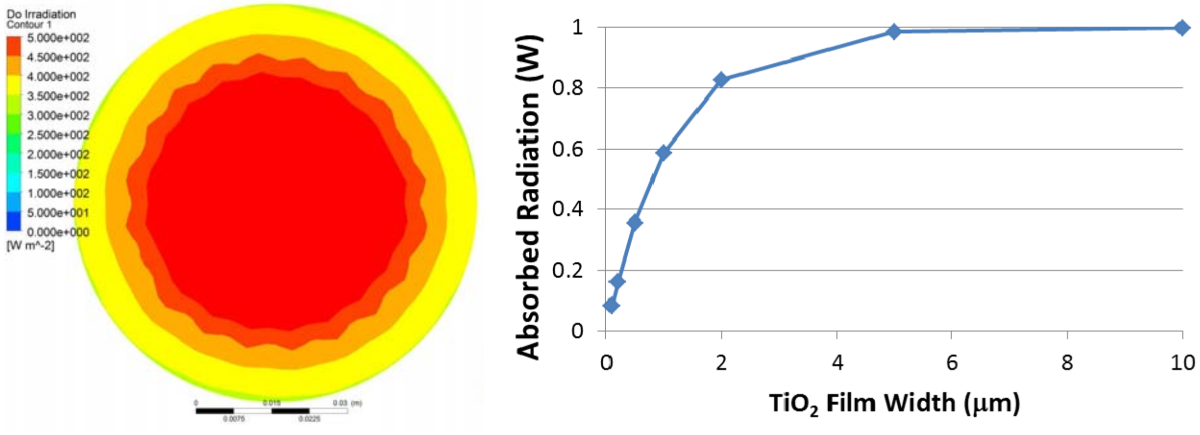

Figure 2. Contours of irradiance distribution in the photocatalytic disk (left). Estimation of the optimal thickness of P25 TiO_2 films (right)

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Acknowledgements

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OP-Ph-4

THE PHASE FUNCTION ON THE RADIATION AND ABSORPTION FIELD IN A PHOTO-CREC WATER-II REACTOR

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Abstract

The phase function is a critical parameter for the photocatalytic reactor simulation determined in this study, using both Monte Carlo and experimental radial irradiation profiles. A novel optical probe coupled with a fiber optic spectrophotometer system is used to measure irradiation inside a Photo-CREC-Water reactor at various radial positions. It is shown that the forward scattering mode, namely g = 0.83 for the Henyey-Greenstein phase function parameter is prevalent. This allows better suited calculations for the photon absorption field or LVRPA.

Keywords

Local Volumetric Rate of Photon Absorption; Monte Carlo, Photoreactor Engineering

Introduction

In this study, irradiation profiles, Local Volumetric Rate of Photon Absorption (LVRPA) and Total Rate of Photon Absorption (TRPA) are used to obtain and validate scattering phase functions for Degussa P25 in a Photo-CREC Water-II annular reactor.

A Monte Carlo algorithm for solving the radiation equation was used to calculate the LVRPA for the annular photoreactor at different photocatalyst concentrations. *Figure 1* reports the LVRPA for a 50 mg L^{-1} concentration with an isocratic phase function ($g \to 0$).

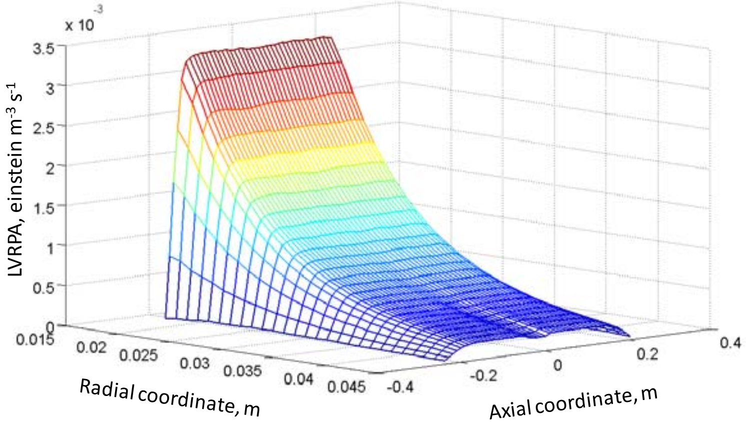

Figure 1. 3D profile of the LVRPA inside the Photo-CREC Water II for 50 mg l^{-1}, Isocratic phase function ($g \to 0$)

Photon trajectories and absorption positions were obtained by considering the UV Lamp emission spectra. Absorption and scattering coefficients were considered

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wavelength dependant as suggested by Cabrera et al. (1996). Boundary conditions at the wall were chosen in agreement with experimental data in the Photo-CREC-Water. Henyey-Greenstein (H-G) and binomial phase functions where used to simulate isocratic, forward and backward scattering as shown in *Figure 2.*

Figure 2 shows that there are large deviations from the isocratic phase function. This is particularly true for 50 mg l l^{-1} (a) and 200 mg l^{-1} (b), with high forward scattering parameters (e.g. g=0.85).

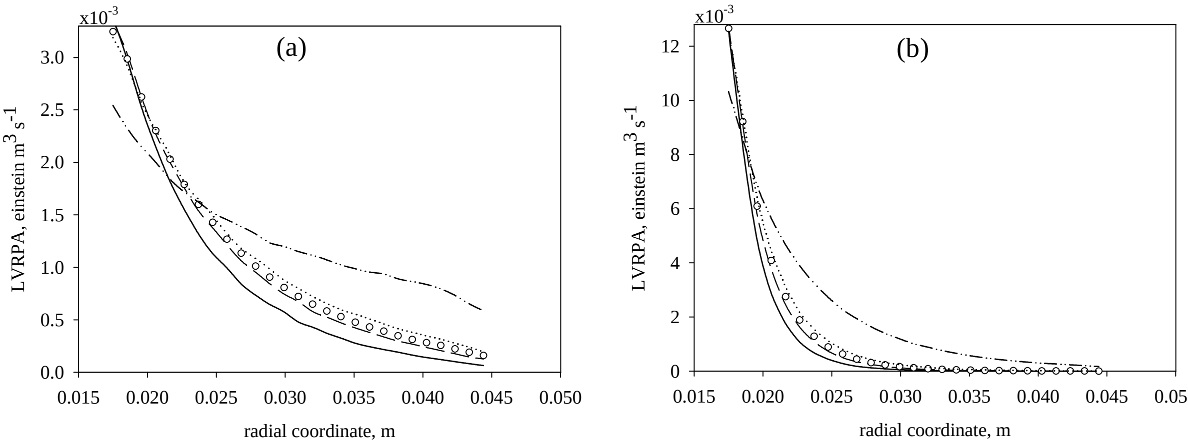

Figure 2. Radial irradiation profiles for (a) 50 mg l^{-1} and (b) 200 mg l^{-1} (○) isocratic, (—)H-G for g = -0.85 (---) H-G for g = -0.2 (••••) H-G for g = 0.2 (–••–) H-G for g = 0.85

Thus, the use of an adequate phase function is critical to establish a proper radiation distribution inside a Photo-CREC-Water Reactor. To assist in this task, a novel probe was designed. This probe (refer to *Figure 3*) allows one to measure irradiation at different radial positions while the TiO_2 particle slurry is being recirculated.

This optical probe was placed in the middle axial window position. As a result, radial radiation profiles were measured for different catalyst concentrations. The obtained data was fitted to simulated results with the “g” parameter being adjusted. *Figure 4* shows that the H-G phase function parameter that better fits the experimental profile is g = 0.83. This 0.83 value shows that there is a dominant forward scattering in the Photo-CREC-Water with Degussa P-25.

Furthermore, when the simulated TRPA was calculated from the data of *Figure 4*, it was found that the Monte Carlo Model predicts an optimum catalyst concentration close to 150 mg L^{-1}. This result is in agreement with experimental values reported by Moreira et al. (2011).

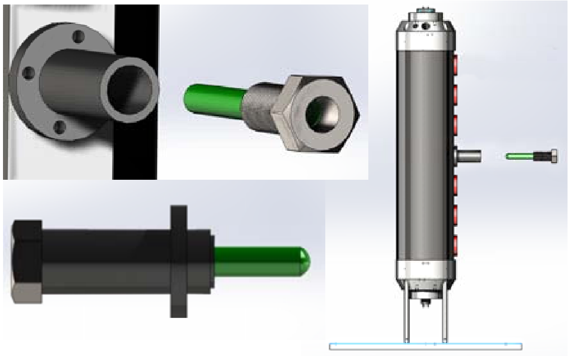

Figure 3. Basic geometry of the probe attached to the reactor

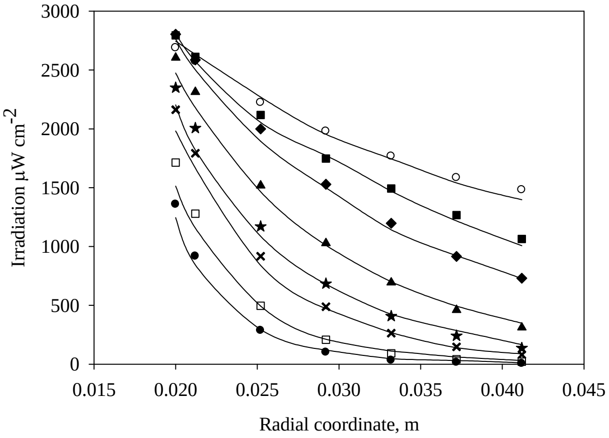

Figure 4. Experimental and Monte Carlo simulated irradiation at various radial positions for H-G with g = 0.83

Conclusions

An experimental and simulation method is proposed for calculating scattering phase functions in photocatalytic reactors. The determined phase function values are found to be valuable for establishing both radial LVRPA and TRPA profiles and their changes with photocatalyst concentration.

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EFFECTS OF AGGLOMERATE FORMATION ON PERFORMANCE OF PHOTOCATALYTIC SLURRY REACTORS

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Introduction

Evaluation of the photocatalytic activity of semiconductors in liquid phase reactions is often performed in slurry reactors. These reactors contain the photocatalyst as a dispersed solid phase and are illuminated with either internal or external light sources. Besides by the intrinsic catalyst properties, the performance of a photocatalytic slurry reactor is largely determined by the light distribution profile in the reactor. Light propagation and distribution in slurries is determined by a combination of forward and backward scattering, as well as light absorption by catalyst particles [1]. In turn, a major factor affecting light scattering and absorption is the extent of agglomeration of the slurried catalyst particles. Some groups have quantified the influence of agglomerate size on the optical properties of photocatalyst particles [1-3]. The agglomeration tendency of the catalyst particles is the result of Van der Waals and electrostatic forces. The pH, and adsorption of solvent, reactant and product molecules often results in a change in surface properties, which consequently influences the interaction of the particles and the state of agglomeration. [3] Usually the state of agglomeration and the optical properties of the reactor are considered constant throughout a photocatalytic experiment, while changes in agglomeration as a function of time are very likely profound in studies evaluating reaction kinetics in photocatalysis.

Experimental

In this contribution the effect of various process parameters on the rate of changes in state of agglomeration, and its contribution to changes in photocatalytic rates will be discussed. To this end, we have used a set-up which allows determination of light transmission in slurries by variation of the distance of an optical probe in the slurry relative to the external illumination source (led to the reactor by an optical fiber bundle). We have combined this light intensity measurement with in-situ measurements of agglomeration (FBRM probe technology), and pollutant degradation by UV-Vis measurement.

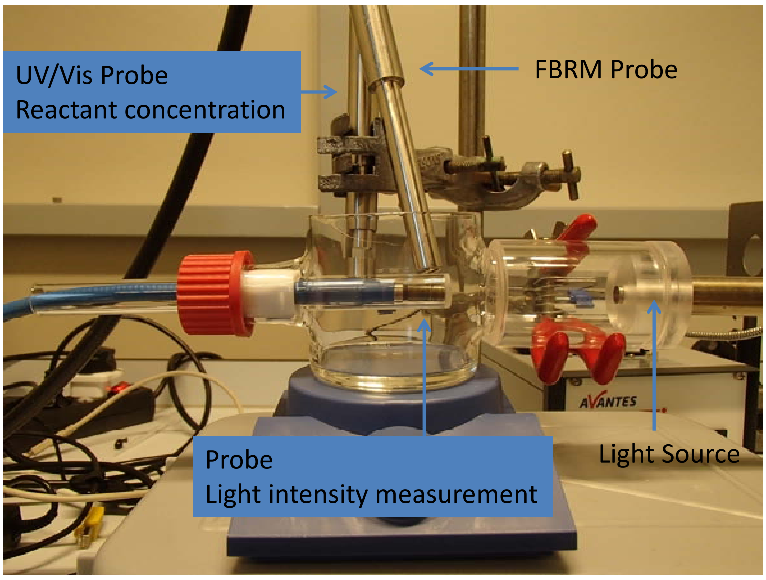

Figure 1: Image of the setup for photocatalytic reaction evaluation.
This setup includes the measurement of light transmission (spectrometer), agglomeration (FBRM) and reaction progression (UV-Vis).
Both the FBRM probe and the UV-Vis probe are inserted in the liquid.
If needed, a pH probe can also be added to the vessel

During the presentation, first the methodology of Focused Beam Reflectance Measurements will be discussed. Second, the correlation between process parameters including pH, catalyst loading, catalyst composition and/or morphology, and the rate of changes in agglomeration of TiO_2 (and other, novel and promising photocatalytic materials such as C_3N_4), will be demonstrated. Also the transients in optical properties of the slurry (by the transmission measurements) will be quantified. Finally, the consequences of the changing agglomeration distribution for photocatalytic kinetics will be evaluated.

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PHOTOCATALYTIC DEGRADATION OF PHENOL USING LEDs – MODELLING AND CONTINUOUS REACTOR DESIGN

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Tom Van Gerven[1]

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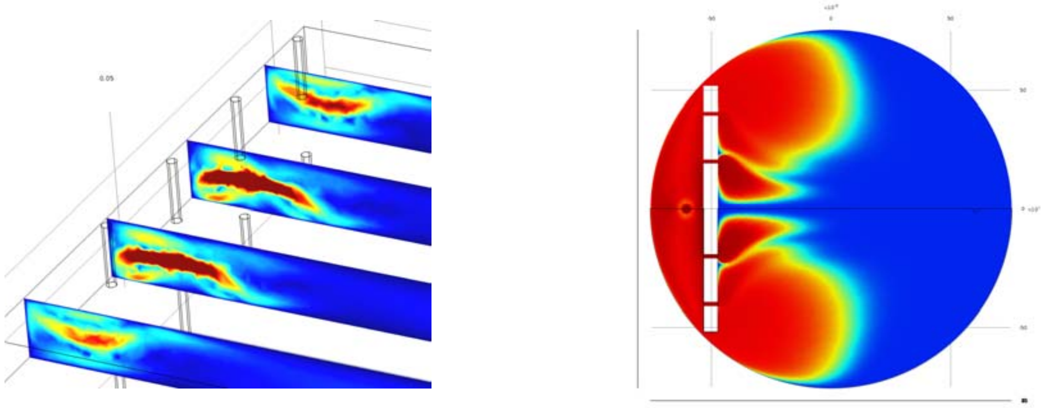
Introduction

Degradation of aqueous phenol containing effluents by photocatalysis is studied within the scope of this work. Phenol can be found as a potent pollutant in the effluents of various industries including paper, pharmaceuticals, and plastic raw materials. Phenol elimination using a semiconductor catalyst, namely TiO_2 has been studied and reported in detail [1–3]. Chemical reaction kinetic data and operating parameter optimization for this process are widely available for batch, slurry reactors [4] as well as continuous thin film reactors [1].

The focus of this work is to investigate the performance of LEDs which emit near UV radiation (375nm) in photocatalytic phenol degradation process. LEDs have much more monochromatic spectra compared to the mercury vapour lamps. Moreover, the light output efficiency of LEDs is widely known to be several orders of magnitude higher than the mercury vapour lamps. LEDs as light source alternatives were investigated previously for phenol degradation by Vilhunen et al. [5]; however, they used deep UV emitting LEDs (265nm) to excite H_2O_2 directly without using TiO_2 as catalyst. This work also aims to model phenol elimination reactors by using CFD tools coupled to partial differential equation solvers (COMSOL Multiphysics®) while emulating the polluted effluents in the laboratory to back the model outputs with experimental data.

Results

Before performing continuous experiments, a batch slurry reactor was used to obtain the optimum process variables. Up to 87 % degradation of phenol was achieved within 4 hours of reaction. Maximum photonic efficiency was found to be 0.0086 which is comparable to microreactors [6]. Two different angular full widths at half maximum (FWHM) angles, namely 120° and 40° were investigated while the 40° was found to have twice as much of the photonic efficiency as the 120°. The maximum reaction rate was found to be $8.7x10^{-11}$ mol/s in these batch experiments. Two continuous reactors were designed to model the mass transfer and illumination limitations as shown in Figure 1. The circular reactor was built from quartz and can be used for modelling laminar and turbulent flow regimes while the rectangular reactor, which was built from polymethyl methacrylate can be used to model chaotic mixing and its effects on mass transfer, thus reaction rate.



(a) **(b)**

Figure 1. Two continuous reactor designs for modelling and process intensification. Rectangular (a) showing oscillating velocity contours and circular (b) showing the concentration contours at start-up

With the current batch reactor data and the results from the two continuous designs, this work gives up-scalable reference kinetic data and mathematical models on LED photocatalytic reactors for any industry with phenol polluted effluents.

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Acknowledgements

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A SCALE-UP CASE STUDY OF A MULTIPHASE PHOTOCATALYTIC REACTOR – DEGRADATION OF CYANIDE IN WATER OVER TiO_2

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Photocatalysis has various applications including degrading organic contaminants in aqueous solutions, oxidizing liquid hydrocarbons, and reduction of carbon dioxide into valuable hydrocarbons. For conventional catalytic reactors, a wide body of literature exists with criteria to determine the rate-limiting-step, and guidelines for proper reactor design and scaling-up. For photocatalytic reactors, such literature is largely absent. The situation in photocatalysis is more complex: in addition to a non-uniform concentration field, the optical field variable of relevance, *i.e.*, the rate of photon absorption by the particles, is also not constant throughout the reactor. This local volumetric rate of photon absorption appears in the kinetic expression. Gradients in the rate of photon absorption lead to gradients in the reaction rate, which in turn lead to concentration gradients, even if the catalyst is homogeneously dispersed and particle-level gradients can be ignored.

In recent years, we developed guidelines and design rules for slurry [1] and bubbly slurry photocatalytic reactors [2] derived from simple mathematical models. Our approach was to develop simple analytical expressions based on logical simplifications, avoiding complex numerical simulations. To achieve this, we used a 1D description of the reactor, considering both low and high light intensities, leading to a linear and square root dependence of reaction rate on the local volumetric rate of photon absorption, respectively. Such analytical expressions can be used to predict the quantum efficiency, quantify photon losses at different steps of the chain of photocatalytic events, and to calculate the relevant optical thickness for kinetic measurement studies in slurry photocatalytic reactors. With a similar approach, we recently provided a simple criterion to determine whether or not the performance of an unmixed phtotocatalytic slurry reactor is limited by diffusion [3].

In the current paper we will present a scale-up strategy for photocatalytic processes, based on the design rules obtained in our previous papers. We will focus on a case study on degrading organic pollutants in the effluent of an integrated gasification coal combustion plant over TiO_2, with the target of degrading cyanide to below its allowable emission threshold set by European legislation [4]. We consider a simple 1D photonic description of a photoreactor, in the direction of incident solar light, and implement a bidirectional scattering model for photocatalytic particles and bubbles to calculate the local rate of photon absorption and the photon absorption efficiency in the photoreactor.

We show the interplay of different efficiencies that determine the overall apparent photonic efficiency and the reactor volume required to achieve a certain objective in conversion. The main losses in the overall photonic efficiency are in the electron-hole trapping and surface-reaction steps. The chosen reactor configuration is rectangular slurry-bubble-columns-in-series to ensure a good mass transfer rate per photoreactor while approaching plug-flow behavior as a sum, and a high reactor surface-area-to-volume ratio for a good capture of incident photons (see Fig. 1). We will show that for the reaction studied there is no need to separate the aeration and the photocatalytic reaction into two unit: integration of these two functions reduces the reactor size and is a good example of process intensification. We show that the large-scale degradation of cyanide to below European emission limits is achievable.

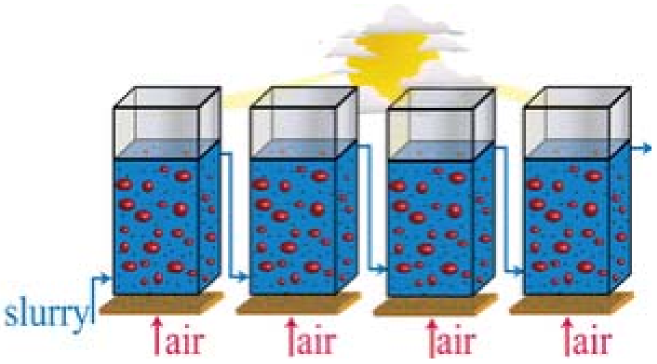

Figure 1. slurry-bubble-columns-in-series are a good option for photocatalytic water cleaning using sunlight

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POSTER PRESENTATIONS

A TECHNOLOGY: VALUE-ADDED DERIVATIVES OF GLYCEROL FROM BIODIESEL INDUSTRY

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Glycerol is one of the by-products of transesterification of palm-based methyl ester for the production of biodiesel. Value-added product such as hydrogen, wood stabilizer and liquid chemicals from catalytic treatment of glycerol can improve the economics of the biodiesel production process. Catalytic conversion of glycerol can be used for production of value- added liquid chemicals. Strategically, it provides versatility to convert glycerol in a value added product, thus depleting a residue.

Both conventional thermal activation and microwave irradiation are able to selectively transform glycerol into value-added liquid product. This reaction exhibits a double advantage: (1) it provides a selective route for glycerol valorization, and (2) it enables glycerol and a new strategic ramw material for industries producing acrylonitrile. In this work, a systematic work has been conducted to evaluate the effects of operating conditions on palm-based glycerol conversion to liquid chemical products in the presence of heterogeneous acid catalysts.

Keywords: biodiesel, acrylonitrile, heterogeneous catalyst, microwave technology

HYDROGEN PRODUCTION FROM BIO-RENEWABLE FEEDSTOCK IN FIXED-BED REACTOR OVER Co/Ce-La CATALYST

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In the last years, hydrogen production from bio-ethanol catalytic steam reforming reactions has reached a great importance due to the availability of bio-ethanol and the application of hydrogen in fuel cells [1-3]. Within the transition metal oxide catalysts that used in this process, Co based catalysts have received less attention in spite of their high capacity for C-C bond breaking similar to the Ni and noble metals [4, 5]. So in our research, ultra-fine Ce_2O_3-CoO_3 and Co_x/Ce_2O_3-La_2O_3 (x = 4 and 10 %) catalyst was prepared by spray-freezing/freeze-drying technology. The catalysts were characterized by XRD, DLS, TPR, BET-surface area and HRTEM, which confirm the formation of ultra-fine cubic fluorite solid solution structure. The effect of reaction temperature (300-600 °C) and stability of the prepared catalysts were studied in a continuous fixed-bed reactor under atmospheric pressure (Fig. 1), with ethanol/water molar ratio of 1: 10, during 15 h. It was shown that, ethanol conversion increase as a reaction temperature increase to reach 100 % conversion at 600 °C, while the addition of La^{3+} cation to Ce_2O_3-CoO_3 catalyst lead to complete conversion of ethanol at lower reaction temperature. The product analysis indicated that H_2, CO_2, CO and CH_4 are the major bio-ethanol steam reforming products. It

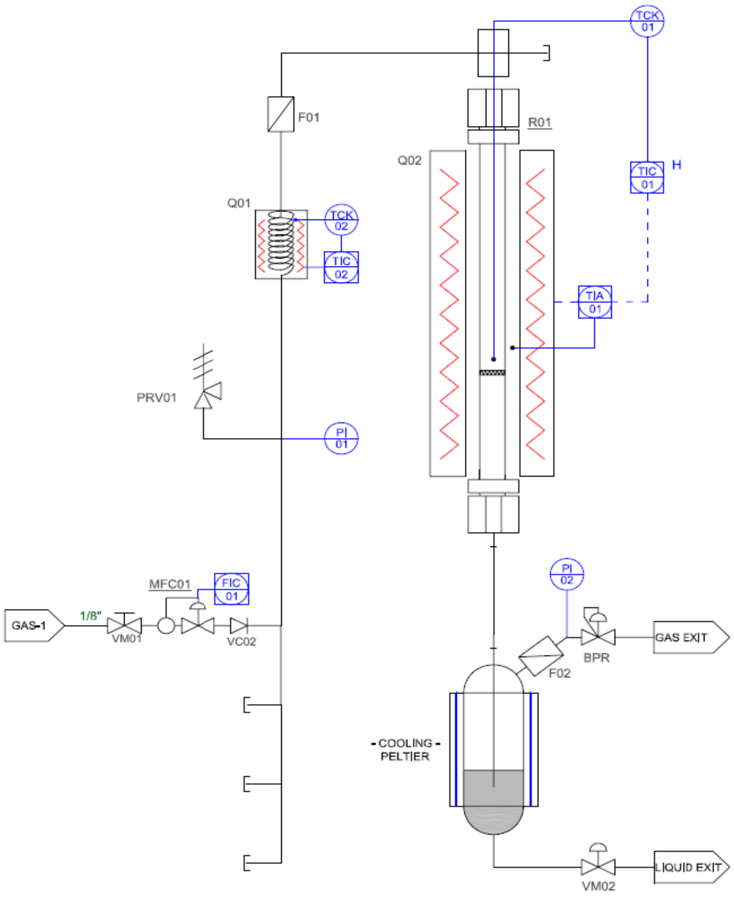

Fig. 1: Schematic diagram of catalytic flow system

is worse to note that, hydrogen selectivity was higher on CeO_2-CoO_2 catalyst than on those catalysts contain La cation and its selectivity increase by increase Co content. Moreover, Co_x/Ce_2O_3-La_2O_3 catalysts provided more deactivation resistant during 15h than Ce_2O_3-CoO_3 catalyst. XRD of spent catalysts revealed that, the addition of La as a promoter to Ce_2O_3-CoO_3 catalyst preventing sintering at high temperatures and also able to gasify the coke and decrease CO through the formation of $La_2O_2CO_3$ oxy-carbonate species. On the other hand, TGA analysis of catalyst after 15 h reaction indicate, the formation of very small amounts of amorphous carbon was deposited on the Co_x/Ce_2O_3-La_2O_3 catalyst, while on Ce_2O_3-CoO_3 catalyst, the CNT was formed which responsible for deactivation processes (TEM Fig. 2).

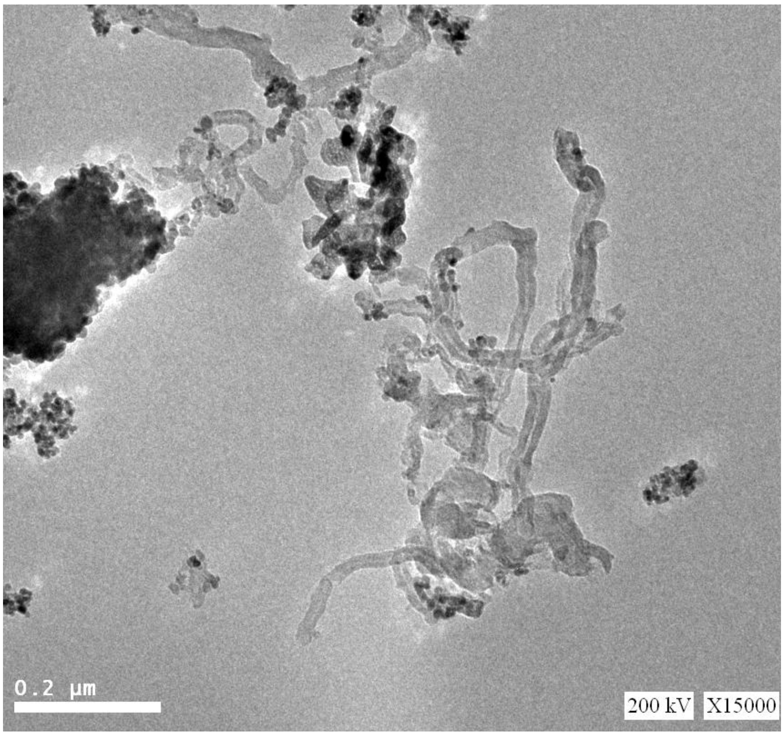

Fig. 2: TEM for Ce_2O_3-CoO_3 catalyst

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DI-METHYL ETHER CONVERSION INTO OLEFINS OVER HZSM-5: EFFECT OF SiO_2/Al_2O_3 RATIO ON SURFACE CHEMISTRY AND REACTIVITY PROPERTIES

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Objectives

This study investigates HZSM-5 as a potential catalyst for light olefins production from di-methyl ether (DTO). The aim of this study is to provide an in-depth understanding of the unique effect of SiO_2/Al_2O_3 ratio on the physico-chemical and reactivity properties of the HZSM-5 zeolite.

Materials and Methods

This study was carried out using three commercial $NH4^+ZSM$-5. The ammonia ZSM5 precursors were calcined to have ZSM-5 in the protonic form (H^+ZSM-5). The HZSM-5 with SiO_2/Al_2O_3 ratio of 30, 80, and 280 are denoted hereto as ZSM5-30, -80, and -280. For reactivity investigation, HZSM-5 was pelletized by adding 5 % binder (α-alumina monohydrate (Al(OH)O)) and 70 % filler (Fused Alumina (Al_2O_3)). N_2 isotherm and XRD tests were performed to assess the structural and porosity properties. NH_3-TPD experiments were carried out to establish acidity and provide insights on intrinsic desorption kinetics. Desorption parameters were estimated numerically using MATLAB® solver. Pyridine FTIR was also employed to evaluate the influence of Brønsted and Lewis acid sites while changing the SiO_2/Al_2O_3 ratios of the HZSM-5. The reactivity runs were performed in a gradientless Berty reactor unit operating at 9.5 h^{-1} weight hourly space velocity of pure DME, 5 hrs time-on-stream, 1 barg total pressure, and 330, 410, and 450 °C temperatures.

Results and Discussion

N_2 adsorption and desorption display isotherms with hysteresis, with this pointing to micropores and intercrystalline mesopores. Zeolite SiO_2/Al_2O_3 ratio shows however, no effect on specific surface area, pore volume and pore size distribution (Table 1). NLDFT cylindrical model confirmed the characteristic 5.5 Å micropores in HZSM-5 framework. NH_3-TPD results shown in Table 2 exhibit weak and strong acid sites in which both of these acidities being reduced with increasing SiO_2/Al_2O_3 ratio.

NH_3-desorption kinetics allows prediction of desorption activation energies and the intrinsic rate constants for both strong and weak acid sites. Kinetic desorption parameters are reported with the following statistical indicators: a) small spans for the 95 % confidence interval, b) degree of freedom (DOF = data points-2) in the 170-330 range, and c) cross-correlation coefficients between parameters consistently much smaller than one (refer to Table 3 and Table 4). It is on this basis shown that the HZSM-5 studied displays higher activation energy for the stronger sites (39-61 kJ/mol) and lower activation energies for the weaker sites (30-50 kJ/mol). Additionally, Table 5 reports that changes of NH_3-desorption kinetic constants with a SiO_2/Al_2O_3 ratio follow similar trends to the ones observed for NH_3-TPD acidity areas and Pyridine-FTIR peaks areas. One can also observe that there is a decrease of the weak to strong acidities' fraction with increasing SiO_2/Al_2O_3 ratio. These findings demonstrate that acidity in HZSM-5 zeolites can be correlated with Al_2O_3 content.

Regarding DTO over HZSM5, one can postulate an "in series" reaction where the formed olefins may continue reacting and yielding heavier paraffin and aromatic hydrocarbons. In this respect Figure 1 reports lower conversion with less deactivation as SiO_2/Al_2O_3 ratio increased. Conversely, HZSM-5 become more selective towards olefins as Al_2O_3 content is reduced as reported in Figure 2.

Conclusions

A thorough understanding of SiO_2/Al_2O_3 ratio on HZSM-5 physical and reactivity characterization leads to a significant olefin selectivity optimization in the context of the DTO process. To our knowledge and in spite of their great significance for DTO future implementation, there is no reported study addressing these topics in the open literature.

Table 1. N_2 isotherm results (NLDFT cylindrical model)

Sample	Pore surface area (m^2/g)			Pore volume (ml/g)			Pore diamater(Å)	
	Micro-A_p	Meso-A_p	Total-A_p	Micro-V_p	Meso-V_p	Total-V_p	Micro-d_p	Meso-d_p
ZSM5-30	861	101	962	0.12	0.095	0.215	5.22	59
ZSM5-80	1036	106	1142	0.14	0.108	0.248	5.22	70
ZSM5-280	728	98	826	0.104	0.085	0.189	5.58	50

Table 2 NH_3-TPD at $\beta = 15$ K/min

Sample	NH_3 Acidity (μmol/g)		
	Weak	Strong	Total
ZSM5-30	429	210.5	640
ZSM5-80	165.2	166.7	331.9
ZSM5-280	43.7	62.6	106

Table 3. Optimized kinetic constants for NH_3 desorption

Parameter	Sites	ZSM5-30			ZSM5-80			ZSM5-280		
		Value	95% CI	DOF	Value	95% CI	DOF	Value	95% CI	DOF
[illegible]	Weak	1.534	±0.03	196	0.443	±0.018	206	0.122	±0.007	172
	Strong	1.297	±0.007	264	0.46	±0.012	302	0.365	±0.01	332
[illegible]	Weak	29.9	±1.4	196	49.4	±3.7	206	50.4	±5.3	172
	Strong	38.7	±4.6	264	54.7	±3.3	302	60.6	±1.4	332

Table 4. Cross-correlation coefficients for NH_3 desorption

Sites		HZSM5-30		HZSM5-80		HZSM5-280	
		k_{d0}	E_d	k_{d0}	E_d	k_{d0}	E_d
Weak	k_{do}	1.00		1.00		1.00	
	E_d	0.05	1.00	0.08	1.00	0.37	1.00
Strong	k_{do}	1.00		1.00		1.00	
	E_d	0.48	1.00	0.27	1.00	0.41	1.00

Table 5 Measured and estimated weak to strong acidity ratios

Sample	W/S[a]	W/S[b]	k_{d0W}/k_{d0S}
ZSM5-30	2	1.61	1.2
ZSM5-80	1.0	1.46	0.96
ZSM5-280	0.7	1.35	0.33

[a] weak/strong acidity ratio based on NH_3-TPD.
[b] weak/strong acidity ratio based on Pyridine-FTIR.

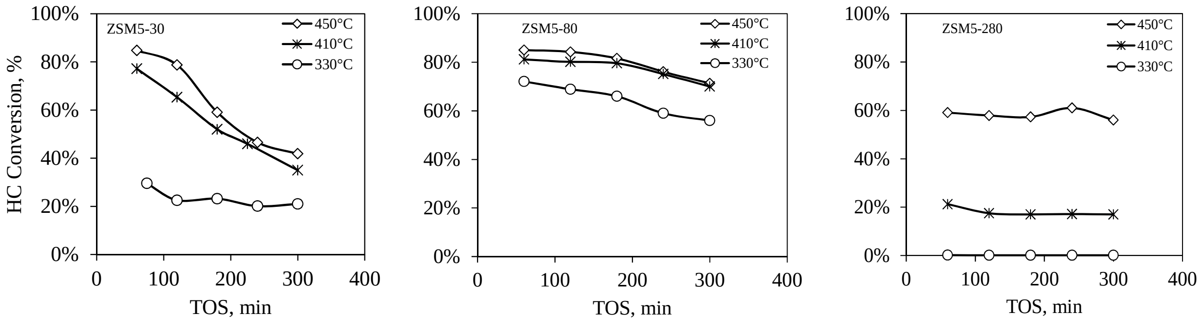

Figure 1. HC Conversion of DME vs Time on stream (TOS)

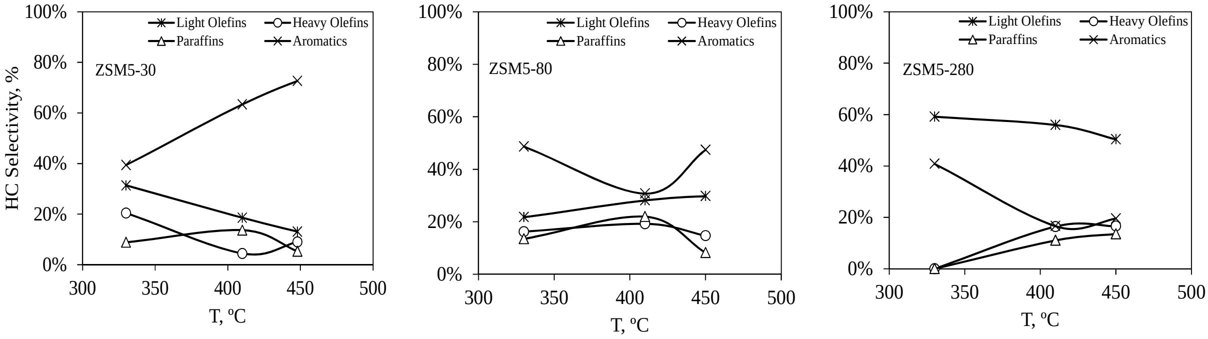

Figure 2. Effect of temperature on HC product selectivity

QUALITY BY DESIGN APPLICATION IN PETROCHEMICALS TECHNOLOGY DEVELOPMENT

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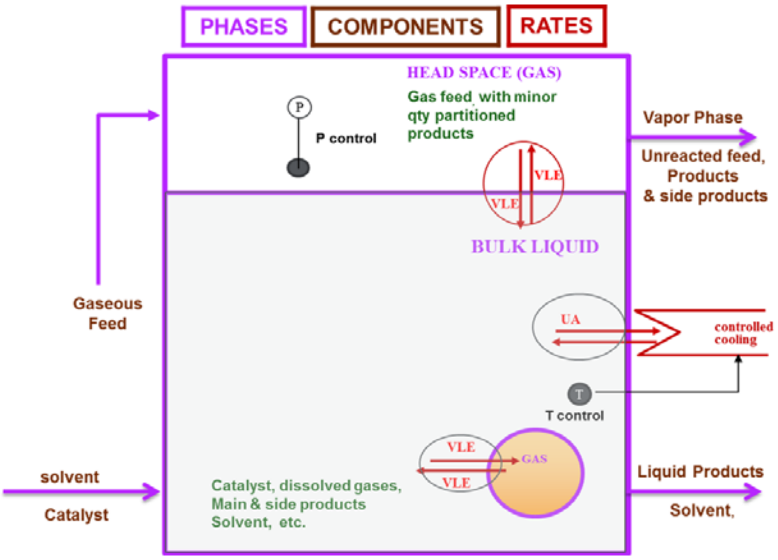
Quality by Design (QbD) has gained acceptance in the pharmaceutical industry as an efficient way of designing and controlling processes to meet regulatory requirements. QbD approach seeks to use mechanistic, risk-based, holistic and proactive approach to build-in quality into new product development processes. The key steps involves defining design space, conducting risk assessment on process parameters and identifying critical quality attribute. Current as well as future technology development in petrochemical industry are expected to face greater challenges including market uncertainty, better process (product) performance amidst higher technical uncertainties and stricter environmental sustainability requirement. In this context, SABIC Technology and Innovation (T&I) has recently incorporated QbD approach into earlier stages of its new technology development projects.

QbD implementation approach using Dynochem inclued five steps:

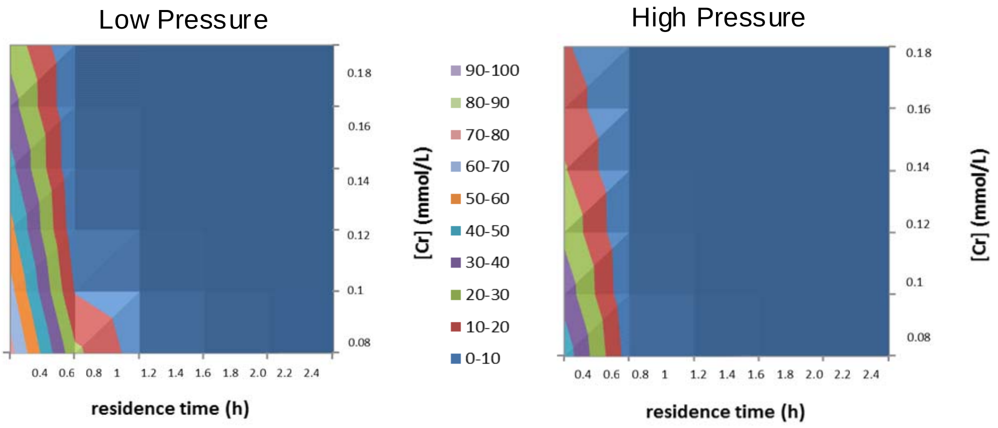
1. Develop predictive model (intrinsic kinetics)
   - Establish and demonstrate process understanding (Figure 1)
   - Further experiments for model verification and to reduce uncertainty
   - Scale-dependent factors should be screened out or understood
2. Explore parameter space to locate optimum conditions that meet set target
3. Determine probability of meeting the targets at select optimized condition
4. Validate QbD at piloting scale
5. Scale-up process and implement at commercial scale

This work describes the steps involved in applying QbD concept to new petrochemical process development using an example of one of SABIC technology development. We provide examples of how mechanistic reaction kinetic model was coupled with statistical DoE to enhance chemical process understanding, support assessment of parameter criticality, and help in defining parametric design space which ensure that targeted catalyst activity, products selectivity and purity are achieved at commercial scale.



Figuer 1: Initial step of QbD, development of model and validate with experiment

As illustrated in Figuer 2, using CSTR as one of rectoer type option, at low pressure operation gives higher probability (60-70 %) for meeting the target, whereas at higher pressure operations, lower probability (40-50 %) is achuived. Joint probability of meeting all targets at commercial scale is further reduced.



Figuer 2: Results of incorporateing probability of meeting targets at deffrent operating pressuer

Future roles of mechanistic models to support QbD application in chemical/petrochemical process are discussed. The concept can helpe in defining technology design space, identifing reactor type and configuration selection for meeting technology targets, and reducing time to market and development cost.

Acknowledgements

Andrew Bird: Scale-up Systems - Dynochem support team, Linde AG: Technology development partner and SABIC T&I team.

PP-5

RENEWABLE HYDROGEN PRODUCTION FROM BIODIESEL BY-PRODUCT USING $LaNiO_3$ AND $LaCoO_3$ NANO PEROVSKITE

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Glycerol, a byproduct derived from the production of biodiesel, is currently in an over supply crisis worldwide. One approach to alleviate this problem is to transform glycerol into valuable chemicals such as hydrogen [1]. Among the various non-fossil feedstock source, glycerol (1,2,3-propantriol) is one alternative because it has a relatively high hydrogen content, it is non-toxic, and its storage and handling is safe [2]. In this work the catalytic steam reforming of glycerol to obtain hydrogen was evaluated using $LaNiO_3$ and $LaCoO_3$ nano perovskite catalysts prepared by reverse microemulsion method. The mixed oxide precursors and the corresponding derived fresh catalysts were characterized by TG/DTA, XRD, TPR and HRTEM, while the spent catalysts were investigated by XRD and TEM. All catalysts were investigated on glycerol steam reforming with special focus on the resistance to deactivation. The effect of reaction temperature (400-700 °C) and the stability of the prepared catalysts were studied in a fixed-bed flow system under atmospheric pressure with glycerol/water molar ratio of 1: 10, during 15 h. The conversion of glycerol gradually increases along with reaction temperature until reaches 100 % at temperature higher than 500 °C. The conversion to gaseous products and the production of H_2 are very high when the reaction performed on $LaNiO_3$ than on $LaCoO_3$. Catalytic activity seems to be mainly determined by the easiness of reduction of the catalysts, which is related to the availability of oxygen from the lattice [3]. The stability studies showed a progressive deactivation of the catalyst accompanied by a decrease of conversion to gas products. $LaNiO_3$ provided more deactivation resistant along to 15 h than $LaCoO_3$ catalyst. XRD analysis of spent catalysts revealed the presence of $La_2O_2CO_3$ phase [4]. Measuring the carbons deposited removal from the catalyst by TGA showed that, only minor amount of more reactive carbon can deposits on the $LaNiO_3$ catalyst, while on $LaCoO_3$ more ordered structures graphite carbon was formed.

Fig. 1. Photo of catalytic flow reactor

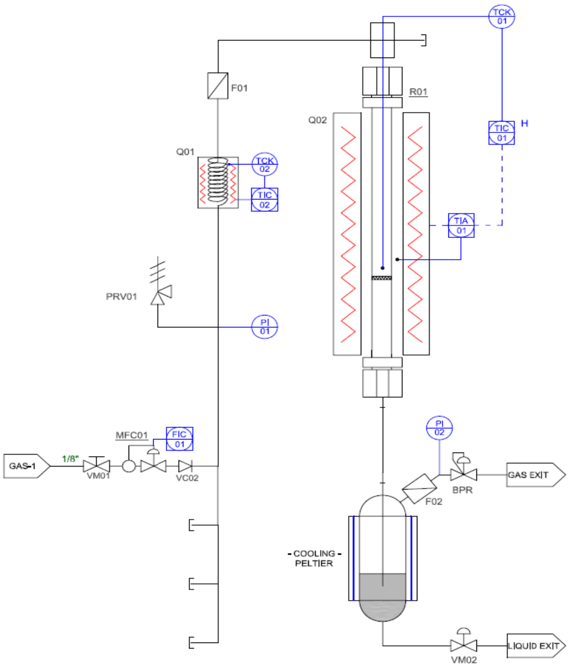

Fig. 2. Schematically diagram of catalytic flow reactor

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BIODIESEL PRODUCTION FROM USED FRYING OILS. EFFECT OF FREE FATTY ACIDS CONTENTS ON BIODIESEL YIELD AND PURITY

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In the present work the synthesis of biodiesel from used frying oils (UFOs) samples with different free fatty acids (FFA) contents, as an alternative feed stocks, using KOH as catalyst, has been studied and optimised by application of the factorial design of experiments. The influence of the oil FFA contents on biodiesel yield and purity regarding to mono-, di- and triglycerides (MG, DG and TG) contents.

The main effects of variables that affect the process, temperature and catalyst concentration were found to have significant influence on conversion and purity. Results show that the FFA content of the samples influence on biodiesel yield and purity. It has been observed that the yield of methyl ester decrease from 97.2 % to 95 % by increasing the FFA content of the oil from 0 % to 4 %.

Key words: Biodiesel quality, Used frying oil, Free Fatty Acids, Optimization.

PRODUCT DISTRIBUTION FROM MICROWAVE INDUCED PYROLYSIS OF DRIED BLACK LIQUOR

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Microwave induced pyrolysis of dried pulverized black liquor was performed in this experimental work. Microwave radiation offers several advantages such as volumetric heating, rapid turnover as well as efficient energy conversion. The objectives this works were to study microwave heating pyrolysis technique and resulting products as well as conversion efficiency. Weak black liquor used in this experiment was taken from soda and kraft pulping process from local pulp mill which was then dried and sieved. Pyrolysis was performed in quartz reactor heated in microwave using silicon carbide as microwave receptor. It was found that the reaction temperature may reach 545-1067 °C within 10 mins by employing microwave heating depending on the amount of dried black liquor used (Fig. 1). The obtained gas products were quantified by gas analyzer. Char and tar were collectively analyzed by weight measuring.

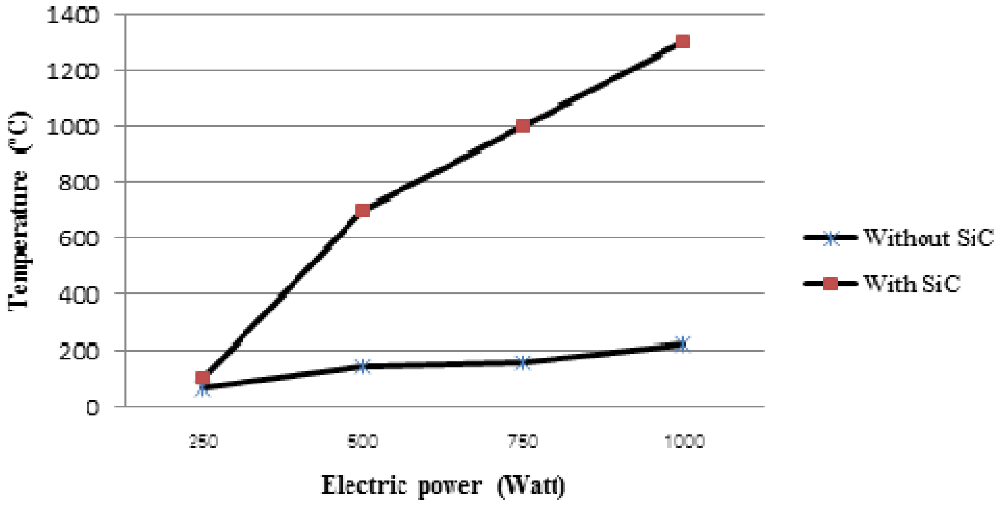

Fig. 1 Temperature profile of black liquor during the microwave induced heating.

Results indicated that optimum operating conditions were pyrolysis of kraft liquor achieved at microwave power of 625 watt, black liquor 10 g., silicon carbide ratio 1:1 and residence time 10 mins where percentage of accumulate to carbon and hydrogen fuel gases (H_2, CO, C-CH_4, H-CH_4 and CO_2) were 76.62, 33.26, 3.23, 10.58 and 0.80 %, respectively (Fig. 2). The H_2 content in produced gas was the highest of 25.90 vol. % at 6 minutes, 625 watt and syngas (H_2 and CO) increased from 17.62 vol. % and 12.20 vol. % to 25.90 vol. % and 16.30 vol. %, respectively, when increased temperature from 832 °C to 1123 °C. Section of soda liquor showed that seem conditions with kraft. The H_2 content in produced gas was the highest of 16.06 vol. % at 625 watt and syngas (H_2 and CO) increased from 4.88 vol. % and 4.02 vol. % to 16.06 vol. % and 9.60 vol. % when increased temperature from 734 °C to 1076 °C. It was observed that yields of gas product increased, while the yield of solid char decreased. Comparison of the results suggested that microwave heating had obvious advantages over conversional heating in terms of more valuable products and energy efficiency.

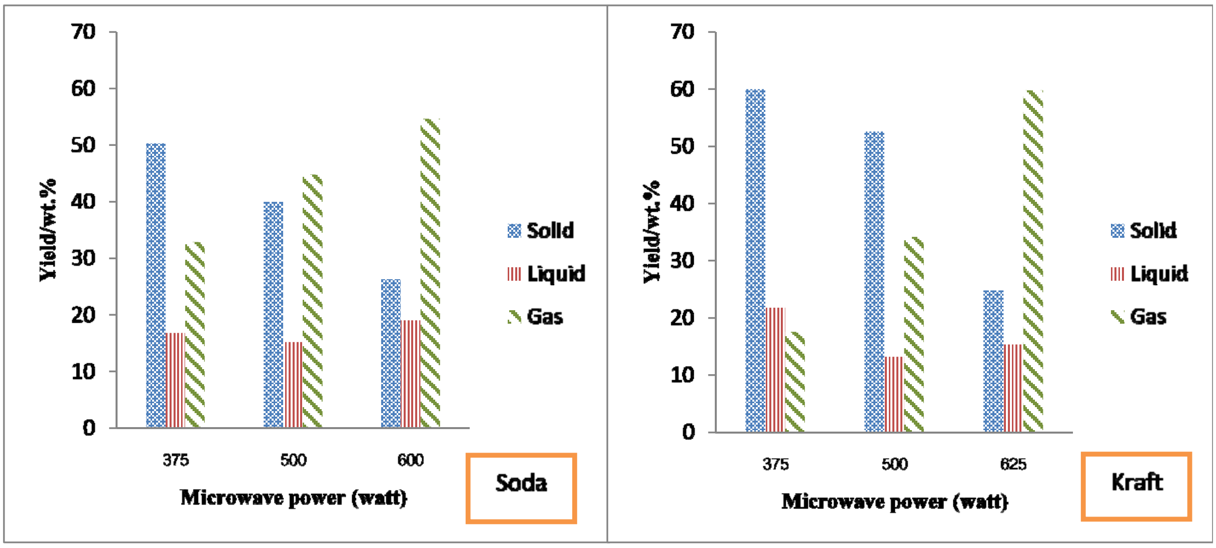

Fig. 2. Product distribution under different power level

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A NEW CORRELATION FOR MEAN PARTICLE DIAMETER ESTIMATION INSIDE A BUBBLING FLUIDIZED BED REACTOR

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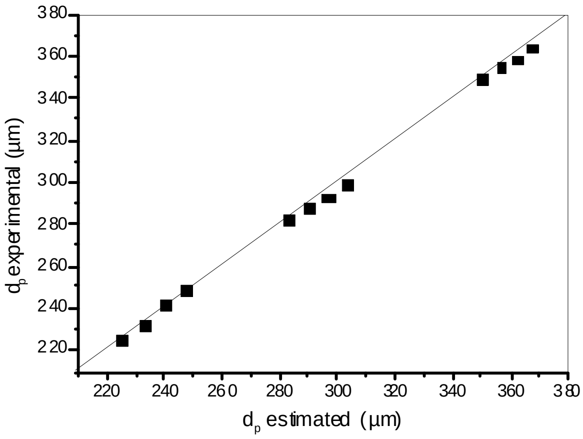
Fluidized bed reactors provide an effective mean of gas–solid contact. They promote good mixing between solid particles and the fluid, therefore high rates of mass and heat transfers. Many fluidized beds involve operations during which the mean particle size of the bed materials may change progressively. As a consequence, finding a tool to estimate the mean particle size at any moment of the operation of fluidization is of utmost importance**.**

On account to its strong dependence on the hydrodynamics of the bed, the standard deviation, which physically measures the width of the pressure time signal, is ideally suited to be used for this purpose.

In this paper, we have demonstrated that pressure fluctuation analysis can accurately be used to monitor the change in particle's mean diameter in a semi continuous fluidized bed reactor. The investigation was performed in a 90 mm ID stainless steel column with several sizes of Geldart B glass beads material. First, a new correlation was established linking the mean amplitude to the excess velocity, the bed height, the probe position as well as the mean particle size. In a second part, we have compared, in three sets of experiments, between the mean size predicted from our correlation and that obtained from sieve analysis. Results have shown, that our model was able to accurately estimate the evolution of the mean particle diameter within an uncertainty of less than 4 μm.



A comparison between the experimental and predicted mean diameters for the different experiments

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FUEL FROM WASTE ANIMAL FATS

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The hunger of the modern human society for energy is tremendous, which is increasing with the increasing population and with the pursuit of higher standards of living. A significant proportion of this energy demand is made up by the different fuels which ensure mobility. Based on environmental and energetic considerations, a larger proportion of this energy is tried to be covered with renewable energy sources on the whole world. In case of Diesel-engines, the most widely utilized bio derived fuel is the biodiesel, but because of its disadvantages, a new product has been developed and have been utilized to some extent, the bio gas oil. During the production of the bio gas oil, a triglyceride containing feedstock is converted via heterogenous catalytic hydrogenation to a mixture of iso and n-paraffines, which are the most important and best quality components of conventional diesel fuels also. The production of bio gas oil can be made by itself or as a co-process quality improvement process if the triglyceride is mixed with gas oil stream [1]. Almost without exceptions, the triglyecride feedstocks of these processes are some kind of vegetable oil with low content of impurities, so pretreatment before the hydrogenation step is not necessary or only a slight cleaning is needed. Nevertheless the commercial price of this kind of feedstocks can be high besides in some cases they may have high iLUC (indirect land use change) value as well [2]. The solution can be the processing of various triglyceride containing waste materials. Such material is the waste cooking oil, which also does not require a high degree of purification, but its large scale collection is not solved (apart from some experimental systems [3]) yet. However, relatively large amounts of triglyceride and free fatty acid containing fatty materials are formed everywhere in the rendering facilities, which can be a feedstock for bio gas oil production. In these plants various fatty materials, meals, fodders are made from the waste of the slaughterhouses and carcasses of livestock. One high amount product of these rendering plants is technical brown grease, which should not be used for animal feeding. However, this material can be a cheap feedstock for bio gas oil production after proper pretreating. The biggest problem with these materials is that their solid contaminant content, metals and phosphorus can be high, therefore pretreatment/cleaning is required, otherwise the high concentration of impurities greatly shorten the life cycle of the catalysts. In the course of the food grade vegetable oil production various cleaning processes are used, but they are have to be examined in detail of their applicability for this type of material. During our experiments we investigated the hydrogenation of expediently pretreated waste fatty material of animal origin in co-process with gas oil fraction (10/90 ratio of fat/gas oil) on a hydrodesulphurization catalyst widely used in refining, and on a Pt/carrier isomerization catalyst developed by us, applying a wide range of process parameters (hydrogenation: 300-380 °C, 20-80 bar, 0.75-1,0-1.5 h^{-1}, 600 Nm^3/m^3; favourable parameters of isomerization: 345 °C, 40 bar, 1.8 h^{-1}, 350 Nm^3/m^3). The yields of the gas oil boiling point range fraction well approached the *theoretical yields (96.3-96.7 %, *97.9-98.2 %) during the hydrogenation step. During this, the triglyceride part was fully converted, and the heteroatom removal and aromatic saturation of the gas oil part also greatly occurred. The cetane number of the products were 56 after the hydrogenation, while their CFPP values were about 8 °C. After the isomerization step, which served for the improvement of the cold flow properties, the product yields were 92.6-93.6% on the basis of the triglyceride containing feedstock. The cetane number of the final product was 54, while the CFPP value between –15 °C and –20 °C. During the product analysis we determined, that these kind of waste fatty materials can be appropriate feedstocks for the production of bio component containing gas oils after a proper pretreatment. In addition, these materials are cheap, their iLUC value is practically zero, and as waste materials they count as twofold inside the EU when calculating the ratio of renewable fuels respectively [4].

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TECHNOLOGICAL BASIS AND APPARATUS EQUIPMENT FOR THE MANUFACTURING PROCESS OF NEW GLASS-POLYMER COMPOSITION MATERIALS USING THE TETRAFLUOROETHILENE OLIGOMERS (TELOMERS) AS A BINDER

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The polymeric composition materials on the base of glass-fiber (glass fabric, fiberglass) are now the most used and demanded type of the polymeric composite materials. These materials are widely standing in need for the building trade, radio, electronics, shipment, aviation, sport equipments and cars production industry, etc. The demand for such materials is constantly increasing.

As the binders for the fiberglass materials manufacturing the producers are used a wide range of various thermoplastic and thermosetting polymers, resins and their compositions, but from this large class is almost excluded the very outstanding polymer namely poly-tetrafluoroethylene (fluoroplast), having many considerable properties (high resistance to the high and low temperatures, resistance to corrosive media, high frictional and adhesion characteristics, dielectric parameters, etc). The main reason of this paradox situation is that it is impossible to transfer fluoroplast into a flow-viscous state or into a solution.

There are only few works producing the fluoro-polymer glass-fabrics based composite materials by using the traditional for fluoroplastic items production technology of powder mixture sintering, because it don't assure conditions for the fluoroplast penetration into the cavities between the binders filers. For the lack of any adhesion between the glass and fluoroplast the conditions are favored to a polymer splitting out from the armoring fiberglass and the material or item continuity. Such technologies require to introduce an essential amounts of polymer and indeed the content of expensive fluoroplast in these composite items is very high (about 50-80 mass.% !)

In present work a principally new technology is proposed for the fiberglass-based polymeric composition materials with a fluoroplastic binder. The main idea is that the fluoroplasts are introducing into a fiberglass matrix by impregnation of a base material with the liquid media containing a fluoropolymeric component. As impregnation media the solutions of low-molecular fractions (with the chain length 10-30 units) are used. The key factor of this technology realization becomes the discovery (in IPhC RAN) a radiation process of the low molecular and soluble (in organic solvents) poly-tetrafluoroethylene formation.

Using the mentioned radiation chemistry method of telomers synthesis in the technology allows to create a principally new type of glass-polymer composition material production and authors were planning hopes on the combination of some new factors: 1) the application of the telomer solution as an impregnation media make available its an effective introduction into the intercapillary spaces and reliable wetting of every elemental filament; 2) the presence of the solvent active functional units on the telomer ends (which maintain the chemical or chemoabsorptional couplings between molecules and give a necessary orientation to the polymer molecule on the filament surface); 3) a possibility of fiberglass filler chemical and physical activation by the acidic etching accompanied by a formation of a filament surface microrelief or texture with formation of the nanopores and chemically active fragments into the near surface layer.

For the fiberglass filler material impregnation and studies of the formed composition materials characteristics the telomer solution in acetone was used with mass concentration 4% and poly-tetrafluoroethylene chain length in 5-20 units range.

The filler specimens used in experiments were prepared from the standard alumo-boro-silicate glassfiber, having the simplest wearing structure and being in the most abundant for the technologies of the commercially used fiberglass composition materials.

The filler specimen impregnations were carried out by their immersing into a bath with the telomer solution followed by the natural air-drying from solvent at the mild temperature range 40-50 °C. The described impregnation procedures were carried out repeatedly many times (in present work to 5 dipping) with the specimen mass growth determination after every impregnation. The telomere mass up growth (relative to filler mass) was only a few percents (it will be recall that the fluoropolymer content for the traditional powder mixture sintering technology is about 80 mass %).

Naturally, for to evaluate the strength and properties of the telomer coupling or adhesion with the glassfiber it is necessary to define the hydrophobicity level of the produced composition material. It was shown that the specimens studied take on a very high hydrophobic properties ("superhydrophobicity") after the impregnation, drying and mild thermal treatment.

The basically important characteristic of the created fiberglass composition material is its high resistance to the aggressive media action. In the frame of this investigation program a primary trial of the composite sample acid resistance was carried out and it had shown that this parameter for the produced composite material is radically increasing.

At last we considered the problem of thermal stability of the composite items produced by the suggested technology. This characteristic was studied using DTA method. The samples were 5 times subjected to the impregnation in the telomere solution (with fluoroplast content 4-4,5 mass. %). It was shown experimentally that under the samples temperature scanning in the temperature range up to 500 °C an appreciable loss of the item mass was not detected.

In conclusion we note that above the first stage of investigation is described. Main aim of the study was the search of the basic technology elements for production of a new fiberglass composition material based on fluoroplast with its lowest content, but preserving into items the basic properties of poly-tetrafluoroethylene. This stage of work is completed. The fields of the possible practical applications of such technology are very wide. For example we can note the glass fabric materials with the fluoroplast properties, hydrophobic fabrics for the temporary constructions coating, the physiologically inert fabrics for medical applications, the thermally and chemically resistant materials for conveyers in food industry, the new filtrating materials resistant to aggressive media, etc.

