XXIII International Conference on Chemical Reactors

CHEMREACTOR-23

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

- **Section I.** Advances in Chemical Reactor Fundamentals;
- **Section II.** Chemical Reaction Engineering and Reactor Design – Novel Experimental Approaches, Modeling, Scale-Up and Optimization;
- **Section III.** Chemical Reactors and Technologies for Targeted Applications;
- **Section IV.** Advanced Processing of Conventional and Unconventional Hydrocarbon Feedstocks.

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SCIENTIFIC TRENDS

Advances in Chemical Reactor Fundamentals

Chemical Reaction Kinetics

Energy & Mass Transfer in Chemical Reactors and first principles calculations

Fundamentals of Hydrodynamics and Fluid Flow in Chemical Reactors

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

Mathematical Simulation: Multiscale Analytic and Computational Studies of Chemical Reactors

Development of Chemical Reactors and Flow-Sheeting of Reactive Processes

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

Process Intensification and Novel Approaches in Multifunctional Reaction Processes (e.g., Microwave/Induction Heated Reactors, Ultrasonic Reactors, Unsteady-State Forcing and Sorption Enhancement in Chemical Reactors, Multifunctional Reactors, Nature-Inspired Engineering of Reaction Processes, High-gravity, High-Shear Reactors)

Chemical Reactors and Technologies for Targeted Applications

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Reactors for Polymers and Other Novel Materials with Targeted Properties

Processing of Biomass and Renewable Feedstocks

Electrochemical and Photochemical Reaction Engineering

Biochemical Engineering

CO_2 Sequestration and Utilisation

Advanced Processing of Conventional and Unconventional Hydrocarbon Feedstocks

Modern Reactive Technologies for Natural Gas, Oil and Coal Processing

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PLENARY LECTURES

A Professor Mikhail Slin'ko Honorary Lecture

CATALYSIS FOR SUSTAINABLE PRODUCTION OF FUELS AND CHEMICALS

Jens K. Nørskov

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The lecture will discuss some of the drivers for a new energy and chemical production industry. In particular, the rapidly decreasing cost of solar and wind electrical energy provides arguments for a shift towards using electrons to drive chemical transformations. In most cases we do not have suitable catalysts for electrocatalytic reactions of interest in the production of fuels and chemicals, and some of the main scientific challenges to catalyst design will be discussed. The lecture will also discuss approaches to molecular level catalyst design. Specific examples will include the electrochemical water splitting and the carbon dioxide and di-nitrogen reduction reactions.

PL-2

AUTOTHERMAL REACTOR DESIGN FOR CATALYTIC PARTIAL OXIDATIONS

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The terms "autothermal reactor" or "autothermal operation" (AO) are used to describe intentional operation of a reactor in the region of multiple steady-states (MSS). In AO, there is no heat addition to the reactor (except during start-up) and there is no intentional heat removal by cooling through reactor walls (except for some heat loss to surroundings). The existence of MSS, and in particular, an ignited high conversion (and high temperature) steady-state that may co-exist with one or more partially ignited or quenched steady-states, is essential for AO. In practice, MSS (with an ignited state) may be generated by either forced (convective) heat exchange between reactants and products with an internal or external heat exchanger (type I), periodic flow reversal (type II) or sufficient heat conduction (or thermal back-mixing) within the reactor (type III). Classical examples of autothermal catalytic reactors are the ammonia reactor (type I), reverse flow reactor for destruction of volatile organic compounds (type II) and gauze reactors used in HCN synthesis and ammonia oxidation (type III). In general, the first two types are suitable for low to moderate adiabatic temperature rise (ΔT_{ad} in the range 20 to 200 K) while the third type for high adiabatic temperature rise (in the 200 to 1200 K range). Some well-known advantages of AO are: compact reactor (or minimal catalyst requirement), and/or operation with low (and possibly ambient) feed temperature, and/or high per pass conversion of limiting reactant, and/or high productivity, especially for highly active catalysts. The present work deals with the design and analysis of reactors for AO of type III in the context of catalytic partial oxidations.

In the first part of this work, we use a hierarchy of reactor models of increasing complexity to determine the boundary of the region of autothermal operation. Specifically, we show that for a fixed adiabatic temperature rise and space time, the largest region of AO (measured by the difference between feed temperature at ignition and extinction) is obtained when the heat Peclet number approaches zero, mass Peclet number approaches infinity, there is no intra-particle diffusional effect and no heat loss (adiabatic case). From a practical point of view, this leads to a reactor design which is a thin and high conductivity bed with small particles (or if we use a monolith, a thin disk made-up of high conductivity substrate and properly chosen channel and washcoat dimensions). We also present some novel results on AO with longer beds (and any bed scale heat Peclet number) by using larger particles leading to multiple solutions at the particle level. However, when the particle size exceeds some critical value, intra-particle concentration gradients can reduce the effective activation energy and can eliminate the particle level multiplicity. In practice, intra-particle gradients can be avoided by using eggshell type catalyst, or for the case of monoliths, using appropriate washcoat thickness. We determine the particle (channel) size, catalyst layer (washcoat) thickness and other bed properties for obtaining the largest region of AO. Finally, we examine the impact of heat loss on the region of AO.

In the second part of this work, we illustrate autothermal reactor design for two specific examples. The first case is that of Oxidative Coupling of Methane (OCM) for which the adiabatic temperature rise is very high (900 to 1200 K) and it is impractical to design a multi-tube reactor with heat removal. We show that AO is possible with shallow-bed or “pancake-reactor” for practical range of methane to oxygen ratios even with some heat loss. We compare the calculations with recent laboratory and pilot scale experimental results and examine the selectivity to C_2 products on the ignited branches. The second example is that of an oxidative dehydrogenation of a hydrocarbon with moderate adiabatic temperature rise (200 to 400 K). For this case, we compare the traditional cooled multi-tubular reactor design (with high inlet feed temperature and near isothermal operation) with that of an autothermal reactor with ambient feed with no heat removal and near adiabatic operation. We demonstrate the advantages of AO, especially for highly active catalysts.

Acknowledgements

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PL-3

MULTI-LEVEL BRIDGE BETWEEN REACTION ENGINEERING AND COMPUTATIONAL CATALYSIS

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Sustainability of chemical process requires more energy-efficient processes, utilization of renewable energy, such as solar and wind, to drive reactions and separations, better catalysts to improve activity and selectivity and thus to reduce separation cost and energy demand, new technologies that are more efficient, and our ability to tap into underutilized and renewable resources, such as offshore and stranded gas, biogas, and biomass. The distributed nature of many underutilized and renewable resources and the low energy density begs for distributed manufacturing, which can be achieved with modular systems and process intensification, such as plants on wheels. The design of such systems needs much more intimate process integration with high fidelity models. A cross cutting need in all of these systems is the need for better materials, whether catalysts, adsorbents, battery materials, or electrocatalysts, to improve performance, reduce cost, catalyst stability, and robustness.

Over the past two decades, multiscale modeling has advanced tremendously, and several algorithms currently exist [1, 2]. Yet, our ability to apply first principles modeling to process design and materials discovery is seriously limited due to multiple challenges. In this talk, we will outline these challenges and introduce computational methods to overcome them. Specifically, we will discuss how to handle complex reaction networks with first principles accuracy but at a very low computational cost [1, 3], how to estimate and reduce errors in multiscale models [4], how to determine the active site of a catalyst [5], and how to predict novel combinations of active sites to drive activity and selectivity. The concepts of small data, correlations in energies and entropies, correlative uncertainty quantification, machine learning for catalysis, and atomistic optimization for improved activity and stability, will be discussed. These concepts will be illustrated with examples focusing on ammonia decomposition chemistry and electrocatalysis in alkaline media focusing on the oxygen reduction reaction (ORR).

It will be shown that model uncertainty is significant in process modeling and that experimental data fusion into multiscale models is essential. On the other hand, prediction of materials incurs very low error. Comparison of computational to experimental data demonstrates that a main uncertainty arises from the lack of knowledge and predictive ability of catalyst microstructure. We reveal correlations of vibrational frequencies [9] and discuss how *in situ* spectroscopy and machine learning can be integrated to provide the actual catalyst structure and close the materials gap. Finally, we will show that machine learning can be used with statistical mechanics to develop surrogate models that capture efficiently the active site microenvironment. Equipped with these methods, optimal catalyst prediction can be accomplished. It is shown that defect engineering can improve reactor performance by at least one order of magnitude.

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PL-4

METHANOL TO OLEFINS: CONCEPT TO COMMERCIALIZATION

Clayton Sadler[1], **John Senetar**[2], **Geoffrey Fichtl**[3]

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As the global demand for light olefins steadily increases, particularly in developing markets, the need for new alternative technologies has emerged. Conversion of methanol to olefins (MTO) is a means to produce light olefins, ethylene and propylene from feedstock derived from sources other than crude oil or condensates. Methanol is widely produced from natural gas and coal at locations with abundant reserves. By using methanol derived from these cost-advantaged raw materials, MTO enables low production costs for ethylene and propylene, which are critical building-block molecules.

This lecture will cover the development of this technology from the initial process concept based on a new molecular sieve, SAPO-34, to the commercialization of UOP's Advanced MTO process. The focus will be on the reactor and regenerator technology selection, modeling and scale-up. There currently are three Advanced MTO units in operation, including the largest MTO unit in the world, and several more due to start up in the next two years.

SOLVENT SELECTION AND TUNING FOR SUSTAINABLE CHEMICAL PROCESSES

Kai Sundmacher[1,2], **Steffen Linke**[2], **Kevin McBride**[1]

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In many chemical processes solvents are used for dissolving or diluting gaseous, liquid or solid substances. The majority of solvents are liquids at atmospheric conditions. The most important functionalities of solvents in the reaction steps of a chemical process are a) thermal control of highly exothermic reactions, b) stabilization of transition states, c) avoiding side reactions, d) homogeneously contacting reactants and catalysts. In downstream processing the addition of (anti-)solvents enables or supports the separation of components, e.g. in crystallization, precipitation, extraction, chromatography, and azeotropic distillation. When selecting a suitable solvent for a chemical process one must take into account multiple aspects, in particular 1) the full functionality of the solvent in the process, 2) the (total annualized) costs when using the solvent in the process, and 3) the solvent impact on environment, health and safety (EHS).

Over the past 100 years, a set of classical organic solvents was established, that contains substances with well-known properties satisfying major process-relevant functionalities. Due to stricter *EHS regulations* (e.g. REACH), and the paradigmatic shift towards *Process Intensification (PI)*, today *non-classical solvents* are taken into account for many industrial applications [1,2]. The most important classes of these solvents are ionic liquids (IL), supercritical fluids (SCF), thermomorphic multicomponent solvents (TMS), micellar solvents (MLS), deep eutectic solvents (DES), and perfluorocarbons (PFC). Among all classical and non-classical solvents, there is a subset of substances fulfilling sharp EHS criteria, called "*green solvents*" [3], which, if properly selected and used, offer a great potential for improving significantly both, the sustainability and the productivity of chemical processes.

The target-oriented identification of a fully functional process solvent is achievable by systematic screening methods applied to existing data banks containing many substances potentially suitable as solvents. In the past, solvent selection was performed by use of semi-empirical concepts, e.g. the *Hansen parameters*, used in industrial chemistry for quite a long time [4]. Moreover, *group contribution (GC) methods* (e.g. UNIFAC) were used to optimize the molecular structure of solvent molecules [5], partly together with the flowsheet structure of the whole chemical process by means of Mixed Integer Nonlinear Programming (MINLP) approaches. Over the last 25 years, *quantum chemical (QC)* computational approaches penetrated into the chemical engineering practice, in particular the COSMO solvation model [6]. By means of this model, electronic structure information of molecules is accessible at relatively low computational cost and usable for the prediction of thermodynamic properties of pure solvents and solvents in mixtures with other components [7].

Although the predictive power of theoretical methods has increased continuously, one still needs experimental data for validation purposes. To maximize the information content and relevance of these data *for integrated solvent selection and process design*, experiments should be harvested in an optimal manner. Once a single solvent or a combination of several solvents fulfilling key functionalities of the reaction and separation steps has been identified, the *reaction-separation-recycle process concept* can be derived. This concept is the starting point for the detailed process design, including *fine tuning* of the solvent properties by adjustment of individual temperature and pressure levels as well as chemical compositions in the different process units.

The overall *solvent selection and process design workflow* sketched above is illustrated for an innovative reaction example of industrial interest, namely the conversion of long-chain olefins from renewable resources into amines via hydroformylation and subsequent reductive amination. Both reactions run in the liquid phase by use of homogeneous transition metal catalysts.

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KEYNOTE LECTURES

PREDICTION OF REACTION RATES FOR IMPROVED CATALYST DESIGN AT THE ATOMIC SCALE

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First-principles calculations have emerged as a key contributor towards the fundamental understanding of heterogeneous catalysis and the educated discovery of improved catalytic materials. By choosing the example of formic acid (HCOOH) decomposition on transition metals and alloys, we demonstrate how a deep mechanistic understanding of selective versus unselective routes can help with designing more selective catalysts. HCOOH is a simple molecule that is an abundant product of biomass processing and can serve as an internal source of hydrogen for oxygen removal and upgrading of biomass to chemicals and fuels. In addition, HCOOH can be used as a fuel for low temperature direct fuel cells. We start by presenting a systematic study of the HCOOH decomposition reaction mechanism starting from first-principles and including reactivity experiments and microkinetic modeling. In particular, periodic self-consistent Density Functional Theory (DFT) calculations are performed to determine the stability of reactive intermediates and activation energy barriers of elementary steps. Mean-field microkinetic models are developed and calculated reaction rates, orders, etc are then compared with experimentally measured ones. These comparisons provide useful insights on the nature of the active site, most-abundant surface intermediates as a function of reaction conditions and feed composition. Trends across metals on the fundamental atomic-scale level up to selectivity trends will be discussed. Finally, we identify from first-principles alloy surfaces, which may possess better catalytic properties for selective dehydrogenation of HCOOH than monometallic surfaces, thereby guiding synthesis towards promising novel catalytic materials.

KL-2

The NETmix Reactor: Concepts, Technology and Products

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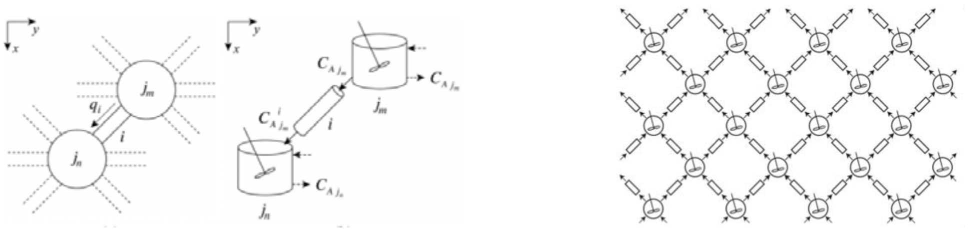
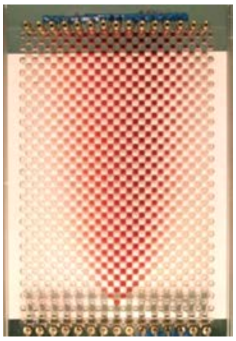
NETmix is a novel static mixing technology consisting on a network of unit cells, comprising chambers interconnected by channels. The NETmix original conceptual model [2] formed the basis for a flow simulator coupled with chemical reaction to study the impact of macro and micro-mixing effects in the network. The chambers were modelled as perfectly mixing zones and the channels as perfectly segregated zones. A mixing intensity parameter was introduced as the ratio between the chambers volume and the whole network volume.



Network branching (left) and analogy with cascade of continuous-flow reactors (right) [1].

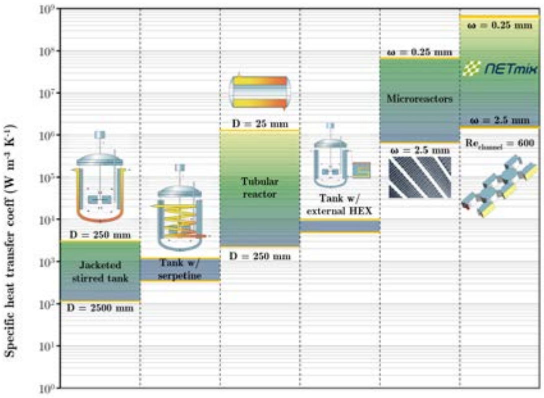
Experimental validation of the NETmix concept [2] was performed in a transparent unit constructed to enable the characterisation of the mixing mechanisms at the local scale. Tracer flow visualisation experiments showed that the mixing characteristics in the NETmix unit, depend on the Reynolds number both for macro-mixing and micro-mixing, and a critical Reynolds number for the onset of mixing was observed. Chemical reaction experiments done using test reactions sensible to mixing, have shown selectivity dependence on the reactant’s injection scheme. For high Reynolds numbers, theoretical predictions obtained with the network model were found to be in agreement with experimental data.



Chemical test reaction experiments using the visualization injection scheme [2].

The NETmix reactor technology was successfully applied industrially in 2008 [3], for the synthesis of hydroxyapatite nanoparticles, HAp. The technology is capable of producing tailor-made HAp nanoparticles with controlled size and morphology, high surface areas, purity and crystallinity.

The heat transfer performance of NETmix has been explored by carrying out hydrodynamics and heat transfer simulations [4]. Based on CFD simulations, it was shown that heat transfer capabilities are one order of magnitude greater than in other microreactors, and 2–5 orders of magnitude greater than the most commonly used mixing devices in industry.



Specific heat transfer capacity of typical heat exchangers equipment [4].

At the 2016 CHISA conference [5], it was reported that large heat transfer capacities, within the range of 1 000- 3000 W/m2/K, can be obtained in NETmix, capable of handling large exothermal reactions in multiphase gas-liquid systems, such as CO2 hydrates formation. In 2017 a patent application was submitted for a new NETmix heat exchanger device [6].

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APPLICATION OF NEURAL NETWORKS TO APPROXIMATE AND GENERALIZE EXPERIMENTAL DATA

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Models based on artificial neural networks (ANNs) exhibit the rule-following behaviour without any explicit representation of those rules. A fundamental information on neural networks can be found in the literature of subject, particularly this concerning neurophysiology, biocybernetics, applied mathematics and informatics, however nowadays ANNs are also extensively employed in different branches of science and technology. The main applications of neural networks in chemical engineering and biotechnology are related to process control, data analysis and transformation as well as to process modelling.

In this study a comprehensive survey of neural networks application in chemical engineering and biotechnology is given, in which approximation of data and modelling of processes are particuraly characterized. First, a fundamental theory of neural networks is presented and a special attention is focused on feedforward neural networks and their abbilities to approximate functional dependencies of any complexity. Then, two fundamental types of neural models, a global and a hybrid one, respectively are distinguished and described. With global neural models entire phenomenon, process or apparatus can be described with a single net, basing only on an appropriate set of experimental data without any identification of governing rules and/or mechanisms. These kind of models have quite good interpolation abilities, however rather poor ability to knowledge generalisation. With hybrid neural models – e.g. those applied to describe a performance of chemical reactors - all accesible knowledgy can be utilized (among others there are usually balance equations), while not sufficiently recognized elements or phenomena (in this case usually the reaction kinetics) are represented with neural net(s). Hybrid neural models are more robust than the global ones and they have much better abilities to generalise a knowledge.

Finally new aspects of neural modelling are consisdered, which are related to posibility of utilization of ANNs for practical impemmentation of the third paradigm of chemical engineering. Since the end of the 20th century – despite the fact that both praradigms, the first and the second one, are still widely used – the third paradimg is introduced. With this new paradigm the synthesis of many products can be currently examined from the view point of the plant, the reactor, hydrodynamics, transport phenomena, catalysis design, reaction chemistry and molecular modlling. This new approch is still widely discussed, improved and supplemented and the multi-scale modelling to design process for manufacturing products of strictly defined structure and properities is employed. Following a general concept of multi-scale modelling, data obtained at the nano-scale have to be transferred into the micro-scale model and further sucessively to the macro full-scale model. Such transfering is essential for efficiency of multi-scale modelling and ofers a significant improvement of process and reactors modelling and optimization. Application of ANNs to approximate the results obtained in nano-scale, then transfering them into the micro-scale can significantly helps to speed-up and improve the whole multi-scale procedure of modelling and designing. A case study is presented as an example to demonstrate the entire procedure and characterize the abilities of neural nets.

In summary some conclusions for practical application of ANNs for modelling is given, among others:

- the way of chosing a set of input-output signals representative for the considered problem,
- the formulation of the optimal net architecture,
- the choice of the learning method as well as learning data set(s).

Also condensed characterisation of ANNs is presented and discussed. Some of them read as follows:

- neural modelling is a method based on experimental data, so quality of these data decide on accurcy and robustness of neural models,
- ANNs work as a “black box” and their parametres (weights) have no physical meaning. However ANNs do not develop the theory, they can help to undersand fundamental principles of the described phenomenon indicating the relevant input-output signals (variables) and important areas for fundamental investigations,
- in conventional models values of their papameters contain always consequences of introduced assumptions and/or simlifications, while neural models are free of them.

KL-4

INTENSIFICATION OF CATALYTIC PROCESSES WITH STRUCTURED CATALYSTS AND REACTORS

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Intensification of catalytic processes requires catalysts with high activity per unit of reactor volume. For this to be practiced, a suitable catalyst arrangement is also required in the reactor to ensure sufficient flow of reagents and products and heat transfer in the proper direction. These flows are controlled by the external diffusion processes (from the bulk fluid phase to the catalyst surface or the inverse), internal diffusion (in the porous network of the catalyst) and by the heat transfer within the catalytic bed. Such processes depend on both the properties of the fluid and the operating conditions as well as on the characteristics of the catalyst, the substrate in the case of structured catalysts and the reactor itself in the case of structured reactors such as microreactors. To enhance the external diffusion rate it is convenient to increase the linear velocity of the fluid and the turbulence, but looking for a trade-off with pressure drop that is favored by the same conditions [1]. As for the internal diffusion in the porous network of the catalyst, we were able to enhance it by increasing the diameter of the pores and reducing the diffusion path which is usually achieved by reducing the catalyst particle size. However, this reduction in particle size also leads to an increase in pressure drop in fixed-beds. Finally, heat transfer requirements are usually solved in fixed-bed reactors adopting multitubular configurations which provide higher surface-to-volume ratios. In response to the opposite effects of the process variables on diffusion limitations and pressure drop, structured catalysts and reactors have been developed. In particular, monoliths with parallel longitudinal channels have reached their highest degree of development in the catalytic converters for exhaust gas emissions control. But it is known that conventional ceramic monolithic catalysts operate under a quasi-adiabatic regime which is not suitable for chemical reactions with large thermal exchange.

The purpose of this talk is to show several examples of the work developed in our laboratories that demonstrate the advantages offered by structured catalysts and reactors for the intensification of catalytic reactions with high thermal effect involved in fuel conversion processes as well as energy and environmental applications.

External diffusion. Its effects have been studied by comparing the performance of monoliths with longitudinal parallel channels, stacked wire mesh monoliths and foams on different reactions: VOC removal, selective butadiene hydrogenation and Fischer-Tropsch synthesis (FTS). In the case of meshes for VOCs removal, kinetic analyses explained their greater activity compared to longitudinal channel monoliths which was due to enhanced turbulence [2]. Metallic foams applied to the above-mentioned reactions have always shown improvements compared to the longitudinal channel monoliths both in activity and selectivity due to the increased turbulence produced. The fundamental role of turbulence is also evidenced by the improvement obtained with the increase of the linear pore density (ppi) of the foams or the decrease of the mesh opening.

Internal diffusion. Studies performed with both monoliths and foams in the FTS showed that thicknesses of the catalytic film exceeding 50 microns produced a significant decrease of the selectivity to C5+ and a slight CO conversion decrease. Therefore, the best strategy for the intensification of this reaction is the use of monoliths with very high cell densities, thus allowing to increase the geometric surface area exposed by the substrates and therefore reducing the thickness of the catalytic film for a given catalyst loading [3]. Another strategy to reduce the limitations of internal diffusion is to increase the porosity of the catalytic layer. Studies done incorporating macroporosity to the catalytic layer (hierarchical porosity) showed a paradoxical effect. Macroporosity resulted in a decrease of the catalytic coating density which produced an increase of the layer thickness for the same amount of catalyst. This led to an increased diffusion path that produced so negative effects that rendered irrelevant the incorporation of macroporosity [3].

Thermal conductivity effects. According to Tronconi et al. [4], the effective thermal conductivity of a structured catalysts depends fundamentally on the conductivity of the substrate and that of the solid deposited on the substrate. Our studies on methanol steam reforming with metallic monoliths of different cell density showed an a priori unexpected result: the methanol conversion increased as the cell density of the monolith decreased. Accurate temperature measurements showed marked temperature profiles for the same core monolith temperature depending on the cell density of the substrate. This caused the average temperature to increase as the cell density decreased due to the lower effective thermal conductivity. These results were confirmed through CFD simulations thus explaining the experimentally observed methanol conversion evolution [5].

The FTS is very exothermic, so temperature control is critical and a high thermal conductivity is necessary to avoid hot spots that produce temperature runaway leading to the sole and undesired production of CH_4 and CO_2. Conventional metallic monoliths fabricated by corrugation exhibited high thermal conductivity when manufactured with a very high cell density (> 2000 cpsi) or with a highly conductive alloy (such as aluminum instead of steel), which allowed a good control of the FTS temperature [6]. In these circumstances, a remarkable intensification of the process is possible since by increasing the temperature a high volumetric productivity of C5+ can be obtained, much higher than that presented in the literature and very close to that of the much more sophisticated and expensive monoliths obtained by extrusion [6].

Therefore, structured catalytic systems with metallic substrates offer substantial improvements over conventional catalytic reactors for reactions presenting high thermal exchange. By properly selecting geometry and materials, the turbulence and the thermal conductivity can be enhanced thus avoiding important limitations associated to transport phenomena of reactants and products together with a better control of the reaction temperature.

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KL-5

NUMERICAL SIMULATION OF COMBUSTION: FROM FUNDAMENTALS TO APPLICATIONS

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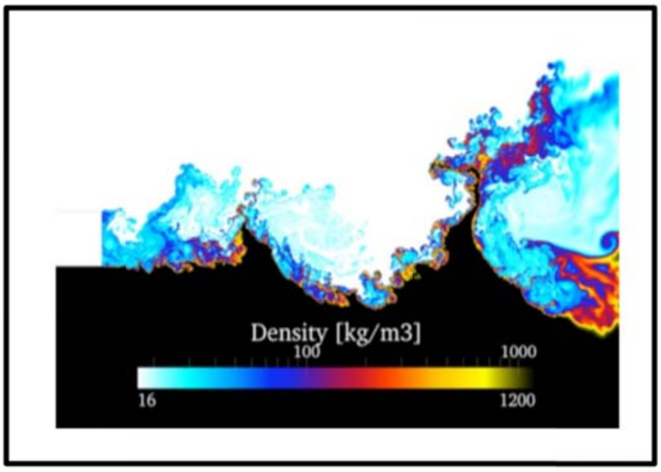
With the constant increase of massively parallel computing power, Large Eddy Simulation (LES) has emerged as a powerful numerical approach to address complex problems, such as turbulent reacting flows. LES is able to provide reliable predictive solutions of both academic and real industrial systems, and gives new insight into the underlying physical phenomena. Moreover, to alleviate some uncertainty associated to boundary conditions, LES can be coupled to other solvers to include complementary system elements and physics in the computation.

In the case of turbulent combustion, many different and complex physics must be described and coupled. This includes turbulence, chemistry, heat transfer, two-phase flows and phase change when the fuel is liquid, solid particles dynamics and chemistry for soot prediction, or acoustics to study combustion instabilities. Non-linearity, associated to a wide range of space and time scales, make the full resolution of turbulent combustion not affordable, and modelling is necessary. Models must be efficient, accurate and reliable, and also describe the interactions between the various physics.

The application of LES to turbulent combustion to real industrial systems, characterized by complex geometries, calls for specific numerical strategies based on unstructured meshes and high-order discretization schemes. It also requires the use of massively parallel computing with the highest possible computing efficiency.



In the lecture an overview of the physical models used for LES of turbulent combustion will be first given, focusing on the most recent and successful approaches. This will be followed by the description of numerical methods and High Performance Computing (HPC) techniques which allow today to reach a high code scalability. Finally a selection of applications will be presented, from aeronautical engines to reactors and furnaces, to illustrate the methods previously presented. Comparison with experiments and results analysis will allow to demonstrate the capacity of LES and coupled multiphysics to tackle complex problems with accuracy and efficiency.

TechnipFMC's SWIRL FLOW TUBE® RADIANT COIL: FROM PATENT TO APPLICATION

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Cracking reactions are endothermic and are driven by the energy supplied to the radiant coils by the combustion of fuel gas in the radiant box. Ethylene yields are favored by low pressures, high temperatures and low residence times in the coil.

Residence time can be reduced by reducing the length of the coils but this implies higher heat fluxes through the coils and higher tube metal temperatures. Currently TechnipFMC (and other ethylene licensors) design coils close to the maximum feasible tube skin temperatures. Further increase in heat transfer rates are inhibited by the metallurgy of the radiant coils. Therefore any technology that reduces the tube skin temperatures of radiant coils is interesting.

The SFT technology of TechnipFMC is such a technology. TechnipFMC acquired the SFT technology for application in radiant coils of steam cracking furnaces. The SFT is a helical pipe, which has a significant technological advantage over other coils with special attributes. This swirl flow enhances the heat transfer by a more intense mixing in the circumference compared to the classical straight tubes.

TechnipFMC has developed bending equipment to fabricate SFT coils from any straight radiant coil tube and from any supplier. The helical shape of the coil is formed by induction bending which is a well-established technology with over 30 years of experience in the field of bending radiant coil material.

This paper will describe the SFT technology, its validation, its fabrication process, its applications possibilities and its benefits for the clients and feedback from the first application.

ORAL PRESENTATIONS

Section I.

Advances in Chemical Reactor Fundamentals

TESTING THE INVARIANT FOR THE NON-LINEAR CHEMICAL REACTION

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Invariants are functions of state variables that remain constant during the non-steady-state transformations. Searching for invariants is one of the most important goals in many sciences such as chemical kinetics and chemical engineering [1-3]. The well-known invariants, widely used in chemistry and chemical engineering, i.e. element conservation laws and stoichiometric relationships, are linear [4, 5]. Since 2011, other invariants of thermodynamic origin for first-order, reversible reactions have been found [6-9]. It was proven that they are related to the famous Onsager's reciprocal relations [10, 11].

In this paper, the first non-Onsager thermodynamic invariant for non-linear chemical system was experimentally found using 'the dual kinetic experiment'. In a batch reactor the esterification of ethanol with acetic acid was studied jointly with the hydrolysis of ethyl acetate. Figure 1 presents the non-linear invariant (K) dependence of the dual experiment in comparison with the quotients of esterification (QI) and hydrolysis (QII) which change in the course of reaction. The obtained experimental result is a justification of the theory developed previously [9].

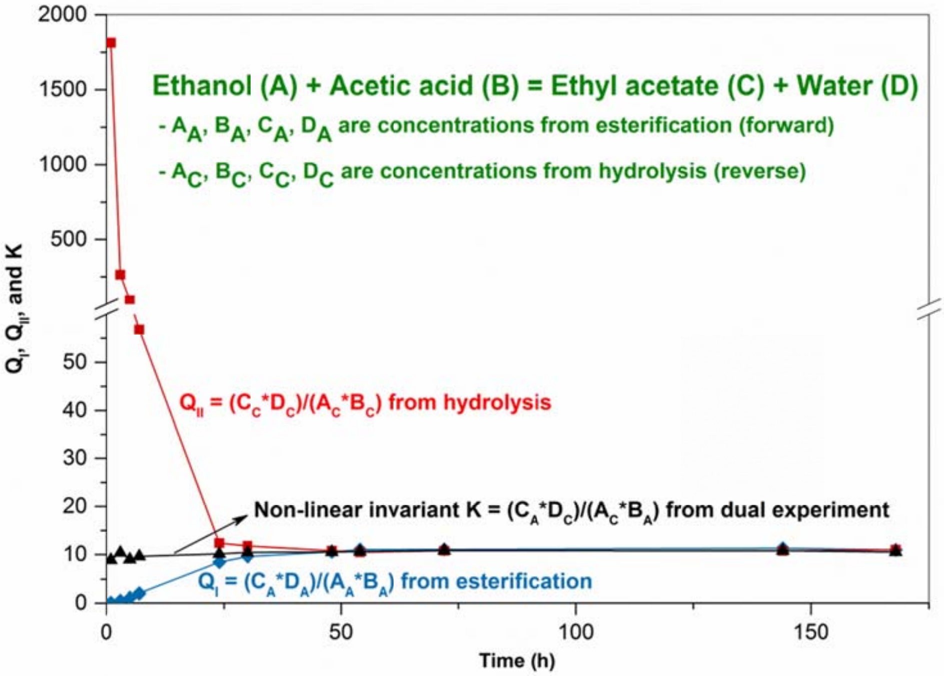

Figure 1. Comparison of quotients $Q_I = (C_A*D_A)/(A_A*B_A)$ for esterification, $Q_{II} = (C_C*D_C)/(A_C*B_C)$ for hydrolysis, and non-linear invariant $K = (C_A*D_C)/(A_C*B_A)$ as a function of time at 30 °C. A_A, B_A, C_A, and D_A are dependences of concentrations of A, B, C, D obtained in the reaction primed with substances A and B; A_C, B_C, C_C, and D_C are dependences of concentrations of A, B, C, D obtained in the reaction primed with substances A and B

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A MODEL-BASED DATA MINING APPROACH FOR OUTLIER DETECTION IN KINETIC MODELLING STUDIES

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Whenever a kinetic model structure is proposed to describe the dynamics of a reacting system, its validation relies on experimental data. Data are in fact required for: i) the estimation of the kinetic parameters appearing in the model [1]; ii) the validation of modelling hypotheses [2]. A frequent issue that modellers have to face in the course of the model validation activity is the presence of outliers in the dataset. Outliers represent data whose observation is extremely unlikely under the postulated modelling assumptions. The presence of a small fraction of outliers in the dataset (realistically between 1 % and 10 %) shall always be expected even if there is high confidence on the appropriateness of the modelling hypotheses and the experimental protocol is followed with extreme attention [3].

The detection and removal of the outliers from the dataset is of paramount importance in the kinetic model identification task. Outliers may be classified in three categories: 1) *type-1*: data affected by gross measurement errors [3]; 2) *type-2:* data collected in the presence of significant external disturbances (resulting in poor experimental reproducibility); 3) *type-3:* data collected outside the domain of model reliability (i.e. data collected at conditions where the modelling assumptions are not valid) [4]. A popular approach used to label “bad” data in kinetic experiments is the method of the *material balance*, which consists on quantifying the discrepancy in the atom balances between the inlet and the outlet of the reactor. Kinetic experiments in which this discrepancy is above a certain threshold (typically chosen between 5 % and 10 %) are considered too inconsistent to be used for kinetic modelling and are removed from the dataset. A major drawback of the *material balance* approach is that it only supports the detection of some *type-1* and *type-2* outliers.

A *model-based data mining* (*MBDM*) method was recently proposed by the authors to prompt a more effective identification of the outliers [4]. The method can be regarded as a robust regression method that is insensitive to the presence of *type-1*, *type-2* and *type-3* outliers in the dataset [5]. The effectiveness of the *MBDM* method is demonstrated in this work in a case study where the aim is the identification of a kinetic model of catalytic esterification of benzoic acid and ethanol in a flow microreactor [6]. A first order steady-state kinetic model was selected and fitted to a dataset consisting of concentration measurements collected in 33 experiments. As one can see from Table 1, if no experiments are removed from the dataset, the model fails the χ^2-test with 95 % of significance, suggesting either the presence of outliers in the dataset or the presence of inappropriate modelling assumptions. The employment of a *material balance* on carbon as outlier detection criterion leads to the exclusion of 3 experiments from the dataset (i.e. experiments 11, 28 and 31). Despite the exclusion of 3 experiments, the model still fails the goodness of fit test, suggesting that the model may be an inappropriate description of the system. The employment of *MBDM* as outlier detection method suggests the exclusion of only one experiment, i.e. experiment 8, leading to a significant improvement in the goodness of fit and the "validation" of the modelling hypotheses through the χ^2-test (see Table 1). Further analysis indicated that experiment 8 was a *type-2* outlier, where the disturbance was of unknown nature. Data records showed that experiment 8 was the first performed after an overnight pause in the experimental campaign. A small leak in the system, sustained through the overnight interruption, may have caused experiment 8 to be an outlier.

Table 1. Comparison of performance between outlier detection methods

Outlier detection method	Experiments removed from dataset	95 % χ^2-test (value/reference)	Goodness of fit Test Result
None	no exp. removed	**113/83**	**Failed**
Material Balance (>5 %)	exp. 11; 28; 31	**87/77**	**Failed**
Model-Based Data Mining	exp. 8	**51/81**	**Passed**

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REDUCTION OF LUMPED REACTION NETWORKS BASED ON GLOBAL SENSITIVITY ANALYSIS

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Introduction

Chemical reactor design requires comprehensive information about the reactions present. For complex processes, however, detailed kinetic parameters are often unavailable because of the very large number of species and reactions present. In such cases different lumping methods are widely used to model the process. However, the reliability of the results are often not addressed. The number of defined component lumps or the number of reactions taking place between them are usually axiomatic. On the other hand, with the application of global sensitivity analysis (GSA) methods the uncertainty of model parameters can be quantitatively addressed. However, application of GSA is not straightforward as multiple different methods are available. Pianosi et al. suggested that good practice in GSA has the following three attributes: comparison of multiple GSA methods, assessing the robustness of GSA methods and lastly, visualizing the results [1]. Therefore, it is necessary to compare the performance of different GSA methods.

Numerical methods

In this work, uncertainty of reaction kinetic parameters of pyrolysis of real platic waste is studied. The performance of five different GSA methods (Table 1) is compared on an exampe of a lumped reaction network consisting six lumps and ten reactions. The suggested network was constructed arbitrarily but it was proven that it and the underlying model can reproduce the experimental results.

Results and conclusion

Performance of GSA methods are compared in Table 1. Comparison was made based on convergence (i.e. necessary sample size, also directly proportional to computational cost) and ease of implementation (e.g. how many parameters have to be manually tuned in order to apply them). Based on the results, the Fourier Amplitude Sensitivity Test raises most interest as it does not have any additional parameters to be manually set or tuned (even the sample size is determined by the number of search variables) and has the best convergence. It is suitable for model reduction purposes, i.e. it can be applied to eliminate reactions for that the sensitivity of the model is low. On this basis, five reactions were eliminated from the full reaction network, leading to a reduced model with a significanly lower number of parameters to be identified, while the results remain essentially the same (Figure 1). However, it should be taken into consideration that the established ranking of these methods might be problem specific, therefore at this point none of the GSA methods should be admitted unsuitable.

Table 1. Comparison of GSA methods

Method	**EET** [2]	**FAST** [3]	**PAWN** [4]	**RS-HDMR** [5]	**VBSA** [6]
Sample Size	3300	1641	2000	3000	3000
Additional parameters	1	0	3	3	1

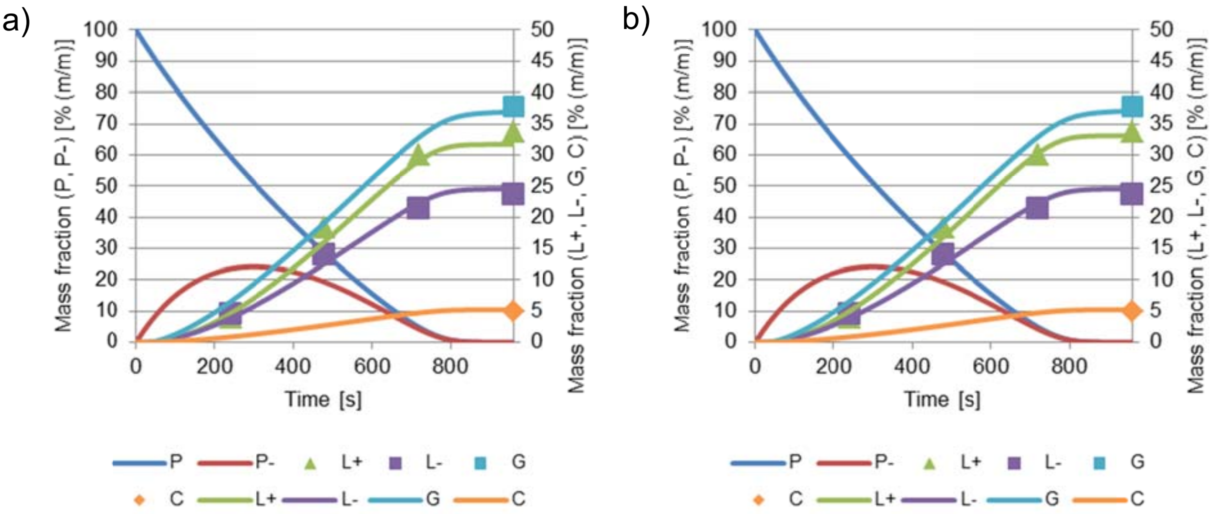

Figure 1. Results of (a) full, (b) reduced reaction network – experimental (markers) and simulation (lines)

The identification of the kinetic parameters of the reduced reaction network could lead to more reliable kinetic parameters, therefore the obtained reduced model can be used in reactor design more effectively.

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OP-I-4

MECHANISM OF CO OXIDATION OVER Pt-GROUP METALS UNDER HIGH PRESSURE CONDITIONS: LANGMUIR–HINSHELWOOD OR MARS–VAN KREVELEN?

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Although oxidation of CO seems to be a rather simple reaction, the fundamental understanding of the reaction mechanism under atmospheric pressure is still matter of debate [1]. In the literature there is still no general agreement concerning the more active state of Pt, Pd and Rh catalysts in CO oxidation reaction. Gao et al. [2] showed that the most reactive phase of Pt and Pd at low and high pressures is identical and corresponds to the reduced metal. On the other hand, it was claimed that the rate of CO oxidation is higher when the surface is oxidized [3]. In some cases, the conclusions have been based on the fact that the amount of surface oxide matched the catalytic activity during the oscillatory behavior and is thus responsible for the catalytic conversion [4,5]. Moreover, basing on the study of the oscillatory behavior during CO oxidation over Pd carried out by such modern methods as in-situ high-pressure STM [4] and operando surface x-ray diffraction (SXRD) [6] the authors concluded that the traditional Langmuir–Hinshelwood (L-H) mechanism was not valid any more, and the new Mars–van Krevelen (M-vK) mechanism had to be used instead.