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DEVELOPMENT OF THE CONCEPT OF THE EARTH’S CRUST AS A “GIANT CATALYTIC REACTOR” (EXPERIMENTAL MODELING OF THE HETEROGENEOUS-CATALYTIC MECHANISMS OF FLUID TRANSFORMATION IN THE EARTH’S CRUST EXEMPLIFIED BY THE METHANE VAPOR CONVERSION ON “SERPENTINITE”)

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It is well known that fluids play an important role in processes of the chemical and physical evolution of the crustal and mantle rocks. Fluids accelerate by in orders of magnitude reaction rates between minerals, growth or dissolution of mineral grains. They intensify melting processes and polymorphic transformation, which influence on various types of deformations and re-crystallization in mineral aggregates. However, the opposite process, i.e. a catalytic effect of rocks and minerals on the chemical reactions between fluid components, is a very poorly studied topic of geochemistry related to the fluid-mineral interactions. However, there are many strong arguments in favor of significant role of the catalytic mechanisms in the fluid transformations in the course of their infiltration through the crustal rocks:

- crustal rocks with compositions based mostly on SiO_2 and Al_2O_3, modified by the catalytic active “metal” components, represents an analogue of the traditional catalytic systems widely used in the industrial technologies;
- temperature and pressure conditions of the fluid fluxes in the Earth’s crust and mantle are favorable for production of many known industrially important catalytic processes;
- components forming the fluid fluxes (H_2O, CO_2, CO, CH_4, H_2, N_2, SO_2, NH_3), can be considered as a raw material for a catalytic generation of a wide spectrum of the products.

An analysis of the catalytic transformation of fluids in the Earth’s crust demonstrates a possibility for many processes analogous to the known industry technologies, such as:

- synthesis of hydrocarbons and their oxygen-bearing derivatives as a result of H_2O, CO, CO_2, H_2 reactions via mechanism well known as the Fisher–Tropsch reaction used for the production of synthetic fuel (so it can be considered as the possible mechanism for a reproducible abiogenic formation of the hydrocarbons under the Earth’s crust conditions);

- reactions of the vapor, air and carbon dioxide conversion of CH_4 and other hydrocarbons, similar to the well known technological process of so called synthesis-gas production;
- catalytic pyrolysis of heavy hydrocarbons (oils) known as the catalytic cracking, platforming, reforming;
- reactions of hydrocarbon transformation to solid carbon, i.e. the catalytic "overcarbonization" process;
- ammonia catalytic synthesis from H_2 and N_2 known as the Haber synthesis.

Present study shows results of the experiments on the catalytic activity of serpentinite, the common rock in the Earth's crust, with respect to the methane vapor conversion reaction (the reaction of "synthesis-gas" formation). Fluids containing $CH_4 + H_2O$ are common type of fluids in the Earth's lithosphere. In turn, serpentinite by its composition ($MgO\text{-}SiO_2$ – base, legated by the catalytically active components Fe, Ni, Cr) and structure (delicately fibrous and porous matrix) is very close analogue of many synthetic catalytic materials used in the industrial catalysis processes.

A massive serpentinite rock sample from Bogorodskii deposit (Southern Urals) was used in the experiments. The serpentinite sample was not subjected to any preliminary chemical treatment apart from the grinding. The granulometric fraction 0.5-0.71 mm of the crushed rock was used in the experiments.

The experiments were carried out using a flow-type catalytic reactor manufactured from quartz glass. A volume of serpentinite catalyst loaded into the reactor vessel was 5.3 cm^3 with the catalyst layer thickness of 1 cm. Methane volume consumption (20 cm^3/min) was regulated automatically and the water content in the flow was sustained by temperature changing in a bubbler element (this parameter was calibrated using the water loss from the bubbler element). The H_2O/CH_4 volume ratio in the reaction zone varied from 8/1 to 10/1, the linear velocity of the reaction flow through the catalyst layer was kept as 0.5-0.6 cm/sec, and the time of the reaction flux contact with the catalyst layer was 1.5-2 sec.

The experiments were carried out at ambient pressure within the temperature range 500-850 °C. The heating and temperature regulation in the catalyst zone were performed by electronic device with a thermocouple control. The composition of starting gas mixture and products at the reactor output were measured by the Crystall-5000 chromatograph.

The main results of the experiments are following: the degree of methane conversion into H_2 increased with temperature and reached 14 % at 825 °C; the methane conversion to CO and CO_2 at the same temperature was 3 % for every component. An unexpected result of the experiments is a qualitative detection of CH_3OH and C_2H_5OH amongst the reaction products. Such oxygen-bearing compounds do not form in the technological process of vapor methane conversion with the standard catalysts. Presence of more complex oxygen-bearing hydrocarbons in the experiment products is possible. However, their quantitative measurement and estimation of a complete balance of the conversion products require specific analytical equipment that was beyond the present study.

The present experimental results allow conclusion that the “serpentinite” rock, common crustal rock, has a very high catalytic properties with respect to the methane vapor conversion. For very short periods of the fluid vapor-methane flow contact with this rock, a sufficiently high degree of the CH_4 conversion to H_2 and oxygen-containing compounds was recorded.

From a geochemical point of view, such fluid transformations can be produced in the fluid systems accompanying the formation of kimberlite pipes. Serpentine is the main constituent of kimberlites, whereas the temperature of the kimberlite magma during eruption reaches 800-900 °C. Indeed, the massive H_2 and CH_4 flows (up to 10^5 m^3/day) and presence of hydrocarbons were detected in boreholes of some Yakutian kimberlite pipes, for example in the famous pipe “Udachnaya”.

The present experiments inspire a systematic study of the catalytic properties of wide spectrum of crustal rocks with respect of the various routes of fluid transformations and development of a new branch in geochemistry, namely “catalytic geochemistry”. For this conception, whole total theoretical and experimental potential accumulated in fundamental studies of catalytic chemistry as a part of physical chemistry must be applied. For example, the theory of the catalytic processes “domain instability”, developed for effects of time-spatial structuring of the industrial catalytic reactors, can be used to analyze the deposit “site clustering” in the Earth’s crust. Of cause, to solve these problems, it is necessary to deviate from the classical geochemical approach of thermodynamic equilibrium and take into account that chemical processes in the Earth crust proceed under non-equilibrium regimes.

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MATHEMATICAL MODELLING OF THE CATALYTIC HYDRODEWAXING OF DIESEL FUELS

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The process of hydrodewaxing assigns for manufacturing summer- and winter-grade diesel oil with ultra low sulfur and polyaromatic compounds content, corresponding to the European standards for diesel fuels. Technological conditions of the process depend on chemical composition of the raw materials, catalyst activity, required extent of dewaxing. The object of the present work is mathematical modelling of the diesel fuels hydrodewaxing.

Development of the mathematical model includes estimation of the thermodynamic possibility of the reactions in order to make hydrocarbons conversion scheme, the creation and soft realization of the kinetic model, estimation of the kinetic parameters of the reactions [1].

Thermodynamic characteristics of the reactions were calculated using non-empirical quantum-chemical method DFT realized in the Gaussian software. Theoretical approximation was B3LYP, basis 3-21G. Kinetic model represents the system of the differential equations and initial conditions. The equations of the kinetic model have the following general form:

$$\frac{dC_i}{d\tau} = \sum v_i W_j$$

Initial conditions are $\tau = 0$, $C_i = C_{i0}$, where *i* is corresponding group of hydrocarbons, *v* – stoichiometric coefficient in the correspoding reaction, *W* – reaction rate, *j* – number of the corresponding reaction.

Software realization of the kinetic model was made using programming environment Delphi 7.

In order to estimate of the rate constants of the reactions the inverse kinetic problem was solved using experimental data obtaining during the operation hydrodewaxing industrial unit. The termodynamic possible reactions which represent the hydrocarbons conversion scheme of the process, thermodinamic values and rate constansts are presented in the table 1.

Table 1. Change of Gibbs energy and rate constants of the reactions

Reaction	*ΔG*, kJ/mol	*k*
1. Hydrogenation of polyromatic compounds	– 65,14	$7{,}00\cdot10^{-4}$
2. Hydrogenation of olefins to n-parafins $C_5 - C_9$	– 52,22	2,30
3. Hydrogenation of monoaromatics to naphthenes	– 32,52	$5{,}24\cdot10^{-3}$
4. Hydrocracking of n-parafins $C_{10} - C_{27}$	– 85,16	$0{,}45\cdot10^{2}$
5. Isomerization of n-parafins $C_5 - C_9$	– 5,85	$1{,}8\cdot10^{-2}$
6. Cyclization of isoparafins	– 11,68	$1{,}5\cdot10^{-4}$

Using developed model research of the technological conditions influence was carried out (see Fig. 1 and Fig. 2).

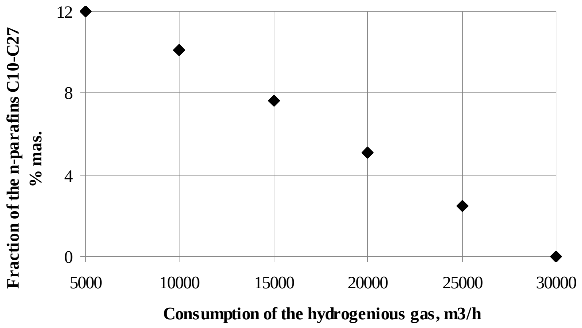

Fig. 1. Dependence of the n-parafins C_{10}-C_{27} fraction in the product on the hydrogenious gas consumption

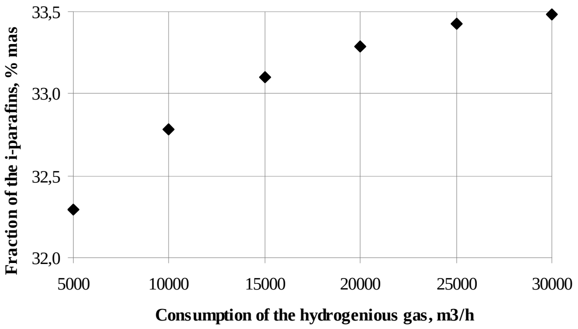

Fig. 2. Dependence of the i-parafins fraction in the product on the hydrogenious gas consumption

As can be seen from the Fig. 1 and Fig. 2 fractions of the n-parafins C_{10}-C_{27} and i-parafins in the product depend on the consumption of the hydrogenious gas significantly. So, the fraction of the n-parafins C_{10}-C_{27} rises on 11,9 % mas. and the fraction of the i-parafins rises on 1,2 % mas. under the increasing of the hydrogen gas comsumption on 25000 m^3/h.

Thus, developed mathematical model of the hydrodewaxing process is based on the physical-chemical laws of the process and allows to carry out optimization of the technological regime for resource efficiency increase.

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METHYLTRIOXORHENIUM SUPPORTED ON MESOPOROUS Al_2O_3 PROMOTED WITH $ZnCl_2$ AS A GREEN HETEROGENEOUS CATALYST FOR METHYLOLEATE SELF-METATHESIS: REACTION KINETICS

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Fats and oils containing carbon-carbon double bonds can undergo transformation *via* metathesis to introduce new chemical functionality or to alter reactant properties enabling synthesis of a wide range of reaction products from pharmaceuticals and cosmetics to polymers and fine chemicals [1]. This metathesis-based modification of fats and oils is regarded as a clean and green catalytic and atom-efficient reaction giving rise to industrially important products without by-product formation [2].

Well-defined homogeneous catalysts are compatible with a wide range of functional groups. These catalysts based on group 6 and 7 transition metals present the advantage of working at rather low temperatures (25–80 °C), giving rise to good selectivity and activities [3]. However, high costs and decomposition hinder their recycling or regeneration. Heterogeneous catalysts, typically from group 6–7 oxides supported on large surface area oxide supports, are robust and can be regenerated by simple calcination. However, they are generally not active with functional groups such as olefin esters unless activators are used [4]. The well-known heterogeneous catalytic system Re_2O_7/Al_2O_3 promoted by R_4Sn is relatively active but is susceptible to poisoning by Sn, which hampers its regeneration [5].

Nonetheless, metathesis of functionalized olefins such as methyloleate and other unsaturated esters such as bulky triglycerides using catalysts supported on mesoporous materials remains largely unexplored. Recently, we demonstrated for the first time that MTO/$ZnCl_2$-modified mesoporous Al_2O_3 is an efficient catalyst for the metathesis of methyloleate, a model molecule of bulky triglycerides present in fats and vegetable oils [6, 7].

This work focuses on Al/Zn molar ratio effect of on the activity and selectivity of the catalyst towards the desired products and also presents the self-metathesis kinetics of methyloleate over this heterogeneous catalyst.

Methyltrioxorhenium impregnated on $ZnCl_2$-modified mesoporous alumina at Al/Zn ratio of 8-12 was revealed as an effective catalyst for self-metathesis of methyloleate at mild reaction conditions.

This research suggests that it is possible to design a stable and green heterogeneous catalyst for the efficient and selective self-metathesis of functionalized olefins such as methyloleate and edible oils, avoiding the utilization of expensive homogeneous catalysts or use of toxic promoters such as R_4Sn.

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ETHANE OXIDATIVE DEHYDROGENATION. REACTION KINETICS

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Oxidative dehydrogenation of ethane (ODE) is an alternative way for ethylene production. Several catalytic systems have been proposed and Mo-V-Te-Nb-O mixed metal oxide catalysts seem to be the most promising ones [1]. Increase of the yield of principal product can be attained by development of a new effective catalyst and an optimization of process regime as well. The last requires thorough reaction kinetics data.

Kinetics study of ODE reaction was done over Mo-V-Te-Nb-O catalysts prepared by slurry method [2]. Kinetic experiments were carried out in the gradient-less flow circulating set-up with on-line chromatographic analysis. Reaction conditions were varied in the following range: temperature from 340 to 420 °C, C_2H_6 content from 3 to 30, O_2 – from 2 to 70 (% vol.), N_2 for balance.

On the base of dependencies obtained kinetic models were proposed and kinetic parameters of the rate of particular reactions were estimated. Average deviations of the calculated and experimental reaction mixture concentrations were 1.1 % for ethane, 2 % for ethylene, 5.3 % for carbon oxides and 0.3 % for oxygen.

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ALUMINA-WASHCOATED STAINLESS STEEL MICROGRIDS: NEW DESIGN OF MICROSTRUCTURED CATALYSTS FOR CATALYTIC APPLICATIONS

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INTRODUCTION

Metallic micro-reactors exhibit important advantages, compared to conventional catalysts, such as high thermal conductivity, high mechanical resistance and the possibility to adopt different geometry and configurations. Much attention has been given to searching for new design concepts of the metallic micro-reactors that can improve the reaction conditions. For instance, the metallic grids are known to provide a uniform gas distribution and homogenize the temperature in the reactor by reducing the excessive temperature gradients. These remarkable properties make this kind of structure applicable, as microstructured catalysts, in diverse gas phase reactions [1]. The present work concerns the preparation, characterisation and activity of CuO/zeolite/Al_2O_3/SS316 and CuO/Al_2O_3/SS316 microstructured reactors (micro-grid type) for SCR of NO_x with NH_3, COTox and COProx reactions and their comparison with conventional catalytic systems. The characterization involved BET, SEM, XRD, H_2-TPR, UV-visible-NIR and XPS techniques.

EXPERIMENTAL

Several methods have been used for the washcoating of alumina on ceramic and metallic monoliths. In the present study the deposition of alumina film was prepared using a modified version of the methods mentioned in the literature [2]. The zeolite/Al_2O_3/SS316 system was a dual-layer monolith with zeolite layer coated on top of alumina-washcoated stainless steel microgrids. For the impregnation of the active phase the alumina/SS316 and zeolite/alumina/SS316 supports were dipped into a stirred aqueous solution of 0.8 M $Cu(NO_3)_2 3H_2O$ for 2 h. Then, the samples were dried at room temperature for 2 h and at 120 °C for 2 h. The impregnation and drying were repeated two and three times to obtain three catalysts with different Cu loadings. Finally, the resulted microstructured reactors, were calcined in air at 600 °C for 10 h with temperature ramp of 1 °C min^{-1}. The results presented in this abstract concern only those obtained on the $CuO/Al_2O_3/SS316$ microstructured reactors. SEM images showed that the preparation method used in this work for the synthesis of CuO/Al_2O_3 films onto stainless steel microgrids resulted in homogeneous and stable coatings with an estimated thickness of 8-10 μm. H_2-TPR, UV-Visible-NIR (Fig. 1(A)) and XPS (Fig. 1(B)) analyses confirmed that CuO exists in three forms in the microstructured reactors: (i) crystallites of CuO deposited on the surface of the substrate, (ii) CuO exhibiting strong interaction with alumina and (iii) a phase where CuO stays in free state.

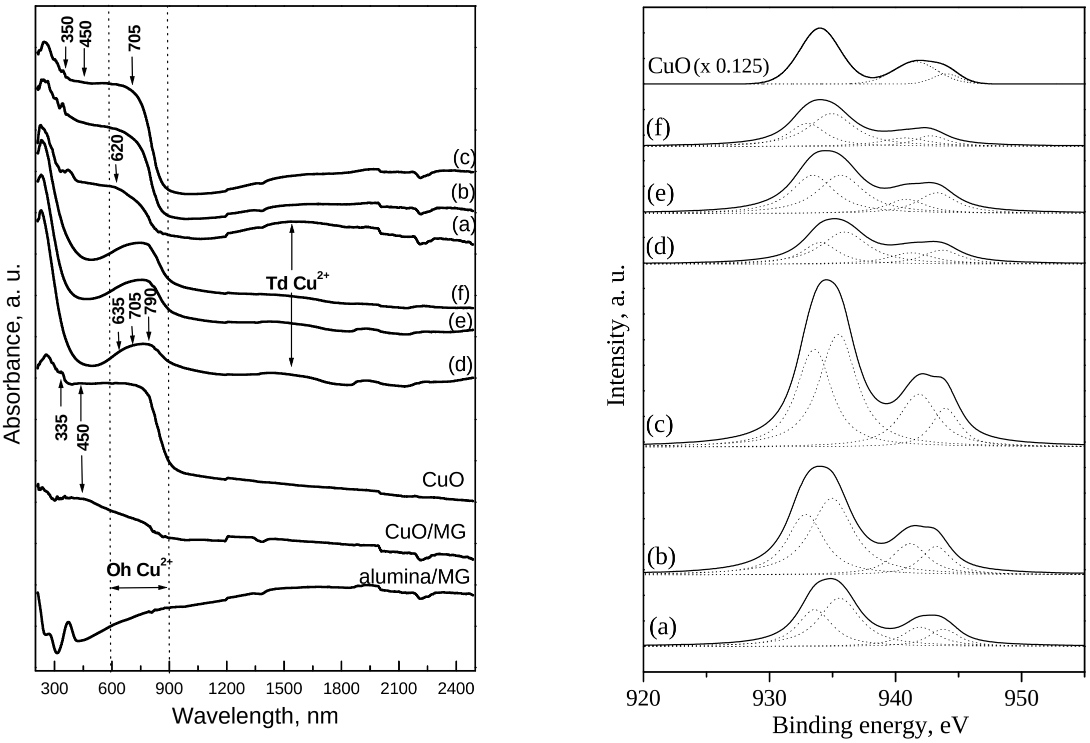

Fig. 1. UV–VIS–NIR (A) and Cu $2p_{3/2}$ XPS spectra (B) of (a) $CuO(10)/Al_2O_3/SS316$; (b) $CuO(14)/Al_2O_3/SS316$, (c) $CuO(18)/Al_2O_3/SS316$, (d) $CuO(10)/Al_2O_3$; (e) $CuO(14)/Al_2O_3$ and (f) $CuO(18)/Al_2O_3$ calcined at 600 °C

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KINETIC MODEL AND MECHANISM OF LOW-TEMPERATURE CARBON MONOXIDE OXIDATION BY OXYGEN

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It was shown before by physical metods (XAS, XRD, SEM) [1] that copper and palladium occur on the surface of γ-Al_2O_3 in the forms of crystalline of $Cu_2Cl(OH)_3$ (paratacamite) and chemisorbed mononuclear $PdCl_4^{2-}$ anions, respectively. DRIFTS spectra indicate that both linear [2159 (Pd(II)), 2114(Cu(I)) cm^{-1}] and bridging (1926 cm^{-1}-Pd(I)) coordinated carbon monooxide emerge upon CO adsorption on the catalyst’s surface. These carbonyls are rapidly disappeared after contact with oxygen and carbon dioxide is appiared at the same time.

The kinetic regularities were studied at 18-40 °C and atmospheric pressure of CO, O_2, N_2, H_2O(gas) mixture in a flow reactor (steady state conditions). The activation energy reaction is found to be negative (–40 kJ/mole*K). The empirically derived equation for the rate of carbon dioxide formation is as follows (1).

$$r_{CO_2} = kP_{CO}^{0.2}P_{H_2O}^{1.7}P_{O_2}^{0.8} \qquad (1)$$

The high kinetic orders for water and oxygen partial pressures allowed us to propose mechanisms with the participation of both (O_2 and H_2O) reagents in the steps of carbon dioxide formation. The most probable mechanism is proposed as a result of advansing and discriminating of hypothetical mechanisms. This mechanism (see below) includes formation of hydroxycarbonyl palladium intermediate on the surface of catalyst. Carbon dioxide is formed as result of interacting this intermediate with oxigen activated by Cu(I) centre (scheme). The equation (2) derived from this mechanism allowed us to achieve good description of the kinetic data (better than for another ones).

$$X_2Pd_2(I) + CO \xrightleftharpoons{K_1} X_2Pd_2(I)(CO),$$

$$X_2Pd_2(I)(CO) + CO \xrightleftharpoons{K_2} X_2Pd_2(I)(CO)_2,$$

$$X_2Cu(I)_2 + O_2 \xrightleftharpoons{K_3} X_2Cu(I)_2(O_2),$$

$$X_2Cu(I)_2(O_2) + CO \xrightleftharpoons{K_4} X_2Cu(I)_2(O_2)(CO),$$

$$X_2Pd_2(I)(CO) + 3H_2O \xrightleftharpoons{K_5} [X_2Pd_2(I)(COOH)]^- H_3O^+(H_2O),$$

$$[X_2Pd_2(I)(COOH)]^- H_3O^+(H_2O) + X_2Cu(I)_2(O_2) \xrightarrow{k_6} [X_2Pd_2(I)(OOH)]^- H_3O^+ + CO_2 + X_2Cu(I)_2 + H_2O,$$

$$[X_2Pd_2(I)(OOH)]^- H_3O^+ + CO \xrightarrow{k_7} X_2Pd_2(I)(CO) + H_2O_2 + H_2O,$$

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

$$r = \frac{k_1^{\text{н}} \cdot P_{CO} \cdot P_{H_2O}^3 \cdot P_{O_2}}{d}, \quad (2)$$

where

$$d = 1 + k_2^{\text{н}} \cdot P_{O_2} + k_3^{\text{н}} \cdot P_{O_2} \cdot P_{CO} + k_4^{\text{н}} \cdot P_{CO} + k_5^{\text{н}} \cdot P_{CO}^2 \cdot P_{O_2} + k_6^{\text{н}} \cdot P_{CO}^2 + k_7^{\text{н}} \cdot P_{CO}^3 \cdot P_{O_2} +$$
$$+ k_8^{\text{н}} \cdot P_{CO} \cdot P_{H_2O}^3 + k_9^{\text{н}} \cdot P_{CO} \cdot P_{H_2O}^3 \cdot P_{O_2} + k_{10}^{\text{н}} \cdot P_{CO}^2 \cdot P_{H_2O}^3 \cdot P_{O_2} + k_{11}^{\text{н}} \cdot P_{H_2O}^3 \cdot P_{O_2},$$

$k_1^H = k_6 \cdot K_1 \cdot K_3 \cdot K_5$, $k_2^H = K_3$, $k_3^H = K_1 \cdot K_3 + K_3 \cdot K_4$, $k_4^H = K_1$, $k_5^H = K_1 \cdot K_3 \cdot K_4 + K_1 \cdot K_2 \cdot K_3$, $k_6^H = K_1 \cdot K_2$, $k_7^H = K_1 \cdot K_2 \cdot K_3 \cdot K_4$, $k_8^H = K_1 \cdot K_5$, $k_9^H = K_1 \cdot K_3 \cdot K_5$, $k_{10}^H = K_1 \cdot K_3 \cdot K_4 \cdot K_5$, $k_{11}^H = k_6 \cdot K_1 \cdot K_3 \cdot K_5 / k_7$ – visible rate konstants.

The mechanisms of low-temperature carbon monoxide oxidation with homogeneous and geterogeneous palladium containing catalysts participation are discussed.

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REDUCTION OF TOC IN INDUSTRIAL WATERS BY THE MEANS OF UV RADIATION

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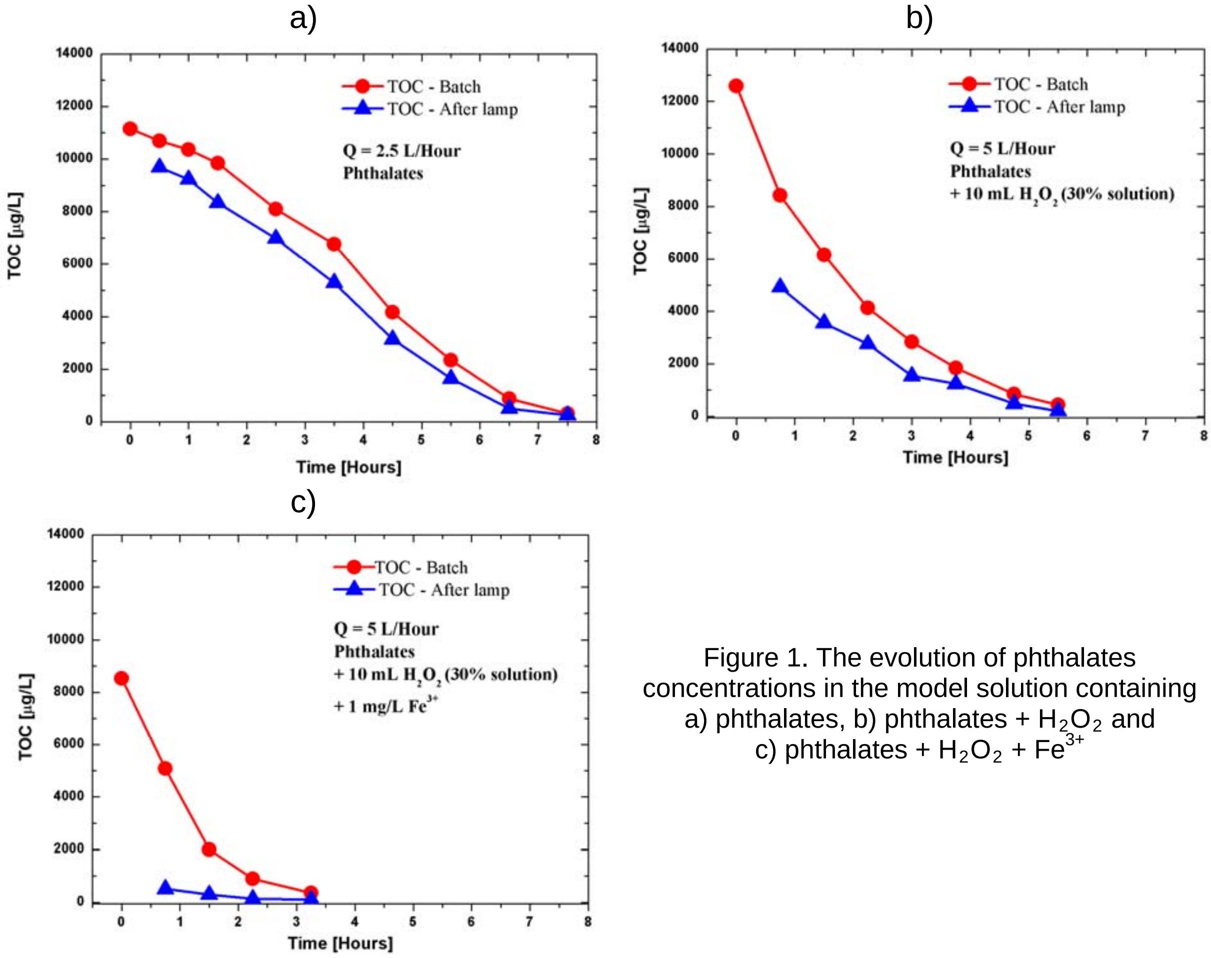
There are several sources of TOC in industrial waters, including organics present in the feed water, organics resulting from system leakage and leaching of various components within the purification or water distribution system and organics from formation of biofilms (bacteria) in the water system. The presence of TOC in industrial waters is adverse, because it can cause severe problems in the consequent technology, e.g. organics fouling on the system walls, thus decreasing of heat exchange or reactions with the material, resulting in the corrosion of the system material [1]. Currently, TOC removal from industrial waters is based on physicochemical and mechanical methods with further biological treatment, which is not sufficient enough for the whole range of organic compounds [2, 3]. Therefore, alternative solution using advanced oxidation processes (AOP), e.g. Fenton process, use of UV radiation or ozone with strong oxidant (H_2O_2), was suggested. The AOPs are characterized by production of OH radicals, which are very reactive species capable of non-selective mineralization of all organic pollutants [3, 4].

In this paper reduction of TOC in industrial waters by the means of UV radiation is presented. Experiments with model solution containing various organic compounds (phthalate, ethylenediaminetetraacetic acid, dodecylsulphate, humic acid) were performed to test UV lamp efficiency. Furthermore, the effect of addition of an oxidizing agent (H_2O_2, $K_2S_2O_8$) and /or metal catalyst (Fe^{3+}) into the solution was studied. The experimental equipment consisted of a feed solution reservoir, from which the solution was pumped into the UV lamp and returned back to the solution reservoir. The experiments were finished when desired TOC concentration (0.5 mg/L) was achieved.

The results of experiment performed with solution containing 11 000 μg/L phthalates are shown in Figure 1a). As it can be seen phthalate concentration in the solution reservoir decreased below desired concentration after 7.5 hours of experiment. H_2O_2 additon into the solution speeds up the phthalate degradation and desired concentration is achieved already after 5.5 hours of experiment, even with double flow of the solution through the UV lamp. The acceleration of phthalate degradation is observed mainly during the first hour of experiment, when TOC concentration is still high (c.f. Figure 1b)). The effect of Fe^{3+} addition into the solution is shown in Figure 1c). As it can be seen presence of metal catalyst together with the oxidizing agent contributes to the phthalate degradation and its degradation is significantly faster than in both previous cases.


a)

b)

c)

Figure 1. The evolution of phthalates concentrations in the model solution containing a) phthalates, b) phthalates + H_2O_2 and c) phthalates + H_2O_2 + Fe^{3+}

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UTILIZATION OF REVERSE OSMOSIS FOR THE BORIC ACID RECOVERY FROM PRIMARY COOLANT AT NUCLEAR POWER PLANTS

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Boric acid is added into the primary circuit of nuclear power plants (NPP) as a source of boron for abosrbtion of neutrons. The boron concentration in the primary coolant varies along the operation cycle of NPP – in the beginning of the operation cycle higher concentrations of boron are required due to higher fuel acitivty producing more neutrons. During the operation cycle, boron concentration in the primary circuit is gradually decreased by the means of coolant drainage. Drained water containing boric acid is then regenerated at the system of evaporators and ion exchangers producing high concentrated boron solution, which can be recycled back to the primary circuit [1]. The operation of the evaporator system is expensive, therefore it was suggested to replace it partially by the reverse osomosis unit. Furthermore, the use of reverse osmosis decreases volume of readioactive waste [2, 3].

Feed solution (primary coolant containing boric) is on the reverse osmosis modulus separated into two streams: permeate (pure water) and retentate (concentrated boric acid solution), which is further purified on the electrodialysis unit and then recycled back to the primary circuit [2].

The efficiency of the reverse osmosis in boron separation is dependent on temperature, applied pressure, feed solution composition and mainly on pH of the feed solution [4, 5].

In order to study the efficiency of reverse osmosis membranes in the boric acid removal form water solutions, experimental apparatus was constructed in our laboratory. It consists of the solution reservoir, pump and reverse osmosis modulus. The arrangement of experiments was batch and the retentate flow was refluxed to the feed solution. Several modulus of commercial reverse osmosis membranes were tested. The feed solution contained various concentrations of H_3BO_3. Furhtermore, various concentrations of KOH, LiOH and NH_3 were added into the solution in order to simulate real primary coolant composition.

To evaluate boric acid removal efficiency, rejection factor was calculated based on the following formula: $R \equiv 1 - \frac{c_P}{c_R}$, where c_P is boric acid concentration in permeate flow and c_R in retentate flow.

As it has been already stated above [4, 5], the efficiency of boric acid removal on reverse osmosis membranes is strongly dependent on the boric acid speciation, which is strongly dependent on pH of the feed solution. The dependence of boric acid speciation on pH of feed solution is shown in Figure 1a). As it can be seen, at high pH values boric acid occurs in a form of negatively charged borates. They are then repulsed from positively charged membrane, which results in increasing boric acid rejection at higher pH values (c.f. Figure 1b)).

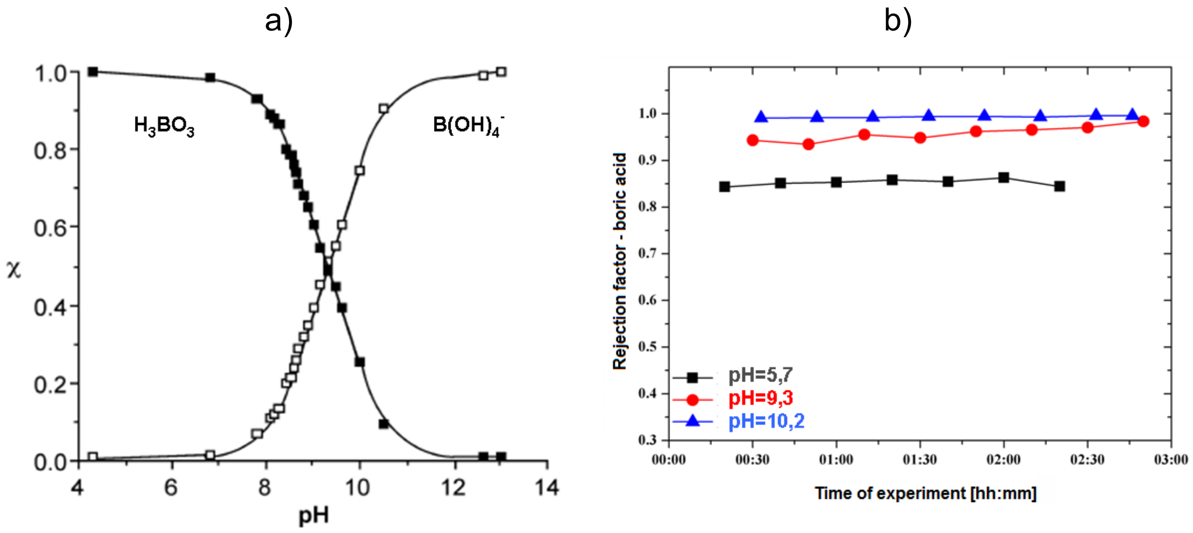

Figure 1. a) The dependence of boric acid speciation on the feed solution pH.
b) The influence of feed solution pH on the evolution of rejection factor of boric acid

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AMMONIA REACTIONS WITH THE STORED OXYGEN IN A COMMERCIAL LEAN NO$_x$ TRAP CATALYST

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Lean NO$_x$ trap (LNT) catalysts work under alternating lean and rich conditions – nitrogen oxides (NO$_x$) are adsorbed on the catalyst surface during the longer lean period (excess of oxygen) and then reduced within the short rich period (excess of reducing agents). During the rich phase, a moving reduction front divides the catalyst into two parts – the region close to the monolith inlet is already reduced, while the downstream part is yet oxidized [1]. Depending on local reaction conditions, several different N-products can be formed: N_2, NH_3, NO and N_2O.

Ammonia is local major product of the NO$_x$ reduction in the fully reduced part. The formed NH_3 is transported by convection downstream into the oxidized zone, where it can react with the stored oxygen and NO$_x$ [1, 2, 3]. Just at the reduction front, however, the reductants initially react with the released NO$_x$ over an incompletely reduced PGM surface, and therefore primary N_2O is likely to form here [4]. Furthermore, the secondary N_2O peak may evolve during the transition from rich to lean conditions – possible sources include ammonia oxidation or interaction of an adsorbed reductant with the residual NO$_x$ [4, 5].

To further elucidate the reaction pathways leading to N_2O formation, we investigate in detail ammonia reactions with the pre-stored oxygen in a commercial LNT catalyst containing platinum group metals (PGM), Ba and Ce. Periodic lean/rich experiments are performed without any NO$_x$ in the feed so that the lean mixture contains only oxygen and rich gas only NH_3 (in N_2 as a carrier gas). The effects of CO_2 and H_2O presence in the feed mixture (relevant to real exhaust gas) are also studied. It is shown that NH_3 reacts readily with the oxygen stored in Ce oxides, resulting in a delayed NH_3 breakthrough after switching to the rich conditions (Figures 1 a,c).

The presence of excess H_2O decreases the extent of this reaction. In contrast, NH_3 consumption increases when only CO_2 (without H_2O) is added into the inlet gas mixture. We propose that CO_2 undergoes a reverse water gas shift reaction leading to CO formation and providing additional oxygen for the NH_3 oxidation. The presence of CO was detected in the effluent gas, confirming this mechanism. Water excess inhibits the whole redox cycle and lowers the NH_3 consumption as it is one of the products (Figures 1 a,c).

The adsorbed CO formed from CO_2 during the rich phase also contributes to the secondary N_2O formation upon switch back to lean conditions (Figures 1 b,d). The appearance of N_2O peaks indicates that although the major part of NH_3 is oxidized selectively to N_2 [3], a certain amount of NO_x can be also produced and immediately stored on Ba sites (no NO_x detected in the effluent). The reaction of adsorbed NO_x species with CO and/or NH_3 has been identified as an important N_2O source [5].

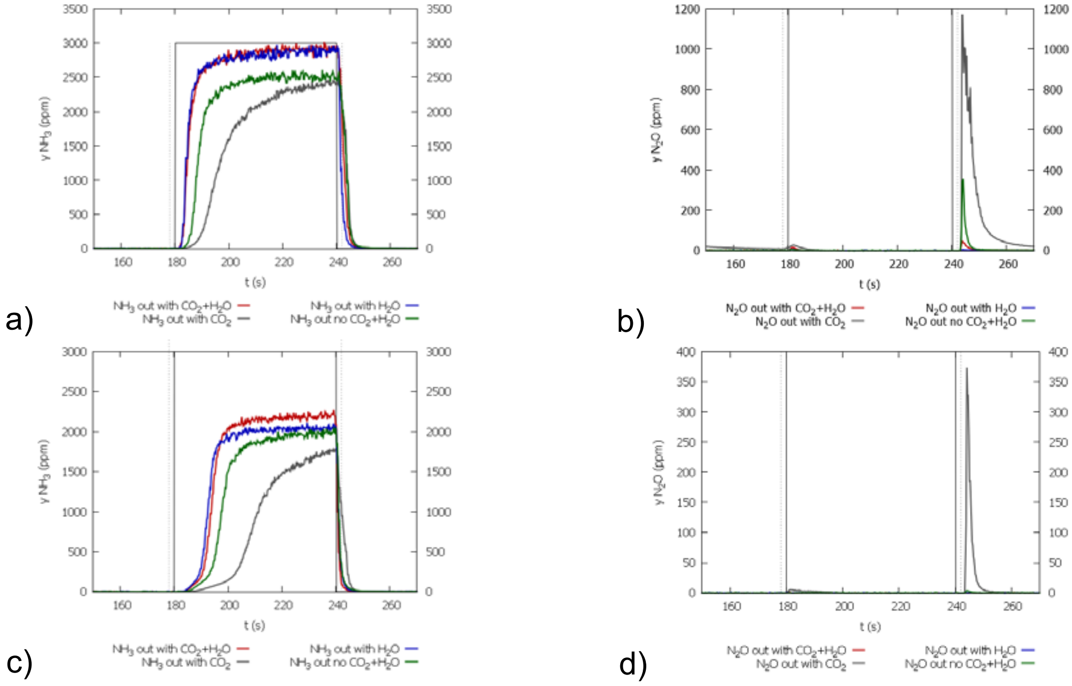

Figure 1. The effect of CO_2 and H_2O on NH_3 and N_2O evolution during oxygen storage and reduction with NH_3-rich inlet mixture at 200 °C (a,b) and 425 °C (c,d)

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STRATEGIC DIRECTION IN THE DEVELOPMENT OF HYDROGEN FUEL COMPLEX IN TRANSPORT, AUTONOMOUS ENERGY AND SYSTEMS OF SPECIAL PURPOSES. TECHNOLOGICAL SOLUTIONS IN THE PRODUCTION OF HYPERFINE HYDROGEN-FILTER FOILS

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Currently, as a general strategy for the development of fuel and energy complex in the field of engine civil and special purpose adopted focus on expanding the use of natural gas as a motor fuel.

The main objective is to transfer engine for compositional, hydrogen-containing fuel, in which hydrogen plays the role of activator that initiates the combustion process component, wherein the engine load required to vary the hydrogen content in the gas mixture from 0 to 100 %.

Developers of this idea attach importance to the problem of creating a promising membrane technology producing high-purity hydrogen (purity – 99.999 %). FSUE "Moscow factory for processing of special alloys," in conjunction with "Chemphyst" is underway to develop the production of ultrathin hydrogen filter foils from palladium alloy, as well as capillary tubes of palladium alloys for new design solutions to create hydrogen generators with high diffusion characteristics.

A NOVEL REACTOR SETUP FOR STUDYING LIMESTONE DISSOLUTION KINETICS

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New stricter emission limits for SO_2 required by the EU Industrial Emissions Directive need to be implemented by 2016 [1]. Moreover, stricter SO_2 emission regulations will also come into force in maritime transport in the Baltic Sea region from 2015. Limestone (mainly $CaCO_3$) is a natural resource and one of the most commonly used reagents in WFGD processes. The dissolution of limestone particles in the lower section of the scrubber (dissolution tank) has been identified as one of the most influential steps determining the rate of the SO_2 absorption process [1]. Limestone dissolution has been widely studied since the 1970's, however, a commonly accepted mathematical model which describes the dissolution kinetics has not been presented so far. The most commonly used approach in modeling is to divide the dissolution into several regions depending on *pH* [2], [3]. This essentially means that either mass transfer or chemical kinetics or a combination of the two determined the overall dissolution rate. Some of the contradictory results found in the literature can arise from differences and uncertainties in experimental setups, including liquid-solid and liquid-gas (CO_2) mass transfer as well as particle size distributions and particle morphology. Moreover, the changing *pH* influences e.g. the thermodynamics of the reaction mixture during the reaction.

A new reactor system was constructed in the present work for studying the dissolution kinetics of two different limestone samples in HCl. The reactor setup comprises a reactor vessel equipped with baffles, intense agitation, an air purging system, on-line temperature and *pH* measurement and a precise *pH* controller. The main advantage with the reactor system is the ability to run in a batch or a semi batch mode in a controlled manner, thus, the influence of different reaction parameters can be separated and studied systematically. The influence of external liquid-solid mass transfer can be evaluated by varying the agitation. The liquid-gas mass transfer can thereafter be studied by introducing varying levels of purging influencing the CO_2 removal from the liquid phase. This is important as CO_2 which is formed in the reaction produces carbonic acid, which influences the *pH* and thus, the reaction rate. Moreover, the influence of the dynamic *pH* on the reaction kinetics can be eliminated by running the experiment in a semi batch mode by keeping the *pH* constant. Different combinations of the running modes, the flexible sampling and on-line measurements, and the accurate temperature control system enable a systematic and controlled approach for gathering data for modeling purposes. The solid phase was studied during the dissolution by laser diffraction, SEM, EDX, and nitrogen adsorption. Experimental results for two different configurations of the experimental set-up are shown in Figure 1.

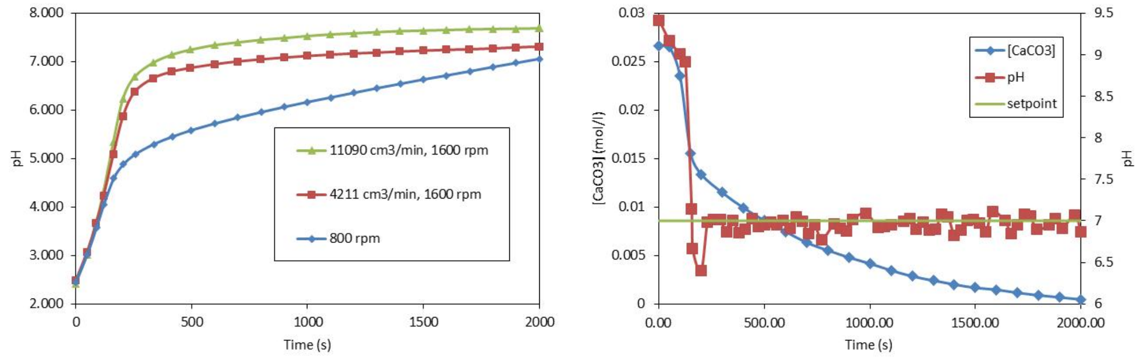

Figure 1. The influence of agitation and purging on the *pH* as a function of time for *pH* drift experiments (left), and the *pH* and conversion as a function of time in a *pH*-stat experiment (right)

As can be observed in Figure 1, the experimental parameters used in the reactor system, i.e. liquid-solid and liquid-gas mass transfer, influence the overall reaction rate significantly. The temperature as well as the concentrations of the solid and liquid phases were varied during the experiments. Mathematical modeling was used to quantify the influence of the different parameters on the overall dissolution rate as well as to assess the performance of the reactor system.

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THE NOVEL Ni-CONTAINING ZEOLITE CATALYSTS FOR PARTIAL OXIDATION OF METHANE (POM)

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The synthesis gas, CO and H_2 mixture, is called a strategic substrate of XXI century. It has industrial application for fuel (Fischer – Tropsch synthesis) and chemical production [1]. The syn-gas is produced from natural gas, carbon, biomass and refinery waste in gasification and reforming processes. One of the most popular ways of syn-gas production is partial oxidation of methane (POM) [1, 2]. This reaction allows to obtain syn-gas with molar ratio of $CO:H_2 = 1:2$, proper to Fischer – Tropsch or methanol synthesis. The advantages of POM reaction are high syn-gas yield and CO selectivity, what allows to avoid of expensive process of CO_2 and H_2O removal from syn-gas. Ni, Pt and Rh supported on Al_2O_3 and SiO_2 are well know as catalysts for POM reaction. In recent years the zeolites have been widely used in various processes. Their high surface area and possibility of good dispersion of metals make zeolites useful in catalytic processes [3].

In this work, the influence of the Ni content, kind of support and reduction temperature on the catalytic activity of Ni_xSiBEA and Ni_xAlBEA catalysts in POM reaction was investigated. The state and nature of Ni species were investigated by XRD, TPR-H_2, TPR-CH_4, TPD-NH_3, FTIR, TEM and ToF-SIMS.

Nickel zeolite catalysts were prepared by two different procedures: I) two steps postsynthesis method (Ni_xSiBEA) and II) classical wet impregnation (Ni_xAlBEA). The first method of preparation allows controlling the incorporation of Ni ions in the zeolite framework [4].

The TPR results show that in Ni_xAlBEA and Ni_xSiBEA nickel is present in three chemical environments which determine their reduction temperature. An isolated pseudo-tetrahedral Ni(II) species strongly interacting with zeolite support is present in the zeolite framework and is reduced at relatively high temperature (400–570 °C). An octahedral Ni(II) species is present in extraframework position and is reduced at much lower temperature 220–340 °C. The reduction at high temperature (about 600 °C) is related to the presence of nickel aluminosilicate ($NiAlO_2H^+$) or nickel silicate ($NiSiO_2H^+$) evidenced by TOF–SIMS analysis. IR studies show the presence of Lewis and Brønsted acidic sites for both Ni_xAlBEA and Ni_xSiBEA. During POM reaction carried out on calcined NiBEA catalysts (Ni_xAlBEA and Ni_xSiBEA) the first step is total oxidation of methane (TOM) and formation of CO_2 and H_2O in temperature range 420–720 °C, than the reduction of NiO phase by CH_4 takes place and partial oxidation of methane (POM) to syngas (CO and H_2) occurs on Ni^0 nanoparticles (from temperature 720 °C) [5]. This mechanism was observed also for supported Ni/Al_2O_3 catalysts [6]. In the case of POM reaction on prereduced Ni_xSiBEA catalysts, the first step is also total oxidation of methane (TOM) (in temperature range 290–390 °C) followed by the partial oxidation of methane (POM) to CO and H_2 (maximum at 600 °C) (Fig. 1). This phenomenon can be related to well dispersed Ni metal phase in close contact with SiBEA zeolite. The similar results was found for Ni/La_2O_3 catalysts [7]. The reduction of Ni_xSiBEA samples at 550 °C for 1 h in H_2 flow leads to the decrease of POM reaction temperature at about 100–200 °C in comparison to reaction carried out on calcined catalysts.

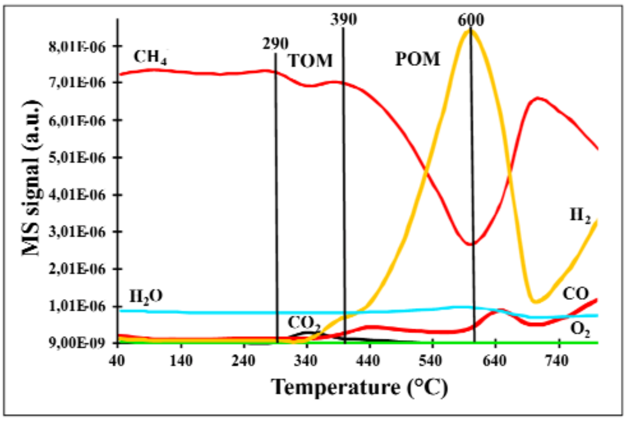

Figure 1. TPSR for $Ni_{5.0}$SiBEA catalyst calcined at 500 °C for 3 h and reduced at 550 °C for 1 h in H_2 flow

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MODELING THE COMPLEX DYNAMICS OF HETEROGENEOUS CATALYTIC REACTIONS

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Discovery of self-oscillations in the heterogeneous reactions of CO oxidation on platinum catalyst and hydrogen oxidation on nickel and platinum in 1972-1973 initiated the application of the theory of nonlinear dynamics in catalysis. The report is devoted to studying different types of generation of complex and chaotic behavior in the small-dimension dynamical systems with a hierarchy of characteristic times (i.e., with fast, intermediate and slow variables). The approach was proposed and firstly developed together with M.G. Slinko [1].

Model of heterogeneous self-oscillations. Consider the kinetic model of catalytic interaction of hydrogen and oxygen

$$\begin{aligned} x' &= K_1(1-x-y)^2 - K_{-1}x^2 - 2K_{30}e^{-\mu_3 y}x^2 y\,, \\ y' &= K_2(1-x-y)^2 - K_{-2}y^2 - K_{30}e^{-\mu_3 y}x^2 y - K_{40}e^{-\mu_4 y+\mu_5 z}y\,, \\ z' &= \varepsilon\left[y(1-z) - \alpha z(1-x-y)\right], \end{aligned} \tag{1}$$

where *x* and *y* are the surface concentrations of adsorbed hydrogen and oxygen, *z* is the concentration of oxygen dissolved into the subsurface layer of the metallic catalyst. The structure of the mathematical model is as follows:

$$x' = \mu f(x,y)\,, \qquad y' = g(x,y,z)\,, \qquad z' = \varepsilon \cdot h(x,y,z) \tag{2}$$

with small parameters ε and μ; i.e., the variables are moderate, fast, and slow. We consider two important cases: $\varepsilon \ll \mu$ и $\varepsilon < \mu$.

Chaotic behavior under condition $\varepsilon \ll \mu$. Fig. 1 shows an attractor and aperiodic time behavior of *z*-coordinate of the solution near the attractor. To be sure in the computational results, we used some special procedures of higher accuracy with a posteriori estimation of the global error of numerical integration.

Homoclinic chaos in the case of $\varepsilon < \mu$. Squeezing and stretching are the necessary properties for existence of some saddle periodic solutions which constitute a “skeleton” of an attractor. Let a Möbius orbit denote a saddle periodic trajectory whose local invariant manifolds are the Möbius sheets. The attractor includes infinitely many Möbius orbits, but there are no steady states. An extremely high parametric sensitivity near the attractor is due to existence of trajectory bundles of a “shower” and “tunnel” type that are generated by transversal homoclinic trajectories to the Möbius orbit.

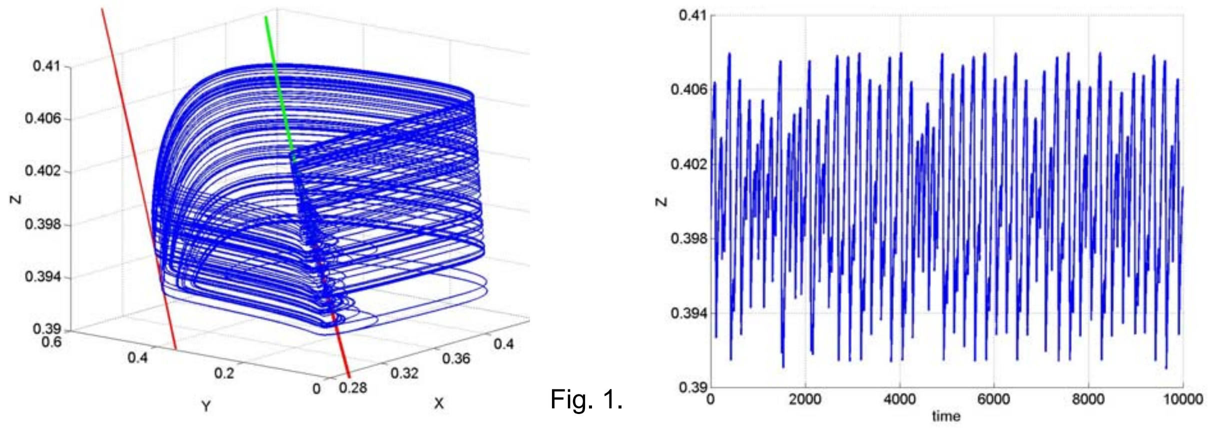

Fig. 1.

Attractor Λ (owing to Slinko and Chumakov) (Fig. 2, *left*) is obtained in result of the Feigenbaum cascade of period-doubling bifurcations of a periodic solution. The partial pressure of hydrogen served here as a control parameter.

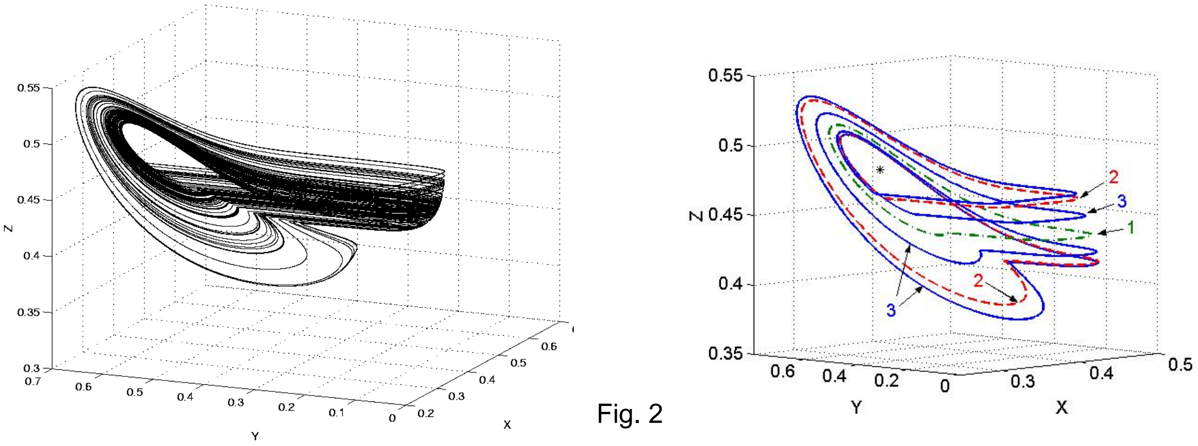

Fig 2

How can we estimate the dimension of a strange attractor? Let Λ be an attractor in the 3-dimensional phase space with the Lyapunov exponents $\sigma_1 > 0 > \sigma_3$, $\sigma_2 = 0$, и $\sigma_1 + \sigma_3 < 0$. Then the *Lyapunov dimension* of Λ (or *Kaplan-Yorke dimension*) is denoted by $D_L(\Lambda)$ and $D_L(\Lambda) = 2 - \sigma_1 / \sigma_3$. The Möbius orbits γ_0 (1), γ_1 (2), and γ_2 (3) in Fig. 2 (right) belong to Λ and have the periods *T*, 2*T,* and 4*T*. The Kaplan-Yorke formula gives the lower estimate of the Lyapunov dimension of Λ: $D_L(\Lambda) \geq 2.075838$.

The developed approach is shown to be rather efficient for studying catalytic reactions with complex dynamics.

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COMBINED STEAM AND CARBON DIOXIDE REFORMING OF METHANE TO SYNTHESIS GAS OVER POROUS NICKEL BASED CATALYSTS

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Currently, combined steam and carbon dioxide reforming (SCDR) of methane to synthesis gas attracts much attention. In comparison with dry reforming of methane, the use of steam in the feed for CO_2-reforming reduces the formation of carbon. By changing the H_2O/CO_2 ratio in the reaction feed, the H_2/CO product ratio can be controlled, and this makes it possible to produce synthesis gas with the H_2/CO ratio of about 2, which is suitable for the methanol and Fisher-Tropsch syntheses. The SCDR of methane enables the production of synthesis gas from such renewable energy sources as biogas, whose main components are methane, carbon dioxide and water.

The major problem encountered towards the application of this process is carbonization of catalysts. This work was aimed at the developing of the nickel catalysts supported on a porous nickel ribbon (pNirb) with a MgO underlayer and studying their catalytic properties in the SCDR of methane to synthesis gas. The use of a catalyst support in the form of a porous nickel ribbon allows us to impart the high thermal conductivity and mechanical strength to the nickel catalysts and to produce structured catalysts [1].

The method of preparation of supported nickel catalysts was developed. The method consisted in supporting of the MgO underlayer (6 wt. %) by impregnation of 0.1 mm thick pNirb, obtained by rolling of the nickel powder (S_{sp} ~ 0.15 m^2/g, V_Σ ~ 0.1 cm^3/g, r_{preval} ~ 5-60 μm). Additional supporting of nickel (1-4 wt. %) and MgO (1-4 wt. %) was performed by impregnation of the support (pNirb + 6.0 wt. % MgO) with a mixture of solutions of $Ni(NO_3)_2$ and $Mg(NO_3)_2$. The catalysts were characterized by XRD, low-temperature adsorption of nitrogen, SEM and TEM in combination with EDX analysis. Catalyst activity in SCDR of methane was evaluated by the flow method (1 atm., 750 °C, $CH_4/CO_2/H_2O/N_2$ = 35/23/39/3, GHSV = 62.5 L/gh). Prior to testing the catalysts were reduced at 750-900°C for 1 hour in H_2 flow.

According to the TEM data supported nickel crystallites are highly dispersed (3–7 nm) and epitaxially bound with the MgO. After testing in the catalysts most of supported nickel crystallites remain in the stable state of dispersed crystallites epitaxially bound with MgO. Figure 1 shows the effect of time-on-stream in SCDR methane (18 h) on CH_4 conversion. The activity of catalyst with low content of MgO (6.7 wt. %) decreased during testing. After reaction in this catalyst no carbon deposits were found on dispersed nickel crystallites epitaxially bound with MgO. However, the islet formation of graphite-like carbon was observed on the large crystallites of nickel ribbon. Thus, the observed decrease in the activity of this catalyst can be attributed to the carbonization of large crystallites of nickel support that are not covered with MgO. The catalysts with high content of MgO (8.6 and 10.4 wt. %) in which the MgO underlayer completely covering the nickel ribbon showed stable activity throughout the test period. After the reaction in these catalysts on the large crystallites of nickel ribbon dispersed nickel crystallites (5-10 nm) epitaxially bound with MgO appeared.

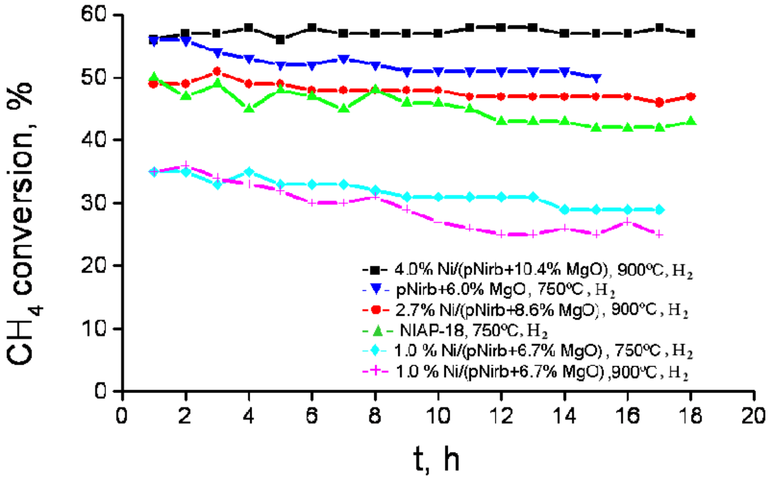

Fig. 1. Methane conversion versus time-on-stream in the steam-CO_2 reforming of methane over the catalysts

The TEM investigation has not revealed any carbon deposits in these catalysts. The resistance of these catalysts to carbonization was attributed both to the formation of nickel crystallites epitaxially bound with MgO and the formation of the MgO underlayer, that completely covers the nickel ribbon and prevents its contact with the reaction medium. The H_2/CO ratio in the reaction products over these catalysts was 2.1-2.2 and over catalyst with low content of MgO this ratio was 2.7-2.8. The catalysts with high content of MgO on the highly thermally conductive nickel ribbon are comparable in activity with commercial catalyst NIAP-18 (10.5 % Ni/Al_2O_3) and surpass it in stability of activity under conditions of SCDR of methane (Fig.1).

Thus, the developed nickel catalysts supported on nickel ribbon with MgO covering are active and stable in SCDR of methane to synthesis gas.

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MATHEMATICAL MODELING OF PROCESS OF NANOSTRUCTURIZATION OF POLYURETHANES

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Metal complex compounds, which are nanostructuring agents for the synthesis of polymer materials, are obtained. The obtained complex compounds reveal catalytic activity in the reactions of low temperature dissociating of urethane groups and the ability to interact with isocyanate groups followed by the formation of azoaromatic derivatives. Establishing step-like fall of volume resistivity of polyureathanes by more than 10, 000 times as the result of metal complex cross-linking of polyurethanes is important both from practical and theoretical points of view. It is found that the interaction of an urethane prepolymer with volumetric coordination compounds leads to the formation of blocks of coordination bound azo groups. The considerable influence of coordination bound rigid blocks on the supramolecular arrangement of polyurethanes and, correspondingly, on the complex of their physical and mechanical properties is shown.