The main goal of this work is to demonstrate that the simplest well-known Sales-Turner-Maple (S.T.M.) model [7], which is based on the L-H mechanism, can describe the main experimental findings regarding the CO oxidation reaction at high pressures. This model shows that in a high activity state the catalyst surface is partially oxidized, but this does not mean that the oxide phase is more active than the metallic phase.

Consider the conventional L-H model of CO oxidation on Pt surface:

$$\frac{d\theta_O}{dt} = 2k_1P_{O_2}\theta_*^2 - 2k_3\theta_O^2 - k_5\theta_O\theta_{CO}\,; \quad \frac{d\theta_{CO}}{dt} = k_2P_{CO}\theta_* - k_4\theta_{CO} - k_5\theta_O\theta_{CO}\,. \qquad (1)$$

OP-I-4

Let the concentration of vacant sites is $\theta_* = 1 - \theta_O - \theta_{CO} - \theta_{ox}$, where θ_{ox} is the coverage of surface oxide. If the reaction rate constant is much larger than the desorption rate constants, then the stationary reaction rate is $R_{CO_2} = (k_2 P_{CO})^2 / (2k_1 P_{O_2})$; it is independent on θ_{ox}, although the oxide inhibits the adsorption. Such solution may exist if oxygen is in excess, but it disappears if a value of θ_{ox} becomes too large. Based on this property of the conventional L-H model, Sales et al. [7] extended the system (1) and suggested a model for oscillations in which adsorbed oxygen can undergo a slow transformation to a tightly bound 'subsurface oxide', which can be reduced via the reaction with adsorbed CO. When the oxide coverage increases past an upper threshold value, the reaction rate abruptly decreases, and the surface begins to reduce. Reduction continues until a low-oxide threshold is reached, then the reaction switches back to a high-activity branch, and the surface begins to oxidize once again.

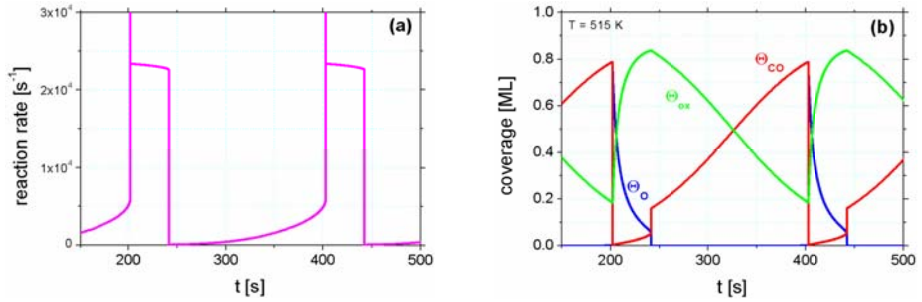

Fig. 1. Oscillations in the model

Fig.1a shows that in the high-activity state the reaction rate is practically constant. Here, the concentration of the oxide is large and one can say that the high-activity state is represented by the oxidized catalyst. At the same time, the conclusion about the larger activity of oxide, which has been done in ref. [4-6], is incorrect. Since the reaction rate constant is large enough and oxygen is in excess, the metallic surface state with $\theta_{ox} = 0$ has practically the same reactivity as the oxidized surface state with $\theta_{ox} = 0.8$ (see Fig. 1b). Thus, the chemisorbed oxygen-covered state may have the same reactivity as a partially oxidized state. The fast decrease of catalytic activity occurs only when a largely oxidized surface is formed. This means that the traditional L-H kinetics, extended by taking into account the oxide formation, can explain the results of experiments [4-6] in which an essential amount of oxide in the high-activity state was detected.

In summary, there is no experimental evidence that the M-vK mechanism is valid. Also, using the kinetic S.T.M.-model coupled with a CSTR reactor model, we could explain the main experimental controversies [1] regarding the temperature dependences of turnover frequencies at various P_{O2}/P_{CO} ratios.

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OP-I-5

THE KINETICS OF FLUE GAS PURIFICATION FOR PRESSURIZED OXY-COMBUSTION

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Pressurized oxy-combustion is a promising new technology for coal-fired power production that can deliver high combustion efficiency with a concentrated CO_2 stream suitable for carbon sequestration or utilization. Combustion takes place at elevated pressure, e.g. 15 bar, such that the dew point of the combustion flue gas is raised and the latent heat is recovered. Prior to final compression for storage or utilization, gaseous pollutants (primarily NO, NO_2 and SO_2) must also be removed from the combustion exhaust stream, otherwise harmful acid condensation can occur in downstream equipment. Pressurized oxy-combustion provides an opportunity for a novel method of pollutant removal, which uses direct water contact for flue gas cooling and latent heat recovery combined with simultaneous purification via pollutant adsorption and complex liquid phase chemistry.

Our experiments investigate the interaction between nitrite and sulfite in the liquid phase, quantifying parallel reaction rates for the formation of nitrous oxide (N_2O) and hydroxylamine disulfonic acid (HADS). The results determine the effects of pH, nitrite and sulfite molar ratio, and temperature in the initial formation period of N_2O and HADS, determining the liquid species composition at each concentration, temperature and reaction time applicable for commercial scrubbing columns. A kinetic model was developed from these results, describing the dependencies experimentally measured.

The larger prototype column has also been constructed and utilizes the liquid phase kinetics and process model to scale up the liquid chemistry as function of gas pressures, temperatures, flowrates, and pollutant concentrations equivalent to a 100-kW_{th} oxy-combustor output. It's primary objective is to optimize parameters to maximize flue gas purification while controlling liquid discharge temperature and heat recovery. The practical implications can lead to a reduction in costs and risk associated with flue gas purification and carbon capture, and can provide an additional efficiency gains for new, low CO_2 coal power plants.

The scale of these experiments have been linked via an an $ASPEN_{TM}$ model to provide a numerical sub-model for integration into a full-scale process model of a Staged, Pressurized Oxy-Combustion power plant.

OP-I-6

DIMETHYL ETHER CONVERSION TO GASOLINE GRADE HYDROCARBONS OVER ZSM-5: KINETIC STUDY IN A RECYCLE REACTOR

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Kinetic models for the conversion of methanol to gasoline grade hydrocarbons (MtG) have limited applicability in case dimethyl ether (DME) is used as feedstock. Considering the increasing interest of DME-to-hydrocarbons (DtH) conversion, we have developed a new kinetic model to describe the conversion of DME to hydrocarbons over a ZSM-5 catalyst.

It is widely accepted that the conversion of oxygenates to hydrocarbons is well described by the dual-cycle mechanisms. The relevant reactions of this mechanism were considered in the kinetic model presented in this research. These reactions include the formation of aromatic intermediates (polymethylbenzenes), which remain adsorbed in the zeolite cages (A); the dealkylation of these intermediates to ethylene and propylene (B); the methylation of low molecular olefins to hydrocarbons of longer chain length (C); the hydrogenation of C_2-C_4 olefins to the corresponding saturated hydrocarbons (D); and the dimerization reactions between C_3-C_4 olefins towards higher hydrocarbons (E). The kinetic investigations were performed in a gradientless fixed-bed external-recycle over a wide range of conditions, with temperatures from 325 °C to 375 °C, weight hourly space velocities (WHSV) from 25 h^{-1} to 125 h^{-1}, a total pressure of 1 bar using undiluted DME as feed.

The performance of the new model has been assessed by calculation of kinetic parameters and evaluation against physicochemical constraints. Moreover, this model was compared to more simplified models reported in literature. The newly developed model allowed better description of the experimental results.

Acknowledgements

The work presented in the current abstract was supported by the European Commission in the scope of the 7th Framework Programme in the Integrated Project BIOGO (www.biogo.eu) under grant agreement 604296.

METHANOL-TO-OLEFINS (MTO) ON ZSM-5: SINGLE-EVENT KINETIC MODELING, MECHANISTIC ANALYSIS AND REACTOR DESIGN

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Lower olefins are widely applied in the chemical industry. The expected growth of their demand cannot be satisfied by current synthesis routes like fluid catalytic cracking or steam cracking [1]. An alternative production method is methanol-to-olefins (MTO) where shape-selective zeolites convert methanol to DME, water, olefins, paraffins and aromatics [2]. In industrial applications, a part of the product spectrum is recycled in order to increase the propene selectivity (methanol-to-propene, MTP) [3]. By doing this, most of the methanol is consumed via olefin methylation. Current research shows that this mechanism seems not to be fully understood yet [4]. Therefore, in this study, microkinetic modeling should afford mechanistic insight which is then applied to reactor design.

Experimental data is obtained with a single tube quartz glass reactor which is filled with a commercial ZSM-5 catalyst and SiC. Methanol and butanol, diluted with nitrogen and water, are used as feed to simulate the industrial co-feed conditions. 40 different combinations of temperature, feed partial pressures and total volumetric flow rate are analyzed at five different contact times each.

A microkinetic model which follows the rules of the single-event concept [5] is created. For this, an existing model for olefin cracking [6] is extended with the methanol related reactions. Different versions of the single-event model for MTO are generated: for example, the methylation via an Eley-Rideal mechanism is compared with a Langmuir-Hinshelwood approach or a description via a co-adsorbed olefin [7]. Moreover, the role of DME as competing methylation agent is investigated. The microkinetic methodology is confronted with a simpler model from literature [8] where mechanistic routes are included, but also a lumping of species is performed. In a next step, the most suitable single-event kinetic model is enriched with side product formation [2] and used for reactor design as it allows vast extrapolation possibilities.

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The influence of different process parameters like the number of adiabatic beds, the temperature rise and both composition and amount of the recycle is analyzed.

Figure 1 shows that the agreement of the single-event kinetic model is high when the methylation is expressed with a co-adsorbed olefin and when a second, faster route for methylation via DME is allowed. The description of the compounds along the reactor can be seen in Figure 2. The strength of single-event microkinetics in comparison to the literature benchmark case [8] is the reduction of the number of unknown parameters [5] which yields significant values with a clear physical background. Nevertheless, some of the assumptions of Huang *et al.* [8] can be confirmed, for example the missing equilibration between oxygenates.

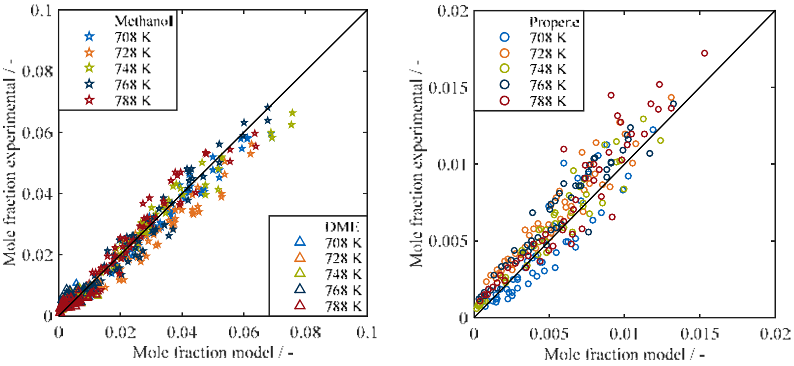

Figure 1. Parity plots for oxygenates (left) and propene (right) resulting from a single-event kinetic model for MTO

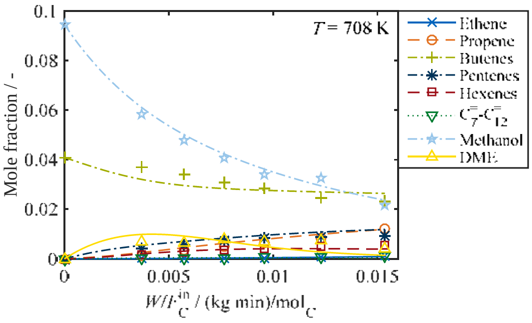

Figure 2. Simulated (lines) and measured (symbols) data;
p_{MeOH} = 114 mbar, p_{C4} = 49 mbar

In summary, the single-event concept allows to describe the reactivity of MTO in a microkinetic way with high agreement and a reasonable number of estimated parameters. Thus, the resulting model can be applied to reactor calculations.

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KINETIC MODEL FOR n-BUTANE TO BUTADIENE DEHYDROGENATION ON Cr-Al CATALYST

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Industrial processes of nonoxidative dehydrogenation of light paraffins are among the most important and widely used ways to produce light olefins, which are a feedstock for organic synthesis and production of polymerization products. Chromia/alumina (Cr-Al) catalysts are commonly used in dehydrogenation processes because of their high activity [1]. It is of great importance to know the kinetics of dehydrogenation reactions to provide ways for dehydrogenation catalysts and technologies optimization.

The aim of the work is to study reaction routes of n-butane dehydrogenation over Cr-Al catalyst, to develop the kinetic model and to determine the kinetic parameters.

Laboratory replica of industrial dehydrogenation catalyst with ca. 13 wt. % Cr [2] was used in this work. Experiments were performed in a fixed-bed reactor at temperatures 550-625 °C, contact times 0.1-0.9 s, initial partial pressures of n-butane 0.1-0.2 bar and different reaction times up to 45 minutes.

Dehydrogenation reactions take place together with cracking and coke deposition on the catalyst surface [3], and to a consequent progressive deactivation. These side reactions are more notable with an olefinic than with a paraffinic feed, which is taken into account in the reaction pathways (Fig. 1).

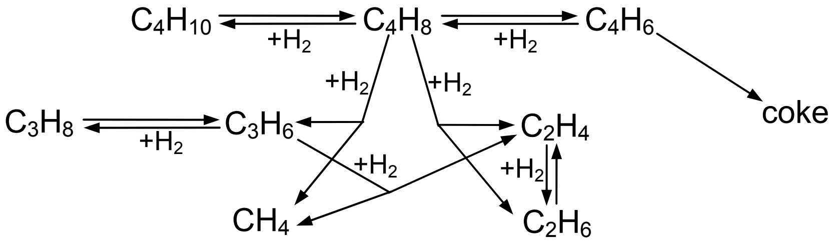

Figure 1. Pathways of n-butane dehydrogenation over Cr-Al catalyst

To estimate the rates of different reactions from Fig. 1 the mathematical modeling was performed. The model of the unsteady-state plug flow reactor taking into account the effect of catalyst deactivation by coke formation was used.

Figure 2 demonstrate the comparison between calculated and experimental data, which were used for the determination of the kinetic equations type and their kinetic parameters. The type of kinetic equations (Langmuir-Hinshelwood) and kinetic parameters (pre-exponential factors and activation energies) were estimated by minimizing the sum of the squared deviations between the experimental and simulated data. The modeling results show a good agreement with experimental data.

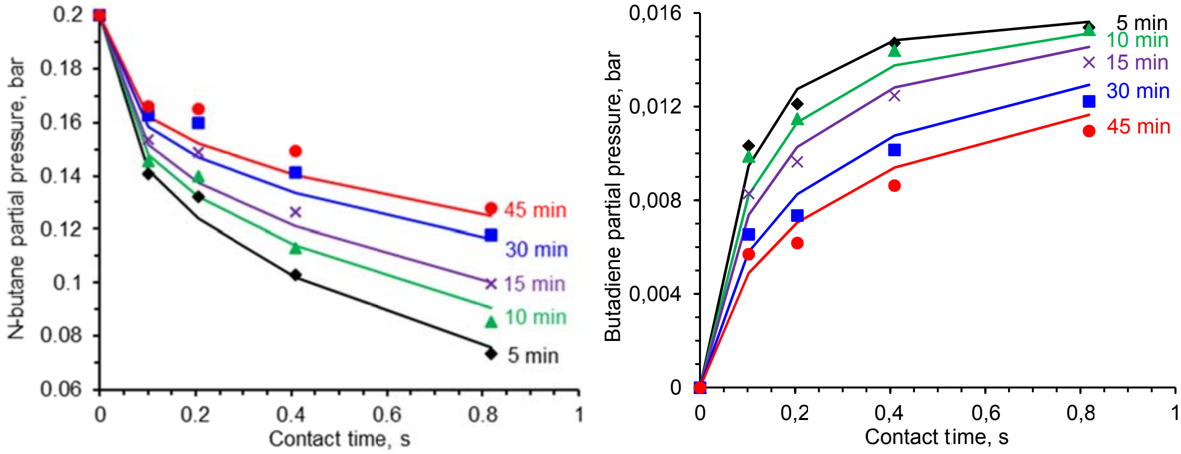

Figure 2. n-butane and butadiene partial pressure vs contact time at 575 °C and different reaction time (points – experiments, lines – modeling)

The kinetics of n-butane dehydrogenation was studied on a Cr-Al catalyst in a fixed-bed reactor. To determine kinetic parameters the model of the unsteady-state plug flow reactor taking into account the effect of catalyst deactivation by coke formation was used. The kinetic model based on Langmuir-Hinshelwood-type equations shows a good agreement with experimental data.

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KINETIC ASSESSMENT OF THE OXATIVE DEHYDROGENATION OF ETHANE USING A NiSnO CATALYSTS

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Ethane oxidative dehydrogenation (ODH-C_2) is one of most promising alternative ethylene production pathways compared with conventional processes [1-3]. Two main challenges are identified with respect to the implementation of ODH-C_2 at the industrial level: (1) the design and kinetic characterization of a catalyst leading to a high activity and selectivity to ethylene; and (2) the design of the industrial reactor accounting for the thermodynamic and kinetic properties of the reaction. Due to their selectivity to ethylene, nickel (Ni) and vanadium (V) based catalysts have been identified as the most promising ones for the ODH-C_2; nevertheless, their overall activity levels remains still low to commercially exploit these materials.

In this work, the ODH-C_2 is performance over a high selectivity NiSnO mixed oxide, which is synthesized by the evaporation method reported elsewhere [4]. To overcome its limitations with respect to activity, this NiSnO mixed oxide is kinetically characterized in a more extended range of operating condition, i.e., at total pressures from 1 to 5 bar, temperatures from 350 to 450 °C, O_2 inlet concentration from 3 to 9 mol %, and W/F_{Ao} from 20 to 70 g_{cat}-h-mol^{-1} to enhance the ethylene production towards industrially relevant levels. The NiSnO catalyst is evaluated in a microreaction unit, MICROMERITICS PID ENG & TECH model MA12216. The NiSnO catalyst is kinetically evaluated via uses an experimental design of the rotatable composite central type, based on a response surface method. The response variables are the ethane conversion (X_{C2H6}) and the selectivity to ethylene and carbon oxides (S_i), whereas the factors are total pressure, temperature, W/F_{Ao} and O_2 inlet concentration. The catalyst stability before actual kinetic experimentation is evaluated in the reaction unit at specific operating conditions (W/F_{Ao} = 47.5, %O_2 = 6 % and T = 400 °C) during ca. 6 h; herein the ethane conversion and ethylene selectivity are maintained during this time at 50 % and 60 %, respectively.

Kinetic experiments, performed under intrinsic conditions, lead to ethylene selectivity from 40% to 65%, for an ethane conversion range from 10 % to 30 %, respectively.

Finally, to relate operating condition with reaction rates and the corresponding reaction mechanism taking place at the investigated operating conditions, kinetic models based on Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Mars-van Krevelen (MvK) formalisms are developed following the pseudo-steady state approach and the reaction scheme presented in Figure 1. Physicochemical and statistical criteria are employed to evaluate LHHW and MvK formalisms to elucidate the macroscopic mechanism involved in the ODH-C_2 over a NiSnO.

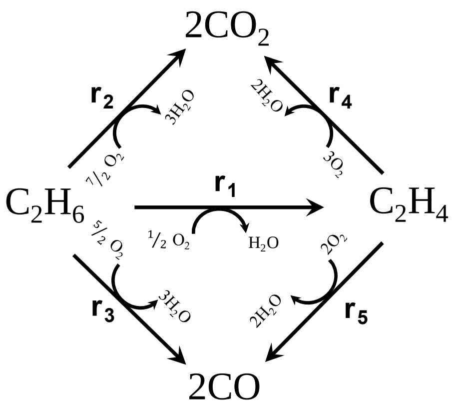

Figure 1. Reaction scheme for ODH-C_2

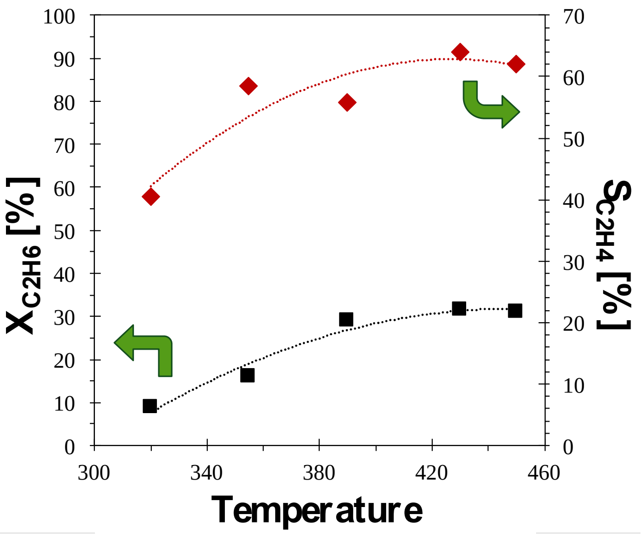

Figure 2. Temperature effect on X_{C2H6} and S_{C2H4} for ODH-C_2, W/F_{Ao} = 44 g_{cat}*h/mol and 3 % mol O_2

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KINETICS OF OXYGEN EXCHANGE BETWEEN NONSTOICHIOMETRIC OXIDES AND GAS PHASE: ANALYSIS OF GIBBS ENERGY RELATIONS IN TERMS OF CONTINUOUS HOMOLOGOUS SERIES

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Nonstoichiometric mixed ionic-electronic conducting (MIEC) perovskites ($ABO_{3-\delta}$) are applied as electrode materials in order to substitute expensive platinum in solid oxide fuel cells, and as membrane materials in catalytic membrane reactors providing simultaneous separation of oxygen from the air and the partial oxidation of light hydrocarbons, e.g., natural gas to value-added products. In this respect study of the mechanism and kinetics of oxygen exchange between the MIEC oxides and a gas phase attracts attention of many researchers for several decades [1-3]. Despite some progress in understanding the mechanism of oxygen exchange there are still many blind spots in this field that do not allow formulating general principles and stages of processes that determine the reaction on the oxide surface [4]. One of the main reasons is due to the fact that MIEC oxides are highly nonstoichiometric compounds allowing for wide variation in oxygen non-stoichiometry (δ) in different conditions of the kinetic experiments which significantly affects measured kinetic parameters. In this work we propose to consider MIEC oxides with different stoichiometry as different compounds forming *continuous series of homologues* that are involved in related reactions of oxygen exchange with the gas phase.

Following the proposed approach, the kinetic measurements are conducted in the iso-stoichiometric regime implying selection of conditions necessary to keep a constant non-stoichiometry δ at different temperatures. An advanced technique of oxygen partial pressure relaxation (OPPR) is used to improve reliability of the measured rate constants [5]. Original experimental setup is used to carry out the kinetic experiments by OPPR technique (Fig.1).

One of the important results of the study of homologous series is the establishment of fundamental principle of Gibbs energy relation between the free energy of activation ΔG_a and standard free energy change ΔG_r^0 of the reaction for related reactions: $\Delta G_a = \alpha \Delta G_r^0 + \beta$ which are commonly referred to as Linear Free-Energy Relationship (LFER).

By means of new approach we have shown that the oxygen exchange rate for two homologous series with different type of conductivity (metal-like $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ - SCF and semiconducting $SrFeO_{3-\delta}$ - SF) obeys the universal principle LFER having the form: $\Delta G_a = \Delta G_a^0 + n\mu O_2^{oxide}$. The electronic structure of two kinds of materials is reflected in the character of dependency between the equilibrium oxygen exchange rate $\Re_0$ and the oxide chemical potential; the enthalpic member gives the main contribution to the free activation energy change in case of the metal-like SCF, while the reactivity of semiconducting SF is determined by the entropic member.

According to a profound analogy between the related charge-transfer reactions involving homologues and electrochemical processes the Brønsted coefficient n corresponds to Tafel charge transfer coefficient α. The value of $n \sim 0.5$ which was obtained in our kinetics studies in the Tafel approach indicates that the transfer of the first electron is the slowest step of multielectron electrochemical reaction. Thus, it can be assumed that $O_2 + e^- = O_2^-$ is a limiting stage of oxygen exchange. This suggestion may be of great importance for understanding the mechanism of oxygen exchange in MIEC oxides requiring further detailed research.

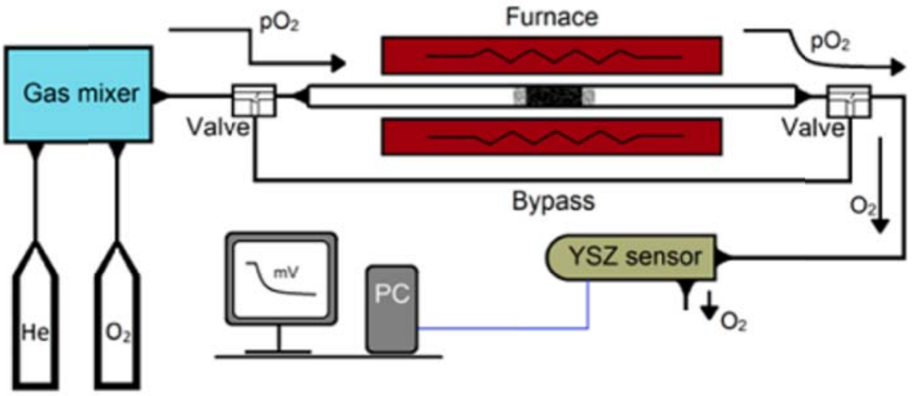

Fig. 1. Experimental installation for obtaining of the kinetic data by means of OPPR technique

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SELF-IGNITION DELAY OF METHANE-ALKANE FUEL COMPOSITIONS

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The problem of utilization of oil associated gas (OAG) which is a mixture of methane with alkanes from C_2 to C_5 or higher remains one of the most serious environmental and economic problems of the oil industry. Despite all efforts and legislative measures, the amount of the world OAG flaring doesn't decrease. The problem has a global scale, and the main reason for the lack of progress in reducing the OAG flaring is the lack of cost-effective low tonnage technology of its use.

A significant part of OAG, in principle, could be used as fuel to meet the power and heat demands of gas-producing companies and the regions. However, this is not a trivial problem. Unlike marketable natural gas OAG does not have any particular composition. Not only are there no two fields with the same gas composition, but the associated gas composition from the same field changes during development.

The presence of a wide range of C_2+ hydrocarbons in OAG, whose reactivity differs by orders of magnitude, hinders its effective use in modern power plants. The admixture of heavy components with low octane (methane) numbers makes OAG prone to detonation and prevents engines from reaching the rated power. The use of such mixtures increases the gumming and sooting processes in the engine, i.e., reduces its life. Existing methods for removing heavy components from hydrocarbon gases require complex equipment, high energy expenditure and are not justified for small (less than 10 MW) power plants.

Recently we have suggested principally new method for reducing the content of heavy components in OAG by their selective oxidative conversion to lighter high-octane compounds [1-3]. However, in all technologies, the required degree of OAG cleaning is closely related to costs, so that the most important issue in determining their costeffectiveness is the maximum permissible residual content of C_2+. In turn, it requires reliable information on the effect of these impurities on methane self-ignition. Available literature data on the self-ignition delay of such mixtures are insufficient.

In this work the effect of C_2–C_5 alkane addition on the self-ignition of methane–air stoichiometric mixtures have been studied to evaluate the degree of cleaning of OAG from heavy components required for its use in modern gas-fueled power plants.

Some preliminary results on the low-temperature self-ignition of binary methane–C_n alkane mixtures have been obtained previously in [4]. In this work we extended the investigation to more complex multicomponent mixtures to check the additivity of different alkanes in promoting methane self-ignition. Besides, the possibility of obtaining certified gas fuel from typical OAG by selective oxidative conversion of heavy components in OAG was checked. Experimental results and detailed computer modeling of self-ignition delay coincide well (Fig. 1). It was reviled, that the influence of all heavier alkanes on the self-ignition of methane is similar enough including the values of activation energies of self-ignition delay, although some abnormalities in C_2-C_5 series were noted (Fig. 1). It allows hoping that it will be possible to describe this influence by some unified equation. If that, it will be significantly easier to estimate necessary degree of OAG cleaning and the efficiency of the used methods thus promoting more wide OAG utilization for power generation.

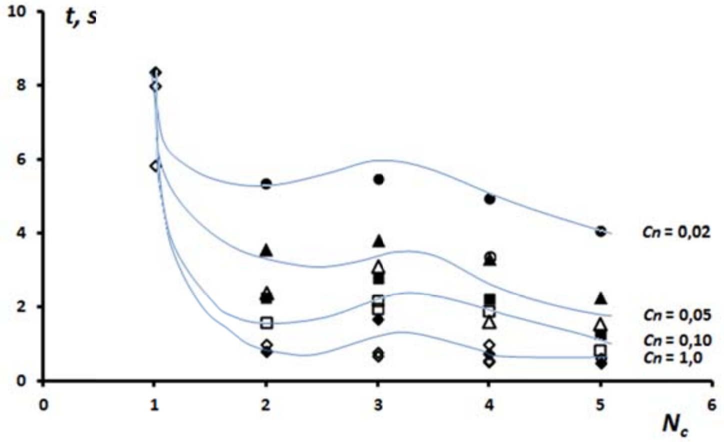

Fig. 1. Dependence of self-ignition delay on the number N_c of carbon atoms in alkane admixed to CH_4 (T_0 = 900 K, P = 1 atm). Empty symbols – experiment, filled symbols – calculations. C_n is the mole fraction of added alkane

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KINETIC STUDY OF CARBON DIOXIDE CONVERSION OF METHANE ON MEMBRANE CATALYSTS UNDER KNUDSEN DIFFUSION CONDITIONS

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The concepts of the organization of the catalytic process in a reactor with a membrane catalyst (extractor, contactor or distributor) differ only in the method of supplying reagents to the membrane catalyst and removing products, while the design of the membrane reactor remains unchanged. Separation properties of the membrane catalyst are required only in the case of an extractor which main function is to remove reaction products from the reaction volume. In other modes, the main function of the membrane catalyst is to control the mass transfer of the reagents in the pore structure (contactor) or reduce the negative effect of the reaction's thermal effect (distributor) [1]. The possibility of combining different ways of supplying reagents to the membrane catalyst with methods for exhausting reaction products opens up wide possibilities for controlling catalytic processes.

Carbon dioxide conversion of methane is an example illustrating such possibilities. From the economic point of view, carbon dioxide conversion of methane is more attractive than steam conversion if its main limitations are overcome.

There are two main shortcomings that prevent the commercial development of this process. First, the absence of a stable catalyst under the conditions of reaction (impossibility of using the existing steam conversion catalyst), and second, the thermodynamic limitations, which require the use of high temperatures and kinetic limitations, leads to low efficiency of using the catalyst surface.

Until recently the use of a membrane reactor for the carbon dioxide conversion of methane was considered only on the traditional way of an extractor reactor with a selective membrane placed in a layer of a bulk catalyst. Although, taking into account the high endothermicity of this process and the kinetic limitations, it was more efficient to apply the distributor mode, which allows achieving a more homogeneous temperature distribution in the membrane catalyst and/or contactor, which, under the conditions of Knudsen transport in the catalyst pores, allows intensifying the catalytic process.

In the case of carbon dioxide conversion of methane, the basis for selecting the best mode should be the kinetic experiment with the membrane catalyst carried out for each of these regimes.

In [2] were quantitatively established that the specific rate constant of the methane dissociation(the limiting stage) under the conditions of carbon dioxide conversion of methane in the contactor mode could increase by several orders of magnitude in a reactor with a membrane catalyst in relation to a traditional reactor.

At the same time, the difference in degree of conversion in the modes of the contactor, distributor and extractor was much less than the difference in these parameters in a reactor with a traditional catalyst. An analysis of the results of the kinetic experiment suggests that the advantages of a membrane catalyst in carbon dioxide conversion of methane are due to the occurrence of Knudsen transport in a membrane catalyst and its design, which makes it possible to use different driving forces, having a positive effect on the transport of reagents and reaction products in the pore structure of the membrane catalyst.

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OPTIMIZATION OF KINETIC DESCRIPTION OF GAS-PHASE AND CATALYTIC OXIDATION OF C1-C2 HYDROCARBONS

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Detailed kinetic scheme of homogeneous oxidation of C_1-C_2 hydrocarbons is the basis for solving the problems of modeling many processes – from gas-phase combustion to heterogeneous-homogeneous catalytic processes. To reflect the main features of the chemical mechanism, such a scheme must meet several requirements formulated earlier [1]. Among the descriptions known to date, the one called ARAMCO v1.3 and developed by the Combustion Chemistry Centre of the NUI Galway [2], apparently, most closely meets such requirements. This model is well documented and validated on a broad experimental basis. However, it includes 253 reactive species and several hundred elementary reactions and, therefore, can not be directly used in computational fluid dynamics (CFD) codes. Unfortunately, any reduction of a detailed kinetic scheme leads to a loss of its mechanistic consistency and decreases the accuracy of simulations. For some technical purposes the first factor is not critical. As to the accuracy, it can be optimized based on the requirements of a particular simulation task.

In this work we tested several reduced versions of the ARAMCO v1.3 scheme in modeling the oxidation of methane and its mixtures with ethane and ethylene over a wide range of conditions. The analysis was performed using the computation instruments included into the Chemical Wrokbench package developed and provided by Kintech Lab [3]. They allowed us to

- simulate reaction development in a wide range of reactors and conditions;
- reduce kinetic schemes using different criteria and procedures;
- reveal differencies in kinetic descriptions (substances, reactions, parameters).

On the first stage of this study it was found that in the case we are interested mainly in the behaviour of C_1-C_2 species, a satisfactory accuracy is preserved if C_{4+} species are not accounted. Thus, the size of the 'basic' description was significantly reduced.

Table 1 demonstrates the numbers of species and reactions in reduced schemes required to describe the reaction with given accuracy in different conditions. It is worth noticing that the sets of reactions in the reduced schemes differ significantly, and the extrapolation of them to different conditions leads to a great loss of accuracy.

By combining the descriptions for the whole range of conditions, we obtained two reduced schemes (Red.1 and Red.2 for 5 and 10 % MAX deviation, respectively).

Table 1.

Temperature, °C	Pressure, atm.	MAX deviation	substances	reactions
650	1	0.05	42	79
650	1	0.1	30	47
650	10	0.05	32	60
650	10	0.1	29	52
850	1	0.05	35	67
850	1	0.1	32	45
850	10	0.05	46	85
850	10	0.1	37	64
650-850 (Red.1)	1-10	0.05	60	141
650-850 (Red.2)	1-10	0.1	49	96

The fact that the Red.2 scheme contains some steps that are absent in Red.1 proves a formal character of the reduction procedure.

Fig. 1 shows that two reduced schemes can satisfactory describe the reaction rate. The same is found for the product distributions. Thus, the scheme can be optimized without a substantial loss of accuracy. In order to adopt such description for catalytic oxidation, one must combine a homogeneous scheme with a set of heterogeneous reactions [1].

The reduction procedure must be applied to the detailed combined scheme, and even the set of gas-phase steps in the final one would differ from those in Red.1 and/or Red.2 descriptions.

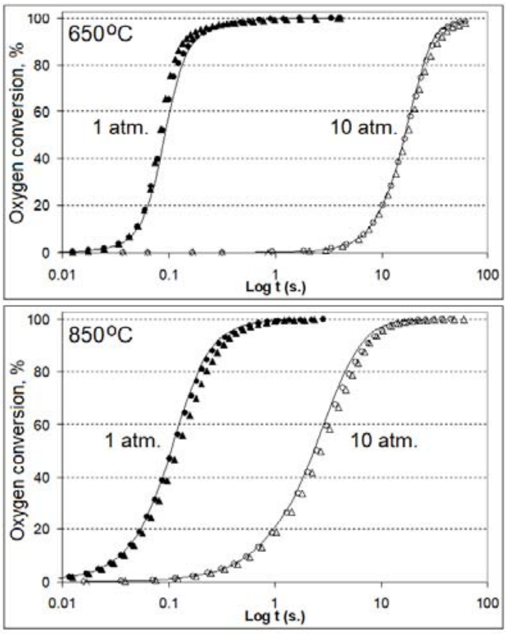

Fig.1. Simulated isothermal oxidation of methane at different temperatures and pressures; $CH_4 : O_2 : N_2 = 84 : 15 : 1$; lines - 'basic' scheme, o-Red.1, ▵-Red.2

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LOW-TEMPERATURE STEAM REFORMING OF LIGHT HYDROCARBONS: KINETIC STUDY ON THE WAY TO SELECTIVE CONVERSION

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Nowadays there is a problem of associated petroleum gas (APG) processing in Russia, Nigeria, Saudi Arabia and north states of USA. Typical APG composition is (vol. %) 50-70 CH_4, 5-10 C_2H_6, 10-30 C_{3+}-hydrocarbons (up to octane), 0-10 N_2, 0-10 CO_2. Due to the presence of C_{3+}-fraction, APG causes engine damage and therefore can not be used as a fuel to generate electricity directly at oil fields. APG also has high hydrocarbon dew point and can not be transported by conventional gas pipelines. Thus, an alternative way of APG utilization is necessary.

Low temperature steam reforming (LTSR) of APG represents a promising method of APG utilization. The process occurs at 250-350 °C and low steam to carbon ratio (H_2O/C_{C2+} mol. < 1). Overall process can be described by two reactions: irreversible steam reforming of C_{2+}-hydrocarbons with the formation of CO_2 and H_2 followed by reversible CO_2 methanation:

$$C_nH_{2n+2} + 2nH_2O \rightarrow (3n+1)H_2 + nCO_2 \quad (n > 1) \tag{1}$$

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \tag{2}$$

It was shown that reactivity of C_2-C_5 hydrocarbons increases with its molecular mass (Fig. 1). Converted APG with high methane content meet the requirements for natural gas: net calorific values are higher than 31.8 MJ/m^3 and Wobbe indexes are between 41.2 and 54.5 MJ/m^3. Reaction orders with respect to C_2-C_5 hydrocarbons are close to one. Reaction order with respect to steam is slightly negative or close to zero. Concentrations of CH_4, CO_2 and H_2 do not significantly affect the hydrocarbon conversion. Effective activation energies for C_2-C_5 LTSR range from 115 to 150 kJ/mol. Comparing the values of reaction quotient (Q_r) and equilibrium constant (K_P) at different temperatures (Fig. 2), we showed that CO_2 methanation occurs in quasi-equilibrium mode at temperature above 250 °C so overall process rate is limited by the reaction of C_2-C_5 hydrocarbons steam reforming. Ni catalysts are not subjected to carbon deposition under the reaction conditions despite this side process being thermodynamically possible.

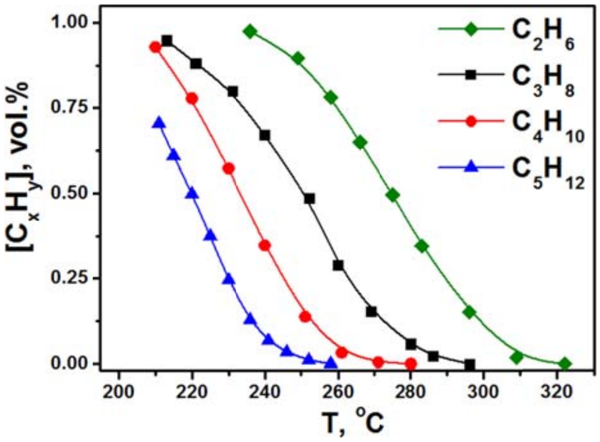

Fig. 1. Temperature dependencies of outlet concentrations (on dry basis) for steam reforming of C_2H_6, C_3H_8, C_4H_{10} and C_5H_{12}. Inlet gas mixture (vol. %): 58.4 CH_4, 0.6 C_nH_{2n+2}, 41 H_2O.
P = 1 bar, GHSV = 3000 h^{-1}

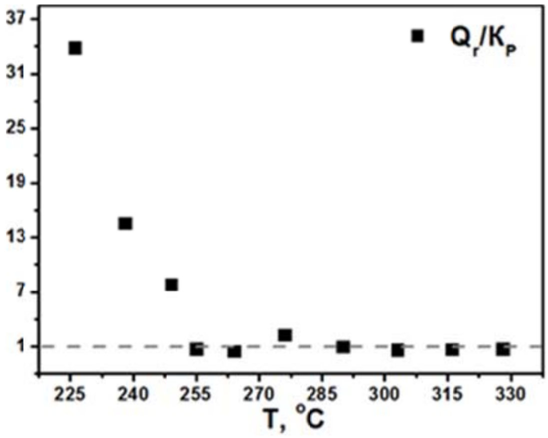

Fig. 2. Q_r/K_P at different T for LTSR of a complex C_2-C_5 mixture. Inlet gas (vol. %): 45.9 CH_4, 9.3 C_2H_6, 5.9 C_3H_8, 2.9 C_4H_{10}, 0.7 C_5H_{12}, 35.2 H_2O.
P = 1 bar, GHSV = 2600 h^{-1}

Based on the novel results obtained, we suggest an extended macrokinetic model which consists of reactions of hydrocarbons steam reforming, hydrocarbons hydrogenolysis and quasi-equilibrium reaction of CO_2 methanation. Fig. 3 shows comparison between simulation results and the experimental data on the LTSR methane-propane and methane-butane. This simple macrokinetic model correctly describes the experimental data and can be used for catalytic reactor design in perspective. The introduction of hydrogenolysis to the model provided correct description of low-temperature region.

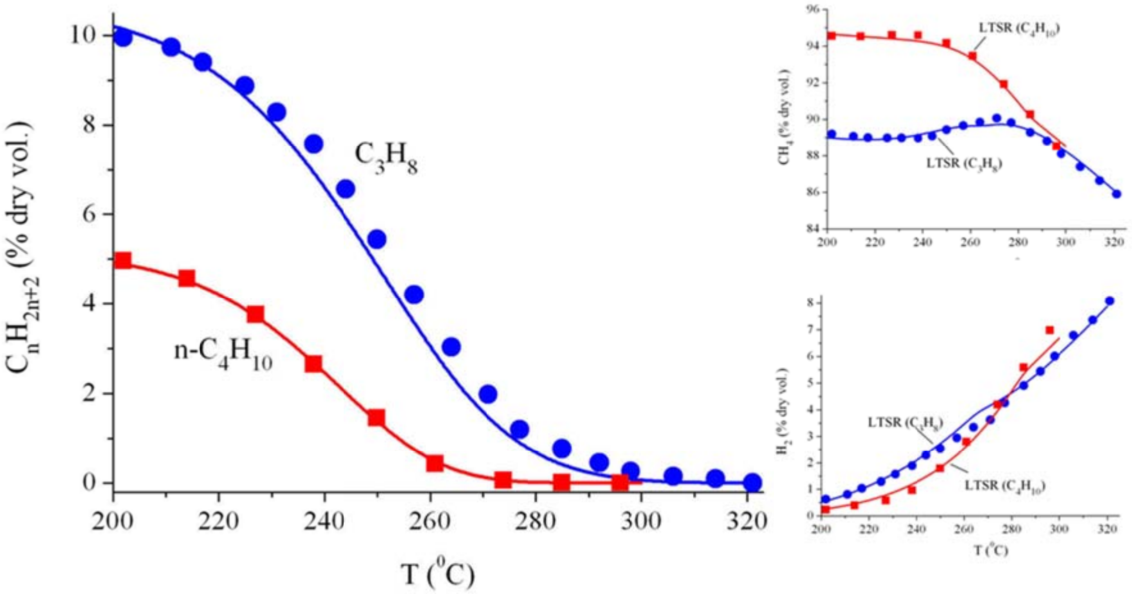

Fig. 3. The temperature dependencies of propane, butane, methane and hydrogen outlet concentrations (on dry basis) in the LTSR of model gas mixtures.
P = 1 bar, GHSV = 1800 h^{-1}. Points are experiment, lines are simulation

MESO-SCALE MODEL OF REACTION-DIFFUSION PROCESS WITHIN A CATALYST PARTICLE FOR MTO PROCESS

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The methanol to olefins (MTO) process provides an alternative approach to produce light olefins from nonoil resources [1]. Industrial MTO catalyst particles consist of meso/macro-porous support and micro-porous SAPO-34 zeolite crystals (active sites). In a region of a catalyst particle, the population of crystal particles and the support around them constitute a mesoscopic structure (see figure 1), which can be quantified by volume fraction, size and spatial distribution of the crystals in the region. The mesoscopic structure can influence the transport resistance and hence catalytic performance.

Different pore sizes (micro-pore and meso/macro-pore) inside the mesoscopic structure indicate the existence of different diffusion mechanisms [2]. For micro-pore SAPO-34 crystal particles, surface diffusion of adsorbed molecular components along the pore wall surface is dominant. While for meso/macro-pores, the bulk (or molecular) diffusion and Knudsen diffusion becomes important. In addition, if the pressure gradient inside the pellet is not negligible, the viscous or Darcy flow should be incorporated.

We developed a meso-scale model, based upon our previously proposed multi-region model [2], to simulate the diffusion-reaction process of mesoscopic structure. The meso-scale model is combined with two parts: the micro-scale reaction-diffusion model for crystal region and the diffusion model for support region. The micro-scale model, based on Maxwell-Stefan diffusion theory and ideal adsorbed solution theory (IAST), was obtained by fitting MTO experiments of SAPO-34 crystal particles. Here a simplified kinetic model [3] based on MTO dual-cyclic mechanism was used. The diffusion model for support region was developed based upon Maxwell-Stefan diffusion theory, including bulk diffusion, Knudsen diffusion and viscous flow. The details of the meso-scale model see figure 1.

The corresponding partial differential equation (PDE) systems, describing chemical reactions, bulk diffusion, Knudsen diffusion, surface diffusion and viscous flow, are converted to ODE systems based on finite volume method (FVM). The resulting ODE systems are solved by combination of Newton iteration, BDF methods, GMRES iteration, and preconditioning method.

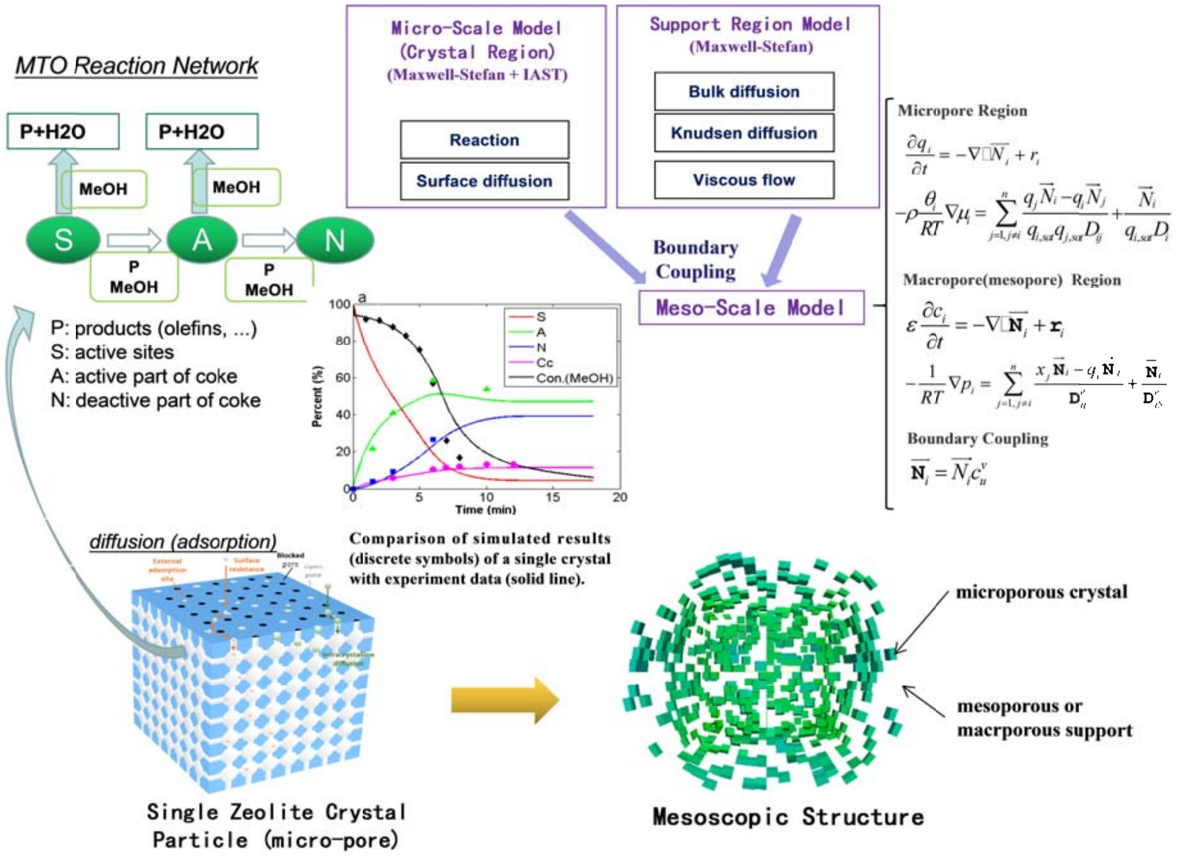

Figure 1. The meso-scale model for MTO process

The meso-scale model could effectively reveal the essence of MTO diffusion-reaction process that are directly related to the molecule-molecule and molecule-pore wall interactions within the catalyst particles. It is of significant importance as a potential bottom to up tool for investigating reaction-diffusion process in porous catalyst pellet.

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PROBING CATALYST DEACTIVATION BY COKE AT THE PARTICLE LEVEL DURING PROPANE DEHYDROGENATION USING A DISCRETE MODEL

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Propane dehydrogenation (PDH) has become an important alternative for on-purpose production of propylene, since the ever-growing demand for propylene cannot been met by the traditional techniques. However, the PDH processes suffer badly from the fast catalyst deactivation by coke. To design robust catalysts against deactivation by coke for PDH, it is essential to understand coking and deactivation at different length scales. Most studies in this field focus on the coke formation mechanisms at the micro-level or the active site level (nm), as well as the coking phenomena at the macro-level or the reactor level (m). However, the coking and deactivation process at the meso-level or the particle level (μm-mm) receives much less attention. In this contribution, at the catalyst particle level, the catalyst deactivation process associated with coke deposition is probed by using a discrete model.

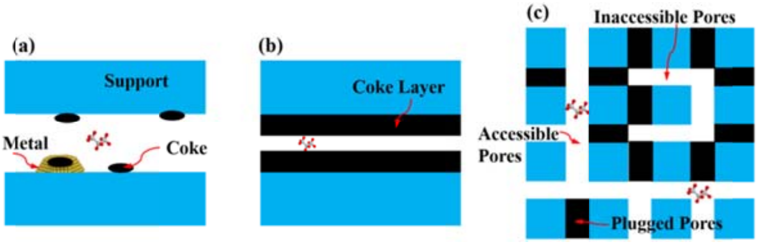

Figure 1. Mechanisms of catalyst deactivation by coke at the particle level.
(a) Site coverage, (b) pore narrowing, and (c) pore blockage [1]

The proposed discrete model describes coupled diffusion, reaction, coking, and deactivation in the catalyst particle; it also includes three mechanisms for catalyst deactivation by coke, namely, site coverage, pore narrowing, and pore blockage (see Fig. 1). There are three steps to build this discrete model: a pore network is firstly built by using the method developed by us [2], to represent the void space in the catalyst particle; then, the corresponding equations describing the complex physical and chemical processes in the catalyst are embedded into the pore network; finally, an algorithm is developed to solve these embedded equations.

With this discrete model, we obtain the representative relation between coke contents and apparent reaction rates, as seen in Fig. 2. The deactivation process can be separated into two stages. R_{app} at stage 2 decreases more rapidly than the one at stage 1, indicating the coke formed at stage 2 has a stronger toxicity to propane dehydrogenation reaction in the catalyst particle, which can be attributed to non-uniformly distiuted activity and the oriented pore blockage by coke (see Fig. 3). Meanwhile, we also probe the effects of coking kinetics, reaction conditions and pore network structure on coking and deactivation processes in the catalyst particle.

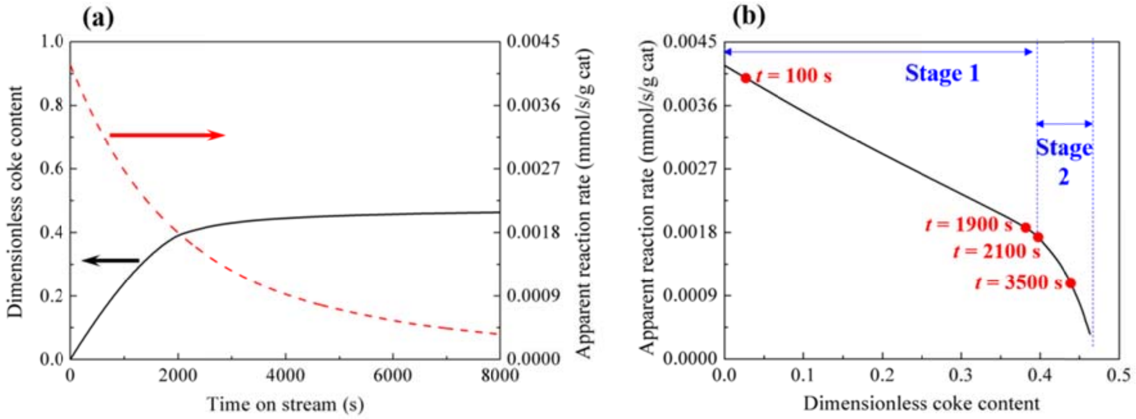

Figure 2. (a) The changes of dimensionless coke content and apparent reaction rate with time; (b) the correlation between dimensionless coke content and apparent reaction rate

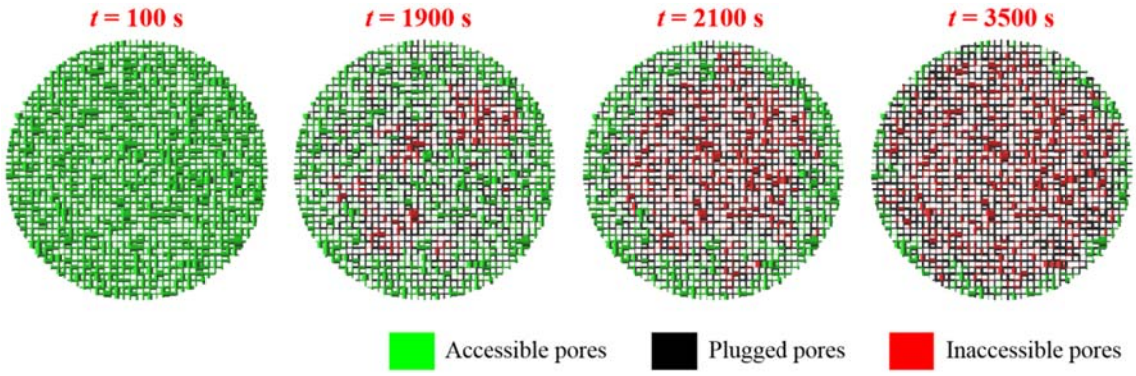

Figure 3. The distributions of coke-plugged pores in the pore network at different times on stream

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OP-I-17

EFFECTIVE THERMAL CONDUCTIVITY IN OPEN CELLULAR STRUCTURES: ANALYSIS OF THE EFFECT OF THE GEOMETRICAL PROPERTIES AND PERFORMANCE COMPARISON

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Heat management and thermal control are key aspects in the design and operability of several catalytic processes. Technical fixed bed reactors packed with catalytic pellets usually suffer from a poor radial heat transfer. To overcome this problem, conductive structured catalysts have been proposed as a suitable solution for the efficient management of strongly exo- and endothermic processes. In this view, open-cell foams and periodic open cellular structures (POCS) are considered among the most promising candidates in the context of process intensification of energy intensive processes. They are respectively random and ordered reticulated interconnected solid structures, whose repeated open cells are composed by solid struts and open windows. The totally interconnected solid matrix promotes high heat transfer rates, being the conduction in the solid matrix the main contribution to the heat transport. The analysis of the heat conduction mechanism is crucial to enable the rational design of these structures. We analyzed the heat transfer in the solid matrix in both structures by means of CFD simulations carried out on virtually reconstructed structures, aiming at deriving engineering correlations for the effective thermal conductivity. We generated the computational domain for the numerical simulations based on accurate digital reconstructions of the geometries. Random open-cell foams are generated according a previously proposed methodology [1,2]. The generation of the computational domain for POCS is carried out starting from the CAD files generated by repeating in the space the basic unit cell, i.e. cubic, diamond, tetrakaidekahedral

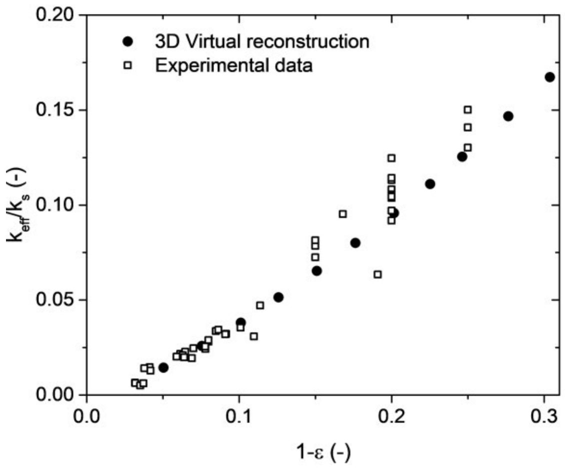

Figure 1. Effective thermal conductivity for open-cell foams evaluated with numerical simulations and experimental activities

(TKKD). The simulations of heat conduction in the solid matrix are carried out by imposing a temperature difference between two opposite faces. The heat flux across the solid matrix is calculated and used for the evaluation of the effective thermal conductivity. The procedure is assessed by comparing the estimated effective conductivities with literature data for open cell foams, as shown in Figure 1. A good agreement has been obtained for porosities higher than 0.85, while widely scattered experimental data are observed at lower porosity. Our results show that the main parameter controlling the heat conduction is the solid volumetric fraction. Moreover, the effect of different cellular structures, e.g. disordered foams, TKKD, cubic, diamond, is investigated. Figure 2 compares the heat conduction performances of foams and POCS. At high porosity, the open-cell foams show poorer heat transfer compared to ordered structures. Conversely, the performances of all the structures are similar at low void fractions. The performances of cubic and diamond cells are usually slightly worse than the TKKD. The different behavior of open-cell foams can be ascribed to the different solid distribution along the strut axis which characterizes these structures. We investigated this effect by varying the ratio of the node to the strut size. As expected, an increase of the ratio reduces the overall performances due to the higher resistance to the heat flow through the reduced strut cross-section, as also reported by Bianchi et al. [3]. As a whole, our analysis provides a full rationalization of the effects of the geometrical properties in open-cell foams and periodic open cellular structures, enabling their advanced design for heat-transfer limited applications.

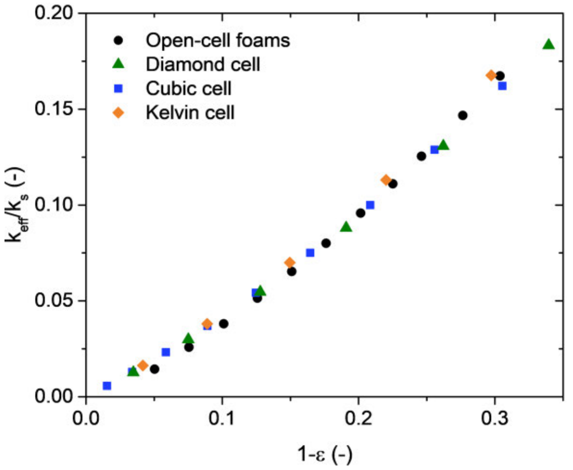

Figure 2. Effective thermal conductivity for several ordered and disordered cellular material

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COUPLING MICROKINETIC MODELING WITH CFD-DEM FOR THE SIMULATION OF FLUIDIZED REACTIVE SYSTEMS

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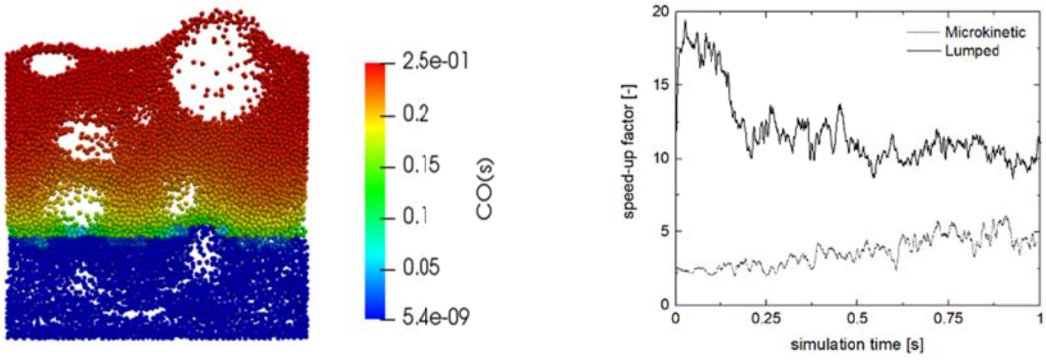
Fluidized bed reactors are a key technology for the management of the most challenging catalytic processes for their high heat transfer efficiency and the easiness of continuous operations. Nevertheless, the fundamental understanding of such systems is still poor and mainly relies on phenomenological models based on empirical correlations, providing limited insight the system. Fluidized beds are characterized by a complex fluid dynamic which determines the mixing and contact time between reactants and catalytic pellets. Therefore, an accurate description of the interplay between the transport phenomena at the reactor scale and the reactions at the catalyst surface is pivotal to accurately predict the system behavior. In this view, fundamental methodologies, such as CFD and microkinetic modeling, are key tools for the accurate analysis of the system. In particular, the microkinetic model accurately predict the surface chemistry on the basis of surrounding conditions provided by the CFD description of the macroscale flow inside the reactor. Here, we coupled the CFD-DEM (Computational Fluid Dynamics - Discrete Element Method) methodology for the prediction of the multiphase gas-solid flow with the microkinetic modeling of catalytic reactions. The solid phase is described by solving the energy and species balances along with site species conservation equations for each catalytic particle (i.e. transport/chemistry step), and the Newton's equations of motion (i.e. DEM step). The gas phase is described by solving the Navier-Stokes equations together with the energy and species mass balances. The accurate description of the chemistry introduces a drastic increase of the computational time (80% of the computational time is related to the solution of the transport/reaction term). Thus, we propose the application of the operator splitting [1] and of the *In-Situ* Adaptive Tabulation (ISAT) algorithms [2], successfully proposed for fixed bed reactor, to overcome these limitations. In particular, the operator-splitting accounts for the gas-solid transport and for the chemical reactions in separate fractional time steps. In this perspective, the transport can be analytically solved, whereas the chemical sub-step requires the solution of a stiff Ordinary Differential Equations (ODE) system. Thus, ISAT algorithm is applied to the reaction substep allowing for a crucial reduction of the computational cost. The proposed framework is capable of describing the complex interactions between the particles and the fluid flow along with the description of the surface reactivity, as shown in Figure 1(a). The operator splitting increases the performances of the system when the relative cost of transport and chemistry in the coupled approach is comparable. This effect enables, in the case of lumped reaction rates [3], a speed-up of the transport/chemistry step of 2 and 12 (Figure 1(b)), with and without ISAT, respectively, corresponding to an overall gain of 1.5 and 4. When a microkinetic model [4] is used, the cost of the solution of the chemistry is much larger than the one required for the solution of the transport. Nevertheless, the application of the tabulation techniques reduces the cost associated to the chemistry, reaching a speed-up around 4 times, as shown in Figure 1(b), when ISAT is employed.



(a) (b)

Figure 1. Snapshot of the fluidized bed where the particles are colored as a function of the fraction of adsorbed CO on the catalyst surface (a); speed-up of the transport/chemistry sub-step for lumped kinetics and microkinetic model (b)

Our analysis highlighted the capability of the operator splitting and ISAT algorithms to overcome the limitation imposed by the broad computational effort involved in the coupled solution of chemistry and transport in the particles. In particular, the reduction of the computational effort provided by the proposed methodologies allows for the fundamental investigation of fluidized bed systems, paving the way for the improvement of design and scale-up of these units.

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Acknowledgements

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2D CONTINUUM MODELS FOR FIXED-BED REACTOR DESIGN: IMPACT OF 2D FLOW FIELD ON INLET REGION CHARACTERISTICS

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Introduction

Modeling fixed-bed reactors by 2D continuum models is a well-established strategy to predict the performance of industrial reactors. Especially at low tube-to-particle ratios $d_{\mathrm{tube}}/d_{\mathrm{p}}$, radial porosity profiles and accompied velocity distributions can have a high impact on the behavior of the reactor [1].

Methodology

The nature of the 2D model arises from radially dependent bed porosities $\varepsilon(r)$. Fixed-beds consisting of ideal spheres can be characterized via the correlation of Bey and Eigenberger [2], while spheroidal catalyst pellets are adequately described with Giese's approach [3]. These correlations are applied to the 2D extended Brinkmann equation in combination with the Λ_r-model of Winterberg et al. [4,5] describing heat and mass disperion in axial and radial direction. Figure 1 sketches the applied solution routine, which enables to efficiently solve the stationary two-dimensional flow field with overall mass continuity segregated from heat and mass balances. Latter are discretized using orthogonal collocation on finite elements, while the flow field is solved via a staggered finite difference scheme. By applying a two dimensional flow field, instead of the popular extended 1D Brinkmann equation, radial flows induced by temperature and/or mole number changes are detectable [3].

Results

From analysis of the 2D flow fields, it can be deduced that perfect spheres and spheriodal particles strongly differ in resulting flow fields inside the packed bed (z=0). Furthermore, Figure 2 shows that the majority of radial flow already occurs before the actual packed bed (z<0). Hence, to adequately describe the impact of 2D flow field in continuum fixed-bed reactor models void inlet regions have to be considered. Impact on the temperature profile is exemplarily shown in Figure 3 for strongly exothermic oxidative dehydrogenation of ethane (ODHE) [6].

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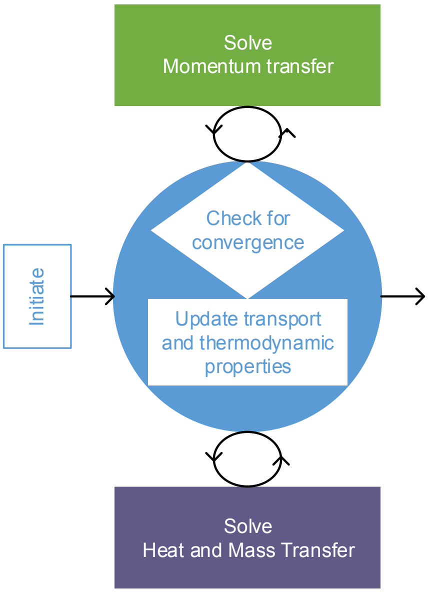

Figure 1. Scheme of solution routine

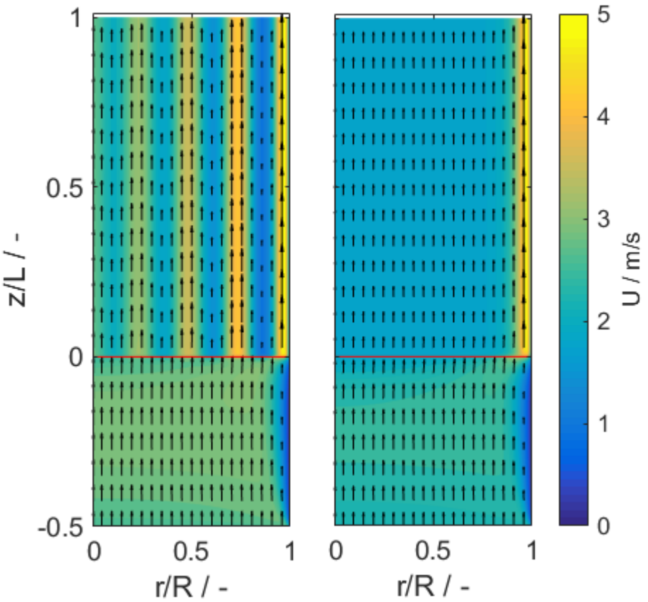

Figure 2. Velocity magnitude for packed bed of spheres (left) and spheroidal particles (right) with a void inlet region (z<0) at $d_{\text{tube}} = 2.54\,\text{cm}$, $d_{\text{tube}}/d_{\text{p}} = 7.5$, $\text{Re}_{\text{p}} = \frac{d_{\text{p}} u_0 \rho_{\text{fl}}}{\eta_{\text{fl}}} = 675$

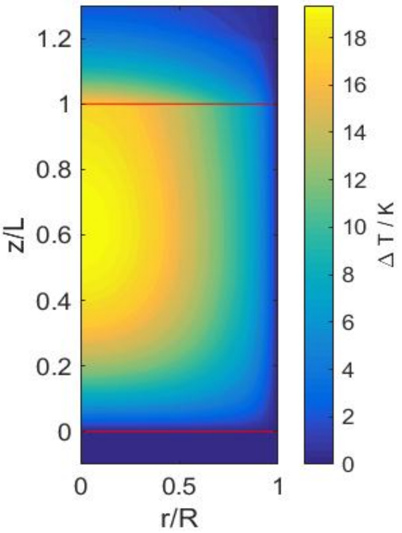

Figure 3. Example of temperature increase for ODH reaction in a spheroidal packed bed with void inlet (z<0) and inert tailing (z>1), a $T_{\text{in}} = 400\,°\text{C}$, $GHSV = 5000\,\text{h}^{-1}$

Furthermore, we compare the pseudo-homogeneous models with constistent heterogeneous model acounting for fluid and solid phase separately. Especially the influence of the inlet boundary condition (Dirichlet vs. Dankwerts) is succesively investigated. Furthermore, the widely applied neglection of radial velocities [6] is critically reviewed. In summary, our results demonstrate the impact of inlet region treatment in modeling of classic continuum fixed-bed reactor models on several reactor parameters.

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CHARACTERIZATION OF HYDRODYNAMICS, HEAT AND MASS TRANSPORT UNDER ABIOTIC AND BIOTIC CONDITION IN A TRAY BIOREACTOR FOR THE PRODUCTION OF PROTEASES OUT OF AGROINDUSTRIAL WASTES

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The solid-state fermentation (SSF) has gained attention in recent years in the biotechnology industry due to its great potential in the production of biologically active metabolites, namely enzymes, biofuels, food additives, precursor molecules for chemical and pharmaceutical industries, among other high value metabolites [1,2]. Despite the technological advances in SSF processes, there have not been sufficient studies related to the characterization, design and intensification of tray bioreactors. However, the state of the art in the fundamentals of reactor engineering offers a useful avenue for the conceptual design and intensification of this class of bioreactors, involving a microscopic characterization of the phenomenological interaction among kinetics and transport phenomena that occurs within the bioreactor.

The objective of this work is to characterize hydrodynamics, heat and mass transport under abiotic and biotic conditions in a tray bioreactor for the production of proteases (SSF) with *Yarrowia lipolytica* using agroindustrial wastes. This work accounts from the design of experiments to the development of models aimed at characterizing transport phenomena and kinetics under abiotic and biotic conditions, respectively.

The bioreactor operates in two stages, the first abiotic operation (without reaction) for the characterization of transport phenomena (hydrodynamics, heat transfer and mass transfer) and the second stage (biotic) consisting of the SSF for the production of proteases. In the abiotic stage, first, the pressure drop is determined at different inlet flows. This information is transferred to the Navier-Stokes equations coupled to Darcy and Forchheimer to describe the velocity field in the tray bioreactor. Second, heat transfer experiments in the absence of reaction allow the determination of the corresponding parameters, namely the wall heat transfer coefficient, and the effective thermal conductivity, fittings the temperature observations with a 2D pseudo homogenous model accounting for hydrodynamics. Third, mass transfer experiments are carried out to determine the mass transfer dispersion coefficient by fitting effluent concentration of CO_2, compound used as the tracer, with a 2D pseudo homogenous model. In the biotic stage, an extrinsic but macroscopic kinetic model, based on the effluent observations of O_2, CO_2, H_2O and protease activity, is developed.

Studies on biotic conditions allow the characterization of how transport phenomena interact with kinetics. Main results of this research are summarized as follows: Figures 1 and 2 display pressure drops and velocity profiles in the tray bioreactor, respectively. In heat transfer, effective thermal conductivity and wall heat transfer coefficient present a value of ca. 0.158 W m^{-1} K^{-1} and 0.0511 W m^{-2} K^{-1} at the studied inlet volumetric flow. In mass transfer studies, the dispersion coefficient presents values ranging from 0.123 to 0.220 m^2 s^{-1} at inlet flows between 200-400 mL/min, respectively. During the SSF, the maximum the production of CO_2, 11.83 mg g^{-1} h^{-1}, and protease activity (40 U g_{ms}^{-1}) were obtained at 36 hours of culture.

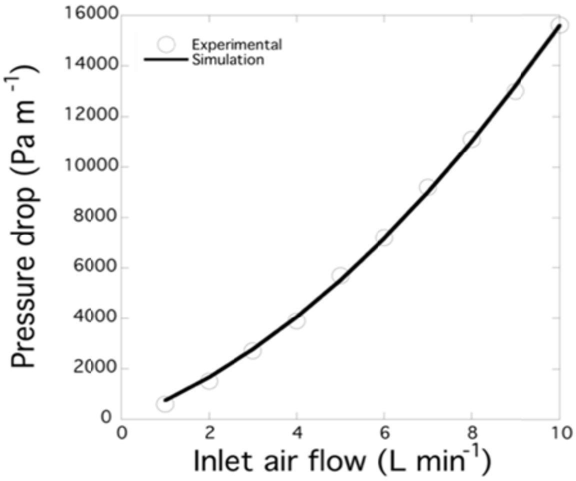

Figure 1. Pressure drop

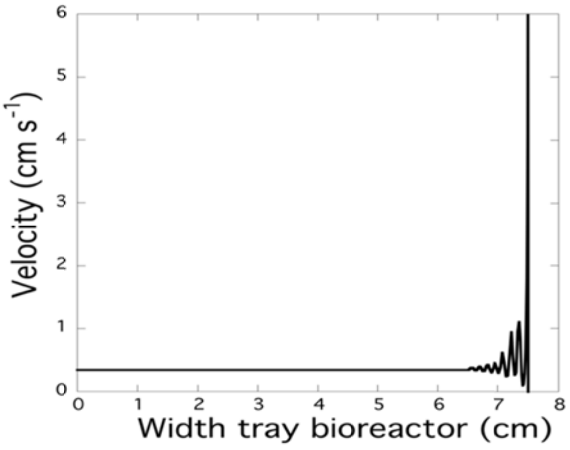

Figure 2. Velocity Profiles

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Acknowledgements

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EXPERIMENTAL ANALYSIS OF HYDROGEN PRODUCTION, LIQUID-TO-GAS MASS TRANSFER AND MIXING IN DARK FERMENTATION PROCESS

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Dark fermentation is an eco-friendly process able to produce second-generation biohydrogen from waste. This follows the same metabolic pathways as anaerobic digestion in which methanogenesis has been supressed, so that biohydrogen coproducts are CO_2 in the gas phase and volatile fatty acids in the digestate. This is considered as a well-established process, but process optimization and scale-up remain key issues, as the effects of abiotic parameters have been disregarded in the literature up to now. Thus, further data are required to better understand the interplay between biochemical processes, mixing conditions and liquid-to-gas mass transfer, as the inhibition of hydrogen production has already been reported in the literature due to hydrogen supersaturation in the liquid phase. The objective of this work is, therefore, to investigate biohydrogen production, measure $k_L a$ and estimate mixing time, not only as a function of agitation conditions, but also as a function of digestate viscosity which is also a key parameter of biohydrogen production processes.

In this work, dark fermentation cultures were carried out in a baffled mechanically-stirred bioreactor (2.0 L volume) equipped with a dual-stage impeller using five levels of viscosity (from $9.0 \cdot 10^{-4}$ to $6.1 \cdot 10^{-2}$ Pa.s) and three levels of rotation speed (40, 120 and 200 rpm). Inter-impeller clearance was also varied. First, biohydrogen production was studied using glucose as the substrate under controlled pH. Then, $k_L a$ was measured using dynamic deaeration/aeration experiments without biochemical rections in the same fluids under the same agitation conditions at a constant gas flow rate (5.0 L/h, i.e. 0.033 vvm), corresponding to the levels reported in the biohydrogen production process. $(k_L a)_{H_2}$was deduced from $(k_L a)_{O_2}$ using the Higbie penetration model. Finally, mixing time t_m was also measured in non-reactive and unaerated flows using Planar Laser Induced Fluorescence (PLIF), chemical decolorization and a local conductimetric method. Tracer injection was operated using two positions, corersponding to the injection positions of the alkaline buffer solution for pH control in dark fermentation process. Experiments were carried out in triplicate.

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Experimental results demonstrated that biohydrogen production and yield presented a maximum in the transitional flow regime as a function of the dimensionless Reynolds number (Re) which accounts simultaneously for the effects of rotation speed and digestate viscosity (data not shown). In particular, hydrogen production fell in established turbulent flow (Re>1000). Even though $(k_L a)_{H_2}$ was also strongly dependent of mixing conditions, it exhibited quite different trends: while hydrogen yield and productivity peaked when Re was about 200, $(k_L a)_{H_2}$ increased slowly below this value and rose steeply when Re>200 (**Figure 1a**). Although this behaviour was measured at constant gas flow rate which did not account for the decrease in hydrogen production under turbulent flow conditions, it emerges however clearly that a compromise between mass transfer enhancement and biogas production must be found in dark fermentation. It also arises from experimental data that neither hydrogen supersaturation nor the access to nutrients were the limiting steps when Re>200, as it can be inferred from mixing time data in **Figure 1b**. Thus, it is probable that turbulent stress applied on microorganisms is responsible for the impairment of biohydrogen production at high Re. Conversely, it seems necessary to approach transitional conditions in **Figure 1b**, as t_m increased steeply when Re decreased below 200. These results were also influenced by inter-impeller clearance and the injection point (data not shown), highlighting the effect of impeller design.

Concludingly, this work underlines the key role of agitation conditions and digestate viscosity, described univocally as a function of Re, on biohydrogen production, liquid-to-gas mass transfer and mixing, for the scale-up of the dark fermentation process.

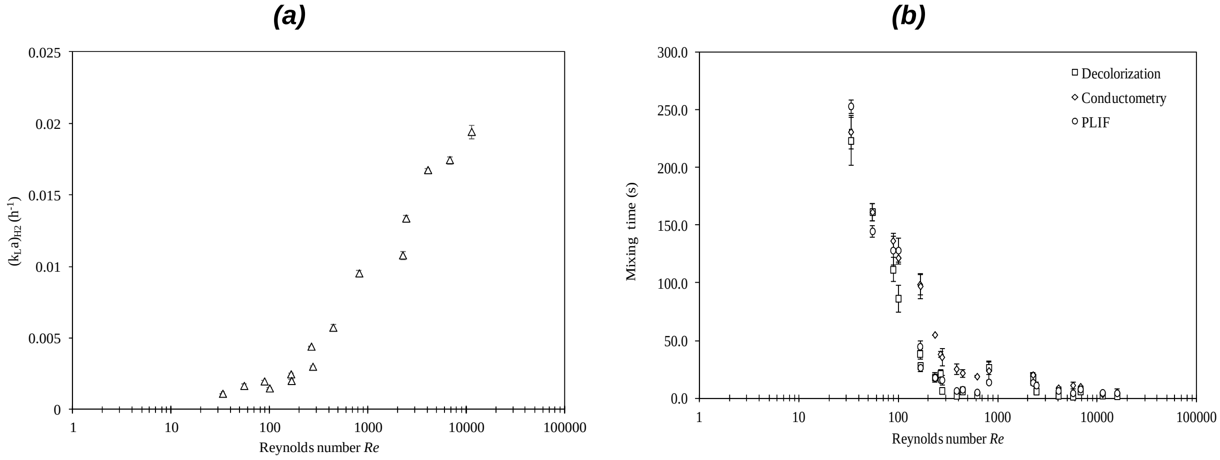

Figure 1. (a) Evolution of $(k_L a)_{H_2}$ as a function of the Re; **(b)** Evolution of the mixing time t_m from PLIF, chemical decolorization and conductimetric experiments as a function of the Re (inter-impeller clearance = 115 mm, injection position = 160 mm, error bars are based on triplicate experiments)

CHARACTERIZATION OF THE LOCAL HYDROMECHANICAL STRESS THROUGH EXPERIMENTAL AND NUMERICAL ANALYSIS OF HYDRODYNAMICS UNDER DARK FERMENTATION OPERATING CONDITIONS

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Dark fermentation is an anaerobic process in which organic waste can be broken down by microorganisms, resulting in the production of biohydrogen, CO_2 and the co-production of metabolites such as volatile fatty acids. In this process, mechanically-stirred bioreactors can generate laminar, transitional or turbulent flows, depending on agitation speed N and the viscosity μ of the digestate, as power input must be maintained below 10 W/m^3 to achieve economic sustainability. As pointed out in a previous work, biohydrogen production and yield could be described by a unique parameter, the dimensionless Reynolds number Re: H_2 production and yield peaked when Re was about 200, i.e. under transitional flow conditions. As many anaerobic bacteria are reputed to be sensitive to hydromechanical stress arising from turbulent conditions, a comparison between the average size of microorganism aggregates measured by laser diffraction (D_b) and the volume-average Kolmogorov length scale derived from power input was used to support this assumption. However, this approach neglects the spatial variability of power dissipation in stirred tanks. So, Computational Fluid Dynamics (CFD) could be an efficient tool for circumvent this issues, but the current turbulence closure models, i.e. the $k-\varepsilon$ models, exhibit a poor predictive ability close to transitional flow conditions. An experimental validation of the simulations is therefore compulsory. Thus, the objective is to analyze the local flow in the agitation and mixing conditions of acidogenic fermentation experimentally using PIV (Particle Image Velocimetry) and numerically using CFD, so that the assumption that turbulent eddies increase the need for cell maintenance and impair H_2 production when their size is lower than D_b can be assessed.

Experiments using PIV were carried out in a fully-baffled 2-L tank equipped with a dual-stage impeller under five levels of viscosity (from $9.0 \cdot 10^{-4}$ to $6.1 \cdot 10^{-2}$ Pa.s) and three levels of rotation speed (40, 120 and 200 rpm). The distribution of the turbulent kinetic energy k, the turbulent kinetic energy dissipation rate ε and the Kolmogorov length scale λ_k were derived from the flow field. In parallel, Reynolds-Averaged Navier-Stokes (RANS) simulations based on CFD (using *Phoenics* from *Cham Ltd.*, UK) were carried out and confronted to PIV data using several variants of the $k-\varepsilon$ turbulence model: namely, the Chen-Kim, Yakhot-Orszag (RNG), Murukami-Mochida-Kondo, Kao-Launder and standard $k-\varepsilon$ models.

First, the influence of turbulence modelling on the predictions of the flow field was assessed using PIV and the estimation of power input from the simulations for various flow conditions (rotation speed and viscosity). A good agreement between simulated and experimental data, including velocity magnitude and k was achieved using the Kao-Launder $k-\varepsilon$ model, as illustrated by **Figure 1a**. As a result, CFD can be considered as a tool robust enough to predict the flow field in the turbulent regime, even close to transitional conditions. Then, Kolmogorov length scale was deduced from local ε values in CFD simulations. This exhibited a strong spatial variation in the tank due to low power input, from the vicinity of the two impellers where it could be far lower than the size of microorganism aggregates to the inter-impeller region where it could be higher, as illustrated by **Figure 1b** that displays the local evolution of the λ_k/D_b ratio.