Nanostructuring organic-inorganic gel is developed which has the ability to dissolve in polymer melts and reactive olygomers. The silica grid in olygomer bulk is formed not only due to the alignment of a chain of bound fractal clusters but it is also formed as a result of the formation of associates of potassium siloxanolate groups at the interphase boundary of thermodynamically incongruent olygomers. Sillica gel is soluble in polymers melts or reactive olygomers owing to the lability of associative bonds at their optimal content. The polymer obtained on the basis of polyoxyethylene glycol containing terminal potassium alkoxide and hydroxyl groups, and polyisocyanate is investigated.

Kinetic investigations of the processes of nanostructuring of polymers have been conducted using the method of mathematical modeling.

Acknowledgements

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REACTOR-REGENERATOR SYSTEM JOINT WORK OPTIMIZATION IN BENZENE ALKYLATION WITH HIGHER OLEFINS UNIT

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Over the last years there has been a huge success in development of aromatic compounds with olefins alkylation processes as environmentally friendly technologies [1]. The most demanded products of petrochemical synthesis are based on synthetic detergents produced from LAB. Such detergents have good foamability and high biodegradability and this fact makes the task of LAB production efficiency enhancing urgent.

The process intensification, in general, involves the modification of technological scheme in order to reduce energy consumption [2], reconstruction of equipment using available raw materials and catalysts [3] or application of innovative technologies [4]. One of the ways of process efficiency enhancing without reconstruction of existing equipment can be an organization of technology-related blocks smooth operation, in this case, joint work of benzene with olefins alkylation reactor and HF- catalyst regeneration column.

Analysis of "reactor-regenerator" system joint work may be carried out at maximum efficiency with mathematical models [5, 6] and computer modeling systems based on them [7, 8] which should take non-stationarity of processes in the reactor into account [9].

The aim of this research is to identify directions of "reactor-regenerator" system work optimization and to analyze their efficiency.

Thermodynamic analysis of heavy aromatics (HAR) hydrofluorination reaction with formation of HAR-F, accumulation of which at the bottom of the column prevents evaporation of HF causing mode failure, occurrence probability was performed with use of quantum chemical methods for thermodynamic functions calculating (Gaussian-98 program).

Analysis of "reactor-regenerator" joint work was carried out with use of chemical processes mathematical modeling methods with software implementation in Delphi-7 programming environment.

The carried out research allowed to reveal following conclusions:

1. The reasons that lead to HF-catalyst regeneration column mode failure were identified. It was shown that substances generated at the bottom of the column during reaction of heavy aromatics hydrofluorination may form a layer with high surface tension and prevent evaporation of HF from the cube. Thermodynamic analysis of hydrofluorination probability of HAR with different structure was carried out.

2. The impact of these failures on benzene with higher olefins alkylation reactor was described. Alkylation catalyst current activity and the rate of its change depending on HAR quantity were calculated.

3. The ways of benzene alkylation rector and catalyst regenerator column joint work optimization were proposed.

4. Positive effect of HF-catalyst optimal activity in alkylation reactor maintaining leads to increase in column smooth operation duration without alkylate quality compromising.

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COPPER BASED CATALYSTS FOR RECEIPT OF ETHYLENE FROM BIOETHANOL

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Increase in energy consumption, reduction of oil reserves make urgent search for alternative raw materials for production of valuable organic products, chemical synthesis. For this reason, the development of producing industrially important products of bio- ethanol is of great interest to researchers in the field of chemistry [1-3].

The aim of this work was to study the catalytic activity of supported copper catalysts in the production of ethylene by catalytic conversion of ethanol. The studies were conducted on the flow installation. The objects of study were deposited copper-containing catalysts Cu/Al_2O_3H-ZSM-5 and $CuCe/Al_2O_3H$-ZSM-5 with a specific surface 281,5 and 282,2 m^2/g, respectively. The influence of the space velocity of the inert gas on the activity of Cu/Al_2O_3H-ZSM-5 catalyst was carried out in the range of 300-13500 h^{-1} catalyst. The results demonstrate that the liquid hydrocarbons, such as benzene, toluene, o-xylene, trace amounts of acetaldehyde are formed at lower space velocities. Selectivity by the liquid phase was 17.8 % and 3.1 at W = 300 and 1500 h^{-1}, respectively. Since W = 3000 h^{-1} the liquid phase is not formed; only gaseous reaction products were detected. Carbon dioxide is released at all space velocities other than W = 13500 h^{-1}. The highest conversion of ethanol (98 %) is observed at W = 1500 h^{-1}. At a given space velocity the maximum yield of ethylene is formed. Selectivity by ethylene increases with increasing of space velocity of the reaction, and the conversion of ethanol decreases passing through a maximum at 1500 h^{-1}. Also the concentration of saturated hydrocarbons decreases with increasing of space velocity.

Effect of modifying additive such as Ce on the activity of 3 % Cu/20 % Al_2O_3-80 % H-ZSM-5 catalyst was investigated. Addition of cerium to the 3 % Cu/20 % Al_2O_3-80 % H-ZSM-5 catalyst has a promoting effect at all space velocities. Ethylene yield on 3 % CuCe/20 % Al_2O_3-80 % H-ZSM-5 catalyst is increased from 85 to 88 % compared with the copper catalyst at 1500 h^{-1}. The highest 93 % yield of ethylene was obtained at space velocity 3000 h^{-1}.

Thus, the results of the research show that the process of catalytic conversion of ethanol on copper catalysts is a promising way to obtain raw materials demanded by the chemical industry-ethylene.

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REFORMING OF METHANE WITH CARBON DIOXIDE

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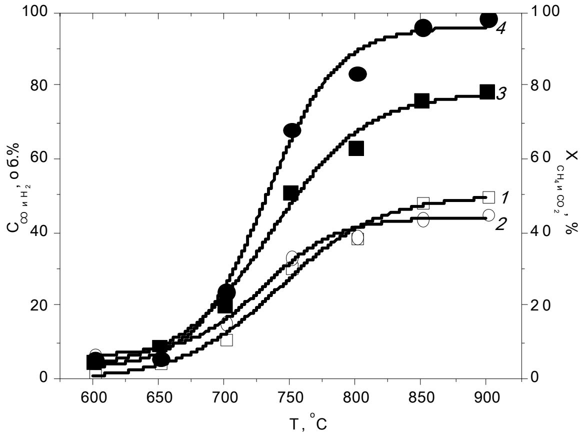
Carbon dioxide reforming of methane (CRM) in the synthesis gas is a promising way to obtaining the starting reactant for the production of hydrocarbons by method-Fischer-Tropsch. Conducting of CRM also has ecological significance, since allows to consume a combination of two greenhouse gas – methane and carbon dioxide [1].

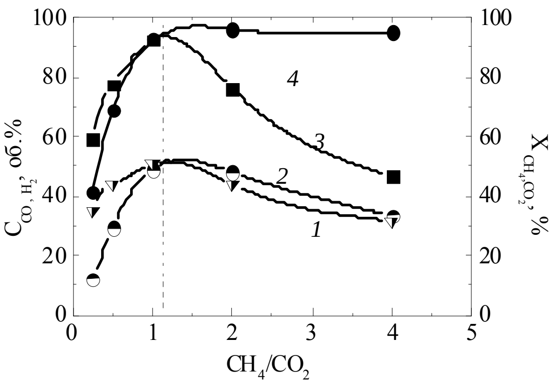
The process of carbon dioxide reforming of methane has not yet been widely adopted in the industry, since the main problem is the carbonization of catalyst. The main efforts in the art directed to the development of active catalysts [2].

In the present work as a catalyst for carbon dioxide reforming of methane was investigated catalyst NiCuNdMo/20%Al_2O_3HZSM-5.

Figure 1 shows the results of the effect of reaction temperature on catalyst activity in the temperature range 600-900 °C at a space velocity of 3600 h^{-1} and a ratio CH_4/CO_2 – 2. As seen from the figure 1, the temperature increase from 600 to 900 °C the conversion of methane increases from 4 % to 78 % and in the case of carbon dioxide – from 5 to 98 %. With an increase in process temperature from 600 to 900 °C the hydrogen concentration is increased from 1.6 to 49.8 vol. %, and carbon monoxide from 6.9 to 45.0 vol. %. In spite of the fact that the ratio of the initial components CH_4/CO_2 = 2 the conversion of the carbon dioxide is considerably higher than that of methane.



1-H_2; 2-CO; 3-CH_4; 4-CO_2
Fig.1. Effect of temperature on the conversion of CH_4, CO_2 and concentrations of major reaction products



1-CO; 2-H_2; 3-CH_4; 4-CO_2
Fig. 2. Effect of the ratio of catalyst activity CH_4/CO_2

However, from the experimental data shows that on this catalyst almost the entire temperature range observed equilibrium yield of CO and H_2. At T = 850 °C to study the effect of ratio CH_4/CO_2 from 0.5 to 4 on the catalyst activity (Figure 2). It is seen that the dependence of methane conversion on ratio CH_4/CO_2 has extreme character with a maximum located in the area close to 1 and corresponds to 92.6 %. Increase of the ratio leads to a fairly rapid decrease in methane conversion. Unlike methane the conversion of carbon dioxide is close to 1 ratio reaches 92.3 %. Curves of formation of the desired product – the hydrogen and carbon monoxide are also the maximum value (H_2 – 49 vol. % and CO – 50 vol. %) with a ratio close to 1 CH_4/CO_2.

Thus, we can conclude that the most favorable ratio for the carbon dioxide reforming of methane is stoichiometric at which the maximum yields of the reaction products and the highest conversion of the starting reagents.

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NUMERICAL SIMULATION OF THE FLUIDIZED BED CHEMICAL REACTOR WITH STRUCTURAL ELEMENTS OPTIMIZATION

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Isobutylene is an important monomer for petrochemical synthesis. On the basis of isobutylene a wide range of materials is obtained, such as synthetic rubbers, films and fibers, high-octane components of gasoline. The main method of isobutylene producing in Russian Federation is the isobutane dehydrogenation in a fluidized bed of catalyst. The catalyst is a complex system consisting of an alumina support and deposited on its surface the active component – Cr_2O_3 and the promoter – K_2O. High activity of alumina-chromia catalyst is detected in the dehydrogenation of isobutane in the laboratory conditions, but not always in the conditions of industrial application. This may be caused by the temperature of the catalyst bed, which is not sufficient to provide a high conversion of isobutane in the endothermic dehydrogenation reaction. To maintain the required temperature, it is necessary to feed of heated catalyst in a fluidized bed. The main task is the effective heating of zone of the fluidized bed with the highest concentration of catalyst.

Currently, one of the ways to determine the properties of large-scale fluidized beds is numerical simulation. In a study of fluidization was extended Eulerian-Eulerian approach, when carrier phase (gas, liquid) and discrete (solid) phase is continuous. To account for movement of features in a fluidized bed, using the kinetic theory of gases added to the equation describing the change in kinetic energy of the granules in consequence of collisions.

This paper presents the results of calculations of chemical reactor with a fluidized bed of pulverized catalyst. The hydrodynamics and heat transfer in a chemical reactor model based on existing industrial unit dehydrogenation of isobutane was studied. In the lower part of the reactor feeder gas feedstock is situated. In the center of reactor there is a vertical pipe feeding from the regenerator. A regenerated heated fresh catalyst is feeding to the zone above the upper grid. Calculations were performed using numerical methods of computing.

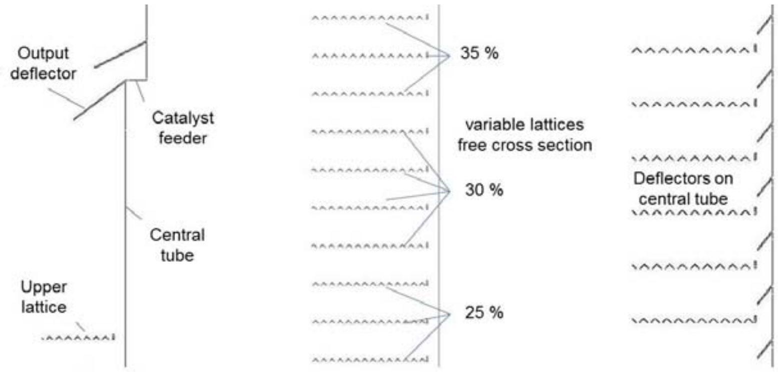

Figure 1. Variants of structural elements modification

Each structural element of the specific apparatus may become critical to overall efficiency. To increase heat transfer in areas of high catalyst concentration were made calculations of reactor with different design variants. There are an “output deflector” in the output of the catalyst feeder; variations of the free cross section of lattices in the reactor; deflectors on the central tube in the lattices zone (Figure 1).

Fields of catalyst concentration, temperature and the function of the chemical reaction efficiency field (which depends on temperature and catalyst concentration) were obtained (Figure 2). The directions and options for modifications are determined that increase the efficiency of the investigated chemical reactor.

Various modifications in the wide range of the fractional composition of the catalyst show different efficiency. Since an increase in small particles some modifications provide to increase the probability of chemical reaction, and others – decreasing. Most effective for the investigated reactor is deflecting elements for the central tube with a simultaneous increase of the lattices free cross section in elevation.

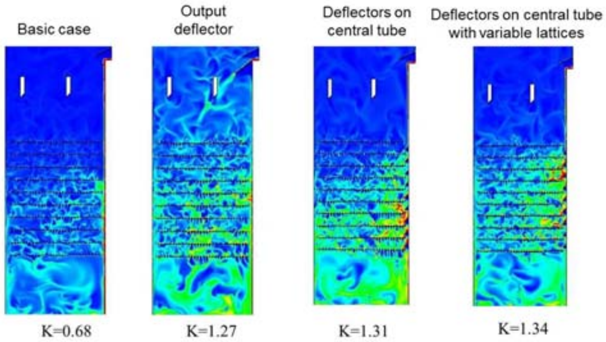

Figure 2. Function of the chemical reaction efficiency fields, K – efficiency coefficient

PP-30

KINETIC MODELLING FOR THE TRANSFORMATION OF 1-BUTENE ON A K MODIFIED HZSM-5 ZEOLITE CATALYST

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The main sources for C_2-C_4 olefin production are: steam cracking (70 %), fluid catalytic cracking (FCC, 18 %) and the methanol to olefins (MTO, 10 %) process. The remaining 2 % is obtained by the “On purpose propylene” (OPP) technologies (in an early research stage), where paraffin dehydrogenation and metathesis are included [1]. The intensification of propylene production from C_2-C_4 olefinic streams obtained from the aforementioned processes, is of great interest in order to satisfy the increasing propylene worldwide demand (annual rate of 5.7 %) [2]. Propylene selectivity is conditioned by the complexity of the oligomerization-cracking carbocationic mechanism [3,4], and so it depends on reaction conditions (especially on temperature) and catalyst properties (acidity and shape selectivity).

This work contributes to quantifying by a lumped kinetic model the effect reaction conditions (temperature, space time and partial pressure) have on the product distribution in the transformation of 1-butene. The study is carried out on a HZSM-5 zeolite catalyst with $SiO_2/Al_2O_3 = 280$ ratio (of moderate acidity) modified with 1 wt. % of K, given that a suitable balance is stricken between conversion, propylene selectivity and stability, which is explained by a limited density and acid strength of the sites that hinder the secondary reactions of aromatization and hydrogen transfer, as well as the reactions of olefin condensation to forme coke [5].

Different lumped kinetic models have been proposed for the zero timeon stream kinetics. The kinetic parameters of best fit for each kinetic model have been calculated by multivariable nonlinear regression. The optimization has been carried out by minimizing an objective function established as the sum of squared differences between experimental and calculated values of composition. The values predicted by the models for the composition of each lump have been calculated using a MATLAB code containing the routines for integration of the mass conservation equation for each lump and for the multivariable nonlinear regression.

Figure 1 shows the kinetic scheme corresponding to the best fit to the experimental results. The products have been grouped into the following lumps: CH_4

(whose formation is significant at high temperature); C_2H_4; C_3H_6; C_2-C_4 paraffins (with low amounts of ethane); and C_{5+} (olefins, paraffins and BTX aromatics). As an example of the goodness of fit, Figure 2 compares the experimental results (points) of lump composition (molar fraction, X_i) and butene conversion (X_B) with those calculated using the kinetic model (lines) for different values of space time, at 400 °C.

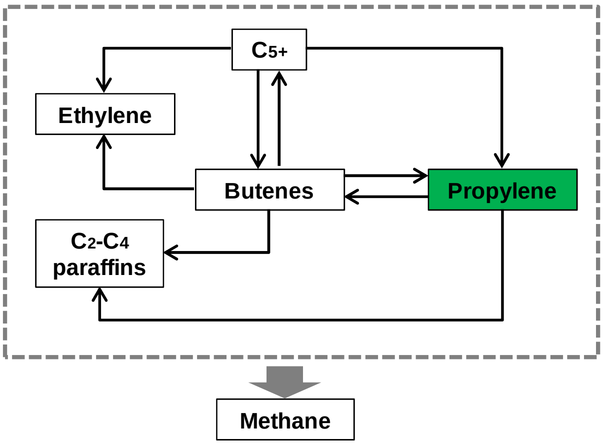

Figure 1. Kinetic scheme proposed

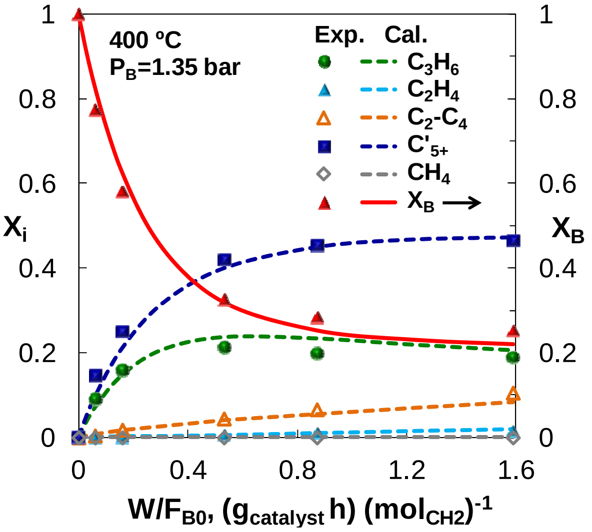

Figure 2. Comparison of experimental (points) and calculated (lines) values for product composition and butene conversion, for different space time values

The kinetic model proposed for the main reaction allows quantifying product distribution at zero time on stream in the 400-600 °C range and in a wide range of experimental conditions: space time, up to 1.6 ($g_{catalyst}$ h)(mol_{CH2})$^{-1}$; and 1-butene partial pressure, 0.375-1.35 bar. In order to progress in the development of the process, this kinetic model will be improved by considering the catalyst deactivation by coke.

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Acknowledgements

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PRODUCTION OF ACROLEIN FROM GLYCEROL IN LIQUID PHASE ON HETEROGENEOUS CATALYSTS

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Introduction

Nowadays, oil is the main energetic resource in the world. Glycerol (G) is the main by-product of transesterification of vegetable oils (triglycerides) and methanol for producing biodiesel. Catalytic conversion of glycerol to acrolein (ACR) by a double-dehydration reaction could offer a sustainable alternative to the present acrolein technology based on propylene. Here, this reaction was studied in liquid phase using heterogeneous catalysis. The main advantage to carry out this reaction in liquid phase with heterogeneous catalysis is that the catalyst can be recovered easily and also it can be reused in other reactions. If sulphuric acid or another mineral acid is employed instead of heterogeneous catalyst, the separation becomes more difficult. So, the catalytic behaviour of several acid solids with Lewis (L) or Brönsted (B) acid sites, such as aluminium phosphate and commercial zeolites (HY and ZSM-5) with different SiO_2/Al_2O_3 ratio, has been studied. Furthermore, the reaction parameters (Temperature of reaction, G/Catalyst ratio and time of reaction) have been optimized in order to obtain the highest yield to acrolein.

Experimental

The aluminium phosphate was prepared by an ammonia gelation method as previously reported [1]. The metal phosphates will be denoted by the corresponding formula and a number indicating the calcination temperature (450 ° and 650 °C). The zeolites ZSM-5 and HY were commercial from Zeolist and glycerol from Sigma Aldrich (99.5 %). The SiO_2/Al_2O_3 ratio was 50 and 30 for ZSM-5 and 5.2 for HY. The glycerol transformation was carried out in a round-bottom flask, using conventional heating and microwave. The analysis of G and product composition was carried out by GC-FID and the identification of products by chromatographic patterns and/or by CG-MS. Conversion (X) and selectivity to products (S_i) are expressed as mol% on a C atom basis. Using conventional heating, the best reaction parameters obtained were: Temperature, 270 °C; catalyst weight, 1 g; G volume, 30 mL; time of reaction, 30 hours. In each experiment a new charge of catalyst was employed. The acidity of the solids was determined by Temperature Programme Desorption (TPD) of pyridine and the acid site nature Brönsted and/or Lewis was determined by Diffuse Reflectance Infrared Fourier Transform Spectrometry (DRIFT) of pyridine.

Result and Discussion

In all the catalysts studied the main product was acrolein. Hidroxyacetone and 1, 3-dioxanol were also obtained. With microwaves, the conversion values were lower than using conventional heating, while the selectivity to acrolein values were almost the same, Table 1. The $AlPO_4$-650 catalyst showed the best yield to ACR (X = 23 %; S_{ACR} = 77 %). This acrolein formation seems to be related with weak Lewis acid sites, being $AlPO_4$-650 which has the most quantity of them. The Brönsted acid sites would favour the glycerine condensation reaction, which takes place over $AlPO_4$-450 catalyst. The lowest capacity of acrolein formation of the different zeolites could be related, not only with the lower acidity that they exhibit, but also with their specific structure. In fact, their cells are smaller than the pores of the aluminum phosphate so these cells could be blocked faster.

Table 1: Surface area; acidity values from Py-TPD; L/B ratio values at two different temperatures of degasification from DRIFT and data of the reaction

Catalyst	S_{BET} (m^2/g)	Py (μmol/g)	L/B 50 °C	L/B 150 °C	X (mol %)	S_{ACR} (mol %)
$AlPO_4$-450	218	146	0.85	-	19	47
$AlPO_4$-650	179	109	2.28	2.10	23	77
$AlPO_4$-650 (*)	“	“	“	“	2	76
ZSM-5(50)	400	195	1.03	0.23	5	65
ZSM-5(30)	425	205	2.88	-	6	72
HY	660	288	21.76	2.37	7	63

(*) values obtained with microwave heating; time of reaction = 1 h

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STRATEGIC AND FUNDAMENTAL PROCESS FOR THE PRODUCTION OF BUTADIENE AND ISOPRENE VIA THE CONVERSION OF LOWER ALCOHOLS

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Butadiene and isoprene are important building blocks for chemical industries; they are majorly produced from petroleum sources. The global demand for butadiene and isoprene is more than 9 million tones, which translates to high demand for their commercially most important polymers some of which are styrene-butadiene rubbers, polybutadiene, styrene-butadiene latex, polyisoprene e.t.c [1,2].

The rapid development of synthetic rubber industry, depletion of oil reserves due to over dependence on fossil fuels, issues related to the environment and climate changes have adverse effects on the production of these petrochemicals and have necessitated the exploration of other alternative resources and research in this direction.

The combination of ethanol and propyl alcohols with different ratios for the combined production of butadiene and isoprene was studied using lebedeev's reaction as a model. The reaction was carried out in a temperature range of 400-420 °C, flow rates between 1-3 h^{-1} and on a bifunctional contact mass K-16 composed of Mg-Si system, proven to be highly active in the conversion reaction of ethanol into butadiene.

The thermodynamic analysis of this reaction showed high possibility of butadiene and isoprene production. There is also a possibility of an in situ reaction of isopropyl alcohol with oxygen to simultaneously produce acetone and hydrogen peroxide - considered to be an initiator for the catalytic conversion process of ethanol

Conversion reactions of the mixtures of ethanol, propyl alcohols and oxygen were carried out, in order to study the ratios of the produced butadiene and isoprene.

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COMPLETE OXIDATION OF VOLATILE ORGANIC COMPOUNDS OVER MANGANESE OXIDE CATALYSTS

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Over 300 chemicals are designed as VOCs by the U.S. Environmental Protection Agency and most of them are highly toxic/carcinogenic substances that contribute to photochemical smog, global warming and so on. Therefore, VOCs are carefully regulared and different technologies have been developed to control their release to the atmosphere [1]. Catalytic oxidation is one of the most widely used techniques to control VOCs emissions at relatively low temperatures: it is less fuel intensive compared to thermal oxidation and it is highly versatile with the possibility to treat waste streams with different VOC concentrations and effluent flow rates [2].

Recent works have demonstrated that manganese oxides are promising catalysts for the abatment of pollutants, exhibiting comparable catalytic activities with noble or supported noble metals. Hence, they could be a cheaper alternative [3]. However, it is known that Mn-based catalysts are structure sensitive for VOC oxidation [1].

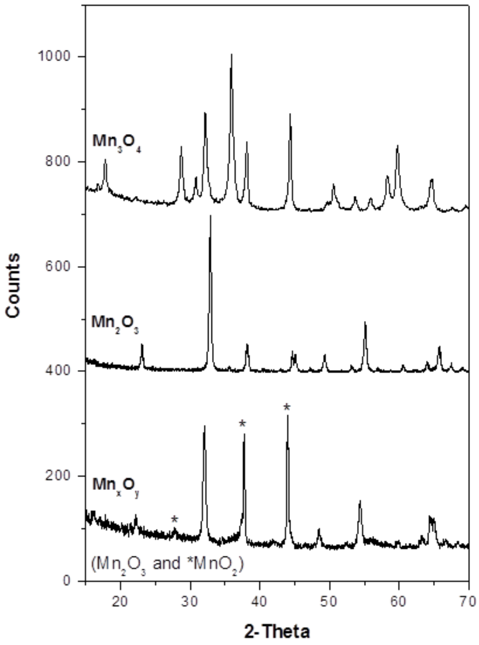

Figure 1. XRD patterns of the prepared catalysts

In this work, a set of highly crystalline MnO_x catalysts (namely Mn_2O_3, Mn_3O_4 and Mn_xO_y) was obtained by the solution combustion synthesis (SCS) [4]. The prepared catalysts were tested for the total oxidation of ethylene, propylene and toluene in air at different temperatures using a fixed-bed laboratory reactor (flow rate: 300 cm^3 min^{-1}; GHSV: 12000 h^{-1}). Stability tests were made (n-cycles and long TOS). Samples were characterized by several physico-chemical techniques, including powder XRD, FE-SEM, N_2 physisorption, H_2-TPR, XPS and IR spectroscopy. As a whole, XRD patterns of both Mn_2O_3 and Mn_3O_4 samples revealed the presence of homogeneous, high-purity and nanocrystalline oxide powders (Figure 1). No peaks for other types of MnO_x phases were detected. On the contrary, peaks due to different cystalline phases were observed with Mn_xO_y (i.e. Mn_2O_3 and MnO_2). Similar textural properties were attained with all catalysts (SSA_{BET} = 30-40 $m^2\,g^{-1}$; V_p = 0.12-0.14 $cm^3\,g^{-1}$) as well as FE-SEM images showed uniform particles size (diameter of ca. 50-100 nm) and spongy (3-D) frameworks. Catalytic activity tests using ethylene as probe molecule confirmed that Mn_3O_4 is the most active catalyst in VOCs oxidation (Figure 2). Similar results where obtained with propylene and toluene (data non reported for the sake of brevity). Indeed, the active phase Mn_3O_4 can be considered as a spinel structure of $Mn^{2+}(Mn^{3+})_2O_4$, in which the presence of both Mn^{2+} and Mn^{3+} cations (= Lewis acidic sites) may favor redox-cycles (i.e. MvK-type mechanisms). On the other hand, this beneficial effect was not observed with Mn_xO_y showing multi-crystalline phases. Hence, the most active catalysts are those that exhibit the best redox properties as confirmed by complementary analysis (Mn_3O_4 > Mn_2O_3 > Mn_xO_y). The flow rate effect on the catalytic activity was also investigated: lower flow rates of VOCs may cause longer residence times of molecules which lead to more complete reactions (deeper oxidations), in agreement with previous studies [5,6]. Since real industrial emissions usually contain mixtures of VOCs, studies of the catalytic activity on a single VOC partially represent the catalyst application. Therefore, the catalytic behavior of MnO_x systems was also investigated with mixtures of VOCs (ethylene, propylene and toluene). Preliminary results suggest that the total oxidation temperature of the mixture strongly depends on the temperature at which the most stable VOC is oxidized. Further catalytic studies could be done with ceramic monolithic supports coated with Mn_3O_4 to better simulate the catalyst working conditions.

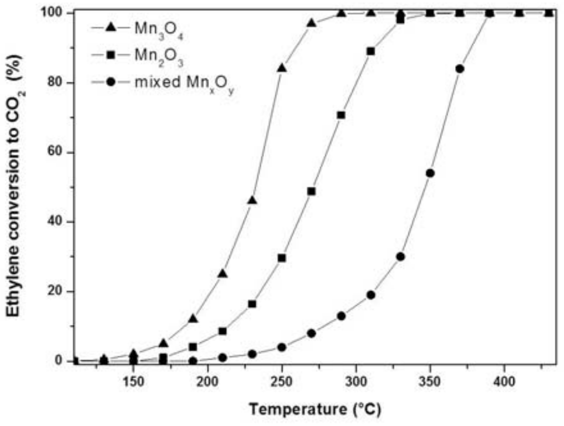

Figure 2. Ethylene conversion to CO_2 over MnO_x catalysts. VOC conc.: 500 vppm in air

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SOLID FOAMS: NOVEL CATALYST SUPPORT IN TRICKLE BED REACTORS

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The trickle bed reactor (TBR), in which gas and liquid flow concurrently downward over a fixed bed of catalyst particles, are widely used in the petroleum industry, mainly in diverse hydrogenation processes of petroleum fractions, e.g. hydrodesulphurisation. The catalyst beads (1–3 mm) are spherical, cylindrical or more sophistically shaped. Due to random character of catalytic beds, several disadvantages may occur, like the hot-spot formation, broad residence time distribution or high pressure drop due to low voidage value (usual void fraction amounts to 0.3 – 0.6). Application of solid foams as alternative catalyst support may be solution of important problems connected with the bed. Solid foams have wide range of applications due to their attractive thermal, mechanical, electrical and acoustical properties. They are being implemented, for example, in heat exchangers, reformers, as static mixers and as structured catalyst supports [1, 2]. The foams can be produced from diverse materials like metals, ceramics, carbon, SiC, polymers, etc. Important advantage of the structures when compared to random packings is large surface area combined with high porosity. But so far, solid foams were not applied as packing in industrial TBRs. Literature data referring to TBR filled with solid foams are very scarce [3 – 6] and this was motivation to undertake the research.

The experiments were performed for the NiCr foam sample (Recemat) with pore density about 30 PPI (pore per inch). The first step was to determine morphological parameters of the foams like porosity and specific surface area. The results proved high porosity and specific surface area of the foam comparing to packed beds, which are shown in Table 1.

Table 1. Morphological parameters for NiCr foam and glass spheres

Packing	Porosity, ε	Surface area, S [m^2/m^3]
glass spherical, d_p = 5 mm	0.388	734.4
glass spherical, d_p = 3 mm	0.38	1240
glass spherical, d_p = 1.5 mm	0.372	2512
NiCr foam (30 PPI)	0.879	2800*

* given by manufacturer (Recemat)

Next, hydrodynamic parameters (liquid holdup, pressure drop) were measured using liquids of different viscosity. The holdup experiments showed that the usual draining time (30 min) was evidently too short thus longer times were applied (up to 20 hours) [6]. Analysis of draining curves showed linear draining volume dependence vs. $t^{-0.5}$. Similar relationship was found by Jaroszyński et al. [7] for structured catalytic packings. The dynamic liquid holdup (ε_{Ld}) and pressure drop ($\Delta P/H$) depends on both liquid (w_L) and gas flow rates (w_g). Physicochemical properties of liquid also influence the hydrodynamic parameters (see Figure 1).

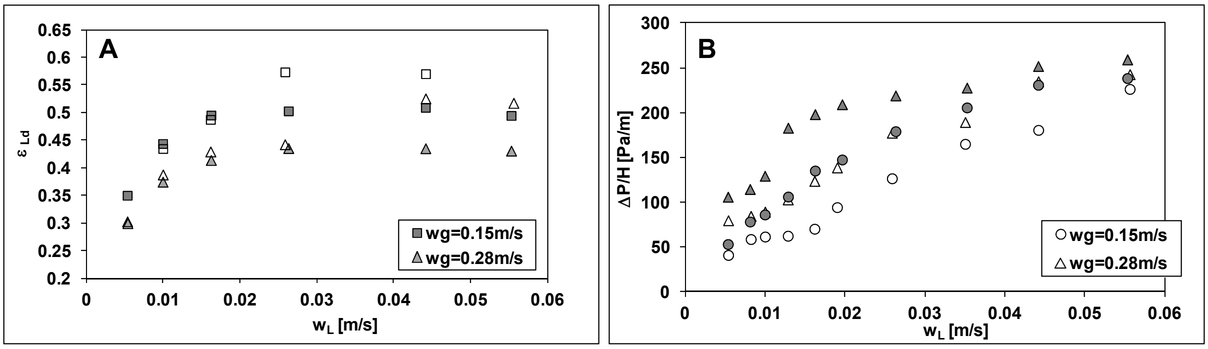

Fig. 1. The effect of operating parameters and physicochemical parameters of the liquid phase on the liquid holdup (A) and pressure drop (B) values. Nitrogen – water system (open points), nitrogen – 30 % glycerol solution (solid points)

The higher liquid viscosity the higher static liquid holdup and pressure drop but the lower dynamic liquid holdup is measured. The hydrodynamic parameters obtained for solid foam were compared to dumped beds. High foam porosity results in significantly lower flow resistance and higher liquid holdup (both static and dynamic). Considering morphological parameters, hydrodynamic characteristics and possible materials, solid foams appear as promising alternative to dumped beds in the TBR applications.

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KINETICS OF CONSECUTIVE-PARALLEL REACTIONS IN A THIN LAYER OF A HETEROGENEOUS CATALYST

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A method for computing of consecutive-parallel reactions with an unrestricted stoichiometry in a thin layer of a heterogeneous catalyst has been considered and realized. The method is based on the principal of pseudo homogeneous kinetics description. It was proposed that in a thin layer of a heterogeneous catalyst autothermal process with the same temperature in the area of consecutive and parallel is realized. The model of plug-flow reactor was used for calculation of the components balance but for the thermal balance the model of mixed flow reactor was applied. Developed algorithm of the considered process was realized by means of MATLAB and checked on the example of consecutive-parallel reactions of synthesis gas production by means of oxygen conversion of methane using known rate constants.

COKE AND METAL INVESTIGATION AFTER OXIDATIVE AND NON-OXIDATIVE REGENERATION METHODS OF SPENT HYDROPROCESSING CATALYSTS

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A comparative study for hydroprocessing spent catalyst from Kuwaiti refineries waste were tested for their activity testing of three types of the same catalyst, namely the fresh catalyst, the non-oxidative and the oxidative reactivated catalyst. The aim of this study to investigate on the coke reactivity after applying different regeneration methods. This regeneration methods is to measure the life cycle of the reactivated catalyst. The coke and metal deposition were removed and reduced after these treatments. A comparison study was conducted for the type of coke and metal formed depending on the feed and operating conditions of the process used in the refinery.

The characteristic analysis using techniques like: Nuclear magnetic resonance (NMR) and Fourier transform Infrared Spectroscopy (FTIR), and C, H, N, S analysis, Refinery Gas Analyzer (RGA) and Energy-dispersive X-ray spectroscopy (EDX) of the treated catalyst confirm the aim of the study.

Keywords: Oxidative and non-oxidative regeneration, spent catalyst, coke hydrotreating.

GIBBS FREE ENERGY MINIMIZATION FOR THE CALCULATION OF EQUILIBRIUM SHIFT IN MEMBRANE REACTORS

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Over the last decades, remarkable advances have been made in developing experimental devises and mathematical models for the synthesis, analysis and design of membrane processes. In fact, process intensification by membrane technologies (e.g., membrane reactors: reaction + pervaporation) has been successfully used for reversible chemical equilibrium limited reactions. Several methodologies have been proposed with regard to predict the extent that membrane reactors can shift the equilibrium of reaction. In an early attempt, Mohan and Govind [1] used a plug flow reactor model for five different dehydrogenation reactions. They analyzed the conversion vs. rector length profile choosing the hydrogen asymptotic value as that corresponding to the equilibrium conversion. Next, Itoh [2, 3] used hydrogen balances and also the condition of equal hydrogen pressures on both sides of the membrane to calculate a maximum conversion. Later, Barbieri *et al*. [4] used a tank in series model for methane steam reforming, removing hydrogen in regular intervals until the partial pressure of hydrogen was equal on both sides of the membrane. When Abashar and Al-Rabiah [5] have applied equations from mass balance on a differential volume using kinetics models, along the reactor length, they observed that the equilibrium was reached when the hydrogen concentration profile was constant. More recently, Rezai and Traa [6] proposed a mole balance approach together with the equilibrium constant and the hydrogen partial pressures on the reaction and permeation sides for calculating the equilibrium shift. In this work, an approach for the minimization of the Gibbs free energy is proposed for the calculation of equilibrium shift in membrane reactors. The model, implemented in MatLab®, was successfully used for the analysis of the catalytic dehydrogenation of cyclohexane, as compared with some reported experimental data [7]. The presented method is easy to implement, robust and can use several thermodynamic models.

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SIMULATION OF AN INDUSTRIAL ADIABATIC MULTI-BED CATALYTIC REACTOR FOR SULFUR DIOXIDE OXIDATION USING THE HETEROGENEOUS DUSTY GAS MODEL

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The manufacture of sulfuric acid from sulfur involves three important steps: (1) the formation of sulfur dioxide, (2) its catalytic oxidation to sulfur trioxide (a reversible and highly exothermic reaction) and (3) the reaction of sulfur trioxide with H_2O in absortion towers. Sulfuric acid is recognized as a very important commodity chemical. Only in 2012, its world production was about 220 million tonnes. Most of it is used for the production of phosphatate fertilizers, calcium dihydrogenphosphate and the ammonium phosphates.

In this work, a rigorous heterogeneous model is developed for the analysis of an industrial adiabatic multi-bed catalytic reactor for sulfur dioxide oxidation, placed in the suburbs of Manizales (Colombia). Most of models used in the literature for this catalytic reaction express the mass transfer by Fick’s law with an effective diffusivity coefficient [1, 2]. Here, a more rigorous model for diffusion and reaction in the catalyst pellet (vanadium (V) oxide supported on silica) was used. It is based on the dusty gas model (Stefan-Maxwell equations). The reactor to be simulated comprises one cylindrical vessel which acts as a fixed bed reactor with four separate beds of catalyst. For a satisfactory yield of sulfur trioxide (above 99.5 % conversion is needed), the used temperature is as low as economically possible. Thus, the heat is removed and recovered from the gas leaving each bed using heat exchangers. The produced sulfur trioxide is removed from the reactor between its third and fourth bed and passed to the next stage, where the sulfur trioxide is converted to sulfuric acid. However, a low amount of sulfur dioxide remains without conversion and is returned to the reactor through the fourth bed of catalyst and then the resulting gases, mainly sulfur trioxide, flow to the next stage of the process. The model, implemented in MatLab®, was successfully used for steady state simulations of the reactor. It allows evaluating truthfully the behavior of each catalytic bed (e.g., concentration, conversion, pressure and temperature profiles). Additionally, the effectiveness factor variation along the reactor was estimated. It should be observed that the reaction mainly takes place in the first two catalytic beds (ca., 54 and 84%, respectively). Only ca. 15.5 % of conversion occurs in the remaining two beds. Thus, temperature profiles became less marked in these last two sections. Effectiveness factor profiles are different for each catalytic bed. In the first one, it starts at ca. 0.63, passes through a maximum of ca. 0.87 (near to the half-length of the bed) and finally decreases sharply to 0.1 at the end of the bed. For the other three beds, it decreases continuously along the each bed, as the rates of this reversible reaction decreases. The developed model and a MatLab®interface make it suitable for operator training.

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PP-39

CO_2 CAPTURE USING POLYSULFONE MEMBRANE CONTACTOR AND [EMIM][AC] IONIC LIQUID

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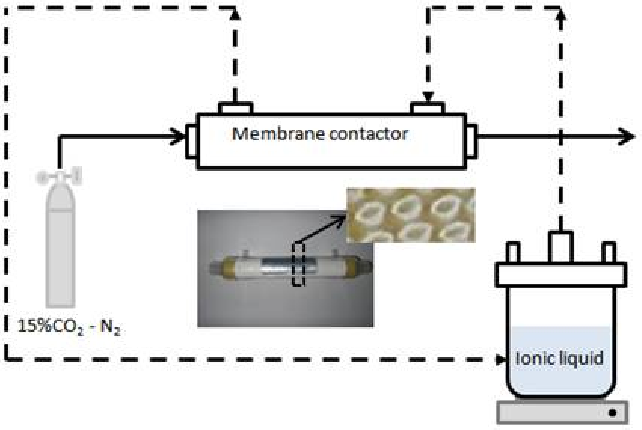
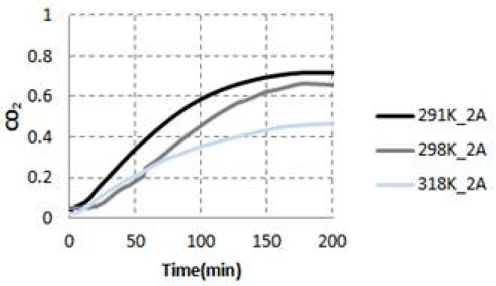
Hollow fiber membrane contactors have been proposed as a way to capture carbon dioxide and so reduce greenhouse gas impacts from fossil fuels in industrial processes because of their main characteristics as a high surface area per unit volume, a controlled interfacial area and an independent control of gas and liquid flow rates respectively. As solvents, ionic liquids (ILs) have emerged as new attractive alternative solvents because of their zero emission features compared to amines [1-2].

In the present work, a commercially available polysulfone (Ps) hollow fibre membrane contactor was used. The ionic liquid 1-Ethyl-3-methylimidazolium acetate ([emim][Ac]) was used as solvent. Its high CO_2 solubility converts the process into a promising alternative to common amine processes.

The aim of this work is to compare the temperature effect on overall mass transfer coefficients and the absorption rate of the reactant in terms of enhancement factor (EA) in CO_2 absorption using a PS membrane contactor and [emim][Ac]. The temperature was studied in the range of 291 to 363K. The overall mass transfer coefficient and the process efficiency are experimentally calculated and discussed in terms of CO_2 recovery.





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SIMULATION OF SYNTHESIS OF OPTICALLY TRANSPARENT MESOPOROUS POLYMERS

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Optically transparent mesoporous block copolymers with controlled sorption capacity are obtained by polyaddiiton of 2,4-toluene diisocyanate to anionic macroinitiators. It is shown that the predominance of the polyaddition reaction over the reaction of trimerization of isocyanate groups underlies the processes increasing the sorption capacity of polymers. It is determined that the nature of a solvent influences considerably the possibility of competing reactions of trimerization and polyaddition of 2,4-toluene diisocyanate to take place; it is shown that urea groups formed by isocyanate groups of 2,4-toluene diisocyanate of ortho-location being involved in the reaction process play decisive role the stabilization of O-polyisocyanate blocks in the given polymer forming system. The binding of neighboring O-polyisocyanate chains by urea makes possible not only the existence of O-polyisocyanate blocks in coplanar trans-configuration but their segregation as well, owing to the specific characteristics of intermolecular quasicyclic hydrogen bonds with the participation of urea. The kinetic constants of the reaction in various media were calculated. It is determined that at the low conversion of isocyanate groups at the gel point the reaction is subordinate to the second order. When the conversion of NCO groups at the gel point is high the reaction is subordinate to the kinetic equation of the first order. It is determined that the formation of transition pores is caused by the geometry of supramolecular structure of block copolymers, the participants of this structure being globules of a macroinitiator and segregated O-polyisocyanate blocks. It is shown that the mesoporous structure of polymer provides the possibility of immobilization of organic chromophores in mesoporous polymers. It is determined that the adsorption of organic functional compounds is accompanied by their concentrating in the polymer matrix. Polymer laser-active media possessing high radiation stability are obtained on the basis of mesoporous polymers doped by organic phosphors.

Acknowledgements

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ANALYSIS OF THE PAST PUBLISHED DATA ON WGS REACTION OVER Pt AND Au CATALYSTS BY DECISION TREES

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For small size proton exchange membrane (PEM) fuel cell applications, steam reforming is a commonly applied method to generate hydrogen gas. However, the hydrogen stream produced by the reforming process contains some amount of CO, which is known to be harmful to the anode catalyst of the PEM fuel cell; hence, it must be totally eliminated [1]. WGS is a commercially well-established process to eliminate CO [2].

The ultimate goal in the catalyst design is to achieve an active, selective, stable and cheap catalyst, and data mining can help to search for such an optimal catalyst. Data mining is the collection of methods (i.e. classification, clustering and estimation etc.), which help to detect trends and patterns, to derive conclusions or to make predictions from a set of data, and their applications in the field of catalysts have also become quite widespread in the recent years [2-4]. Decision tree technique, which is one of the popular data mining methods, can help to derive simple but valuable rules, such as finding the variables leading to high or low catalytic performance levels [4]. In this work, a database for water gas shift reaction over noble metal catalysts (containing 3802 experimental data points) was generated from the published papers between the years 2002 and 2012. Then, the database was analyzed using decision trees.

The decision tree classifying the Pt based catalysts is given in Figure 1 as a sample. The tree shows the ranges of catalyst preparation and operating conditions leading to CO conversion levels as high (more than 75 %), average (between 50-75 %) and low (less than 50 %). As a result of the findings, it was found that analysis of the past data using decision tree classification were quite suitable to give empirical rules that lead to high catalytic performance. It can be concluded that decision trees can be indeed very beneficial to analyze the past data for WGS over noble metal catalysts as well as other similar systems with large number of publications in the literature.

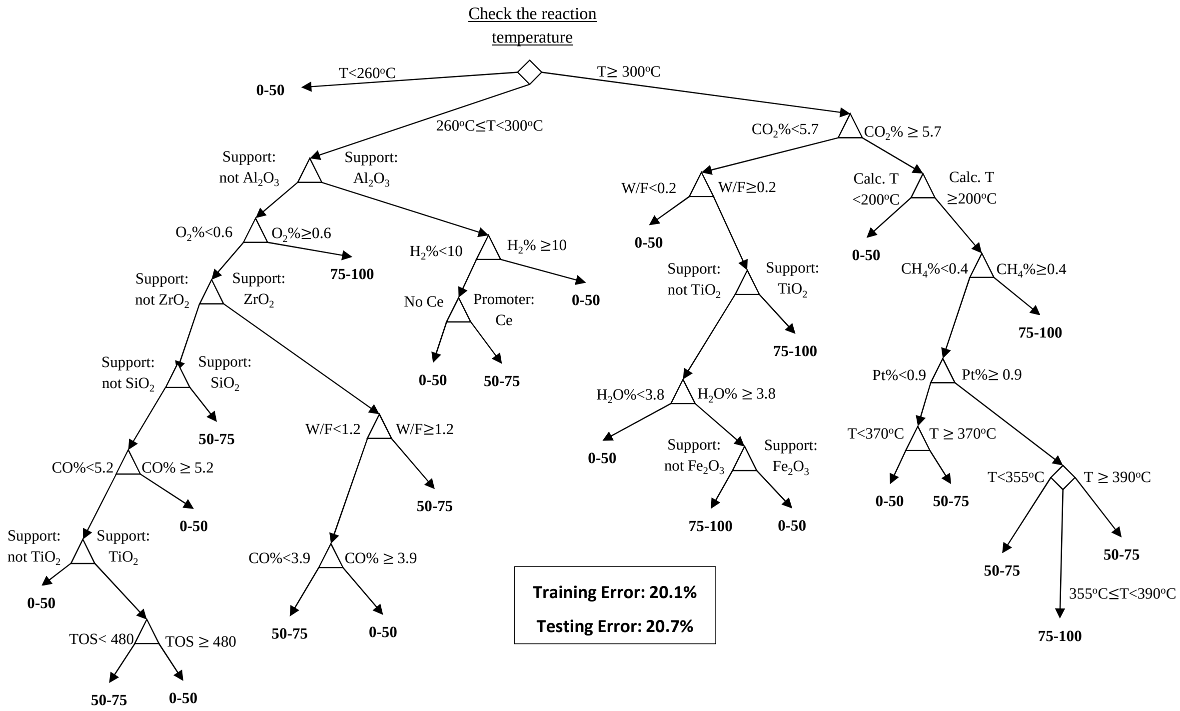

Figure 1. Decision tree classification of Pt catalysts based on CO conversion

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MODELING OF A DOUBLE-LAYER DESULFURIZATION REACTOR

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Fine gas desulfurization is now needed not only for natural gas using chemical processes, especially catalytic ones, but also for the renewable feedstocks (like biogas) processing and direct-reduced iron production.

Manufacturing techniques of sulfur absorbents for fine desulfurization now practically reached their limit as far as sulfur capacity and the rate of absorption or their optimal combinations are concerned.

Thus, a reactor containing two layers of sulfur absorbents having different characteristics (or two cascade reactors loaded with different absorbents) can be considered to check if such a combination can increase the run time of a fixed total volume loading.

Two typical sulfur absorbents were selected for the modeling. The first one (Abs1, tabletted) has low porosity (about 30 %) and, therefore, low diffusivity but high bulk density and, therefore, high sulfur capacity per unit volume.

The second one (Abs2) has relatively high porosity (about 50 %) and, respectively, high diffusivity with moderate bulk density and sulfur capacity per unit volume.

One can see from the results of ref. [1] that speed of H_2S front movement is inversely proportional to sulfur capacity per unit volume and its width – to H_2S diffusivity.

So the dense absorbent should by placed in the frontal layer, and the porous one should by placed after it, downstream the gas flow.

The bulk velocity value was chosen the typical one for industrial desulfurization units as well as target value of purification rate. The fraction of the frontal layer length in the total absorbent bed length was chosen to be a predictor.

Breakthrough curves were calculated using the description of a flow with a small admixture through an absorbent bed from ref. [1]. The curves for the double-layer loading were compared with those for single-layer loadings of Abs1 or Abs2 and the one for the reverse order of Abs1 and Abs2 layers.

The most interesting effects take place roughly in the first half of the period of full exhaustion of bed absorption capacity when high purification rate values are mainly observed (hereinafter referred as “the initial stage of the run”).

The main qualitative results of modeling are as follows:

1. The maximum run time until the breakthrough takes place at equal lengths of Abs1 and Abs2 layers.
2. The purification rate for double-layer loading with the proposed order is better than for single-layer loadings of Abs1 during the initial stage of the run.
3. The purification rate for single-layer loadings of Abs2 is better than for double-layer loading with the proposed order during the very beginning of the run (with extremely high purification rate values). Double-layer loading works better during the rest of the initial stage of the run.
4. The purification rate for double-layer loading with the proposed order during the initial stage of the run is better than for the reverse order.

The approach used here provides quantitative results for specific process configurations and conditions. It can be easily extended to more complex configurations.

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SELECTIVITY ENGINEERING WITH MULTI-SIDE DRAW HYBRID REACTIVE DISTILLATION COLUMN INVOLVING AZEOTROPIC SYSTEMS

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Reactive Distillation (RD), which combines reaction and distillation, can be effectively used to get desired selectivities in multi-reaction systems. The contribution deals with the development of design algorithm for hybrid Reactive Distillation (RD) column with multi-side draws in order to obtain a desired selectivity in a multi-reaction system involving azeotropic mixtures.This work is the continuation of our earlier work on selectivity engineering with hybrid RD columns [1,2,3,4,&5]. A model reaction scheme of van de Vusse type (Eq. 1) is studied as an illustrative exampleand acombined graphical-simulation algorithm is developed using the concepts of attainable region approach.The design methodology utilizes the concept of visualization of the locus of feed stage compositions of nonreactive distillation column and its intersection with that composition (X*) in space at which reaction takes place in a multi-side draw RD column. Based on the desired product selectivity, we determine the surface of reactive stage compositions (SRSCs) in the RD column. If the reaction in the RD column takes place at any of the compositions that belongs to SRSCs then our desired selectivity is ensured. In case of azeotropic systems, nonideal vapor-liquid equilibrium and distillation boundaries are responsible for the contraction of the feasible reactive stage composition region required for the design of RD column. In spite of this difficulty, it is shown that the developed methodology is capable of finding promising designs of RD column with multi-side draws to obtain desired selectivity. Figure 1 shows one such feasible design meeting our requirements, the design specifications of which are given in Table 1.The applicability of this approach, at present, is restricted tothe systems with single reactant. However, the developed methodology holds a potential to be extended to the schemes with multiple reactants and is the next step of this work.

Model Reaction Scheme:

$$\left.\begin{array}{l} A \xrightarrow{desired\ (k_1)} B \underset{desired\ (k_3)}{\overset{undesired\ (k_2)}{\rightleftarrows}} C\ , A \underset{undesired\ (k_5)}{\overset{undesired\ (k_4)}{\rightleftarrows}} D,\ B \xrightarrow{undesired\ (k_6)} E, \\ [\ r_A\ r_B\ r_C\ r_D\ r_E\ ] = [\ -k_1 x_A^* - k_4 x_A^{*2} + k_5 x_D^{*2}\ ,\ -k_2 x_B^* - k_6 x_B^* + k_1 x_A^* + k_3 x_C^*\ , \\ \qquad k_2 x_B^* - k_3 x_C^*\ ,\ k_4 x_A^{*2} - k_5 x_D^{*2}\ ,\ k_6 x_B^*\ ] \end{array}\right\} \quad (1)$$

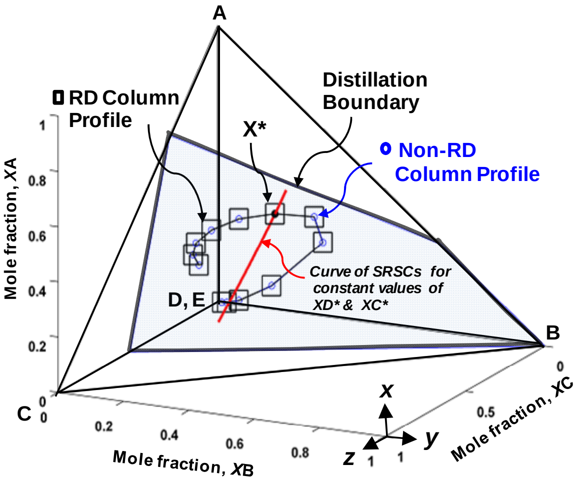

Fig. 1. Identical composition profiles of Non-RD and RD multi-side draw columns in 3D composition space. X*: reactive stage composition

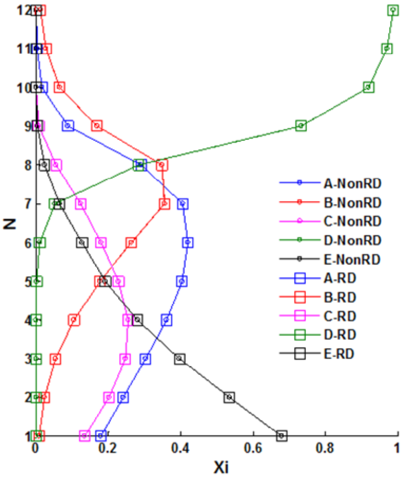

Fig. 2. Column profiles along the length of column. The close overlap indicates that the design is feasible.

Table 1: Design specifications for multi-side draw hybrid RDC

Column configuration	Non-RDC	RDC
Number of components, *NC*	5	5
Volatility , *D>B>A>C>E*	Nonideal VLE	Nonideal VLE
Number of stages, *N*	12	12
Feed location, *Nfl*	6th Stage	6th Stage
Feed flow rate, *F*	1	1
Feed composition, *Xf*	(0.2, 0.1, 0.111, 0.2365)	(1,0,0,0)
Feed stage composition, *X**	(0.42, 0.2627, 0.18, 0.01, 0.1273)	(0.42, 0.2627, 0.18, 0.01, 0.1273)
Side draw location, *S1*	4th Stage	4th Stage
Side draw location, *S2*	8th Stage	8th Stage
Number of reactive stages, *Nr*	-	1
Location of Reactive stage, *Nrl*	-	6th Stage
Damkohler Number , *Da*	-	1.3416
Distillate to feed ratio, *D:F*	0.175	0.175
Vapor to feed ratio, *V:F*	15.7	15.7
Side draw to feed ratio, *S1:F*	0.15	0.15
Side draw to feed ratio, *S2:F*	0.2253	0.2253
End Compositions after mixing the distillate, side draws and bottom streams	(0.2, 0.1, 0.111, 0.2365)	(0.2, 0.1, 0.111, 0.2365)

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HYDRODESULPHURIZATION OF SCRAP TIRE PYROLYSIS OIL (STPO) OVER A NiMo/Al_2O_3 CATALYST. EFFECT OF PRESSURE AND TEMPERATURE

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Processing and valorizing tires has attracted growing interest due to its increasing dumping amount and negative environmental impact. Every year, approximately 7 Mt of waste tires are disposed worldwide, accounting for the 2 wt % of total waste [1]. Incineration could be attractive for recovering part of the calorific power of waste tires (33 MJ/kg, efficiency 41 %). However, the emissions of dioxins, particulates, SO_2 and NO_x keep this process from being environmentally favorable [2]. On the other hand, pyrolysis is a more efficient (70 %) and environmentally friendly alternative (less harmful emissions) that allows tires to be processed along with other types of waste (plastic, biomass) or coal. Pyrolysis products can be co-processed within the standard scheme of a refinery, being the most interesting the liquid product obtained from this process, known as Scrap Tires Pyrolysis Oil (STPO) [3] which is a potential combustion fuel [4]. However, its main drawback is the concentration of contaminants as nitrogen and, particularly, sulphur, which may vary between 0.5-3 wt % depending on the technology employed to produce the STPO. With the purpose of removing undesired and harmful compounds, STPO needs to be hydrogenated, to comply with the environmental protection policies. In this work, the sulphur removal from STPO has been studied by using different pressure in the 300-375 °C temperature range.

The hydrotreating of STPO, diluted (50 wt %) in n-decane, has been carried out in a down-flow fixed bed reactor of 15 cm^3. The reaction conditions were: 25-65 bar; WHSV, 4.15 h^{-1}; H_2/Oil ratio, 1000 (v/v) and time on stream (TOS), 0-24 h. Reaction temperature was modified sequentially in intervals from 375 °C to 300 °C and back to 375 °C again. Liquids were collected and analysed in an Agilent Technologies 7890A GCxGC-MS System using FID and MS detectors. The sulphur content has been measured by GC with a PFPD detector. The original sulphur content on the feed was of 10800 ppm.

Figure 1 shows the effect of process temperature and pressure on the efficiency of sulphur removal on the hydrotreatment of a scrap tire pyrolysis oil (STPO).

High HDS conversions have been reached at the temperature range studied (300-375 °C), obtaining the highest conversion values at the highest temperature and

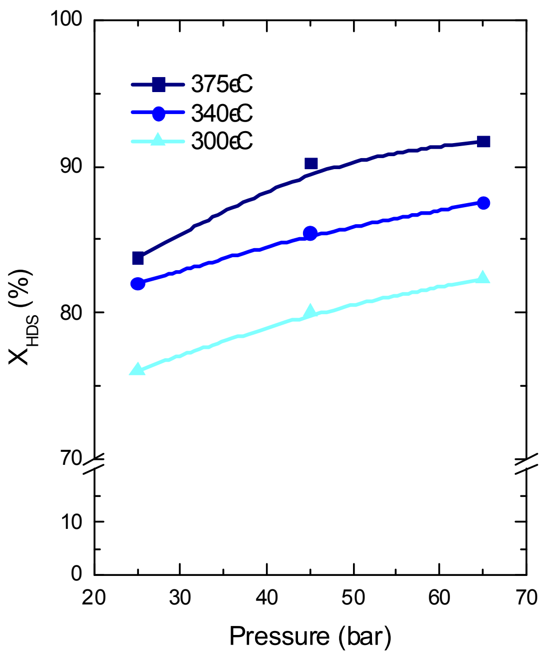

Figure 1. Effect of T and P on the HDS conversion on the hydrotreatment of STPO over a NiMo/Al_2O_3 catalyst.

pressure values studied (91.7 % at 375 °C and 65 bar conditions). When temperatures are lowered at 65 bar, HDS conversion values drop to 87.5 % and 82.3 % for 340 °C and 300 °C, respectively. For lower pressures, lower sulphur removal efficiency was achieved, being the sulphur removal trend: 65 bar> 45 bar> 25 bar. Therefore, lowering operation pressure hinders the HDS equilibrium towards sulphur removal. The effect of temperature was the same for 45 and 25 bar, dropping HDS conversion as temperature decreased (76.1 % in the case of 300 °C and 25 bar conditions).

Qualitatively, the effect of increasing pressure and temperature is the same. Regarding other hydrogenation reactions that take place simultaneously with HDS, decreasing either temperature or pressure hinders the hydrogenation of the heaviest fraction of STPO, rich in polyaromatic compounds, which may block the catalyst pores, keeping active sites from being accessible and thus decreasing its HDS activity.

After the 375-340-300 °C sequence, temperature was raised up to 375 °C again and HDS conversion increased, recovering almost all its initial catalytic activity (90-96 %, data not shown). The catalytic activity recovery was higher for higher pressures.

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BIMETALLIC CATALYSTS FOR PRODUCTION AND CONVERSION OF SYNGAS

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The actual interest in GTL process has grown up in consequence of environmental demands, technological developments and changes in fossil energy reserves. This technology provides the conversion of natural resources into syngas (a mixture of carbon monoxide and hydrogen – $CO+H_2$ in any ratios) and then syngas conversion to clean fuels through the Fischer-Tropsch synthesis (FTS). Syngas may be produced from almost any organic material. At present natural gas, which supplies are abundant and available, is converted to syngas via existing or newly developed processes such as steam reforming, carbon dioxide reforming, and partial oxidation. Among these ways, the carbon dioxide reforming of methane/natural gas appears to be prospective. Both CO_2 and CH_4 are green-house gases, and an interest in the processes is stimulated because converting these gases into a valuable feedstock may significantly reduce the atmospheric emissions of CO_2 and CH_4. Other available and presently non-utilizable source is associated gases still burned at flares. Since both syngas production from and FTS are catalytic processes, their efficiency depends on the catalyst properties. For this reason, the main attempts are directed to creating the high active, selective and stable catalysts with resistance to coke formation.