Concludingly, turbulence seems to impair biohydrogen production and yield even when $\lambda_k/D_b > 1$ in most regions of the anaerobic bioreactor, except the vicinity of the impellers. This highlights that further work may be conducted on the choice of impeller design and even impeller position to enhance dark fermentation.

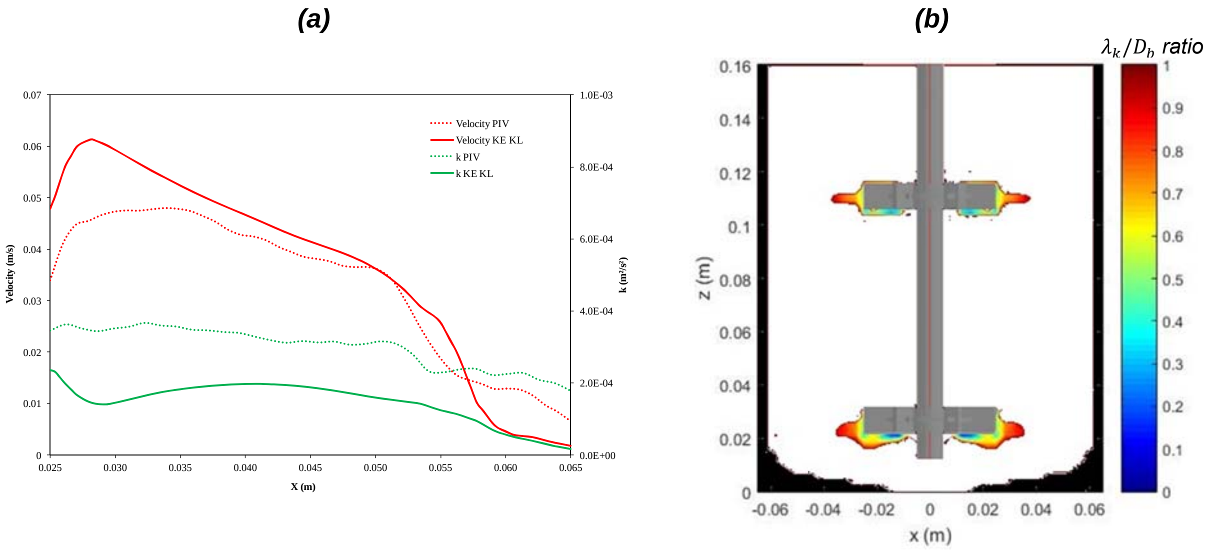

Figure 1. (a) Comparison between CFD and PIV velocity and k in the vertical $x-z$ plane at $\mu = 9.0 \cdot 10^{-4}\ Pa.s$ and $N = 40\ rpm$; **(b)** Corresponding CFD prediction of the λ_k/D_b ratio using the Kao-Launder $k-\varepsilon$ model

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SPATIALLY-RESOLVED REACTION CALORIMETRY WITH PACKED BED REACTOR

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Analysis of the kinetics of heterogeneously catalysed reactions is a complex problem due to a large number of simultaneous processes, including chemical reactions and mass-transfer. One of the known approaches to the analysis of such systems is a steady-state spatially-resolved method. The ability to acquire a spatial kinetic profile of a reaction at the steady state is widely utilised in research of heterogeneous catalytic processes.[1] There have been a number of reported attempts to observe and analyse the temperature profile of plug-flow reactor (PFR), however, only one work was successful in quantification of mass transfer effects, while other works either did not carry out quantitative [2–4] or quantified only integral (independent on kinetics and mass transport) values.[5, 6]

In our work, we analyse and discuss the potential of the continuous PFR with a spatially resolved temperature measurement to study fast mass transfer limited processes. We focus on the steady-state flow reactor with a catalytic packed bed and infrared temperature measurement (**Fig. 1**). This method can be applied to some of the challenging exothermic processes, such as multiphasic oxidations or acid-base reactions. Such flow system would be capable to provide independent observation of time dependant processes (chemical reaction) and spatial processes (mass transfer).

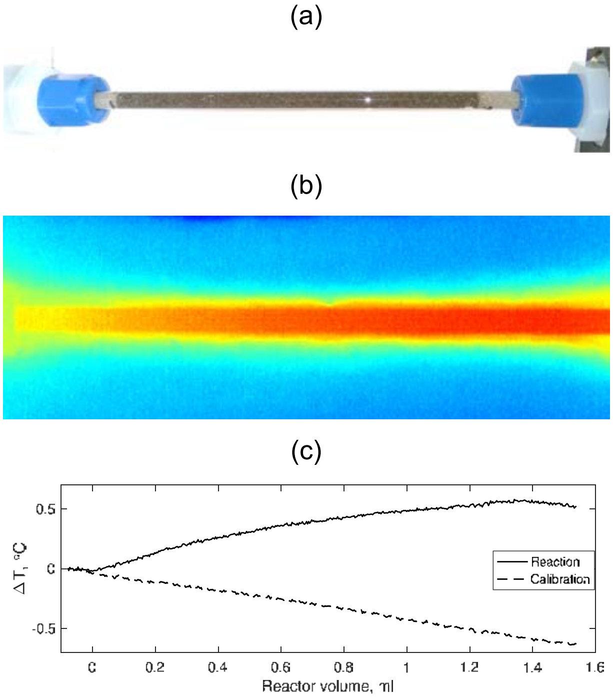
(a)
(b)
(c)

Fig. 1. PFR reactor and visualisation of its thermal profiles. (a) Image of the reactor; b) Thermal image of the reactor; c) Steady state chemical reaction and blank run thermal profiles

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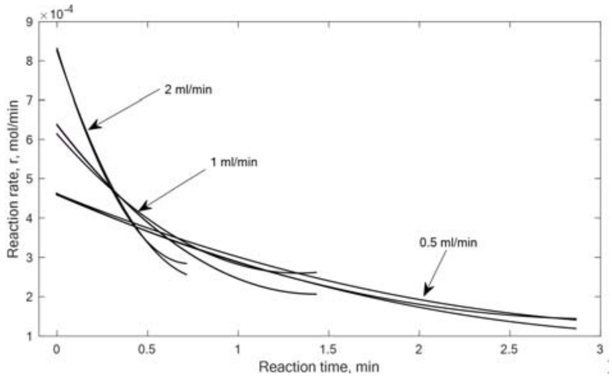

Fig. 2. Kinetic profiles of the hydrogen peroxide decomposition over heterogeneous catalyst at different flow rates

The work is divided into evaluation of the few prototypes of flow calorimeters and analysis of the advantages or disadvantages of some of them. One of the prototypes of the flow calorimeter, comprising of the glass reactor tube and infrared camera was assembled. This reactor has shown the possibility to achieve a steady state thermal profile in the conditions close to adiabatic. Some advantages of the method were illustrated with catalytic decomposition of hydrogen peroxide on manganese oxide. Two main features were displayed:

First feature – the multiple steady state kinetic profiles can be achieved at different flow rates. Comparison of such profiles allow to visualise change in catalyst mass transfer properties as a function of flow velocity (**Fig. 2**);

Second feature – the evolution of the catalyst activity over time can be observed by monitoring the thermal profile as catalyst deactivates.

With the flow calorimeter, it was shown that the mass transfer effects in the packed bed can be observed independently of kinetics of chemical reaction and catalyst deactivation. This provides a powerful tool for better understanding the implications of novel complex multiphasic heterogeneous catalytic processes as well as a fresh view on the already well-studied conventional processes.

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CAPTURING THE EFFECT OF PARTICLE CLUSTERS IN A DOWNFLOW REACTIVE SYSTEM VIA LARGE EDDY SIMULATIONS

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Several 4-way coupled reactive 3D DEM-LES were carried out using OpenFOAM to investigate the effect of particle clusters on the chemical behavior of a downer reactor during the fluid catalytic cracking of gasoil. Particle clusters in pneumatic conveying processes, such as FCC, prevent ideal contact between phases in the reactor and hence induce heat and mass transfer limitations; and reduce the efficiency (low-conversion zones) in both risers and downers.

A one-meter-long cylindrical downer was used as a canonical case to analyze the dynamics of particles via 3D DEM-LES. A fluid mesh of 7.0 10^6 hexahedral cells sufficed to meet the $y^+ < 1$ criterion for wall-resolved simulations. The simulation included 4.8 10^6 particles as inventory under normal operating conditions, which corresponds to a mean particle volume fraction of 0.01 over the simulated volume, a value characteristic of fast fluidization processes. A four-lump mechanism was selected to describe the chemical behavior of the process. This mechanism considers gasoil, gasoline, light gases and coke as lumped species of the process. Validation of the reactive 3D DEM-LES was carried out using experimental data found in literature [1]. The product distribution predicted by the 3D DEM-LES agrees with experimental data at the outlet with maximum differences on the yields of 10 rel.%.These can be attributed to the simplicity of the kinetic mechanism.

The identification of clusters in the downer reactor was carried out using the instantaneous position of the particles in the domain and the inter-particle distance. Information on the position of the particles in a cluster was used to determine the shape, size and distribution of the clusters. The detected clusters tend to be shaped like strands or sticks; particles naturally align in elongated structures to minimize the drag force and hence the shear stresses. The shear forces are reduced at the bottom of the reactor where the reaction rates and, hence, the acceleration accompanying the expansion is low. Besides, because of the change in the gas properties, particles respond slower to external disturbances from the gas phase and, therefore, larger and more stable clusters can be formed at the reactor outlet. This effect reduces the efficiency in the contact time between phases, reducing, as well, the efficiency of the reactor.

As the 3D DEM-LES simulations are computationally expensive, the aim is to include the effect of particle clustering in 1D simulations. Therefore, an artificial effectiveness factor (η_c) capable of capturing the influence of particle clusters in the prevailing chemistry is proposed, based on the cluster characteristics (frequency and mean lifetime) extracted from 3D DEM-LES results. The artificial effectiveness factor was calculated using two empirical correlations obtained from 3D DEM-LES, that provide the values of frequency and mean lifetime of clusters respectively, as function of the particle Reynolds number (Re_p) and the Stokes number (St), which are readily available in a 1D simulation. Figure 1 shows that the simulated gasoil conversion for the the modified 1D model, which considers η_c, is closer to experimental data than the uncorrected 1D model because the effect of clusters in the prevailing chemistry is considered via the effectiveness factor.

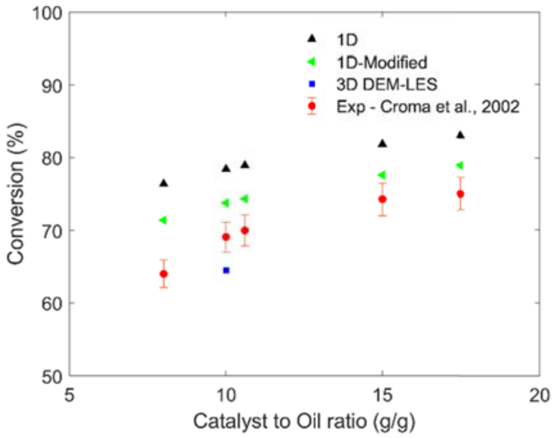

Figure 1. Comparative plot of predicted gasoil conversions using different models and the experimental data from [1]

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The authors would like to acknowledge the financial support from the Colombian Science Foundation (COLCIENCIAS) and the Colombian State Oil company (ECOPETROL S.A.) under contract No. 0423 –2013. LAV and PAR acknowledge financial support from a doctoral fellowship from the Fund for Scientific Research Flanders (FWO). The authors also acknowledge the financial support from the Long Term Structural Methusalem Funding by the Flemish Government–grant number BOF09/01M00409. The computational resources and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by Ghent University, FWO and the Flemish Government – department EWI.

TOMOGRAPHY BASED SIMULATION OF REACTIVE FLOW AT THE MICRO-SCALE: PARTICULATE FILTERS WITH WALL INTEGRATED CATALYST

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Introduction

Due to the need for high contact area, most catalytic systems exhibit a micro-scale structure. The standard simulation approach is to not resolve this micro-scale structure which is then described in terms of volume averaged homogeneous model equations [1]. Today, micro-scale geometries can be routinely obtained by X-ray tomography. In this contribution, the application of tomography-based micro-scale reactive flow simulation is demonstrated for the reactive flow in the pores of a particulate filter wall with integrated catalyst (washcoat). It is shown that micro-scale transport effects have a significant effect on the overall catalyst performance.

Simulation of the filter wall

A wall segment of a catalyzed particulate filter was analyzed by X-Ray tomography with a spatial resolution of ~1.4 μm and each volume element was assigned as either pore, substrate or washcoat, where only in the latter the reaction is taking place. The flow field and the concentration profiles were then computed using the PoreChem simulation code [2], assuming a first order reaction in the washcoat. The left side of Figure 1 shows the resulting flow field through a filter wall segment. The conversion in the filter wall was compared to a homogeneous model with the same dimensions and catalyst content, see right side of Figure 1.

Results and Discussion

It was found that the conversion in the pore network is lower than predicted by the homogeneous model, indicating the presence of some kind of in-pore transport limitation. Potential explanations are flow channelization through bigger pores leading to a broadening of the residence time distribution or diffusion limitations within the washcoat. It was found that in our case the reduced conversion can almost entirely be attributed to diffusion limitations in the wall integrated washcoat. If the diffusion in the washcoat was described by a standard effectiveness factor model with the effective washcoat diameter fitted to the results of the full pore scale simulation, a very good agreement between the full simulation and the homogeneous model was found, see right side of Figure 1. The effective washcoat diameter obtained by this fit is surprisingly large, compared to the apparent size of the washcoat particles. This can be explained by the limited accessibility of the washcoat due to the confinement in the pore structure.

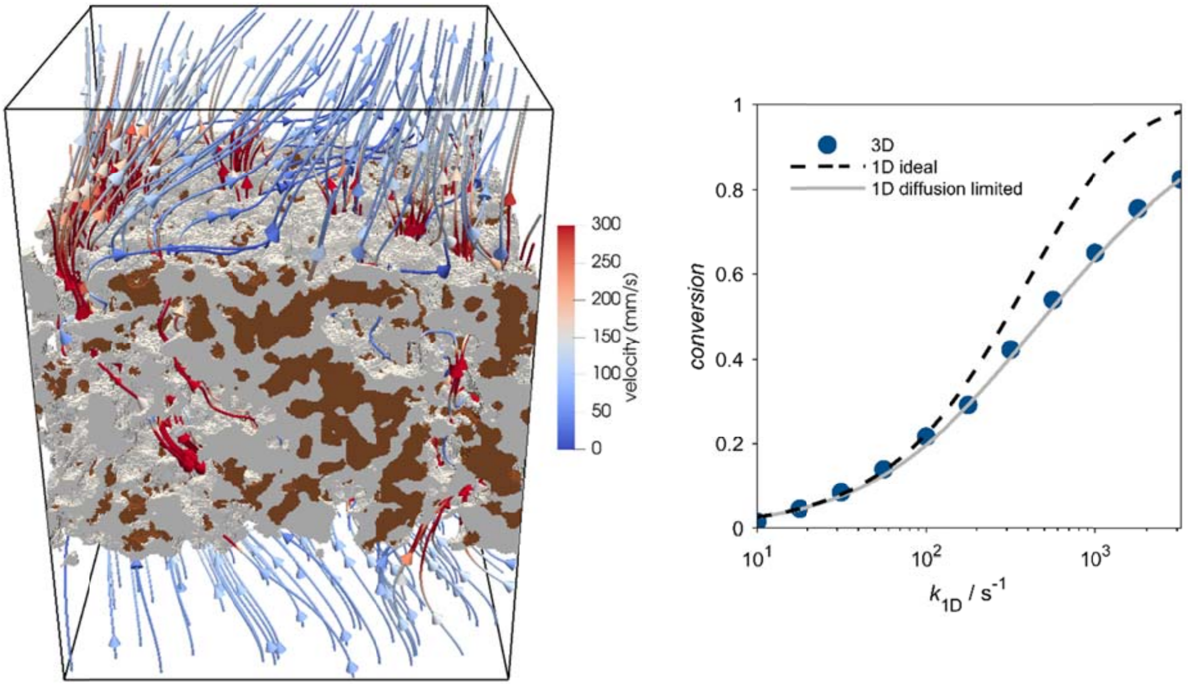

Figure 1. Left: section of the filter wall structure (490×640×490 μm); substrate (grey), washcoat (brown). Lines show the flow field. Right: conversion of the different models versus the reaction rate

Conclusions

In the shown case, micro-scale transport phenomena have significant effect on the overall performance, which would not have been captured by conventional homogeneous models. The result demonstrates the potential of tomography-based simulation for micro-scale catalyst design.

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ORAL PRESENTATIONS

Section II.

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

CFD MODELING OF MICROCHANNEL ENABLED ETHYLENE OXIDE SYNTHESIS WITH INTEGRATED COOLING

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Ethylene oxide (C_2H_4O) is an important intermediate for ethylene glycol, antifreezers, and polyesters. It is commercially produced by partial oxidation of ethylene ($C_2H_4 + 1/2O_2 = C_2H_4O$) on pure or α-Al_2O_3 supported silver catalysts. Under operating conditions total oxidation of ethylene ($C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$) occurs. These two competitive reactions are highly exothermic, making precise temperature control essential for high selectivity towards C_2H_4O. In this respect, use of wall-coated microchannel reactors characterized by heat transfer rates ~10^2 higher than those of conventional packed-beds become promising. Furthermore, ease of integration of cooling function allows microchannel units to operate under isothermal conditions favoring optimization of selectivity and conversion. This study aims to explore the potential benefits of heat exchange (HEX) integrated microchannel reactor operation on ethylene oxide synthesis by means of a detailed parametric study carried out by CFD-based modeling and simulation techniques.

Microchannel reactor is composed of solid wall separated parallel cooling and reactant channels involving counter-current flow of coolant (air) and reaction mixture, both at an inlet linear velocity of 2×10^{-2} m/s at atmospheric pressure. Dimensions for the cooling and reactant channels are the same, 4×10^{-4} m for height, 6×10^{-4} m for width, and 5×10^{-2} m for length. Reactant channel contains 5×10^{-5} m thick Ag/α-Al_2O_3 catalyst layers which are wash-coated onto opposing inner channel walls. Microchannel reactor operation is modeled in 2D on ANSYS 16.0 platform that utilizes finite volume method through which simultaneous solution of steady-state transport of momentum, heat and mass in porous catalyst and fluid phases together with catalytic reactions are obtained. Parametric study is made on reactant and coolant inlet temperatures, molar feed ratio (C_2H_4/O_2), and wall thickness and material which are selected in the ranges of 230-280 °C, 215-275 °C, 1.5-3, 4-8$\times10^{-4}$ m, respectively. Materials are selected as stainless steel, aluminum and cordierite. Details of the microchannel reactor and modeling approach can be found elsewhere [1].

OP-II-1

HEX integrated microchannel model is validated with the experimental data obtained from literature [2] (Figure 1). For this purpose, microchannel is modeled isothermally at 21 bar by varying volumetric flow rate and temperature (C_2H_4:O_2:N_2 = 4:19:77) between 1.21-6.55×10^{-9} Nm^3/s and 240-280 °C, respectively. Ethylene conversion increased with decreasing volumetric flow rate and increasing temperature. Selectivity, defined as the ratio of moles of ethylene oxide produced to moles of ethylene reacted, is found to increase with decreasing ethylene conversion in accordance with the experimental results [2].

Due to highly exothermic nature of oxidation reactions, fast heat removal from the reactor is necessary. Keeping the reactor almost isothermal by integrating cooling function (Figure 2) allows better control over conversion and selectivity. In fact, with HEX integrated microchannel model, selectivity of ethylene oxide is increased from 50.6 % to 54.1 % via elimination of ~50 °C of temperature rise. Reactant inlet temperature has a notable impact on ethylene conversion whereas the effect of coolant temperature is found negligible. Selectivity of ethylene oxide is not affected significantly by reactant or coolant temperature, as similarly stated in [2]. Increasing feed ratio decreased conversion, though selectivity of ethylene oxide is increased since partial oxidation is favored at O_2-lean conditions. Impact of the cooling function is dictated by the thickness and material of construction of the wall between the channels. Possibility of achieving near isothermal conditions by using thicker walls made of higher thermal conductivity materials, i.e. Al and steel is demonstrated.

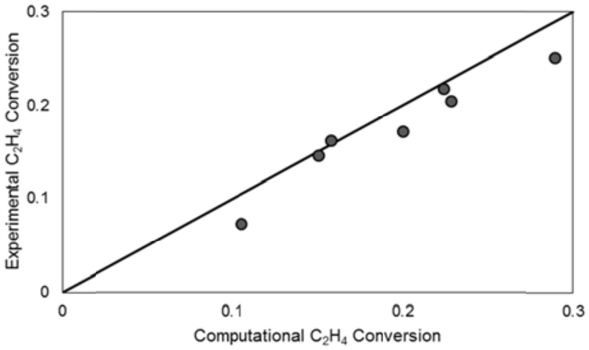

Figure 1. Validation of the model with the experimental data [2]

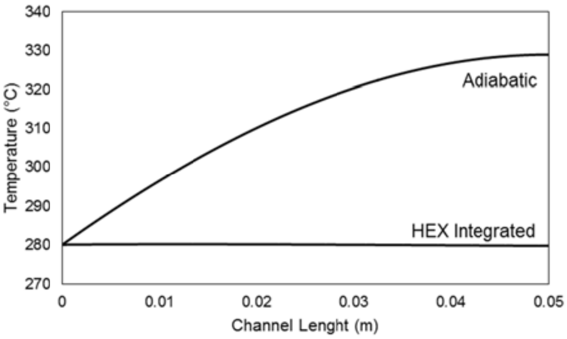

Figure 2. Temperature distribution along the reaction channel obtained in the absence and presence of cooling

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OPEN-CELL FOAMS AND PERIODIC OPEN-CELLULAR STRUCTURES AS ENHANCED SUBSTRATES FOR THE INTENSIFICATION OF ENVIRONMENTAL CATALYTIC PROCESSES

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Stochastic open-cell foams and Periodic Open-cellular Structures (POCS) represent a promising alternative to conventional honeycomb monoliths as catalyst supports for enviromental applications, e.g. automotive exhausts aftertreatment. The former are cellular materials composed by irregular interconnected cells sorrounded by solid struts and permeable windows. The latter are regular arrays of repeated unit cells with well-defined topology [1]. Both geometries provide high surface areas, high void fractions and high external transfer rates [2], besides they allow radial mixing which combined with custom shape design may offer significant advantages. Despite the high interest towards these structures, adequate engineering correlations for the description of gas-to-solid mass transfer and pressure drops are still missing. In this work, we present the results of a combined numerical and experimental investigation of the transport properties in these structures. Experimental analysis were performed running CO oxidation under diffusional limitations [2]. Numerical investigations are carried out on virtual reconstructions of the structures. Open-cell foams are generated according to an accurate reconstruction procedure [3] and the geometrical properties estimated according to a detailed model [4]. POCS are meshed from a CAD file. Infinitely fast surface reaction is imposed to mimic external transport limitations. A generalized correlation able to accurately describe the performances of samples with different geometrical properties and flow conditions is derived for foams and POCS. In contrast with honeycombs, the flow mechanism inside these structures is close to crossflow in tube bundles with the mass transfer coefficients increasing with the Reynolds number (Fig. 1a). This results, as an example, in a volumentric mass transfer coefficient at 5 m/s of ~4800 1/s for a commercial foam (d_c = 600 μm – ε = 0.9), strongly overcoming the conventional honeycomb (900/2.5) performance which is around 1100 1/s. Additionaly, two distinct flow regimes are found: one related to the fully laminar conditions and another one representative of the cross-mixing at high Reynold numbers. Pressure drops of foams and POCS are evaluated with a combined experimental and CFD approach over virtually reconstructed samples and 3D printed replicas. Ergun-type pressure drop correlations are able to describe the effect of the geometrical properties on the pressure losses, see Figure 1b.

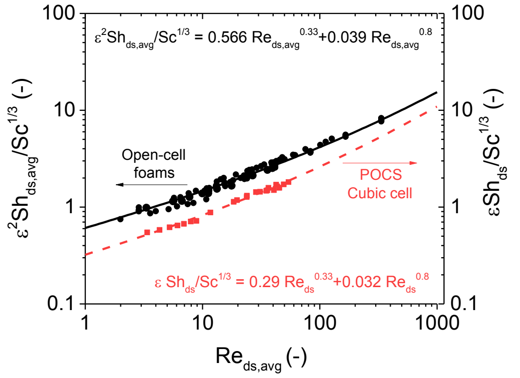

Figure 1a. Mass transfer correlations for foams and POCS and experimental data

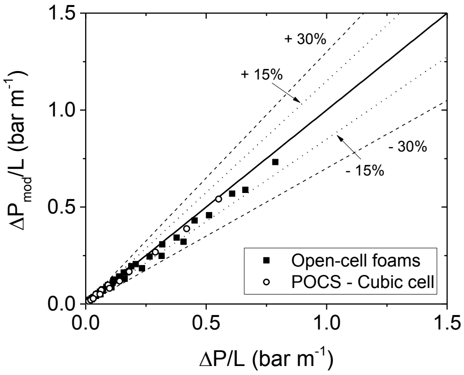

Figure 2b. Parity comparing the predictions of the pressure drops correlations against experimental data

A central aspect in environmental processes is the tradeoff between diffusional mass transfer and pressure drops, which can be described according to a dimensionless merit index introduced by Giani et al. [1]. With the derived correlations, we compare the performances of square channel honeycombs (HC in Fig. 2) with those calculated for these innovative structures. The comparison shows that in a narrow range of geometrical properties and operating conditions these structures are able to outperform current technologies. Moreover, the high degrees of freedom offerd by POCS structures is promising in view of further improving the performances and extending the range of the advantageous operative regimes.

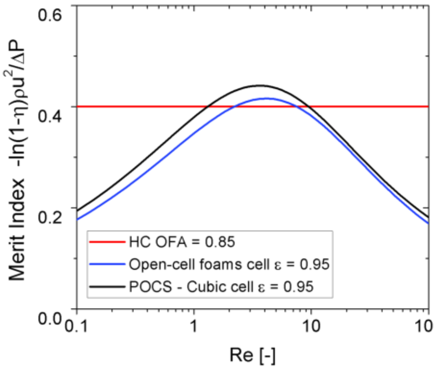

Figure 2. Merit index for different structured supports

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INVESTIGATION OF PACKED FOAMS AS A NOVEL REACTOR CONFIGURATION FOR METHANE STEAM REFORMING

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Structured catalysts represent a highly promising solution for the intensification of non-adiabatic chemical processes, where radial heat transfer represents the major issue which governs the reactor performance and limits considerably the reactor and process scalability [1]. The catalytic activation of metallic structures (i.e. honeycomb monoliths, open cell foams) by washcoat deposition has been widely studied as a promising solution to improve the performance of fixed bed reactors with respect to packed beds; indeed, heat transfer can be improved by the use of highly conductive, interconnected and catalytically active structured substrates [2]. Nevertheless, drawbacks such as smaller catalyst inventory with respect to packed beds and issues like washcoat adhesion and catalyst loading/unloading discourage the application of this technology at the industrial scale [3].

In this work, a novel fixed bed reactor configuration is proposed and tested for the steam reforming of CH_4; it consists of filling the voids of a highly conductive open-cell foam with small catalytic pellets. This reactor layout aims at enhancing the radial heat transfer of the tubular reactor by exploiting the thermal conductivity of the solid interconnected matrix, without losing catalyst inventory.

Tests were performed using a Rh/Al_2O_3 catalyst in form of alumina egg-shell particles, with diameter of 1.8 mm. In the case of the packed foam layout, FeCrAlY open cell foams (Porvair) of 12 PPI with 5 mm cell size and 0.92 void fraction were used; diameter and height of the foam were 29 mm and 25 mm, respectively. Drills were made for the thermocouple-wells. Temperature profiles were in fact recorded longitudinally across the catalytic bed in three different radial positions, namely at the centerline, at 8 mm from the center and at the wall. The foam void volumes were filled with catalytic particles (Fig. 1-a). For comparison, tests in a conventional packed bed system were also performed. In this case, the same load of catalytic particles was loaded in the reactor, mixed with SiC particles (SiC to catalyst weight ratio of 1.54) in order to have the same reactor volume as for the packed foam layout. In both configurations, tests were carried out in a tubular reactor (I.D. =

29.5 mm) externally heated by a furnace; tests were performed in the 600-800 °C range. The feed consisted of a steam/CH_4 mixture with S/C ratio of 3.5. Water was condensed and separated downstream from the reactor. A small N_2 flow was mixed to the dry product stream, as an internal standard. The quantification of reaction products was performed using an on line micro-GC (model GCX by Pollution) equipped with MolSieve and Porapack columns connected to TCD detectors.

Figure 1a. Close-up view of packed foam into the reactor

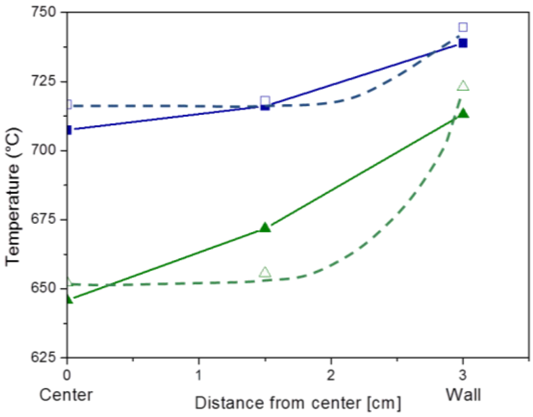

Figure 2b. Temperature profiles at catalytic bed outlet for packed foam (dashed line, open symbol) and packed bed (full line, full symbol) at 5000^{-1} (square) and 10000 h^{-1} (triangle)

At the GHSV of 5000 and 10000 h^{-1} the tests showed an improvement of CH_4 conversion in the packed foam over the packed bed, at fixed furnace temperature (i.e. from 92 % to 95 % at GHSV = 10000 h^{-1} and furnace temperature of 800 °C). Although small, this improvement is significant, given the irreducible role of thermodynamics at these high temperatures. This behavior can be ascribed to the reduced heat transfer resistances from the reactor wall to the catalyst, which enabled smaller temperature gradients and flatter T-profiles along the radial direction thanks to the conductive heat transfer mechanism favored by the open cell foam structure (Fig. 1-b). Such enhanced heat transfer performances were even more evident at higher space velocities. Conversely, at all space velocities, the packed bed with SiC partcles showed more pronounced radial gradients, thus uneven rate distributions within the catalyst mass.

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PORE-SCALE MODELING OF COATED CATALYTIC FILTERS

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Increasingly stringent European legislation for particulate matter emissions in automotive applications requires the use of particulate filters not only for Diesel cars but newly also for cars with gasoline engines [1,2]. Current trend is the integration of catalytic coating for abatement of gaseous pollutants into the filter, making the system more compact. Distribution of the catalytic coating in the porous filter substrate affects the catalytic activity, soot trapping efficiency and pressure drop.

This work presents a novel methodology for pore-scale modeling of flow, diffusion and reaction [3] combined with soot particles filtration. The models work with 3D–reconstruction of porous filter wall obtained from X-ray tomography (XRT) scans, describing pore morphology as well as spatial distribution of solid phases (substrate and coating). The XRT images are transformed into simulation mesh suitable for computations in OpenFOAM simulation environment. Processes in the filter wall are decoupled and solved by in-house developed models: (i) flow through filter pores, (ii) gas component convection, diffusion and reaction in the coated zones, and (iii) soot particle transport and filtration, including Brownian motion (Figure 1).

Three coated gasoline particulate filters (GPF) are examined in this work. The samples are based on cordierite substrate and vary in the distribution of Pd–Al_2O_3 coating: (i) in wall, (ii) combined in+on wall, and (iii) on wall. For each sample, eight sections are reconstructed and simulations are repeated in order to obtain statistically representative results. The average pressure drop, permeability and gas component conversion are calculated from steady-state pressure, velocity and concentration fields in the reconstructed domain. The statistics of particle trapping then allows evaluation of filtration efficiency depending on soot particle size. The predicted performance is then confronted with the measured data.

The results suggest that the gas predominantly flows through remaining free pores in the filter wall and cracks in the coated layer. Large domains of compact catalytic coating covering complete channel wall result in a significant increase of pressure drop as the local permeability of the coating is two orders of magnitude smaller than that of bare filter wall. The filtration efficiency and pressure drop are more sensitive to coating distribution than the conversion of gas components. The most promising structure combines in-wall and partial on-wall coating. The developed models open the doors to computer-aided optimization of coating distribution in particulate filters.

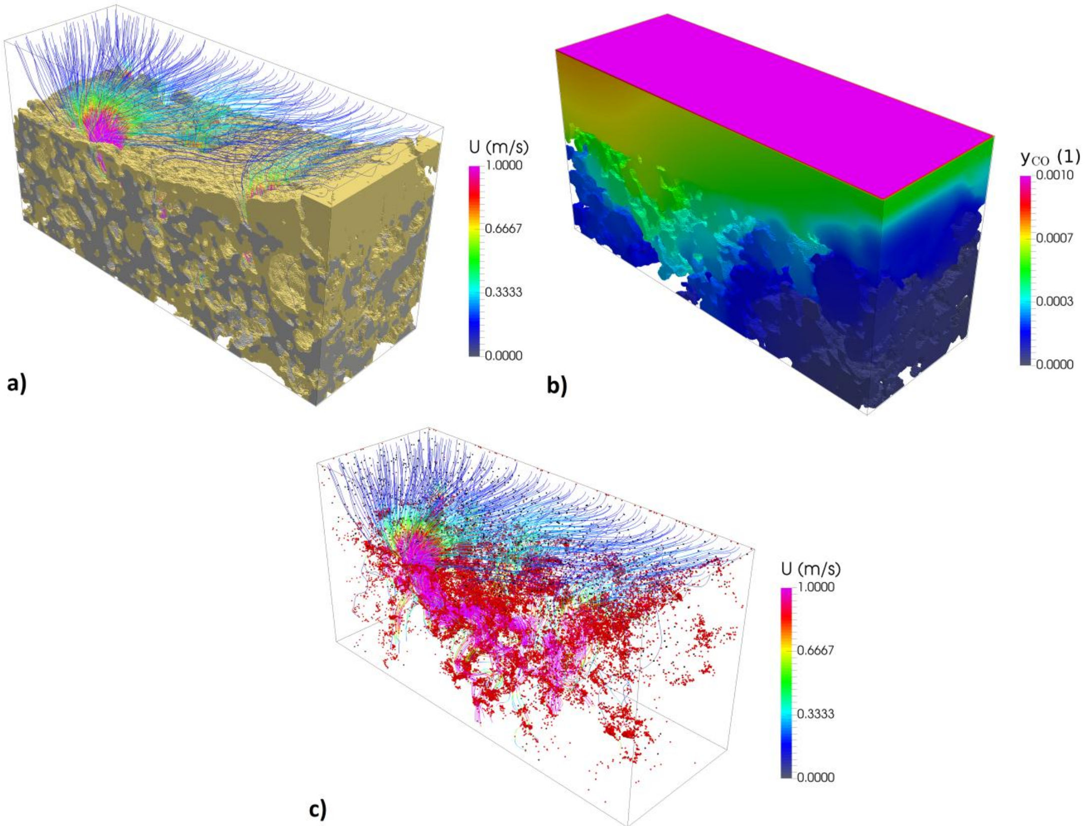

Figure 1. Filter sample with combined in-wall and on-wall coating.
a) Reconstructed wall structure (grey = substrate, yellow = catalytic coating) with streamlines,
b) CO concentration profile, c) soot particles (black = moving, red = trapped)

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Acknowledgements

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MATHEMATICAL MODELING OF HIGHLY EXOTHERMAL PROCESSES IN MICRO-CHANNEL REACTORS

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In the last years, the studies of catalytic processes in micro-channel reactors (MCR) have received great attention. Due to the small sizes of reaction zone, such reactors have advantages over conventional ones, in particular, higher efficiency of heat and mass transfer, which play an important role if the process is accompanied by substantial heat release or heat consumption.

The paper is devoted to the theoretical study of highly exothermal process of methanol to formaldehyde oxidation in MCR. The MCR constitute a brass disc 10 mm thick and 52 mm in diameter with 250 channels filled by the crushed industrial iron-molybdenum catalyst. The diameter of channels is 1 mm. The reactor is heated up to the reaction temperature in the flow of inert gas. Then reacting mixture is fed to the reactor. The oxygen to methanol ratio is 1.5. The influence of methanol concentration (C_m), velocity at the inlet of reactor (u) and temperature (T) on methanol conversion (x) and formaldehyde selectivity is studied.

Mathematical modeling is done on the base of two models:

1) The heating of the reactor in the flow of inert gas is modeled using 3D unsteady-state reactor model which takes into account the convective heat and mass transfer, effective thermal conductivity and diffusion in the cannels with catalyst, thermal conductivity of solid material of the disc without catalyst in channels and heat exchange with furnace. Heat exchange between these two computational domains, solid material of the disk and channels with catalyst, is also considered.

We can see (Fig. 1) that difference in the temperature values at various locations within the reactor is not more than 3 degrees, so we suppose that all channels are in the similar conditions and we consider then only the processes in the separate channel.

2) The influence of the parameters on the process performance is studied using 2D cylindrically symmetric steady-state channel model which takes into account the convective heat and mass transfer, effective thermal conductivity and diffusion in the channel, heat exchange between channel and its wall, catalytic reactions.

We can see (Fig. 2) that the maximal difference between temperature at the reactor axis and at the wall equals to 7 °C for given parameters. Temperature increase at the reactor outlet (Fig. 3) results in the rise of methanol conversion for both values of C_m. Results of modeling are compared with the MCR experiments previously presented in [1]. We obtain a good agreement between calculated and experimental data (Fig. 3).

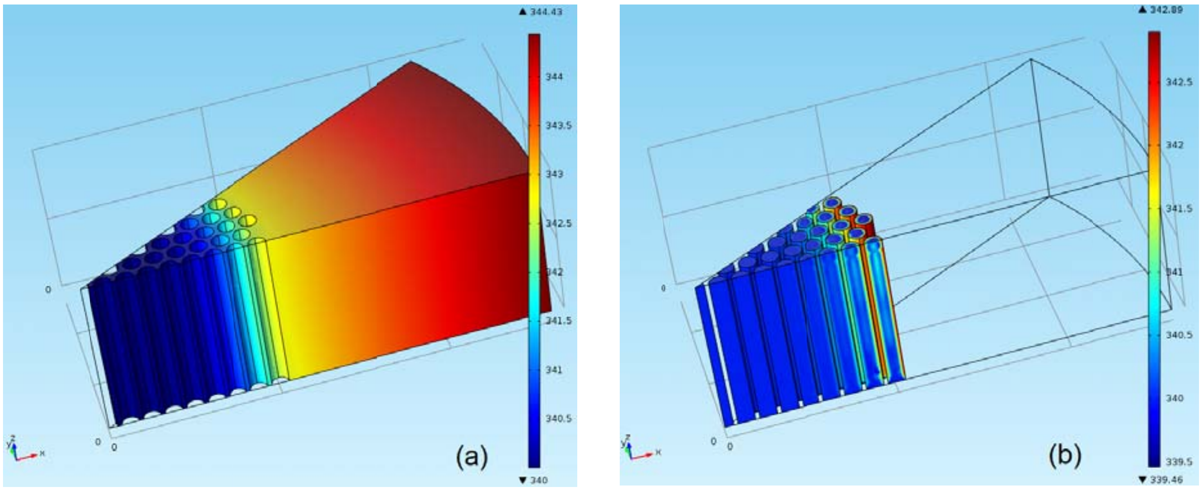

Figure 1. Temperature distribution in the disc without catalyst in channels (a) and in the channels with catalyst (b).Time – 4000 s

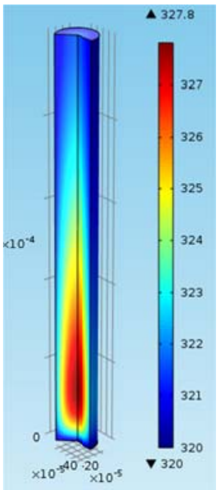

Figure 2. Temperature distribution in the channel.
u – 0.28 m/s, C_m – 6.5 vol. %, T_{in} – 320 °C, x – 92.2 %

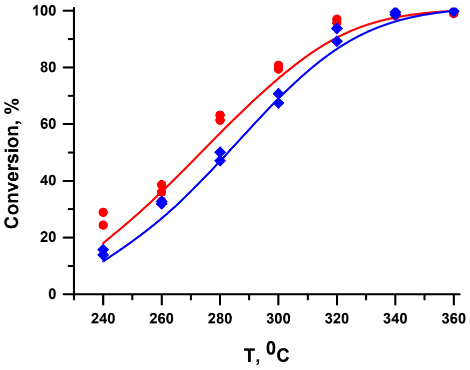

Figure 3. Methanol conversion versus outlet temperature. u – 0.28 m/s, C_m – 6.5 vol. % (red), C_m – 12.0 vol. % (blue). Lines – modeling results, symbols – experimental data [1]. The differential equations of the mathematical models are solved using COMSOL Multiphysics

The result of mathematical modeling shows that all channels have approximately the same walls temperature. The difference in the values is not more than 3 °C. Modeling of a single channel gives a good agreement with experimental data.

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MULTI-SCALE MODELING OF AN ANNULAR STRUCTURED CATALYTIC REACTOR: APPLICATION TO STEAM METHANE REFORMING

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Structured catalytic reactors have shown potential to intensify catalytic processes. An optimized flow pattern allows increased heat transfer and reduced pressure drop compared to conventional packed bed reactors [1-2]. A thin layer of catalyst is coated on the internals of the reactor, allowing high catalyst effectiveness factors. Reactor design, optimization and scale-up requires the development of a detailed reactor model accounting for intrinsic reaction kinetics and transport phenomena. A multi-scale approach is presented for the case of an annular structured reactor for methane steam reforming (ZoneFlow^{TM} Reactor Technologies).