The bimetallic supported catalysts represent a highly interesting class of catalysts because one metal can tune and/or modify the catalytic properties of the other metal as the result of both electronic and structural effects. Besides, due to the effect of both second metal and support, the particle may be dispersed, which leads to enlarging the surface area and decreasing the metal consumption and the catalyst. The preparation method of catalysts has significant effect on catalytic activity and coking resistance for methane conversion to synthesis gas.

Co is an active metal in both reactions: the dry reforming of methane and FTS. In this work, the Co-containing catalysts modified by the second metal (VIII Group) and supported on alumina were studied by a number of physico-chemical methods (TEM, BET, IR-spectroscopy, TPR), and tested in the processes: the production of syngas using the dry and bireforming (combined steam and carbon dioxide reforming) reforming of methane and syngas conversion by FTS.

The results obtained indicate, that the addition of second metal substantially changes the composition, structure, and adsorptive and catalytic properties of Co/Al_2O_3 catalyst. The metal size is decreased to 2-4 nm at the addition of second metal. It occurs due to metal-metal interaction with the formation of bimetallic nano-particles of cluster type. That is indirectly confirmed by the dates of TPR and TEM methods.

The bimetallic nano-particles perform the high activity, selectivity, thermostability, and resistance to the coke formation in both processes: the dry reforming and bireforming of methane and the Fischer-Tropsch synthesis. The complete conversion of methane reaches at comparably lower temperature – 700-800 °C depending on the amount of the second metal and source compositions. Adding water into CH_4-CO_2 feed in amount 10-30 vol. % leads to decrease in process temperature by 15-50 °C and increase in H_2/CO ratio in syngas produced.

In FTS, the degrees of carbon oxide conversion over the same catalysts are 70-80 % depending on the amount of the second metal and process conditions. Basically the liquid hydrocarbons (gasoline-diesel fractions) is produced ($S_{5+} > 70$ %).

Acknowledgements

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CHANGING THE HYDROGEN-RICH GAS CIRCULATION RATIO WITH SAVING THE LIFETIME OF THE C9–C14 ALKANES DEHYDROGENATION CATALYST

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In the alkanes dehydrogenation, which is part of the linear alkylbenzenes (LAB) production [1], one of the most important parameters is the molar ratio between hydrogen and raw material, or the corresponding variable – hydrogen-rich gas circulation ratio. Increasing the molar ratio H_2 : raw stock is known to decrease the coke formation on a Pt-catalyst surface, and, therefore, prolong its lifetime. However, using larger volumes of circulating gas in the plant leads to bigger equipment and piping sizes, and raises energy costs as well.

Obviously, on active plants the H_2 : raw stock ratio is defined by technoeconomic studies that consider how the hydrogen-rich gas circulation ratio affects yield and quality of products depending on raw material contents and catalyst activity.

Earlier before, our team had shown that the coke formation intensity might be decreased with the water injected into industrial reactor environment, and the amount of that water is defined by the process temperature, raw stock contents, and catalyst type and deactivation extent [2].

This paper is dedicated to determining if the dehydrogenation catalyst life can be saved even with decreasing the hydrogen-rich gas circulation ratio to 6 : 1 from 7 : 1, and to calculations of demineralized water injection schedule for dehydrogenation reactor, considering the different raw stock contents and different yields of final products (linear alkylbenzenes).

Our studies let us suggest that the coke formed on the surface of dehydrogenation Pt-catalyst is mainly amorphous type [1]. Quantum chemistry calculations have shown that the reactions of intermediate coke products hydrogenation are as possible as the reactions of their oxidation [2, 3]. Hence, there exists some optimal activity of the catalysts, corresponding to equilibrium between coke formation and hydrogenation/oxidation.

Along with that, the necessary condition for a steady equilibrium of coke conversion with water is increasing the water injection rate into the reactor over time. This can help avoid spending too much valuable hydrogen-rich gas on this process while it can be used in other hydrogenation processes at the refinery.

To go into more details of this issue, we have built a computer modeling system for the processes involved in linear alkylbenzenes production. It includes mathematical descriptions for each stage of that production: a) dehydrogenation of C9–C14 alkanes; b) hydrogenation of by-products; c) HF-alkylation of benzene with alkenes.

We used different target alkylbenzenes yields (173.8, 175.1, and 176.4 tons per day, corresponding to 8.7 %, 8.8 %, and 8.9 % mass yields of alkenes in the product stream from the reactor).

The calculated lifetimes for alumina-platinum catalysts, economies of hydrogen-rich gas, and linear alkylbenzenes yields are given in the Table. As shown, the more the dehydrogenation plant productivity, the less its catalyst life. Increasing the alkene yield by as little as 0.1 mass % leads to decreasing the catalyst lifetime for 20–25 days.

Table – Calculation results

Raw stock	Выработка ЛАБ					
	173.8 tons of LAB/day (alkenes 8.7 mass %)		175.1 tons of LAB/day (alkenes 8.8 mass %)		176.4 tons of LAB/day (alkenes 8.9 mass %)	
	Days	Hydrogen-rich gas saved, $m^3 \cdot 10^6$	Days	Hydrogen-rich gas saved, $m^3 \cdot 10^6$	Days	Hydrogen-rich gas saved, $m^3 \cdot 10^6$
Composition 1	405	74.35	385	70.68	365	67.01
Composition 2	398	73.07	375	68.85	355	65.17
Composition 3	373	68.48	353	64.81	330	60.58

Thus, our calculations prove the possibility of saving the lifetime of platinum dehydrogenation catalysts while decreasing the hydrogen:raw stock molar ratio at the same time. The requirement for that is changing the demineralized water injection schedule due to temperature changes, as shown by curves in the plot. Moreover, the water injection must start to be increased 10–12 days earlier than at H_2 : raw material ratio of 7 : 1.

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REACTION RATE IN STRUCTURED REACTORS: ANALYTICAL METHODS FOR DETERMINATION OF CATALYST AMOUNT

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In structured reactors reaction rate is commonly referred to the catalyst geometrical area [1]. A reason for it is that it seems the easiest to measure. Such rate representation, however, does not necessary reflect the performance of the catalyst deposited onto the surface of a monolith or structured carrier. In order to compare catalyst and reactor performance an intrinsic reaction rate defined as a turn over frequency on a single active centre should be determined. In this case, however, the number of active centres cannot be always easy determined especially when catalyst is deposited on the surface of the carrier. To measure the number of active centres the *in situ* spectroscopic methods using surface probe molecules are the most adequate and precise [2]. To approach this value the amount of the catalyst deposited on the surface of the carrier should be measured at least, but even this poses a complicated analytical problem. The first issue is about selection of an analytical method and another is about the meaning of a physical response of the analytical tool.

In this study three commonly available analytical techniques: as X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Spectroscopy (EDX) and X-ray Fluorescence (XRF) are compared and discussed using as an example palladium and ceria promoted cobalt oxide catalysts deposited on the precalcined kanthal steel carriers and tested in methane combustion. Although it is known that the listed methods are the surface sensitive methods which provide information about top layers with XPS being limited to few monolayers, a question arises what are the differences of depth penetration between them and resulting differences in determined catalyst amount. XRF, but also Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Atomic Absorption Spectroscopy (AAS), can be used to analyze the total amount of the catalyst when it is transferred into a solution but an issue is a proper calibration of the method.

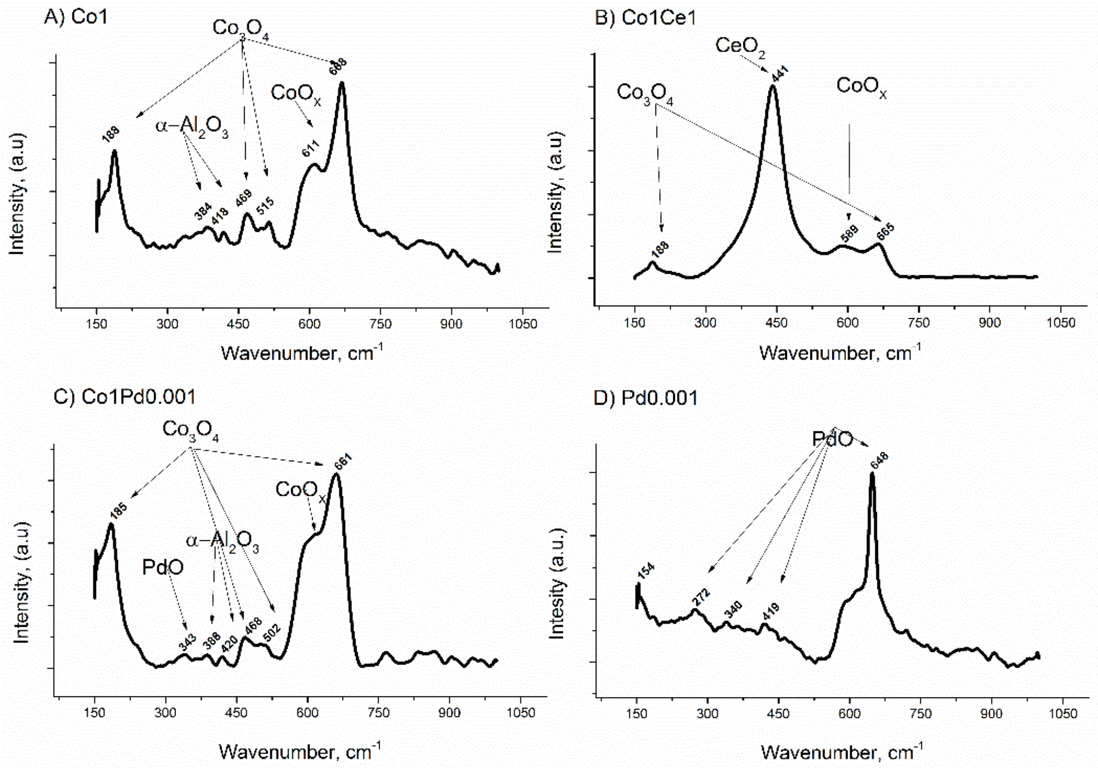

Figure 1. Raman spectra of prepared samples; A) Co1, B) Co1Ce1, C) Co1Pd0.001, D) Pd0.001

Not only did the results of XPS, XRF and EDX provide the reaction rate normalizing factors but also when combined with Raman analyses of surface structure the information on the metal oxide distribution throughout the deposited layers (Fig. 1). The results revealed that unlike ceria promoted catalysts the palladium doped cobalt catalyst surface is practically covered with highly dispersed palladium oxide. This explained extremely higher activity of this catalyst in comparison with commercially applied for methane combustion palladium alumina supported catalyst.

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GAS PHASE AND SURFACE REACTION KINETICS FOR CCl_4-H_2 SYSTEM IN TUBULAR CHEMICAL VAPOUR DEPOSITION REACTOR

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Chemical vapour deposition has proved to be the promising method to produce pure components in bulk or as thin films. Poly crystalline diamond can be used as a substrate material for integrated circuits, as a low friction- durable coatings and for various other applications [1]. Chloromethanes have the potential to grow diamond nanofilms at low temperatures [2]. Many researchers have worked on deposition of polycrystalline diamond nanofilms through the reactions of CCl_4 and H_2 ([3], [4]). In this work, efforts have been made to deposit smooth surfaces of diamond nanofilms in a tubular atmospheric pressure chemical vapour deposition (APCVD) reactor and to develop a kinetic model for gas phase and surface reactions. Hydrogen is bubbled through a tank containing CCl_4 and the comosition of the outgoing gas is analyzed throught the temperature and pressure of this holding tank. The mixture is then sent to the reactor whose walls are maintained at constant temperature. Investigation is done on analyzing the deposited product on reactor inside walls to find the reactor temperature and feed concentration required for diamond nanofilm formation. SEM images of the deposited product on reactor walls at various temperatures are shown in figure 1.

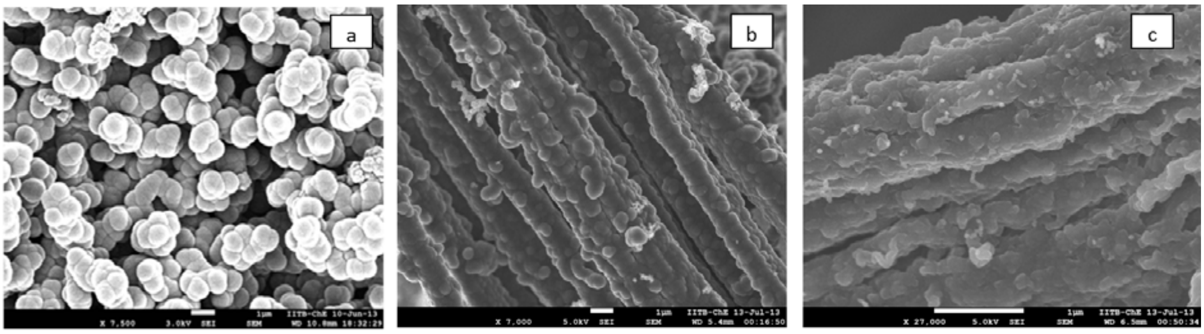

Figure 1: SEM images of the deposited product on reactor walls with a feed compotion of 17 % CCl_4 and 83 % H_2 and reactor wall temperatures of (a) 475 °C (b) 650 °C, (c) 800 °C

A reaction mechanism and a parametric model for the gas phase and surface reaction kinetics is established from the exit gas composition data and average deposition rate obtained through experiments.

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TEMPERATURE EFFECTS ON THE YIELD OF GASEOUS OLEFINS FROM WASTE POLYETHYLENE VIA *FLASH* PYROLYSIS

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Thermal pyrolysis has earned significant reputation in the recovery of valuable chemicals, especially petrochemical based fuels from various materials, including biomass and plastics. Of many available technologies, *fast* pyrolysis was preferred in this study owing to its minimal heat and mass transfer limitations and better control on process conditions. The focus of this study is towards efficient conversion of waste plastics into gaseous products consisting primarily of alkanes, alkenes and aromatics. Lab scale experiments were performed using a flash micro reactor to determine favorable reaction temperature that would result in maximum yield of olefins, primarily the monomer ethylene.

ENHANCEMENT OF OXYGEN GAS-LIQUID MASS TRANSFER IN THE PRESENCE OF HYDROPHOBIC NONWETTABLE PARTICLES

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Oxygen mass transfer intensity to aqueous phase often influences on efficiency of chemical and biotechnological reactors. Oxygen absorption kinetics can influence on the rate of catalytic oxidation, biological purification of waste water and polluted air, microbiological synthesis of various products. A perspective way of O_2 absorption enhancement is addition of dispersed solid particles to liquid phase. Currently, there is a lot of data about influence of wettable particles (e.g. activated carbon) immersed in liquid bulk on O_2 mass transfer. Destabilization of gas-liquid interface under influence of particles is considered as one of the possible mechanisms of mass transfer enhancement in suspensions [1]. It can be assumed that this mechanism will be effectively implemented in the presence of nonwettable particles which constantly float on gas-liquid interface. However, to our knowledge, the effect of nonwettable particles on O_2 mass transfer has not been studied. The aim of this study is to investigate the influence of nonwettable hydrophobic particles on O_2 mass transfer in gas (air)-liquid (water) system.

Absorber with flat gas–liquid interface and mechanical agitation (6-blade turbine) was used for experiments. The effect of the particles was estimated with enhancement factor ($E = K_La/K_La_0$, where K_La and K_La_0 – volumetric oxygen mass transfer coefficients with and without particles, respectively, s^{-1}).

Two kinds of hydrophobic particles were investigated: silica with methyl groups on surface (C_1-silica) and silica with hexadecyl groups on surface (C_{16}-silica). For control experiment unmodified silica particles were used. Properties of the particles are presented in the table 1.

Table 1. Properties of the investigated particles

Particles	Average particles size, micron	Weight fraction of carbon, %	Specific surface area, m^2/g	Average pore size, Å	Pore Volume, cm^3/g
C_1-silica	10	4,9	252	12,0	0,755
C_{16}-silica	10	17,0	160	13,6	0,544
silica	10	-	268	14,9	1,002

Dependences of enhancement factor (E) on the particles concentration in liquid phase were studied (table 2).

Table 2. Dependences of E on the particles concentration at 200 rpm

Particles	Enhancement factor (E)				
	Particles concentration, mg/l				
	0	10	50	100	150
C_1-silica	1,0	1,3	1,7	1,5	1,1
C_{16}-silica	1,0	2,6	1,9	1,3	1,1
silica	1,0	1,0	1,0	1,0	1,0

It was shown that wettability and hydrophobicity of the particles influenced significantly on their ability for oxygen mass transfer enhancement. Hydrophilic completely wettable silica particles did not influence on O_2 mass transfer, while hydrophobic nonwettable floating on the liquid surface C_1- and C_{16}-silica particles enhanced oxygen mass transfer. Ability of nonwettable particles for oxygen mass transfer enhancement grows with increase of their hydrophobicity. Maximal enhancement factor in the presence of more hydrophobic C_{16}-silica ($E = 2,6$) is higher than one in the presence of less hydrophobic C_1-silica ($E = 1,7$). Maxima of enhancement factor (E) were observed at particles concentrations 10 and 50 mg/l for C_1- and C_{16}-silica respectively. These concentrations are quite low in comparison with concentration at which maximal value of E was observed in the presence of wettable particles (activated carbon) investigated earlier [2]. It was shown in paper [2] that maximal value of enhancement factor ($E=3,5$) in the presence of wettable activated carbon particles was observed at much higher concentration (500 mg/l) than in cases of C_1- and C_{16}-silica.

Dependence of enhancement factor on stirring rate in the presence of C_{16}-silica (50 mg/l) was studied. It was shown that increase of stirring rate from 100 to 300 rpm led to growth of E from 1,8 to 1,9.

Thus, obtained data show that hydrophobic nonwettable particles floating on the liquid surface can significantly enhance oxygen gas-liquid mass transfer (up to $E = 2,6$) at low particles concentration.

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INTENSIFICATION OF REACTANTS MIXING DURING BENZENE ALKYLATION WITH ETHYLENE

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One of the fastest growing areas of the petrochemical industry is ethylbenzene used as intermediate in styrene production. In this industry ethylbenzene is produced by benzene alkylation with ethylene, the catalysts for this process are the Lewis acids, preferably zeolites, and $AlCl_3$ is often used in Russia [1].

For the last 10 years the power of alkylation process has increased by 14 % worldwide. As a result, now more than 160 alkylation units are operated. [2]

The purpose of this work is numerical research of benzene alkylation with ethylene and a feasibility assessment of the alkylation reactor mixing equipment reconstruction using methods of computational fluid dynamics.

In chemical engineering, simulation is used to solve various problems, which are mostly focused on the optimization of processes occurring in an apparatus.

A formalized scheme of hydrocarbon transformations in the benzene alkylation with ethylene was compiled and kinetic model was developed [3]. In a hydrodynamic model compiling of the reactor, ideal plug flow regime was passed. The mathematical model allows calculating of major components concentrations in product mixture, and temperature gradient across the reactor.

The adequacy of the model is confirmed by comparing the concentrations calculated which using the model and experimental data which were collected over a long period of the plant operation (calculation error does not exceed 5-6 %). As the result a computer simulation system was developed using a programming environment Delphi 7.

Calculations allow to get recommendations for optimization of alkylation reactor. This mode is determined by the feedstock: with a high benzene/ ethylene ratio ((8-12) kg/1 kg), temperature range: 383-393 K (instead of 408 K) is recommended for alkylation carrying out, which corresponds to the current mode. The recommended ratio of circulating polyalkylbenzene/raw: (0.06-0.09) kg/1 kg. But such hydrodynamic processes study, namely stage of reagents mixing is not possible without the use of modern techniques of computational fluid dynamics.

In 2012, in the Russian ethylbenzene production plant, the mixing equipment upstream of the alkylation reactor was reconstructed. Before this reconstruction ethylene was mixed with a stream of benzene and catalyst. Reconstruction involves retrofitting with new mixing chamber. To evaluate the effectiveness a simulation of this mixer was developed using ABAQUS and FlowVision software systems. It allows problems to be solved in fluid dynamics modeling of liquid and gas flows mixing.

At this stage, benzene and catalyst input options are: a) input through the tubes sequentially, firstly – the catalyst, secondly – benzene; b) input with reverse sequence.

Fig. 1 shows benzene mass fraction variation for the 1st option reactant inlet. From this Fig., the qualitative flow mixing is observed after the second mixing element, set in upper part of the mixer. The mole benzene fraction at the outlet of the mixing device is at 0.7-0.8.

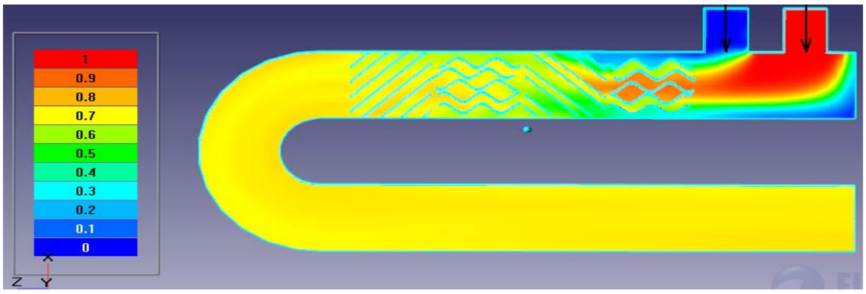

Figure 1 - The molar benzene proportion in a longitudinal device section

Calculations show that it is preferable to use the 1st pipe for the catalyst input and the 2nd pipe – for benzene input: reactants distribution is more uniform in the cross section of mixing elements in the chamber, the mole catalyst fraction in the mixing elements in the chamber will be 0.1-0.15 (with another option: 0.06-0.08). This result is caused by the physical properties of the fluids, as well as a large mass flow rate of benzene in proportion to catalyst complex.

In the future calculations with the flow input variations will be carried out in the plant in order to evaluate the minimum possible value of the catalyst flow rate.

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MODEL-BASED DESIGN OF A LED-BASED PHOTOCATALYTIC REACTOR

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In recent years heterogeneous photocatalysis has attracted a lot of attention due to its large number of applications including air and water purification, water splitting, oxidization of liquid hydrocarbons, recovery of noble metals from wastewater and conversion of carbon dioxide to valuable hydrocarbons. The rate of photocatalytic reactions dependents on both the concentrations of the reactants and the rate of photon absorption by a catalyst. The catalyst has to receive photons with a suitable amount of energy in a uniform pattern for optimal performance [1]. Thus, investigation of the radiation field within the reactor is crucial for the reactor design, optimization, and scale-up [2]. Around 95 % of solar light reaching the earth is visible light and a great deal of research has been conducted on development of photocatalysts with the capability of harvesting visible light [3]. However, TiO_2 is still the most frequently used photocatalyst due to its high photocatalytic activity, non-toxicity, low cost and long-term stability. TiO_2 needs to absorb ultraviolet light to be activated. Classical UV lamps such as black lights, Mercury and Xenon lamps have been widely used for laboratory or commercial photocatalytic applications. There are several studies dedicated to the analysis and modelling of the radiation field within a reactor based on conventional lamps as the light source [4]. However these lamps are fragile and toxic and offer less flexibility in term of reactor design. Alternatively, light emitting diodes (LEDs) are non-toxic, compact and can be applied flexibly. Several studies have shown the feasibility of using light emitting diodes as a promising light source for photocatalytic applications.[5] However, how to systematically model and optimize the radiation field produced by LEDs within a photocatalytic reactor remains an important question.

This work aims to model and optimize the radiation field from LEDs as a light source to find the optimum design parameters of a LED-based photocatalytic reactor. A model to define the radiation field in a LED-based photocatalytic reactor is proposed. The model includes the emission model in order to compute the superficial rate of light absorption by a TiO_2 film coated on the reactor wall as function of reactor and LED-array design. Fig. 1 shows a preliminary result of the simulated irradiance pattern from a UV-LED module on a catalyst film surface in a one dimensional reactor.

The reactor will be modelled by combining a radiation field model and mass balances for a model compound with well-known kinetics from literature. The model will be validated experimentally in future research and the effect of the design of the LED array on the reactor performance will be investigated.

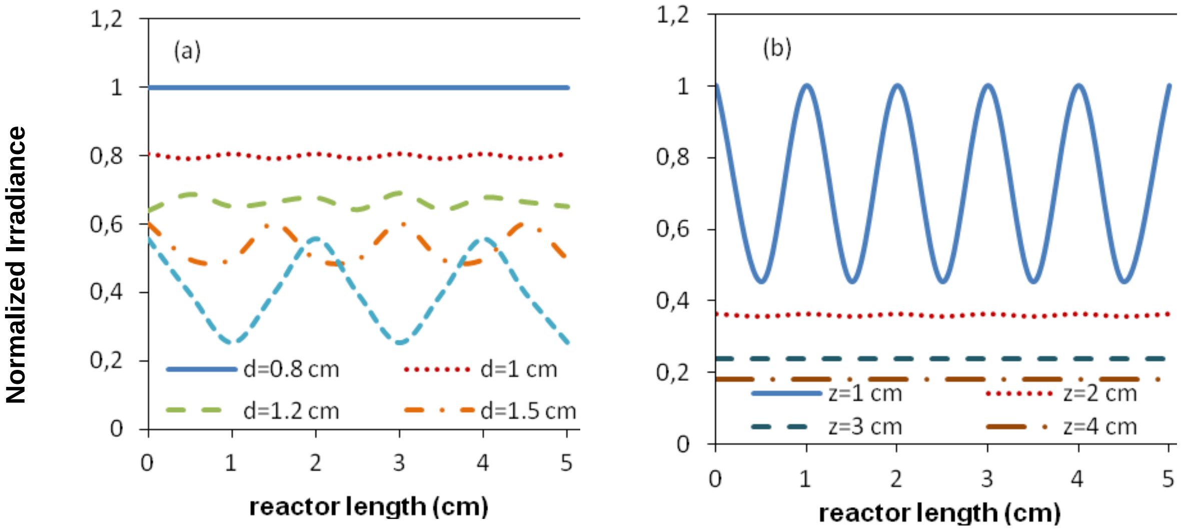

Fig. 1 Predicted 1-D Irradiance profile along the reactor a) for various LED-to-LED distances (d) at z = 2 cm b) for various distances of LED module from catalyst surfaces (z) at d = 1 cm

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CATALYTIC PROPERTIES OF BEA AND MWW ZEOLITES IN ALDOL CONDENSATION OF FURFURAL AND ACETONE

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The negative effect of our industrial activities on environment is the main driving force of the intensified research and development of new technologies for using energy from renewable raw materials. Pyrolysis of waste biomass and catalytic transformation of various biomass-derived intermediates results in a variety of compounds with a broad distribution of molecular weights. Upon direct hydrodeoxygenation many of them are converted into low value products; as a consequence, efficiency of biomass processing is decreased. A promising strategy is based on aldol condenation of small aldehydes and ketones into larger molecules.

Aldol condensation of aldehydes and ketones proceeds in the presence of both acidic and basic catalysts. Homogeneous basic catalysts are industrially used in the reaction because of their high activity and selectivity toward the desired reaction products. However, due to their environmental friendliness, processes using heterogeneous catalysts are highly desirable. A list of such potential catalysts includes hydrotalcites and other mixed oxides (basic materials) or zeolites (acid materials). The advantage of using zeolites as catalysts in aldol condensation is in their predictable and tunable physico-chemical properties as well as in their stability to regeneration.

It was shown [1] that the acidic zeolites possessed rather good activity in aldol condensation of furfural and acetone. Their catalytic properties were determined by the structural type, as well as by their textural and acidic characteristics. It was also shown that during the reaction the activity of all investigated zeolites have decreased due to the formation of carbonaceous deposits inside their micropores. Therefore, careful design of textural properties (pore size and dimensionality, internal and external surface area) and acid properties (type and strength of acid sites and their location) of zeolites is necessary to opimize their properties in aldol condensation. Layered materials should exhibit a better accessibility of their active sites than the classical zeolites and could thus make the activity enhancement possible. Materials of MWW or UTL structural topology are of particular interest because they combine the features of both zeolites due to the presence of microporosity and layered (or laminated) materials as they consist of zeolitic layers with a thickness of 25 Å. The aim of the present work was the comparison of the catalytic properties of 2-D and 3-D materials in aldol condensation and the determination of factors responsible for the increase of zeolite catalytic activity and for the improvement of their stability to coking.

The objects of investigation included wide-pore three-dimensional BEA zeolite as well as a number of microporous materials with MWW topology: MCM-22, MCM-36, MCM-49 and MCM-56. All the samples under study were characterized by XRD, SEM, N_2 physisoprtion, FTIR of adsorbed d_3-acetonitrile and di-tert-butyl-pyridine, TGA/DTG. Their catalytic properties were examined in aldol condensation of furfural and acetone using a batch stirred reactor. The performed experiments indicated that the activity of all MWW samples in the reaction is higher in comparison with the activity of BEA zeolite. These results proved the advantage of using 2-D microporous materials over 3-D zeolites as catalysts in aldol condensation. The main reaction products were C_8 and C_{13} compounds as products of aldol condensation of furfural and acetone. Additionally, C_{16} compounds were formed by the dimerization of primary C_8 product that would afford C_{16} branched hydrocarbon products upon deoxygenation. The presentation will discuss in detail the effect of individual parameters of the samples on their activity and selectivity in aldol condensation of acetone and furfural. The obtained results can be used to address some the challenges of biomass upgrading.

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MODELING OF MASS AND HEAT TRANSFER FOR HONEYCOMB CATALYSTS WITH CHANNELS OF DIFFERENT SHAPE

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In the last decades, the wide application of catalytic monoliths for air pollution control has attracted the interest of researches to study how to develop other processes by using monolith reactors. They were found to be promising for catalytic combustion, hydrocarbon processing for fuel cells, etc. Modeling of structured systems helps to understand the peculiarities of interactions of chemical reaction and transport processes and search out a decision of design problems [1].

This work continues the CFD study reported in [2], where it was shown that exothermic reaction in the honeycomb catalyst with porous walls occurs with significant innhomogeneity of the reaction rate and temperature caused by the aerodynamics of the gas flow. More detailed information about the rates of mass and heat transfer in the system is required for further analysis.

The comprehensive spatial distribution of gas flow velocities in the honeycomb catalyst with triangular or square channels is obtained by solving the system of Navier-Stokes equations with FLUENT software. A single channel model is used assuming the permeability of the walls for the gas flow. The impact of catalyst structure and operation conditions on mass and heat transfer rates is studied, and methane oxidation is taken as a model reaction.

Local distributions of gas velocities were determined: near and inside face-to-face part of the catalyst particle, along the axial line inside the catalyst wall and normal to channel surface, along the channel axis and the axial line near channel edges. The transfer rates in the parts of catalyst volume differ significantly. Such difference is observed for all conditions under study, both channel shapes with the equal hydraulic diameter of 1.18 mm and open porosity 40-60 % are considered at inlet gas velocities 0.5-3 m/s and the range of temperature 400-800 °C.

For example, along the channel axis the flow velocity increases more than in 5 times because of heterogeneous flow distribution over the cross-section area. As the gas flow approaches the face-to-face surface of the catalyst, the gas velocity lowers sharply near the inlet, in about four orders. The ratio of average axial velocity at the catalyst top to normal regarding the catalyst wall surface is more than two orders. The strong innhomogeneity of gas flow distribution defines the system behavior generating significant gradients of reaction rate, concentration and temperature in the catalyst, similar dependences are observed for all conditions studied.

Axial profiles of methane concentration for triangular channel as an example of modeling results are given in Figure 1. In spite of low velocities of gas penetration in the top part of the catalyst wall, the sharpest gradients arise in this zone.

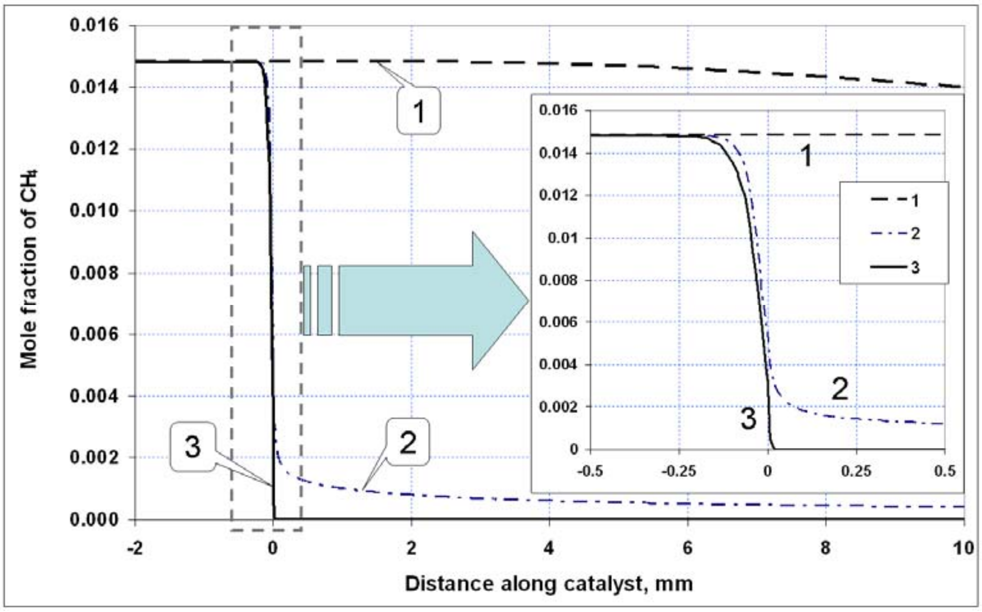

Fig. 1. Axial profiles of methane concentration for triangular channel along the middle lines at the channel axis (1), at the channel surface (2), and inside the catalyst structure (3)

Local and average parameters of mass and heat transfer between channel walls and the gas flow in the interface layers formed in the near-wall region were determined along the channel, and the comparison of average values was performed with these parameters evaluated by using plug-flow model of the process in monolith. For the majority of data, especially in the upper channel part, significant difference is observed, but the regions are assigned where 1D approximation could give acceptable results.

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CARBON MONOXIDE AND HYDROGEN CO-ADSORPTION OVER PLATINUM CATALYST

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The investigations of the interaction between hydrogen and carbon monoxide on metal surface and their competitive adsorption is of great interest in the context of PROX reaction (preferential oxidation of CO in the presence of H_2). In the PROX system, next to the oxidation of CO, oxidation of hydrogen may occur [1]:

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \tag{1}$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \tag{2}$$

Therefore, the knowledge about the co-adsorption of CO and H_2 on catalyst surface is of significant importance to get a deeper insight into the mechanism of PROX reaction. Supported Pt catalysts are the most active and widely studied in this reaction.

The aim of this work was to know the nature the co-adsorption of CO and H_2 over 1 % Pt/Al_2O_3. The catalyst was prepared by the wet impregnation of Al_2O_3 (Fluka, S_{BET} = 125 m^2/g) using aqueous solution of H_2PtCl_6. In order to obtain samples with differentiated platinum dispersion they were pretreated (reduced) *in situ* by heating in hydrogen at given temperature from the range 500-800 °C for 1h.

The co-adsorption was measured by using pulse technique in PEAK-4 apparatus [2] with an application of Infrared Gas Analyzer. The experiment was based on the injection of 0.05 mL of gas mixture : 1) **CO/He** (*6 % vol. CO + 94 % vol. He)* or 2) **CO+H_2/He** (*6 % vol. CO + 44 % vol. H_2 + 50 % vol. He)* into the carrier gas (He) at room temperature. The amount of adsorbed CO vs. reduction temperature was presented in Fig. 1. After sorption measurements, temperature programmed desorption (TPD) was performed. The nature of adsorbed on Pt/Al_2O_3 CO species in the presence or absence of hydrogen were studied by FTIR spectroscopy. The co-adsorption measurements were also performed on pure support (Al_2O_3).

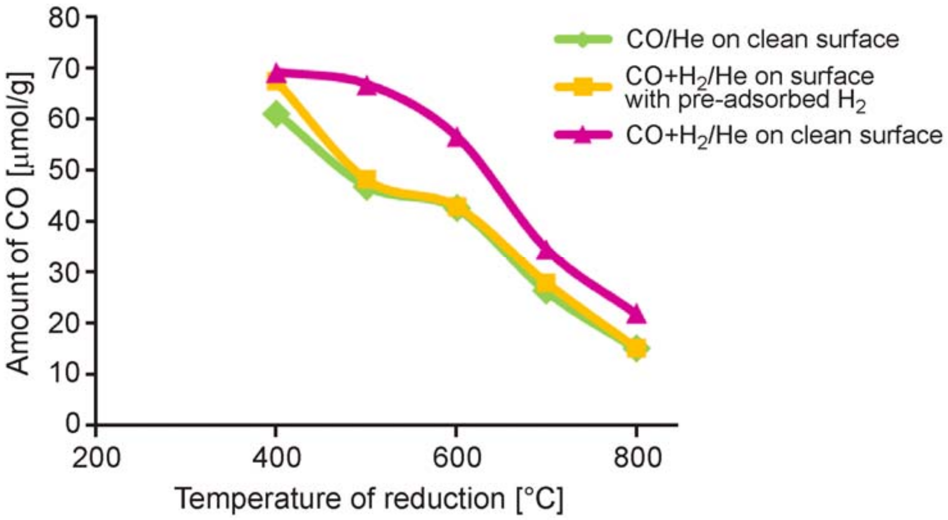

Fig. 1. The amount of CO adsorbed on Pt/Al_2O_3 from the CO/He and CO+H_2/He mixtures vs. temperature of catalyst's reduction

Basing on the obtained results one can conclude that:

- the sorption of CO both on clean surface and that with pre-adsorbed hydrogen is similar, what indicates no influence of hydrogen on CO adsorption,
- the amount of adsorbed CO from the mixture CO+H_2/He is higher when that from the mixture CO/He,
- with the increase in reduction temperature the sorption of CO decreases,
- the sorption of CO on the support Al_2O_3 is not observed.

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Acknowledgements

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BIO-PROPYLENE GLYCOL TECHNOLOGY FROM RENEWABLE SOURSE

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The efficiency of bio-propylene glycol synthesis from lactate ammonium was described. The technology consists of three stages:

- Fermentation of sugar containing solution with ammonium lactate formation;
- Ammonium lactate esterification with butyl lactate formation;
- Butyl lactate hydrogenation with bio-propylene glycol formation.

On fermentation stage glucose and molasse were used as a raw materials. Fermentation was carried out in a continuous mode in a membrane bio-reactor when cells remain inside reactor during all run time (as a bio-catalyst). Lactic acid yield was non less then 95 %.

Esterification was carried out in a reaction-rectification apparatus in a mode when water and ammonia were separated from top of rectification column while butyl lactate was forming in bottom. Butyl lactate yield on this stage was 90-95 %.

Hydrogenation of butyl lactate was carried out in a gas phase tube flow reactor with fixed bed of Cu/SiO_2 catalyst. Bio-propylene glycol yield was about 99 %.

Analysis of obtained data showed that elaborated method provides production of bio-propylene glycol by an economical efficiency competitive with that of petrochemical derived propylene glycol.

CHARACTERIZATION AND KINETIC STUDIES OF DeNO$_x$ REACTION OVER Cu-SSZ-13 SYNTHESIZED ON METALLIC FOAMS

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Biofuel cogeneration power generators offer the capability of producing economical power and heat from a renewable fuel. Such process requires, however, appropriate catalytic technology for the treatment of exhaust gases to meet the new European Waste Incineration Directive (WID) devoted to stationary emission sources. Although the cleaning installations for VOC and NO$_x$ are known and work successfully in power stations there are several important problems typical of biogas engine exhaust. These include reduction of the size of cleaning installation, ammonia slip, thermal deactivation (hot spots) and high cost of catalyst based on nobel metals. The remedy can be the application of the reactors based on metallic short channel structures of enhanced mass and heat transport [1] that are able to considerably shorten the reactor length. However, to exploit the benefits of such structures, active catalysts need to be employed.

In this paper, a short channel structure based on metallic foam with in-situ synthetized SSZ-13 zeolite is characterized and tested in Selective Catalytic Reduction of NO$_x$ (SCR) with ammonia. The catalyst performance is expressed in terms of reaction rate and kinetic parameters. The kinetic parameters were derived from the results of experiments where the process parameters, ammonia over nitric oxide ratio, nitric oxide level, space time and temperature, were varied over a wide range.

The short channel structure catalyst was prepared by hydrothermal in-situ synthesis of a SSZ-13 zeolite on precalcined metal foam surface using modified procedures described in [2,3]. The copper ions were introduced by ion-exchange from 0.5 M $Cu(NO_3)_2$ solution. As-prepared catalysts were examined by various analytical techniques: X-ray diffraction (XRD) for phase identification, SEM for crystal morphology and XRF for copper content.

The catalytic activity of structured catalyst and reaction kinetics was examined in NH_3-SCR of NO in a gradientless flow reactor directly connected to FTIR THERMO spectrometer with photoacoustic low volume gas analysis module. The catalytic reaction was typically carried out in the presence of oxygen (5 %) in the temperature range 200–500 °C, whereas the feed concentrations of NH_3 and NO were varied between 150 and 1000 ppm. Overall N-balances at steady-state were evaluated within 5 % error. Internal and external gradients were ruled out by theoretical diagnostics of limiting criteria. The kinetic expressions was determined in a broad temperature range (200-500 °C). The scale-up experiments were performed to validate the evaluated kinetic rate expression.

In all, the kinetic tests demonstrated high overall SCR activity and almost 90 % selectivity to N_2 of the in-situ synthesized catalysts SSZ-13 on structured foam reactor. The kinetic model of NH_3-SCR reaction is discussed and difficulties for ammonia oxidation at temperatures above 300 °C are accounted.

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PP-58

OCM REACTION OVER VARIOUS STRUCTURED FORMS OF $Mn/Na_2WO_4/SiO_2$ CATALYST

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The increasing energy cost and environmental problems such as global warming seem to make the conversion of natural gas into some valuable products such as ethylene significant for petrochemical industry [1]. Oxidative coupling of methane (OCM) to C_2 hydrocarbons (ethane and ethylene) has been researched for a long time as a potential process [2]. In this work, the oxidative coupling of methane (OCM) over various forms of $Mn/Na_2WO_4/SiO_2$ catalyst was investigated.

The reactions were performed using a 2mm ID and 10 mm ID micro-flow quartz tube reactor at various temperature from 600 to 750 °C with a changing CH_4/O_2 ratio from 3, 7 to 10 in various structures such as particulate fixed bed, wall coated in metal microchannel, wash coat monoliths and single monolithic structures as in Figure 1. Three different methods (incipient to wetness to impregnation method, sol-gel method and direct hydrothermal synthesis method (MCM-41)) were applied to synthesize the 2 wt % Mn/5 wt % Na_2WO_4/SiO_2 catalysts. The catalyst contents of the active metal remains 2 wt % Mn and 5 wt % Na_2WO_4 the same all the preparation ways.

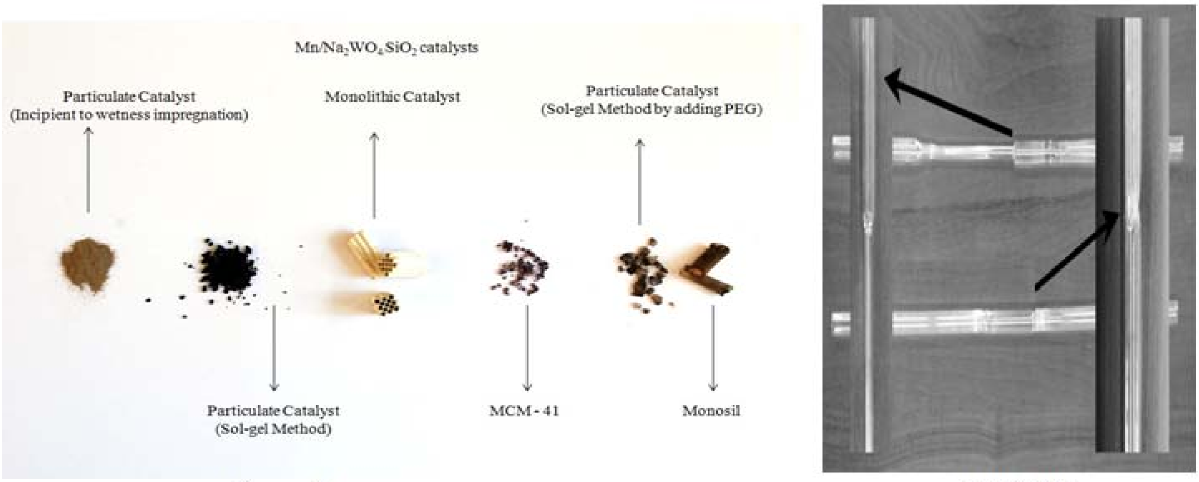

Figure 1a

Figure1b

Figure 1. a) various types of catalysts prepared through different methods
b) 10 mm and 10 to 2 mm narrower ID quartz fixed-bed down flow reactor

Some of the results can be seen in Figure 2. The catalysts prepared by incipient to wetness impregnation resulted the highest selectivity, followed by the catalyst prepared by sol-gel method with PEG while the colloidal coated catalyst gave way to 14.69 yield and 5.43 C_2 selectivity, which is significantly low. In addition, decreased 10 mm to 2 mm initial diameter after the catalyst bed in the quartz reactor inside diameter improved the C_2 selectivity significantly but did not changed the conversion. Additionally, the low C_2 yield was achieved in the micro-structured reactor tests of coated particulate $Mn/Na_2WO_4/SiO_2$ catalyst on the FeCrAl alloy plate probably due to the weak adhesion and metal poisoning.

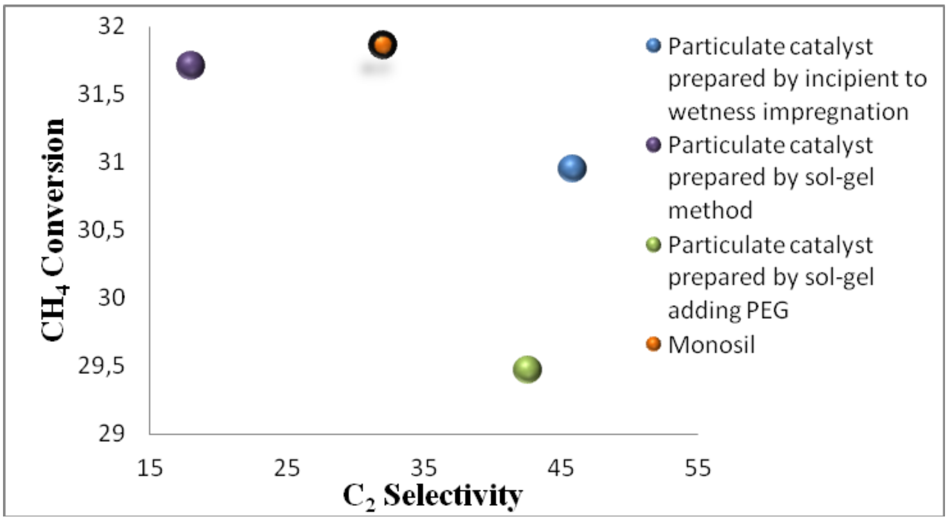

Figure 2.Comparasion of the catalysts prepared by different methods (reaction temperature at 700 °C, CH_4/O_2 ratio is 10)

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Acknowledgements

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SEPARATION OF LINEAR AND BRANCHED PARAFFINS FROM A REAL FEED BY FIXED BED ADSORPTION USING A CARBON MOLECULAR SIEVE

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The study of the effect of the temperature (175 to 325 °C) on the separation of real feed (multi-component hydrocarbon mixture) was performed by fixed bed adsorption experiments using a carbon molecular sieve (CMS-IMP12) obtained from the pyrolysis of a poly-(vinylidene chloride-co-vinyl chloride (PVDC-PVC) polymer commercially known as Saran^{TM} as adsorbent material.

Material balances of the breakthrough experiments showed that total adsorption capacities went from 128 to 86 mg/g$_{ads}$ at temperatures starting at 175 to 325 °C and as a result, octane numbers of the non adsorbed product (10 to 15 % of the total feed) were at least 10.8 units higher. The octane number of the non-adsorbed could be increased by reducing the yield.

To simplify the description of the feedstock and products the hydrocarbons were classified as: non branched, monoalkyl, gem and non gem dialkyl, and trialkyl alkanes and cycloalkanes, respectively. Gem refers to the relationship between two methyl groups that are attached to the same carbon atom. The results of this separation showed that the material was able to separate them by number of carbons and type of branching in the main chain. Linear and cyclic and non-cyclic non-gem hydrocarbon were readily adsorbed; 3,4-dimethylbutane, cyclopentane, cyclohexane and 1c,2-dimethylcyclopentane presented an intermediate behavior, while tri-branched, and cyclic and non cyclic gem-branched hydrocarbons were absolutely precluded for the material.

In a further classification to facilitate the mathematical modelling, compounds that were easily adsorbed named “Adsorbed HCs” involved mono alkyl and non gem di-alkyl alkanes except 2,3-dimethylbutane, and all the non gem di- and trialkyl cycloalkanes. The non adsorbed compounds named as “Not Adsorbed HCs” were all the gem di- and trialkyl alkanes and gem di- and trilalkylcycloalkanes, Cyclopentane, cyclohexane , 2,3-dimethylbutane and 1c,2-dimethylcyclopentane were considered moderately adsorbed compounds and named as such. Values for the adsorption process of the lumped “Adsorbed HCs” and “Moderately adsorbed HCs” were fitted by kinetic and equilibrium based Langmuir models. The kinetic model fitted better the experimental data than the equilibrium Langmuir model. This result indicated that the overall adsorption rate is governed by the adsorption process per se; meaning that the deposition of the hydrocarbon molecules to the surface of the adsorbent was the slowest stage and the influence of mass transfer was not prevailing. Average estimated heats of adsorption (ΔH) showed that “Moderately adsorbed HCs” presented higher adsorption heats than “Adsorbed HCs”.

Therefore, Saran derived CMS-IMP12 seems to be a promising material for high octane-low environmental impact gasoline production by an adsorption process in gas phase.

THERMODYNAMIC AND KINETICS OF ADSORPTION OF NITROGEN COMPOUNDS FROM MODEL MIXTURES AND REAL FEEDS: EXPERIMENTS TOWARDS ULSD

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The production of ultra low sulfur diesel (ULSD) is so essential to protect life on earth that many stringent environmental regulations for this nonrenewable fuel have been established worldwide in spite of the sustained decrement in the crude oil quality. Several technological alternatives have been developed to overcome those challenges; for example: the withdrawal of the nitrogen compounds (N-compounds) in the feedstocks processed for diesel fuel production due to its hydrodesulfurization (HDS) inhibition capabilities.

In this work, the adsorption process of the nitrogen compounds present in the feed for diesel fuel production was studied in four commercial adsorbents.

Experimental. Silica gel (BET 645 m^2/g; pv 0.82 cm^3/g), selexorb CD (BET 410 m^2/g; pv 0.48 cm^3/g), selexorb CDX (BET 460 m^2/g; pv 0.48 cm^3/g), and activated carbon (BET 870 m^2/g; pv 0.80 cm^3/g).

Thermodynamic and kinetic studies were performed using model mixtures (300 ppm quinoline, 300 ppm indole or 150 ppm carbazole in 1:1 toluene:hexadecane) and a straight run gas oil (SRGO, 285 ppm) sample.

The experiments were carried out in a vessel were 15 ml of the model mixture and 1 g of the adsorbent of choice were mixed for an hour at 30-35 °C taking samples at different time intervals and the nitrogen content were analyzed (Antek multiTek equipment for nitrogen and sulfur analysis). The thermodynamic parameters were obtained by fitting the experimental data to Langmuir and Freundlich models. The effective diffusivity model was chosen for the kinetic treatment.

Results from model mixtures. In silica gel the only compound adsorbed was quinoline (12.3 mg N/g_{ads}). In selexorb CD and selexorb CDX the adsorption capacity followed the order: quinoline (4.5-5.3 mg N/g_{ads}) > indole (2.7-2.8 mg N/g_{ads}) > carbazole (2.9-1.2 mg N/g_{ads}). In the activated carbon the order was: indole (6.7 mg N/g_{ads}) > carbazole (4.2 mg N/g_{ads}) > quinoline (3.7 mg N/g_{ads}). The total adsorption capacity followed the order: activated carbon (14.3 mg/g_{ads}) > selexorb CD (13.1 mg N/g_{ads}) > silica gel (12.3 mg N/g_{ads}) > selexorb CDX (9.3 mg N/g_{ads}).

Regarding the kinetic data, quinoline was adsorbed in silicagel at 17.2 x 10^{-2} min^{-1}. In activated carbon, order was: quinoline (18.5 x 10^{-2} min^{-1}) > indole = carbazole (4.6 x 10^{-2} min^{-1}). Important difference between adsorption rates were not observed for quinoline, indole or carbazole in selexorb CD and selexorb CDX (2.2-3.5 x 10^{-2} min^{-1}).

Results from SRGO. When performing the adsorption process of the nitrogen compounds present in the SRGO, the adsorption capacity followed the order: silica gel (32.0 mg N/g_{ads}) > activated carbon (11.3 mg N/g_{ads}) > selexorb CDX (8.3 mg N/g_{ads}) > selexorb CD (6.3 mg N/g_{ads}). The adsorption rates for nitrogen compounds in the four adsorbents followed the order: silicagel (20.3 x 10^{-3} min^{-1}) > selexorb CDX (13.7 x 10^{-3} min^{-1}) > selexorb CD = activated carbon (7.3 x 10^{-3} min^{-1}). Noticeably, adsorption rates of the nitrogen compounds present in a real feed were at least one order of magnitude lower than the rates observed in the experiments using model mixtures.

Conclusions. Commercial applications of this type of materials will require higher N-adsorption capacities than that achieved by the adsorbents studied in this work.

A Py-GC/MS STUDY ON THE IN SITU UPGRADING OF BIOMASS PYROLYSIS OIL BY VARIOUS ZEOLITE CATALYSTS

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The growing demand and the environmental problems resulting from the use of fossil fuels has induced the need for the utilization of different types of biomass. More specifically, lignocellulosic biomass is the only renewable source that leads to the production of liquid, solid and gaseous fuels, as well as high added-value chemicals. The *biomass fast pyrolysis (BFP)* is considered as an attractive process for the thermochemical conversion of lignocellulosic biomass into liquid products (pyrolysis oil or bio-oil) [1]. Bio-oils are dark brown, free-flowing organic liquids that are comprised of highly oxygenated compounds, including ketones, aldehydes, carboxylic acids, sugars and phenolics. Due to its composition, bio-oil exhibits some undesirable properties, such as low heating value, incompatibility with conventional fuels, high viscosity, relatively high acidity and corrosivity, incomplete volatility and chemical instability. Thus, bio-oil must be upgraded, mainly via deoxygenation, if it is aimed for the production of hydrocarbon based transportation fuels.

The *in situ* upgrading of bio-oil can be achieved by the use of appropriate catalysts during the BFP process [2]. A variety of fast pyrolysis processes and reactors can be applied for the catalytic fast pyrolysis of biomass, at both pilot and industrial scale, including mainly fluid bed & circulating fluid bed reactors [3]. In laboratory scale experimental research, the method of fast pyrolysis in combination with gas chromatography/ mass spectrometry (Py-GC/MS), serves as a useful tool for understanding the reaction pathways and rationalizing the composition of bio-oil [4]. In addition, many groups are also working with bench-scale fixed bed reactors [5] or dual-fluidized bed reactor set-up, consisting of a fluidized bed reactor, a biomass screw feeder and a set of four coolers and four gas quenchers [6].

This study presents the results of the catalytic and non-catalytic fast pyrolysis of lignocellulosic biomass (beech wood, Lignocel HBS, 150-500) and its individual components (cellulose, hemicellulose, lignin), using the Py-GC/MS technique. The experiments were carried out at 470-600 °C using a series of catalytic materials, consisting of strongly acidic microporous zeolites (H-ZSM-5, H-Beta, H-Y, USY, H-Mordenite, H-Ferrierite) with different micropore structure. All the acidic microporous zeolites induced pronounced de-oxygenation of the bio-oil via reducing the content of acids, ketones, aldehydes and phenols (in some cases). In addition, specific zeolites, such as ZSM-5, Beta and USY facilitated the formation of mono-aromatics and polycyclic aromatics (PAHs) due to their increased Brönsted acidity strength and micropore morphology.

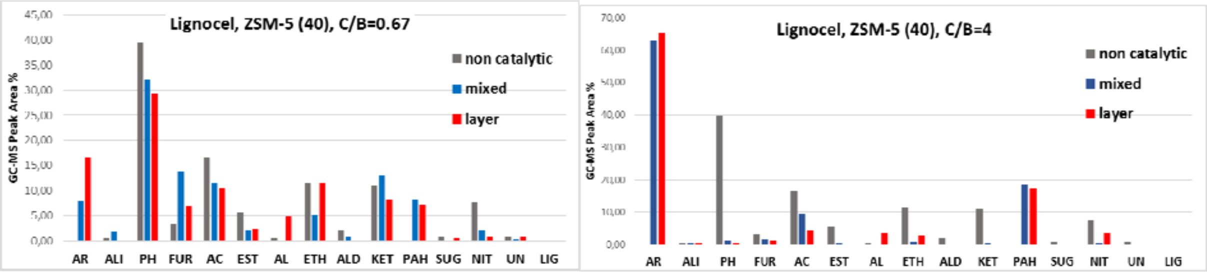

Fig. 1. Effect of the different catalytic bed configuration & the catalyst to biomass ratio (C/B) for the fast pyrolysis of biomass with zeolite H-ZSM-5 (Si/Al=40) at 500 °C

The different catalyst bed configuration and the catalyst to biomass ratio (C/B) has also been studied, and as can be seen from the results of Figure 1, the "mixed" bed (physical mixture of biomass with catalyst particles) is less effective towards the formation of aromatics and decrease of oxygenated compounds, at low C/B ratio, compared to the "layered" bed (separate catalyst and biomass beds). However, at higher C/B ratio these differences are minimized.

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Acknowledgements

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STRUCTURED CARTRIDGES WITH REINFORCED FIBER-GLASS CATALYST FOR FUEL COMBUSTION IN THE FLUIDIZED BEDS OF THE INERT HEAT-TRANSFER PARTICLES

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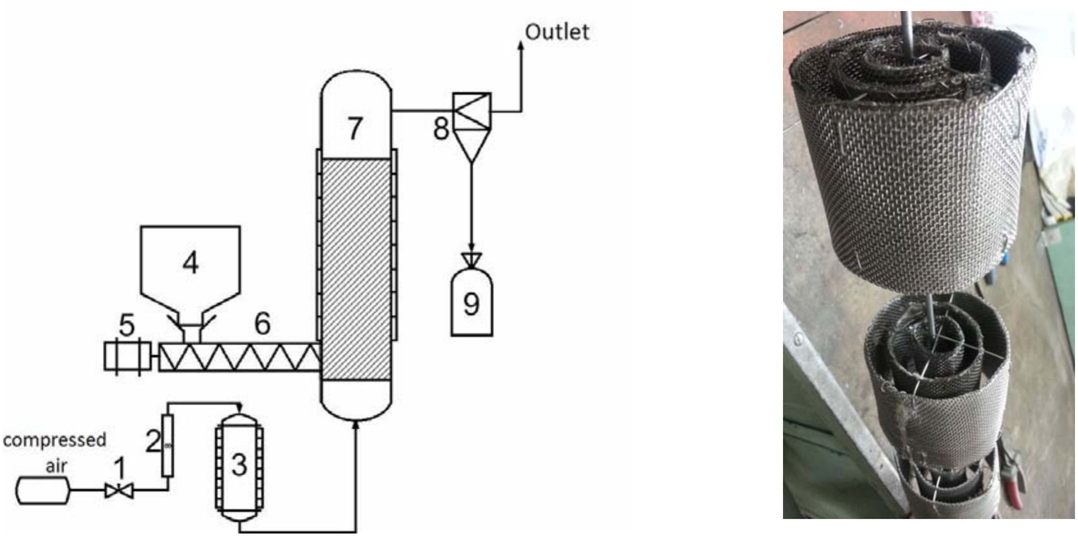
Catalytic fuel combustion is a basis for the efficient and environmentally safe heat energy production. The promising technology in this area is the combustion of various fuels including solid fuels in the fluidized bed of the inert heat transfer particles equipped with a packed bed of the catalyst [1,2]. Such technology provides increased energy efficiency and minimizes the amount of harmful admixtures (CO, hydrocarbons, NOx) in the flue gases.

The catalysts for this process must be structured in the form of cartridges with high value of void volume and wide gas passages preventing the clogging of the catalyst by heat-transfer particles. Another specific requirement is high catalyst resistance to attrition in the highly abrasive media of moving particulates.

The proposed catalytic system for this process was based on the catalytic element consisting of domestic Pt-containing (~0.07 % mass Pt) fiber-glass fabric catalyst IC-12-S111 and was reinforced by the stainless steel gauze from both sides [3]. The selected size of the cell in the gauze (2x2 mm) was less than the typical size of heat-transfer particles (sand, 3-4 mm) thus preventing the direct contact between particles and catalyst fabric and providing efficient protection of the catalyst from attrition. At the same time, such cell size is sufficient to provide the efficient diffusion of the gaseous reactants (CO, hydrocarbons) to the catalyst surface. The steel gauze also play a role of the structuring body giving the way to produce the catalytic cartirdges of any shape and size (Fig. 1).

Fig. 1. Structured cartridges with fiber-glass catalyst, reinforced with metal gauze

The produced cartridges of different shape were tested in the pilot experimental stand using the dispersed coal particles as fuel. The scheme of the stand is given in Fig. 2a. The most stable performance and complete absence of clogging was observed at the series of the concentric type cartridges (Fig. 2b).



(a) **(b)**

Fig. 2. Scheme of the pilot stand (a) and catalytic cartridges (b).
1 – valve; 2 – flowmeter; 3 – heater; 4 – fuel vessel; 5 – electric engine; 6 – screw feeder; 7 – electrically heated reactor; 8 – cyclone separator; 9 – ash vessel

Table. Results of the tests at the pilot heating unit at 750-840 °C, fuel – coal (fraction <1.25 mm)

No.	Parameter	Results		
		No catalyst	Glass-fiber Pt catalyst	Cermet CuCrAlOx [4]
1.	Residual CO content in outlet gases, ppm	4244	584	432
2.	Residual hydrocarbon content in outlet gases, % vol. (re-calculated for methane)	0,05	0	0

According to the test results (see the table) the cartridges with glass-fiber catalyst demonstrated the performance comparable with the most efficient conventional catalysts. The discharged cartridges had no traces of catalyst attrition and no sign of catalyst deactivation. The developed cartridges were recommended for further tests in the conditions of the commercial heat production unit.

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THERMO-OXIDIZING CRACKING OF HEAVY OIL RESIDUES

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Russia is one of the leader in crude oil production but the depth of oil refining is still much less then in the developed industries and is equal about 72 % while this indicator is equal 85 % in Europe and 92 % in USA. So the deeping of oil refining is one of the most important task for russian oil refining industry.