The intrinsic kinetics of steam methane reforming and water-gas shift reactions on a new Ni-based, intrinsically bound thin-layered catalyst adhered on a metal substrate were experimentally studied [3]. The experiments were performed in a tubular packed bed micro-reactor, designed to avoid transport phenomena limitations [4]. Estimation of the parameters and discrimination between the competing models followed from non-linear regression and statistical and physicochemical testing [5-7]. Intra-catalyst diffusion limitations were accounted for using a pseudo-continuum model [8].

The commercial reactor performance is also determined by the complex flow pattern. A Computational Fluid Dynamics (CFD) model was developed. The Reynolds-Averaged Navier-Stokes (RANS) approach was adopted and turbulence was accounted for through the k-ε model. Thermal conduction in the walls and the internals of the reactor was accounted for and radiation was described by means of the Rosseland-Weighted Sum of Gray Gases Model. The CFD code was coupled with the intrinsic kinetic model and effectiveness factors independently calculated were imposed. The model parameters were determined from a combination of cold flow pressure drop tests and hot inert and reactive flow tests in different pilot plant units. The complete model was finally used to perform simulations of a commercial steam reformer. Comparison with a conventional packed bed reactor is made [8-10] to demonstrate the process intensification potential of the annular structured reactor.

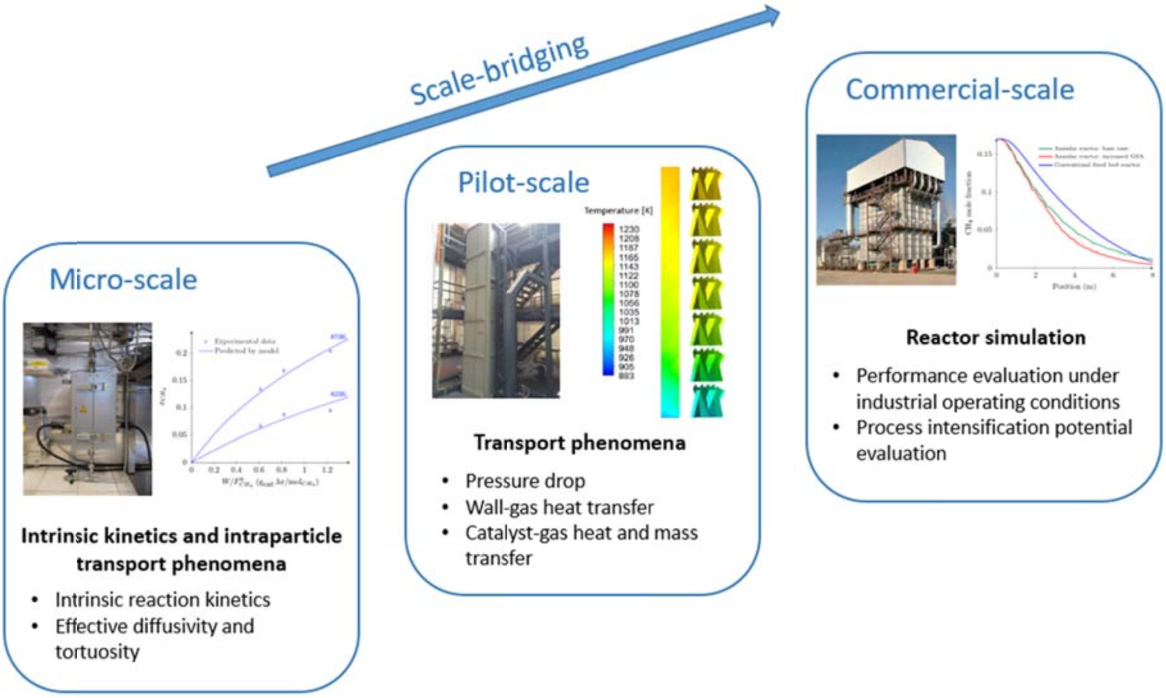

Figure 1. Multi-scale approach for the development of a reactor model

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DESIGN AND EVALUATION OF PHOTOCATALYTIC MICROSTRUCTURED REACTOR MODULES

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Photocatalysis is a promising technology for a wide area of applications like water purification, pharmaceutical ingredients synthesis and energy storage. Although the great opportunities that photocatalysis is offering, almost no industrial photocatalytic processes exist. This lack of practical application is mainly due to the suboptimal reactor design. This work focuses on the development of microstructured photocatalytic reactors which can easily be scaled-up to industrial throughputs. There are three aspects related to photocatalytic reactor engineering we have to address: photon transfer, catalyst load and mass transfer. A high catalyst load can be achieved by using thick catalyst layers. However, this will cause internal mass transfer as well as photon transfer problems. Thus, a thin catalyst layer is preferred but this means only low catalyst loadings can be applied and the unabsorbed photon energy will be lost. Keeping these limitations in mind, microreactors are interesting devices because they solve the three limitations simultaneously due to very high surface to volume area. Despite the fact that microreactor kinetics are fast, they are not very productive[1]. A strategy to achieve microreactor kinetics while maintaining productivity is to create large photocatalytic structures consisting of microchannels.

In this work a reactor structure was build out of spheres with a maximum diameter of 3 mm. This size ensures microchannels of maximum 750 μm inside the structure. Spheres can be packed easily while maintaining good light distributing properties. Using this structure a surface to liquid volume area of up to 15000 m^2m^{-3} could be reached and catalyst loads of 15 $g \cdot L^{-1}$ while keeping the catalyst layer thickness below 500 nm. Methylene blue degradation was selected as a model reaction for testing the reactor performance and the concentration was monitored using an online UV-VIS spectrophotometer. As a light source, a custom-designed LED array was used with a mean cone angle of 30° to minimize light losses and ensure a homogeneous light field of 200 W/m^2.

To benchmark the reactor, the apparent first-order rate constant, a measure for reaction speed, and the photocatalytic space-time yield, a measure for productivity in function of energy consumption, were evaluated for our system. It was found that the apparent first-order constant can be increased from order 10^{-2} to order 10^{-1} 1/min while the photocatalytic space-time yield can be increased with 10 to 50 orders of magnitude due to the efficient light consumption of the reactor together with efficient light source design.

In summary, a new, scalable microstructured photocatalytic reactor was proven effective to increase the efficiency and throughput of continuous photoreactors. The formed microstructure and the thin catalyst layer were shown to lead to a faster and more productive reactor which can be used in the future on an industrial scale.

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THE SORBENT AND THE PROCESS: CO_2 AND H_2O SORPTION ENHANCEMENT IN CHEMICAL REACTORS

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Chemical industry has tremendously improved the processing of materials, resulting in jobs, new materials, and products. To maintain its role in a sustainable society, industry now needs to respond to two challenges, namely (1) the efficient and effective capture and storage of CO_2 [1], and (2) the efficient and effective re-use of CO_2 as circular carbon [2]. While processes for carbon capture and utilisation (CCU) exist, intensified multifunctional processes can overcome equilibrium limitations and enhancing both efficiency and effectiveness of CCU. Here, developments of sorption-enhanced gas-solid chemical reactors are presented, focussing on chemistry and kinetics on the micro scale and the way these manifest themselves on reactor scale.

Sorption-enhanced water-gas shift (SEWGS) is exceptionally suited for CO_2 capture from industrial gases, producing hot decarbonised H_2 by in situ CO_2 adsorption [3]:

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad\qquad CO_2 + \bullet \rightarrow \bullet CO_2$$

Hydrotalcite-based adsorbents were developed for pressure swing adsorption, showing high stability with sufficiently high cyclic working capacity. Experimentally, it has been shown that different relevant adsorption sites exist [4–6]. Reactor models based on a understanding of the functioning of these sites have allowed for design and optimisation of SEWGS [7]. Comparative analysis has shown that SEWGS outperforms conventional technologies, based on its inherently high CO_2 capture ratio. Currently, a SEWGS pilot installation is being operated on blast furnace gas [8].

Utilisation of CO_2 can be facilitated by in situ steam adsorption on LTA zeolite adsorbents in several relevant processes. Sorption-enhanced reverse WGS reaction ('COMAX') aims to convert CO_2 into the more versatile feed gas CO [9]:

$$CO_2 + H_2 \leftrightarrows CO + H_2O \qquad\qquad H_2O + \bullet \rightarrow \bullet H_2O$$

COMAX cycle design will be presented, addressing the selectivity and the prevention of consecutive reactions at higher pressures. Sorption-enhanced methanation (SEM) increases the yield and reduces the concentration of unconverted H_2 [10]:

$$CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O \qquad H_2O + \bullet \rightarrow \bullet H_2O$$

Conventional methanation and SEM in series allows for near-complete conversion of H_2 in a power-to-gas process and achieving the specified dew point for delivery to the natural gas grid. Sorption-enhanced dimethyl ether (DME) synthesis (SEDMES):

$$2CO_2 + 6H_2 \leftrightarrows CH_3OCH_3 + 3H_2O \qquad H_2O + \bullet \rightarrow \bullet H_2O$$

has more recently been demonstrated experimentally [11], showing increased yield of DME, an improved selectivity, and strongly reduced CO_2 content in the product. It was found that regeneration of the system [12] and the scale of mixing of different catalyst functions are crucial for functioning of both catalyst and adsorbent.

In conclusion, sorption enhancement in chemical reactors offers clear advantages in overcoming equilibrium limitations, improving selectivity, and improving the efficiency of separation. It will become reality, provided that a fundamental understanding of micro scale phenomena is properly translated into process design.

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HYDROGEN PRODUCTION BY SORPTION-ENHANCED STEAM REFORMING OF HYDROCARBONS WITH AUTOTHERMAL SORBENT REGENERATION IN A SUPER-ADIABATIC HEAT FRONT OF CATALYTIC COMBUSTION REACTION

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Active development of hydrogen-based energy technologies is in a great extent limited today by availability of efficient and low-cost hydrogen production. The most promising technological way in this direction is application of sorption-enhanced catalytic methane steam reforming. This approach, first formulated even in 19-th century [1], has received a lot of attention in modern practice since 1980-s and now is developing extremely fast by numerous research groups worldwide [2]-[6].

The sorption-enhanced catalytic methane steam reforming concept except usual methane and carbon monoxide steam conversion catalytic reactions, widely applied in conventional technologies

$$CH_4 + H_2O \Leftrightarrow CO + 3\ H_2 \tag{1}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{2}$$

also includes the adsorption of product CO_2 by solid sorbent:

$$MeO + CO_2 \Rightarrow MeCO_3 \tag{3}$$

leading to favorable equilibrium conditions for reactions (1), (2) and to achievement of high yield of high-purity hydrogen in one conversion stage. After saturation of sorption capacity of the sorbent it is necessary to provide its regeneration according to backward reaction

$$MeCO_3 \Rightarrow MeO + CO_2 \tag{4}$$

Though the research efforts in this area are very intensive and active, the achieved level of process efficiency is still far from ideal. While performance of basic reaction cycle (reactions 1-3) is well studied, the source of most complications is sorbent regeneration reaction stage (4). The method here is “isothermal” sorbent regeneration, meaning external bed heating during regeneration stage, characterized with high level of inefficient energy losses. Moreover, efficient and uniform heating of the bed in this case is possible only in reactors with relatively small diameter and this factor limits the scale of approach application or requires unreasonable complication of reformer design.

Much more promising, but much less studied, regeneration method is adiabatic or autothermal regeneration, meaning heating of the catalyst-sorbent bed by exothermic reaction performed directly inside the bed [7],[8]. In this case CO_2-sorbent regeneration is performed according to reaction (4) with supply of heat, necessary for regeneration, by oxidation of available combustible substances (say, hydrogen or methane) in the air flow directly in the adiabatic sorbent-catalyst bed:

$$H_2 + \frac{1}{2} O_2 \Rightarrow H_2O \tag{5}$$

$$CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O \tag{6}$$

As shown by mathematical modelling, both process stages may be performed in a periodical “traveling heat wave” regime and in this case, it becomes possible to create at each process stage the axial profiles of catalyst temperature, optimal for performance of next stage. Especially efficient operation mode may be realized by application of counter-current (or reverse flow) operation, when methane/steam and air/fuel mixtures are fed into processor bed in opposite directions.

The evident advantage of the proposed regeneration mode is that combustion heat produced is distributed uniformly around the bed sequence and, therefore, the regeneration efficiency does not depend upon the bed diameter. This circumstance opens the way for creation of cheap and reliable adiabatic packed bed methane processors of unlimited processing capacity instead of either conventional single-tube reactors with external heating with very limited productivity or expensive and complicated multi-tubular reactors for high capacities.

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OP-II-10

FLEXIBLE PRODUCTION OF SYNTHETIC METHANE: DYNAMIC OPERATION AND CONTROL OF FIXED-BED METHANATION REACTORS

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The current trend towards a more flexible production to react on markets as well as on volatile inputs (e.g., coming from renewable sources), contains many new challenges and requires concepts for dynamic process operation. Thus, the interest in prediction of the process dynamics has become more important than ever before [1-3]. The present work deals with the dynamics of fixed-bed reactors for carbon dioxide methanation by use of hydrogen generated via water electrolysis, an important example of power-to-X production processes. Particularly in view of vehicles fuelled with compressed natural gas (CNG), synthetic methane (SNG) is a very attractive, easy-to-distribute substitute fuel. Moreover, carbon dioxide methanation is a key reaction in the context of chemical conversion networks for the storage of electrical surplus energy. However, the reaction is strongly exothermic such that distinct hot-spots are formed within the catalytic fixed bed that can influence the catalyst stability and process safety [4]. By tracking the reactor dynamics and making use of advanced control methods, such as Nonlinear Model Predictive Control, one can identify non-conventional operation strategies which enable the reactor to operate more flexible, and with reduced hot-spot formation, guaranteeing a long term process operation.

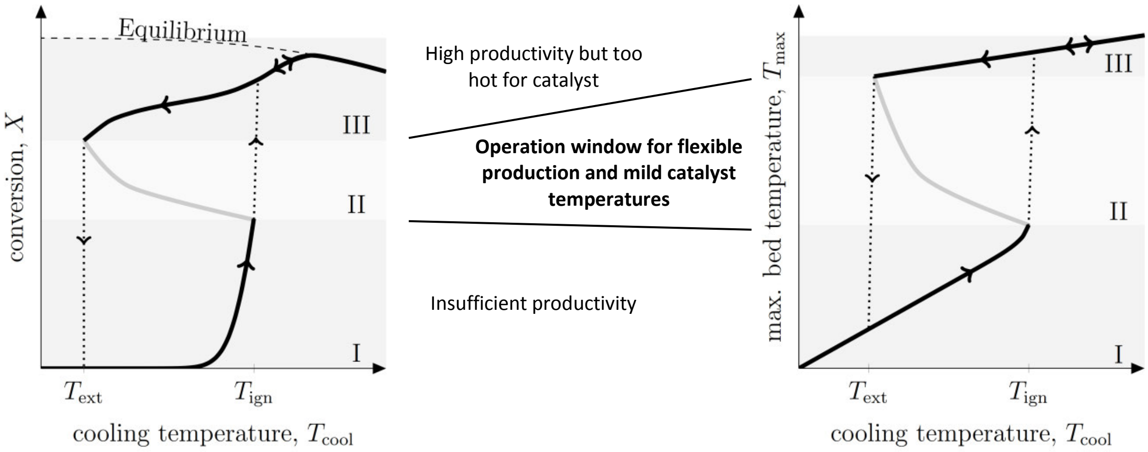

Figure 1. Operation regimes of exothermic fixed-bed reactors; conversion (left); maximum bed temperature (right); stable low conversion regime (I); stabilized via feedback control (II); stable high conversion regime (III); Arrows indicate the reactor's history

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OP-II-11

A POWERFUL CO_2 METHANATION REACTOR WITH Ni/CeO_2 STRUCTURED CATALYST: ESTIMATION OF MASS AND HEAT TRANSFER PROFILES

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The CO_2 methanation is the hydrogenation of CO_2 to produce CH_4 ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, $\Delta H^0_{298K} = -165\ kJ\cdot mol^{-1}$) for the power to gas technology (PtG) [1]. We have introduced the Ni/CeO_2 structured catalyst for CO_2 methanation under high flowing CO_2 rate with effective heat exchange and lower pressure drop [2]. In this study, heat and mass transfer properties for methanation over various types of structured catalysts were investigated from the viewpoint of chemical reaction engineering. A plain-type with straight-flow channel, a stacked type with random-flow channel, and segment-type having the divided flow-path unit with gap distance were employed in this investigation. It was found that the proposed methanation system had a powerful potential for reduction and utilization of CO_2.

A structured catalyst was prepared by the following processes; (i) preparing a Ni(10 wt %)/CeO_2 granular catalyst by impregnation [2], (ii) coating such granular catalyst (300mg) on an aluminum fin-substrate by wash-coating method. As shown in **Fig. 1**, three types of substrate with 18 mmϕ x 50 mm, 100 cpsi were used. Prior to the CO_2 methanation, the catalyst was reduced by H_2 at 500 °C for 1 h. Then feed gas ($CO_2/H_2/He$ = 1/4/5 molar ratio) was introduced to the reactor under feeding flow rate of 70-3,000 mL/min.

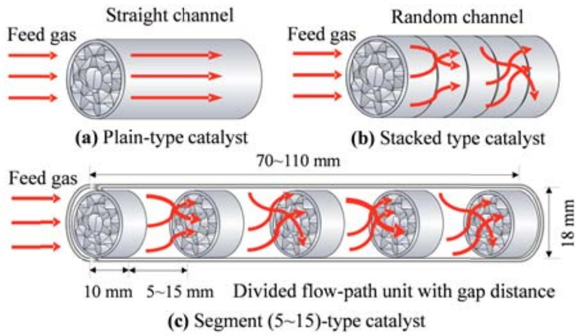

Figure 1. Schematic of various structured catalysts.

Fig. 2 shows methanation property of various structured catalysts. As shown in **Fig. 2(a)**, CO_2 conversion at 250-350 °C increased due to the random-flow channel and the

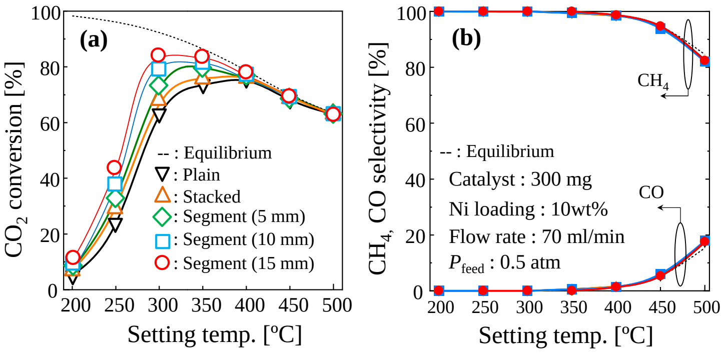

Figure 2. (a) CO_2 conversion and (b) CH_4 and CO selectivity.

segmented gap, compared to the straight-flow channel of the plain-type catalyst. In addition, the longer gap distance, the higher conversions were obtained. It was attributed to the improved heat and mass transfer properties. Moreover, in **Fig. 2(b),** all CH_4 selectivity achieved the equilibrium at all temperatures.

Heat balance in the reaction zone is described by overall heat transfer coefficient (U) in **Eq. 1**. Heat transfer property was estimated through U values. Based on the gas film theory, a relation of mass transfer rate and reaction rate is represented by **Eq. 2**. By rearranging and assuming 1storder methanation, the relation of overall reaction rate constant (K), reaction rate constant (k_r), and mass transfer coefficient (k_c) is obtained in **Eq. 3**. In this study, mass transfer property was estimated through K values. The mass balance for unit cell of the structured catalyst is formulated in **Eq. 4**. The K values in **Eq. 5** can be obtained by an integration of **Eq. 4** with boundary conditions of $C_z = C_0$ at z = 0, and $C_z = C_{out}$ at z = L.

$$UA\Delta T_m = \sum_i\left(\dot{n}_{i,in}\widehat{H}_{i,in}\right) - \sum_i\left(\dot{n}_{i,out}\widehat{H}_{i,out}\right) + \dot{n}_{CO2,in}X\sum_i\{S_i(-\Delta H_i)\}\ \ldots(\mathbf{1}),\ J = KC_m = k_c(C_m - C_w) = k_r{C_w}^n\ \ldots(\mathbf{2}),$$

$$\frac{1}{K} = \frac{1}{k_r} + \frac{1}{k_c}\ \ldots(\mathbf{3}),\ F(C_z - dC_z) - FC_z - KC_z\cdot\pi d_h\left((z+dz) - z\right) = 0\ \ldots(\mathbf{4}),\ K = -\frac{F}{\pi d_h L}ln(C_{out}/C_0) = -\frac{F}{A}ln(1-X)\ \ldots(\mathbf{5})$$

A : surface area of honeycomb cell [m^2], C_m,C_w :concentration of bulk and at wall [mol/m^3], d_h :hydraulic diameter [m], F: gas flow rate [m^3/s],
$\hat{H}_{in}$, $\hat{H}_{in}$: specific enthalpy [J/mol], ΔH_i : reaction heat [W], J: flux of feed gas [mol/m^2·s], L:catalyst length [m], $\dot{n}_{i,in}$, $\dot{n}_{i,out}$:mole flow [mol/s],
S : product selectivity [—], ΔT_m:mean temp. difference of wall and center [K], X:conversion [—], Z:direction along the catalyst length [m]

Fig. 3 shows the estimated U and K values of the structured catalysts under the performance shown in **Fig. 2**. The U and K values, which are normalized with those of the plain-type catalyst, increased significantly. The random-flow channel and the gap space improved the well mixing feed gas. In **Fig. 3(b)**, the K value of the segment-type catalyst (gap =15 mm) increased almost twice times at 250 °C compared with that of the plain-type. It was found that the structured methanation system has a powerful performance of heat and mass tranfer properties, which will open an wide application of the PtG technology.

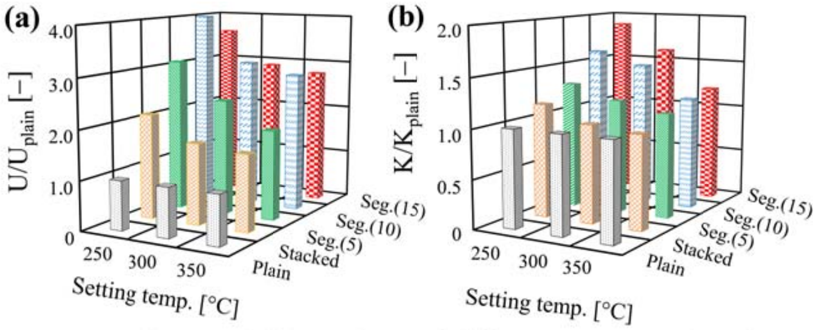

Figure 3. (a) U and (b) K values of different structured catalysts.

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SYNGAS PRODUCTION FOR SOFC VIA CATALYTIC OXIDATION OF DIESEL FUEL

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Hydrogen is widely considered as a clean energy carrier for the future. Steam reforming (SR), partial oxidation (PO) or autothermal reforming (ATR) of hydrocarbon fuels are recognized as commercially competitive methods to produce hydrogen. Catalytic autothermal reforming is considered as one of the most effective methods of producing hydrogen from heavy hydrocarbon fuels for solid oxide fuel cell (SOFC) which can directly use CH_4 as well as CO as fuels with the addition of sufficient steam feeds [1]. Diesel is an attractive fuel because of high energy density, wide applications and well – constructed infrastructure. Much attention is focused in the world now on the development of catalytic reformers of liquid hydrocarbons [2,3].

Optimization of the reformer design, associated with a number of technological details such as fuel evaporation, mixing and feeding, and the selection of the optimuml reaction conditions are the main trends in the development of diesel-fuelled SOFC-based power plants. However, the performance of a reformer is highly dependent on its catalyst. Many types of catalysts have been investigated for improving the performance of diesel reforming catalysts [4,5].

The novel sorption-hydrolytic deposition technique enables production of highly dispersed catalysts based on noble metal (Pt, Ru, Rh) particles of 1-2 nm in size [6]. The method is easy to implement and has a great potential for catalyst industry applications. In this work, composite oxide $Ce_{0.75}Zr_{0.25}O_{2-\delta}$ supported Rh, Ru and Pt in amount of 0.1 mmol/g (1 wt. % Ru and Rh, 1.9 wt. % Pt) were tested in SR of n-hexadecane (HD) and ATR of diesel fuel. Among the catalysts tested in SR under the following operating conditions: $H_2O/C = 3$, GHSV = 23,000 h^{-1}, T = 550 °C, the Rh-based sample showed the best activity – it provided complete conversion of the fuel during 8 h on stream and the outlet concentrations of H_2, CO_2, CO and CH_4 close to the equilibrium values (Fig. 1).

The catalysts supported on structured carriers (FeCrAl blocks) provide controlled reaction conditions throughout the reactor volume that favorably competes, for example, fixed bed reactors. The use of the structured catalysts provides efficient heat and mass transfer, decreased gas dynamic resistance, improved catalyst performance that allows reducing the catalyst quantity per unit volume of the reactor. The opportunity to perform the process under controlled optimum conditions allows to increase the selectivity and minimize undesirable side reactions, such as coke formation.

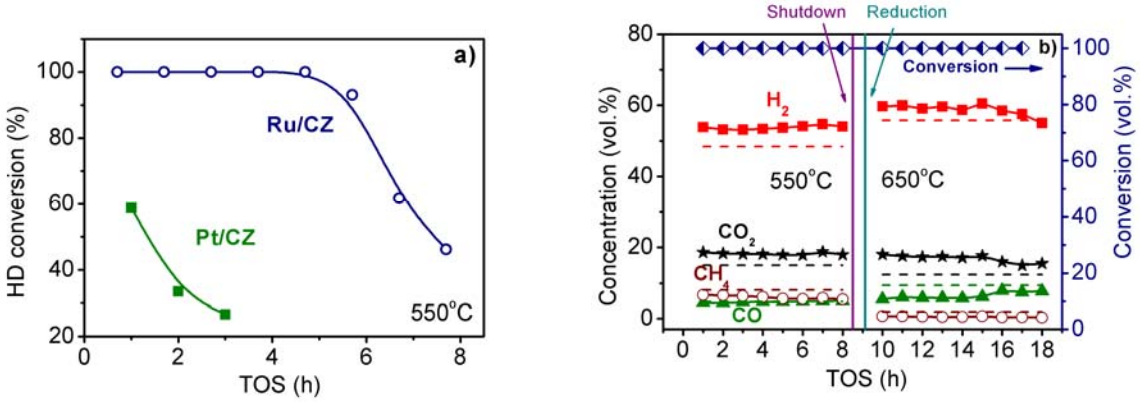

Fig. 1. The HD conversion and products distribution over 1.9 wt. % Pt/CZ, 1 wt. % Ru/ CZ (a) and 1 wt. % Rh/ CZ (b) in the SR as a function of time on stream

In the present work, active component Rh/CZ was supported on FeCrAl metal meshes using Al_2O_3 as a binding structural component. The obtained catalyst Rh/CZ-η-Al_2O_3/FeCrAl was tested in the reactions of SR and ATR of HD and diesel at various temperatures and gas flow rates. Operating conditions were found to provide a 100 % conversion of n-hexadecane and diesel and stable catalyst activity for a long time-on-stream exposure.

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NUMERICAL SIMULATION OF INDUSTRIAL SCALE AUTOTHERMAL CHEMICAL LOOPING METHANE REFORMING FOR SYNGAS PRODUCTION IN A DUAL FLUIDIZED BED REACTOR

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Methane reforming is one of the important technologies for the production of syngas. Steam methane reforming (SMR), the dominating methane reforming technology, emits on average about 7 kg of CO_2 per kg of H_2 [1]. The related industrial one that produces about 75 % of word's total hydrogen, is responsible for around 3 % of the worldwide CO_2 emissions. Converting methane to syngas more efficiently and environmentally friendly is of vital importance to address global warming. Autothermal Chemical Looping Reforming (a-CLR) is a process that has the potential to reduce CO_2 emissions and minimize energy losses [2]. It is generally realised in a dual-fluidized bed reactor with a fuel reactor (FR) and an air reactor (AR), respectively. The oxygen carrier (OC) particles are oxidized by air in the AR, while in the FR, the OC is reduced by the syngas and acts as catalyst for methane reforming. Most prevous studies focused on the development and characterization of the solid. Tests with experimental demonstration units have also been reported. The functioning and potential performance at commercial scale has, however, not been studied in sufficient detail.

In this work, a 1-D model was developed to simulate an industrial scale a-CLR. It couples fluidised bed hydrodynamics including interfacial transfers, with intrinsic reaction kinetics including catalyst deactivation. A unit equivalent to 50 conventional SMR pipes was simulated as schematically shown in Figure 1. A Nickel based OC/catalyst was considered due to its high activity. The required design and operating conditions to reach a target operating temperature and CH_4 conversion were studied. The effects of the main operating parameters on the design and performance of both reactors were analyzed.

Unlike in Chemical Looping Combustion (CLC), the OC is only slightly oxidized in the AR to maintain sufficient catalyst activity in the FR. Nevertheless, autothermal operation can be guaranteed. Interfacial transfer limitations affect the performance of both the AR and FR. Because of the relation between the minimum fluidization velocity, terminal velocity and the particle size, the latter is also seen to have a significant effect on the reactor performance. The operating temperature of the FR affects the conversion of the OC in the AR due to a higher oxidization rate of Ni. A higher temperature difference between the AR and FR allows to lower the solids circulating rate, while hardly affecting the oxygen/fuel ratio. Energy recovery of the outlet gas of both reactors, as shown in Figure 1, allows to increase the hydrogen production.

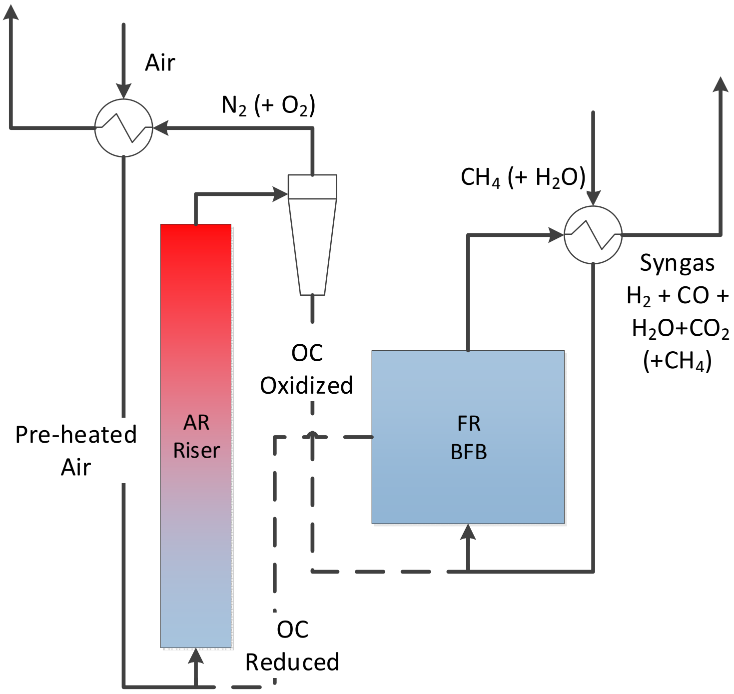

Figure 1. Schematic description of autothermal Chemical Looping Reforming

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PERFORMANCE AND SELECTIVITY COMPARISON OF PACKED BED AND TUBE REACTORS IN SELECTIVE HYDROGENATION

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Despite advances of the continuous flow manufacturing in the pharma and fine chemical synthesis, heterogeneously-catalyzed gas-liquid reactions attract rather little attention. It is particularly surprising considering that catalytic hydrogenation constitutes at least 10 % of the fine chemical reactions. Compared to the state of the art batch processes, hydrogenation in flow improves productivity, process efficiency and process safety. Quality by design can be achieved with online process monitoring, and repetitive non-productive operations eliminated such as heating or substrate loading. Low-volume flow reactors make dealing with explosive hydrogen or toxic compounds safer because an unlikely leak results in a limited release.

Packed-bed reactors are simple and therefore widely studied for hydrogenation in flow. The reactors, unfortunately, may show the non-uniform distribution of gas and liquid that decreases the product selectivity and the reactor throughput. Small particles of the widely used catalysts create very narrow fluids pathways and result in high pressure drop. Therefore, a lot of energy is consumed on pumping with severe barriers for process scalability.

In the work presented, we compared the micro packed-bed reactors (6 mm ID, 5-30 mm long) with catalyst-coated tube reactors (1.27 mm ID, 5 m long) in hydrogenation reactions of 2-methyl-3-butyn-2-ol (MBY) over a 5 wt % Pd/ZnO catalyst, cinnamaldehyde (CAL) over a 12 wt % Pt/SiO_2 catalyst, as well as oleic acid over a 5 wt % Pd/C catalyst. The comparison was performed with the same catalyst amount under identical conditions; the tube reactors were provided by Stoli Catalysts Ltd.

The tube reactors showed a high selectivity of 97-98 % in the MBY hydrogenation and above 80 % in CAL hydrogenation. The packed-bed reactors demonstrated a 20-40 % lower selectivity under the same conditions. The packed-bed reactors, moreover, required a longer residence time to reach complete conversion compared to the catalyst-coated tubes. The difference is caused by internal and external mass transfer limitations in the packed-bed reactors facilitated by the limited interphase gas-liquid boundary and uneven distribution of the fluid velocity profile across the reactor cross-section.

A significant difference between the catalyst-coated tubes and the packed bed reactors was observed in terms of the pressure drop. The catalyst-coated tube reactors with the opening of 1.27 mm showed a low pressure drop even despite their length of 5 m. The packed-bed reactors demonstrated the pressure drop a factor of 3-40 higher even despite a substantially shorter length of 5-30 mm. The Pd/C catalyst even had to be diluted by inert particles to perform experiments.

Therefore, the work shows that the catalyst-coated tube reactors provide a significantly higher selectivity and performance compared to the packed-bed reactors under the same reaction conditions. The pressure drop, moreover, is significantly lower in the catalyst-coated tubes allowing to connect them in series for the higher reaction throughput. As an example, a single 5 m tube allows for a 100-300 g/day throughout in MBY and oleic acid at a low hydrogen pressure.

Acknowledgements

We acknowledge the support of the European Research Council Proof of Concept grant (project Micarf 693739) and InnovateUK grant (900041) for funding this research.

THE EFFECTS OF INTRAPARTICLE DIFFUSION PHENOMENA ON DIMETHYL ETHER DIRECT SYNTHESIS

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Introduction

Dimethyl ether (DME) is considered a valid alternative to liquefied petroleum gas (LPG) and diesel fuel. Traditionally DME is produced from syngas in a two-step process consisting in methanol synthesis followed by methanol dehydration (indirect synthesis) [1]. To improve the process efficiency, many efforts have been made in the last decades to develop the one-step direct synthesis, combining methanol ($Cu/ZnO/Al_2O_3$) and dehydration catalyst (zeolites or γ-Al_2O_3). The two catalysts can be either mechanically mixed or intimately coupled by producing hybrid pellets [2]. The intraparticle diffusion phenomena have a strong influence on the reaction kinetics, which in turn affects the thermal behavior of the reactor, especially under industrial relevant conditions. However, these effects have not been deeply investigated in literature.

Methods

In order to compare the two configurations (bed of mixed pellets vs. bed of hybrid pellets), heterogeneous models of a single tube of a multi tubular fixed bed reactor for the direct DME synthesis have been developed. The models consist of i-species mass, energy and momentum 2D balances for the gas-phase, coupled with i-species mass and energy balances for the catalyst phases (one solid phase for the hybrid pellets, two solid phases for the mixed pellets) accounting for concentration gradients (1D) in isothermal pellets. A reaction scheme including methanol (MeOH) synthesis from CO_2, Reverse Water Gas Shift (RWGS) and MeOH dehydration has been adopted with kinetics taken from the literature [3]. The model equations have been implemented in gPROMS® for the numerical resolution of the boundary value problem.

Results

The simulations have been performed considering different feed compositions (consisting of H_2, CO, CO_2, CH_4) obtained from biomass gasification. The results show that the hot-spot temperature of the solid phase of the reactor loaded with hybrid pellets is much higher compared to that reached with the mechanical mixture configuration (Fig. a), and the DME yield is favored when the hybrid pellet configuration is adopted (Fig. b). These results can be explained considering that, in the hybrid catalyst pellet, the DME synthesis reaction consumes the methanol produced by the MeOH synthesis, while WGS removes H_2O produced by both MeOH and DME syntheses. This results in a synergistic effect on the conversion rate with respect to the mechanical mixture, where, due to intraparticle diffusion limitation, the catalyst efficiencies (Fig. c-d) decrease both in the MeOH catalyst pellets, because of the equilibrium approach, and in the DME catalyst pellets due to combined effect the lower methanol concentration and the higher water content.

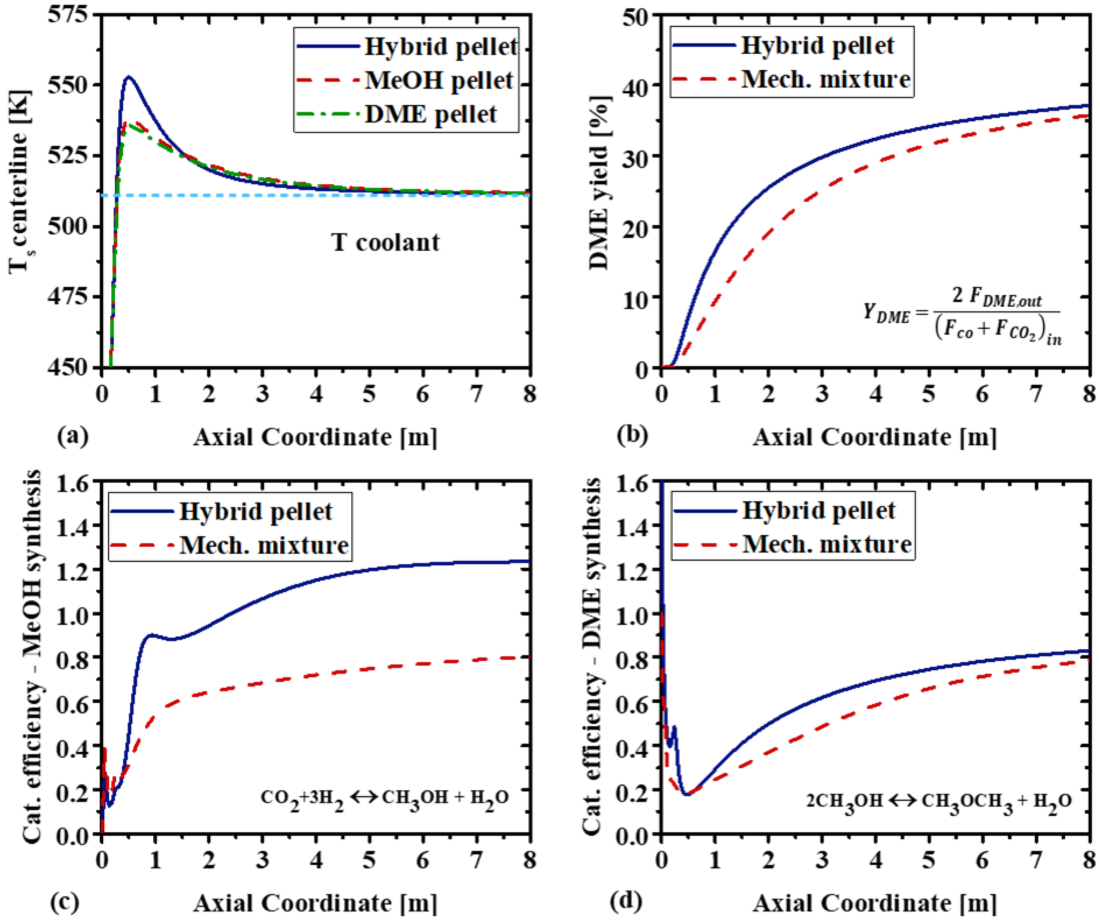

Figure. Hybrid pellets vs mechanical mixture. Upper panels: catalyst temperature profile (a) and DME yield profile (b); lower panels: catalyst efficiency profiles for MeOH synthesis (c) and for DME synthesis (d). Tube dimension: L = 8 m; D = 1 inch. Operating conditions: T_{in} = 323 K; P_{in} = 30 bar; GHSV = 1407 h^{-1}

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ETHANOL-TO-ETHYLENE DEHYDRATION ON RING-SHAPED ALUMINA CATALYST IN TUBULAR REACTOR

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In the past decade, the alternative routes of ethylene production from the renewable oil-independent sources have been successfully commercialized [1]. For the low-tonnage production of ethylene and ethylene-based innovative materials, the process of bioethanol catalytic dehydration to ethylene appears to be economically promising. The process is strongly endothermic and requires energy supply around 1.7 GJ per 1 ton of C_2H_4; thus, the proper temperature control in the reactor is a key operation factor for this process. Pilot-scale studies and process simulation in the tubular reactor on industrial alumina catalyst as cylinders were carried out in [2]. Further, more active acid-modified alumina catalyst was proposed [3].

In the present paper, experimental and theoretical studies of the ethanol dehydration process on the ring-shaped alumina based catalyst developed by BIC SB RAS were performed. Replacement the cylindrical granules with the ring-shaped ones allows to intensify the radial heat transfer inside the tube, as well as to increase the yield of ethylene and to reduce the hydraulic resistance of the bed.

To simulate the process in the multi-tubular fixed bed reactor, a pseudo-homogeneous 2D model [2] was used. Taking into account the requirements for activity and mechanical strength, the ring sizes were determined as follows: outer diameter (D) 5.6…6.0 mm, height (h) 2.0…6.0 mm, wall thickness (δ) 0.8…1.0 mm.

Ethanol-to-ethylene dehydration on acid-modified ring-shaped alumina catalyst 6×6×1 mm ($D \times h \times \delta$) was studied experimentally in the pilot-scale setup with U-tube reactor 27.3 mm (ID). The process parameters were varied within the ranges as follows: the linear flow velocity 0.29-0.63 m/s, the temperature of the heating agent (Tw) 380-450 °C, and the height of the catalyst bed was 1.19 m or 1.42 m.

Under the conditions given above, the best ethylene yield on the ring-shaped alumina catalyst in the tubular reactor was as high as 98.0 mol %; it was obtained at Tw = 420 °C and GHSV = 920.5 h^{-1}.