This report is devoted to Thermo-Oxidizing Cracking (TOC) of oil residues – the new method of conversion of mazut (atmospheric residue) and tar (vacuum residue) into the more valuable products (light fractions and bitumen).

TOC is carried out in a presence of oxygen which is highly efficient initiator of radical processes. TOC process runs in a mixed-flow reactor at 430-450 °C and 4-10 bar. Parameters of TOC process were optimized on the bench-scale installation having capacity of 3 kg of raw material per hour.

TOC technology provides conversion of mazut into about 70 % of motor fuel fractions and 25 % of bitumen or into 50 % of motor fuel fractions and 45 % of furnace fuel depending of customer's desire.

Vacuum residues can be converted by TOC into 35% of light fractions and 60% of bitumen.

The advantages of TOC are that its efficiency is higher then one of visbreaking and that existing visbreaking installations can be easy modified into TOC installations.

MODIFIED $AlPO_4$ FOR DEHYDRATION OF GLYCEROL IN GAS PHASE

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Introduction

The global annual biodiesel production is projected to be about 41 billion liters in 2019 (OECD-FAO). Glycerol (G) is the major by-product of biodiesel production.This has led to a drastic surplus of G in the chemical markets, while its current demand remained unchanged. Selective dehydration of G to acrolein (ACR) is a promising eco-friendly alternative to the present commercial acrolein production process, leading to oil saving and cost lowering. Here we report on the catalytic behaviour of a series of aluminum phosphate (AlPO) and the modified AlPO, with addition of Cu, Cr and Co, in the production of acrolein in gas phase. The final goal of this research is to obtain acrylic acid in one step. The textural properties and structure of the solids have been determined by X-rays, UV-Vis and ^{31}P and ^{27}Al NMR. Their acidic properties from TPD and DRIFT of pyridine have been also studied.

Experimental

The catalysts were prepared by an ammonia gelation method as previously reported [1].The AlPO (P/Al=1) was modified with a 1 wt % of transition metal, being the molar ratio P/(Al+M)=1. As a comparison, in one of the catalysts, the $AlCl_3$ was added first and dissolved, after that, the $Co(NO_3)_2$ was added. The solids were denoted by the corresponding formula and a number indicating the calcination temperature.

The G transformation was carried out in a continuous-flow fixed-bed microreactor under atmospheric pressure. Reaction products together with unconverted G were collected in an ice trap and analysed by GC equipped with a FID. The catalyst (ca. 50 mg) was pretreated at 220 °C 2h in a N_2 flow (50 cm^3/min). A 36 wt % glycerol (99.5 %, Sigma-Aldrich) aqueous solution was fed at 0.3 mL/h. The reaction was usually conducted for 22 h at 280 °C. The absence of homogeneous reactions and the inactivity of the reactor were determined with a blank test. The reaction products were identified through patterns and/or CG-MS. The response factors were obtained for each identified product. Conversion (X) and selectivity to products (S_i) are expressed as mol % on a C atom basis.

Results and discussion

The XRD patterns of catalysts showed only a very broad band characteristic of the amorphous metal phosphates. All the catalysts were mesoporous. UV-VIS spectrum of the solids showed characteristic bands assigned to Co(II,III), Cu(II), Cr(III,IV). ^{31}P and ^{27}Al NMR showed the presence of mainly P y Al in tetrahedral coordination. The acidity as well as the S_{BET} values increased with the modifications, the catalysts calcined at 650 showed lower acidity and surface. In all the solids predominated the Lewis sites.

The main products obtained under the experimental conditions studied were ACR and hydroxyacetone (H), other by-products were phenol, glycerol formal, glycidol and ethyl hydroxyacetate. The steady state was reached at 6-7 h of time on stream and the catalysts did not undergo changes in conversion after 22 h of operation. The modified AlPO showed higher values of G conversion (X) and selectivity to ACR (S_{ACR}) than the AlPO. Those calcinated at 650 exhibited the best catalytic behavior at 3h of time on stream, Table 1. In fact, the AlCoPO650 showed the best yield to ACR (52 %) at 3 h. The S_{ACR} decreased with the time on stream while the S_H increased. This fact could be related with changes in the balance between Lewis and Brönsted acid sites due to the presence of water in the feed [2]. A direct relationship between the acidity and the production of ACR of the solids was not found so the participation of other active sites in the dehydration of G could be to take into consideration.

Table 1. Surface area; acidity values versus pyridine (Py); conversion and selectivity to acrolein (at different time of reaction) at 280 °C on all catalysts studied

Catalyst	S_{BET} (m^2/g)	Py (µmol/g)	X (mol %)			S_{acr} (mol %)		
			3 h	6 h	22 h	3 h	6 h	22 h
AlPO450	215 ± 1	131	28	65	93	58	23	13
AlCoPO450	256.1±0.6	150	84	94	94	49	31	21
AlCoPO650	225.6±0.6	141	100	100	96	52	40	29
Al-CoPO450	253.8±0.5	159	72	84	94	54	33	21
Al-CoPO650	243.8±0.7	154	94	88	85	54	28	24
AlCuPO450	213.4±0.7	140	63	88	95	59	34	22
AlCuPO650	201.6±0.7	127	96	99	85	46	32	24
AlCrPO450	243.8±0.7	163	80	91	95	47	37	22
AlCrPO650	262.6±0.7	152	100	100	99	52	37	27

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STUDY OF METHANOL TO FORMALDEHYDE OXIDATION IN THE MICROCHANNEL LAB-SCALE REACTOR

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Past two decades, micro-channel reactor (MCR) technologies have been moved forward and applied in various scientific areas, such as catalysis, power engineering, green chemistry, organic synthesis etc. This is a world trend that apart from scientific applications, MCR-technologies are being widely commercialized. High efficiency and low energy consumption are mandatory for modern industrial technologies, in particular, for catalytic processing and fine chemicals production. Micro-channel systems, such as micro-reactors, micro-mixers and micro-heat-exchangers can meet the requirements for chemical processes intensification significantly better, compared to conventional technologies.

In this paper, MCR were used for investigating the problem of intensification and increasing the efficiency of highly exothermic catalytic processes on the example of methanol to formaldehyde oxidation. Conventional process occurs in multi-tubular reactors at methanol input concentration ca. 6.5 % vol., that is, below the lower explosive limit of methanol-oxygen mixture. Significant temperature gradients along the tube length and across the tube radius are typical for highly exothermic process like this and can reach 50-150 °C [1]. This results in a low specific productivity of the catalyst loading and a high metal capacity of the apparatus. The experimental study and modeling were focused on methanol to formaldehyde oxidation conditions in MCR, aimed at improving the process productivity. Selective oxidation of methanol over Fe-Mo catalyst proceeds after the reaction scheme as follows [1]:

$$CH_3OH + 0.5O_2 \rightarrow CH_2O + H_2O + 159\ \text{kJ/mol}$$

$$CH_2O + 0.5O_2 \rightarrow CO + H_2O + 230\ \text{kJ/mol}$$

$$CH_3OH + O_2 \rightarrow CO + 2H_2O + 394\ \text{kJ/mol}$$

Fig. 1. A view of MCR catalytic unit.

Lab-scale MCR catalytic unit consisted of evaporation chamber, flow distributing device and microchannel plate shown in Fig. 1. A brass perforated plate, 52 mm dia. and 10 mm thick had multiple through channels, 1.0 mm dia and 1.25 mm pitch. The central part of 499 channels was filled by Fe-Mo catalyst as 0.25-0.5 mm fractures and worked like tubes in a multitubular reactor. Annular part of 596 channels was air-flowed for the reaction heat removal. MCR design provided low pressure drop, while high metal conductivity and small channel diameter secured excellent heat withdrawal from the reaction area [2]. Experiments were performed at the following conditions: $VHSV$ = 3,600-11,000 h^{-1}, C_0 = 6-6.5 % vol., catalyst load *ca.* 4 ml. Both commercial Fe-Mo catalysts and the samples tailored on-purpose were studied.

The catalytic process in MCR was simulated using the 2D continual mathematical model [1]. Each channel was considered as a separate catalyst tube with the reaction heat removal; uniform flow distribution over the cross-section of the plate was assumed. Fig. 2 shows the temperature profiles along the tube axes expressed as the difference ΔT between the computed temperature in the catalyst bed T and the wall temperature Tw.

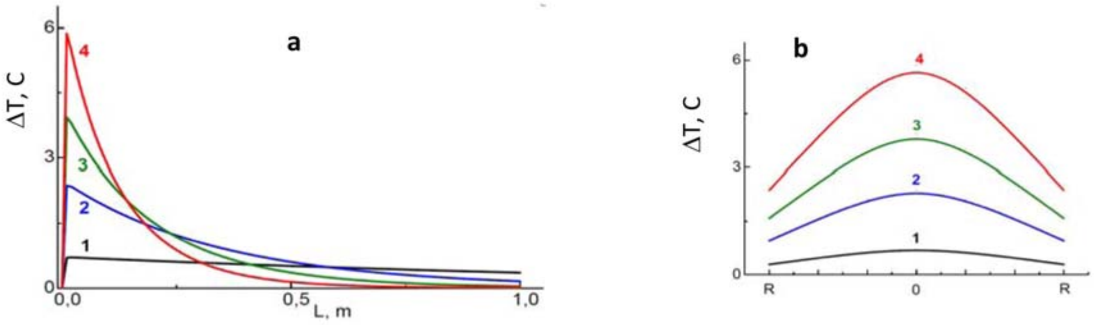

Fig. 2. Linear (a) and radial (b) T-profiles of temperature in the microchannel at *Tw* = 270 (**1**), 320 (**2**), 350 (**3**) and 380 °C (**4**). *Tw* = *Tin*, *[MeOH]* = 6.5 % vol., $[O_2]$ = 7 %, $VHSV$ = 10,909 h^{-1}

Results of preliminary modeling showed in Fig. 2 reveal the existence of only small temperature gradients inside the channels; therefore the process can be intensified by applying higher methanol input concentration. Note that formaldehyde yield is favored by elevated temperatures, because the activation energy of the target product reaction rate is higher than that of the by-products. Thus, at the highest temperatures *Tw* = 320-380 °C, high performance values of methanol conversion *X* = 93-99 % and formaldehyde selectivity *S* = 94-96 % can be reached in miniaturized reactor. Operation conditions in MCR allow increasing the catalyst specific productivity by the factor of 1.5-1.8 compared to conventional reactor.

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NOVEL HETEROGENEOUS CATALYSTS FOR TRANSESTERIFICATION PROCESS OF VEGETABLE OIL

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Transesterification process of vegetable oil is an important opportunity of diesel fuel production. Usually this process is carried over homogenous catalysts – mainly sodium and potassium hydroxides. Application of homogenous catalysts have a number of disadvantages: impossibility of catalysts reuse, soap formation and many others. Heterogeneous catalysts exhibit lower activity but they are more suitable for transesterification process.

In this work the transesterification process was studied over spinel based catalysts containing alumina and oxides of Ca, Mg, Sr, Ba. Catalysts were prepared by coprecipitation method from aqueous solutions of appropriate nitrates. Then the samples were dried and calcined in temperature range: 600-1200 °C. Transesterification process was performed in autoclave in temperature range 80-180 °C. As a substrate the mixture of methanol and rapassed oil with the molar ratio 6:1, 9:1 and 12:1, respectively. Total amount of substrate was about 40 ml and the catalyst weight was 1, 1.5 and 2 g. The product was analyzed using LC-MS technique. The results show that oil conversion depends strongly from reaction temperature (33 % for 100 °C and 90 % for 160 °C). The products contains mainly methyl esters of fatty acids (40-90 %), unreacted oil (8-67 %), traces of mono and diglycerides. The highest activity was achieved for catalysts previously calcined at 900 °C.

Acknowledgements

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PP-67

STEADY STATE MULTIPLE REACTION-DIFFUSION PROBLEM REDUCTION BY STOICHIOMETRY RELATIONS

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Introduction

When a non-reactive system of “nc” compounds is treated, the mass conservation condition reduce the complexity of mass transfer by diffusion to “nc-1” independent compounds, being the remaining one obtained as a linear combination of the rest. When a set of “nr” chemical reactions is involved the complexity of mass transfer by diffusion is reduced up to a “nk” number of independent fluxes equal to the rank of the matrix of stoichiometry. The remaining diffusive fluxes can be obtained as linear combinations of those “nk” independent ones.

This work is devoted to provide a background for the development of calculation methods for multireacting effectiveness factors. Thus, although the complexity reduction by stoichiometry relations can be obtained for dynamic systems too, here steady state is a basic assumption.

Methodology

The starting point for the present analysis is a general description of an isothermal diffusion-reaction process within a porous catalytic pellet, with tortuosity tensor “**T**”, given by equation (1).

$$\oiint_{A_p} \overline{N} \bullet T \bullet n dS = \iiint_{V_p} \rho_p [\nu] \bar{r} dv^{\bullet} \qquad (1)$$

The matrix of stoichiometry “[ν]”, considered a set of “nc” numerical vectors of change, each one formed from “nr” numbers, defines a vector space of rank “nk”, which means the number of linearly independent vectors that integrate a base “[ν_b]” in that space. The “nk” compounds corresponding to the vectors in the base are commonly referred as key compounds.

The set of combinations of the base vectors producing the matrix of stoichiometry is represented as a matrix “[Γ]” of “nc” vectors formed from “nk” numbers, here called matrix of stoichiometry relation (MSR). This is in agreement with equation (2)

$$[\nu] = [\Gamma][\nu_b] \qquad (2)$$

MSR provides, through the set of molar balance equations, the combination of key compound molar fluxes producing the set of “nc” individual fluxes.

The constitutive equation being used to represent the mass transfer, which may be the Generalized Fick’s Law or the Maxwell-Stefan equations, works as a transformation rule between two vector spaces: the molar fluxes and the mol fraction gradients. Through this rule and the MSR, a relation between the set of mol fraction gradients and the key compounds’ is obtained.

Results

Once applied the mentioned reductions, the “nk” descriptive equations of the diffusion-reaction problem to be solved take the shape shown in equation (3)

$$\frac{\partial[\beta]}{\partial\bar{x}}[\alpha^{\bullet}][\beta]\nabla\bar{x}_b \bullet T \bullet \nabla\bar{x}_b + [\beta]\{T^{T}\overset{\bullet}{\bullet}\nabla(\nabla\bar{x}_b) + \nabla\bar{x}_b \bullet (\nabla \bullet T)\} = -\rho_p[\nu_b]\bar{r} \tag{3}$$

Which should be solved coupled to the relation given as equation (4)

$$\nabla\bar{x}_{nb} = [\alpha_{nb}^{\bullet}][\alpha_b]^{-1}\nabla\bar{x}_b \tag{4}$$

The subscript “nb” stands for non-base.

Conclusions

1. The most general equations to be solved in diffusion-reaction modeling were obtained from linear algebra and vector calculus concepts.

2. The tortuosity tensor commonly considered in academic books is a constant and isotropic one.

METHANOL-DME TO LIGHT OLEFINS OVER SAPO-34: EFFECT OF FEED TYPE ON PRODUCT DISTRIBUTION AND CATALYST PERFORMANCE

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As a main process for Olefin production, Methanol to Olefin (MTO) process is highly concered in catalyst studying institutions. This operational process is operating, based on two main catalysts: SAPO-34 and H-ZSM-5. The feedstock for MTO is mostly limited to Methanol, if SAPO-34 is used. Actually, studying MTP (Methanol to Propylene) as the previous and basic form of MTO shows that DME (Dimethylether) is also known as a feedstock which seriously helps lifetime and product distribution to be improved. This clue, introduced a new theory for changing the feedstock followed by studying MTO performance in both feeding systems, which showed an increase in ZSM-5 catalyst’s lifetime from 2 to 80 days. Close behaviour of SAPO-34 and ZSM-5 during MTO process, presents the possibility of spectacular raise in lifetime. There are three important Factors must in cosideration for MTO Process if SAPO-34 is used as catalyst: Lifetime, Selectivity and Economy.

Studying DME production processes, it is mostly manufactured using methanol over γ-Alumina in a stable fixed bed reactor however, Ogawa et. al. (DME Development Co., Ltd) developed a new process to synthesize DME from Natural Gas directly [1]. This new acheivement showed a qualified performance because the main Thermodynamic Resistance occurred during indirect production of DME is removed spontaneously. Also, this modified process is economically improved while two main reaction units are combined.

During this study, SAPO-34 was synthesized By the modifed method obtained from Delphine et. al. [2], then characteristics tested (basically crystal phase, surface area and acid site densities using: XRF, BET, TPD and XRD) and finally examined in a fixed bed reactor for product distribution analysis. Also, effect of several parameters such as Temperature, WHSV and feed type was also studied for both DME and Methanol feeded operations. Figures 1 shows XRD pattern plot of the synthesised catalyst. Obviously, main peakes are recognized in 2θ of about 10, 20 and 30.

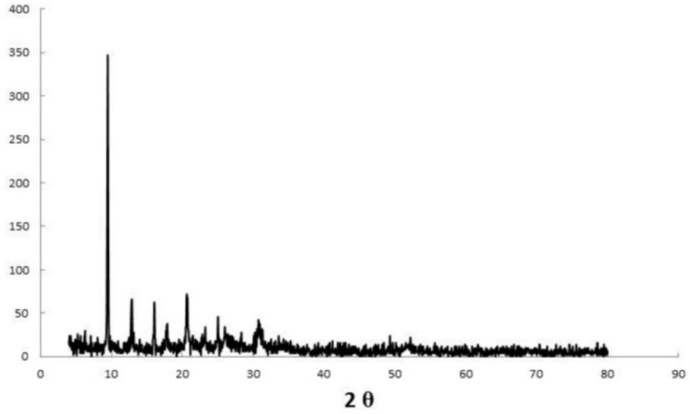

Figure 1: XRD pattern of synthesized SAPO-34

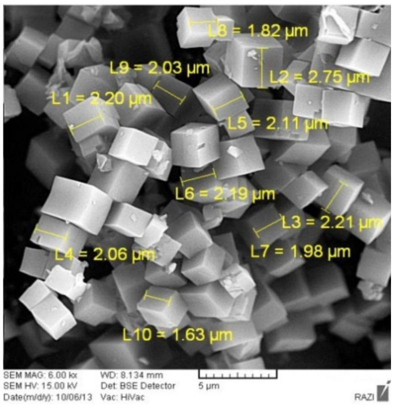

Figure 2: SEM plot of the SAPO-34 catalyst, by Razi Metallurgical Research Center

SEM test analysis showed that crystalization was proceed successfully. Also uniform size and shape of crystals, infulenced the results especially product distribution. Figure 2 shows the SEM plot of the catalyst.

Reaction performance of catalysts were studied using special Multipurpose-Multireactor setup in Gas Engineering Research Center-Petroleum University of Technology (Figure 3). while reactor outlet products were analyzed using 2 yunglee Gas Chromatograph Units.

Figure 3: Schematic view of reastion test setup, petroleum university of Technology

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Acknowledgements

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THE EFFECT OF GOLD ON THE COPPER CATALYST DURING STEAM-OXYGEN REFORMING OF METHANOL

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The main goal of this work is to explain the correlation between the composition of active component in mono and bimetallic catalysts with their activity results in steam-oxygen reforming of methanol. In order to achieve the goal of this work monometallic Cu catalysts were prepared using wet impregnation method. However, in the case of bimetallic Au-Cu catalysts, gold phase has been introduced into Cu/MWCNT catalyst by deposition-precipitation method. The physicochemical properties of the catalytic systems were studied by XRD, SEM-EDS, TPR-H_2 and FTIR techniques.

In this work steam-oxygen reforming of methanol (SORM) process was carried out over monometallic Cu/MWCNT and bimetallic Au-Cu/MWCNT supported catalysts. Steam-oxygen reforming of methanol process was performed in a flow quartz reactor under atmospheric pressure in the temperature range 160-300 °C. The ratio of the reactants in the studied reaction was $CH_3OH : H_2O : O_2 = 1 : 1 : 0.4$. The steady – state activity measurements at each temperature were taken after at least 2 h in the stream. The analysis of the reaction products was carried out by an on-line gas chromatograph.

The activity results performed for investigated catalytic systems confirmed the promotion effect of gold on catalytic activity and selectivity. The higher selectivity to hydrogen formation of bimetallic Au-Cu catalyst can be explained by the Au-Cu alloy formation during activation process. It should be emphasized that in the case of a copper catalyst promoted by gold there was no formation of carbon monoxide. It was observed that the conversion of methanol increased with increasing of copper content. Among the copper catalysts the optimum conversion of methanol in SORM reaction exhibited catalyst containing 60 % wt. Cu, further increasing the content of copper in the catalyst system did not lead to an increase in methanol conversion. It is worth to noticed that the activation process led to an increase of the catalytic activity of studied catalysts in investigated process. The composition of the resulting product was strongly dependent on the composition of the starting reaction mixture.

Acknowledgements

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NANOPOROUS FELT-LIKE ACTIVATED CARBON FIBER MODIFIED BY CONCENTRATED HNO_3 FOR THE ADSORPTION OF THE DIBENZOTHIOPHENES

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Hydrogen-treated activated carbon fiber (ACF) samples was oxidized with 65% HNO_3 at two temperatures (i.e., 25 and 100 °C) to two different levels of surface acidity for examining adsorption of dibenzothiophene (DBT), and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) in single-solute systems from n-hexane solutions as thiophenic compounds (TC) solutions. The surface chemistry and textural properties of all tested adsorbents were characterized by Boehm titration, Fourier transform infrared spectroscopy (FTIR) and N_2 adsorption. Oxidation at 25 °C did not noticeable change in the porosity of ACF sample, whereas the oxidation at 100 °C significantly reduced the BET surface area, total pore volume, and micropore volume. nitric acid oxidation at 100 °C produced highly acidic carbons and especially carboxyl and phenol groups' concentration significantly increases but oxidation at 25 °C is low efficient for increasing the oxygen functional groups on the ACFHO25 surface than oxidation at 100 °C. Oxidation at 25 °C leads to increasing about 10-40 % thiophenic compounds adsorption capacity. At sever oxidation condition (100 °C), the adsorption capacity of the activated carbon samples decreases 46-54 % due to pore blocking and porous structure devastating. Due to the presence of functional groups, the DBTs molecules with higher aromatic rings and methyl group can be adsorbed to the surface via acid–base and active site interaction mechanism.

Keywords: Nanoporous Carbon Fiber, Adsorption, Oxygen Functional Groups, DBT, 4,6-DMDBT

CARBON MONOXIDE REMOVAL USING HOPCALITE CATALYST AT LOW TEMPERATURE

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Carbon monoxide removal is a practical method with the most potential for reducing concentrations down to tolerant levels.

The hopcalite catalysts are prepared by combination of precipitation and redox method. The samples calcinated at 300 °C were investigated using micro activity equipment, for carbon monoxide oxidation in different reaction conditions (temperature in range 25-80 °C, pressure 0.2-1 bar, various initial CO concentration).

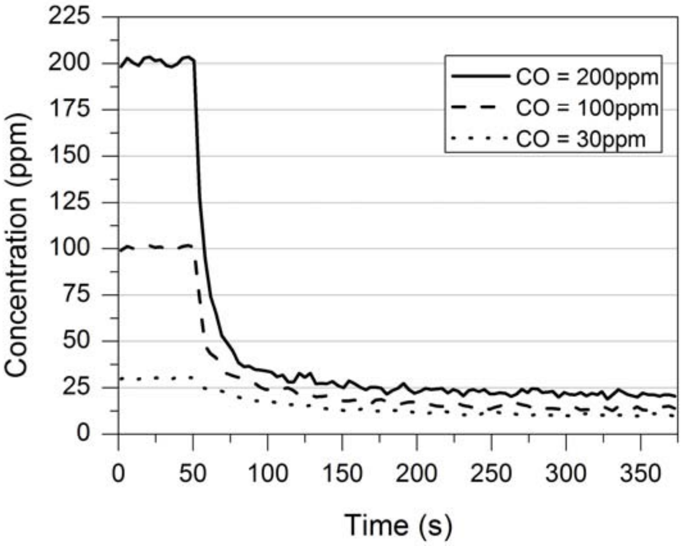
In this study, copper manganese oxides were prepared using a novel method and their catalytic performances for CO oxidation at ambient temperature under different conditions were studied. This novel method allowed for room temperature synthesis of amorphous copper manganese oxides with good surface areas, and high catalytic activity for CO removal at ambient temperature. In addition, the structural, morphological, and catalytic properties of hopcalite prepared using the redox and co-precipitation method are compared to those of a commercial Hopcalite catalyst.

The catalytic tests were performed in a continuous flow fixed quartz tubular bed micro reactor (PID Eng&Tech – MICROACTIVITY-Reference).

The prepared hopcalite exhibited steady performance in the micro activity reactor for 72 h while reducing carbon monoxide content down to residual contents.

The influence of the CO concentration in the initial gaseous gas in optimized conditions is presented in figure. The amount of CO decreases gradually, so that after less than a minute, the mixture contains proper CO concentration for use as filter in various environmental domain.

The experimental results justify the opportunity and possibility of using hopcalite containing potassium, prepared by combining the redox method with the double precipitation for reducing CO from inlet concentrations of hundred ppm levels to residual content.



The performances of hopcalite on optimized conditions:
25 °C temperature, 1 bar pressure, 50 ml/min flow rate

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CATALYTIC PARTIAL OXIDATION OF METHANE OVER COBALT CATALYSTS SUPPORTED ON SYNTHESIZED CERIA

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INTRODUCTION

Among the several available technologies for syngas production, catalytic partial oxidation of methane (CPOM) presents the interesting characteristic of being theoretically capable of providing syngas with H_2/CO molar ratio of 2, which is ideal for the Fischer-Tropsch synthesis [1]. In contrast with the non-catalytic process, the CPOM can be conducted at relatively low temperatures with acceptable yields in the presence of a suitable catalyst. Noble metals, specially Rh, are the most active catalysts for this reaction. Nevertheless, transition metals such as Ni or Co supported on refractory supports have been proposed as cheaper alternatives although there are less reports on the use of these catalysts, particularly Co [2]. In this work, Co supported on synthesized ceria have been investigated as CPOM catalysts.

EXPERIMENTAL

Ceria was prepared by precipitation from an aqueous $Ce(NO_3)_3 \cdot 6H_2O$ solution after mixing with another solution of the cetyltrimethylammonium bromide (CTAB) surfactant under vigorous stirring. Then a NH_4OH solution was added until a stable pH was achieved. The precipitate was then filtered and washed with deionized water in order to remove ammonia, nitrate ions and the surfactant. The resulting solid was dried overnight at 100 °C and finally calcined at 750 °C for 2 h. The synthesis conditions were varied between 25 and 85 °C, pH values between 8 and 10.5, synthesis time within the 2-5 h range, and [CTAB]/[Ce] molar ratios between 0 and 0.8. The supported catalysts (10 wt.% Co) were prepared by incipient wetness impregnation of the supports with a $Co(NO_3)_2 \cdot 6H_2O$ solution. The resulting solids were dried overnight at 100 °C and calcined at 750 °C for 2 h. Catalysts were caracterized by TPR, N_2 adsorption at 77 K and X-Ray diffraction.

CPOM in air was carried out at atmospheric pressure in a quartz tubular fixed-bed reactor. The catalyst was diluted with SiC particles of similar particle size range forming a bed of about 15 mm in length. CPOM reactions were performed at space time of 0.08 $g_{cat}/(NL\ CH_4 \cdot h^{-1})$, O_2/CH_4 molar ratio in the feed stream of 0.49 and temperatures between 700 and 500 °C. Prior to reaction the catalyst was treated under 50 NmL·min^{-1} of H_2 for 2 h at 700 °C and then with 50 NmL·min^{-1} of He for 30 min. On-line analyses of the feed and products streams were performed on a gas chromatograph equipped with FID and TCD detectors.

RESULTS AND DISCUSSION

A positive effect of the presence of CTAB during the synthesis of the support has been observed (Figure 1), that led to Co catalysts that allowed reaching at 700 °C virtually equilibrium CH_4 conversion and syngas with H_2/CO ratios close to 2. However, the use of CTAB in excess seems to be detrimental for the CPOM activity. These results were consistent with that of the physicochemical characterization. The textural and structural properties of ceria improved when using CTAB for its synthesis.

Figure 1

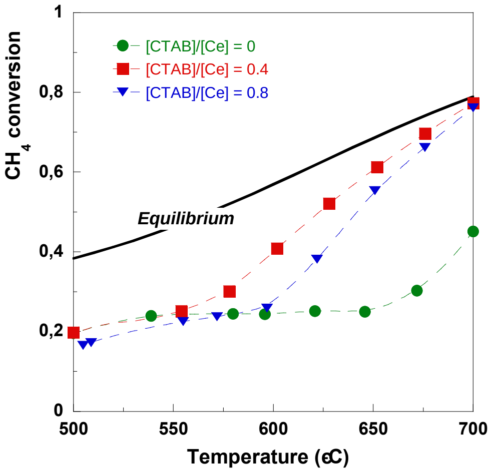
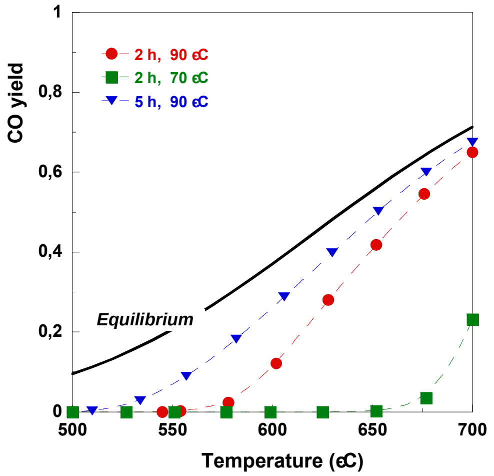


Figure 2



The performance of the catalysts also improved as the synthesis temperature and time increased, as shown in Figure 2 for the yield of CO. On the other hand, it was found that a pH value between 8.0 and 8.5 was suitable for cerium hydroxide precipitation. It has been found that one of the reasons of the activity decrease at temperatures below about 650 °C is the oxidation of metallic Co. In conclusion, a synthesis method of ceria has been developed that allows obtaining very promising Co/CeO_2 catalysts for the CPOM. Research is under progress to optimize the catalytic performance and extend it to lower reaction temperatures.

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SCALE UP AND PERFORMANCE OF MONOLITHIC CON-FLOW SILICA MICROREACTORS

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Silica-based continuous-flow monolithic microreactors are extremely promising for cost-effective production of *fine chemicals* owing to their unique, bi-continuous structure of monoliths in which flow-through macropores are connected to an extensive network of meso- and micro-pores present in a solid skeleton [1]. This gives lower backpressure, higher permeability and much better overall performance compared to packed columns [2]. The monoliths feature high porosity and surface area, but their mechanical strenght is low. So far, the microreactors were made by embeding the monolith either into a heat-shrinkable PTFE tube [1] or polymeric body [3].

To achieve reactors with more robust structure and also suitable for high temerature operations the concept of "monolith in monolith" (MM) was proposed and proved viable by our group [4]. It relies on filling the channels of the well know ceramic monolith (cordierite) with silica monoliths possesing hierarchical pore structure. While simple in concept it appeared somewhat diffucult to achieve a perfect contact between two materials, otherwise we could expect a by-pass of fluid. To overcome that a special treatment of cordierite surface was proposed. Composition of the solution applied, temperature and time of treatment were investigated. Figure 1 shows the images of cordierite monoliths hosting silica monoliths with well preserved structure. In case of the treated cordierite the connection is tight (left), whereas large voids could be seen (right) when untreated cordierite was used. In terms of permeabilty and mass transfer the MM microreactor was found to be similar to those obtained for a single rod monolithic microreactor, but the applied flow rates could be significantly larger.

The catalytic properties of monolithic reactors (functionalized with sulphonic acid groups) were investigated in esterification of acetic and lactic acids with butanol. The performance of both reactors (MM and single silica rod) were compared. Good catalytic stability during repeated cycles was confirmed.

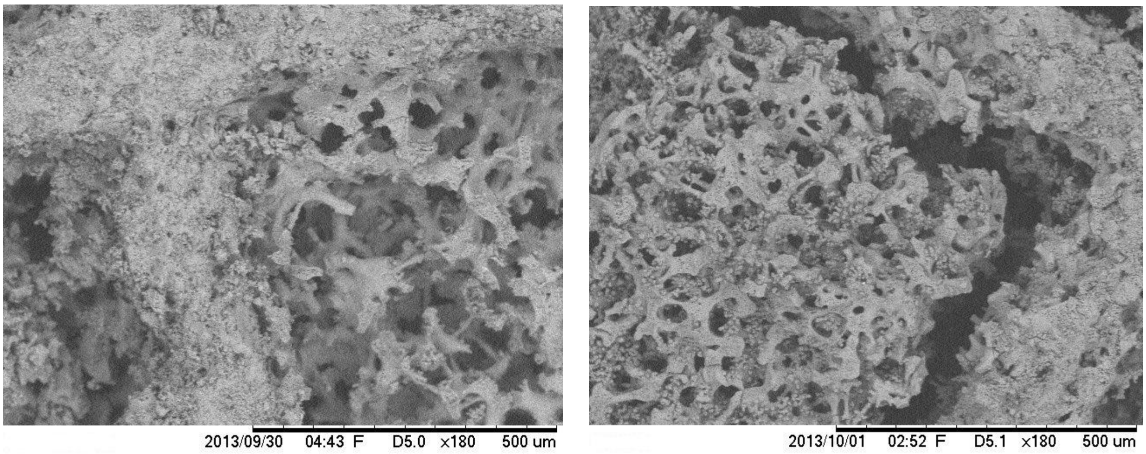

Fig. 1. SEM images of MM microreactors: left – cordierite treated; right – without treatment

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LOW BACKPRESSURE MONOLITHIC ENZYMATIC MICROREACTOR FOR PROTEIN DIGESTION

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Recently much attention has been paid to the development of immobilized enzyme reactors [1] (IMERs) especially for proteolysis [2]. In addition to high digestion efficiency, they can also be easily coupled with separation and detection systems to achieve automated and very effective systems for protein analysis [2].

In this work monolithic silica rods 6 x 40 mm (length), exhibiting very open (total pore volume 3.8 $cm^3 \cdot g^{-1}$) and uniform 3D hierarchical pore structure of 35-50 μm flow-through macropores and ca. 20 nm mesopores, were synthesized using the sol–gel method combined with pore templating and phase separation (MH-1). These monoliths were successfully converted into miniaturized, multichannel continuous-flow reactors (Fig. 1A) which (for a single rod) could operate at flow rates of up to about 800 $mL \cdot cm^{-2} \cdot min^{-1}$ at pressure drop not exceeding 60 $kPa \cdot cm^{-1}$ (Fig. 1B). Monoliths with smaller macropores (4-5 μm, MH-2 [3] and 8-10 μm, MH-3 [4]) were also made and the pressure drop/flow rate dependence was determined (Fig. 1B). Decrease in macropore diameter from 35-50 μm to 4-10 μm resulted in even 100 fold increase in backpressure (flow backpressure coefficient for MH-2 and MH-3 were $1.2 \cdot 10^{12} - 4.7 \cdot 10^{12}$ m^{-2} whereas for MH-1 it was $5.2 \cdot 10^{10}$ m^{-2}). The lower pressure drop eliminates the need for application of HPLC pumps.

After immobilization (adsorption or covalent bonding) of trypsin, potentials of the microreactors were tested in BAPNA hydrolysis and Myoglobin digestion. It was found that after trypsin adsorption onto functionalised silica carriers the activity in BAPNA hydrolysis was higher than when it was attached covalently, but the stability was much lower owing to protein leaching. When proteins were covalently attached about 90 % of sequence coverage was observed for Myoglibin at flow rate of

0.1 mL·cm^{-2}·min^{-1} (Fig. 1C). When it was increased to about 1 mL·cm^{-2}·min^{-1} sequence coverage decreased to 45 %, but it is still considered as a very good result. The reactors retained initial activity for at least 12 h of continuous work.

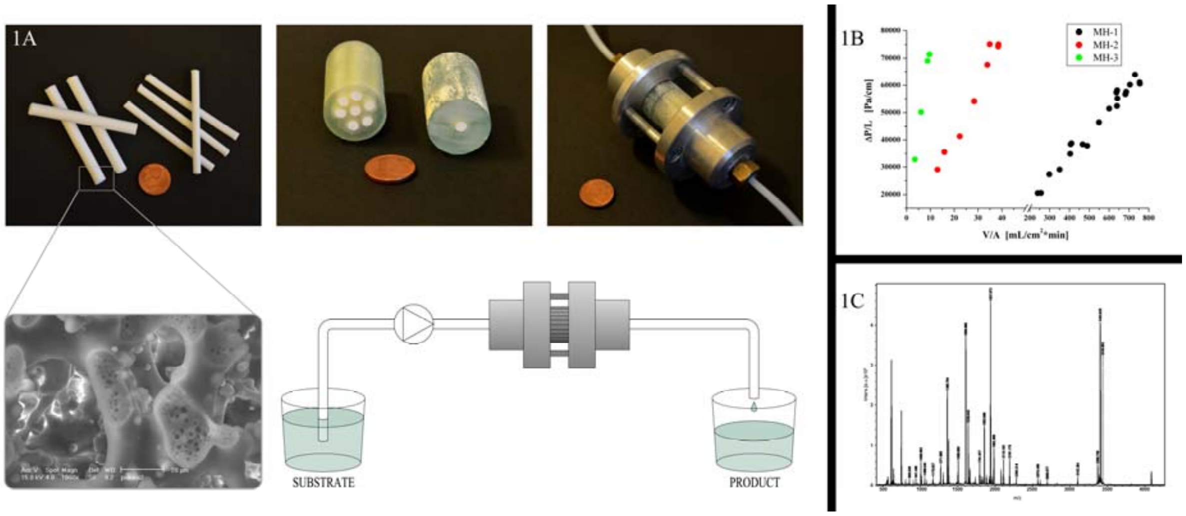

Fig. 1. Scheme of microreactor (A), Pressure drop in microreactors with different pore size (B), Myoglobin digestion by trypsin immobilized on MH-1(C)

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VALIDATION OF A TORREFACTION REACTION MODEL FOR A CONTINUOUS SCREW CONVEYOR REACTOR

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Introduction The torrefaction of biomass is a thermochemical conversion process involving the application of heat at moderate temperatures (200 °C – 300 °C) to biomass in non-oxidising atmospheres. The elevated temperatures drive thermal degradation reactions of the various biopolymers that are present within the biomass, thereby resulting in the production of non-condensable gases, condensable vapours and a solid product (torrefied biomass) which has improved fuel characteristics over the original biomass. This work discusses the validation of the a numerical torrefaction reaction model against the experimental results obtained at the Department of Biosystems Engineering at Ghent University.

Purpose of the Work This work falls into a bigger project involving torrefaction reactor and process design. The reaction model will be used to test different reactor configurations (screw conveyor reactor, moving bed reactor, rotating drum, etc.) and will also incorporate the effect of both feed material selection and feed particle size distribution. This will finally result in determining the optimal reactor and process design and the overall economic benefit of such a process.

Approach The reaction model is based on a combination of sub-models: modelling the transfer of heat to the biomass particle; modelling the drying of the biomass particle; modelling the rates of the thermal degradation reactions; and estimating product yields and qualities. The models for the heating and drying of the biomass particle are taken from literature. The thermal degradation is based on a reaction model from literature and the intrinsic reaction rates were determined experimentally for the different biomass types used in this study. The results from the reaction model are compared against the performance of a continuous (2.5 kg/h feed) screw conveyor reactor. Experiments have been performed to estimate the mean particle residence time in the reactor since this has been seen to deviate from estimates based on the linear, forward propagation rate of the screw relative to the shell of the conveyor. Experiments have also been performed to determine the effective heat transfer coefficients within the reactor (which form part of the boundary conditions of the reaction model). The quality of the products that are formed under different conditions is estimated by a regression of the product properties (calorific value, elemental analysis, grindability) against the anhydrous weight loss observed during the experiments – this information is necessary for further evaluation of the process economics.

Scientific innovation and relevance Torrefied biomass has been identified as a possible “drop-in” substitute for fossil coal. The improved characteristics of torrefied biomass allow it to be utilised in existing infrastructure (pulverised-coal boilers, gasifiers) with a greater efficiency than biomass. This benefit comes at the cost of torrefying the biomass. Several companies, particularly in the Netherlands, have started to commercialise torrefaction processes based on different reactor concepts with varying degrees of success. There is a limited amount of academic literature on the relative benefits of these different reactor concepts and this work attempts to address this.

Results and Conclusions Continuous torrefaction experiments (based on pine chips) have been performed where-steady state operation was achieved for at least 1 hour with mass balance closures above 95 %. The solid and gaseous products were analysed and were found to be highly correlated to the anhydrous weight loss resulting from torrefaction. The expected influence of torrefaction temperature and reactor residence time on the torrefied biomass yield was observed. The reaction model was able to predict the performance of the experimental setup to a good degree of accuracy. Further improvements to the model could improve its accuracy, however, such improvements (predicting particle size reduction, improved heat transfer estimation) could be highly complicated.

Explanatory section The continuous rotating screw reactor setup has been built by BTG, (The Netherlands) and is shown in Figure .

Figure 1. Screw Conveyor Torrefaction Setup

STEAM REFORMING OF BIOGAS FOR SYNGAS PRODUCTION

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Biogas is one of the most abundant and versatile energy sources in the world. It is formed in large amounts by the anaerobic digestion or bacterial fermentation of biomass or as a result of organic source processing. Biogas is considered a very important source of renewable methane, the content of which is 45-70 %. The second most prevalent component of biogas is carbon dioxide (30-45 %). Biogas also contains traces of other gases, such as hydrogen sulphide, ammonia, hydrogen, nitrogen, oxygen, and water vapour, depending on the nature of the primary feedstock and the biogas formation conditions. Biogas can be utilized for various applications. In addition, a mixture of carbon dioxide and methane can serve as feed for the catalytic production of syngas by the dry reforming of methane (DRM) according to the reaction (eq.1). This reaction is a very attractive way to utilize both greenhouse gases – methane and carbon dioxide.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \text{(eq.1)}$$

Syngas consisting of a mixture of CO and H_2 in various ratios is an alternative to oil feedstock for the chemical industry. At present, the efficiency of synthesis gas production is in need of improvement because the demand for this raw material is steadily growing every year. The direction of syngas use significantly depends on its composition, namely, its H_2/CO ratio. Syngas formed by DRM has a ratio of $H_2/CO = 1$ (eq.1). The steam reforming of methane (SRM) yields a ratio of $H_2/CO = 3$.

Biogas enriched in methane up to 75 % could not be completely converted into H_2 and CO alone via the dry reforming reaction because the CH_4/CO_2 ratio is higher than the stoichiometric ratio (eq.1). The excess of methane would cause significant carbon deposition, resulting in the rapid deactivation of a catalyst. Steam at its introduction to biogas can be used as an additional oxidant to eliminate carbon. The combination of DRM with SRM (bi-reforming of methane) will provide syngas with the desired hydrogen to carbon monoxide ratio by the easy adjustment of the feed composition. Indeed, with steam addition, both the C/H ratio and the C/O ratio in the feed decrease, resulting in reduced carbon formation. The main challenge is to develop the catalyst, which should be active in both the dry and the steam reforming of methane and resistant to coke formation.

The main goals of this study are the synthesis and testing of new and more durable catalysts based on Co with adding second metal supported on alumina. The catalytic performance of the catalysts has been investigated in the dry and steam conversion of biogas to assess the feasibility of the process, which seems to be a promising method for the efficient production of synthesis gas using biogas as a renewable energy source.

In the work, authors have used a model biogas with an equal content of CH_4 and CO_2. For the steam reforming of biogas, steam in amount of 10-40 vol. % has been added. The bimetallic supported catalysts – 5 wt. % Co-M_2/Al_2O_3 with varying amount of M_2 within 0.25-0.5 wt. % have been used in both the steam reforming and for comparison in dry reforming of biogas. The processes were carried out in a flow quartz reactor supplied with the programmed heating and controlled feeding velocity under conditions: P = 0.1 MPa, GHSV = 1000 hr^{-1} and varying temperature 300-800 °C.

Almost complete methane conversion (97.5-99.0 %) depending on the amount of the second metal in 5 wt. % Co-M_2/Al_2O_3 catalysts has been observed at steam reforming of biogas under conditions: P = 0.1 MPa, T = 745 °C, V_{H2O} = 20 vol. %, GHSV = 1000 hr^{-1}. The syngas produced has a ratio of H_2/CO = 1.05-1.15.

In dry reforming of biogas, methane conversion is less (96.2-96.4%) under the same conditions. Also, the H_2/CO = 0.86-0.89 is less in dry reforming of biogas.

Degree of carbon dioxide conversion decreases in steam reforming of methane – 73.4-85.0 %, while in dry reforming $X(CO_2)$ = 89.3-92.6 %.

The catalysts developed provide both the dry and steam conversion of biogas. Steam reforming is more effective process in view point of decrease in the process temperature and higher yield of hydrogen. The physic-chemical methods show the high dispersive state of metals in the catalysts. The catalysts developed are stable and resistant to coke formation.

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SUPPORT VECTOR MACHINE CLASSIFICATION OF WGS REACTION OVER Pt AND Au CATALYSTS FOR KNOWLEDGE EXTRACTION FROM LITERATURE

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Water gas shift reaction is an essential step for hydrogen enrichment and CO reduction in syngas. Due to their high activity and stability, noble metal catalysts (such as Pt, Rh, Pd, Ru and Au) over various supports (such as CeO_2, Al_2O_3, ZnO and MgO) have been investigated extensively for fuel cell applications in the recent years.

Data mining is a field of computer science to extract knowledge from a database that helps to spot the patterns that are too hard to detect by naked eyes, and use these patterns to derive significant conclusions. Classification, clustering and estimation are the most common techniques that are applied for this purpose. This approach could also be used in the field of catalysts to extract knowledge from the publications in the literature [1-3].

In this work, an extensive literature search for water gas shift reaction was made and a detailed database (containing 3802 experimental data points) on water gas shift reaction (WGS) over Pt and Au based catalysts was constructed using the data obtained from the published papers between the years 2002 and 2012. This database was analyzed and modeled by using support vector machine (SVM) technique, which is one of the most popular and efficient methods for knowledge extraction [4].

First, the data was separated into six classes according to CO conversion levels (0-50, 50-60, 60-70, 70-80, 80-90 and 90-100 %); then, SVM classification was performed on the data. According to the SVM classification results of Au, the experimental data of 15 out of 25 publications were correctly classified with accuracies higher than 75 %. Similarly, the results of 55 out of 70 publications for Pt catalysts had such correct classification accuracy. The confusion matrix, which gives the details of SVM prediction accuracy, was presented for Au catalysts in Table 1 as an example. As a result of the findings, it can be suggested that SVM's can be used in catalytic systems to extract the essential knowledge and experience from the published experimental data. This way, the experimental results related to the catalysts that were prepared and operated in different conditions can be predicted successfully without actually doing the experiments, and this may help the researchers in planning the future experimental works more effectively.

Table 1. Confusion matrix for Au catalysts indicating predicted and experimental number of data points in each CO conversion level

		Predicted classes					
		0-50	50-60	60-70	70-80	80-90	90-100
Experimental classes	0-50	**312**	10	2	0	0	0
	50-60	11	**32**	14	0	0	0
	60-70	2	31	**20**	4	0	0
	70-80	0	4	22	**24**	12	0
	80-90	1	0	7	13	**56**	13
	90-100	0	0	1	2	46	**58**

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CRITICAL SUPERFICIAL GAS VELOCITY FOR SUSPENSION OF SOLID PARTICLES IN A SLURRY BUBBLE COLUMN REACTOR FOR HYDROCONVERSION PROCESSES

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Fluid-dynamic parameters in bubble column reactors have been studied for many years. It has been produced a large experimental database about design, scale-up and operation of these vessels. However, a few research works have been done on critical gas velocity required for suspension of solid particles in bubble columns. In some hydroconversion processes an up-flow scheme of gas-liquid-solid through a tubular reactor is used. Eventually, solids have to be suspended by gas flow in order to have a stable and reliable operation. In order to breakdown all variables affecting the critical superficial gas velocity; 72 experiments in a 120-mm-id Plexiglas column without any gas sparger were performed. Three-phase experiments were carried out using air, mineral oil, coke and resins. The column was operated in an up-flow semi-batch scheme with gas velocity ranging from 0.5 to 6 [cm/s] using three solid concentrations. These results have shown that critical gas velocity is less than 6 [cm/s] for the solid concentration range tested. Also, it was found that critical gas velocity proportionally increases with the density of the different additives used (coke and resins). Based on these experiments, the numerical methodology proposed by Pandit and Joshi (1987) was improved.

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SMALL SCALE PRODUCTION ORGANIC COMPOUNDS: TECHNOLOGY PECULIARITIES

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Industrial production of organic compounds most often involves many stages yielding a lot of wastes. E-factor value for basic organic synthesis is 1-5, and for fine organic synthesis it attains 5-50 [1]. With this regard there is a need for new approaches in the field. In the table below one may see how chemical production processes are classified according to the product tonnage:

No	Production tons per year Specific features	Differencies
1	Micro scale up to 0,1	Wide and quickly replaced range of products
2	Small scale 0,1-10	
3	Medium scale 10-1000	
4	Large scale 5-10 thousand	Stable range of products
5	Super large scale More than 100 thousand	

Processes of groups 4 and 5 are based on continuous technologies and differ by complex and specific equipment required. Processes of groups 1 and 2 involve chemical processes performed in batch reactors. To compete well small scale processes should be flexible regarding the product assortment change. Industrial setups capable of single product production have no perspective. Therefore it is necessary to develop flexible process schemes (FPS) for batch technologies substitution. Let us note that methodology of FPS is not yet developed, since small scale production is strongly market dependent and thus functions in the field of target product uncertainty. Therefore, FPS development is possible only in active relationship with fundamental science providing new methods and ideas. Moreover, it is necessary to consider that FPS themselves are the market infrastructure elements.

In this work it is shown that application of catalysts, microreactors and complex approach improves the economics and ecology of processes developed at the Boreskov Institute of Catalysis SB RAS. Among these processes are the small scale productions of rubber vulcanizing accelerators (2-mercaptobenzothiasole, 2,2-dibenzothiasoldisulfide), carbonic acids (butanedioic acid), amines (diphenylamine, triethanolamine) [2-4]. The engineering capacities of Volgograd Department are considered regarding their use for the small scale production of organic compounds

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CAPE OPEN COMPONENT FOR THE SIMULATION OF A DIESEL HYDROTREATING REACTOR

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Hydrotreating is a heterogeneous catalytic process to remove impurities contained in the petroleum cuts, as sulfur, nitrogen, oxygen and metals through chemical reaction of the hydrocarbon with hydrogen. Additionally, reactions to modify molecular structures are carried out, as saturation of olefins and aromatics compounds, and hydrocracking reactions. The process allows formulating environmentally friendly fuels, protecting downstream refining processes, and converting vacuum residue into valuable distillates [1]

The objective of this work was to develop a model for a fixed bed reactor of light gasoil hydrotreatment according to the CAPE OPEN standard for interoperability in chemical process simulation [2, 3]. The model was conceived as a combination of two process modeling components (PMC). One of them is a unit operation that 'wraps' the calculations related to the reactor model itself. The other PMC encapsulates the properties and phase-equilibrium calculations. The implementation was accomplished using C++ as the programming language.

In relation with the reactor model, it makes use of a set of pseudocomponents to represent the hydrocarbon feed and total liquid product and assumes an ideal plug-flow reactor behavior with no considerations about diffusion or fluid-dynamic effects. In addition, it is assumed an isothermal operation and linear pressure drop. The reactions considered are: hidrodesnitrification (HDN), hydrodesulphurization (HDS), olefins hydrogenation (HDO), aromatic hydrogenation (HDA) and hydrocracking (HCK). HDS reactions are modeled using the Langmuir-Hinshelwood approach. The reactions are considered as first order in relation with hydrocarbons while higher order is taken into account in relation with hydrogen.

Model results were validated with experimental data of pilot plants with conditions for pressure and temperature in the neighborhood of 11000 KPa and 370 °C respectively. In addition, the availability of the model developed in different commercial process simulators without additional coding efforts was verified.

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FLOW RESISTANCE, TRANSPORT AND MORPHOLOGY OF METALLIC FOAMS APPLIED AS CATALYST CARRIER

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Application of solid open-cellular foams extends to e.g. mechanics or aeronautics [1]. Due to their distinctive features, like high porosity and large specific surface area, foams are considered as promising catalyst carriers [1,2]. In this paper, experimental and modelling study on flow resistance and heat/mass transfer for the NiCr 30 ppi foam (Recemat) is presented. The results are compared to dumped bed (2 mm spherical grains) and 100 cpsi (channel per square inch) monolith.

The heat transfer and flow resistance experiments were performed using the laboratory-scale test reactor with a rectangular cross-section of 45x30 mm. The foam was heated by strong electric current (150A) and temperature measured by several small thermocouples. The results are presented in terms of Fanning friction factor and Nusselt (or Sherwood) number versus Reynolds number. The independent mass transfer experiments were not done, the Chilton-Colburn analogy was used to derive the mass transfer description. The foam was investigated using computer microtomography (CT) (SkyScan), optical microscopy (OM) and helium pycnometry (HP) to determine basic geometrical dimensions, porosity (void fraction) and specific surface area.

CT gave an average pore diameter of 0.64, close to that from OM (0.572 mm). However, OM distinguishes between cells and window. The OM derived average cell diameter is 0.852 mm and the window diameter 0.293. The porosity 0.879 (CT) slightly differs from that from HP (0.94); CT derived specific surface area is 7875 m^2/m^3 while the value given by the manufacturer is 2800 m^2/m^3.

The experimentally derived friction and transport characteristics are presented in Fig. 1. There, the results are compared with packed bed of spherical 2 mm beads and with classic 100 cpsi (channels per square inch) monolith.

The transfer and friction phenomena of the foam studied were modelled using the developing laminar flow concept; such an approach seems a novelty. The modelling results presented (Fig. 2) show good agreement between the experiments and theoretical modelling (not shown here in details). The crosswise dimension assumed (model channel diameter D = 0.293 mm) is equal to the window diameter while the channel length (L = 0.852 mm) to the cell diameter. Mean error amounts to 18.5 % (Fanning factor) and 17 % (Nusselt number). The friction and transfer are calculated according to the theoretical equation of Shah [3] and Churchill and Ozoe [4] with L/D = 2.9.

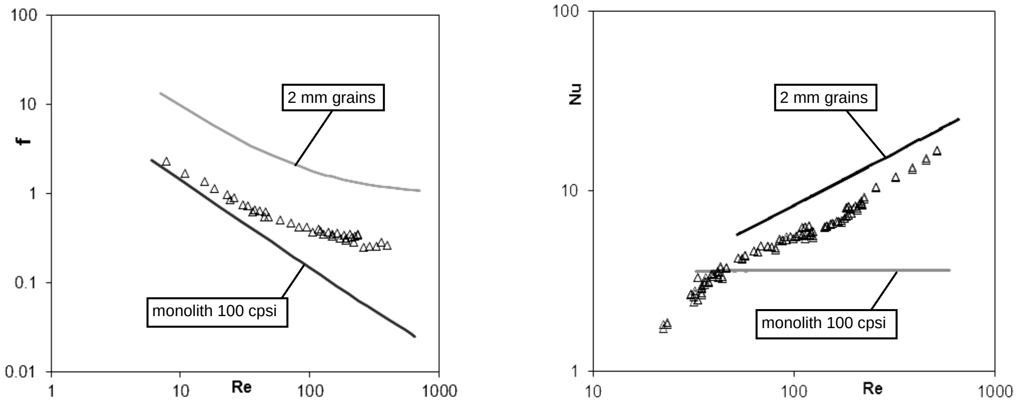

Fig. 1. Comparison of Fanning friction factors and Nusselt numbers for NiCr foam (points), packed bed of 2 mm grains and monolith 100 cpsi (lines)

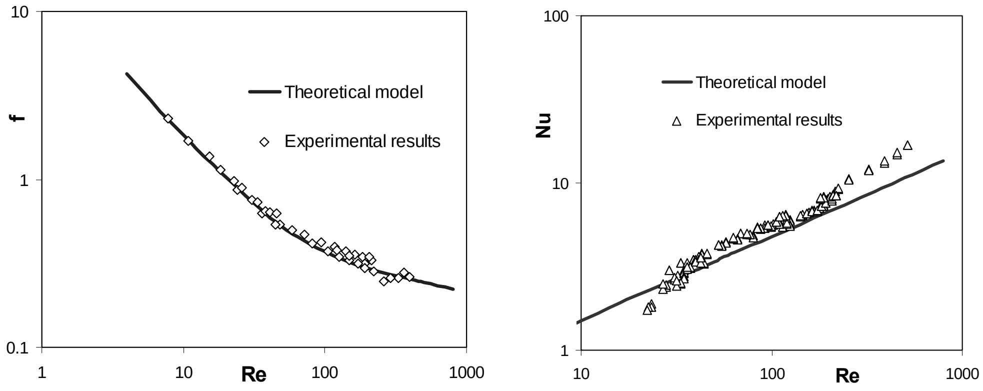

Fig. 2. Experimental results compared with the theoretical model derived

Metallic foams appear as promising catalyst carrier for many fast catalytic reactions. The foam display surface area high enough and it can be regarded as an intermediate between monolith and packed bed. To prove the developing laminar flow nature for foams, more examples should be considered.

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CATALYTIC HYDROGENATION OF LEVULINIC ACID TO γ-VALEROLACTONE IN A CONTINUOUS PACKED-BED REACTOR

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Introduction. Levulinic acid (LA), derived from lignocellulosic biomass, is recently selected as one of the 15 most promising carbohydrate-derived platform chemicals by the US Department of Energy [1]. The presence of a ketone and carboxyl group makes it a versatile component, which can be converted to a number of interesting derivatives. Among these, γ-valerolactone (GVL) is identified as a sustainable platform chemical for the production of carbon-based chemicals and fuels [2]. A significant amount of literature is available about the production of GVL in batch set-ups with the use of different solvents and catalysts [2]. However, despite the high interest, limited studies have been reported about the production of GVL in a continuous manner. Keeping scaling up to industrial scale in mind, a continuous process is favorable above a batch process [3].

This study is focused on the catalytic hydrogenation of LA to GVL in water environment in a continuous packed bed reactor with an emphasis on catalyst activity and stability. In our work we have addressed the possible influence of both intraparticle and external transport limitations on controlling observed rate of reaction.

Results and discussion. A catalyst screening study with heterogeneous catalysts was performed using ruthenium on different supports (Ru/C, Ru/Al_2O_3, Ru/TiO_2). Ruthenium loading in the catalysts was varied in a systematic manner (0.3-5 wt %). The catalyst Ru/C demonstrated highest activity and stability over 6 hours on stream whereby it was chosen as base catalyst for further process kinetic studies

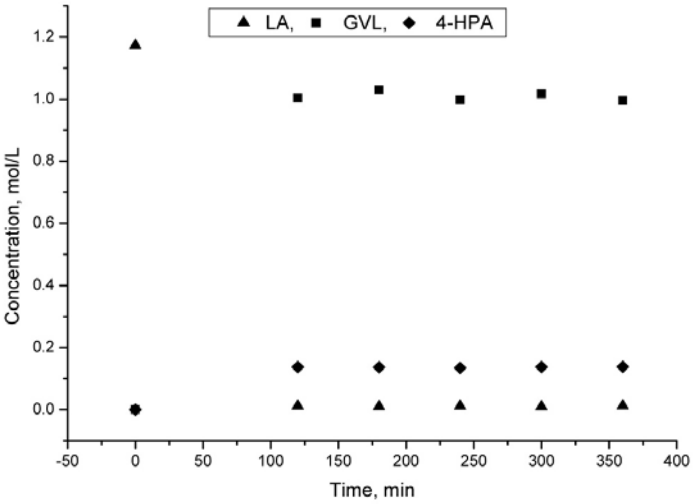

Figure 1. Levulinic acid hydrogenation profile using Ru/C (0.5 wt % Ru) at 130 °C

(Figure 1). Under these conditions, the intermediate 4-hydroxypentanoic acid (4-HPA) is also clearly observed Reaction conditions like temperature (90-130 °C), hydrogen volumetric flow rate (30-120 mL/min) and initial LA concentration (0.1 mol/L – 97 %) were varied to optimise the volumetric production rate (mol GVL/m^3·h) and the data ere modelled using an reactor engineering model including mass transfer limitations.

Finally, a long duration test (52 hours on stream) was performed with LA using Ru/C (0.5 wt. % of Ru) as catalyst. A small reduction in LA conversion was observed over 52 hours on stream (from 95 % to 82 % at the end). To gain insight into possible reasons for catalyst deactivation, the fresh and spent catalysts were characterized in detail. TEM-HAADF analysis demonstrated a significant sintering of Ru particles after 52 hours on stream, which was concluded a main reason for catalyst deactivation.

Conclusions. The hydrogenation of LA acid to GVL in water using Ru based catalysts was explored in detail in a continuous packed bed reactor. Best catalyst performance regarding activity and selectivity to GVL was obtained using Ru/C as the catalyst. The results were modeled using a reactor engineering model including the intrinsic kinetic data obtained in batch.

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CeO_2-BASED CATALYSTS WITH ENGINEERED MORPHOLOGIES FOR SOOT OXIDATION

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Ceria-based catalysts are among the most active systems for soot oxidation either under O_2 or in a NO_x/O_2 atmosphere. Indeed, ceria alone or in combination with other oxides is effective towards the oxidation of particulate matter. Among the various properties of ceria that could affect the surface reactivity, the redox capacity and the availability of surface oxygen species are likely the most important. Moreover, the number of soot-catalyst contact points may influence the activity of ceria for soot oxidation and hence it is necessary to maximize the interactions between the soot particles and the catalyst [1].

In the present work, a set of CeO_2-based nanoparticles (namely cubes, rods and 3-D-mesoporous systems) was prepared to study the role of morphology on the reactivity of ceria. Indeed, recent results displayed that soot oxidation is a surface-sensitive reaction [2]. Since the overall activity is largely influenced by the surface area of the catalyst, we also prepared a sample with CeO_2 nanocubes dispersed on the surface of ZSM-5 zeolite.

Briefly, i) ceria nanocubes (Ceria-NC) and nanorods (Ceria-NR) were synthesized by using the procedure reported in literature [3]; ii) Ceria-ZSM-5 was prepared by wet impregnation of ZSM-5-type zeolite; iii) Mesoporous ceria (Ceria-M) was synthesized by nanocasting from SBA-15 silica.

The prepared samples were characterized by complementary techniques to investigate their physico-chemical properties. Catalytic activity tests for soot oxidation (either with O_2 or NO_x/O_2) are currently under investigation.

The diffraction profiles for the three types of materials are reported in Figure 1. As a whole, the main reflections can be indexed to (111), (200), (220), (311) and (222) planes according to a pure fluorite cubic structure.

Low-angle XRD pattern of Ceria-M (not reported for the sake of brevity) shows that the replication of the SBA-15 template was only preserved to some degree, since the characteristic reflections at 2θ values of *ca.* 1°, related to the presence of the mesostructure, are observed. The latter sample exhibits SSA of 75 m^2g^{-1} and total pore volume of 0.12 cm^3g^{-1}.

The isotherms reflect the N_2 adsorption jump at *P/P°* ≈ 0.5-0.8, characteristic of capillary condensation in the mesopores (pore size ≈ 6 nm). On the contrary, the SSA of both Ceria-NC and Ceria-NR are very low (ca. 5-7 m^2g^{-1}) and hence the ZSM-5 support (SSA 450 m^2g^{-1}) was used to obtain a better dispersion of the active phase. Moreover, ZSM-5-type materials may favour total oxidation reactions due to longer residence times of gas-phase molecules [4,5]. This also suggests that under NO_x/O_2 atmosphere the possible formation of NO_2 (a stronger oxidant than O_2) can promote the soot oxidation over ceria-based catalysts. FESEM images confirm the textural properties of the prepared materials: both Ceria-NR and Ceria-NC range in the size from 100 to 250 nm, whereas Ceria-M shows mesoporous structures with smaller particles (size between 50 and 100 nm).

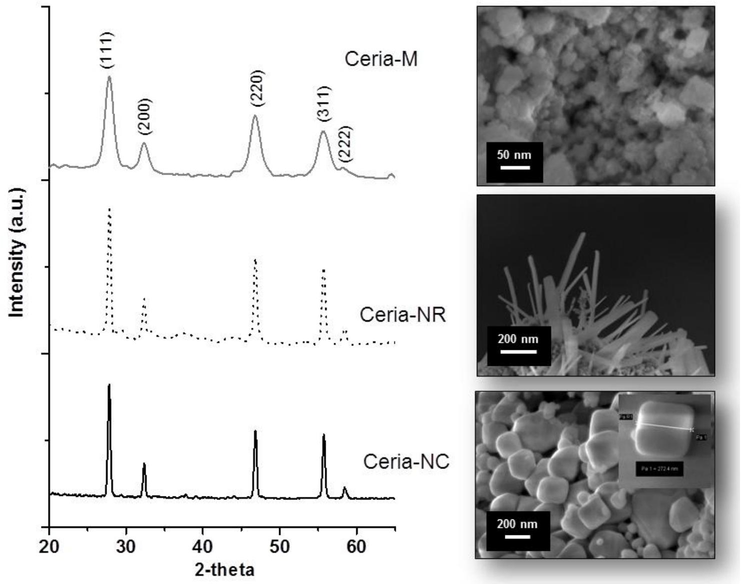

Figure 1. Powders XRD patterns of the prepared catalysts (left) and FE-SEM images (right).

Although the surface properties of the prepared materials are still under investigation it is expected a relationship between the morphological features of such CeO_2 nanomaterials and their activity towards the soot oxidation.

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KINETICS OF ACETALDEHYDE SYNTHESIS FROM ETHANOL OVER A COPPER ON CARBON FIBERS CATALYST

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Copper supported on different materials is a well known catalyst for ethanol dehydrogenation. However, a choice of a carrier plays a crucial role for the catalyst effectiveness. Granular metal oxides such as Al_2O_3 or SiO_2 are commonly used but they provoke side products due to the surface acid or basic sites of the carriers. Besides the form of catalyst can limit the variety of reactor design, that can be especially important for the small scale synthesis such as acetaldehyde production. Different results must be expected when activated carbon fibers (ACF) are used. In this study fabrics of ACF (Taiwan Carbon Technology CO) were applied. The diameter of one filament, that serves as a support for an active component, is 3-5 μm; several fibers twisted into threads of 1 mm in diameter: those organize a matt structure. Hence, ACF combines advantageous of carboneous materials, like high surfase area, thermostability, inertness in the ethanol dehydrogenation process [1], as well as advantegeous of structured but not over-structured support [2] like improved external heat and mass transfer, low pressure drop, original geometry and high flexibility. To use all these benefits of the catalyst for developing a proper reactor construction kinetics of the process of acetaldehyde synthesis must be inverstigated.

The experiments were carried out in a fixed-bed flow reactor under the atmosphere pressure. The structured catalytic bed (5 % Cu/ACF prepared by wetness impregnation) represented several round layers in the middle of the reactor with the diameter which corresponds to the inner diameter of the quarts reactor applied. Ethanol deluted with argon (1:2 mol) was used as a feed stream. The kinetics were studied by observing the effect of residence time and the effect of temperature on the ethanol conversion. From the data obtained frequency factors at different temperatures (250, 300 °C), activation energy (Ea = 41 kJ/mol) and the order of the reaction were calculated. In addition, to determine the adsorbtion coefficient of ethanol an experiment with different ethanol to argon delution (1:4 mol) was made.

Finally, three kinetic model equations for the rate of ethanol dehydrogenation were offered (fig.1). The first one considered the first order reaction, as it is usually mentioned in the literature [3]. The second one included the reaction order of 0,9 calculated in this study, while the third one allowed for the ethanol adsorbtion coefficient (b_{EtOH} = 1.71). According the results variance factor ($\hat{S}^2_y$) was calculated and the third model was proved to be more appropriate.

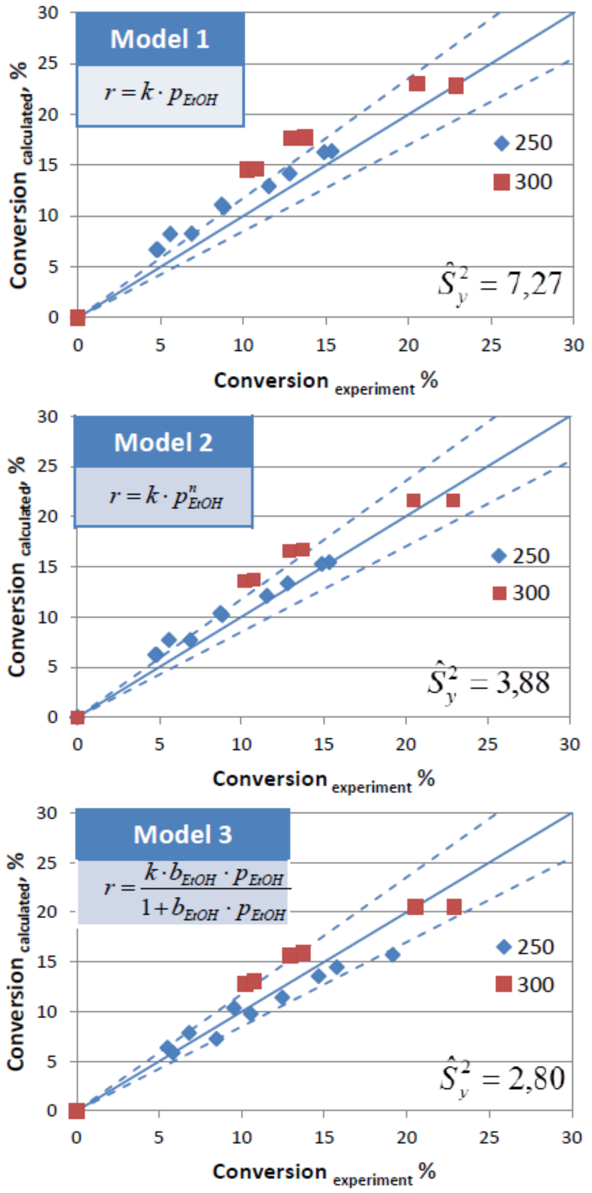

Figure 1. Comparison of measured and calculated ethanol conversion by different models

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KINETIC STUDIES OF GASEOUS ETHANOL OXIDATION OVER Pt/Rh AND Pd MONOLITHIC CATALYSTS IN A SPINNING-BASKET FLOW REACTOR

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Ethanol has been being used both as an alternative fuel and as gasoline additive for the operation of automotive vehicles, all over the world. As a consequence, there has been a rapid growth in demand for fuel ethanol since 2000 [1]. Specifically, almost 35 % of the Brazilian fleet runs on ethanol as fuel, whereas the rest fleet uses gasoline that contains 22 % v/v anhydrous ethanol on average [1]. In the United States of America (USA), 15 % of the gasoline sold contains gasoline at some percentage [2]. India has already made the first steps to add ethanol in gasoline and diesel at percentage 10 % v/v and 15 % v/v, respectively [3]. Although the ethanol use in fuels is still comparatively limited in Europe, bio-ethanol is promoted as gasoline and diesel additive since it has become legally-bound that traditional fuels such as gasoline and diesel should contain a minimum of 2 % biofuel by 2005, with this figure to increase to 5.75 % by 2010 [4]. It is evident that ethanol market is steadily growing worldwide.

As a result of the addition of ethanol into fuels, automotive exhaust emissions contain increased amounts of gaseous ethanol [5]. Its fate on catalytic systems is of great interest since its partial oxidation may lead to toxic or photochemically active compounds [5]. A number of experimental studies is devoted to ethanol catalytic oxidation. Ismagilov et al. [6] studied the catalytic oxidation of ethanol (10^{-3}-10^{-1} μmol/mL) in the gas phase from 150 °C to 220 °C for various oxygen concentrations (10-85 % v/v), using three catalysts, namely CuO, CuO/Al_2O_3 and Pt/Al_2O_3 in a continuous stirred flow reactor. Acetaldehyde at considerable concentrations was formed in all cases, whereas small amounts of carbon dioxide were also detected. The authors proposed that ethanol oxidation to carbon dioxide over copper catalysts proceeds through partial oxidation to acetaldehyde according to the following scheme:

$$CH_3CH_2OH \rightarrow CH_3CHO \rightarrow 2CO_2$$

In the case of Pt/Al_2O_3 catalyst, in parallel with the above scheme, ethanol was also directly converted to carbon dioxide. Barresi and Baldi [7] investigated the oxidation of ethanol in a wide range of ethanol and oxygen concentrations over a Pt/Al_2O_3 catalyst. They proposed the following reaction scheme for temperatures up to 180 °C:

$$CH_3CH_2OH \rightarrow CH_3CHO$$

$$CH_3CH_2OH \rightarrow 2CO_2$$

At higher temperatures and up to 350 °C, they proposed the following reaction scheme:

$$CH_3CH_2OH \rightarrow CH_3CHO \rightarrow 2CO_2$$

$$CH_3CH_2OH \rightarrow 2CO_2$$

The development of more efficient catalysts on ethanol oxidation requires the knowledge of reaction intrinsic kinetics. In the present work, the catalytic oxidation of ethanol in the gas-phase over Pt/Rh and Pd monolithic catalysts was performed in a spinning basket flow reactor with the aim of studying intrinsic kinetics. The reactor was operated under atmospheric pressure and reaction temperature was varied between 50 and 300 °C. The inlet concentrations of ethanol and oxygen ranged in 0.0060-0.0240 μmol/mL and in 0.10-10.0 % v/v, respectively. Various kinetic models were tested in the analysis of the experimental data obtained. The model that takes into account the surface reaction between adsorbed reactants was found to yield the most successful fit for both catalysts. According to this model, the activation energy of ethanol catalytic oxidation over Pt/Rh and Pd is estimated as 7903 cal mol^{-1} and 6571 cal mol^{-1}, respectively.

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EFFECT OF TEMPERATURE IN THE PROCESS OF DME CATALYTIC TRANSFORMATION TO PROPYLENE USING A K MODIFIED ZSM-5 ZEOLITE CATALYST

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The conversion of dimethyl ether (DME) to light olefins (DTO process) is an interesting route in order to obtain a high propylene yield, whose growing demand is not satisfied by the steam cracking technology [1]. The DME can be obtained from coal, natural gas and biomass, and is also feasible to co-feed the syngas with CO_2 [2,3].

In this work the effect of temperature in the process of transformation of DME to propylene has been studied with the aim of maximizing the selectivity of propylene and of other light olefins.

For that purpose, a catalyst based on a HZSM-5 zeolite of SiO_2/Al_2O_3 = 280 ratio (Zeolyst Int.) modified with a 0.2 wt. % of K by wetness incipient impregnation method has been synthesized. The zeolite has been agglomerated with pseudo-bohemite (30 wt. %) and Al_2O_3 (20 wt. %) that confer a matrix with meso- and macropores to the catalyst particle which contribute to attenuating deactivation.

Table 1 summarizes the physical and acid properties of the catalyst. The microporous structure has been analyzed by N_2 adsorption-desorption (ASAP Micromeritics 2000) and the total acidity and average acid strength have been determined by adsorption-desorption (cracking) of tert-butylamine, by combining termogravimetric techniques and differential scanning calorimetry.

The experiments were carried out in a fixed bed reactor at atmospheric pressure, at different temperatures (300-400 °C), a space time of 2.5 $g_{catalyst}$ h $(mol_C)^{-1}$ and time on stream of 4h. The products were continuosly analyzed in a gas cromatograph (Micro-GC Agilent CP-490). It is noteworthy the thermal cracking of DME above 400 °C, with formation of CH_4 and CO.

Table 1. Physical and acidic properties of the catalysts

	S_{BET} (m^2/g)	**V microp (cm^3/g)**	**Total acidity (mmol t-BA/g)**	**Average acid strength (KJ/mol t-BA)**
0.2 K / HZ-280	296	0.041	0.28	97

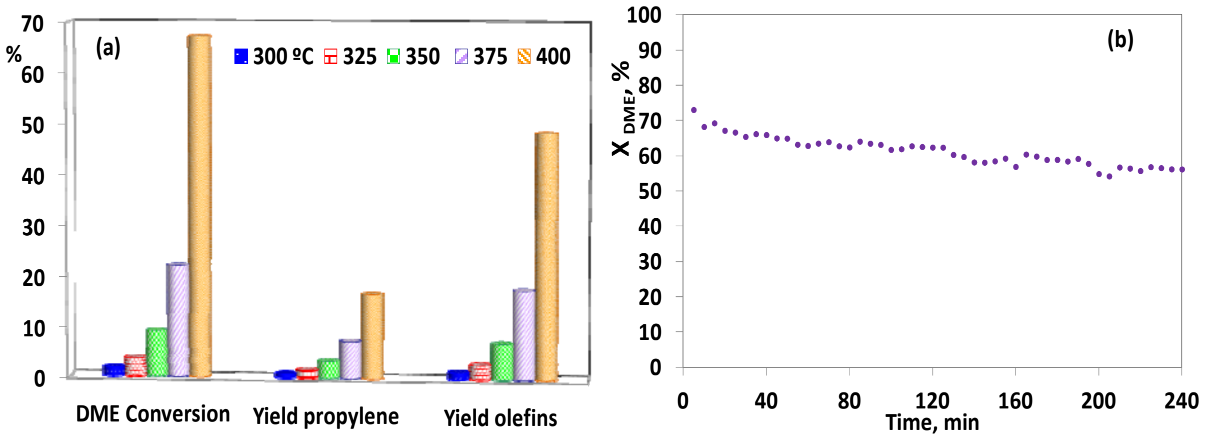

Figure 1. Effect of temperature on DME conversion, propylene and light olefin yield (a) and the evolution with the time on stream of DME conversion at 400 °C (b)

Figure 1a shows an exponential increase with the temperature of the reaction indices (DME conversion and propylene and light olefin yield), where a maximum yield of light olefins of around 50 % is observed at 400 °C, with a DME conversion of 68 % and a propylene yield of 18 %.

Figure 1b shows that catalyst deactivation at 400 °C is very slow, which is an advantage over the SAPO-34 catalyst, that although it is more selective to propylene, it deactivates considerably faster.

The amount of coke deposited on the catalyst is lower than 1.4 wt % for all the temperature range studied. Based on the good behavior, HZSM-5 zeolite catalyst (SiO_2/Al_2O_3 = 280) doped with 0.2 wt % of K can be considered as an alternative to SAPO-34, of high deactivation rate in the conversion of DME to light olefins with high propylene selectivity.

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CATALYTIC CRACKING OF PROPANE AND BUTANE OVER La-P/HMFI ZEOLITES TO PRODUCE LIGHT OLEFIN

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The influence of Lanthanum and phosphorus modification on the performance of La/P/HMFI zeolites in the catalytic cracking of propane and mixed butane to light olefins has been studied in a fixed bed reactor, separately. The catalysts were characterized by means of NH_3-TPD, XRD, and SEM. The yield of light olefins, i.e., ethylene, propylene, and butene was increased to 55 wt % at 650 °C in the presence of lanthanum. The similar yield of light olefins was also obtained over HMFI, but the formation of $C5^+$ hydrocarbons was observed in the catalytic cracking of C4 alkanes over HMFI from the start of the run, while it was not produced over La/HMFI after 180 min of the reaction. The modification of La/HMFI with phosphorus decreased the yield of light olefins about 7 wt% due to the lower acidity of La-P/HMFI catalyst. Catalytic cracking of propane over La/HMFI catalyst has resulted in 30 wt % ethylene and propylene.

Introduction

The recent researches depict that catalytic cracking of C4 alkanes over the modified MFI zeolites results in high yield of light olefins [1-4]. Propane, iso-butane and n-butane are the main components of LPG (Liquefied petroleum gases), which is produced abundantly in the Middle East due to great sources of natural gas. In the present research, catalytic cracking of mixed butane (isobutene, n-butane) has been studied over Lanthanum and phosphorus modified HMFI. Catalytic cracking of mixed butanes has been investigated over HMFI (SiO_2/Al_2O_3 = 40), 10 % La/HMFI, and 10 % La – 2 % P/HMFI separately to evaluate the influence of lanthanum and phosphorus on catalytic cracking of butane at the same operating condition. Furthermore, catalytic cracking of propane over the above-mentioned catalysts has been studied for the first time.

Experimental

The loading of rare earths and the phosphorus on the zeolites was conducted by impregnation using aqueous solutions of lanthanum nitrate salt ($La(NO_3)_3{\cdot}6H_2O$) and diammonium hydrogen phosphate salt ($(NH_4)_2HPO_4$), respectively. HMFI powder was impregnated with the aqueous solution of ($La(NO_3)_3{\cdot}6H_2O$) to produce 10 wt % Lanthanum over La/HMFI. A quartz tube fixed-bed flow reactor (i.d. = 10 mm, length = 500 mm) was used for the cracking experiments.

Catalyst characterization

X-ray diffraction patterns of HMFI, 10 % La/HMFI, and 10 % La 2 % P/HMFI zeolites were indicated that La/HMFI and La-P/HZSM samples keep well the framework structure of HMFI. SEM images depicted that the crystalline shape of the HZSM-5 zeolites was not changed by La loading. NH_3-TPD results showed that the strong and weak acidic amount of HMFI has been considerably reduced with the introduction of lanthanum and phosphorus.

Results and discussion

The product yields of butane cracking over modified HMFI catalysts are shown in Fig. 1. The product yields of propane catalytic cracking over La/HMFI catalysts are shown in Fig. 2.

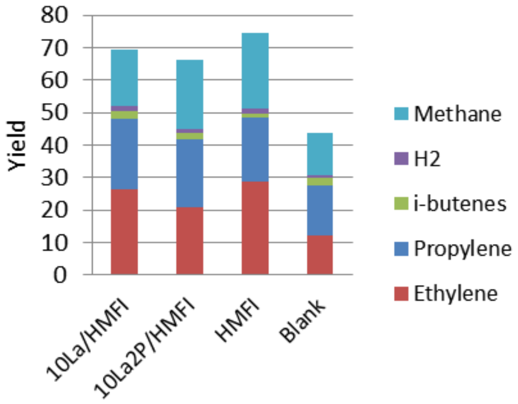

Fig. 1. Product distribution in catalytic cracking of butanes on La and P - loaded HMFI catalysts

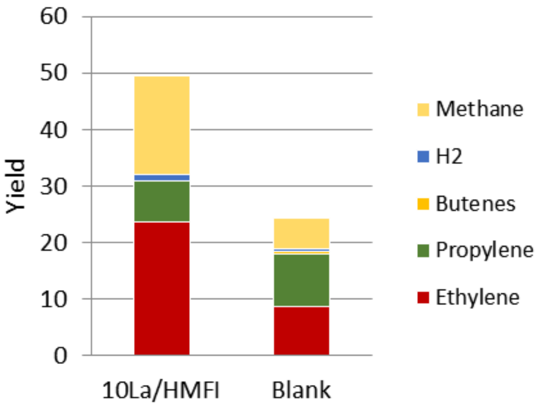

Fig. 2. Product distribution in catalytic cracking of propane on La loaded HMFI catalysts

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TETRACHLOROETHYLENE HYDROFLUORINATION TO PENTAFLUOROETHANE: INFLUENCE OF Cr-Mg CATALYST HEAT TREATMENT CONDITIONS, KINETIC STUDY

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The pentafluoroethane $CHF_2–CF_3$ (refrigerant R-125) is obtained by gas-phase hydrofluorination of tetrachloroethylene $Cl_2C=CCl_2$ in the presence of chromium-containing catalysts on various supports, in particular, chromium–magnesium catalysts [1,2]. The activity and selectivity of the chromium-containing catalyst will depend on the composition and properties of the catalytic system (precursor of the catalyst) and the activation mode is determined (pretreatment). The catalyst is finally formed under the action of fluorine containing mixtures under conditions of a catalytic reaction or fluorinating preactivation.

In this work, we studied the influence of the heat treatment conditions (temperature and gas phase composition) on the physicochemical and catalytic properties of chromium–magnesium catalysts and kinetic study on the most active sample.

The precursor of catalysts samples was prepared by impregnation of powder magnesium fluoride with aqueous solution of CrCl3. The BET specific surface area was equal to 60 m^2 g^{-1}. The catalyst contained 12 wt. % of chromium chloride. The physicochemical properties of the catalytic systems obtained by heat treatment of the precursor in nitrogen and air between 120 and 500 °C and their influence on the catalytic activity in tetrachloroethylene hydrofluorination were studied by thermal analyses (DTG,DTA), X-ray diffraction analysis, and specific surface are measurements.

It was shown that by changing the activation conditions can form the catalysts with very different catalytic properties for the same initial catalytic system. More efficient way of enhancing the catalytic activity procedure involving heat treatment in air.

Kinetic regularities of the vapor-phase hydrofluorination of perchloroethylene were studied at the total pressure of 0.4 MPa, temperature 300–380 °C, contact time 0.5–5 s and the molar ratio HF : PCE = 10. The experimental setup included a reactor placed into a heat chamber, which permitted one to vary the temperature of the reactor from 300 to 390 °C. The reactor was built as a U-type nickel tube (i.d. 0.6 cm, volume 6 cm^3). The concentration of PCE in HF was set via saturation of the gaseous hydrogen fluoride flow with the perchloroethylene vapors in an evaporator. The gaseous product mixture was passed through a scrubber with dry alkaline metal carbonate, in which HF and HCl were converted into CO_2 and H_2O, and then was analyzed by chromatography on-line.

The overall process includes a large number of possible reaction routes and, apart from its main products, might yield the products of sidereactions like isomerization, elimination and disproportionation [3]. Based on the experimental data, the pathway of perchloroethylene fluorination with HF was identified. The process involves several consecutive reactions for the formation of main fluorination products and parallel reactions for the formation of by-products. The rate constants and activation energy of the PCE conversion was obtained on the assumption of the first order of the reaction rate.

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PP-89

MACROSCOPIC MODELING OF TURBULENT FLOW IN A RADIAL FLOW FIXED BED REACTOR

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Turbulent flow in two possible configurations, CF-π and CP-π, in a radial flow fixed bed reactor (RFBR) is studied [1]. The characteristics of the turbulent flow in the hybrid region, involving both a catalytic fixed bed region and the channel fluid region were simulated.

The turbulent flow in the channels and in fixed beds can be described by the RANS equations.

The macroscopic continuity and momentum equations [2, 3] in the channels and in fixed beds are expressed in a cylindrical coordinate system:

$$\frac{\partial U_z}{\partial z}+\frac{1}{r}\frac{\partial U_r r}{\partial r}=0 \tag{2}$$

$$\frac{\partial U_z^2}{\partial z}+\frac{1}{r}\frac{\partial r U_z U_r}{\partial r}=-\frac{1}{\rho}\frac{\partial P}{\partial z}+2\frac{\partial}{\partial z}\left(\upsilon_\varepsilon\frac{\partial U_z}{\partial z}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left[\upsilon_\varepsilon r\left(\frac{\partial U_z}{\partial r}+\frac{\partial U_r}{\partial z}\right)\right]-\left(\xi_1+\xi_2\sqrt{U_z^2+U_r^2}\right)U_z \tag{3}$$

$$\frac{\partial U_z U_r}{\partial z}+\frac{1}{r}\frac{\partial r U_r^2}{\partial r}=-\frac{1}{\rho}\frac{\partial P}{\partial r}+\frac{2}{r}\frac{\partial}{\partial r}\left(\upsilon_\varepsilon r\frac{\partial U_r}{\partial r}\right)+\frac{\partial}{\partial z}\left[\upsilon_\varepsilon\left(\frac{\partial U_z}{\partial r}+\frac{\partial U_r}{\partial z}\right)\right]-\frac{2U_r}{r^2}\upsilon_\varepsilon-\left(\xi_1+\xi_2\sqrt{U_z^2+U_r^2}\right)U_r \tag{4}$$

where $\xi_1=150\upsilon(1-\phi)^2/(\phi^3 d_k^2)$ and $\xi_2=1.75(1\text{-}\phi)/(\phi^3 d_k)$ are Ergun's parameters; d_k is diameter of grains of a catalyst bed; ϕ represents the porosity.

The last two terms in Equations (3) and (4) represent the drag force due to the presence of the fixed bed. The generalized model (Eq. (3) and (4)) can be reduced to the RANS equations in the channels if the catalytic bed disappears, as $\phi\to 1$.

The eddy viscosity ν_t is a function of kinetic energy k and its rate of dissipation ε as:

$$\nu_t=C_\mu f_\mu\frac{k^2}{\varepsilon} \tag{5}$$

Subsequently, to close the problem transport equations for k and ε are required. The macroscopic $k-\varepsilon$ turbulent model of Nakayama and Kuwahara is given by [6]:

$$\frac{\partial}{\partial z}(U_z k)+\frac{1}{r}\frac{\partial}{\partial r}(rU_r k)=P_k+\frac{\partial}{\partial z}\left[\left(\upsilon+\frac{\upsilon_t}{\sigma_k}\right)\frac{\partial k}{\partial z}\right]+\frac{1}{r}\frac{\partial}{\partial r}\left[r\left(\upsilon+\frac{\upsilon_t}{\sigma_k}\right)\frac{\partial k}{\partial r}\right]+G_k-\varepsilon \tag{6}$$

$$\frac{\partial}{\partial z}(U_z\varepsilon)+\frac{1}{r}\frac{\partial}{\partial r}(rU_r\varepsilon)=C_{\varepsilon 1}\frac{\varepsilon}{k}P_k+\frac{\partial}{\partial z}\left[\left(\upsilon+\frac{\upsilon_t}{\sigma_\varepsilon}\right)\frac{\partial \varepsilon}{\partial z}\right]+\frac{1}{r}\frac{\partial}{\partial r}\left[r\left(\upsilon+\frac{\upsilon_t}{\sigma_\varepsilon}\right)\frac{\partial \varepsilon}{\partial r}\right]+C_{\varepsilon 2}\left(G_\varepsilon-\frac{\varepsilon^2}{k}\right) \tag{7}$$

where $G_k = \frac{1.75(1-\phi)}{\phi}\frac{(U_jU_j)^{3/2}}{d_k}$ is the extra generation rate of *k* due to presence of the fixed bed; $G_\varepsilon = 4.55C_\varepsilon\left(\frac{1-\phi}{\phi}\right)^2\frac{(U_jU_j)^2}{d_k}$ is the extra production rate of ε due to presence of the catalyst bed; C_ε is a dimensionless constant; $P_k = \left(-\overline{u_iu_j}\frac{\partial U_i}{\partial x_j}\right)$; *f*$_1$ and *f*$_2$ are the damping functions; and C_ε, $C_{\varepsilon 1}$, $C_{\varepsilon 2}$, σ_k, σ_ε are dimensionless constants [4]. These extra terms G_k and G_ε vanish in the limiting case when non porous medium is present, or when the porosity and the permeability are extremely high $\phi \to 1$, meaning that the transport equations of *k* and ε are recovered to the clear fluid region.

At the channels and the fixed bed interface the classical continuity boundary conditions are applied for simplicity [5].

The calculation results of the proposed macroscopic model of turbulent flow in two possible configurations, CF-π and CP-π, in RFBR depending on the operating parameters (resistance layer and the Reynolds number) are presented in the following research. In comparison with CP-π configuration calculated data of the CF-π shows the best flow distribution in the fixed bed. Influence of Reynolds number on the flow distribution in a radial flow fixed bed reactor due to the variation of its value from 83 250 to 832 500 at the inlet channel is shown.

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MICROWAVE SYNTHESIS OF ION EXCHANGE RESIN FROM USED TIRE

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Nowadays, as the growth of economics and industries, waste of used tire became a serious problem because of the huge amount of used tire is produced each year, and it is hardly degradable in environment. Besides using as recycled tire or land-fill materials, some research groups proposed the methods to convert them into value-added products such as adsorbents for environmental remediation [1-3].

D. Danwanichkul and D. Dechojarasssi reported the adsorption of Hg^{2+} in aqueous phase using granular of used tire. The adsorption efficiency reached as high as 88.8 % in dynamic adsorption in column pack [1]. S. Katyaem and co-workers proposed the removal of phenol from the contaminated water using small particle of used tire [2]. E. Manchon Vizuete and co-workers reported on the modification of used tire by heat treatment at 400 °C incorporated with the chemical treatment by immersing used tire in H_2SO_4, HNO_3 or mixture between H_2SO_4 and HNO_3. The used tire which was modified by heat treatment showed higher Hg^{2+} adsorption than the chemical treatment method [3].

Used tire waste is considered to be an important hydrocarbon source. The structure of used tire usually contains double bonds that are derived from isoprene unit of natural rubber and butadiene copolymer unit of synthetic rubber (Figure 1). Both units contain carbon-carbon double bond, which are useful for the chemical modification.

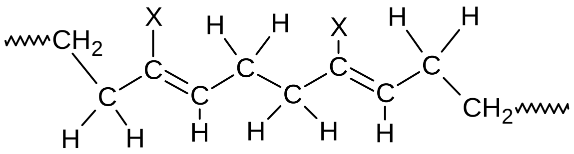

Figure 1. The chemical structure of polyisoprene (X = $-CH_3$) and poly 1,3-butadiene (X = H)

In this research, used tire was modified by amination of these double bonds, and followed by protonation to give ion exchangeable site ($-NH_2R^+Cl^-$) in the structure (Figure 2).

In the experiments, 5 g of used tire was added to 50 mL of ethylenediamine. The mixture was heated by microwave irradiation at 450 W for 30 minutes. Then it was washed by distilled water and dried. It was protonated by immersing in 0.2 M HCl solution for 1 night. It was washed by distilled water and dried to give the modified used tire. The ion exchange capacity of modified use tire was measured by titration.

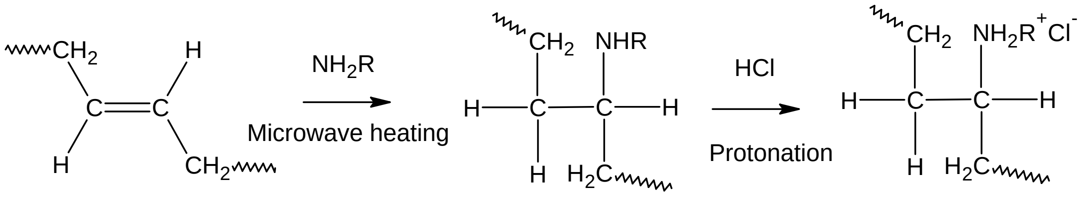

Figure 2. Reactions for preparation of ion exchange resin from used tire.

As a result, the used tire, which was modified by ethylenediamine showed 0.95 meq/g of ion exchange capacity. The ion exchange capacity was higher than that of the raw used tire (0.05 meq/g). The similar reaction performed at 300 W and 600 W of microwave irradiation but the obtained modified used tire showed lower ion exchange capacity. Finally, the ability for removal of anion such as phosphate ion and chromate ion was evaluated. It was found that the modified used tire could remove both ions much better than the raw tire and natural rubber.

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PEROVSKITE – TYPE OXIDES AS CATALYSTS OF THE PROX REACTION

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Hydrogen and fuel cell technologies are considered as an important solution of the 21st century energy problems. The crucial requirement for the proton exchange membrane fuel cells (PEMFC) is to deliver clean hydrogen to the anode, which is rapidly poisoned by traces of CO. The removal of CO to the level below 10 ppm can be achieved by using the catalysts which are able to selective oxidizing of CO in the presence of hydrogen (PROX – preferential oxidation).

A number of catalysts have been investigated for this reaction and among the most effective are Pt-based [1] and Au-based [2] systems. In the beginning the importance was attached to Pt/Al_2O_3 catalyst [3]. This kind of catalysts was proposed by Los Alamos National Laboratory in the sixties of XX century as an effective one for preferential oxidation of CO in the H_2-rich gas mixture.

Over Pt/Al_2O_3 catalyst, carbon monoxide, hydrogen and oxygen compete for the same adsorption sites on the metal surface. In order to provide separate sites for CO and O_2 adsorption, appropriate supports for noble metals (i.a. surface reducible oxides like TiO_2) should be used. For such systems, the synergetic effect consisting on the reaction of carbon monoxide adsorbed on the metal surface with oxygen retained by the support, can be anticipated.

Perovskite – type oxides with the general formula ABO_3, are an interesting catalytic materials for many oxidation processes, showing very high activity in the oxidation of hydrocarbons (methane, propane) and carbon monoxide [4]. Thus, one can expect that some of such oxides would be good candidates for application as supports of platinum in the catalysts of PROX reaction.

This work reports the results of our studies on selective oxidation of carbon monoxide in the presence of hydrogen over $Pt/BaSnO_3$, $Pt/LaMnO_3$ and $Pt/LaCoO_3$ catalysts.

1 wt. % of platinum was loaded on oxides with an aqueous solution of H_2PtCl_6 by a wet impregnation method. The samples were dried at 110 °C and calcined in air at 600 °C for 4 h. The samples were characterized by different physico-chemical methods such as (TPR-H_2 and TPR-CO), the pulse of H_2 chemisorption, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and temperature programmed desorption of oxygen (TPD-O_2).

The catalytic tests were carried out in a conventional flow, fixed-bed reactor at atmospheric pressure. The reaction mixture consisted of H_2 (75 vol. %), CO (0.15-1.5 %) and O_2 (0.3-3%). The concentration of two last gases for given measurement were described by lambda parameter (λ), defined as:

$$\lambda = \frac{O_2/CO}{(O_2/CO)_{Stoich}}$$

$\lambda = 1$ when O_2/CO ratio is stoichiometric. The measurements of catalytic activity were carried out in a wide range of λ (0.5 – 8). The outlet gas mixture was analyzed by IR method using Fuji Gas Analyzer.

1 wt. % Pt/$BaSnO_3$ catalyst shows very high activity and selectivity in PROX reaction connected with its high capacity to oxygen adsorption and the reducibility of support. The selectivity of Pt/$LaMnO_3$ and Pt/$LaCoO_3$ is rather poor although Pt/$LaMnO_3$ catalyst shows good catalytic activity in CO oxidation in the absence of hydrogen.

Basing on the obtained results, we proposed a mechanism of PROX reaction over Pt/perovskite oxides catalyst. The important role was ascribed to the CO spillover phenomenon and anionic vacancies over catalyst surface. In the presented mechanism an amount of accessible anionic vacancies is considered as crucial for catalytic activity. The role of adsorbed and lattice oxygen and different types of carbonate and formate species is also discussed.

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PP-92

PERFORMANCE OF CONICAL SPOUTED BED CONTACTOR FOR DRYING OF BIOMASS WASTES

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Exploitation of biomass as energy resource supposes not only environmental benefits, but also social and economic profits. Moreover, biomass is considered one of the key renewable resources of the future. It already supplies 14 % of the world's primary energy consumption. Directive of the European Parliament and the Council 2009/28/CE [1], establishes mandatory targets consistent with a 20 % share of energy from renewable sources by 2020.

As biomass wastes usually have high moisture content, in order to increase the efficiency of exploitation treatments, it is advisable to reduce the humidity by previous drying. The exploitation of a renewable energy source as biomass by spouted beds technology can be considered as an alternative that guarantee sustainable development. This technology in conical geometry of the contactor is very useful for applications where a vigorous movement of the solids is required, as in the handling of sticky solids, of irregular texture and with a wide particle size distribution [2-4]. Moreover, the conical spouted bed is successful for wastes treatment, especially biomass wastes [5-8]. Since the first application of spouted beds for drying of grain [9], several authors have dried granular materials [10-12], and other materials such as biomass [13-14], foods [15], pharmaceuticals [16], sludge [17-19], pastes, suspensions [20].

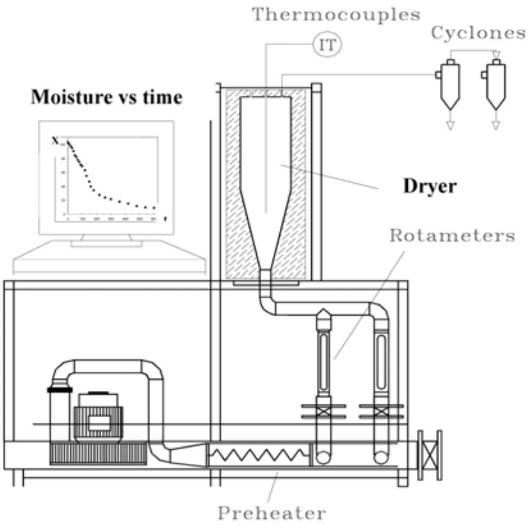

Figure. Experimental equipment and evolution of moisture content of biomass with the time.

The experimental unit, Figure, designed on a pilot scale consists basically of a conical dryer, a blower, two high efficiency cyclones, two mass-flow meters, an electrical preheater and thermocouples, gas inlet diameters between 0.03 and 0.05 m and stagnant bed heights, between 0.05 and 0.25 m. The biomass wastes studied have been agroforestal and derivatives of wood

Industry of pinus insignis (sawdust, branches, wood chips and shavings) of density, ρ_S, 560 kg/m^3, with Sauter mean diameter, $\overline{d_s}$, between 0.95 and 5 mm.

In this paper in order to determine the performance of conical spouted beds for drying of biomass wastes, the stable operation conditions at inlet gas temperature range of 25-120 °C have been determined. In adittion, the good behaviour of the spouted bed dryer has been proven for drying of mixtures of biomass wastes at different temperatures. The evolution of biomass moisture content has been measured with time, Figure, and also the influence of the operating conditions on drying has been analyzed.

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BUBBLE COLUMN REACTOR FLUID DYNAMIC EVALUATION AT PILOT PLANT SCALE FOR RESIDUE AND EXTRA – HEAVY CRUDE OIL UPGRADING TECHNOLOGY

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Bubble column reactors are multiphase contacting devices used in a wide variety of industrial application, due to their easy construction, operation, high heat transfer rate and overall mass transfer coefficient [1]. Venezuelan Oil Company Research Center has been developing technologies to convert extra-heavy crude oil that use this type of reactors [2]. Volumetric gas hold up, average gas bubble size, average interfacial area, residence time distribution (RTD) and dispersion coefficient are important design parameter for bubble column reactor and for a proper scale up of them. Several cold model experiments have been proposed to determine the previously mentioned parameters at atmospheric conditions, using a plexiglas bubble column reactor at pilot plant scale unit (12 cm diameter). It was also evaluated our own design of internal plates or trays inside the reactor. Air-tap water and air-light oil systems have been used. The light oil has similar physical and chemical properties to the real feedstock (vacuum residue) on real operating conditions. A wide operating condition range was applied, superficial gas velocity between 0.5-10 cm/s, liquid flowrate between 15-65 L/h. General speaking, without internal plates was found that gas hold up increase along the reactor and it was possible to identify heterogeneous bubble, transition and churn turbulent flow regime areas at different superficial gas velocities for the air-light oil system [3]. It was also determine that average gas bubble size increase along the reactor at bubble regime from 2-5 mm, but at turbulent regime, stay oscillating between 1-3 mm [4]. The air-light oil system always showed gas hold up higher than the air-tap water system. At the same reactor height, average gas bubble size decreases with the gas superficial velocity. Average interfacial area increases exponentially with superficial gas velocity at any reactor height, till 1412 m^2/m^3 for the air-light oil system but, at bubble flow regime, the average interfacial area is lower than 100 m^2/m^3, which will negatively impact the reactor performance [5]. Internal plates in the reactor always increase gas hold up at any condition or system used. Residence time distributions curves, Peclet numbers and dispersion coefficients founded, show that this reactor with internal plates still tends to be a complete mixing reactor under the operating conditions used [6]. The new RTD curve was displaced on time because the death space created by the internal plates inside the column.

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KINETIC AND REACTOR MODELING FOR THE METHANATION OF CO_2

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Background

Changing the energy supply from conventional power plants towards renewable resources implies the need for adequate energy storage technology and capacity as a consequence of the unsteady onset of wind and solar energy. The electrolysis of water and the reaction of hydrogen with carbon dioxide to methane offer a possible next generation storage technology [1]. Being a feasible chemical energy carrier, methane can easily be stored, transported and converted back into electric energy. Though the methanation of carbon dioxide has been well known since the beginning of the 20th century, no commercial process has been established and essential questions concerning catalytic systems, kinetics and reaction engineering have not been answered.

Methodology

Ni-, Ru- and Pd-based systems have been reported to be catalytically active and to show a high selectivity to methane. In this study, we address the modeling of the intrinsic kinetics of the methanation of carbon dioxide on a Ni catalyst system based on a dataset measured in our lab in a single-pass fixed-bed reactor under isothermal conditions in absence of transport limitations. For the kinetic modeling, a 1D PFR model is implemented in Athena Visual Studio and used for parameter estimation. The study focuses on empirical power law approaches and Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics. The derivation of LHHWs rate equations will be based on mechanisms postulated in literature, e.g. see references 2 and 3. By varying the rate determining step and most abundant surface intermediates, different rate equations will be derived. Besides, it will be tested if literature models [2,4] for the methanation are applicable, though they were derived and parameterized under different conditions.

Results & Outlook

$$r = k' \cdot e^{\frac{E_A}{R}\left(\frac{1}{T_b}-\frac{1}{T}\right)} \left(p_{CO_2}^{n_{CO_2}} p_{H_2}^{n_{H_2}} - \frac{p_{CH_4} p_{H_2O}^{2}}{K_{eq} p_{CO_2}^{1-n_{CO_2}} p_{H_2}^{4-n_{H_2}}} \right)$$

Preliminary results show that the dependence of carbon dioxide and hydrogen can be described according to an order of close to 0 and 1/3 respectively under a wide range of conditions if the conversion is kept low. Accordingly, a simple power law allows for an excellent description of the data under these conditions (see parity plot in figure 1). However, as soon as the thermodynamic equilibrium is approached, a systematic deviation is observed: The power law model systematically overestimates the reaction rates and fails to describe approaching the equilibrium. To solve this issue, the dataset has been extended to feed compositions that also contain methane and water so that their influence can be evaluated. The introduction of an empirical water inhibition in the power law or rate equations of LHHW type allow now for a better description. Different LHHW rate equations will be discriminated according to statistical tests, e.g. Bartlett's test, and checked for physical consistency.

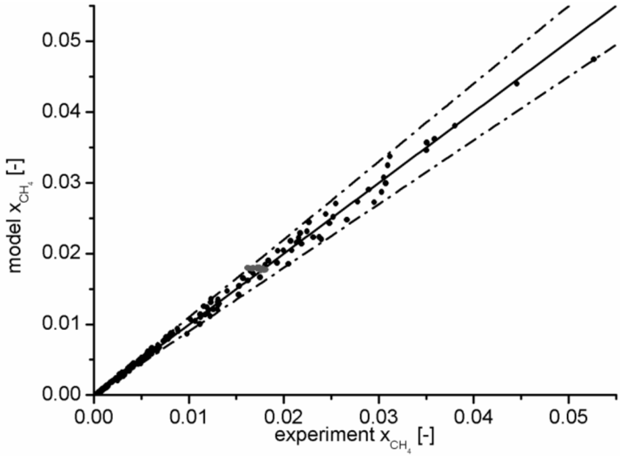

Figure 1: Parity plot for a dataset constrained to low conversion

The kinetics will also be implemented to a 1D heterogeneous polytropic reactor model accounting for intraparticle and external heat and mass transfer in order to be able to transfer the kinetics measured in the lab to a fixed-bed reactor of technical dimensions.

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THE SYNERGETIC EFFECT AND OSCILLATORY BEHAVIOUR DURING CO OXIDATION OVER A BIMETALLIC COMPOSITE CATALYSTS

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Bimetallic composite and nanocomposite catalysts have found many practical applications because they can exhibit a so-called *synergetic catalytic effect,* i.e., an effect when a composite surface can exhibit catalytic properties that are very different from those of the monometallic surfaces [1]. For example, Pt–Rh catalysts are used for oxidation of ammonia and also in three-way catalytic converters.

The goal of our study is to simulate the reaction of CO oxidation over a Pt-Rh composite surface with realistic values of kinetic parameters in order to obtain a fundamental understanding of how the presence of a second metal can change the overall activity of a composite surface. The reaction mechanism (of the Langmuir-Hinshelwood type) includes the elementary events of adsorption-desorption of CO and O, as well as the reaction between CO_{ads} and O_{ads} which gives CO_2 in the gas phase. The model is represented by the system of 4 differential-algebraic equations (DAEs). The macroscopic state variables are the CO_{ads} and O_{ads} coverages on Rh (type-1) and Pt (type-2) surfaces: $\theta_{CO,1}$, $\theta_{O,1}$, $\theta_{CO,2}$, $\theta_{O,1}$. Two algebraic equations describe the quasi-equilibrium conditions (i.e., the equality of chemical potentials for two surfaces). The model assumes that the quasi-equilibrium state is attained due to fast diffusion of CO and O. The algebraic equations contain the important parameters ΔE_{CO} and ΔE_O, which denote the difference in the binding energies of CO and O, respectively, on the two surfaces of composite catalyst.

First, we analyze a simplified mathematical model (with $\Delta E_{CO} = \Delta E_O = 0$) which has an analytical solution. It demonstrates some simple cases when a composite catalyst can improve the overall activity. In particular, we show that a difference in the CO sticking coefficients on two surfaces is sufficient to provide a positive synergetic effect, but this effect can be observed only in a certain range of the external parameters.

Next, we discuss the synergetic effect between Pt and Rh for CO oxidation reaction using realistic values of kinetic parameters, in particular, using $\Delta E_{CO} = 0$, $\Delta E_O = -35$ kJ/mol. The simulations give a semi-quantitative description of the experimental data presented in [2]. Fig. 1 shows a temperature dependence of the CO_2 formation rate for monometallic Pt and Rh, as well as for composite Rh/Pt.

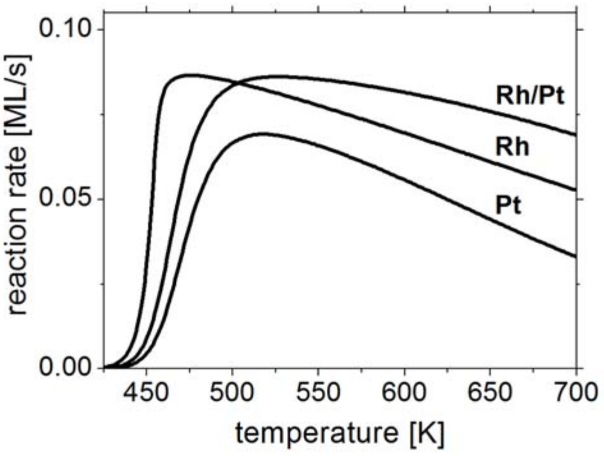

Fig. 1. Calculated temperature dependence of the steady-state CO_2 formation rate at $P_{CO} = P_{O_2} = 10^{-6}$ mbar. Three curves correspond to different catalysts.

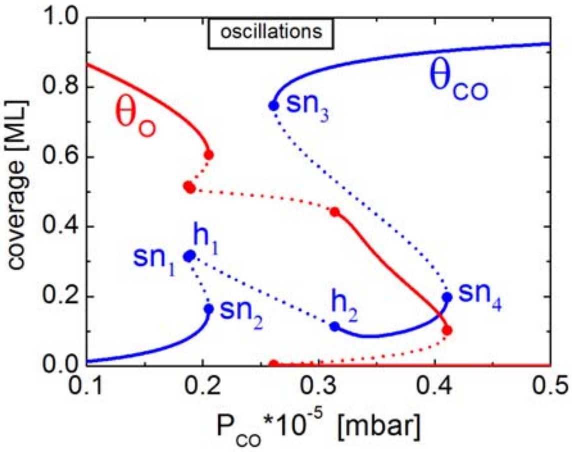

Fig. 2. Bifurcation diagram for the composite catalyst at $P_{O_2} = 10^{-5}$ mbar, T = 450 K. There are several Andronov-Hopf (h_1 and h_2) and saddle-node bifurcations (sn_i).

One can see that at temperatures above 505 K the Rh/Pt composite catalyst gives the highest rate of CO_2 formation. At low temperatures, however, the Rh surface is the most active. The main reason of the observed synergetic effect is the larger sticking coefficient of CO on Pt as compared to Rh. On a composite surface, the reaction proceeds mainly on Rh, while Pt serves only as a source of adsorbed CO and O.

The DAEs model has been analyzed using the bifurcation analyses and the parameter continuation. It turned out that the model can produce an oscillatory behaviour. Fig. 2 shows an example of the one-parameter bifurcation diagram. Finally, we analyze a new mechanism of kinetic oscillations in the model of the CO oxidation reaction. The main reason for oscillations was shown to be a large difference in the binding energy of O_{ads} on Rh and Pt.

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OPTIMISATION OF OPERATING CONDITIONS OF CATALYTIC REFORMING CATALYST IN INDUSTRIAL REACTORS BY METHOD OF MATHEMATICAL MODELLING

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Nowadays mathematical modeling of industrial processes has become the universally recognized method of solving problems on increase of efficiency and creation of new technological processes and apparatuses.

The methodical bases of catalytic processes modeling were laid in the works of such Russian scientists as academician of Russian Academy of Sciences (RAS) Boreskov G.K. and corresponding member of RAS Slynko M.G., and also in the works of foreign researchers Amudson N.A. and Aris R. This method consists of division of complex chemical technological process into physical and chemical constituents, studying them separately and creation of common mathematical model from mathematical models of individual parts of complex process.

Optimization of industrial processes is one of the most important stages of mathematical modeling. It should be found a big amount of optimal process parameters: temperature, pressure, reaction mixture composition, its flow rate and etc.

The modern modifications of Pt-Re-catalysts of catalytic reforming process allow to get high – octane product with 96-98 octane number and selectivity can achieve 87-90 % mass. However, there is a question about their stability during the operating process, which is determined by carbon composition of raw material, technological operating condition and characteristics of reactor unit. It's wrong to lead this multifactorial task to division of catalysts into «Russian» and «Foreign» by surface characteristic without physico-chemical regularities of target and adverse reactions. It's only possible to solve catalyst work prediction problem by using kinetic model, which takes into consideration complex influence on deactivation of coke formation processes, poisoning and aging. Besides, it's necessary to add technological exploitation catalyst level.

The most important condition of optimal exploitation of bifunctional reforming catalyst is the balance of acid and metal activity. Chlororganic compounds are fed in the reforming reactor unit, and, transformed into hydrogen chloride, promote of increase of hydrocarbon conversion selectivity on the surface and increase the depth hydrocarbon raw material conversion and product octane number. It's necessary to take into consideration reversibility of chlorine adsorption on the active catalyst surface. Physico-chemical process model allows to determine optimal technological conditions and hydrocarbon composition of raw material, making increase of efficiency by a balance between acid and metal catalyst activity, i. e. to realize industrial reactor optimization with different modes of operation.

For a complete monitoring of the reforming catalyst operating condition taking into account its actual activity potential and quantitative evaluation of optimal activity (activity, corresponding to condition of thermodynamic equilibrium of coke formation reactions and reactions of intermediate products compaction) Catalyst Operating Condition Control System was designed. This system allows asses the degree of involvement of all factors into the regulation process of technological operating condition of unit, which determine the realization catalyst potential. There are dependent and independent factors. Independent factors are carbon composition of raw material and benzene octane number, and also the degree of purification of raw materials from contaminants. Dependent factors (which can be changed during process regulation) include reagent consumption, temperature, and feed of chlororganic compounds.

Multiparametric regulation is the most effective in the presence of generalized criterion, which characterizes as a catalyst potential, as a degree of its realization. We use coke formation on the catalyst surface, duration of raw material cycles and total volume of recycled raw material as the criterion.

CORRELATION BETWEEN THE XYLITOL AQUEOUS PHASE REFORMING ACTIVITY AND NATURE OF VIII GROUP METAL CATALYSTS

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Biomass can be regarded as a renewable source of platform chemicals, biofuels and energy-rich materials [1-4]. Aqueous phase reforming (APR) has attracted a lot of attention, since this process is efficient and tunable in terms of hydrogen and light hydrocarbons production from biomass-derived sugars and sugar alcohols. Pt supported catalysts have been shown to be the most effective among monometallic catalysts for APR of polyols [5]. Recently APR of xylitol over Pt and PtRe supported on Al_2O_3 and TiO_2 was studied considering the effect of the support and Re insertion as well as the reaction mechanism [6]. In the current work we have studied catalytic behaviour of different carbon supported Pt, Ni, Ru, Re and PtNi, PtRe, PtRu materials in xylitol APR under comparable reaction conditions in order to relate activity/selectivity with the size/structure as well as the metal nature of VIII group metals nanoparticles.

Monometallic Pt, Ni, Ru, Re and bimetallic PtNi, PtRe, PtRu catalysts were prepared by incipient wetness impregnation of Sibunit (S_{BET} = 380 m^2/g, fraction. 40-70 μm) with Cl-containing metal precursors followed by reduction in H_2 under TPR conditions, while Ru and Ni catalysts were also prepared by a colloidal method via reduction with ethylene glycol of PVP stabilized nanoparticles (NPs) under reflux conditions. Metal NPs were characterized by HRTEM, XPS, TPR, XRF, and XRD. The catalysts were tested in APR of 10 wt % xylitol in water at 225 °C and 30 bar overall pressure in a continuous fixed bed reactor. Liquid samples were analyzed by HPLC (Aminex HPX-87H, eluent 5 mM H_2SO_4, flow rate 0.6 ml/min, 45 °C, 70 min, RI

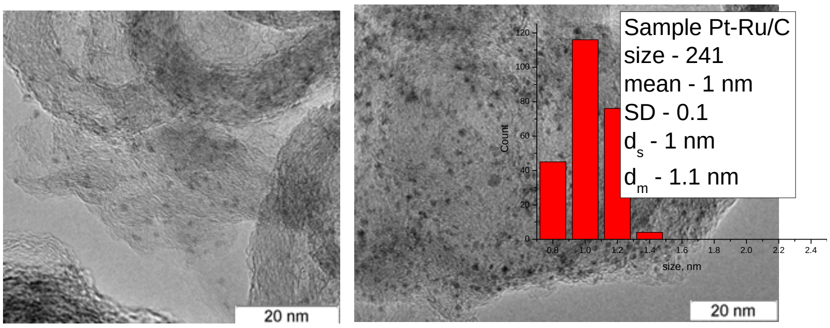

Fig. 1. TEM images of 3%Pt3%Ni/C (left) and 3%Pt3%Ru/C (right).

detector). The gaseous products H_2, CO_2, CO, CH_4, linear hydrocarbons C1–C4 were analyzed by micro-GC (Agilent Micro GC 3000A) equipped with four columns: Plot U, OV-1, Alumina and Molsieve. Total organic carbon was monitored giving 95–100 % for all measurements (TOC instrument).

According to HRTEM analysis all prepared catalysts contained an active metal of the cluster size 1-3 nm with a narrow NPs size distribution (Fig. 1). Preliminary catalysts reduction at TPR maximum temperature provided mainly the metallic state of the active component confirmed by XPS. Catalyst screening has demonstrated the highest activity and selectivity to H_2 of Pt compared to other catalysts (Fig. 2). Among bimetallic catalysts PtNi demonstrated better selectivity to H_2 while PtRu system showed the least selectivity to H_2 under the same conversion. PtRe catalyst provided 100 % xylitol conversion with the same selectivity to H_2 as Pt. Differences in hydrogen selectivity can be attributed to the difference in the metal cluster size and addition of the second metal. Carbon supported bimetallic catalysts were more active toward hydrogen formation than monometallic ones contrary to alumina and titania supported catalysts [6].

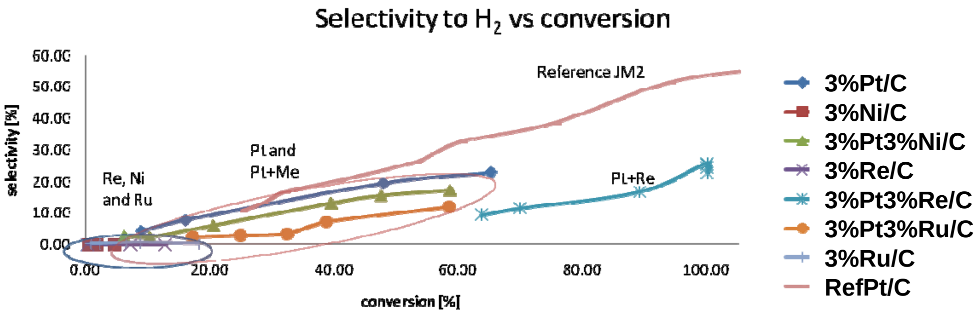

Fig. 2. Xylitol APR over mono- Pt, Ni, Ru, Re and bimetallic PtNi, PtRe, PtRu catalysts.

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TRANSFORMATION OF LIGNOCELLULOSE DERIVED C5 ACID INTO GREEN DIESEL FUEL COMPONENTS OVER Pd SUPPORTED ON METAL OXIDES

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Due to the depletion of crude reserves and the increasing demand for clean hydrocarbon fuels production of renewable fuels has emerged in the past decade as a method to solve at least partially these challenges [1]. Green fuels should replace at least in part gasoline, jet fuel, and diesel, currently derived from petroleum In the case of green diesel, its increasing demand could reach 900 million tons by 2020 [2]. Valeric acid, a product of levulinic acid conversion obtained by dehydration of glucose [3-5], can be upgraded to *n*-nonane, a green diesel component. In this work we have studied valeric acid conversion consisting of valeric acid ketonization to 5-nonanone followed by hydrodeoxygenation into *n*-nonane over Pd and Pt catalysts in H_2 atmosphere (Fig. 1). Both catalytic reactions were studied separately in order to be performed thereafter in a cascade mode over the best bifunctional catalyst, which turned out to be Pt(Pd)/M_xO_y.

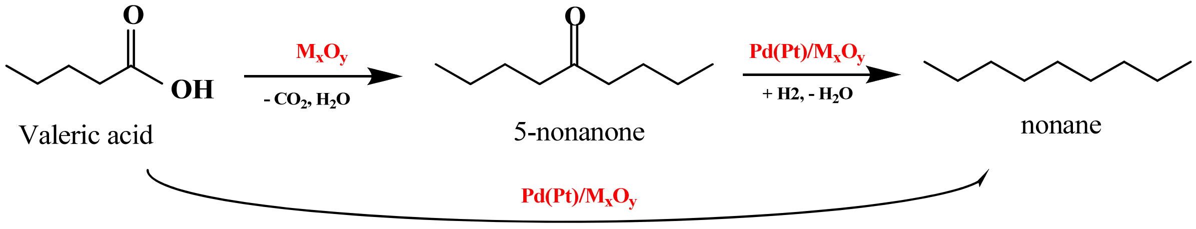

Fig. 1. Scheme of C5 acid conversion to n-nonane

Ketonization of valeric acid was carried out in a fixed bed flow reactor over ZrO_2 and 10 wt.% CeO_2/ZrO_2 ($m_{catalyst}$ = 0.5 g, fr. 0.25÷0.5 mm) at 573-678 K and 1 bar, both under H_2 and N_2 flow rate (10-33 cm^3/min). Hydrogenation of 5-nonanone was performed over 2 wt.% Pd supported on ZrO_2, and 10 % CeO_2/ZrO_2 at 573-673 K under P_{H2} 1-10 bar. The reaction products were analyzed by “Chromos 1000” GC (FID) with fused silica column Stabilwax-DA (50 m/0.32 mm/0.5 μm) (USA) at 373-473 K with ramp 10 K/min.

The effect of the reaction and support calcination temperature, CeO_2 loading, and residence time on the conversion and selectivity to the desired products were investigated. Regardless the carrier gas 10 % CeO_2/ZrO_2 was found to show higher

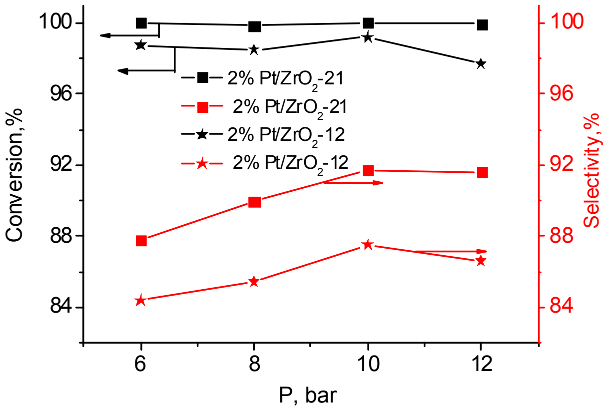

Fig. 2. Hydrogenation of 5-nonanone over 2 % Pt/ZrO$_2$ with the different dispersions at 628 K and PH$_2$ 6 bar.

catalytic activity (79 % selectivity at 93 % conversion) compared to neat zirconia (78 % selectivity at 83 % conversion) and other ceria modified zirconia while neat ceria exhibited very low catalytic activity. All catalysts provided higher valeric acid conversion in H_2 than in N_2 whereas selectivity to 5-nonanone was insensitive to gas atmosphere. XRD, FTIR, UV-Vis DRS, XPS, HRTEM methods were applied to characterize catalysts in reduced and unreduced states simulating the corresponding reaction conditions during acid ketonization. The mechanism of ketonization on the basis of FTIR and UV-Vis in-situ study was suggested [6] being consistent with the results previously reported in [7-9].

Pt(Pd)/M_xO_y catalysts with the highest dispersion showed similar (85-90 %) yields of *n*-nonane in deoxygenation of 5-nonanone at 628 K and 6 bar (Fig. 2). Pd/ZrO_2 catalyst was tested in one-pot process ketonization/deoxygenation of valeric acid to *n*-nonane under T = 628 K and P = 6 bar. A correlation between catalytic activity and structural and electronic properties of catalysts was found according to analysis by XPS and HRTEM.