A comparative study of the BIC's proprietary catalyst in the form of a ring and of the industrial catalyst in the form of a cylinder was carried out in tubular reactor under similar conditions, namely, 96 wt. % ethanol, Tw = 438 °C, GHSV = 923 h^{-1}. The yield of ethylene was 97.4 and 86.1 mol. % with ethanol conversion 98.9 and 99.9 mol. % on rings and cylinders, respectively. An index CI (t/t) characterizes the specific ethanol consumption per 1 ton of ethylene, while index P_{CAT} ($kg \cdot g^{-1} \cdot hr^{-1}$) demonstrates the unit catalyst productivity for ethylene per year. Both indexes are plotted in Figure.

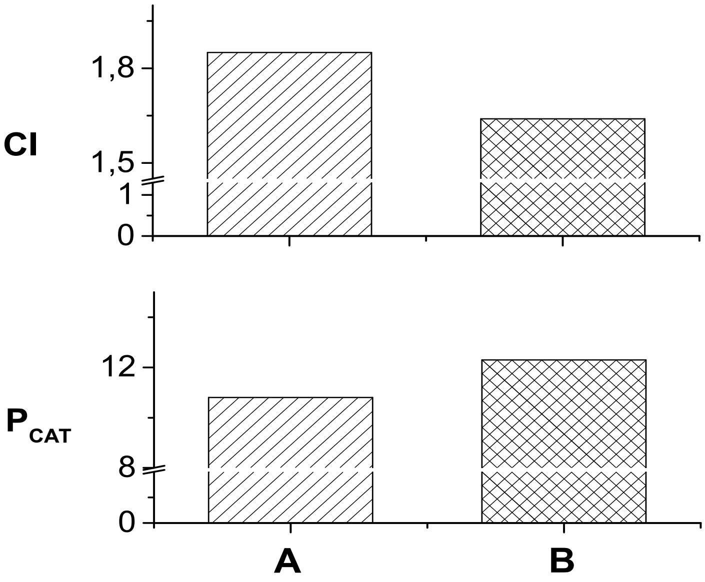

Figure. The comparison of the process performance indexes for cylindrical (A) and ring-shaped (B) catalysts

As a result of this study, we can conclude that on the ring-shaped particles ethanol-to-ethylene dehydration proceeds more efficiently than on cylindrical ones; the specific ethanol consumption is 11.4 % lower, and the catalyst productivity for ethylene is 14.5 % higher. Thus, the acid-modified alumina ring-shaped catalyst 6×6×1 mm in sizes may be recommended for practical use in the ethanol-to-ethylene dehydration process in multi-tubular reactor.

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OP-II-17

MODELING OF CO_2 ADSORPTION ON SUPPORTED AMINE SORBENTS IN A MULTISTAGE FLUIDIZED BED

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Introduction

In the natural gas treatment chain, the removal of sour gases such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S) is intensive in terms of capital and operational expenditure (CAPEX and OPEX). Currently, sour gases from natural gas are mainly removed by absorption in aqueous alkanolamines. These processes have a high energy consumption because of heating, cooling and partly evaporating an aqueous stream with a high heat capacity. The use of adsorptive sour gas removal can be energetically attractive because adsorbents have generally a lower heat capacity and avoid solvent evaporation. In addition, fast adsorption kinetics and gas-solid mass transfer are expected, thereby decreasing the equipment size.

Large scale production requires a continuous gas-solid process. A countercurrent multistage fluidized bed (MSFB) is attractive to achieve deep removal of sour gas (<3.5 ppm H_2S). This deep removal was demonstrated in a five stage fluidized bed (Fig. 1) [1]. Recently, MSFBs were also proposed for post-combustion CO_2 capture employing amine sorbents [2].

In this work a reactor model is developed which describes single component sour gas removal at a single fluidized stage. This model is experimentally validated by adsorbing CO_2 from a nitrogen stream on an commercially available amine sorbent in a single stage fluidized bed (0.10 m diameter). The challenge in this work is to investigate the effects of adsorption kinetics, mixing and mass transfer on the sour gas removal efficiency.

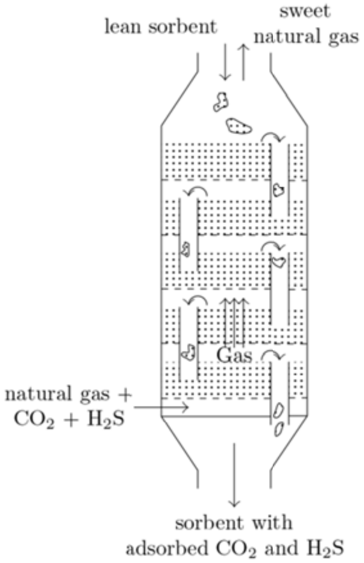

Figure 1. Schematic of a multistage fluidized bed for sour gas removal

Model

The model is based on the Van Deemter two phase model for bubbling fluidized beds [3]. This model employs two fictitious phases for the gas phase: the bubble and the emulsion gas phase. The bubble phase is assumed to be in plug flow, whereas the emulsion gas phase is assumed to be (partially) mixed. The model uses an interchange between the two gas phases. In addition, a third (partially mixed) solid phase is introduced to account for the CO_2 adsorption on the sorbent. A linear driving force model in combination with an effectiveness factor is used to describe the adsorption kinetics and intraparticle mass transfer respectively. The apparent adsorption kinetics and the gas interchange were fitted independently with dedicated experiments.

Results and discussion

The experimental results look promising: the uptake of CO_2 on the sorbent is very fast. As an example, 70 % of the supplied CO_2 is adsorbed in a single stage (75-150 mm bed height) whereas the gas residence time is only 0.2 s, assuming a typical void fraction of 0.5 m^3_G/m^3_R (Fig. 2). The effects of superficial velocity, solid flux, inlet concentration and overflow height were investigated experimentally.

The model developed fits the experimental results for changing gas and solid fluxes at a given overflow height (Fig. 2). However, the model is not yet able to predict variations in bed height. At the moment of writing, work is ongoing to capture this effect and mixing effects in the model. The first results indicate that gas-solid contacting is good, most likely because bubbles stay small in these shallow fluidized beds. This is supported experimentally by the fast uptake of CO_2, which would not be possible with poor gas-solid contacting.

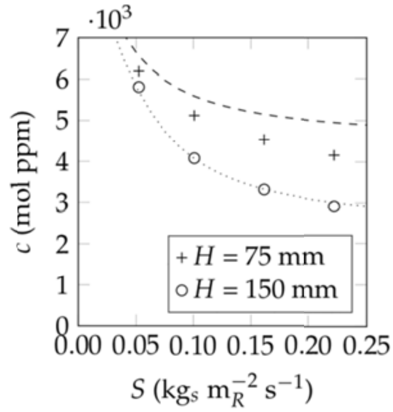

Figure 2. Outlet CO_2 concentration as function of solid flux. The dotted and dashed lines are model predictions. (inlet concentration = 10000 mol ppm, superficial gas velocity = 0.32 m/s)

Conclusion

A model is developed which describes single component sour gas adsorption on an amine sorbent in a shallow single stage fluidized bed. The proposed model fits well to CO_2 adsorption experiments. The uptake of CO_2 is fast: 70 % of the supplied CO_2 can be adsorbed in 0.2 s. This indicates good gas-solid contacting.

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CHARACTERISATION AND DESIGN OF SINGLE PELLET STRING REACTORS USING NUMERICAL SIMULATION

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Conventional design criteria for catalytic testing result in long packed bed reactors with tube diameters much larger than the catalyst pellet size, as otherwise poor axial and radial dispersion within the bed would be expected, which makes it difficult to interpret results of kinetic experiments. These criteria lead to relatively large and costly reactors which require substantial gas flow rates, are rather complex and may pose a significant level of hazard.

On the contrary, a reactor concept where pellets are packed in a tube of only slightly larger diameter came up in the 1960s and was named Single Pellet String Reactor (SPSR) by Scott et al. in 1974 [1] who already describe the similarity of the reactor's flow behaviour to conventional packed beds. But are SPSRs suitable for kinetic experiments and catalyst performance testing? Recent publications [2-4] demonstrate a renewed interest in this reactor concept, including its use for catalyst testing.

In this work, an attempt is made to systematically characterise SPSRs of spherical, non-porous particles in cylindrical confining walls using computational fluid dynamics. A parameter study on the reactor geometry is conducted whilst keeping the space time, defined here as ratio of fluid volume across the catalytic bed to the volumetric flow rate, through the reactors constant. Residence time behaviour as well as the conversion of a hypothetical first order irreversible gas phase reaction at the pellet surface which is considered both isovolumetric and isothermal, are evaluated and compared to

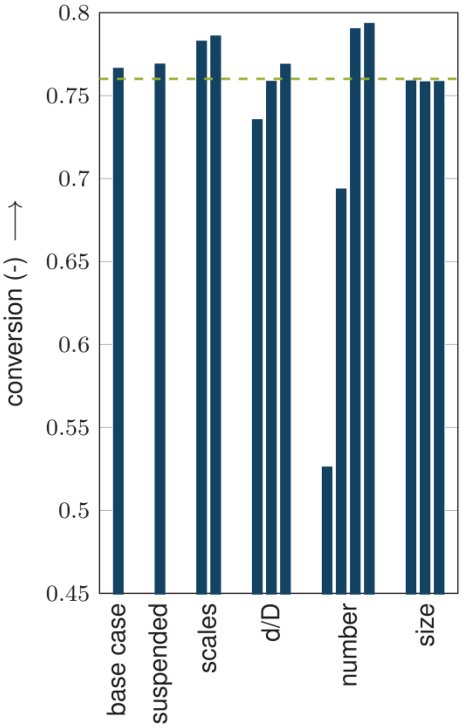

Figure 1. Conversion results for SPSR scenarios; dotted line indicating 5 % deviation to ideal PFR behaviour

corresponding plug flow conditions. Finally, a design criterion is derived for which SPSRs show a behaviour close to ideal plug flow.

Overall bed conversion results of various simulated SPSR scenarios are shown in Fig. 1, where the base case corresponds to a reactor with 20 pellets and a particle-to-cylinder-diameter ratio of $d/D = 0.8$. A reactor with similar geometry, except that the pellets are now stacked along the tube axis on top of each other, yields a slightly larger conversion. Bed conversion is also increased with the scale of the reactor, with an increase in pellet size at constant cylinder diameter as well as with increasing pellet number, as expected by criteria for conventional fixed-bed reactors (cf. [5,6]). Introducing a variability in catalyst size has the opposite effect. Though not shown here for brevity, the residence time distributions are in between the ideal functions for laminar flow and plug flow with behaviour closer to plug flow where conversion results indicate near plug flow behaviour. A design criterion relating the deviation to plug flow conversion to reactor geometry, flow condition and diffusion coefficient is proposed as indicated in Fig. 2.

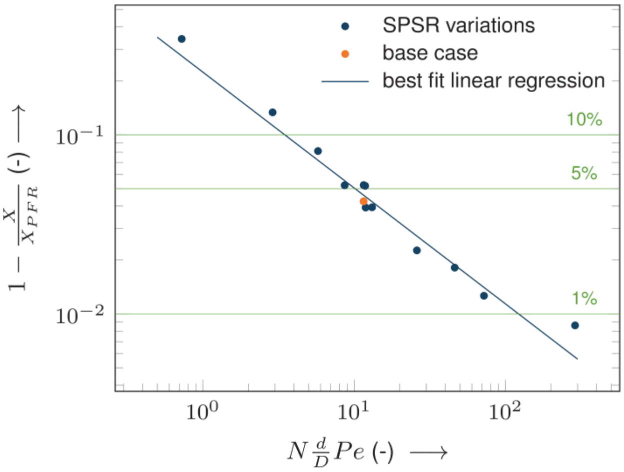

Figure 2. Trend analysis showing deviation to PFR conversion as function of pellet number, pellet-to-cylinder diameter ratio and Péclet number

Conversion results deviating less than 5 % from ideal plug flow can readily be achieved with SPSRs. They are a well suitable reactor concept for kinetic experiments, reducing the required gas flow rates and levels of complexity, cost and hazard substantially. Single pellet string reactors deserve a revival after falling into oblivion decades ago.

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HYBRID CATALYSIS: A NEW REACTOR DESIGN FOR ONE-POT SYNERGISTIC COUPLING OF ENZYMATIC AND HETEROGENEOUS CATALYSIS

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The use of enzyme for fine chemicals production has been the subject of many researches over the last decade. In this context, the recent concept of hybrid catalysis emerged: a coupling of chemical and enzymatic catalysis [1]. The aim the project (GLYCYBRIDE) is to convert glycerol into valuable chemicals (target reaction) by taking advantage of the synergy between enzymatic and heterogeneous catalysis.

Our aim is to design a one-pot reactor able to perform three phase hybrid catalysis. Part of the challenge lies in different reaction conditions (temperature, stirring speed, oxygen concentration) required by heterogeneous and enzymatic catalysis. The design of the reactor must allow us to work under different conditions, preferably in the same reactor, which means having a temperature and/or oxygen concentration gradient, as well as different stirring speed (Fig. 1) for each catalyst.

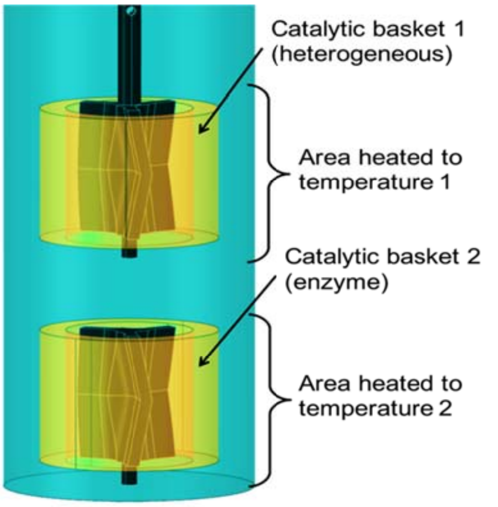

Fig. 1. Simplified scheme of the designed reactor

In the present work, a CFD-based modeling of the reactor and an experimental validation of the design by means of a model reaction were performed.

For the first part of the study, the ANSYS© Fluent software was used to perform CFD modeling. A MFR model for stirred tank reactor was used [2]; the hydrodynamic and then the mixing properties were modeled for Liquid/Solid system. Then, the energy balance was added to model the temperature gradient that can be obtained under different conditions (heating system, stirring, presence of catalytic basket, etc.). Experimental characterization of the reactor was performed to validate the models: conductivity experiments for the mixing, and axial temperature measurements for the heat transfer.

For the second part of the study, a two-step model reaction (requiring an efficient mass transfer of oxygen like the target reaction) was developed by coupling two well-known reactions (mechanism, kinetic parameters): an enzyme catalyzed isomerization of fructose to glucose [3] and a heterogeneously catalyzed oxidation of glucose to gluconic acid [4].

A preliminary kinetic study was performed for each step (Enzyme = Michaelis-Menten – Heterogeneous catalyst = Langmuir–Hinshelwood) to provide a kinetic model of the one-pot reaction (batch). The kinetic parameters were estimated using Matlab® (lsqnonlin function + ODE45 solver). A simple model of one-pot isothermal slurry reactor (“slurry model”), will serve as a reference for the more elaborated compartmentalized reactor model.

A first one-pot slurry test showed that both steps could be combined (Fig. 2). However, the reaction rates were lower than expected by the slurry model (Fig. 2(a)). This can be due to deactivation or strong inhibition of the catalyst by carboxylic acid groups, a well-known phenomenon. A better curve fitting is indeed achieved (Fig. 2 (b)) when considering strong inhibition by products. Further investigation is under progress to exclude other additional causes (limitation of oxygen transfer, deactivation, enzyme inhibition etc...) and optimize the coupling of both steps.

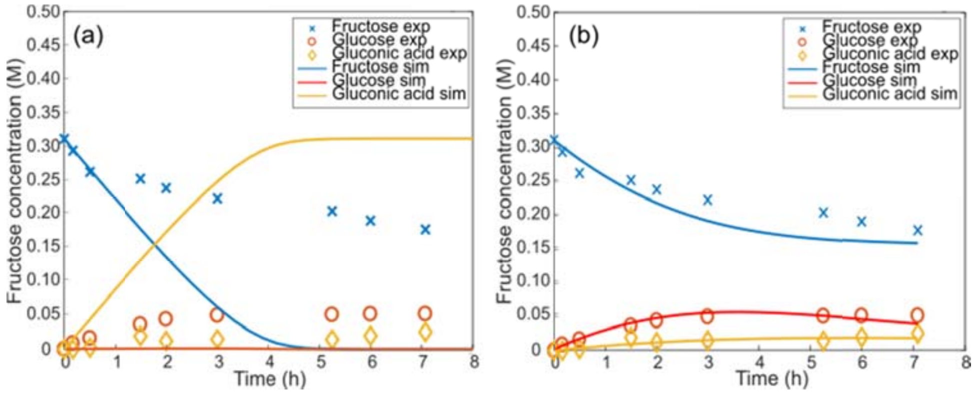

Fig. 2. One-pot slurry reaction results: (a) Fitting with parameters calculated for each step; (b) New fitting with strong inhibition by products

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MULTIPHASE REACTOR MODELING FOR REACTIVE PROCESSING OF POLYOLEFINES

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The post-polymerization functionalization of polyolefins with polar monomers is a useful technique allowing the incorporation of advanced properties to the virgin material, thus expanding its commercial applications [1]. The main industrial route employed for polyolefin functionalization is free-radical induced grafting (FRIG) [2]. The mechanism of FRIG involves the formation of mid-chain macroradicals (MCRs) via hydrogen abstraction caused by the attack of primary free radicals, created during the decomposition of the chemical initiator (usually a peroxide). Grafting points are formed by the addition of MCRs to the double bond of the vinyl monomer. This step is usually refered to as grafting "from". However, primary radicals are not selective during their attack, and they can directly add to the unsaturation of the vinyl monomer, producing homopolymer radicals as by-product. Nonetheless, by the recombination of homopolymers with MCRs, further functionalization can be achieved, leading to the formation of grafting "to" points. Furthermore, the reactive mixture could become multiphasic due to the incomplete solubility of monomer and chemical initiator in the molten polyolefin. The selection of the type and initial amount of polyolefin, initiator, monomer, the temperature, the pressure, the mixing efficiency, and the reactor have a crucial effect on the performance of this type of reactive process [3]. Thus, due to the multiple variables involved, and despite of being a mature and well-stablished industrial process, there are still issues to be addressed to enhance the process and properties of the final product during the post-polymerization functionalization of polyolefins via FRIG [4].

Recently, an advanced model for the kinetics of functionalization of polyolefins with vinyl monomers via FRIG was developed at LCT [5]. The kinetic model, based on the kinetic Monte Carlo (kMC) technique, assumed in a first istance isothermal conditions and perfect macromixing (single homogeneous phase model). Furthermore, it accounts for diffusional limitations on the microscale. Because the reaction temperature is close to the ceiling temperature of the vinyl monomer, depropagation steps are also taken into account. In order to accurately perform the random sampling of macromolecules during hydrogen abstraction reaction events, a mass-weighted CLD for the polyolefin is employed in the kMC algorithm. The model allows the calculation of parameters to evaluate the extent of reaction, such as monomer conversion, grafting selectivity an yield, as well as the complete microstructural characterization of the macromolecular product, such as grafting "from", grafting "to", crosslinking density, number of grafts and crosslinks per individual chain, and the chain length distribution (CLD) of homopolymer, polyolefin and grafted chains.

In the present contribution, the single-phase homogeneous model is extended toward phase segregation, due to the incomplete solubility of monomer, initiator and solvent in the molten polyolefin. Hence, two phases are assumed, one rich in monomer and one rich in polyolefin so that the model becomes applicable to describe the reactor performance during reactive processing. The monomer-rich phase will produce mostly homopolymer chains, whereas grafted polyolefin and homopolymer will be brought about in the polyolefin-rich phase. The reactants and products formed in one phase can be transferred to the other phase until the saturation point (given by the solubility of the components in each phase) is reached. It is assumed that the polyolefin is not transferred from the polyolefin-rich phase to the monomer-rich phase, due to the low affinity of non-polar long chains with more polar compounds. The mass transfer over the interface is accounted for based on fundamental principles. The extended model can also be applied for multiple temperature zones and injection points. Hence, the model can be applied for a variety of industrial reactor operation modes.

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PROOF OF CONCEPT CFD STUDY OF POLYSTYRENE PYROLYSIS IN A GAS-SOLID VORTEX REACTOR

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Polystyrene (PS) is a type of plastic with numerous applications in different sectors, like packaging and construction. PS represents 6 % of the polymers produced in Europe [1]. However, due to its high chemical stability, polystyrene waste has large environmental impacts for a long period of time. A promising route to PS recycling is pyrolysis. Large yields of the styrene monomer are obtained. Styrene can be reused for the production of new polystyrene. PS pyrolysis thus offers a path towards a plastic-based circular economy.

Nowadays, the fluidized bed reactor is one of the preferred technologies to apply for multiphase processes like pyrolysis due to its ease in design and operation. However, fluidized bed reactors suffer from operational limits, eg the maximum fluidization gas flow, while mass and heat transfer rates are moderate. These limits are observed to decrease in a fluidized bed operating in a centrifugal field. Gas-Solid Vortex Reactors (GSVRs) sustain a rotating solid bed by continuous tangential injection of fluidizing gas through multiple small injection slots. GSVRs are known to offer advantages over conventional fluidized bed reactors in the gravitational field; the bed is densely packed, giving higher gas-solid slip velocities. The latter results in enhanced heat and mass transfer.

At the Laboratory for Chemical Technology (LCT, Ghent University), fluidization in a GSVR is visualized and studied in a GSVR demonstration unit. The goal is to further optimize the operational benefits for a GSVR in processes like biomass fast pyrolysis, oxidative coupling of methane, and more. Additionally, Computational Fluid Dynamics (CFD) simulations of these processes have demonstrated various capabilities of vortex technology, as compared to conventional fluidized bed reactors [2] [3]. The work presented here focuses on a computational study of the applicability of GSVR technology for the pyrolysis of PS. Three-dimensional multiphase, Eulerian-Eulerian simulations have been performed with ANSYS Fluent using a basic kinetic model for PS pyrolysis taken from the literature [4]. The kinetic model considers thermal degradation of PS into several products: non-condensable gases, light olefins, aromatics and styrene monomer. Combining the kinetic model with the CFD model allows to study PS degradation into a useful liquid fraction, more particular into the styrene monomer by optimization of the process conditions and the reactor design.

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CFD SIMULATION OF A NOVEL GAS-LIQUID REACTOR SYSTEM

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A novel system for contacting gases and liquids, which is suitable for many applications involving gas-liquid contact such as CO_2 capture and brine desalination, has been developed and experimentally characterized [1, 2]. The system consists of a vertical vessel with gas and liquid ports and inert particles that enhance mixing and provides high gas–liquid interfacial area. The optimum conditions for CO_2 capture and brine desalination where statistically demonstrated using Minitab software [3], and verified experimentally to be at low gas flow rate; however, the gas velocity can have a major effect on the motion of inert particles inside the reactor. Uniform particles motion and hence good mixing within the reactor ensure efficient absorption and stripping process; at the same time, the inert particles volume fraction has significant effect on CO_2 capture and minimum effect on desalination [2]. The Computational Fluid Dynamics (CFD) models which will be presented in this work will show the minimum gas velocity that insure high mixing through monitoring the flow patterns inside the reactor. Flow patterns variables were studied in a semi-batch and continuous mode flow. These variables and ranges are: Gas flow rate of 500-3500 ml/min, particle average size of 5-15 mm, particles volume fraction of 0-10 vol. %, orifice diameter of 1-4 mm, brine flow rate of 10-40 ml/min. in the continuous mode and brine volume of 1-3 L in the semi-batch mode using CFD software packages ANSYS Fluent. The flow domain was constructed on Design Modeller, two dimensional CFD of gas through high salinity brine in both semi-batch and continuous mode flow. In the semi batch-mode, the setup of the mesh is assumed to consist of four sections, namely, gas inlet, gas outlet, water body and space, while in the continuous mode two more section, the brine inlet and outlet, have been introduced. Volume of fluid (VOF), Mixture and Eulerian multiphase [4-6] models well be compared to investigate the hydrodynamic flow behavior in the system which consist of stainless steel cylindrical vessel with 78 mm internal diameter, 700 mm height, and a total working volume of 3000 ml. The simulations were carried out under transient and gravitational acceleration conditions. The realizable k-ε model is taken to consider the turbulence effects of the flow of gas through brine water. The residual tolerance was set to 0.0001 for all factors to show convergence of the calculations. Each model has been run in double precision mode to increase the accuracy of calculation. The momentum and pressure equation was solved using the coupled pressure-velocity scheme with volume fractions. The gradient was calculated using Least Squares cell based method. Pressure interpolation was determined using PRESTO scheme. A third order MUSCL scheme is used to solve the momentum and turbulence equations [7-9]. Figures 1-3 show the geometry and mesh structure for the reactor system in the semi-batch mode, and Figures 4-9 show some results for the VOF model as contours of pressure, mixture velocity, water and air volume fraction, turbulence kinetic energy and Eddy viscosity for the semi-batch mode without mixing particles at gas velocity 1 m/s after 10 seconds of flow. Mesh independent study for each model will be presented to make sure that results are independent of the mesh resolution [10].

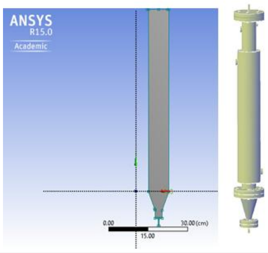

Fig 1. Reactor system diagram and 2D geometry

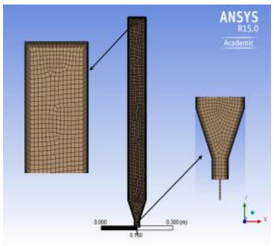

Fig 2. Mesh structure in semi-batch mode

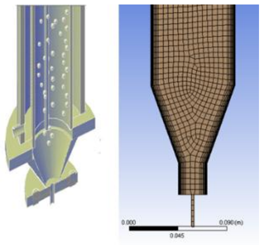

Fig 3. Conical part of reactor system with mesh structure

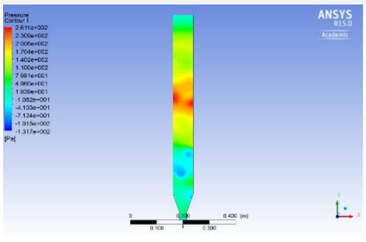

Fig. 4. Contours of the pressure

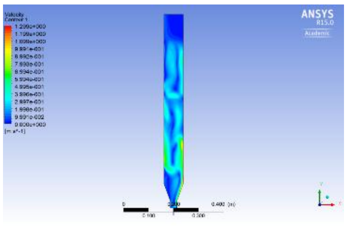

Fig 5. Contours of the velocity

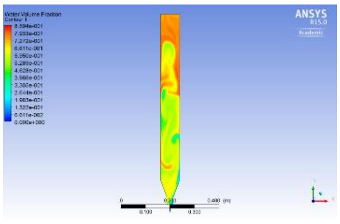

Fig 6. Contours of the water volume fraction

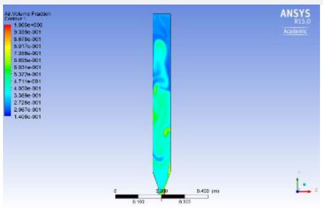

Fig 7. Contours of the air volume fraction

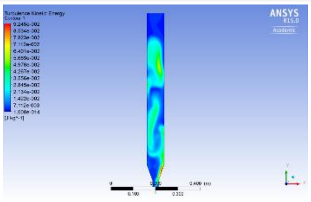

Fig 8. Contours of turbulence kinetic energy

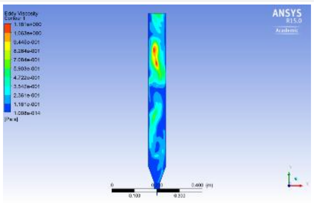

Fig 9. Contours of Eddy viscosity

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OP-II-23

X-GTL: A STUDY OF THE PROCESS OPTIONS USING A MULTI-PHASE PROCESS MODELLING FRAMEWORK

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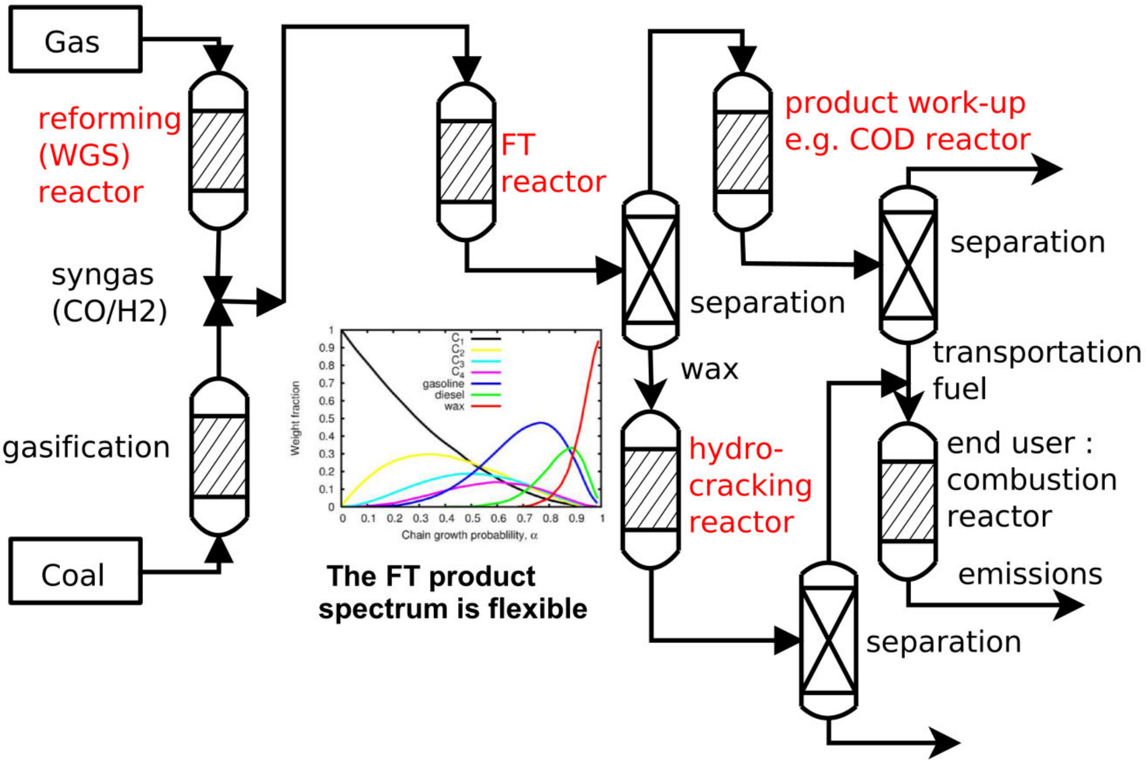
Although massive progress is being made in the use of renewable materials as a source of energy, the dependence of heavy duty long distance transportation (cars, trucks, ships, aircraft, etc) on petroleum based fuels remains dominant. This is supported by continued heavy investments in maintaining and developing large scale petroleum based refineries. However, the feed to these refineries, which historically was only crude oil (and in the case of SASOL, coal), is changing rapidly. The “new” technology is dominated by gas to liquid (GTL) plants, but there is no restriction on the source of the gas and or liquid which could come from renewables, such as biogas, municipal waste, tyres, plastic and so forth. Interestingly, any large scale plant making transportation fuels from these feedstocks have much the same downstream processing units, whether going via Fischer-Tropsch or methanol. They comprise of some or all of the following: Fischer-Tropsch (FT), hydrocracking, oligomerisation, hydrocracking with or without recycle and separation. The challenge here is that the best operating mode of these reactors and systems depend on the feed used and the inter-connectivity of the units, which could be considerably more variable that in the past.

One of the challenges in developing new flow sheets is to reduce the capital cost and optimise the operations by better integration. Large capital cost savings can be achieved by using air in the reformer in place of oxygen. This has signifcant consequences to the downstream operations, in particular the operation of the FT reactor, which currently is optimised to work at conversions of 60 % with recycle now has to operate in once through mode at high conversion to offset recycling the nitrogen [1]. Moreover the FT product distribution represented by the alpha value has to be optmised to maximise the distilate yield from hydrocracker. These concepts can be studied by combining elementary multi-phase, multi-species models into a flow sheet.

A simplified flow sheet of potential flexible process is showen below. These reactors operate in multiphase mode which makes operation and prediction of their behaviour considerably less intuitive than single phase reaction systems. This work reports on progress towards developing a modelling framework which proposes to use multi-species, multi-phase reactor units, incorporating multi-species reaction kinetics sufficiently complex to describe elementary phenomena and phase equilibrium of the real system. The development will focus on coupling reaction systems which operate with up to 200 carbon numbers within a flow sheet. The process flow sheet will be used in sections and as a whole to study the influence of nitrogen content on the downstream performance and the effect of the alpha value on the distillate yield of the process.



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OP-II-24

NICOTINIC ACID PRODUCTION AT ELEVATED β-PICOLINE LOADING: THEORETICAL STUDIES OF THE POSSIBILITY TO INTENSIFY THE PROCESS

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Some technological processes operate at low inlet concentration of raw materials, due to the thermal runaway, explosive limits, and other kinds of restrictions. Evidently, increasing the reactant's load would greatly improve the process productivity provided that existing technological facilities meet the new requirements. Synthesis of nicotinic acid (NA) by heterogeneous catalytic oxidation of β-picoline (βP) is carried out at the initial concentration as low as 0.8-1.2 %. To be efficient, the exothermic process under consideration should proceed within a narrow range of the process temperature. On the one hand, this excludes the condensation and/or crystallization of the products; on the other hand, this will ensure the thermal stability of the catalyst and will limit the undesirable increase in by-products formation [1]. Besides, due to kinetic reasons it is necessary to maintain a significant excess of oxygen and water vapor with respect to βP as the reactant to be oxidized [2].

In the present paper, the role of factors that could contribute to the intensification of the process of NA synthesis in a multi-tubular reactor at the increased concentration of βP, has been investigated by methods of mathematical modeling [3]. To solve the problem, we used a 2-D quasi-homogeneous model of a tubular reactor, and the detailed kinetic reactions model on V_2O_5-TiO_2 catalyst [1] as well. In simulation, we varied the initial ratio βP:O_2:H_2O, coolant temperature, linear gas velocity, length of the catalyst bed, and the inner tube diameter. Increasing the initial βP concentration up to ~3 % leads to an increase in the specific catalyst productivity by 1.5-2 times. For a given production capacity, the process intensification can reduce by 2-5 times the number of tubes with respect to the conventional multi-tubular reactor.

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TRANSIENT OPERATION: A NOVEL WAY TO ENHANCE SELECTIVITY IN GLUCOSE ISOMERIZATION REACTION

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Over the last decade, the dependence on fossil feedstock has become a source of preoccupations for chemical industry highlighting the need to move towards renewable raw materials. In this sense, carbohydrates constitute three quarters of the available renewable biomass. Simple carbohydrates, such as mono- and disaccharides, are obtained by catalytic hydrolysis of cellulose, hemicelluloses and starch, and their further transformation into useful derivatives in an obvious way forward. Glucose isomerization is an important step in its subsequent transformation into platform molecules, for example, 5-hydroxymethylfurfural (5-HMF), which can be further processed into fuel additives, paints, and a variety of fine chemicals. While fructose can be converted into 5-HMF in a rather straightforward way, glucose remains the main building block of lignocellulosic biomass, and its conversion towards fructose and further planform chemicals remains challenging. Glucose isomerization is a complex chemical process characterized by formation of numerous side products.

In this work we present a novel approach for glucose isomerization to fructose based on a combination of a nanostructured heterogeneous catalyst and transient operation in flow. A 5 wt. % Ru supported onto hypercrosslinked polystyrene (HPS) catalyst was synthesized via conventional wet impregnation method following the previously reported protocol [1]. The temperature modulations were realized using induction heating of magnetic microparticles in a trickle bed reactor following the approach developed in our previous study [2]. The catalyst particles were mixed with magnetic microparticles to create a uniform catalyst bed. When exposed to an AC magnetic field at a frequency of 100 kHz, magnetic microparticles undergo a magnetization reversal process leading to energy losses which generate heat in the catalyst bed. Glucose (concentration: 0.5 mol/L in water) was fed with an HPLC pump and gas (H_2/N_2 mixture) was fed with a set of MFCs. In all experiments, the pressure was maintained at 17 bar with a back pressure controller, the temperature was varied in the range of 110-130 °C and the period of temperature modulations was varied in the range of 23-210 s.

The steady state reaction over the supported Ru catalyst yields sorbitol as the main product with a selectivity to fructose below 10 %. However under periodic temperature modulation, the selectivity to fructose increases to 82 % at the same conversion level. In order to shed some light on the origin of this exceptional selectivity switch, time averaged coverages with glucose and hydrogen species were estimated using a transient kinetic model previously developed for hydrogenation of glucose over the Ru/HPS catalyst [3]. The model was based on two kinetics with competitive adsorption for hydrogenation and isomerization reactions. The kinetic model qualitatively described the behavior observed. The higher fructose yield under transient operation was explained by much higher time-averaged glucose coverage. A rather high hydrogen concentration in gas phase was required to maintain high catalyst activity and stability. At steady state conditions, the replacement of hydrogen with an inert gas drastically reduces the rate of hydrogenation without any enhancement in the isomerization pathway.

A similar selectivity switch was observed in the transformation of maltose in the flow reactor. Hence, it can be concluded that the concept of fast temperature modulation can be extended to a wide class of reactions over Ru/HPS catalysts.

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SPATIOTEMPORAL OSCILLATIONS IN BATCH REACTORS PROMOTE LIGNOCELLULOSIC BIOFUEL PRODUCTION

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1. Introduction

Biological self-assembly renders the cellulose polymers in plant cell walls resistant to deconstruction to monomeric sugars. Here we show experimentally that non-equilibrium spatiotemporal oscillatory states formed via autoregulatory (autocatalytic/ auto-inhibitory) reactions – either catalytic or enzymatic – in batch reactors fuelled by external energy sources result in faster hydrolysis of lignocelluloses leading to higher production of cellulosic biofuels. Enzymatic hydrolysis of hemicelluloses [1] in unmixed tubular reactors lead to activator-inhibitor type unsteady state limit cycles, while ionic-liquid mediated catalytic conversion of non-edible lignocelluloses [2] in batch reactors heated by oil-baths result in chemical chaos, characterized by chaotic strange attractors with fractal dimensions and positive Lyapunov coefficients.

2. Methods

A. Catalytic conversion of lignocellulose (Sunn hemp fibre) to biofuel precursors is performed in 15 ml well-mixed (at 500 rpm) batch reactors at 110 °C using ionic liquid ([Bmim]Cl) as a solvent and $CuCl_2$ as catalyst. Water is added every half-hour at the rates of 25, 28.33, 33.33, 37.5 and 42.8 μl/gm/hr, and the concentrations of glucose, fructose, hydroxymethyl furfural (HMF), levulinic acid (LA) and formic acid (FA) are measured every half-hour for 24 hours of the reaction time.

B. Enzymatic hydrolysis of hemicellulose (xylan) is performed for 3 days with endo-xylanase enzyme at 40 °C in unmixed tubular reactors of 10 mm diameter kept in an incubator. The concentrations of the activator and inhibitor (xylose and xylobiose) are measured at every 3 cm interval along the reactor length at regular intervals of time.

3. Results and discussion

The catalytic hydrolysis of lignocellulose produces chaotic strange attractors with fractal dimensions and positive Lyapunov coefficients on product phase spaces. All the 5 products (glucose, fructose, HMF, LA, FA) exhibit aperiodic (i.e., non-repetitive) temporal oscillations, peaking at 5 hours for all water-addition rates, suggesting 5 hours to be the optimum hydrolysis time in the domain of chemical chaos.

37.5 μl/gm/hr of water-addition maximizes the concentrations of glucose, LA, FA – at all times, with their average yields peaking at 5 hours to 67.45 %, 12.42 %, and 4.97 %, respectively. The non-oscillatory yields of glucose, LA and FA at 5 hours for water addition of 45 μl/gm/hr (or higher) are much lower – 58.25 %, 3.51 % and 1.39 %, respectively. Bioethanol yield of 78 % is obtained after 15 hours of *Saccharomyces cerevisiae*-mediated batch fermentation of glucose separated from the ionic liquid.

The enzymatic hydrolysis of hemicellulose produces limit cycles at various times in the activator-inhibitor phase space all through the 3 days of hydrolysis, where the activators are the soluble sugars with Degree of Polymerization of 3 to 11, while the inhibitors are the monomer (xylose) and the dimer (xylobiose). These limit cycles correspond to the unsteady-state oscillatory spatial (longitudinal) patterns formed due to the inhibitor-activator reaction kinetics and the faster diffusion of the inhibitor along the length of the tubular reactor. As the hydrolysis proceeds, the limit cycles change from circular to elliptical. Initially, the rates of inhibitor formation and activator depletion are nearly equal, resulting in circular limit cycles, but as the hydrolysis progresses, the rate of inhibitor formation exceeds that of activator depletion, resulting in elliptical limit cycles. We observe that the non-equilibrium oscillatory patterns in the tubular reactor enhance the yield of reducing sugar by 8.7 % and 14.1 % over no mixing and continuous mixing, respectively, after 1 day of hydrolysis, while xylose yield increases by 3.6 % and 7.9 %, respectively.

4. Conclusions

Thus, we show that non-equilibrium states constituting of spatiotemporal oscillatory patterns significantly promote the yields of biofuel precursors in batch reactors, e.g., by 16 % in catalytic conversion of lignocellulose, and by 14 % for enzymatic hydrolysis of hemicellulose. This new technology of employing non-equilibrium spatiotemporal oscillations in batch reactors to enhance the yields of biofuel precursors accelerates and promotes the overall production of second generation lignocellulosic biofuels.

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LOW-TEMPERATURE CHEMISORPTION-ENHANCED CATALYTIC DECOMPOSITION OF HYDROGEN SULFIDE: THERMODYNAMIC ANALYSIS AND PROCESS CONCEPT

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Active development of hydroprocessing technologies and hydrogen energy require the development of new efficient ways for production of hydrogen, prefereably from non-hydrocarbon feedstocks.

Hydrogen sulfide seems to be the very attractive feedstock for this purpose. First, it is the conventional waste from oil and natural gas processing facilities. Second, the bonding energy of hydrogen in H_2S is the lowest among all natural hydrogen-containing compounds.

Unfortunately, the reaction of hydrogen sulfide decomposition

$$H_2S \Leftrightarrow 1/n\ S_n + H_2 \tag{1}$$

is characterized with severe equilibrium limitations. The complete H_2S decomposition requires the extra-high temperatures (above 1500 °C), leading to high energy consumption, necessity to apply expensive thermostable materials and risk of backward element recombination at cooling stage. In (very typical) case, when the carbonaceous compounds (CO_2, hydrocarbons) are present in the gas feedstock, such temperatures may also cause side reactions with formation of undesired products (coke, CO, COS and CS_2). Due to these reasons, still there is no feasible technology for H_2S decomposition in wide practical application.

The new process approach [1] is based on the chemisorption enhancement of the decomposition reaction (1). The process, involving metal sulfide chemisorbent-catalyst, includes cyclic alteration of two reaction stages technologically separated in time and space:

$$H_2S + MeS_n \Rightarrow H_2 + MeS_{n+1} \tag{2}$$

$$MeS_{n+1} \Rightarrow MeS_n + 1/n\ S_n \tag{3}$$

As shown by thermodynamic calculations (Fig. 1), the reaction (2) is exothermic and the corresponding equilibrium conversion of H_2S may reach 100 % at ambient temperature. Reaction (3) requires moderately increased temperatures (200-400 °C).

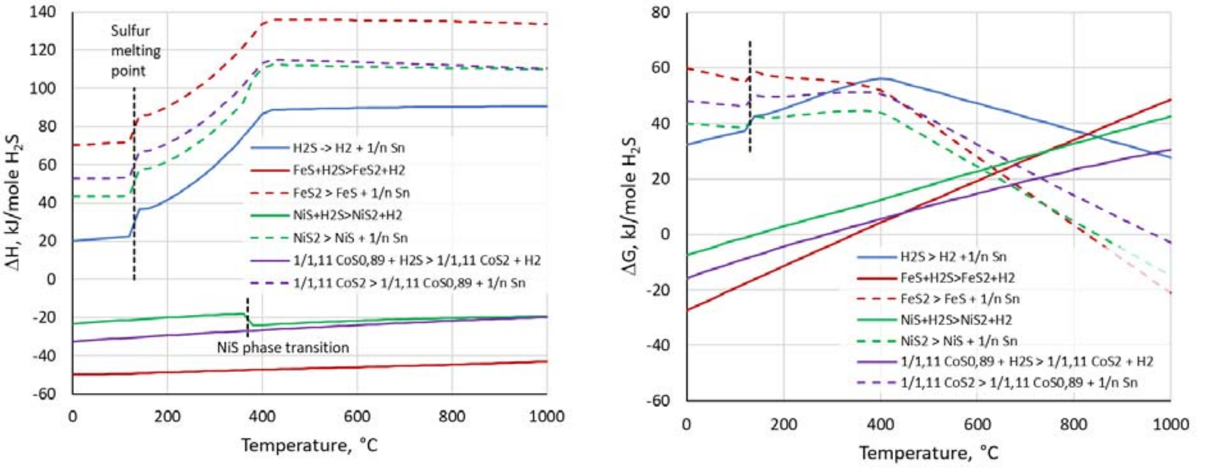

Fig. 1. Calculated enthalpy (left) and Gibbs free energy (right) changes in reactions (1-3) vs temperature

The whole process may be thus realized at moderate temperatures with achievement of complete H_2S decomposition, the backward recombination of elements is prevented by technological separations of stages (2) and (3) – hydrogen is not persent at stage (3).

Low operation temperatures provide decrease of heat losses to environment, resulting in increased energy efficiency of the process. The process may be based on cheap standard equipment from conventional materials, thus significantly minimizing the capital costs. Besides, the low temperature at H_2S chemisorption stage (2) makes possible to process feedstock gases, containing carbonaceous admixtures, without risk of their involvement to reaction and formation of undesired side products.

The presentation will include overview of the available related experimental data and discussion of the possible process flow-sheets with their comparative analysis.

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MODELING THE CONVERSION OF DIMETHYL ETHER INTO OLEFINS CONSIDERING THE HZSM-5 BASED CATALYST DEACTIVATION

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The conversion of dimethyl ether (DME) into olefins is an attractive route for complementing the production of olefins by steam cracking and catalytic cracking of naphtha. Moreover, it is an interesting alternative to MTO process (methanol to olefins) since DME is more reactive than methanol and its production is thermodinamically favored compared with that of methanol [1]. Deactivation of acid catalyst by coking is inevitable in this process and it is one of the main drawbacks for its industrial implementation [2]. In this sense, the understadning of the mechanism of DME conversion into olefins and its evolution caused by catalyst deactivation turn out to be crucial for advancing in the reactor and process design.

In this work, a lumping model for the conversion of DME into olefins has been developed and several deactivation equations have been proposed in order to establish a global kinetic model that succesfully predicts the evolution of product concentrations with space time and time on stream. Accordingly, an acid catalyst was prepared by the agglomeration of a HZSM-5 zeolite (Si/Al = 140) with pseudoboehmite as a binder (30 wt %) and α-alumina as inert fill (20 wt %). Experimental data were collected from reaction runs that were carried out in a fixed bed reactor using the following conditions: 325-375 °C; 1.5 bar; space time, 0-6.5 g_{cat} h mol_C^{-1} and time on stream 0-18 h.

A methodology based on the Levenberg-Marquardt algoritm has been developed in order to simultaneously fit the kinetic parameters at zero time on stream and the deactivation kinetics [3]. **Figure 1a** shows the lump-based kinetic scheme of DME conversion into olefins. This scheme involves the direct formation of olefins from DME (and methanol), hydryde transfer, oligomerization-craking and cyclizacion-aromatization pathways. Each step of the kinetic scheme follows a classical Langmuir-Hinshelwood equation, considering that the adsorption of methanol and water attenuates the rates of reaction:

$$r_j = \frac{k_j P_j a}{1 + K\left(P_{MeOH} + P_{H_2O}\right)} \tag{1}$$

Figure 1b shows the evolution of the yields of each lump with the space time. As observed, the model allows for achieving an accurate estimation of the yields of light olefins (O) and paraffins (P), aromatics BTX and long chain hydrocarbons (C5+). Nontheless, catalyst deactivation is noteworthy during the reaction and therefore, a catalytic activiy variable was included in the kinetic model (a in eq. (1)). Several deactivation equations were tested for fitting the experimental data of evolution of yields with time on stream (dots in **Figure 1c**). The best fitting (lines in **Figure 1c**) is obtained considering that DME, O and BTX are the main precursor of coke and the presence of water attenuates the catalyst deactivation:

$$-\frac{da}{dt}=\frac{k_d\left(P_{DME}+P_O+P_{BTX}\right)}{1+K_W P_W}a^{5.8} \tag{2}$$

Regarding the results, it can be stated that this lump-based model allows predicting with relatively good accuracy the product distribution of DME conversion into olefins in a fixed bed reactor considering the deactivation of the HZSM-5 catalyst.

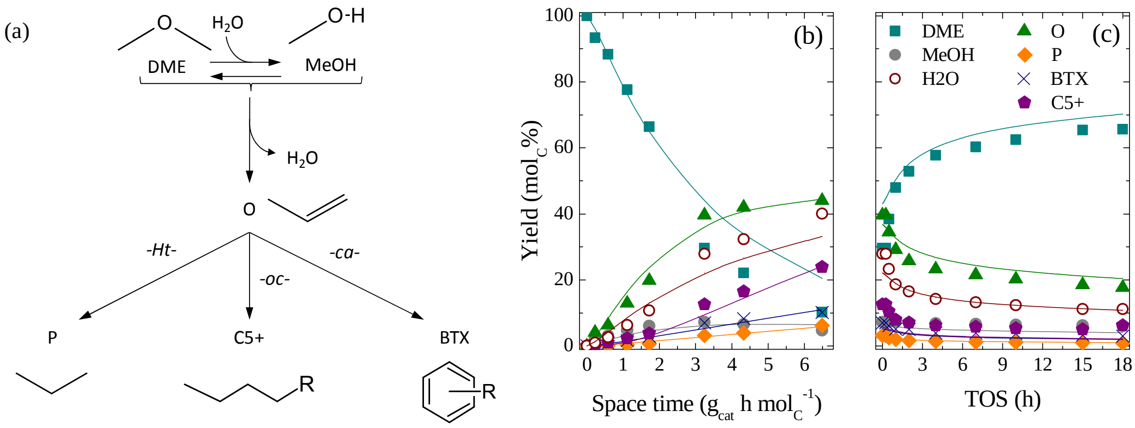

Figure 1. (a) Kinetic scheme for the transformation of DME into olefins and evolution of the lump concentrations with (b) space time and (c) time on stream at 350 °C. (dots are experimental data and lines are the model predictions)

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PLASTIC WASTE PYROLYSIS IN A SEMI-BATCH REACTOR

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Introduction

The generation of plastic waste is increasing year by year. In the context of processing waste from electric and electronic equipment (WEEE) recycling the electric cable waste has attracted increasing attention in recent years. Therein, priority is generally given to the recycling of the conducting metal, due to its higher value and, as a consequence, large amounts of plastic from electric cable waste are released into the environment without an effective disposal [1]. This incorrect disposal causes great problems to the environment, since, plastics (part of electric cable) do not degrade quickly and can remain in the environment for a long time [2], A large part of this waste is disposed of in landfills or is incinerated [3]. New processes are needed to increase the percentage that is reccycled. The use of feedstock recycling, for example by resorting to pyrolysis may be an attractive alternative since it provides an opportunity to obtain a broad distribution of products including char, oil/wax and combustible gases from plastic wastes [4]. In this work, the influence of temperature on the thermal pyrolysis of the electrical cables waste (ECW) will be analysed.

Experimental

The ECW were provided by Pyroplas. The samples were washed and crushed but their particle size lacks homogeneity. The thermal pyrolysis experiments were carried out using an unstirred glass reactor in semi-batch operation at atmospheric pressure. The reactor was initially flushed with N_2, then about 10 g of the plastic waste material were placed in the reactor which was heated at 10 °C min^{-1} to a final temperature ranging from 450 to 500 °C. The final temperature was maintained for 90 min. On top of the eactor a condenser was installed and the coolant fed to the condenser was controlled by a thermostat at 20 °C to control the product in the gaseous phase.

Results and Discussion

The mass yield of the products obtained for thermal pyrolysis are described in Table 1, for the three temperatures studied the reaction time was 90 min after reaching the final temperature.

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Table 1. Effect of temperature on thermal pyrolysis yields (wt %) at 90 min

Temperature (°C)	Solids	Liquids	Gases
450	98.8	0.0	1.2
470	97.0	0.6	1.4
500	94.1	1.2	4.7

It is observed from the results of Table 1 that the largest amount of products formed is in the solid phase (wax), results which are in accordance with Chaala [5]. For the lowest temperature (450 °C) it was not possible to collect any liquid phase products. It is important to note that the increase of 50 °C in the system did not cause significant changes in the yield of the products in the liquid and gaseous phase.

The distributions of the products collected in the gas and liquid phase for the thermal pyrolysis are shown below in Figures 1a and 1b respectively.

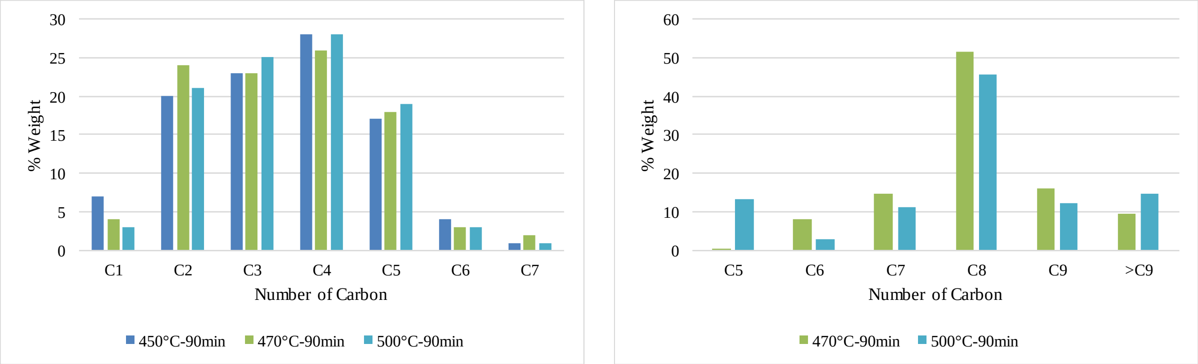

Figure 1. Product distribution (a) Gas phase and (b) Liquid phase

The product formed in the gas phase is in the range of C1-C7 but with the major portion being between C2-C5 while the products collected in liquid phase are heavier but with a large portion of C8 being formed. The solid products formed are mainly waxes of high molecular weight.

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MODELING OF MICROWAVE IRRADIATED AND HETEROGENEOUSLY CATALYSED EPOXIDATION OF VEGETABLE OILS

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Oil extracted from plants, seeds and wood is a vast biomass resource, which can be used to elaborate a wide range of products, for instance, by epoxidation. Epoxidized vegetable oils are used for developing bio-lubricants, PVC-derived plastic-ware, as well as intermediates for the synthesis of polyols, glycols, olefinic compounds and stabilizers for polymers. Moreover, microwave irradiation (MW) is considered as one of the best process intensification technologies [1]. The Prileshajev oxidation is the most common method to epoxidize vegetable oils, by using peroxycarboxylic acid formed in situ from hydrogen peroxide and acetic acid. To enhance the reaction rate a solid catalyst can be used. The aim of this work is to develop an improved method for producing epoxidized vegetable oils with high yields, using less energy and shorter reaction times, applying MW technology combined with special mixing technology and a solid catalyst. Finally, a kinetic model was developed for the epoxidation reactions under different reaction conditions.

Methods. Epoxidation of oleic acid was performed in a semi-batch reactor, by the so called Prileschajew oxidation. The perhydrolysis reaction (peroxyacetic acid formed in situ from acetic acid and H_2O_2) was enhanced by using a solid catalyst resin. The reactor system comprised a loop where the mixture was pumped through a cavity in which microwaves were irradiated and immediately recirculated back to the reactor. Experiments conducted under MW were compared with identical experiments carried out under conventional heating. A special mixing technology (Spinchem^{TM}) was incorporated, which allowed to minimize mass transfer limitations of the bifacial system and to immobilize a solid resin catalyst. The reaction kinetics was modeled mathematically by applying numerical methods for the solution of stiff differential equations and optimization algorithms for parameter estimation. With this model the numerical values of the kinetic parameters were obtained and the model can be used to predict the progress of the reaction. Maxwell's equations were included to describe the microwave heating in the energy balance, which defines the interaction of each substance present in the reaction under microwave irradiation.

Results. The epoxidation kinetics accomplished with microwave heating were compared to conventional heating without any solid catalyst [2] as well with solid resin catalyst present. A detailed kinetic model for the reaction was developed which took into account the perhydrolysis reaction and decomposition reactions in the aqueous as well as the solid catalyst phase, and the epoxidation reaction and the ring opening reactions in the organic phase. Also, the mass transfer of the components between the phases were taken into account.

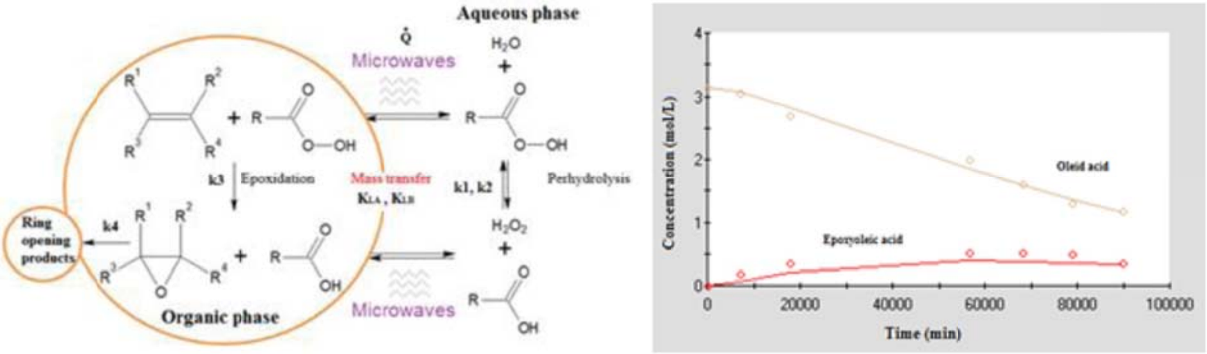

Figure 1. LEFT: Epoxidation reaction scheme. RIGHT: Example of data fitting for non-catalytic conventional heating at 40 °C

The kinetic model for epoxidation of vegetable oil showed to have a good correspondence between experimental and calculated values. Rate constants and activation energies for the reactions involved were obtained by nonlinear regression analysis.

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NOVEL REACTOR DESIGNS FOR THE HYDROFORMYLATION OF LONG-CHAIN OLEFINS: FLEXIBILITY AND AUTOMATION ASPECTS

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Introduction

The design of new novel reactors can be done in many different ways. Especially for the production of fine chemicals highly flexible systems are needed. In our group dynamic optimizations were performed o identify the most promising reactor network for the homogeneously catalyzed hydroformylation of 1-dodecene using a thermomorphic multicomponent solvent (TMS) system for catalyst recycling [1]. The reaction network and kinetics are complicated; therefore it is not possible to apply standard reactor design methods. Two reactor systems were found to be most promising: (1) a repeated semi-batch reactor (RSBR) followed by a continuously operated stirred tank reactor (CSTR), (2) a helically coiled tubular reactor (HCTR) followed by a CSTR.

Results and Discussion

Both reactor concepts have been constructed and operated for long time periods with closed catalyst recycle (Figure 1) [2,3,4]. In this contribution, both concepts will be compared regarding their performance while taking also the effort of the construction and operation into account. Our model-based predictions (see [1]) and the experimental results indicate, that both candidates feature almost the same performance (yield, selectivity) when using identical reaction parameters (catalyst concentration; total volume flow; residence time). But the efforts during operation and construction for both setups are very different. For the integration of the batch-wise operated reactor into the continuous process, two buffer vessels in front of and after the RSBR had to be installed. During the operation, charging and discharging of the reactor has been done manually, which lead to a strict procedure and high effort for the operator. Regarding the operational effort, the continuous operated tubular reactor is exactly the opposite of the RSBR. In order to reduce the space required, the reactor tube was coiled up helically with a total length of 270 m. The construction was done in a way that it opens the possibility of changing the length of the reactor

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tube. This leads to a good flexibility when the reaction conditions have to be changed, e.g. due to varying quality of the raw materials, catalyst concentration changes or variation of the reaction temperature.

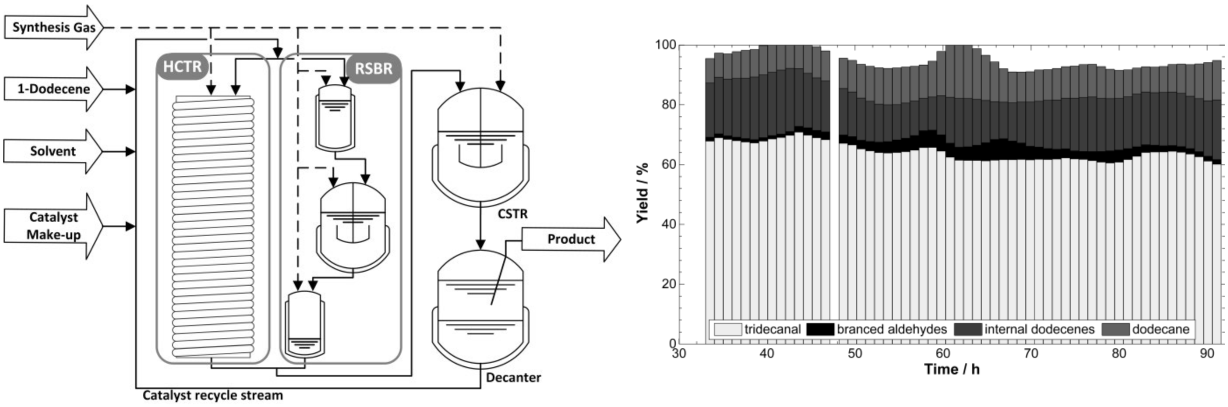

Figure 1. Left: Simplified process flowsheet with the two reactor concepts (HCTR, RSBR); right: C13-aldehyde yield over time obtained with the RSBR-CSTR-setup [3]

Conclusions

Both reactor concepts show almost the same performance for the hydroformylation of long-chain alkenes, but feature quite different efforts in terms of operation and construction. The coiled tubular reactor is much easier to operate, because it runs continuously, whereas the RSBR is much more challenging to operate. However, the latter is much more flexible with respect to the reaction parameters that can be changed from batch to batch. In the end, the decision for or against a certain reactor system will be guided mainly by aspects of plant flexibility and the automation effort.

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ORAL PRESENTATIONS

Section III.

Chemical Reactors and Technologies for Targeted Applications

DIRECT SYNTHESIS OF DIMETHYL ETHER (DME) FROM CO/CO_2 IN A MEMBRANE REACTOR

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Dimethyl Ether (DME) has a great interest as domestic fuel (similar vapor pressure to liquified gases) and automotive fuel (high cetane number), as well as raw material for the production of H_2 (through steam reforming) and olefins (substituing methanol). Direct synthesis of DME on a bifunctional catalyst shows an important thermodynamic advantage in comparison to the methanol synthesis and its dehydration towards DME in two-steps. Due to the use of a single reactor for both reactions, the methanol synthesis equilibrium is displaced [1]. This lower thermodynamic limitation justifies that the direct DME synthesis is suitable for the conversion of CO_2 on a large scale, co-fed with syngas [2]. Simulation studies of a packed bed membrane reactor (PBMR) with different sweeping strategies have been performed, analyzing the effect of H_2O removal from the reaction medium regarding the DME production and CO_2 valorization enhancement compared to a fixed bed reactor (PBR) [3, 4]. Although these simulation results are encouraging, since using a PBMR both DME production and CO_2 valorization are improved, is key to synthesize a H_2O perm-selective membrane and stable under the reaction conditions (high temperature and pressure) required in this process [5].

Based on the simulation results, in this experimental work, an original reaction system with a PBMR is designed and installed, in order to carry out reaction runs and compare the DME yield and CO_2 conversion with a PBR. Figure 1a shows a PBMR operation scheme. The catalyst used is CuO-ZnO-ZrO_2 / SAPO-11 and the external wall of the catalytic bed is a LTA zeolite membrane, selected among other microporous zeolites such as MOR or SOD. This type of microporous zeolite is hydrothermally stable and its H_2O permeance under 30 bar and 300 °C is 1.09×10^{-3} mol$\cdot$m$^{-2}\cdot$s$^{-1}\cdot$Pa^{-1}. The reaction runs were carried out under the following reaction conditions: Feed gas, H_2+CO+CO_2; CO_2/(CO+CO_2) molar ratio, 0,0.5 and 1; H_2/(CO+CO_2) ratio in the feed, 3; temperature, 275, 300 and 325 °C; pressure, 30 bar; space time, 10 g_{cat}h $(mol_c)^{-1}$. The sweeping gas flow on the permeate side in co-current mode is 60 ml·min^{-1} with the same feed concentration. In Figure 1b DME yields obtained with a PBR and PBMR are compared at different temperatures and CO_2/(CO+CO_2) molar ratios in the feed between 0 and 1. It can be observed that the DME yield is significantly higher with the PBMR for all the different studied conditions. Moreover, it has been determined that the conversion of CO_2 is also greater with the PBMR (results not shown). The advantage of the PBMR for this purpose (valorization of CO_2) is higher increasing the CO_2 content in the feed. These results are encouraging in terms of its industrial scale-up substituing the conventional PBR for the PBMR and, besides, permit the evaluation of subsequent studies like sweeping strategies and reaction conditions optimization.

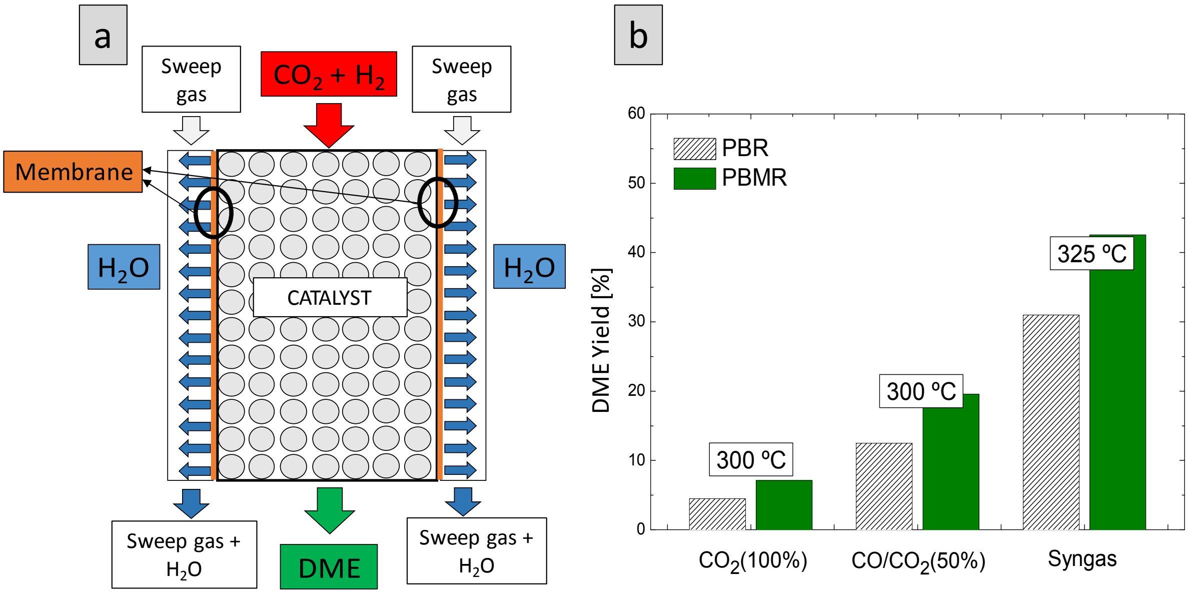

Figure 1. a) Operation scheme of the PBMR. b) Experimental comparison between the DME yields with a PBR and a PBMR

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Acknowledgements

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INTENSIFIED DME PRODUCTION FROM SYNTHESIS GAS WITH CO_2

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In recent years production of clean fuels alternative to crude oil-based gasoline, diesel and LPG has been drawing increasing attention. Among such fuels, Dimethyl Ether (DME) is considered as a strong candidate for replacing their conventional counterparts in the near future due to its attractive properties such as easy transportation and handling, and pollutant (i.e. CO, NO_x) free combustion characteristics. DME production involves exothermic equilibrium reactions, namely synthesis gas-to-methanol conversion and subsequent dehydration of methanol, which are commercially carried out indirectly, i.e. in two sequential packed-bed reactors involving $CuO\text{-}ZnO\text{-}Al_2O_3$ and a solid acid such as $\gamma\text{-}Al_2O_3$ as catalysts, respectively. In the direct synthesis approach, however, reactions run within the same reactor on a bed composed of either a physical mixture of the synthesis and dehydration catalysts or of a single, hybrid catalyst in which active phases for synthesis and dehydration reactions exist on the same support. Success of the direct synthesis approach, which offers significant reductions in capital and operating expenses and suppresses the limiting impacts of thermodynamic phenomena, depends strongly on facile removal of the heat released by synthesis and dehydration of methanol from the reaction medium. In this respect, wall-coated microchannel reactors come into play with their heat transfer rates that are $\sim 10^2$ higher than those of their packed-bed counterparts. Moreover, ease of integration of cooling function allows microchannel units to operate under isothermal conditions allowing precise balance of the kinetic and thermodynamic effects. This study involves a quantitative parametric study for providing insight into the potential benefits of heat exchange (HEX) integrated microchannel reactor operation in single-step DME synthesis from synthesis gas involving CO_2, which further increases the detrimental effects of thermodynamics and calls for the requirement of precise temperature control of the catalyst bed.

HEX integrated microchannel reactor concept [1] consists of stainless-steel walls separating cooling and reaction channels in which coolant (air) and reaction mixture are fed counter-currently with the same velocity and pressure of 1.17×10^{-1} m/s at

50 bar, respectively. All channels have the same size, 4×10^{-4} m for height, 6×10^{-4} m for width, and 5×10^{-2} m for length. Inner walls of the reaction channels are washcoated with 5×10^{-5} m thick layers of homogeneously mixed $CuO\text{-}ZnO\text{-}Al_2O_3$ and $\gamma\text{-}Al_2O_3$ catalysts (mass ratio = 1:1). Prior to their use in the simulation of the HEX-integrated reactor, expressions describing the rates of methanol synthesis via hydrogenation of CO and CO_2 on $CuO\text{-}ZnO\text{-}Al_2O_3$ and of methanol dehydration on $\gamma\text{-}Al_2O_3$ are validated by incorporating them into a one-dimensional pseudomogeneous model that is used to simulate a packed-bed reactor whose experimental data is reported in [2]. Upon successful validation (Figures 1 and 2), air-cooled microchannel DME synthesis reactor is modeled in 2D on ANSYS 16.0 platform which uses finite volume method to solve steady-state heat, mass and momentum transfer equations in both porous catalyst and fluid phases along with catalytic reactions simultaneously. Effect of reactant and coolant inlet temperatures, molar feed ratios (H_2/CO and H_2/CO_2) and wall thickness are studied in the ranges of 190-250 °C, 200-275 °C, 1-3, 2-10 and $4\text{-}8\times10^{-4}$ m, respectively. The results show that, in all parametric combinations, temperature change along the catalyst layer can be kept below ~10 °C which sets path for the optimal management of single step DME production from synthesis gas involving CO_2.

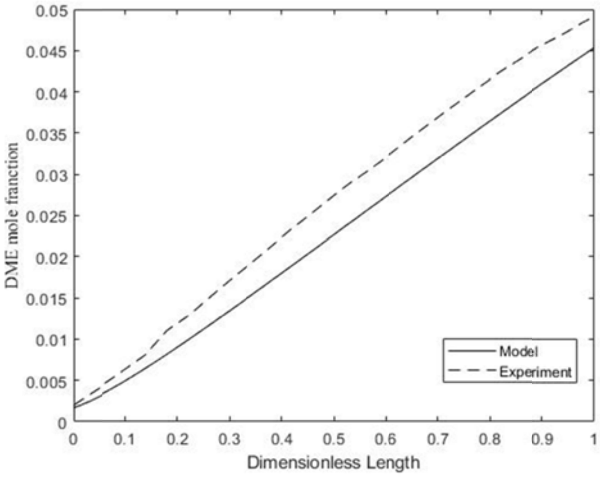

Figure 1. Comparison of computed DME mole fraction with experimental data [2]

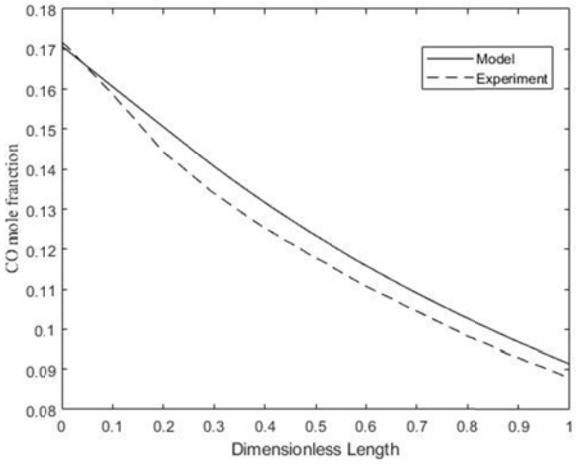

Figure 2. Comparison of computed CO mole fraction with experimental data [2]

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CO_2 CONVERSION ENHANCEMENT IN A PERIODICALLY OPERATED SABATIER REACTOR: NONLINEAR FREQUENCY RESPONSE ANALYSIS AND SIMULATION-BASED STUDY

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The increasing levels of global CO_2 emissions has prompted research in utilizing CO_2 as a feedstock for generating synthetic fuels and chemical [1]. The current industrial usage of CO_2 is limited to processes such as synthesis of urea, salicylic acid and polycarbonates. Conversion of CO_2 into synthetic CH_4 (the Sabatier reaction, $CO_2 + 4H_2 = CH_4 + 2H_2O$, normally accompanied by reverse water gas shift and CO methanation), has recently gained increasing interest as a technologically advantageous route for CO_2 utilization [1]. Microchannel, monolith, three-phase slurry, fluidized bed, and packed bed reactors were suggested as design solutions [2, 3]. Thermal management remains one of the main problems, as the overall process is highly exothermic requiring efficient heat removal to drive the CH_4 formation and, importantly, to prevent catalyst deactivation [2, 3]. It is of crucial importance therefore to increase the CO_2 conversion at low temperatures. Herein, we demonstrate the use of the Nonlinear Frequency Response (NFR) technique to predict the CO_2 conversion enhancement induced by periodic operation.

The nonlinear frequency response (NFR) method is an approximate, analytical method, mathematically based on Volterra series and generalized Fourier transform, which uses the concept of higher order frequency response functions (FRFs) in order to predict whether, at which conditions, and to which extent, a reactor performance can be improved by periodic modulation of one or more input variables [4]. In this work the NFR method was applied to analyse the kinetic flow model of the Sabatier reaction described by a set of dimensionless material balances [5]:

$$\frac{du_i}{d\tau} = u_{if} - u_i + Da\left(\alpha_{i1}\kappa_1 f_1 + \alpha_{i2}\kappa_2 f_2 + \alpha_{i3} f_3\right)$$

where u_i is a dimensionless concentration (*i* stands for CO_2, H_2, CH_4, CO, and H_2O), f_1-f_3 are dimensionless reaction terms with stoichiometric coefficients α_1-α_3, κ_1 and κ_2 are normalized reaction rate constants, and Da stands for the Damköhler number.

OP-III-3

A typical output from the NFR analysis is shown in **Figure 1**, where a substantial improvement in CO_2 conversion obtained by the periodic modulation of the inlet flow rate is demonstrated. This improvement was validated by numerical simulations using a kinetic flow model described above, **Figure 2**.

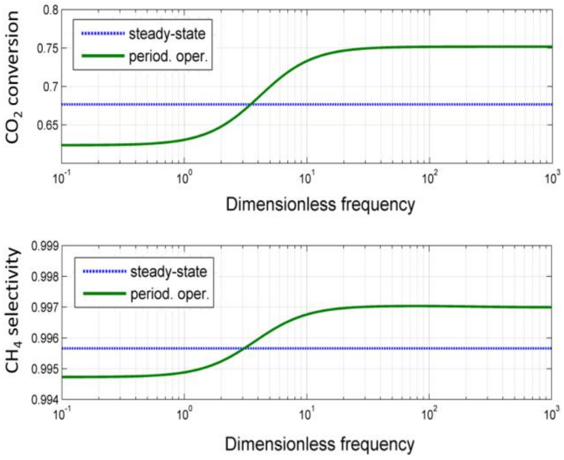

Figure 1. NFR analysis applied on the Sabatier reaction system: blue lines represent steady state conversions obtained with constant input

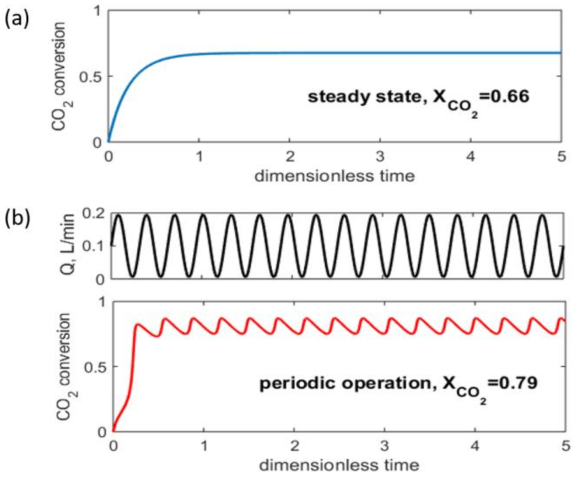

Figure 2. Numerical simulations of the flow model, Eq. (4) with constant and modulated feed rate (same average feed flow rate)

For the first time, we have demonstrated that the Nonlinear Frequency Response (NFR) analysis can be used to predict the enhancement of the conversion of CO_2 in the Sabatier reaction at low temperatures [5]. Our findings are of great importance for advancing the field of the thermocatalytic CO_2 conversion.

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APPLICATION OF DIELECTRIC-BARRIER DISCHARGES REACTOR IN CO_2 HYDROGENATION

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High consumption of carbon-based energy causes significantly and continuously increasing of the atmospheric CO_2 concentration, which results global warming and even leads to many other disasters [1]. As CO_2 is a C_1 resource available at low cost, chemical utilization of CO_2 has attracted considerable interest [2]. However, relatively high temperature is needed to active CO_2 because of its high kinetic stability, which is inefficient. A bigger drawback is the deactivation of the catalysts due to carbon deposition on the surface at high temperature [3]. Aiming at this problem, non-thermal plasma technique is applied to CO_2 hydrogenation in this work. Among various plasma, dielectric-barrier discharges (DBD) is most commonly used because the high-energy electrons generated have typical energies 1-10 eV, enough to break most chemical bonds [4]. The application of plasma could help active CO_2 at low temperature, avoiding carbon deposition and enhancing stability of the catalysts. The DBD reactor is shown in Fig. 1. The high-field electrode is located at the central axis of the reactor tube with an 8 mm inner diameter and connected with plasma generator, choosing quartz as the discharge medium and surrounding the grounding electrode around the outer wall of the quartz tube, which has a 10 cm length discharge interval.

In this study, incipient wetness impregnation method is used to prepare a series of metal catalysts precursor with ZSM-5 as the support (15 wt % metal loading). The catalyst precursor was packed in the discharge interval of the DBD reactor, pretreated in H_2 plasma flowing in 80 ml/min for 40 min (input power = 12 W), and then switch the reaction gas to 1/3 CO_2/H_2 (input power = 14 W), reacting in-situ for 3.5 h with the synergy of plasma. The product was monitored by gas chromatography. It is found that among various metals, Co and Ni/ZSM-5 get high selectivity of CH_4 and even C_2-C_4 appears in the products. Co/ZSM-5 has the highest C_2-C_4 selectivity, which is 4.88 % (alkane) with 38.97 % CO_2 conversion. By changing the cobalt catalyst supports, the C_2-C_4 selectivity also changes in such sequence: bulk Co>ZrO_2>SiO_2>ZSM-5>SAPO-34>Al_2O_3, among which, C_2-C_4

selectivity of bulk Co catalyst is 11.41 % (alkane : alkene = 2.29 : 9.12) with 39.37 % CO_2 conversion. The yield of lower hydrocarbons is much higher than that produced by conventional methods [2].

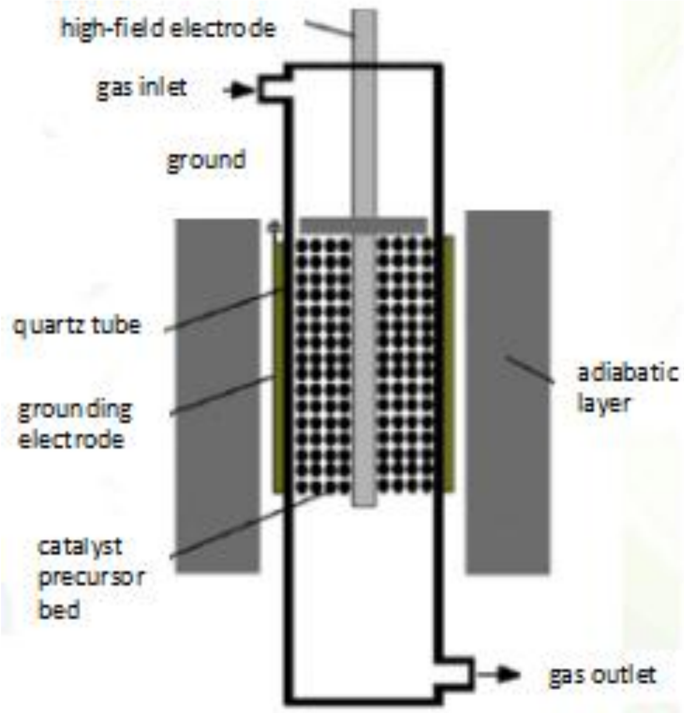

Fig. 1. Structure of DBD reactor

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OPTIMAL REACTOR DESIGN FOR CO_2 METHANATION ON Ru/Al_2O_3

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The CO_2 methanation reaction is a promising process to combine CO_2 reutilization and energy storage. In fact, the CO_2 recovered from atmosphere can be reacted with hydrogen produced by electrolysis with the excess energy to form methane. Methane can then be fed to the natural gas network or stored in the appropriate storage systems. The CO_2 methanation is a strongly exothermic reaction (ΔH_R (298 K) = -165 kJ/mol) and is subject to thermodynamic equilibrium. In the industrial operation, where the gases are fed not diluted in the reactor, the heat management of the reaction is the key parameter for an efficient control of the reaction. In fact, the rate of reaction changes drastically with the axial coordinate of the reactor, according to temperature and advancement of the reaction. Ru/Al_2O_3 is the most active catalyst for this reaction and the only material which allows CO_2 conversion higher than 95 %. In our study, we applied the method of elementary process functions [1] to find the optimal reactor for the synthesis of methane from CO_2 and H_2. Using the kinetic model of Lunde et al. [2], it was possible to determine the optimal absolute reaction path in terms of conversion and temperature profiles. The results are shown in figure 1. In this phase, the results do not refer to any particular equipment, but only to the physical properties of the system. In the second step, the reaction is modeled taking into account also the properties of the technical system, introducing limitation to heat and mass transfer. Since the reaction has different requirements according to the advancement stage, it is not possible to efficiently approximate the optimal conditions with a single reactor. Three main zones with different requirements are present (figure 2):

1. Preheating zone, where the reactant gas mixture must be quickly heated to the operation temperature in order to start the reaction;
2. Cooled zone, where the cooling system is crucial to limit the hotspot temperature and remove the reaction heat;

3. Isothermal zone, where the temperature is kept at an appropriate value in order to complete the reaction.

The third step of the reactor design concerns the development of a technical solution to approximate the heat requirements of the optimal reaction pathway. The proper heat and material fluxes have to be considered in order to define a technical solution capable of approximating the optimal path defined in the previous steps. According to the properties to optimize (e.g. residence time or maximal temperature), the fluxes to adjust for good reaction control are different. In this study, we defined and compare various reactor configurations in order to define the most suitable reactor for the CO_2 methanation and achieve high conversion. The results obtained allow the design of an optimized reactor for integration in a PtG system, generating significant savings in terms of investment and operation costs.