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ADVANCED HYDRO REFORMING OF SPENT PULPING CHEMICALS FOR FUEL GENERATION

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Hydro reforming via supercritical water gasification (SCWG) for conversion of spent pulping chemicals to fuel products was carried out in this work. Spent pulping chemicals also called black liquor can be considered as one of the most important renewable energy resource due to its high energy content as well as tremendous annual production from pulp and paper making industries. Two major chemical recovery processes which resulted in black liquor are soda and kraft which are the principal methods for pulp liberation widely used in the industry [1]. The crucial difference of two processes is the addition of cooking chemical, sodium sulfide (Na_2S) in the later process leading to dissimilarity between resulting spent pulping chemicals. Black liquor can be considered as feedstock for power generation as well as for fuel gas production via thermal conversion processes such as gasification. However, high moisture, alkali, and sulfur contents make the conventional thermal conversion of black liquor (recovery boiler) an inefficient process. For this reason, the water content in black liquor is used as oxidizing agent in the SCWG for fuel gas production. The SCWG was carried out in a miniature fused quartz tube reactor which allowed quick turn over and rapid experimental processes. The influences of temperature, pressure, Na/S ratio, black liquor concentration on fuel gas production, and carbon and hydrogen conversion efficiency were investigated. During the experiment, the capillary quartz tube was filled with black liquor sample and subsequently airtight sealed. The black liquor filled quartz tube was then heated inside a fluidized bed reactor for superior temperature control. The fluidized bed reactor and quartz tube holder are shown in Figs. 1a,b. The high pressure required for SCWG reaction was achieved by vaporizing of content inside the quartz tube in a very small volume. The reaction temperature was regulated from 400-600 °C while the pressure was a dependent variable which may be estimated by thermodynamic principles. After each trial, the quart tube reactor was crushed in a special gas container to release and capture the produced gas for further analysis. Fig. 1c displays the liquor filled quartz tube before and after SCWG process.

(a) (b) (c)

Figure 1. a) Fluidized bed reactor, b) quartz tube holder and
c) black liquor filled quartz reactor tubing, before and after the reactions

The results showed that the gas yield mainly composed of H_2, CO, CH_4, CO_2, and light hydrocarbon gases with some char presented and very little tar formation. Pressure has minor effect on total gas production but obvious influence on gas speciation which may be described by several hydrogasification reactions involved. Temperature is the most important parameter which greatly effect gas yield, qualitatively and quantitatively. The most suitable condition for conversion of black liquor to fuel gas (mainly CO, CH_4, and H_2) was 600 °C and about 300 bar with the carbon and hydrogen conversion efficiencies of over 89 % and 82 %, respectively. It may be suggested from normalized conversion results that lower black liquor concentration would increase total conversion to gas species. For the case of kraft liquor, varied sodium to sulfur ratio also lea\d to change in reaction activity due to the catalytic effect of sodium on the gasification process while increase sulfur resulted in catalytic deactivation which adversely affect the total gas yield. Further experiments on direct addition of promising catalysts to black liquor should be carried out in order to achieve more than 97 % carbon conversion typically required for black liquor conversion process.

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IN SITU CATALYTIC UPGRADING OF BIOMASS FAST PYROLYSIS VAPORS WITH ACID-BASE MIXED OXIDES DERIVED FROM LAYERED DOUBLE HYDROXIDES (LDHs)

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The catalytic fast pyrolysis of lignocellulosic biomass is applied for the *in situ* upgrading of bio-oil, mainly by reducing undesirable organic acids and other oxygen-containing compounds and increasing aromatic hydrocarbons compared to non-catalytic fast pyrolysis. This can be achieved by the use of acidic catalysts, such as zeolites or mesoporous aluminosilicates which convert pyrolysis vapors through a series of cracking, decarbonylation, decarboxylation and aromatization reactions and remove oxygen in the form of CO, H_2O and CO_2 [1-2]. However, the most studied catalyst, the microporous acidic ZSM-5 zeolite is costly (about 7,000 €/tn) and suffers from pronounced decrease of the organic fraction of bio-oil towards gas and coke formation. Layered double hydroxides are crystalline materials and are constituted from positively charged brucite-type layers [$Mg(OH)^{2+}$] on which Mg^{2+} ions have been partially substituted by a trivalent metal (ca. Al^{3+}). The calcination of such layered structures leads to the production of mixed oxides with a fine metal dispersion, relatively large surface areas and tuned physicochemical characteristics (chemical composition, porosity, acid-base and redox properties) [3].

In this work, we studied the activity of mixed oxides with basic or acid-base properties derived from the thermal decomposition of layered double hydroxides (LDH) containing various metals, such as Mg, Al, Ni, Co, etc., aiming at a "mild" pyrolysis of biomass and higher yields of bio-oil with desired properties. The catalytic performance of these oxides in bio-oil composition and products yield was compared with the use of an acidic ZSM-5 catalyst and the use of a strongly basic MgO catalyst.

These basic and acid-base oxides (with acidity varying from 3 to 70 μmol NH_3/g and basicity varying from 50 to 250 μmol CO_2/g) facilitated different upgrading reaction mechanisms than those observed with acidic catalysts (Fig.1). Ketonization reactions converted acids to ketones and increased oxygen removal in the form of CO_2 (which is preferable than CO; Fig. 1a and Fig. 1b). In addition, basic catalysts are known to facilitate carbon-carbon coupling reactions, converting small gas molecules to larger ones that end up in the liquid product [4]. Increase in the acidity of the mixed oxides (ca. MgNiAl catalyst) seemed to enhance the production of aromatics and polycyclic aromatic hydrocarbons, a behaviour similar to that of the acid ZSM-5 catalyst.

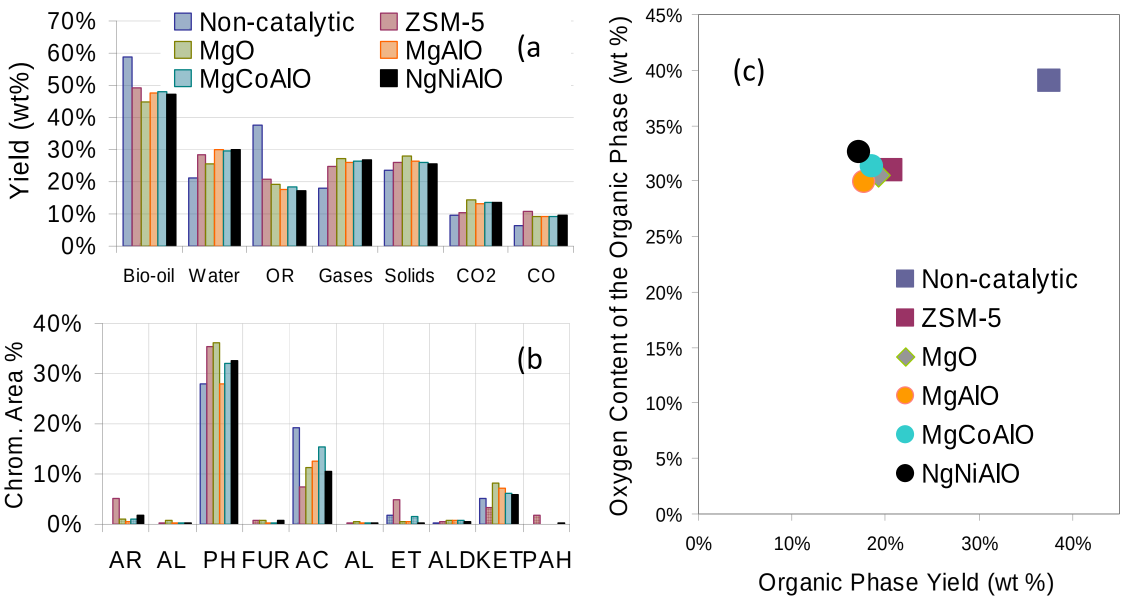

Fig. 1. (a) Product Yields, (b) GC-MS analysis of the bio-oil's organis phase and (c) organic phase yield versus oxygen content in the organic phase

Thus, tailoring of the physicochemical characteristics of the mixed oxides derived from LDHs structures can lead to the development of interesting catalytic systems for biomass pyrolysis producing a bio-oil with comparable oxygen content (Fig. 1c) to that derived by the use of commercial acidic ZSM-5 formulations via different reaction routes.

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CATALYTIC HYDROGENATION OF FURFURAL

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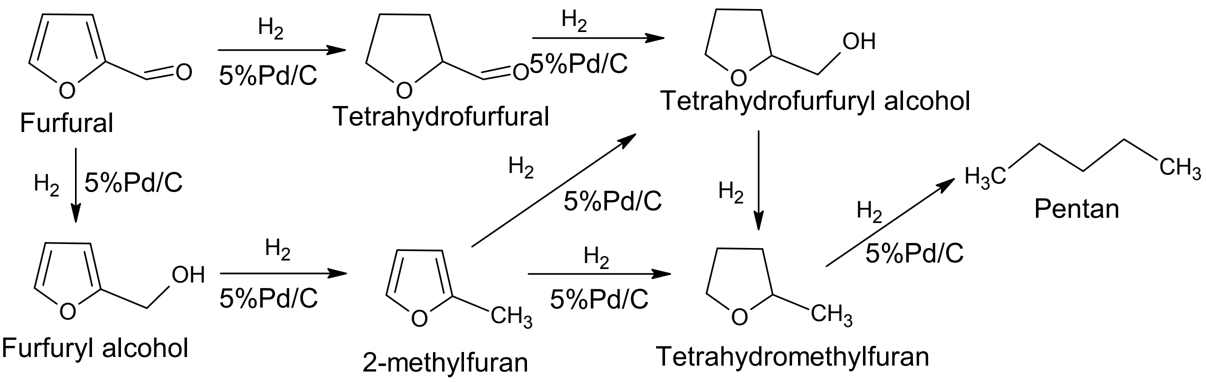
Rapid increase a non-renewable fossil source of carbon has led to global ecological crisis. This circumstance was powerful impact for the search of alternative renewable sources, which can be used in the energy sector [1-2]. Biomass has received considerable attention as a sustainable feedstock that can replace diminishing fossil fuels for the production of energy, especially for the transportation sector. This research is especially important in the transportation fuel sector which is strongly dependent on petroleum, a non-renewable fossil source of carbon [3]. Catalytic hydrogenation of furfural is an important industrial reaction for obtaining biofuels perspective and valuable raw material for chemical industry [4]. However, the existing catalysts don`t in able to deeply reduce of furfural to key products – furfuryl alcohol and tetrahydrofurfuryl alcohol. These products is mainly used for the production of dark thermostatic resins resistant to acids, bases and various solvents; liquid resins for galvanic bath-tube, and resins used for strengthening ceramics [5].

During the catalytic hydrogenation of furfural, various products may be produced, as shown in the following reaction scheme:



This work is devoted to furfural hydrogenation under H_2 over various carbon-supported Pd catalysts at H_2 pressure of 6 MPa, temperature range from 443 to 473 K. The main products were found to be furfuryl and tetrahydrofurfuryl alcohol.

The maximum conversion obtained over absorbent carbon 5 % Pd (5 % Pd/C) catalyst at 453 K and 6 MPa was 15.72 % with 87 % selectivity to furfuryl alcohol. Increasing conversion furfural from 0.68 % to 30.5 % was observed in the temperature range 443-473 K while the formation of furfuryl alcohol and tetrahydrofurfuryl alcohol selectivity decreased from 100 to 84 %. Furthermore, it should be noted increasing the temperature above 473 led to rapid furfural polymerization over surface active sites and catalyst deactivation. Thus, the effective hydrogenation catalyst furfural should have a minimal amount of acid-base centers to reduce polymerization processes.

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LACTULOSE ISOMERISATION OVER MAGNETIC NANOPARTICLES

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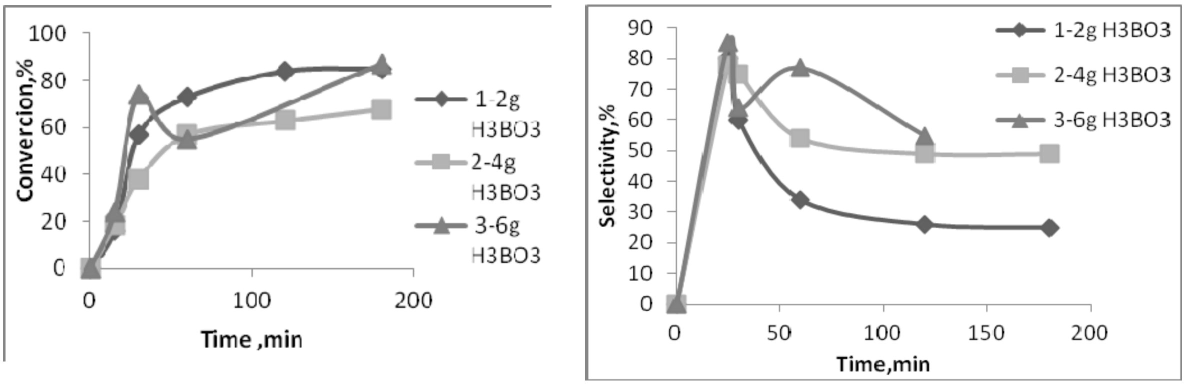
Lactulose is a synthetic ketose disaccharide that has valuable pharmaceutical application. Lactulose has considerable medical interest for the treatment of portal systemic encephalophathy and chronic constipation. It is also used as a Bifidus factor in nutrition and is known to be an important humanizing factor in infant formulas. This sugar has greater sweetness compared to lactose and therefore it can be used in baking and confectionery applications.

To carry out the experiment the solutions of lactose with pre-calculated mass concentration were prepared. The reaction was performed in Parr Series 5000 Multiple Reactor System (six blocks) in a nitrogen atmosphere. While carrying out the experiments such reaction condition as the ratio of the catalyst mass to the mass of lactose taken was varied. During the reaction at given intervals samples were taken, the sample volume was 4 ml.

The reaction was carried out with the catalyst – boric acid supported on magnetic particles. The maximum selectivity was 87 % at 70 % conversion. The increase in conversion results in considerable decrease of selectivity up to 30-60 %. The most conversion 80 % was observed in experiment 1 (Fig. 1). The increase in nanoparticles content leads to the increase in conversion and selectivity.



a b

Fig. 1. Reaction curves for lactose isomerisation process
a) Conversion dependence on the time in the isomerization of lactose (at 60 °C, pH 7)
b) The selectivity versus time in the isomerization of lactose (at 60 °C, pH 7)

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CATALYTIC HYDROGENOLYSIS OF BIOMASS

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Cellulose is the world's largest organic raw material resource. It has been estimated that 10^{11}–10^{12} tons of cellulose are photosynthesized annually [1]. Being rich in hydroxyl groups, cellulose conversion to polyols is one of the most favored routes to cellulose utilization [2]. Cellulose is hydrolyzed into glucose which is then hydrogenated in the presence of catalysts to form sorbitol, mannitol and other C_5–C_2 polyols.

In this paper a new type of Ru-containing catalyst for the process of cellulose conversion into polyols is suggested. To stabilize ruthenium nanoparticles hypercrosslinked polystyrene of various types: HPS MN 270 without functional groups, HPS MN 100 functionalized by amino groups and sulphonated HPS MN 500 was used. The catalysts on the basis of HPS (1.0 % Ru/HPS MN 270, 1.0 % Ru/HPS MN 100 и 1.0 % Ru/HPS MN 500) were tested in the process of cellulose hydrolytic hydrogenation under the following conditions: t = 245 °C, P (H_2) = 60 bar, reaction duration 5 min, 0.028 mM Ru, 1 g cellulose, 30 ml H_2O. As a comparison the commercial catalyst 5.0 % Ru/C (J. Matthey, Materials Technology, U.K.) was used in the same process. The efficiency of the catalyst action was estimated according to the value of the total yield of hexitols (sorbitol and mannitol). The catalysts on the basis of HPS MN 100 and MN 500 were revealed to be inappropriate for the process discussed. The yield of hexitols made 12.7 and 1.8 % accordingly. The catalyst 5.0 % Ru/C also showed unsatisfactory result – 19.3 %. The use of 1.0 % Ru/HPS MN 270 resulted in the highest yield of hexitols (50.4 %).In this case cellulose conversion was 84.3 %. Physical chemical study of the catalysts showed that compared to other catalysts 1.0 % Ru/HPS MN 270 has larger specific area, narrow pore size distribution and active phase monodisperse particles with a diameter of 1.4 ± 0.3 nm. Triple use of the catalyst 1.0 % Ru/HPS MN 270 did not lead to any noticeable decrease of its activity. The analysis of the liquid phase by the method of atomic absorption spectrometry showed that the particles of the catalyst active phase do not leak.

In the future, hypercrosslinked polystyrene-supported Ru-containing catalysts can form the basis for highly effective catalytic systems for cellulosic biomass conversion into feedstock for chemical synthesis and production of second-generation biofuel.

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DEACTIVATION BEHAVIOUR FOR Pd-Ag/α-Al_2O_3 CATALYST IN ACETYLENE SELECTIVE HYDROGENATION PROCESS

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In the manufacturing of polymer grade ethylene, the removal of acetylene from hydrocarbon mixtures obtained in cracking plants is an important step. An elegant and widely used method is the catalytic hydrogenation of acetylene to ethylene. This process must be highly selective since the acetylene content has to be reduced to less than 5ppm, while higher ethylene losses are economically intolerable. Bimetallic catalyst systems and especially Pd-Ag/Al_2O_3 were established in the industry and are still used by today. As a result of the great economic relevance of palladium-based catalysts in industrial technologies, many investigations have been performed to study their physico-chemical properties in more detail and to reveal the various reasons for the loss of activity or selectivity [1-3]. The objective of the present research is to study the deactivation behaviour of the synthesized catalysts for acetylene selective hydrogenation.

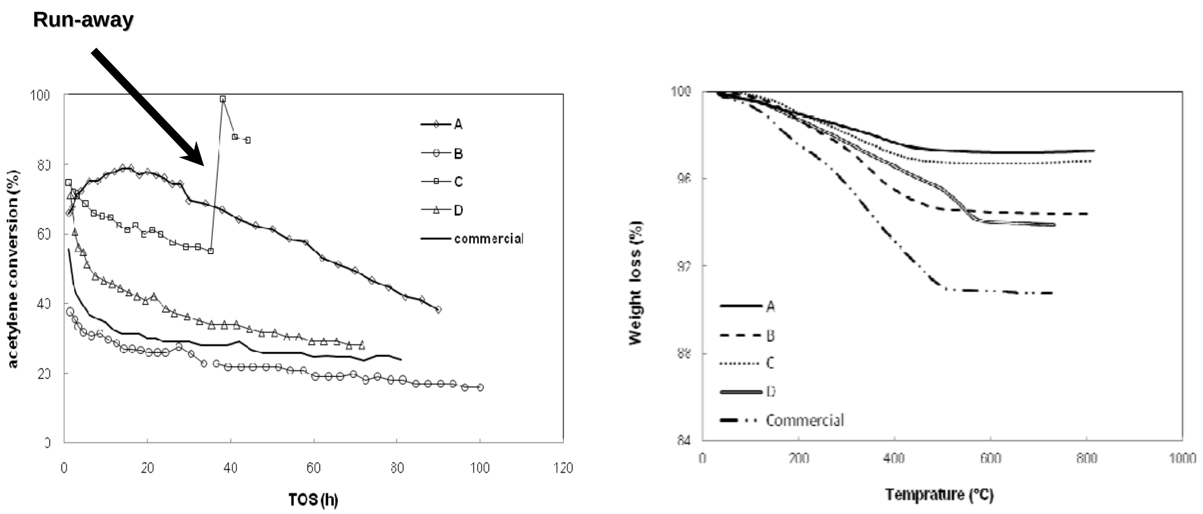
Bi-metallic Pd-Ag/Al_2O_3 catalysts were synthesized by wet impregnation (sequential and co-impregnation) of α-Al_2O_3 support with $PdCl_2$, $PdNO_3 \cdot 2H_2O$ and $AgNO_3$ solutions. XRD, BET, ICP and CO-chemisorption techniques were used for characterization of the fresh samples and TG/DTA was used to evaluate the amount of coke deposition on the used samples. The performance of catalysts for tail-end selective hydrogenation of acetylene was evaluated using a high pressure set-up and compared with that of a commercial sample.

Samples A, C and D were synthesized by sequential impregnation while co-impregnation was used for sample B. CO-chemisorption analysis revealed that Pd dispersions were 12.87 %, 4.76 %, 12.81 % and 9.66 % for samples A to D respectively.

Long-term tests of about 80 h were carried out in a fixed-bed reactor. The results are shown in Figure (1a) as acetylene conversion versus time on stream. The poorest results are observed for sample B prepared by co-impregnation method. On the other hand, this sample had the lowest Pd dispersion. It could be concluded that co-impregnation is not a suitable synthesis method for this catalyst as it gave a sample with low dispersion and consequently low activity.

In order to investigate the amount of coke deposited on catalysts, after each long-term catalytic run, samples were analyzed by TG/DTA method, the results of which are depicted in Figure (1b). The lower the weight loss of a sample, the lower is the amount of coke deposited on catalyst. The trend of graphs for all samples except D was the same indicating the presence of a similar type of coke. The amount of deposition was in the order: commercial > D > B > C > A

Coke deposition amounts over the spent catalysts showed a good correlation with catalyst activity (Figure (1a)), indicating that coke formation was the main cause of catalyst deactivation.



(a) (b)

Figure 1. Long-term behaviour of catalytic samples; (a) acetylene conversion at T = 60 °C, P = 10 bar, H_2/C_2H_2 = 1.5, (b) TG graph for used catalysts

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SIMULATION OF AN INDUSTRIAL HYDROTREATER FOR HGO-VEGETABLE OIL CO-HYDROPROCESSING

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The ever increasing energy consumption in the last decades has led to the development of new techniques for the substitution of fossil fuels in the transportation sector. An alternative route for the production of bio-components resembling diesel is hydrotreatment (HDT) of vegetable oils and their derivatives [1], [2], [3], [4]. This is a promising process that can partially substitute diesel fuel. Hydrodeoxygenation of vegetable oils can occur at even milder conditions than hydrodesulphurization of gasoil. Thus, the necessary infrastructure already exists in refineries and no further or only limited capital investment is required. The scope of the present work is the study of the co-hydroprocessing of palm oil with gasoil under deep-hydrodesulphurization conditions over a commercial $CoMo/Al_2O_3$ catalyst for the simultaneous desulphurization of gasoil and deoxygenation and conversion to diesel-like hydrocarbons of the vegetable oil. Technical kinetic equations for HDS and hydrogen consumption were derived from the treatment of experimental data, and they were used for the simulation of the operation of an industrial hydrotreater.

Experiments were carried out in an integral, isothermal, laboratory bench-scale trickle-bed reactor. The inner diameter of the reactor tube was 2.54 cm and its total length was 47.5 cm. The catalyst used was a commercial $CoMo/Al_2O_3$ one in cylindrical form with a mean diameter of 1.4 mm. The active section consisted of 40 g catalyst mass, while 50 g of fine SiC particles with a mean diameter of 0.25 mm were used for the dilution of the catalyst bed for better catalyst wetting, avoidance of liquid maldistribution and application of the plug flow assumption in bed mass balances. Before and after the catalyst bed, impeded zones from glass spheres were loaded in order to secure uniform liquid distribution and support the catalyst bed. The liquid feeds tested were mixtures of palm oil 5 and 10 wt% in gasoil (0.55 wt% S), along with neat gasoil. The experiments were conducted at three temperatures 330, 350 and 365 °C and total pressure 33.0 ± 0.5 bar. The mass liquid flow rate was in the range of 34–56 g/h, corresponding to weight hourly space velocities (WHSV) 0.85–

1.4 h^{-1}. The flow rate of the hydrogen feed was 20–22 Nl/h. The assessment of the effect of the vegetable oil presence on this process is attempted by examining their effect on the desulphurization rates. Moreover, the hydrogen consumption is studied because this is an important parameter of the process economics while the hydrogen consumption reactions are exothermic and control the temperature profile along the length of the industrial fixed bed reactors.

For the simulation of the industrial hydrotreater, 120 tn of catalytic mass was considered while typical flow rates of hydrogen at the reactor inlet and the quench zones were taken into account. The simulations were performed at WHSVs within the range of 0.8-2.4 h^{-1}, for inlet reactor temperatures up to 370 °C and for vegetable oil content in the feed within the range of 0-10 %. Profiles of the sulphur content, temperature and hydrogen consumption along the industrial reactor were calculated. The effect of the operating parameters such as the vegetable oil content in the feed, the inlet temperature and WHSV, on the hydrodesulphurization, the hydrogen consumption and temperature was also tested. The conditions that a deep hydrodesulfurization was achieved (sulphur content in product less than 10 ppm), when vegetable oil is co-hydroprosseced, were calculated. According to the simulation results the vegetable oil is fully converted through the first two beds, depending on the inlet temperature and WHSV. The hydrogen consumption increased about 1.7-2.2 Nl_{H2}/Kg_{feed} and the temperature increased about 1.0-1.5 °C per 1 % of the vegetable oil content in the feed, within the whole range of WHSVs and inlet temperatures tested.

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CATALYTIC SYNTHESIS OF FUEL COMPOUNDS FROM ORGANIC RAW MATERIALS

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Biomass has received considerable attention as a sustainable feedstock that can replace diminishing fossil fuels for the production of energy, especially for the transportation sector, which is strongly dependent on petroleum, a non-renewable fossil source of carbon [1].

Among the various fuels-from-biomass investigated, fatty acid methyl ester biofuels obtained by transesterification of triglycerides from natural oils and fats with methanol have received considerable attention. However, there is growing concern about the fungibility of these fuels with conventional petroleum-derived diesel due to the oxidative and thermal instability. Various processes including hydrogenolysis, decarbonylation, and decarboxylation have been proposed to transform the biodiesel into the hydrocarbon based fuel [2].

The most promising way of biofuel obtaining in the form of saturated hydrocarbons from the oxygen-containing compounds is hydrodeoxygenation. Biofuel produced via hydrodeoxygenation is usually called the second generation of biodiesel or “Green” diesel [3]. “Green” diesel has numerous advantages such as high cetane number, good low-temperature properties, superior thermal and storage stability, and materials compatibility in comparison with both petrol diesel and biodiesel [4]. Besides, “Green” diesel is the product which does not depend on raw materials origin, and is mixing easily with common diesel fuel.

Another perspective and valuable raw material for chemical industry and for obtaining of fuel components is furfural, which can undergo catalytic hydrogenation [5]. However, the existing catalysts do not allow reducing furfural completely to key products – furfuryl alcohol and tetrahydrofurfuryl alcohol. These products are mainly used for the production of various resins and solvents [6], however they can also serve as a source of linear hydrocarbons (i.e. pentane).

In this work the catalytic hydrotreatment of stearic acid, which is potential feedstock to produce the second generation of biodiesel, as well as furfural was investigated using both conventional Pd/C catalyst and new Pd-containing catalyst based on polymeric matrix of hypercrosslinked polystyrene (HPS) with different metal loading (from 1 % up to 5 % (wt.)). The processes were conducted in stainless steel batch reactors at variation of reaction temperature and hydrogen pressure.

It was revealed, that the main product of the reaction of stearic acid hydrodeoxygenation was *n*-heptadecane. The selectivity of the process (regarding to n-heptadecane) reached up to 98.8 % at 100 % of substrate conversion. As a result of investigation the possible transformation paths were proposed. The hydrodeoxygenation process was found to proceed via decarbonylation mechanism. Besides, cracking of hydrocarbon products was found to occur. Synthesized HPS-based catalysts were observed to be more stable and selective in comparison with commercial Pd/C catalysts.

In the case of furfural hydrogenation the main products were found to be furfuryl and tetrahydrofurfuryl alcohol. Conversion and selectivity (regarding to furfuryl alcohol) reached up to 35 % and 87 %, respectively. For Pd/C catalysts, the existence of acid-base centers and the increase of reaction temperature above 473 K were found to result in rapid furfural polymerization and catalyst deactivation.

Catalysts used in this investigation were characterized by low-temperature nitrogen physisorption, transmission electron microscopy, X-ray photoelectron spectroscopy, thermogravimetric analysis and differential scanning calorimetry.

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HYDRODYNAMIC MODELING EFFECTS ON MIXING IN SUBMERGED MEMBRANE REACTOR

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The aim of this work is to simulate mixing conditions in an anaerobic dark fermentation process devoted to biohydrogen production from the fermentation of organic waste (2nd generation biofuels). The experimental set-up is a submerged membrane bioreactor (SMBR) consisting of a stirred tank reactor equipped with a two-stage radial impeller and coupled with an external hollow fiber membrane module in a forced circulation loop. The final objective is to optimize the simultaneous production of volatile fatty acids (VFA) and bio H_2, which will constitute a key in the design of a two-stage bioreactor process able to convert lignocellulosic wastes into lipid biofuels.

Mixing plays a key role in SMBRs: impeller speed enables the suspension of organic waste, it homogenizes local concentrations, and enhances hydrogen desorption, but high speed may disturb the biological process. Also, the inlet of the membrane module must be placed carefully, avoiding the aspiration of suspended solids in the loop, but where VFA concentrations are maximum. The computational strategy consists of the combination 1D and 3D CFD methodologies [1], using a comparison between experimental data on RTD and mixing time based on a conductivity tracer technique with the simulations. Mixing experiments were carried out for both batch and fed-batch configurations to investigate the flow pattern in the different sections of the SMBR.

The experimental results show that laminar flow pattern was observed in the membrane unit and remained unaffected by the permeate flow. Conversely, turbulent flow was reported in the stirred tank reactor. In the batch configuration, mixing time decreased as the inverse of the impeller rotation speed. The value of the dimensionless mixing time was close to 30. Finally, the bioreactor was shown to correspond to a perfectly mixed tank with space time τ, connected to a laminar loop of space time $\tau/10$. CFD approach was able to predict the local velocity and concentration fields in the SMBR. The simulations using transient flow and k-ε turbulence model showed a fairly good agreement with the experimental data in the tank, using the transient evolution of concentrations for mixing analysis. This gave access to the critical features of local flow in the stirred tank and, subsequently, on the optimized position of the inlet of the membrane separation module.

As a conclusion, these findings confirm the potential interest of the optimization of the operating conditions of the anaerobic SMBR in terms of mixing, bio H_2 mass transfer and permeate flow, before continuous operation can be driven.

Keywords: submerged membrane bioreactor, CFD, mixing, hydrodynamics.

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CATALYTIC UPGRADING OF BIOMASS FAST PYROLYSIS OIL

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The bio-oil or also called pyrolysis oil is being produced via fast pyrolysis of lignocellulosic biomass (BFP) and can be utilized as source of valuable chemicals or as bio-crude for the production of hydrocarbon fuels. It contains mainly oxygenated compounds, such as phenols, ketones, furans, aldehydes, carboxylic acids, sugars and heavier oxygenated fragments [1]. Due to its composition, bio-oil is considered as a low quality fuel (low calorific value), it is acidic, not easily miscible with petroleum fractions, and unstable upon prolonged storage. The down-stream upgrading of bio-oil via hydrodeoxygenation or other catalytic process has been investigated over the last years [2]. However, another route for improving the composition and properties of the bio-oil is the catalytic fast pyrolysis (CFP) of biomass where the initially produced pyrolysis vapors are being directly converted into de-oxygenated compounds, mainly mono- and poly-cyclic aromatics, at the same time reducing the acids, ketones and other "undesirable" components [3-5]. Various acidic catalysts have been studied so far and ZSM-5 zeolite has been recognized as one of the most promising catalysts for de-oxygenating bio-oil and producing an organic fraction rich in aromatics [6-8]. The potential commercial application of CFP using ZSM-5 zeolitic catalysts has been also investigated on various types of pilot scale reactors, such as circulating fluid bed reactors [9].

Although promising results have been obtained recently on the CFP process, optimization of catalyst properties and reactor/process configuration is still necessary before full commercial exploitation. In the present work, we studied the effect of the textural, morphological and acidic characteristics of ZSM-5 on its catalytic performance in biomass fast pyrolysis. The effect of addition of transition metals or noble metals with specific (de)hydrogenation and oxidation properties has been also investigated at both bench-laboratory and pilot scale reactors. In general, the classical strongly acidic microporous ZSM-5 zeolite leads to increased production of water and coke and decreased yield of the organic fraction of bio-oil with parallel formation of aromatics (Fig. 1), pronounced decrease of oxygenated compounds (i.e. acids, ketones, etc.) and moderate decrease of phenolics. Introducing intracrystal mesoporosity or larger external surface area via reducing the crystal size, leads to enhanced catalyst reactivity accompanied with possible selectivity tuning, especially when small intracrystal mesopores (i.e. 2-5 nm) are utilized. Tailoring of the acidic properties or taking advantage of the metal function in the metal-modified ZSM-5 catalysts offers a tool for better control of the reactions that take place and the final product selectivity to desirable products such as aromatics or phenolics.

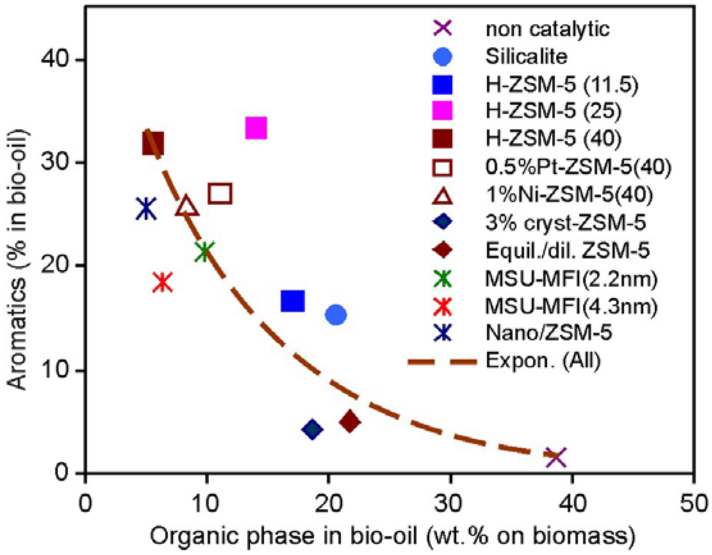

Fig. 1. Correlation between the concentration of aromatics and the yield of organic fraction of bio-oil

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SELECTIVE PRODUCTION OF SYNTHESIS GAS IN CATALYTIC MICROREACTOR

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Obtaining of synthesis gas from which subsequently receives the various useful chemicals is the first step in the processing of natural gas. Synthesis gas is a valuable intermediate of organic synthesis [1,2]. The study of Pt-, Ru- and Pt-Ru/2 % Ce/($\theta+\alpha$)-Al_2O_3 catalysts with different ratios of Pt to Ru in the selective catalytic oxidation of methane to synthesis gas at short contact times in microreactor and conventional flow reactor are presented. The activity of catalysts in the SCO of CH_4 was determined in flow set at atmospheric pressure in a quartz micro reactor with an internal diameter of 4.5 mm. Initial reaction mixture $CH_4 : O_2 : Ar = 1.6 : 0.8 : 97.6$, (%), at T = 1173 K, space velocity (V) = 9×10^5 h^{-1}, contact time (τ) = 0.004 s was supplied into reactor.

The study of oxidation of 1.6 % CH_4 in the presence of 0.8 % O_2 at 1173 K and short contact time showed that the process is completely (X_{CH4} = 100 %) to produce a synthesis gas without by-products ($H_2/CO = 2.0$) with high selectivity by H_2 and CO (100 %) only when the atomic ratio Pt : Ru = 2 : 1, 1 : 1 from the series of Pt : Ru catalysts with different ratios of elements after reduction of catalyst at 1173 K.

A similar Pt-Ru/2 % Ce/($\theta+\alpha$)-Al_2O_3 catalyst supported on the ceramic and metal block was tested in a conventional flow reactor with varying the reaction temperature, contact times (space velocity) and concentration of initial reaction mixture. It was established that 0.36 s (V = 1×10^4 h^{-1}) is the optimum contact time for the oxidation of methane to synthesis gas on 0.55 % Pt - 0.45 % Ru/2 % Ce/($\theta+\alpha$)-Al_2O_3 catalyst supported on the ceramic block of the honeycomb structure. 100 % selectivity by CO and H_2 at 63-80 % methane conversion was achieved by varying the concentration of CH_4 - from 4.4 to 34.0 %, O_2 - from 2.2 to 17.0 % at 1173 K. Methane conversion has increased to 91% in the case of adding the water vapor to the reaction mixture (steam-oxygen conversion).

Catalytic oxidation of methane was performed on 1,0 % Pt-Ru/2 % Ce/($\theta+\alpha$)-Al_2O_3 supported on the metal block, while maintaining the ratio of $CH_4 : O_2 = 2 : 1$ in the initial reaction mixture with varying the concentration of CH_4 at 1173 K, $V = 1\times10^4\ h^{-1}$, $\tau = 0{,}36$ s. It was shown that the CH_4 conversion is reduced up to 11.7 % while maintaining a maximum 100 % values for selectivity by H_2 and CO with the increase of initial concentration of methane from 4.4 to 34.0 %. However, 100 % conversion of methane into synthesis gas with an optimal ratio of $H_2/CO = 2.0$ was established when processing of 4.4 % CH_4.

Investigation of the effect of catalyst composition on desorption of hydrogen in different temperature regions was carried out. It is assumed that occurs the adsorption of hydrogen on Pt^o, Ru^o, Pt-Ru clusters on 2% Ce/(θ+α)-Al_2O_3 as two molecular forms H_2ads and H_2^+ads, Hads and atomic hydrogen (T_{des} > 873 K) associated with the oxidized Pt and Ru ions, which form chemical compounds with Al_2O_3 and $CeAlO_3$ upon heating. This conclusion is also confirmed by transmission electron microscopy studies of catalysts. Further quantum chemical calculations were carried out to determine the ability of platinum-ruthenium clusters to activate a molecule of methane. It has been shown that the interaction of CH_4 with Ru-Pt clusters has a complicated character, since there is no unambiguous correlation between the energy of interaction, transfer of electron density from methane molecules on cluster and lengthening of the C-H bond. However, it is assumed that the Ru-Pt catalysts with atomic ratios (1:1) are more optimal catalysts according to the calculation, which agrees with experimental results.

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MICRO REACTOR SYSTEMS FOR HYDROGEN PRODUCTION BY ETHYLENE GLYCOL REFORMING

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Hydrogen production and its utilization, as a fuel or for energy production, seem to be a promising way to minimize the actual dependence on fossil fuels. This dependence should be gradually decreased not only owing to the fossil fuels depletion, but also because of the environmental problems that entail their utilization. In this sense the use of bio-renewable organic sources, such as polyalcohols, seem to be a promising and sustainable alternative in an intensified process through the use of a micro reactor [1].

Figure 1: *Micro reactors*

In this work the validation of ethylene glycol (EG) as raw material for hydrogen production by steam reforming (SR) and oxidative steam reforming (OSR) reactions was studied using microchannel testing reactors. The experiments were carried out at a steam to carbon ratio (S/C) of 4.0, several temperatures and atmospheric pressure. Rh based catalysts were designed using α-Al_2O_3 modified with different contents of CeO_2 or La_2O_3 oxides as their supports. Different temperatures were tested for SR experiments (725, 675 and 625 °C) at a volume hourly space velocity (VHSV) of 200 NL/h·g_{cat} as well as different VHSV (300 and 100 NL/h·g_{cat}) at a constant temperature of 675 °C. In the case of OSR experiments, only the effect of the VHSV was studied at 675 °C. A long term experiment was carried out with the 2.5Rh/20Ce catalyst which lasted over 115 hours in stable conditions. The catalysts physicochemical properties were studied by their characterization using the following techniques: N_2 physisorption, ICP, TPR, H_2 chemisorption, TEM, XRD and XPS.

Almost full conversion was achieved by all tested catalysts and only the 2.5Rh-10Ce catalyst obtained a bit lower conversion at the temperature of 725 °C. Attending to the hydrogen selectivity plot, the 2.5Rh-cm catalyst obtained lower values at the highest temperature which can be related to the by-product formation measured. As far as the remaining catalysts are concerned, very similar hydrogen selectivity values were measured.

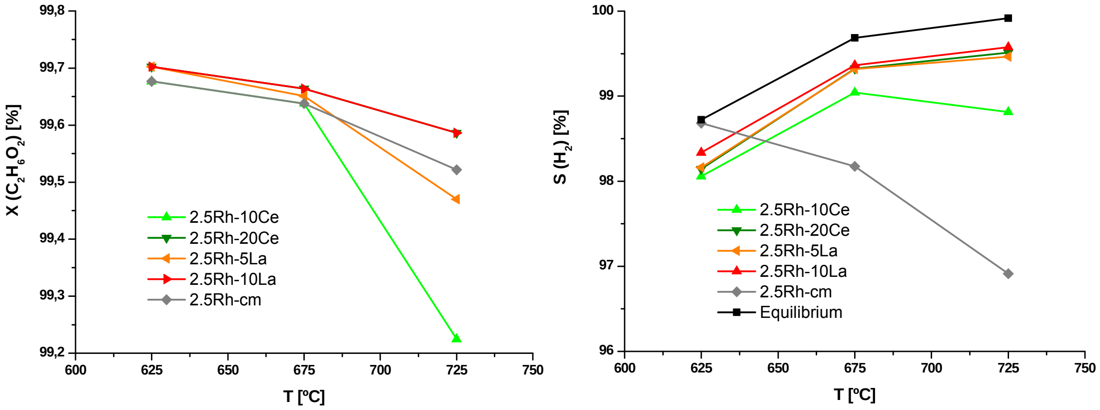

Figure 2: Ethylene glycol conversion (left) and hydrogen selectivity (right) vs. reaction temperature as obtained for all catalysts investigated under the conditions of SR; VHSV of 200 L/(g_{cat} h)

Almost full ethylene glycol conversion was achieved by all tested catalysts also for the OSR process. Attending to the existing small differences, the 2.5Rh-cm catalyst achieved a bit lower conversion, and really small differences can be observed among the catalysts containing additives. In addition, only the 2.5Rh catalyst was smoothly affected by the VHSV increase.

As a conclusion, the 2.5Rh-20Ce catalyst showed the highest surface area and pore volume. In addition, the reduction peaks measured for this catalyst were the highest ones at the highest temperatures. This can be due to stronger metal-modifier and support-modifier interactions. Regarding the activity results, conversions close to the ones predicted by the equilibrium were achieved by all tested catalysts for both SR and OSR processes. For the OSR process the addition of modifiers improved the stability and the hydrogen yield. For the conducted long term experiment under SR conditions, at a VHSV of 200 L/(g_{cat}h) and the lowest reaction temperature of 625 °C, the 2.5Rh-20Ce catalyst was selected. The results showed complete conversion and a constant and stable process during 115 h.

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PRESSURE DROP AND MASS TRANSFER IN THE STRUCTURED CARTRIDGES WITH FIBER-GLASS CATALYST

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Novel catalysts, supported on fiber-glass woven support [1] has attained a lot of attention recently both from theoretical and applied points of view. Recently, the various structured cartridges were proposed for packing of the glass-fiber catalyst (GFC) fabric were proposed [2]. Such cartridges are convenient for construction of catalyst beds of any size and geometry. At the same time, engineering properties of such cartridges (e.g. pressure drop, mass transfer) were not studied enough yet.

In our previous research [3] we have proposed the equation for the pressure drop in GFC cartridges. It provided good description of the experimental data, but for limited variety of cartridge designs. In the current study we have proposed new equation which may be applied for GFC cartridges of practically any shape and construction:

$$\Delta P = \zeta \frac{\rho v^2}{2} \frac{S_{SP}}{\varepsilon^3} L ,$$

$$\varsigma = 0.418\,\mathrm{Re}^{-0.153}$$

ρ – flow density, v – flow velocity, S_{sp} – specific external surface area of cartridge elements, ε – cartridge void fraction, L – cartridge length, ζ – friction factor, *Re* – Reynolds number

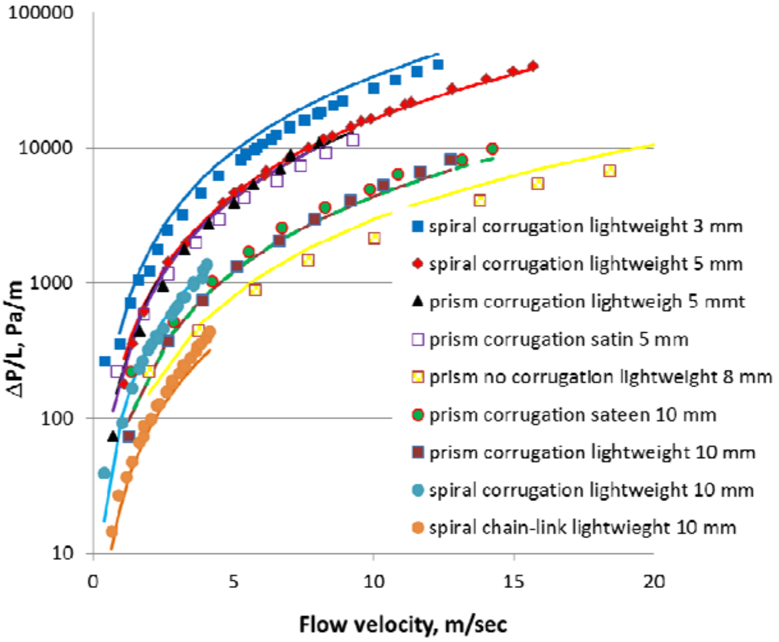

Fig. 1. Experimental (points) and calculated (lines) data on pressure drop of GFC cartridges

Fig. 1 demonstrates that good description of experimental data for ΔP is provided in wide range of channel size (3-10 mm) for cartridges of spiral and prismatic shape, with lightweight and sateen GFC fabric, with corrugated and chain-link structuring wire gauzes, as well as without structuring gauze.

Mass transfer properties of the GFC cartridges were studied in the reaction of deep oxidation of ethylbenzene in air flow at the Pt-containing (~0.07 % Pt mass) commercial GFC IC-12S111 (BIC, Russia). As confirmed by special experiments, the reaction performance at temperatures above 250 °C provided realization of pure external diffusion limitation regime. Experiments included variation of the cartridge geometry (variation of flow passage width from 3 to 12 mm) and air flow superficial velocity (0.1-0.4 m/sec). The obtained data may be described by criterial equation

$$Sh = 0.0695 \cdot Re^{0.93} \cdot Sc^{1/3}$$

$Sh=\beta d/D$ – Sherwood number, $Sc=\mu/\rho d$ – Schmidt number, β – external mass transfer coefficient, d – equivalent flow passage size, D – ethylbenzene diffusion coefficient, μ – air flow viscosity.

Such equation provides adequate description of the experimental data (Fig. 2) – mean absolute error of conversion calculation for the whole experimental array is ~5 %.

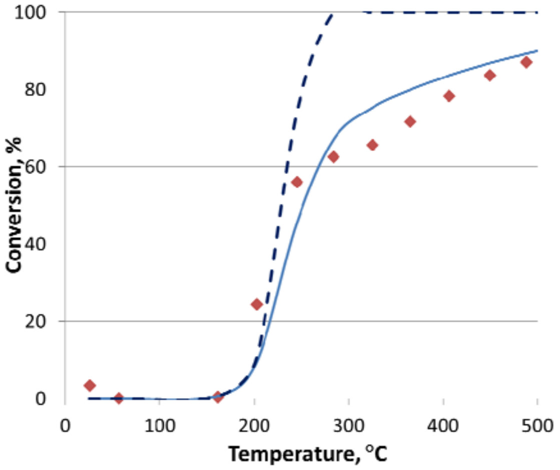

Fig. 2. Experimental data (points), calculations with (solid line) and without (dashed line) account of external diffusdion limitations for ethylbenzene oxidation

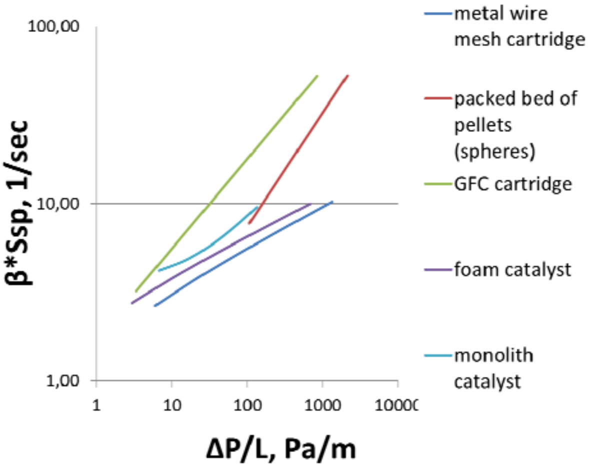

Fig. 3. Relationship between mass transfer efficiency and pressure drop under variation of the flow velocity for different forms of catalysts

Analysis of the relationship between value of the mass transfer coefficient and pressure drop is the universal criterion which may be used to compare different types of catalysts [4]. As seen from Fig. 3, GFC cartridges provide better mass exchange at lower pressure drop than all known forms of catalysts, thus highlighting the great engineering potential of structured fiber-glass catalytic systems.

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FERRUM-MOLYBDENIC CATALYSTS WITH USING OF HUMATE SILICATE IN THE QUALITY OF INERTIAL MATRIX FOR METHANOL OXIDATION INTO FORMALDEHYDE

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Now industrial receiving of formaldehyde is carried out in two ways: oxidizing dehydrogenation of methanol on the silver catalyst and methanol oxidation in the superfluity of air oxygen on the oxidic iron-molybdenum catalyst. The oxidic FeMo-catalyst used in world practice is effective until 400 °C after which sinters and is irreversible reduces the activity. It forces to carry out process in isothermal conditions, providing intensive cooling of the tubular reactor. According to it, now in a number of works there is a search of inert carriers in which the oxidic iron-molybdenum catalyst is dispersed.

We developed and tested in the process of methanol oxidation the new nanostructured iron-molybdenum catalyst on silicahumate.

Experiments made in the automated universal flowing catalytic reactor PKU-1. The simultaneous analysis of all components of steam-gas mixture carried out on a gas-chromatographic complex on the basis of the chromatograph CHROMOS GH-1000 (Development and production – JSC "SOLO" / JSC "Center "Hromosib"). IR spectrums of catalysts studied by means of IR-spectrometer Vertex-70 (Bruker). The thermogravimetric analysis is carried out on the derivatograph 1500D (Hungary).

In the catalyst the structuring and stabilization of a metal-oxide composite is carried out by means of the silicate humate received from oxidized coals of Kazakhstan and liquid glass (sodium silicate). The choice of this matrix is caused by SiO_2 properties to fast hardening that is convenient at a catalyst granulation. Besides, the part of SiO_2 in the process of the catalyst granulation reacts with molybdate ions and the microphase of silicon molybdate is formed in the process of annealing. As a result of researches it is established by us that after the oxidic iron-molybdenum catalyst with Mo/Fe ratio = 2,2:1 dispergating in the matrix of SiO_2 or Si–O–Al its activity decreases to level, characteristic for catalysts with Mo/Fe ratio = (1-1,5):1.

Optimum conditions of the process of silicate humate receiving are the following parameters: concentration of sodium silicate – 2 %, process temperature – 30-40 °C; duration of the process of silicate humate dealkalization – 30-40 minutes; dispersion of coal particles – from 0-3 to 0-5 mm.

In IR- spectra of the silicate catalyst the wide strip is observed at 1090 cm^{-1} which corresponds to antisymmetric fluctuation of bond Si–O in Si–O–Si in a tetrahedron; the strip 803 cm^{-1} which is responsible for symmetric fluctuations of a tetrahedron SiO_4 is also observed. Absorption strips in low-frequency area of spectrum from 668 to 614 cm^{-1} related to Fe–O in Fe_2O_3 group and the strip in the area of 820 cm^{-1} corresponds to Mo-O group. Besides typical peaks of silica-gel, there are strips of water absorption on spectrum. In IR-spectrum there is no the absorption strip corresponding to free silanol group that points to progress of humate sorption on these groups. The analysis of thermograms specifies that at the direction besides loss of hygroscopic moisture there is the humic component partial destruction assuming the decomposition of superficial –COOH and –OH groups. At that the continuous exothermic effect with two peak which corresponded to an oxidation of aliphatic groups and destruction of aromatic fragments of structure is observed on DTA curve at temperature increasing unto 500 °C.

During performance of work it is established that the catalyst possesses high activity in the process. Extent of methanol transformation fluctuates in the range from 92,3 to 99,9 %, a formaldehyde production – from 87,3 to 99,9 % at the process selectivity from 99,6 to 100 %. The main impurity are products of deeper methanol oxidation – formic acid (till 3,4 %), carbon dioxide (till 1,3 %).

Optimum conditions of methanol oxidation in the presence of silicate catalyst are: correlation Mo / Fe > 2, the methanol containing in the initial mixture CH_3OH-O_2-N_2 is 6,0-10,0 %, oxygen – 9,0-13 %, the speed of a gas stream is 34 ml/min. Extent of methanol transformation in optimum conditions is at the level of 99,8 % at 100 % selectivity of its transformation into formaldehyde.

MESOPHILIC ANAEROBIC FERMENTATION OF BIOMASS IN THE PRESENCE OF IRON COMPLEXES IMMOBILIZED ON HUMIC ACID

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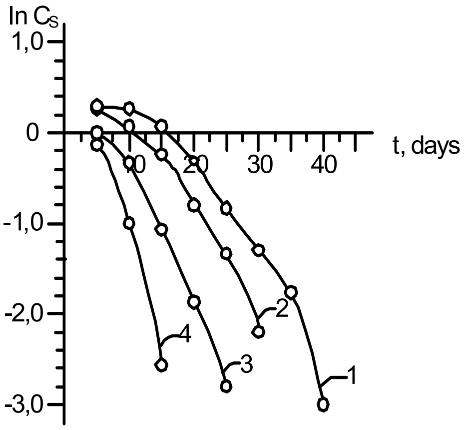
The findings on methanogenic bacteria recovery from the chicken manure, horse and cow dung are presented in the work. By means of the chromatographic analysis on the coming out of methane it is demonstrated that the best gas formation happened in a sample with the horse dung at the using of acetate as a part of a culture medium. The attribution of separated methanogenic bacteria on grounds of morphological and fiziological-biochemical evidences is carried out. Besides the results of an anaerobic methanoic fermentation of a chicken manure in the 35-40 °C temperature interval at pH 5,5-7,5 in the presence of iron complexes immobilized on the natural polymr – humic acids are introduced. The kinetic exploring demonstrated that in the explored conditions the biomass methane fermentation rate increased thrice in the presence of the elaborated catalysts – analogs of natural catalysts – ferments.

All progress of fermentation is limited by possibilities and state of methanogenic bacteria population, extremely responsive to temperature conditions and have small growth rate (1).

$$dS / d\tau = k[S][E]; \; dS / S = k \cdot d\tau; \; \ln S = k \cdot \tau \qquad (1)$$

Semilogarithmical anamorphoses in coordinates of the first order are introduced in figure 1. Two sectors with a different declination pointed to two slow stages proceeded with different constants are marked on the dependences $\ln S = f(\tau)$.

In the beginning of process, when the quantity of substrate exceeded quantity of microorganisms, accumulation of them during fermentation determined rate of methane producing. In the end of experience the rate dropped because of exhausting of raw. On the basis of what it is possible to conclude that anaerobic destruction of biomass is effected through hydrolysis of substrate followed by stages which could be viewed as processes of the pseudo-first order.



in the presence of the 1% humate applicated on $FeSO_4$: 1 – 1%, 2 – 3%, 3 – 5%, 4 – 7%

Figure 1 – Semilogarithmical anamorphoses of a mesophilic anaerobic fermentation of biomass

The elevation of iron humate positively affected to constants of the first order as for the stage of microorganisms accumulation during fermentation and at the stage of anaerobic destruction of biomass.

The kinetic constants of a first and second stage equalized in the optimal conditions at C_{FeSO_4} = 5-7 %.

MICROSPHERICAL SORBENTS FROM TECHNOLOGICAL RAW OF THERMAL POWER STATION – CATALYSTS OF SULFUR DIOXIDE OXIDATION BY OXYGEN

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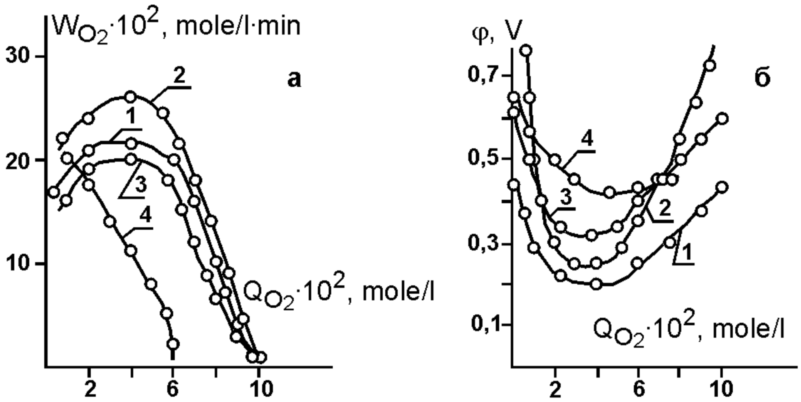
Ash dumps of coal thermal power stations – a classic example of that, what geologists termed as a technogenic deposit. These are aggregations of mineral matter on the ground surface formed as a result of reworking of useful minerals (in our event – combustions of coal) and applicable by quantity and quality for cost-effective industrial application. We discover that the modified microspheres of furnace dust of the thermal power station worked on the coals of the Ekibastuz deposit are high-activity catalysts of SO_2 oxidation by oxygen in water solution.

Na_2SO_3 was used in the quality of a source of SO_2 inasmuch in experimental conditions at pH = 10-12 in water solution SO_2 is in the shape of SO_3^{2-}, and reaction (1) was actually studied.

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \qquad (1)$$

Fractional conversion of Na_2SO_3 attained 100% in optimum conditions, maximum oxygen saturating rate are equal to 6,8 ml/minutes.

Typical conversion curves in coordinates $W_{O_2} = f(Q_{O_2})$, where W_{O_2} – oxygen saturating rate in mole/l·min.; Q_{O_2} – quantity of absorbed oxygen in mole/l, as well as potentiometric curves in coordinates $\varphi = f(Q_{O_2})$, where φ (V) – potential of a platinum electrode in relation to calomel half-element introduced in figure 1. Initial redox-potential of the system Na_2SO_3-Al-O-Si-Fe-MH-H_2SO_4-H_2O (where MX – the modifying component) are in the interval 0,8-0,45 V, at that $d\varphi / C_{Na_2SO_3} < 0$, $d\varphi / dC_{Na_2SO_3}$ passes through maximum, $d\varphi / dT > 0$. These results allow to suppose that the pair Fe^{3+} / Fe^{2+} are the redox-determinative pair in this case. The conversion curves in coordinates $W_{O_2} = f(Q_{O_2})$ (fig. 1a) and potentiometric curves in coordinates $\varphi = f(Q_{O_2})$ (fig. 1b) demonstrated that with the Na_2SO_3 introducing in system the redox-potential sharply pass in the cathode field on 0,5-0,25 V, and oxygen absorption begins at once. The jump of potential depended on a correlation of components in system. In the course of experiment the potential returns in anodic field, in optimum conditions – to a reference value that pointed that fact that products of the reaction don't modify structure and composition of the catalyst and works with high stability in the given conditions.



T = 313K, P_{O_2} = 0,1 MPA;
a, b: $C_{Na_2SO_3}$ = 0,2 mole/l,
$C_{H_2SO_4}\cdot 10^2$ mole/l: 1 - 1,75,
2 - 3,50, 3 - 5,25, 4 - 7,0

Figure 1 – The sodium sulfite oxidation by oxygen in the presence of microspherical aluminosilicates

In out-of-limit conditions the potential remained on certain value, without return to initial, the disorder of stoichiometry of reaction (1) observed for the same conditions (the curve 4 in fig. 1a). Chemical composition are introduced by oxides of aluminium, silicon, iron (4,5-5 mass. %), calcium and titanium.

The microspheres sizes varied from 20 to 250 microns, ultimate compression strength – 150-280 kg/sm^2, Moos' scratch hardness – 5-6. We used spectroscopic methods for analysis of microspherical compositions. The infrared spectrum of aluminosilicate catalyst are introduced. The intensive absorption band in the frequencies interval 1200-1000 cm^{-1} are observed. This frequency interval are characteristic for groups Si–O, Al–O, Si–O–Al: ν 1100, 1066, 1022, 1050, 900 cm^{-1}. Absorption bands in a low-frequency range of spectrum from 668 to 614 cm^{-1} related to Fe-O in group Fe_2O_3.

Data of EPR demonstrated that iron (3+) is basically in two shapes: single ions Fe^{3+} in a glass and in particles of magnetic-ordered phase of spinel structure with size 30-50Å at the content of iron 3-4 mass. % Fe_2O_3. At the content of iron in the cenospheres below 2 mass. % Fe_2O_3 iron (3+) is predominantly in the form of single ions. Thus, the microspherical aluminosilicate nanostructured iron-containing composite which was tested in the quality of a sorbent of NO_x and SO_2 and after modification in the quality of SO_2 oxidation catalyst are elaborated.

KINETICS OF FREE FATTY ACID ESTERIFICATION IN USED COOKING OIL USING ION EXCHANGE RESINS AS CATALYST

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A kinetic study of free fatty acid esterification was carried out using Purolite D5081 as a catalyst. Esterification reaction was carried out using 1.25 % (w/w) catalyst loading, 6:1 methanol to oil feed mole ratio, 350 rpm stirring speed and reaction temperatures ranging from 323-335 K. The experimental data from the esterification reaction were fitted to three kinetic models: pseudo homogeneous (PH), Eley-Rideal (ER) and Langmuir-Hinshelwood-Hougen-Watson (LHHW) models. A built-in ODE45 solver in MATLAB 7.0 was used to numerically integrate the differential molar balances describing the concentration of FFA in the system. The influence of temperature on the kinetic constants was determined by fitting the results to the Arrhenius equation. It was found that the forward rate constant, k_f increased with an increase in reaction temperature. However, the increase of reverse rate constant, k_r values with the increase in reaction temperature are considered to be very small and this indicates that the reverse reaction (hydrolysis process) hardly took place in the reaction. The activation energies for the esterification and hydrolysis reactions were found to be 53 and 107 kJ mol^{-1}, respectively. These results proved that the hydrolysis reverse reaction requires more energy to occur as compared to esterification reaction, hence validated the proposed model.

Keyword: *biodiesel, free fatty acids, esterification, biodiesel, heterogeneous catalyst, kinetics, used cooking oil.*

HIGHLY EFFECTIVE ION – CLUSTER MECHANISM OF SELECTIVE EXCITATION OF ARGON LEVELS IN JETS OF MIXTURES

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The excitation of argon radiation in condensing supersonic jets of argon mixtures with methane, monosilane and carbon dioxide upon electron-beam activation of the flow is investigated experimentally. It is found that, at certain condensation stages, the radiation intensity at some atomic argon lines increases anomalously. It is shown that the effect appears at the initial stages of condensation and is damped upon the formation of large mixed clusters.

For the first time the phenomenon of abnormal increase of intensity of radiation of separate lines of an atomic argon in a mix with monosilane, activated by an electrons, was revealed in [1]. The authors have connected the registered effect with a process of condensation in a flow. However use of the continuous expiration of a gas jet from a stationary source essentially has limited a level of achievable density in a jet and has not allowed to determine the borders of action of the effect. Application in the present work of pulse engineering of flow formations, overlapping in measurements of methods of an electron-beam spectroscopy and molecular-beam mass-spectrometry, and also large set of investigated gas mixes have ensured an opportunity of more detailed study of mechanisms of the found out effect.

The experiments are executed on a complex of experimental set-ups LEMPUS at the Novosibirsk State University [2]. The optical emission spectra excited by an electron beam in pulsed supersonic jets were measured in the range 0–1500 kPa of stagnation pressures P_0. The easily condensable methane, monosilane and carbon dioxide were 5 % impurity in argon jets. The intensities of the resonance emission lines of argon atom (549.6 nm) and ion (461.0 nm) were studied as functions of the stagnation pressure. From a comparison of given electron-beam (upper figure) and mass-spectrometric experimental data it is possible to as certain the following. In the some range of stagnation pressure P_0, limited from above and from below, at increase of P_0 the nonlinear growth of intensity of radiation of separate lines of atomic argon is observed at electron beam activation of a mix jet. This effect is observed in a mixes of argon with molecular impurities and is not observed in a pure argon, and also in a mix of argon with helium. In the investigated range of stagnation parameters the diagram of dependence of intensity of radiation of an ion Ar^+ from a current of an electron beam is linear (Fig. 1).

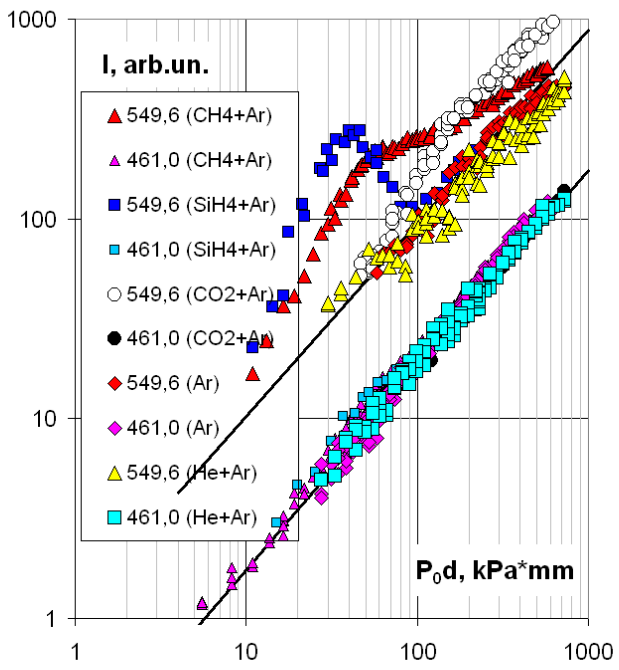

Fig. 1.

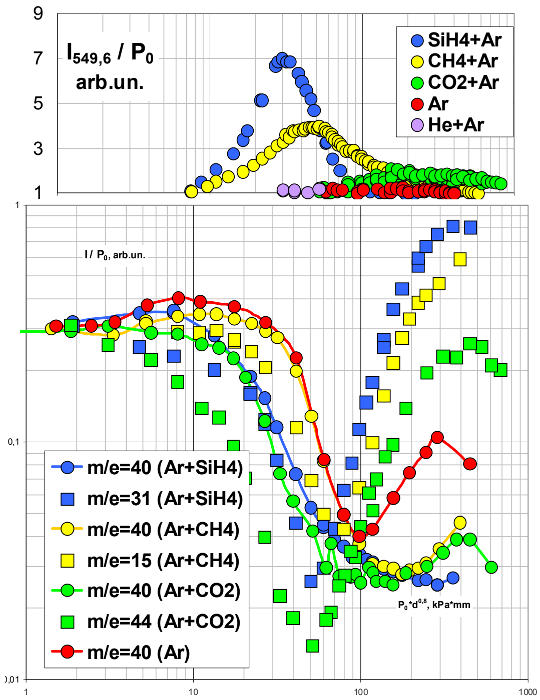

Fig. 2.

The excitation of levels of Ar is not quite selective: the abnormal effect is observed for the lines appropriate to the transitions from several levels, close located on energy. The beginning of effect correlates with the beginning of condensation in a flow, and its ending – with formation of large clusters in a flow (mass-spectrometry measurements, lower graph in Fig. 2). The exited condition with the large lifetime (more than 10 ms) participate in this process. In result in conditions of display of abnormal excitation of atomic argon the jet of a mix shines on all length. The process is characterized by very high efficiency.

Thus, in mixes of argon with methane, monosilane and carbon dioxide the process of abnormal excitation of atomic argon, caused by the highly effective ion – cluster mechanism of selective settling of levels of argon is observed.

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MATHEMATICAL MODELLING AND PILOT TESTS OF THE ADSORPTION-CATALYTIC PROCESS FOR ABATEMENT OF ORGANIC POLLUTANTS IN LEAN WASTE GASES

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Removal of volatile organic compounds (VOCs) from industrial waste gases is a very important problem of atmospheric air protection. Particularly there is an acute problem in cleaning gases with the very low VOC concentrations (below 0.1 g/m^3) as their treatment requires high energy consumption. In this respect the adsorption-catalytic processes, including adsorption of VOC at the catalyst surface at ambient temperature with periodical incineration of accumulated VOC at elevated temperature [1] are of particular interest. But as mathematical modeling showed they have some disadvantages, such as possible desorption of unoxidized VOC to gas stream during regeneration [2, 3], thus reducing purification degree. So, there is the need to develop new technological approaches aimed to minimize such desorption losses.

To confirm the results of mathematical modeling of considered adsorption-catalytic process the pilot tests were conducted. During the experiment, airflow with toluene or styrene vapors was fed into the reactor with adsorbent-catalyst.

The inlet airflow moves in the reactor through the catalytic bed vertically upward. The catalytic bed in the reactor consisted of CuCrAl oxide ICT-12-8 catalyst in the form of the Raschig rings with 10.5 x 10.5 x 2.5 mm size. The total volume of catalyst is 2.4 l, the diameter of catalytic bed is about 10 cm and the height is 36 cm. The heating coil for regeneration initiation was situated in the bottom of the reactor. The temperature was measured in the 11 points of the bed, both along the reactor axis and the catalyst bed border.

During the experiment, the adsorption-regeneration cycles were realized with variation of input VOC concentration, airflow velocity and heating time during the regeneration stage.

Fig. 1 shows the output VOC concentration dynamic at the adsorption stage. The experimental (solid) and model (dashed) curves are rather close.

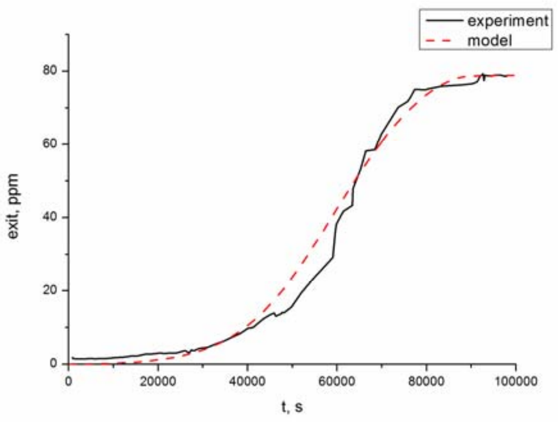

Fig. 1. The output VOC concentration. Adsorption stage

At the regeneration stage, it was found that in all range of varying parameters we have a higher purification efficiency with styrene (97-99 %) vapors than toluene (70-80 %). It comes from the better adsorption of styrene, so we have not such significant desorption losses. This fact may be accounted in the model by the greater value of the adsorption equilibrium constant in the styrene case.

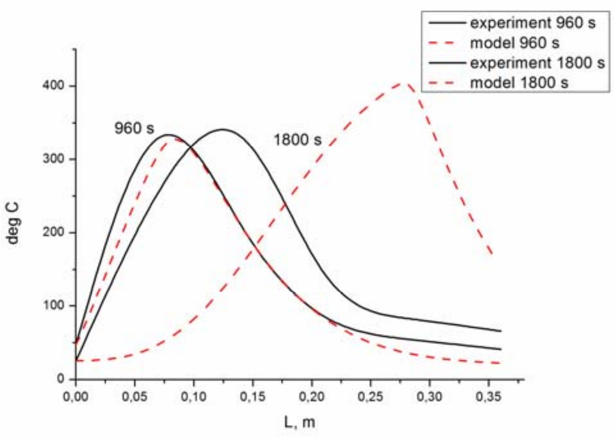

Fig. 2. The gas temperature profiles along the vertical reactor axis during the regeneration stage

Fig. 2 shows the gas temperatures profiles at the regeneration stage. We can see that the model gives generally adequate description of the experimental data, though some difference is seen in the value of maximum temperature and heat front movement velocity, especially evident in the end of regeneration cycle. This disagreement is most probably caused by the heat losses and heat dissipation in the reactor. This disagreement may resolved by account of the heat capacity of the reactor heat insulation and reactor body in the apparent reactor heat capacity.

In general, we can see a good agreement between experimental and modeling results. The pilot tests gave us an opportunity to ascertain some model parameters that we can use for the scale-up of the adsorption-catalytic process.

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LIQUID-SOLID REACTION KINETICS OF DIASPORIC BAUXITE DISSOLUTION IN BAYER PROCESS

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The qualified bauxite ore in China to produce Alumina through Bayer Process is almost disporic, containing multi-solid phases, among which Si and Al are primarily focused for their determining role in resource efficiency.

The leaching of alumina on diaspore bauxite with different alkaline solutions was carried out at various temperatures from 170 °C to 250 °C under the pressure from 0.4 to 6.0 MPa. And the reactive energy was measured as 56.2 kJ/mol.

The Kaolinite,as well as Illite in the bauxite was almost reacted when the diasporic was dissolved, therefore, the silicate in the leaching liquor would be removed. The supersolubility of silica in supersaturated aluminate solution and the sodium aluminosilicate precipitation nucleation mechanism from the clear solution were investigated The inferred activation energy (Ea) of the homogeneous nucleated reaction was 14.9 kJ/mol, and that of the heterogeneous 50.5 kJ/mol.

The separation of Al and Si in red mud from Bayer process in digestion with concentrated NaOH solution was investigated as well. The recovery rate of Al_2O_3 could reach 79.22 % and A/S in the final mud decreased to 0.30 even 0.15 under appropriate condition. In the improved mild hydro-chemical process, 87.8 % of Al_2O_3 and 96.4 % of Na_2O were extracted from the red mud at optimized conditions, and The Na_2O content in the residue could be reduced to less than 1 %.

PRODUCTION OF METHYLETHYLKETONE BY OXIDATION OF N-BUTENE. THE KINETICS OF REGENERATION OF THE HOMOGENEOUS CATALYST (Pd + HETEROPOLY ACID) BY OXYGEN, THE KEY STAGE OF THE PROCESS

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Methylethylketone (butanone, MEK) is an organic solvent widely used in many industries. We suggested a method of MEK preparation by the direct catalytic oxidation of *n*-butenes by oxygen via reaction (1) [1].

$$n\text{-}C_4H_8 \; + \; {}^1/_2\, O_2 \xrightarrow{\text{Pd(II) + HPA}} CH_3COC_2H_5 \qquad (1)$$

Aqueous solutions containing Pd(II) complex and various Mo-V-P heteropoly acids (HPA) are used as catalysts for this process. Since the reduced forms of HPA (H_mHPA) are able to be oxidized with O_2, therefore HPA's in the MEK-process are *reversible* oxidants. In the catalytic process (1), the vanadium atoms in the HPA solution undergo redox transformations ($V^V \leftrightarrow V^{IV}$).

Reaction (1) is performed via two stages (2) and (3) which are accomplished in *two* different reactors **1** and **2**, respectively.

$$ {}^m/_2\ n\text{-}C_4H_8 + HPA + {}^m/_2\ H_2O \xrightarrow{Pd^{2+}} {}^m/_2\ CH_3COC_2H_5 + H_mHPA \qquad (2)$$

$$H_mHPA + {}^m/_4\ O_2 \longrightarrow HPA + {}^m/_2\ H_2O \qquad (3)$$

Such two-staged method excludes the direct contact between $n\text{-}C_4H_8$ and O_2 and permits to obtain high selectivity (97–98%) in target reaction (2). After finishing reaction (2) in the butylene reactor **1**, MEK is distilled off from the reduced catalyst (Pd + H_mHPA). Next the catalyst is regenerated at t >100 °C, P_{O_2} = 2–4 bar in the reactor **2** via reaction (3) and again used in reaction (2). Consequently, reactions (2) and (3) compose the *catalytic cycle* of reaction (1).

Recently, we have begun to use modified (*non-Keggin-type*) Mo-V-P HPA solutions as a basis of the (Pd + HPA) catalysts in MEK-process [1]. Their composition is expressed by general formula $H_aP_zMo_yV_{x'}O_b$ (HPA-x'), where z > 1, and x' > 4. The HPA-x' solutions have high thermal stability (up to 180 °C) and therefore can be fast regenerated at elevated temperatures (160–170 °C) without decomposition.

Reaction (3), the catalyst regeneration, is a *key stage* that determines manufacturability of the total MEK-process. Kinetic peculiarities of this reaction are studied in the present work. Kinetics of target reaction (2) was studied in our previous work [2].

Study of oxidation of the reduced HPA-x' solutions by O_2 was carried out at 140–170 °C and stirring in a stainless steel autoclave equipped by a glass beaker.

After cooling of the regenerated solution, its redox potential E was measured, and the corresponding $[V^{IV}]$ value was determined using the calibration curve $E = f([V^{IV}])$.

The rate of reaction (3), W_3, continuously decreases over time. To determine an apparent order of this reaction with respect to V^{IV}, the W_3 values were calculated for various reaction times. The order, $n_{V(IV)}$, proves to be increased from the 1st, if $[V^{IV}]$ is higher than 0.8 M, to the 3rd at lowering V^{IV} concentration during reaction (3).

It was also found that reaction (3) is the first order with respect to oxygen in the pressure range 1-8 bar. Further increase in P_{O_2} does not change W_3.

At 140–170 °C, the apparent activation energy is 37.5 kJ mol^{-1}. These kinetic peculiarities may be written by the equation:

$$W_3 = k_0 \cdot P_{O_2} \cdot [V^{IV}]^{1-3} \cdot e^{-\frac{37.5}{RT}}$$

This kinetic equation was used for calculation of a perfect-mixing air reactor **2** in a pilot plant for the MEK-process. The technological scheme of this plant was shown and discussed in the previous work [2].

Our pilot testing of MEK-process showed that regeneration of the homogeneous catalyst (Pd + HPA) in the perfect-mixing reactor **2** was successful. This raises the prospect of the implementation MEK-process.

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COATING OF PARTICLES IN A FLUIDIZED BED REACTOR USING ATOMIC LAYER DEPOSITION

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Core-shell nanoparticles and other nanostructured particles have high potential in several practical applications, such as catalysis and energy conversion and storage. However, a hurdle in their utilisation is that typically large amounts of such materials are required. Gas-phase coating using atomic layer deposition (ALD, a variant of chemical vapour deposition) can be used to provide the surface of a particle with either an ultrathin conformal coating or a decoration of nanoclusters. ALD has its roots in experiments made in the Soviet Union in the 1960s and in Finland in the 1970s, but it only started to attract substantional attention in the 1990s [1]. Up to now, the majority of work reported in literature is aimed at coating stagnant substrates such as wafers. However, when applied to a fluidized bed, ALD offers an attractive way of producing nanostructured particles [2,3]. In this way, both coat micron-sized particles and nanoparticles can be coated. In the latter case, very dilute agglomerates consisting of a large number of primary particles are fluidized.

In the presentation, we will show that ALD applied to particles has a number of important advantages. First, it can be used to deposit a large range of materials on particles, since we can benefit from all the ALD schemes that have been developed for stagnant substrates. Recently, Miikkulainen et al. [4] gave an overview of all the known chemical schemes. Second, it is a technique that guarantees efficient use of the precursor. We will demonstrate this both with modelling and experimental results. Third, it is a technique with good scale-up potential. By already using a fluidized bed at the lab-scale, we pave the way for carrying out large-scale production in a similar device. Fourth, it is a technique that allows precise control of the structure and composition characteristics of the deposited material [5]. In the case of particle decoration (i.e., deposition of nanoclusters), a homogenous distribution of nanoclusters of similar size is obtained; see Fig. 1. In the case of deposition of a hermetic film, sub-nm control over the film thickness is achieved. Fifth, ALD applied to particles leads to high-quality (low impurities level) end-products with excellent properties. For example, we found that a Pt-TiO_2 catalyst with only 0.12 wt % Pt yields five times higher photocatalytic activity compared to native TiO_2 nanoparticles.

These five advantages make ALD applied to nanoparticles and micron-sized particles an attractive method to produce novel, nanostructured materials. We will give an outlook to the opportunities, but also to the challenges ahead.

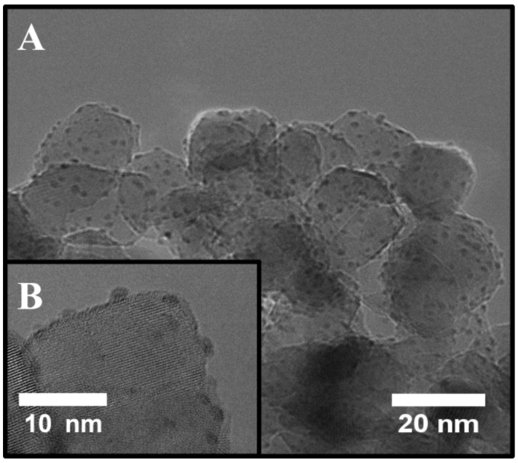

Figure 1. (A) TEM image of the Pt nanoclusters, deposited by ALD, decorating the surface of nanoparticles. The nanoclusters are typically 1-2 nm in size; TiO_2 nanoparticles contain 1.0 wt % of Pt. (B) A zoom-in of the decoration at the edge of the TiO_2 crystal

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PP-121

A CONCEPT OF POLYMER COMPOSITES FILLED WITH CARBON NANOTUBES PRODUCTION: USAGE OF BIOETHYLENE DERIVATIVES

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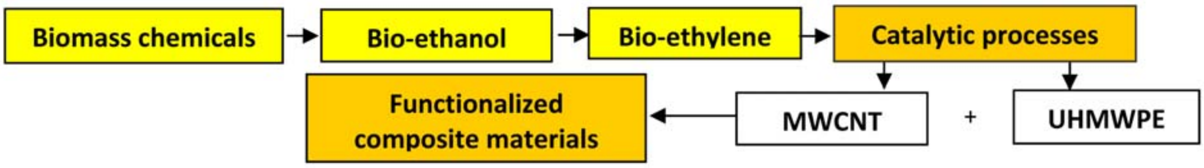
This is a world trend that polymer composite materials are widely applied now for numerous commercial applications. Expansion of the source of raw material used for their production by involving renewable bio-ethylene feedstock may reduce the consumption of petrochemical ethylene. Composite materials on the basis of multi-wall carbon nanotubes (MWCNT) and ultra-high molecular weight PE (UHMWPE) have much-better thermomechanical, tribological, flame-retardant, and electrical conductive properties even at low nanotube loadings [1-6] and can be employed for different applications, such as extreme conditions, mechanical engineering, medical instrumentation, sporting goods etc.

In this paper, a general concept of polymer composite UHMWPE-MWCNT production from bio-ethylene derivatives is presented.



Bio-ethylene is produced by catalytic dehydration of bio-ethanol [7] which can be obtained by fermentation of agricultural products. Carbon nanotubes with controlled properties are produced from bio-ethylene in the fluidized-bed reactor over different Fe/Co-based catalysts [8]. The methods of MWCNT-UHMWPE composites preparation includes *in situ* ethylene polymerization using the Ziegler-Natta catalyst complexes immobilized on the MWCNT's surface [9].

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VIRTUAL PRESENTATIONS

ELECTROMAGNETIC CATALYTIC REACTOR OF WATER TREATING FROM OILS AND HYDROCARBONS

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The problem of clearing of water resources from oil pollution is rather actual now. Annual total emission of mineral oil in the seas and oceans as a result of consequences of extraction and emergencies is estimated on different sources, including the National academy of sciences the USA on the average from 6 up to 8 million tons. Nevertheless, the problem of operative and effective liquidation of consequences of similar emissions is far from the decision in view of low efficiency of existing technological decisions, and including, absence high-efficiency the reactor equipment. The majority of known processes of clearing of water environments from oil pollution is based on use the methods of oxidation [1], flotation [2], absorbtion [3], and also methods of biological clearing [4]. Under the total characteristics, including productivity, a degree of clearing, simplicity of technological decisions, the economic and power efficiency, the mentioned ways are conditionally suitable for the decision of similar problems.

The clearing process of water environments from oil pollution and dangerous hydrocarbons aromatic and olefinic the lines, based on use is developed and tested in industrial scale as basic reactionary unit of the device of electromagnetic processing water environments. The principle of work is based on the phenomenon of acceleration microparticles association of mineral oil in conditions of interaction of an external variable magnetic field with ferromagnetic sorbent which particles have own constant magnetic field. As a result of such interaction there are intensive association processes the hydrocarbonic components being consequence of concentration in places of impacts of ferromagnetic particles of electromagnetic, thermal and mechanical energies. Further, passing through the polysorbtional layers, the integrated particles of hydrocarbons are absorbed much faster, than similar particles of smaller diameter.

Working parameters of a reactor electromagnetic association:

Initial concentration of mineral oil – 100 ÷ 1 mg/L
Final concentration of mineral oil – 0,5 ÷ 0,05 mg/L
Working volume of a reactor – 30 L
Productivity on initial water – Up to 100 m^3/h
Operating mode – Continuous
Working temperature – 0 ÷ 50 °C
Working pressure – 0 ÷ 1,0 MPa

Besides direct use of the specified installation during water treating, there are variants of her modification, allowing her use in a number of adjacent tasks of oil extracting and processing. In particular, her use is planned during preliminary processing, tars, bitumen sand, in manufacture of dyes, etc. spheres.

The general distinctive characteristics of installation:

1) High efficiency;
2) Stability to a high level of pollution of communications (a rust, sand, fine stones);
3) Standardization of a design with an opportunity of fast replacement of elements (a grid, a pipe, nozzles and so forth);
4) Absence of a problem of deterioration in case of use the plastic case of a reactor.

Installation has passed industrial tests in a zone of the Caspian pool: Russia, Republic Dagestan.

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KINETIC STUDIES FOR THE CHELANT ASSISTED EXTRACTION OF HEAVY METALS FROM SPENT CATALYST

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Environmental concerns associated with the elevated metal concentrations in environment can be colligated with increased consumption of metal ores in the industry which also cause generation of large amount of industrial waste with significant content of heavy metals present in it. Chelant assisted extraction of heavy metals from spent catalyst is a widely known illustration of solid-liquid extraction process which includes formation of metal-chelate complex and transportation of the complex from solid surface into aqueous phase. Mass transfer limitation and effects of process parameters have been investigated extensively in the available literature to design and optimize a sustainable chelant assisted green approach for metal extraction [1, 2]. However, extraction kinetics associated with the metal extraction form spent catalyst using chelation concept has not been explicated sufficiently in literature.

In the present study, efforts have been made to investigate the extraction kinetics of a diffusion controlled non-catalyzed chelant assisted metal (Cobalt and Molybdenum) extraction process. Various empirical models (Peleg Model, Elovich Model, Parabolic Diffusion Model, Weibull's Distribution Model) were employed to look into the possible kinetics [3] and to suggest an optimum empirical kinetic model based on its accuracy of fitting the experimental data obtained at different operating conditions. Effect of molar concentration of chelating agent, solid to liquid ratio and reaction temperature was investigated to extract heavy metals at stirring speed of 400 rpm, particle size 100-300 μ and reaction pH 10. Error analysis was performed by calculating the linear correlation coefficient (R^2), root mean square error (% RMSE) and average relative error (% ARE).

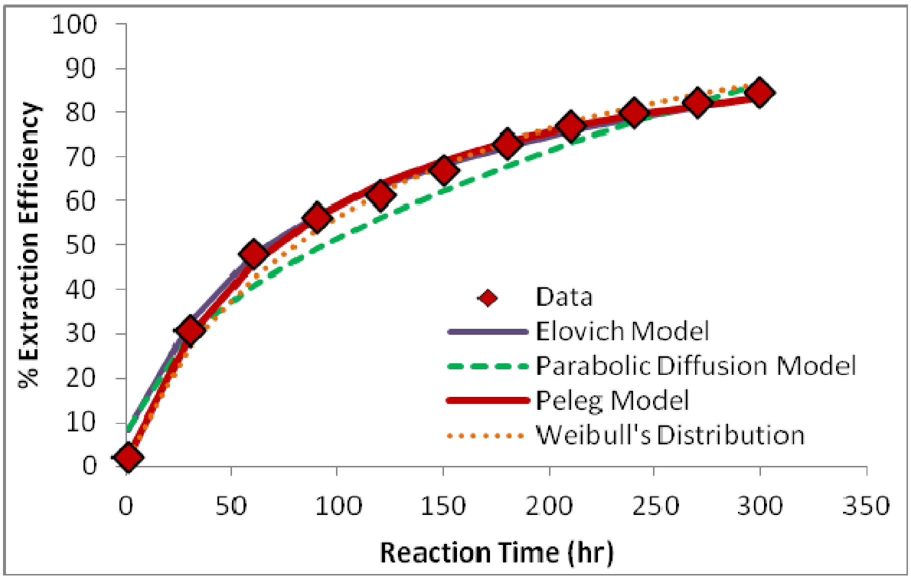

Figure 1: Comparative analysis of different empirical models for extraction kinetics of Mo (Reaction temperature 120 °C, S/L = 1:15, molar conc. of EDTA 0.4 M, particle size 100-300 μ and stirring speed 400 rpm, pH 10)

Figure 1 illustrates the concordance between experimental data and calculated values of the extraction yield for the various empirical model. All empirical models gave a good fit to the experimental data (root mean square error (RMSE) ±10 %, Average relative error (ARE) < ±10 %, linear correlation coefficient (R^2) > 0.95), however, Peleg Model, having the lowest value of RMSE (±2.07 %), ARE(±0.967) and the highest value of R^2 (0.9958) was selected as the best model for the metal extraction kinetics. Thermodynamic parameters were also evaluated for the metal extraction process which confirmed the the endothermic diffusion controlled process [4] with an activation energy 24.8 Kj/mol.

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MATHEMATICAL DESCRIPTION OF MOISTURE TRANSFER IN A VIBRATED BOILING LAYER

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In 2010 we presented the developed vibrating multifunctional chemical reactor, allowing to carry out in a single reaction volume without depressurization and contact with the environment almost all chemical processes [1]. As a further development of this trend the constructive solution of vibrating reactor, which allows to obtain monodisperse fraction of crystalline product of desired particle size distribution was presented [2]. Essence of the new process for separation of suspension into fractions is that the polydisperse suspension is fed not on a single filtering baffle, whose mesh size is smaller than the smallest particles trapped and set on a vibrating filter partition, arranged with clearance one above the other in order of decreasing size cells. This lets successively extract solids from entering suspension flow decreasing its dispersion. Since the developed method is not subject to the ordinary laws of filtration it was necessary to develop mathematical description of establishing dependence of residual moisture content of precipitate from the main vibration parameters. A mathematical description of moisture transport in vibrating layer was obtained on the basis of the Navier-Stokes equations for one-dimensional flow of a viscous incompressible fluid based on a number of assumptions. The effluent from the feed zone of suspension monodisperse precipitate layer on each of partitions presents a pore structure of unconsolidated winding with pores penetrating the layer in all directions. Under the action of vibration occurs its periodically sealing and loosening, and, consequently, the change in time and space, of characteristic dimensions of the elementary pores. They can vary from maximum value at the cubic packing of particles to minimum corresponding the most dense hexagonal packing. Liquid phase that fills the pore space of sediment layer, held there by capillary cohesion and surface tension and can theoretically change its state by action of vibration from original rope to capillary – fragmented. We will present real layer of precipitate in the form of plurality of vertical locally capillaries filled with liquid and immersed in the lower ends. By this the curvature of the lower meniscus is equal to infinity, thus simulated free, not constrained by edge effects nature of liquid outflow from capillary. Because sediment layer on each of partitions is monodisperse, particle size of solid phase is known and corresponds to a size of its cells, the radius of capillary model we take to be 0.15 of radius particles of solid phase, which corresponds to minimum size at elementary pores of the densest packing of particles. The initial height of liquid in the capillary is conventionally assumed equal to height of sediment layer. This assumption as underutilization capillary potential to compensate occurring periodically loosening sediment layer and an increase in pores size. In this case the only variable that characterizes process of extracting liquid - (or humidity changes), will be the current linear dimension of liquid column. We accepted that without any external influence of fluid flow does not occur, consider wetting complete and neglect of hydraulic resistance partitions. Then, based on the concept of absolute motion of fluid in capillary under influence of vibration consisting of relative motion along the walls of capillary and a laptop with him, after transformations we obtain an expression of fluid velocity in the capillary in vibration exposure. After conversion and bring to dimensionless form of equation, we obtain the dependence of residual moisture from the vibration parameters, physical properties of phases and timing of the process, i.e. the kinetics of moisture transfer. Based on the results of experiments on suspensions of quartz sand – water, sand – transformer oil, bentonite clay - ethanol can be concluded that the experimental and calculated values are in satisfactory agreement for the layer height (in static) max 40 mm [3].

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DIRECT METHANE CONVERSION OVER Mo/ZSM-5 CATALYSTS

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In recent years, the non-oxidative conversion of methane into aromatic hydrocarbons over Mo/ZSM-5 catalysts has attracted a considerable attention. The study of this process is of a great interest both to develop an efficient method for conversion of natural gas into valuable petrochemical feedstock and to solve a complex catalysis problem connected to activation of methane, whose molecules are the most stable and symmetric [1, 2].

This paper presents the results of investigation of the effect of conditions for thermal treatment of Mo/ZSM-5 catalyst on its composition, reactivity and stability during a non-oxidative methane conversion.

Catalysts where prepared by mechanical mixing of ZSM-5 zeolite with the molar ratio SiO_2/Al_2O_3 = 40 and Mo nanopowder. The resulting mixtures were calcinated in air at 250-650 °C for 1 hour. The concentration of Mo in the zeolite was 4.0 wt %. The Mo nanopowder, calcinated at different temperatures was investigated using a Bruker™ D8 DISCOVER X-Ray diffractometer.

The nonoxidative conversion of methane (99.99 % purity) was performed in a flow setup at 750 °C and atmospheric pressure, methane was supplied at a space velocity of 1000 h^{-1}. The reaction products were determined by gas chromatography.

The data on the effect of temperature of Mo/ZSM-5 catalyst calcination on its reactivity and stability in the course of methane conversion are shown in Fig. 1.

It is seen that the reactivity of catalyst increases with increasing temperature of calcination. The maximum conversion of methane (17.2 %) is achieved during the first hour of the catalyst calcination at 350 °C. Further temperature increase of Mo/ZSM-5 catalyst treatment results in a decrease of its initial reactivity. However, as the reaction runs, the reactivity of samples calcinated at 400-650 °C becomes higher than that of the samples calcinated at lower temperatures. The highest stability was exhibited by the sample calcinated at 650 °C, which indicated its higher resistance to coking. The effect of temperature of Mo/ZSM-5 catalyst calcination on its catalytic properties is due, apparently, to the state and localization of molybdenum in the zeolite matrix. The method of thermal analysis was applied to study the changing of Mo nanopowder state in the course of its oxidation in air within the temperature range 20-800 °C. With increasing the temperature of oxidation, a gradual increase in the sample weight was observed, which increased sharply when the temperature has reached 526 °C. The increase in the weight of catalyst continued until the temperature of 730 °C has been reached, and then it decreased due to the sublimation of molybdenum. Total weight of the sample was increased by 44.4 %. A phase composition of Mo nanopowder calcinated at different temperatures was determined by X-ray analysis. Mo nanopowder calcinated at 250 °C contained up to 2 % of MoO_3 phase. With increasing calcination temperature an increase in the amount of MoO_3 phase was observed and Mo has been completely oxidized to MoO_3 at 550 °C. It is found that the amount of MoO_3 active phase (26 %) formed during the calcination of Mo nanopowder at 350 °C was sufficient for activation of methane molecules and its further aromatization involving the acid sites of the zeolite. The increase in the calcination temperature up to 650 °C results only in slightly increased catalytic reactivity and stability, in spite of substantially increased MoO_3 phase in the catalyst. Thus, the Mo nanopowder used to obtain an efficient zeolite-containing catalyst for methane dehydroaromatization allows reducing the temperature of its pre-activation.

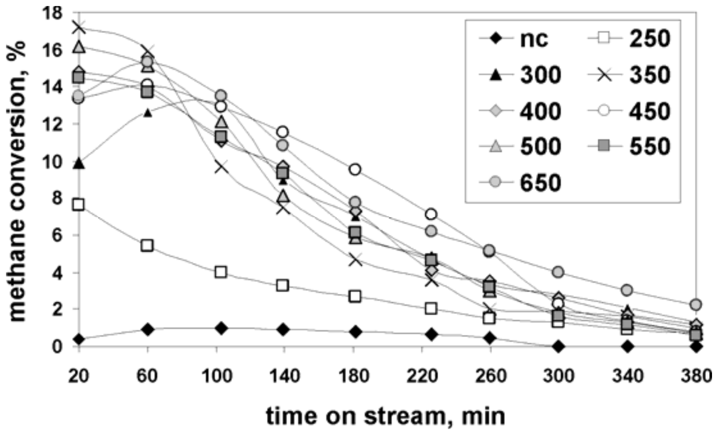

Fig. 1. Changing of the methane conversion vs. the lifetime of Mo/ZSM-5 catalyst calcined at different temperatures (°C)

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STD-PROCESS OVER MIXED CATALYSTS: KINETIC STUDIES AND MATHEMATICAL MODELING

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Dimethyl ether (DME) is produced from synthesis gas using two consequent reactors: the first reactor is used for methanol synthesis, while the second one is used for methanol dehydration to DME. Currently, the STD-process (synthesis gas conversion to DME) is extensively studied. In this case both reactions of methanol synthesis and its subsequent dehydration take place in a single reactor with interlacing of layers of catalysts used separately in two above mentioned processes [1]. This can shift the equilibrium and, thereby, intensify the process of DME synthesis.

The aim of the present work was to develop a kinetic model of the process of DME synthesis and mathematical model of the reactor on the basis thereof. To implement the STD-process a series of samples of catalysts, namely, Cu/Zn/Al methanol synthesis catalyst and gamma-Al_2O_3 catalyst of methanol dehydration to DME, was synthesized.

Kinetic studies of the most active samples were carried out in a wide range of reaction conditions: contact time was 0.02-0.1 min, reaction temperature range was 493-553 K, and component molar ratio were $CO:H_2 = 1:2, 1:6$, $CO:CO_2:H = 1:0,1:6$. On the basis of experimental data and the results of physical research a kinetic model of the process of conversion of methanol to DME was developed, and model parameters were determined.

On the basis of the results obtained the mathematical model of the reactor with variouslayered charge of the catalyst was developed. It was shown that the use of layer interlacing of the abovementioned catalysts significantly increases the yield of the desired product compared to the one obtained in two-reactor scheme.

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MATHEMATICAL MODELLING OF THE CATALYTIC HYDRODESULFURIZATION OF DIESEL FUELS

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Hydrodesulfurization of petroleum fractions occupy one of the leading places in the oil refining, due to the high quality requirements – diesel fuel. Main objective of the diesel hydrotreater – reducing the sulfur content in the product.

In diesel fraction sulfur compounds (CC) represented sulfides, thiophene benzologami homologs and, to a lesser extent mercaptans and disulfides. Compared with gasoline fraction diesel fraction contains sulfides to order more. If the fraction of 40 ... 200 °C, the content may be up to 0.34 wt. %. The fraction of 200 ... 360 °C – to 7.33 wt. % In the distillate. Disulfide sulfur content in diesel fractions of less than 0.006 wt. %. Exception – distillates mercaptan oils. The content of disulfides and mercaptans of higher boiling point fraction increases slower than the content of sulfides and thiophenes.

The main representative class of organosulfur compounds in the diesel fraction are compounds containing a sulfur atom in the aromatic heterocycles comprising – thiophenes, benzothiophenes and their alkyl substituted homologs.

Development of the mathematical model of the hydrodewaxing includes estimation of the thermodynamic possibility of the reactions in order to make hydrocarbons conversion scheme, the creation and soft realization of the kinetic model, estimation of the kinetic parameters of the reactions. Thermodynamic characteristics of the reactions were calculated using non-empirical quantum-chemical method DFT realized in the Gaussian software. Theoretical approximation was B3LYP, basis 3-21G. Kinetic model represents the system of the differential equations and initial conditions. The equations of the kinetic model have the following general form:

$$\frac{dC_i}{d\tau} = \sum v_i W_j$$

Initial conditions are $\tau = 0$, $C_i = C_{i0}$, where i is corresponding group of hydrocarbons, v – stoichiometric coefficient in the corresponding reaction, W – reaction rate, j – number of the corresponding reaction.

Software realization of the kinetic model was made using programming environment Delphi 7. In order to estimate of the rate constants of the reactions the inverse kinetic problem was solved using experimental data. The termodynamic possible reactions which represent the hydrocarbons conversion scheme of the process, thermodinamic values and rate constants are presented in the table 1.

Table 1. Change of Gibbs energy and rate constants of the reactions

Reaction	ΔG, kJ/mol	k, ч$^{-1}$
1. Hydrodesulfurization of mercaptans	– 80,14	5,6
2. Hydrodesulfurization of sulfides	– 77,45	4,2
3. Hydrodesulfurization of disulfides	– 54,30	4,6
4. Hydrodesulfurization of thiophenes	– 31,06	3,7
5. Hydrodesulfurization of benzothiophenes	– 12,24	2,7
6. Hydrodesulfurization of dibenzothiophenes	– 7,68	2,9

Using developed model research of the desulfurization grade influence was carried out (see Fig. 1).

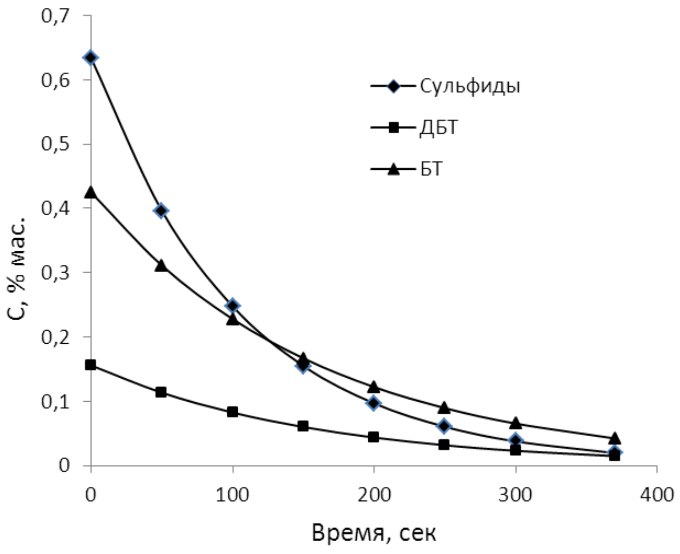

Fig. 1. The kinetic curve of concentrations of constansts

Kinetic transformation model is developed sulfur homologs, preferably belonging to the thiophene type compounds, in the hydrotreating of diesel fuels. The degree of removal of sulfur compounds is 98 % by weight.

The obtained values of the rate constants for the conversion of individual sulfur compounds and their temperature dependencies can be used to predict the residual sulfur content.

Thus, developed mathematical model of the hydrodewaxing process is based on the physical-chemical laws of the process and allows to carry out optimization of the technological regime for resource efficiency increase.

OBTAINING ARTIFICIAL LIQUID FUEL BY THERMOLYSIS OF ANIMAL WASTE

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Human activity associated with the permanent formation of various waste and constant need for energy.

In the context of the approaching scarcity of fossil fuels oil and gas constantly recycle organic waste generated by their processing into electrical energy not only improves the environment of the environment, but also contributes to the production of "green" energy [1,2].

So urgent is the problem of processing animal waste into useful fuel products whose disposal by thermolysis synthetic liquid fuels will increase the relative volume of production and consumption of electricity from renewable energy sources.

In thermolysis organic part of the waste is converted into gaseous, liquid and solid fuels. Part of the fuel gas is burned in the pyrolysis reactor to maintain the required flow temperature – air. The remainder of the gaseous fuel and liquid and solid fuels.

Basic physical and chemical characteristics of the studied sample of liquid animal waste thermolysis product are shown in Table 1.

Table 1. Results of tests of the liquid product of the thermolysis

Indicator	Unit	Results of measurement
Mass fraction of water	wt %.	0,58
Density at 20 °C	kg/m^3	930,7
Kinematic viscosity at 20 °C	mm^2/s	291,9
Mechanical impurities	wt %.	0,025
Sulfur content	wt %.	0,336
Mass fraction of asphaltenes	wt %.	6
Mass fraction of resins	wt %.	27,5

According to the indicators of the density and viscosity of artificial liquid fuel to the high content of asphaltenes and resins, it can be attributed to the type of bituminous oil.

The results of determining the fractional composition according to GOST 11011 - 85 are shown in Table 2. The largest part of the sample of artificial liquid fuel represented residue with boiling temperature above 320 °C and in appearance resembling oil. This allows the sample to confirm the ratio of bituminous type of oil. The lighter fraction boiling in the range 38-180 °C 180-320 °C are not characteristic color and odor of petroleum. It should be noted that, together with light fraction with a boiling temperature of up to 180 °C stood water – 8.8 % vol.

Table 2. Fractional composition of synthetic liquid fuels

Indicator	Value,% vol.
start of boiling – 180 °C	27,9
180 °C – 320 °C	16,3
residue >320 °C	52,4
losses	3,4

Main characteristics of fuel oil obtained by distillation from the direct synthetic liquid fuels are presented in Table 3.

Table 3. Physico-chemical characteristics of the residue > 320 °C

№	Indicator	Unit	Results of measurement
1	Mass fraction of water	wt%.	0,00
2	Sulfur content	wt%.	0,163
3	Kinematic viscosity at 100 °C	mm^2/s	63,2
4	Flash Point COC	°C	246
5	Ash content		0,047
6	Congelation point	°C	+12
7	Density at 20 °C	kg/m^3	980
8	Heat of combustion (lower)	kcal / kg	8944,49

Thus, semi-liquid fuel obtained by thermolysis zhivotnovodcheskth waste can be a source of raw materials for the production of bitumen, motor fuels, lubricating oils, synthetic chemicals, road and building materials.

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PARTIAL OXIDATION OF PROPANE-BUTANE MIXTURE TO OXYGENATES OVER Mo – CONTAINING MODIFIED CATALYSTS

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The problems of optimum selection of raw material and catalysts for different processes are very important for decision due to the rapid development of a petrochemical industry at the last decade in Kazakhstan and world. Under the forecasts for the nearest period C_1-C_4 saturated hydrocarbons not only will keep, but also will strengthen the positions as raw material for manufacture unsaturated hydrocarbons. In these conditions there is urgent problem the search of ways of effective processing of saturated light hydrocarbons into various oxygen-containing compounds. It is necessary to expect formation of unsaturated hydrocarbons, aldehydes, acids and alcohols at the partial oxidation of propane and butane as against of methane and ethane, which form compounds, giving less complex composition. Only optimum selection of catalysts can purposefully carry out the process with primary formation of one of the listed products. The heterogeneous catalysts investigated in reaction of partial oxidation of propane and butane, represent as individual oxide [1,2], polyoxide catalysts [3,4], and also supported on various carriers, including zeolites [5-7].

The purpose of the work is investigation of supported polyoxide catalysts on a base of Mo and natural clays in the process of oxidative conversion of propane-butane mixture, determination the influence of reaction temperature, space velocity and ratio of components in a reaction mixture. The investigations were carried out on installation of a flowing type at atmospheric pressure in tubular quartz reactor with the fixed layer of the catalyst. The catalysts were characterized by XRD. The determination of surface, porosity and element content of samples are carried out. The catalysts on the basis of elements - Mo, Bi, Ce, Ni, W, Sb, Mn, Fe, Ga, and Cr were synthesized. White and red clays are used as the carriers. The temperature range was 300-600 °C at the space velocity 7500-15000h^{-1}. Reactants and products were analyzed by chromatographic method.

The influence of the reaction temperature on direction of oxidative conversion of propane-butane mixture on MoCrGa/white clay. The content of reaction mixture: hydrocarbons – 60,0 %, O_2 – 8.4 %, N_2 – 31,6 %, W – 7500 h^{-1}.

Acetone, methanol, acetaldehyde and other oxygen containing products are the basic products. Besides ethylene is the basic product in a gas phase. 300-350 °C – the optimum temperature by methanol and acetaldehyde, 450-500 °C – by acetone, 500-600 °C – by acetic acid. Also it was shown that the content of ethylene in waste gas at 500-600 °C is increased from 5-up to 17 % during rise of temperature. The conversion did not exceed 50 %.

The results on oxidation of propane-butane mixture on granulated catalysts have shown, that the homogeneous oxidation practically does not take place. The conversion of propane-butane mixture is higher on the clean carrier. Use of the catalyst sharply raises the conversion at all temperatures.

The influence of processing of the catalyst before experiment on the content of acetone in catalyzate. The content of acetone grows at high-temperature processing by acid. The same behaviors were observed for others oxygen-containing compounds. The influence of space velocity on the contents of oxygen-containing compounds in catalyzate was investigated at oxidation of propane-butane mixture on MoCrGa/clay. 7500h^{-1} is the optimal space velocity for acetone at 450-500 °C and for methanol at 300-350 °C, 7500h^{-1} and 9000h^{-1} is optimal for ethylene. The influence of the content of oxygen in reaction mixture on the content of acetone and methanol in catalyzate over MoCrGa/clay. The content of acetone in catalyzate is increased during raising the content of oxygen [8].

The analysis of composition of products of C_3-C_4 oxidative conversion has shown that the process carries out by complex mechanism including oxidation, oxidative dehydrogenation and cracking.

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GREEN CATALYTIC CONVERSION PROCESSES FOR PRODUCTION OF FUELS FROM RENEWABLE BIOMASS MATERIALS

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In the recent years interest in green fuels has been encouraged due to global warming, depletion of petroleum resources and increased demand for green fuel. Biofuel derived from biomass has received tremendous attention as a renewable and carbon neutral alternatives. The aim of the present research is to identify opportunities and constraints related to the potential future production of biofuels and assess the framework for a successful implementation of renewable biofuel refinery. Pyrolysis and hydropyrolysis of biomass are the promising technologies for the utilization of renewable biomass resources, and these have gained extensive attention in recent years. The biooil produced has an approximate heating value between 22 and 25 MJ/kg. The fuel produced was tested for its physiochemical characterization using ICP-MS, gel permeation chromatography (GPC), Fourier transform infrared spectrometer (FTIR), and Raman spectroscopy. Bio-oils components, such as the water, acids, aldehydes, unsaturated compounds, and oligomers, results in the various undesirable properties of bio fuels, such as higher acidity, higher viscosity and lower heating value. Therefore, it is necessary to upgrade bio-oils to eliminate these undesirable compounds or convert them to desirable ones. For conversion of biomass into transportation fuels, two key molecular transformations are needed: (a) depolymerization, and (b) removal of oxygen. Therefore another focus of our research is on the selection of green catalytic strategies to produce biofuels from biomass pyrolysis and hydrolysis followed by their up gradation. Investigations were made on utilization of non traditional biomass materials (Pongamia pinnata (Jatropha) seed cake/ wheat straw) and provide technologies to process lignocellulosic biomass through pyrolysis and hydro. Effect of temperature and feed rate was studied to maximise the bio oil yield. Further in situ cracking of the oil vapours was done in a separate bed of selected Pd/MCM-22 type catalysts.

The application of sub and supercritical water technology can be a viable option. The technology is based upon the use of water, as reactant and reaction medium for the chemical reaction. Hydropyyrolysis of biomass under subcritical and supercritical conditions can be applied in the processing of nontraditional biomass and microalgae, either whole or its oil extract, with similar yields and efficiencies at a level that can be scaled up. The challenge involves developing a process that can tolerate the complex compositions found with different biomass.

SELECTIVITY OF PALLADIUM-CATALYSED ETHYLENE GLYCOL OXIDATION IN TRICKLE-BED REACTOR

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Selectivity of aqueous alkaline oxidation of ethylene glycol (**EG**) on the granulated 2 % Pd/C catalyst in a trickle-bed reactor is investigated. The operating range of superficial velocities of a liquid ($(3{\div}7)\cdot10^{-4}$ м/с) and gas ($(4{\div}14)\cdot10^{-3}$ м/с) conformed to trickling flow mode [1].

It was shown that the oxidation products composition conforms to sequence of transformations of glycol to sodium glycoleate (**GlNa**) and further to oxalate (**OxNa**) and carbonate:

$$HOCH_2CH_2OH + O_2 + NaOH \longrightarrow HOCH_2COONa + 2\ H_2O. \qquad (I)$$

$$HOCH_2COONa + NaOH + O_2 \longrightarrow (COONa)_2 + 2\ H_2O. \qquad (II)$$

$$(COONa)_2 + ½\ O_2 + 2\ NaOH \longrightarrow 2\ Na_2CO_3 + H_2O. \qquad (III)$$

It was established that process selectivity doesn’t depend on hydrodynamic parameters and at maintenance of alkaline mode of reaction medium essentially is completely defined by glycol conversion.

Concentration influence of liquid-phase reagents on process selectivity is caused not so much by their values, how many their ratio (C_{NaOH}:C_{EG}) that is illustrated by the diagram in figure 1.

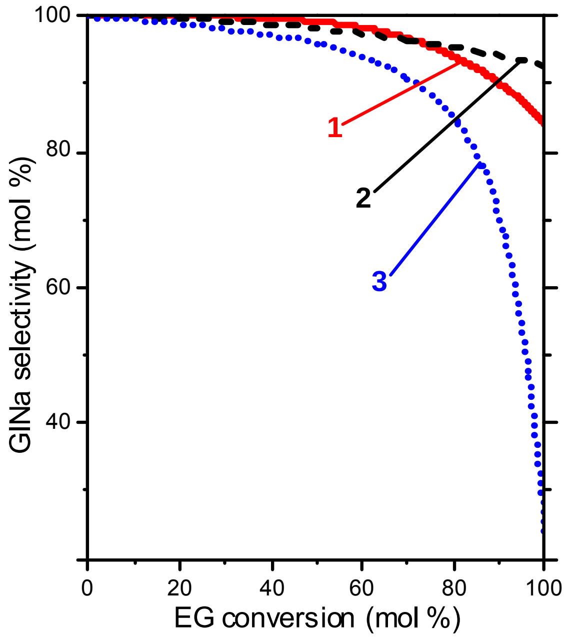

Figure 1. Initial concentration ratio NaOH:ЭГ influence on selectivity at 35 °C.

1 – $(C_{NaOH}:C_{EG})_0 = 1$;
2 – $(C_{NaOH}:C_{EG})_0 = 1.1$;
3 – $(C_{NaOH}:C_{EG})_0 = 2$.

Alkali expenditure stoichiometry on reactions (II) and (III) is more than 1. Therefore at initial ratio $(C_{NaOH}{:}C_{EG})_0 = 1$ alkali is exhausted at 88–90 % of EG conversion then process passes in low-selective alkali-free oxidation mode [2]. Small excess of alkali ($(C_{NaOH}{:}C_{EG})_0 = 1.1$) allows to keep the alkaline medium and high selectivity before practically full exhaustion of glycol. Significant alkali excess ($(C_{NaOH}{:}C_{EG})_0 = 2$) leads to the accelerated progress of consecutive oxidation according to reactions (II) and (III) and to sharp selectivity falling.

The increase of temperature affect selectivity in a similar way to an alkali excess increase. Selectivity decreases to acceleration of reactions (II) and (III) greater than reaction (I) acceleration (Table 1).

Table 1. Dependence of glycol oxidation selectivity on temperature. $C_{NaOH.0} = C_{ЭГ.0} = 1$ M

t, °C	EG conversion, mol %	Selectivity of products, mol %		
		GlNa	OxNa	Na_2CO_3
35	0.713	95.0	5.0	—
50	0.753	93.8	6.2	—
80	0.710	87.3	8.9	3.8

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CaO-CATALYZED ETHANOLYSIS OF SUNFLOWER OIL IN THE PRESENCE OF VARIOUS COSOLVENTS

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The use of ethanol in transesterification reactions of vegetable oils or animal fats has the advantage of nontoxicity over methanol. Also, it is a better solvent of oily feedstocks. Furthermore, the use of fatty acid ethyl esters (FAEE) improves the cold start of the engine because of their lower flash point, compared to fatty acid methyl esters. The CaO-catalyzed ethanolysis of sunflower oil occurs in a three-phase system (oil, alcohol and solid catalyst), where the mass transfer limitation due to immiscibility of the reactants determines the overall reaction rate at the beginning of the reaction. This problem can be overcome by using vigorous mechanical agitation, enhanced reaction temperature or cosolvents [1,2]. The present work deals with the ethanolysis of sunflower oil catalyzed by CaO (calcinated at 800 °C for 2 h) in the presence of various organic solvents such as *n*-hexane, dioxane, tetrahydrofurane, methyl ethyl ketone, ethyl acetate, diethyl ether, triethanolamine, diethanolamine, propylene glycole and triethylamine. The oil/ethanol molar ratio was 1:12 (22.98 g of oil and 14.38 g of ethanol). The CaO concentration was 1.3729 mol/dm^3, while the cosolvent amount was 20 wt. % of the oil mass. The reactor was immersed in a thermostated chamber kept at 70 ± 0.1 °C. The FAEE yields achieved in the 3 h reaction were as follows: tetrahydrofuran 21 %, dioksan 30 %, hexan 33 %, methyl ethyl ketone 40 %, diethyletar 56 %, ethylacetate 68 % and triethanolamine 99 %. The corresponding FAEE yield in the absence of any cosolvent was 47,9 %. Therefore, tetrahydrofuran, dioxane, *n*-hexane and methyl ethyl ketone inhibited the CaO-catalyzed ethanolysis, leading to lower FFEE yields, compared to that achieved in the control reaction without any cosolvent. The ethanolysis efficiency was enhanced in the presence of diethylether (8 % larger yield than that in the control reaction), ethyl acetate (20 %), and triethanolamine (46 %). Thus, trethanolamine was found to be the best cosolvent among the used ones.

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SUNFLOWER OIL ETHANOLYSIS CATALYZED BY COMMERCIAL CaO IN THE PRESENCE OF CHOLINE CHLORIDE-UREA-BASED DEEP EUTECTIC SOLVENT

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Because of its basicity, low solubility and low cost, CaO is commonly used as a heterogeneous catalyst for biodiesel synthesis from vegetable oils [1]. However, its catalytic activity is reduced with forming $CaCO_3$ and $Ca(OH)_2$ on its surface in the reactions with moisture and CO_2 from the air. Therefore, CaO should be calcinated at high temperatures before using to recover the catalytic activity [2]. To avoid the energy demand for calcination, for alternative solution for activating the commercial CaO should be loocked for. A promising way seems to be the use of CaO in the presence of a deep eutectic solvent (DES). The present work deals with ethanolysis of sunflower oil catalyzed by the calcinated (800 °C, 2 h) and not-calcinated CaO in the presence of the choline chloride-urea (1:2 molar ratio)-based DES . The reaction was performed in a three-neck flask at atmospheric pressure equipped with a magnetic stirrer bar, a thermometer and a reflux condenser. The oil/ethanol molar ratio was 1:12 (22.98 g of oil and 14.38 g of ethanol. The CaO concentration was 1.3729 mol/dm^3, while the DES amount was 20 wt. % of the oil mass. The reactor was immersed in a thermostated chamber kept at 70 ± 0.1 °C. The products were determined by a HPLC chromatograph (Agilent 1100Series) using Zorbax Eclipse XDB-C18 column (4.6 x 150 mm with 5 μm particle size). The mobile phase was methanol (reservoir A) and 2 propanol/n-hexane (5:4 v/v; reservoir B). A linear gradient from 100 % A to 40 % A + 60 % B in 15 min was employed. The flow rate of mobile phase was 1 mL/min. Components were detected at 205 nm. The best fatty acid etyl esters (FAEE) yields of 99.63 % and 99.13 % were achieved in 3 and 2 hours using not-calcinated and calcinated CaO, respectively. Hence, the calcination of CaO could be avoided if the transesterification of sunflower oil is conducted in the presence of the DES. Further investigation is undertaken to optimize the reaction conditions.

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THE EFFECT OF ZINC CONCENTRATION AND STATE ON ACTIVITY OF CATALYSTS FOR ETHANE AROMATIZATION

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In view of the continuous deficit of aromatic hydrocarbons, it is challenging to design new catalytic processes for aromatization of the light hydrocarbon stock. The latter is primarily formed by natural gas, oil-dissolved gas, and reject gases contaning C_2-C_5 paraffins. The aim of this work is to study the process of ethane-to-aromatics conversion over Zn-containing zeolite catalysts.

To prepare Zn-containing catalysts, use was made of a hydrogen form of a ZSM-5 zeolite with a molar ratio of $SiO_2/Al_2O_3 = 40$. Zinc, whose concentration was varied from 0.5 to 10-wt%, was introduced by impregnation of the zeolite with an aqueous solution of zinc nitrate. Conversion of ethane was carried out in a flow-type installation equipped with a quartz reactor under atmospheric pressure at the reaction temperature 650 °C and the feed space velocity 800 h^{-1}. The reaction products were analyzed by GLC using a Khromatek Kristall 5000.2 chromatograph. The catalytic activity of the samples was estimated by determining the degree of ethane conversion and calculating the yield and selectivity of the gaseous and liquid reaction products. HR TEM images were obtained in a Jeol JEM-2010 electron microscope (Japan).

The main liquid products of ethane conversion over Zn-containing zeolites are benzene, toluene, xylene, and high-molecular-weight compounds, including naphthalene and its derivatives, and the gaseous products are C_2–C_4 olefins, methane, ethane, and hydrogen. Zeolite, containing 3.0 % of Zn, exhibits the highest reactivity in the course of ethane aromatization. The degree of ethane conversion for the 3.0 % Zn sample is found to be 56.1%, and the yield of aromatic hydrocarbons is as high as 32.2 %. The use of zinc concentration in the zeolite higher than 3.0 % did not result in any significant changes of its catalytic properties in the course of ethane aromatization.

According to the TEM data, particles of the 3.0 % Zn/ZSM-5 catalyst measure several microns in size and have a shape characteristic of high-silica zeolites. The orientation and frequency of lattice absorption bands correspond to the inner channel structure of zeolite, without any individual zinc particles being detected. However, the EDX spectra registered from different areas of the zeolite demonstrate the presence of zinc in the samples before and after testing in the reaction of ethane conversion, which suggests the presence of a cationic form of zinc introduced into the zeolite structure.

In addition, the EDX spectra show that the distribution of zinc over the zeolite crystals in the 3.0 % Zn/ZSM-5 catalyst is nonuniform. The data of elemental analysis indicate very different zinc concentrations in different zeolite crystals, reaching 5.0 % in some of them. Moreover, the content of zinc in the defective zeolite crystals is generally much higher.

An increase in the Zn content to 7.0 % does not result in any significant changes in the structure of catalyst particles; there are the following changes only: an increased zinc content in the crystals and the formation of regions with a thickness of ~1 nm and a length of 10-50 nm near the zeolite surface, which exhibit a modified chemical composition and “island” morphology. The islands located at the edges of the zeolite crystals are responsible for the enhanced contrast in the TEM images and EDX-spectra, which is attributed to zinc. Consequently, we can assume that an introduction of more than 3.0 % of zinc into the sample results in the transfer of its ions to the zeolite surface and their subsequent aggregation to form planar structures.

For the 3.0 % Zn/ZSM-5 sample treated with ethane for 8 hours, the EDX spectra from all zeolite crystals have a similar surface morphology, which implies that all zeolite particles have the same elemental composition. It is very likely that the concentration of zinc in the crystals of the zeolite carrier in the course of ethane conversion gets balanced.

Thus, Zn-containing zeolite catalysts exhibit high catalytic activity and selectivity in the course of ethane aromatization. The most effective catalyst for this process is a zeolite containing 3.0 % zinc. We believe it is unreasonable to increase its content beyond this value, as this does not result in any improvement of the catalyst performance.

TEMPERATURE-SCANNING METHOD FOR THE KINETIC STUDIES OF CO OXIDATION OVER CERIA-ZIRCONIA SUPPORTED GOLD CATALYSTS

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In this work, a variation of the Temperature Scanning Method (TSM) [1] was implemented for analyzing the experimental data of CO oxidation over a series of 2 wt. % Au/$Ce_{1-x}Zr_xO_2$ (x = 0, 0.25, 0.5, 0.75, 1) catalysts [2]. The goal of this work was to develop a tool to determine the optimal reaction conditions of CO oxidation using a new and efficient numerical technique. Thus, the kinetic of this reaction was quantified by conversion–rate–temperature (*X, r, T*) triplets, calculated from raw data obtained using a Plug Flow Reactor, working at stoichiometric conditions (1.6 % CO, 3.3 % O_2, 95.1 % He), with a flow rate of 50 cm^3/min, in the temperature range of 25-300 °C, with a ramp rate of 5 °C/min. The obtained data were fitted to the two proposed mechanistic rate models which differ in their view of the state of the adsorbed oxygen: The Langmuir–Hinshelwood dual site Molecular Adsorption Model (MAM) and The Mars–van Krevelen adsorption model (MvK). The results are presented not only in the terms of the traditional light-off curves in the conversion–temperature plane but also as three-dimensional kinetic plot, such as the (*X, r,* catalyst composition) surface [1]. It offers a useful and intuitive way to review experimental data and to envision the optimal catalyst performance. The obtained kinetic results are discussed on the basis of morphological, structural and redox (using CO-TPR) properties of the studied catalysts.

The most important conclusions of this work can be summarized as follows: (i) The MAM does not fit well all experimental conditions used in this study; (ii) The MvK is able to predict the superficial reaction and the reoxidation of the catalytic surface;

(iii) The sequence of increasing activity follows the progression of increasing reducibility of catalysts, indicating the importance of support redox properties in controlling the performance of the Au/oxide supported catalysts; and (iv) The extended reaction surface, when plotted on the composition plane, allows identifying the optimal reaction conditions.

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