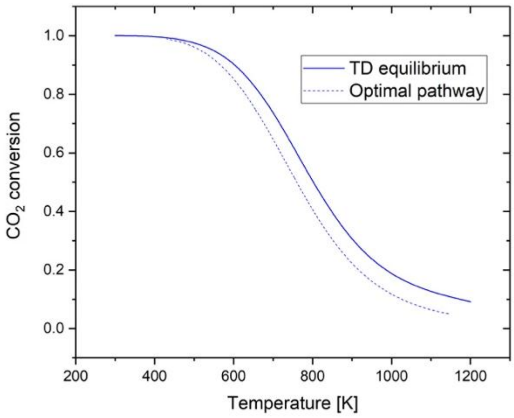

Figure 1. Absolute optimal temperature profile

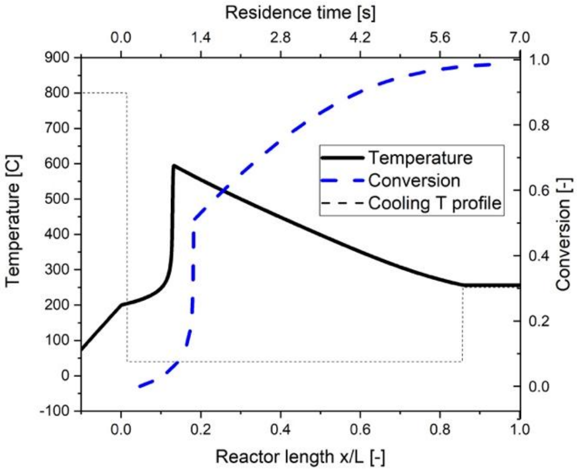

Figure 2. Optimal heat management of the reactor

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COMBUSTION IN THE FLUIDIZED BED OF CATALYST AS AN EFFECTIVE METHOD OF OIL WASTE UTILIZATION

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One of the acute problems is the formation of a huge amount of oil refining waste (including oil production and storage waste) namely the need for their utilization. In general, oil-refining waste includes so-called oil sludge and acid tar. The main groups of components making up such wastes are petroleum products, water, mineral components and mechanical impurities. According to the existing statistical data, from 3 to 5 % of all oil produced in the world goes to the waste. More than 3 million tons of oil sludge and from 220 to 250 thousand tons of acid tar are produced annually in the Russian Federation.

Problems of oil sludge utilization are associated with their high humidity (up to 80 %) and ash content (up to 50 %). The utilization of acid tar containing significant amounts of sulfuric acid and oleum by direct combustion is not acceptable due to high SO_2 emissions.

This work demonstrates the possibility of using the combustion in the fluidized bed of catalyst as a method of oil waste utilization. The technology has successfully proved to be an effective tool for burning various fuels and waste with obtaining a thermal energy. A series of model oil sludge samples with a different oil/water ratio was prepared for the study. Also it was taken two industrial oil sludge of different origin (OS1 and OS2) formed during oil refining at the Ryazan oil refinery. OS1 – is a sample from the floating sludge collector, while OS2 – is a sludge from an oil trap.

The composition of used sludge samples is shown in table 1. The combustion was carried out in the fluidized bed of spherical deep oxidation catalyst ($CuCr_2O_4$/γ-Al_2O_3) with particles size of 1.2-1.4 mm.

Table 1. Composition of oil sludge samples

Oil Sludge	Working mass moisture, W, %	Ash content in working mass, A, %	Petrolium content in working mass, %
Model oil sludge	50.0-80.0	0	20.0-50.0
OS1	80.5	0.6	18.9
OS1	86.3	4.9	8.8

As a result, no any underburning products was found in the exhaust during the combustion of model mixtures and real oil sludge samples in the fluidized bed of catalyst at 700 °C. Moreover, the content of toxic substances such as NO, NO_2, SO_2 in the waste gases was insignificant. At the same time the burnout degree of oil sludge at 700 °C was 99.6 % for OS1, 99.4 % for OS2, and 99.8 % for a model oil/water mixture.

The data obtained as a result of the studies were used to calculate the conditions for the combustion of oil sludge in the fluidized bed of deep oxidation catalyst. Calculation of the heat balance has shown that during the OS1 sample combustion under the fluidized bed conditions additional heat will be released in the amount of 505 kcal per 1 kg of the burned product. Therefore, it is necessary to ensure the removal of excess heat during OS1 combustion. In the case of OS2 combustion in order to provide a temperature regime of 700 °C additional fuel is necessary. Organization of OS1 and OS2 co-incineration allows us to create an autothermal regime without any additional fuel, with a weight ratio of OS1/OS2 = 0.46. This ratio corresponds to an average humidity of 80-85 % and a calorific value of 900-1000 kcal/kg.

Thus, the approach considered in the work compensates practically all the shortcomings of the existing methods for oil waste utilization, has significant advantages and has no direct analogues both in the Russian Federation and abroad.

Acknowledgements

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AN EXPERIMENTAL AND MODELLING STUDY OF FAST BIOMASS PYROLYSIS OIL DROPLET COMBUSTION

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Fast pyrolysis of biomass produces a liquid bio-oil (FPBO) [1] with yields up to 75-80 wt. %, together with some residual char and a fuel gas. Bio-oils derived from different biomass streams are much more uniform compared to the original biomass resources and have typically 5-20 times higher volumetric energy density. Thus, they offer the potential to de-couple liquid fuel production (scale, time, and location) from its utilization [2]. FPBO are completely different from petroleum fuels with regard to both their physical properties and chemical composition [3]. Beside water, bio-oils are complex mixtures of hundreds of organic compounds that belong to acids, aldehydes, ketones, alcohols, esters, anhydrosugars, furans, phenols, catecols, guaiacols, syringols, vanillins, nitrogen containing compounds, as well as large molecular oligomers (holocellulose-derived anhydro-oligosaccharides and lignin-derived oligomers) [4]. The modelling of each individual constituent of the bio-oil is not feasible, therefore these complex mixtures are characterized in terms of a limited number of representative chemical components (surrogate mixture). The challenge is to characterize both the chemical properties (gas combustion and liquid fuel craking leading to cenoshperes) and physical propeties (evaporation, atomization).

Fundamental research activity is performed inside the Residue2Heat project [2], which aims at developing a concept for renewable residential heating using FPBO, to develop a proper surrogate mixture able to mimic the behaviour of the real bio-oil. A nine-component mixture (made of water, acetic acid, ehylene glycol (EG), glycol aldehyde, vanillin, HMW-lignin, levoglucosan, 2,5-Dimethylfuran, oleic acid) has been defined and exeprimentally verified in comparison with the corresponding FPBO in single droplet experiments [5]. It also contains the heavy lignin component to represent the Heavy Molecular Mass (HMM) fraction of the FPBO and can be extended to include Pyrrole to model the Fuel-Nitrogen. Physico-chemical properties were defined to evaluate the evaporation behaviour of the FPBO and the combustion characteristics. The comparison with experimental results showed that this surrogate is able to mimic the main chemical and physical characteristics of pyrolysis oils in terms of volatility, density, heating value, elemental and chemical compositions.

The experimental analyses and kinetic model development were performed hyerarchically, starting form pure components (such as acetic acid and EG), then moving to their mixtures and finally the compelete surrogate. A kinetic mechanism able to describe the FPBO combustion is described in this work, toghether with the comparison with experimental data in both ideal reactors and in the single droplet experiments, which are modeled using a transient droplet multi-phase model which describes liquid heating, evaporation and combustion in the gas phase [6].

The complex combustion features of FPBO droplets, suspended on a thin thermocouple in order to follow their thermal history, were studied in a single droplet combustion chamber by means of high speed shadowgraphs [5] to investgate droplet swelling and sputtering, as well as homogeneous and heterogeous combustion.

The comparisons show that the model is able to reproduce the effect of the different volatility of FPBO components. This includes the effect of evaporation, cracking reactions, and reactivity in the gas-phase which control the formation of carbonaceous residue, the heat release rate, and the flame temperature.

The kinetic model contains a revision of ethylene glycol, acetic acid, and a new vanillin kinetics.

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THERMOPHORETIC DEPOSITION COMBINED WITH AEROSOL CVD SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBES FOR THIN, CONDUCTIVE, AND TRANSPARENT FILMS OF EXCEPTIONAL CHARACTERISTICS

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Carbon nanotubes are one of the most studied materials of the last 25 years, but still one of the most attracting for investigation. Indeed, efforts of the last two decades did not completely revealed the mechanism of the carbon nanotube growth or provided technique to produce single-walled ones with controlled and single chirality. Nevertheless, implementation of the fluidized bed reactors facilitated industrial production of both single-walled and multi-walled carbon nanotubes resulting in more than 3 000 ton/year capacity. This might enhance the application of the nanotubes as substrates or as component of composite material.

However, when considering electronics, not the scalability but the material properties play as barrier for wide application requiring carbon nanotubes of specific morphology, defectiveness, structural characteristics. Aerosol CVD synthesis of the single-walled carbon nanotubes – a specific case of floating catalyst with low volume concentration of catalytic particles – is one of the best techniques to control the characteristics of individual carbon nanotubes and the ratio and the morphology of the agglomerates providing the state-of-the-art devices – thin, transparent, and conductive electrodes, transistors etc. Although low yield of the carbon nanotubes from the reactor cross-section prohibits this approach to challenge fluidized beds in the field of composites, the aerosol CVD occupies specific and certain niche of flexible electronics, nanophotonics, nanoelectronics *etc*.

In this work we examine the design of aerosol CVD reactor in terms of catalytic performance and carbon nanotube properties using a comprehensive set of the methods: the analysis of differential mobility of the aerosol particles, optical spectroscopy, scanning and transmission electron microscopy, Raman spectroscopy *etc*. Thorough kinetic analysis has allowed us to reveal fundamental aspects of the activation of the active component of the catalyst.

While aerosol CVD (floating catalyst) method has proven itself to provide versatile and tailorable source for the thin films, transfer of carbon nanotubes from gas phase to a substrate offers bonus opportunities for fine tuning. Here, we also discuss thermophoretic deposition of carbon nanotube aerosol – non-invasive approach for direct tangential transfer of aerosol structures under the temperature gradient providing, for example, films of extremely low thickness (sub-percolation surface concentration) on non-porous substrates. In the present work we systematically asses the influence of intrinsic properties of carbon nanotubes (length, morphology, diameter etc.) on the thin film performance with special attention to the origins and peculiarities of carbon nanotube behavior within the field of high temperature gradient. We considered theoretical description of the process taking place as most of existing concepts fail to predict the experimental results of the thermophoretic deposition of the carbon nanotubes.

The results obtained allowed us to improve the performance and the morphology of the carbon nanotube thin films enhancing the development of the next generation devices.

Acknowledgements

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PYROLYSIS OF LIGNIN: EFFECTS OF MOLECULAR WEIGHT AND BOND TYPE

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Lignin is an abundant natural aromatic polymer, which provides structural strength to plant cell walls. Generally, it is burned as a low-value fuel. However, lignin being aromatic in nature might be a potential source for the production of mono-aromatics (BTX type) and other value-added chemicals. Depolymerisation of lignin via fast pyrolysis is widely studied over a wide range of temperature and in different setups. Slow heating rates (in TGA) and online detection of volatiles (e.g. in Py-GC/MS), offers limited information about true primary products because a major fraction of the pyrolysis products are composed of large molecules and remain therefore undetected. The goal of current work is to investigate the primary products, underlying primary reactions and the behaviour of different inter-unit linkages (e.g. β-O-4, β-β, β-5) under minimal mass and heat transfer limitations.

In this work, five different lignins were characterized for elemental composition, molecular weight distribution and bond types. Subsequently, their fast pyrolysis was carried out in a dedicated screen-heater reactor. In which, lignin is rapidly heated (>5000 °C s^{-1}), formed products are quickly removed (~20 ms) from the hot pyrolyzing site by applying vacuum and are instantaneously quenched by using liquid nitrogen [1]. Analysis of obtained bio-oils is carried out by using GC-MS, GPC, and quantitative 2D NMR. A clear trend for the lumped product yields (bio-oil, solid residue, and non-condensable gases) as a function of lignins molecular weight (Mw) was observed. Additionally, a relation between molecular weights of lignins and molecular weights of bio-oils was measured see (Figure 1) which could be explained by a model including cracking and polymerization reactions and ejection/evaporation of fragments from the reaction zone.

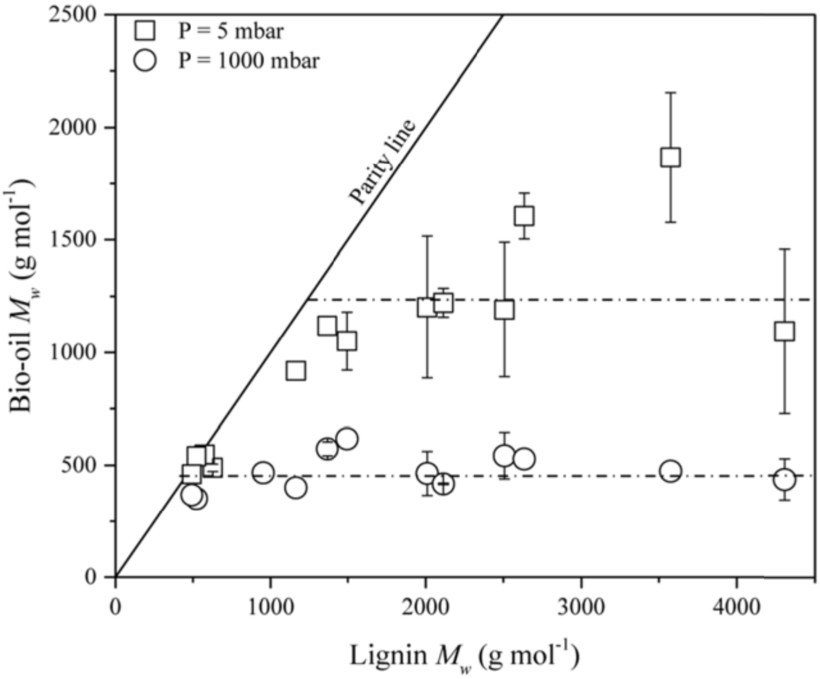

Figure 1. Mw of bio-oils against lignin Mw as a function of pressure (5 mbar and 1000 mbar) at 530 °C

The quantitative 2D NMR of bio-oils (obtained at 5 mbar and 1000 mbar) enabled us to track alterations occurring, during fast pyrolysis from which a "Bond Balance" could be performed. Lastly, the pyrolysis of model compounds, representing different linkages present in native lignin, offered insights into the interplay of mass transfer and chemistry. We will present a new data set on lignin pyrolysis, interpret the data with engineering models and will discuss the implications of the results for the valorisation processes of lignin.

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MUCIC ACID HYDRODEOXYGENATION OVER METAL CATALYSTS

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Environmental concerns are pushing chemical industry towards the search for new and cleaner chemical production routes. One of the most environmentally harmful processes is the conventional oil-based production of adipic acid, where a lot of NO_x is emitted into the atmosphere. Substituting oil with biomass would bring about a tremendous improvement. Cellulose, especially waste cellulose, is one of the most promising types of biomass, from which a wide range of platform chemicals can be made. For instance, its monomer glucose can be catalytically converted into adipic acid.

Glucose can be first oxidized into glucaric acid and then, under high hydrogen pressure, deoxygenated into adipic acid. Our work focused on the last part, *i.e.* hydrodeoxygenation (HDO) of mucic acid, which is an optical isomer of glucaric acid. The objective was to develop a reaction mechanism for HDO of mucic acid over different metal catalysts on diverse supports. Experiments were performed in a 250 mL high-pressure stainless steel batch autoclave, operated as a three-phase system. Mucic acid was dissolved in water; solid catalyst particles (diameter < 100 μm) were added afterwards. After purging the system with an inert gas, 5 MPa of hydrogen was introduced into the autoclave. We heated up the whole system to the desired temperature with a heating ramp of 5 K min^{-1}. The total reaction time was 180 min. During the reaction, liquid samples were taken and analyzed on HPLC and GCMS. For GCMS analyses intermediates and products were extracted into diethyl ether and treated with a TMS derivatization reagent.

Based on experimental results, a reaction scheme was proposed, as showed in Figure 1. In the first step, hydroxyl (–OH) groups are gradually removed as double bonds form, which are then quickly hydrogenated to yield sp^3 bonds. Cyclic products can form during the HDO and, if using highly efficient catalyst at high temperature, complete deoxygenation leading to fully saturated hydrocarbons is observed. Several side products due to C-C bond splitting were detected, such as pentanoic acid, hydroxyl pentanoic acid, pentenoic acid and, levulinic acid.

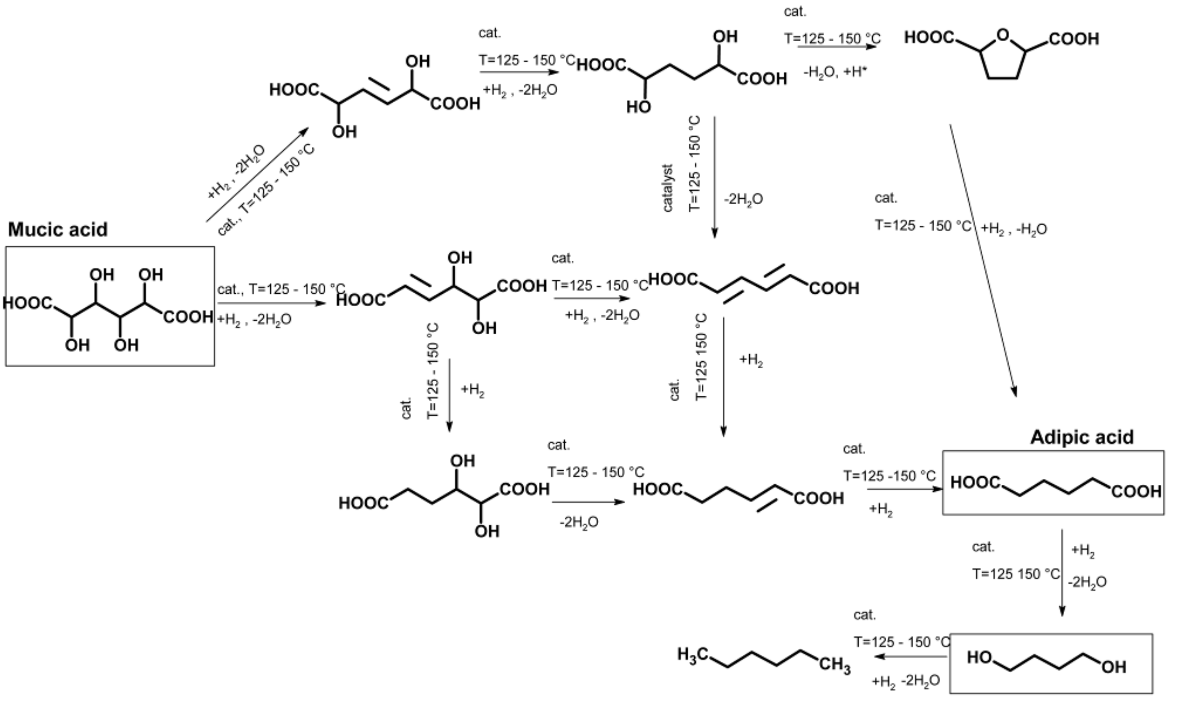

Figure1. Propsed reaction pathway for catalytic HDO of mucic acid

The desired product of HDO of mucic acid is adipic acid. After catalyst screening, all effort was directed to improving selectivity and obtaining higher yields. Reaction conditions, such as temperature, pressure and solvent, were varied in the process.

Experimental work was supported with first-principles (DFT) calculations. For the tested catalysts, adsorption energies and reaction energies of particular reaction steps were calculated. In conjunction with experimental data, these findings were used to construct BEP relationships and volcano plots, justifying the ultimate choice of the catalyst.

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MULTI-PHASE, MULTI-SPECIES MODEL FOR THE CONVERSION OF RECYCLED PLASTIC TO DIESEL

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Plastic recycling is carried out globally to reduce the volume of waste plastics produced and the need for landfill. The conversion of waste plastics such as polyethylene into useful fuels such as diesel is a viable recycle alternative. Literature[1] has measured the degradation of plastic as well as well established chemistry of the idealised radical degradation mechanisms. However, a practical plastic to diesel reactor system operates in a two phase mode, in which the long hydrocrabons are liquified at high temperature, thermally cracked and the lighter species evaporate out of the mixture to be recovered by distillation with or without heavy cut recycle. The dynamics of the liquid phase and thus also the reactor performance and the kinetic behaviour is strongly influenced by these factors. Literature [1] has failed to capture these important design features and thus rigorous design of such systems is not yet feasible. Moreover, in order for the kinetic model to fully represent the reaction system and be used with rigorous phase equilibrium calculations, the elementary kinetics must exceed carbon numbers of 4000, which yields 100000's of chemical species and is completely intractable for the design task. Thus there is a need for a progressive lumping scheme that retains the kinetic features, uses real chemical species and thus also real VLE calculations and has a limited number of species yield a tractable reactor model. This paper evaluates the ability of the progressive lumping scheme to represent the elementary kinetics as well as its impact on the computational requirements. The model prediction is validated against experimental data [2].

The model is developed in two stages. In stage one, the ratios of the kinetic constants of the progressive lumping kinetic scheme which uses the following groups, L1: [C1,C2,...C100], L2: [C102,C105,...C498], L3: [C504,C513,...C1998], are tuned to an elementary kinetic scheme over a range of conversions with fast single phase calculations. Special development is needed at group bounsaries to ensure molar balances are conserved. Figure 1 shows that the lumped kinetic scheme precicely represents the elementary reaction scheme.

The second stage models the pyrolysis reactor as a multi-phase continuous stirred tank reactor (CSTR), with embedded vapour liquid equilibrium using the Peng-Robinson equation of state, and only a vapour stream leaving. The production of only a vapour product stream provides severe limitations to the operational flexibility of the process.

Figure 2 shows that temperature has a strong influence on the product distribution while figure 3 shows that the present model can represent experimental data very well.

A process model was developed with the addition of separation and recycle to the reactor model, and has been used to study the operating strategies and develop design criteria for the operation of such a process.

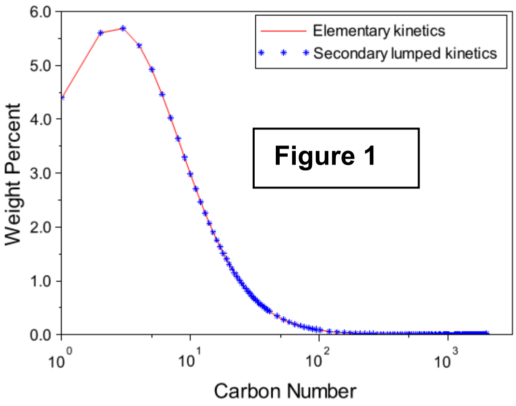
Figure 1

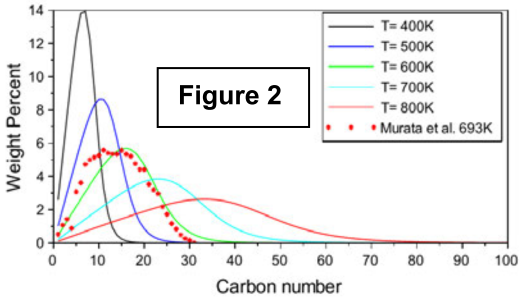
Figure 2

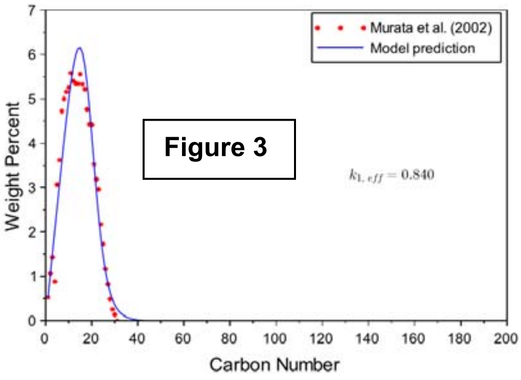
Figure 3

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CATALYTIC DEHYDROGENATION COUPLING OF ALCOHOLS TO ESTERS: MECHANISM AND KINETIC STUDIES FOR MODELLING PURPOSES

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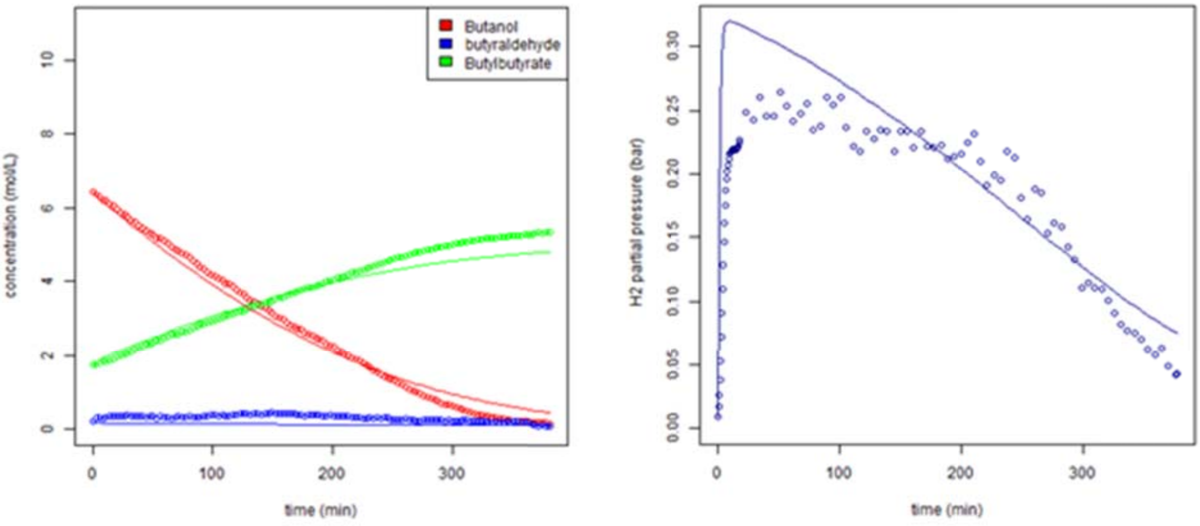
Fatty esters from bio-based feedstock are an important source of heavy molecules in green chemistry. There valorization is a daily challenge in economies that wish decreased there dependency on fossil sources. One of the main outlet is the production of wax ester (WE) for cosmetic applications. Such products can be obtained by classical esterification reactions between fatty acid derivatives and fatty alcohols with the known limitations for those reactions. An alternative for the synthesis of symmetric WE is the homo-coupling of the corresponding alcohol. In the last decade, contributions in the field of Acceptorless Alcohol Dehydrogenation (AAD) for the preparation of ester significantly grew. Several groups described novel metallic complexes with impressive catalytic activities usually based on ruthenium with non-innocent polydentate ligands [1], [2].

The first works on our project led to the optimization of a promising catalytic system based on ruthenium and PNP ligands (Ru-MACHO) and tested on n-butanol and several other heavier alcohols [3]. The mechanistic aspects were mainly studied through the synthesis of plausible intermediates and there spectroscopic characterizations as well as control experiments. The current work has proposed in a first part to collect kinetic and thermodynamic data to (1) clarify our understanding of the mechanism (2) find an accurate kinetic model for modelling purposes. The second part has been to study several scaling-up strategy through chemical reactor simulation and comparison : (1) classical batch stirred tank (2) inovative continuous membrane milireactor.

For the kinetic studies, experiments have been performed in a Batch stirred tank reactor under various conditions. The mixture composition has been monitored by gas chromatography (GC) and/or by in situ IR analysis post treated with multivariate method (PLS regression). The H_2 gas produced during the reaction has been followed by online gas chromatography. Besides all the advantages of online system, IR have allowed us to report the observation of aldehyde, a key intermediate.

Specific attention was also carried about H_2 transfer and reaction reversibility. Based on experimental data and mechanistic hypothesis, detailed and simplified kinetic models have been proposed and estimated thank to Levenberg Marquardt optimization and ODE resolution programs from R software.



(a) **(b)**

Figure 1. Example of reaction profiles for n-butanol dehydrogenation. (a) Concentrations of liquid species. (b) hydrogen partial pressure. Model predictions are in full lines, experimental values from (a) online IR and (b) online GC in points. Initial conditions are [butanol] = 6.9 mol·L^{-1}, [butylbutyrate] = 1.7 mol·L^{-1}, catalyzer = 256 ppm, temperature = 383 K

The second part deals with the choice of reactor technology for scaling-up. The transfer from batch system to continuous process has been considered since “Tube-in-tube” (TiT) membrane milireactor technology seems very promising for continuous H_2 segregation [4]. TiT technology has been validated experimentally and short term works in reactor simulation, using kinetic models, should rapidly lead to a compleat and quantitative comparison of this technology with the more classical batch stirred tank.This work was applied on n-butanol and n-octanol model molecules.

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MAGNETICALLY SEPARABLE BIOCATALYSTS BASED ON IMMOBILIZED ENZYMES

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One of the most significant catalytic processes of fine organic synthesis that serves for synthetic biologically active compounds production is selective oxidation reaction [1, 2]. The researchers' efforts, nowadays, are focused on the increase in the selectivity and stability of the catalytic systems. In this regard, the development of heterogeneous biocatalysts in particular magnetically separable catalysts is the most important [1-3]. Catalytically active sites formed on the surface of such catalysts combine the advantages of enzymatic (selectivity and activity) and heterogeneous/magnetically separable (easy separation and modification possibility) catalysts. Depending on the characteristics of enzyme, support, and modifier the catalytic properties of such systems can be varied.

In the present work, the innovative method of D-gluconic acid production by enzymatic oxidation method using biocatalysts primary magnetically separable catalysts was developed. These methods can be considered an ecologically friendly alternative to the existing methods with a high yield of the target product [4, 5].

The direct synthesis of magnetic particles of Fe_3O_4 by the hydrothermal method is proposed [6, 7]. The synthesis conditions variation in the suggested method and the combination of Fe^{+2} and Fe^{+3} salts will allow controlling the morphology and obtaining nanoparticles with the extended surface which will be optimal for the functionalization and further enzyme immobilization.

The biocatalysts were synthesized via the immobilization of enzymes of oxidoreductase group (glucose oxidase EC 1.1.3.4) on inorganic supports including magnetically separable particles. The effective influence of amino-containing modifiers and linking agents on enzyme immobilization process was studied. By changing the ratio of support/modifier/linking agent/enzyme it is possible to vary the catalytic properties of biocatalysts.

In the present work, we developed novel magnetically recoverable catalysts using magnetite nanoclusters, coated with silica modified with amino groups. The glucose oxidase covalent attachment has been carried out via the reaction with a glutaric dialdehyde. Exceptional catalytic activity and stability of the catalyst developed to make it promising for practical applications. The characterization of the obtained Fe_3O_4 magnetic particle samples and biocatalysts by physicochemical methods: transmission electron microscopy, X-Ray photoelectron spectroscopy, X-Ray diffraction, FTIR spectroscopy and low-temperature nitrogen physisorption was studied.

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OP-III-14

CONTINUOUS CATALYTIC AEROBIC OXIDATION OF BENZYL ALCOHOL IN A SLURRY TUBE-IN-TUBE REACTOR USING Au-Pd/TiO_2 CATALYST

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The need for large catalyst particles in order to reduce pressure drops in packed-bed reactors, inevitably leads to a reduction in the catalyst efficiency. Additionally, homogeneous temperature conditions are not always guaranteed in these reactors. Liquid-solid slurry reactors can overcome these problems by allowing the use of small particles and enhancing the mixing properties between the catalyst and the liquid reactants [1]. In this work, a new reactor configuration that combines the advantages of using a slurry tube reactor with a high recycle ratio and a tubular membrane contactor (Teflon AF-2400) for safe oxygen delivery has been realized. A slurry made of Au-Pd/TiO_2 and benzyl alcohol flows inside the tubular membrane, while oxygen gas is stagnant and pressurised outside the membrane and inside a steel tube. The slurry catalyst mixture circulates inside a loop to which the tube-in-tube reactor is connected and the products are continuously withdrawn by means of a stainless steel crossflow filter, designed for this application. A schematic of the setup is shown in Figure 1.

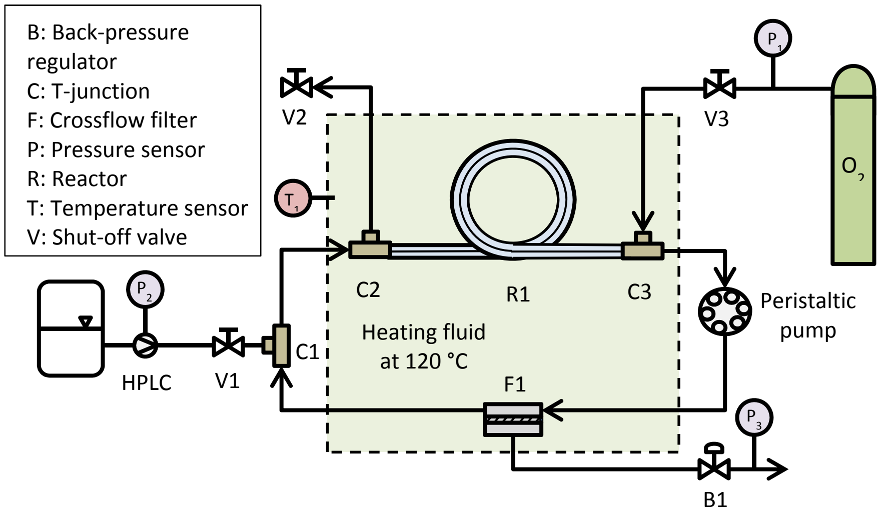

Figure 1. Schematic illustration of the slurry reactor with a tube-in-tube membrane for the oxygen delivery. The reactor and the crossflow filter are immersed in a bath filled with a heat transfer fluid at a constant temperature

15 mg of 1 % (Au-Pd)/TiO_2 catalyst powder was mixed with 3 mL of pure benzyl alcohol (Sigma Aldrich) and loaded into the loop (0.75 mL). The first campaign was performed by varying the external oxygen pressure. The recycle flowrate was set to 10 mL/min, the liquid pressure to 7.5 barg, the heating fluid temperature was kept constant to 120 °C and the inlet flowrate was 25 μL/min. Conversion and product selectivity are reported in Figure 2.

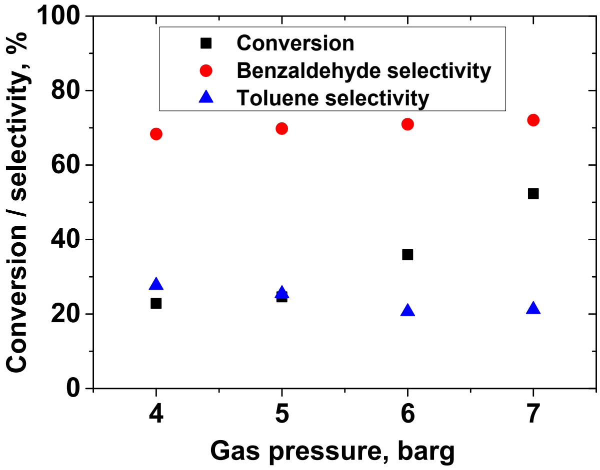

Figure 2. Benzyl alcohol conversion and product selectivity at different gauge pressures. Temperature of the heating fluid was 120 °C, liquid pressure 7.5 barg, recycle flowrate equal to 10 mL/min, inlet flowrate 25 μL/min, catalyst concentration 5 g/L, catalyst contact time: 9.2 g_{cat}*s/$g_{alcohol}$

Increasing pressure has the effect of increasing the oxygen concentration, hence favouring the direct oxidation of benzyl alcohol to benzaldehyde, as highlighted by the increase in conversion. A comparison is made between this Slurry Reactor and a Tube-in-Tube Membrane Microreactor where the same catalyst was packed in the tubular Teflon AF-2400 membrane without liquid recycle [2]. At the same operating conditions, the Slurry Reactor outperforms the Tube-in-Tube Membrane Microreactor by achieving similar conversion and higher benzaldehyde selectivity at 6 barg O_2 pressure, but with approx. 12 times less catalyst contact time and 5 times less catalyst amount. A complete characterization of the process is made by performing further reaction tests aiming at understanding the role of the length of the tube-in-tube reactor, the inlet flowrate and the reaction temperature.

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PROCESS INTENSIFICATION OF ENZYME CATALYSED KINETIC RESOLUTION OF 1-PHENYLETHANOL IN A SPINNING MESH DISC REACTOR

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Biotransformation of racemates into enantiomers using enzymes is an attractive option owing to the high regio, enantioselectivity and a safer alternative to chemical synthesis [1]. One such important reaction is the resolution of 1-phenylethanol via acylation using a suitable acyl donor and catalysed by lipase (Fig 1).

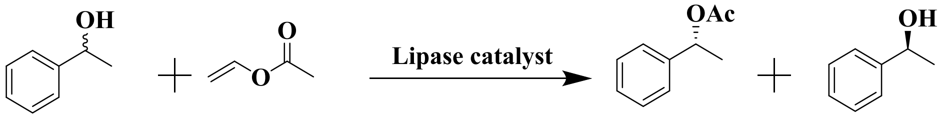

Fig. 1. Kinetic resolution of 1-phenylethanol with vinyl acetate as the acyl donor, catalysed by lipase

It is an important reaction as the chiral derivatives of phenylethanol are often used as starting materials in the pharmaceutical and natural products industries [2]. However, current issues with this reaction are long reaction times, low recoverability of the enzymes, solvent compatibility and process scale-up [3].

The spinning mesh disc reactor (SMDR) is a novel reactor built on a similar concept to the SDR, but additionally houses a cloth with immobilised catalyst resting on the disc surface allowing the centrifugal force of the spinning disc to create a thin film over and within the cloth. This improves mixing and mass transfer within the film, accelerating the reaction, as well as protecting the catalysts from the shear forces associated with the spinning disc [4]. An additional advantage with the SMDR is the use of immobilized catalysts which enables easy catalyst separation, recovery and reuse. The SMDR has so far only been demonstrated for two reaction systems, enzymatic hydrolysis of tributyrin (water-enzyme) [4] and copper catalysed Henry reaction (organic solvent-metal catalyst) [5]. One of the aims of this research is therefore, for the first time, to achieve process intensification of enzyme catalysed synthesis in organic solvents. This will also further demonstrate the versatility of the SMDR.

Lipase immobilisation was carried out by soaking the PEI modified cloth in lipase solution followed by cross-linking with glutaraldehyde [6]. The presence of lipase was confirmed by FTIR, SEM, EDX and XPS. The solvent effects were studied in batch and then the conversion and enantiomeric excess was optimised in the SMDR for different flowrates and spinning speeds for both free and immobilized lipase and compared to batch. Conversion in batch (using both free and immobilized lipase) and in the SMDR showed similar conversion of ~45 % (maximum possible conversion being 50 %) and enantiomeric excess (ee) of 90 %. However, the reaction rate in the SMDR was higher compared to that in batch demonstrating proof of concept and achieving process intensification. Increasing the number of cloths, doubled the initial reaction rate, although the conversion after 5 h remained the same and 83 % of the original lipase activity was retained after three consecutive runs.

These results show the versatility and the applicability of the SMDR and is the first demonstration of novel reactor design for organic enzymatic synthesis. The SMDR thus shows potential to be extended to other enzyme catalysed systems to further improve reaction selectivity and provide a pathway towards scale-up and the continuous processing of organic enzymatic synthesis in the fine chemicals and pharmaceutical industry.

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ORAL PRESENTATIONS
Section IV.
Advanced Processing of Conventional and Unconventional Hydrocarbon Feedstocks

THE SENSITIZING EFFECTS OF NO_2 AND NO ON METHANE LOW TEMPERATURE OXIDATION IN A JET STIRRED REACTOR

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The mutual effects of CH_4/NO_x have attracted considerable attention in the past decade. Although a large number of experimental reports concerning the hydrocarbon-NO_x interactions in ideal reactors are available [1-4], the sensitizing effects of NO_2 on methane low-temperature oxidation in a jet-stirred reactor has not been performed yet. Additionally, the knowledge of some notable intermediate nitrogen species (such as HONO) is not comprehensively understood. In this context, the oxidation of neat methane and methane doped with NO_2 or NO in argon at 107 kPa and temperatures between 650-1200 K with a fixed residence time of 1.5 s has been investigated in a jet-stirred reactor for different equivalence ratios (Φ), ranging from fuel-lean to fuel-rich conditions using four different diagnostics: gas chromatography (GC), chemiluminescence NO_x analyzer, continuous wave cavity ring-down spectroscopy (cw-CRDS) and Fourier transform infrared spectroscopy (FTIR). In case of the oxidation of neat methane, the initial oxidation temperature was above 1025 K while it shifted to 825 K with the addition of NO_2 or NO, independently of equivalence ratio. This indicates that the added NO_2 or NO highly promotes methane oxidation. The consumption rate of methane exhibits the similar trend with the presence of both NO_2 and NO. The search for HONO and CH_3NO_2 species has been attempted. A detailed kinetic mechanism, derived from POLIMI kinetic framework, is used to interpret the experimental data. The agreement between the experimental data and model predictions is very satisfactory. Reaction rate and sensitivity analysis were conducted to illustrate the kinetic regimes. The fact that the addition of NO or NO_2 seems to have similar effects on promoting methane oxidation can be explained by the fact that both species are involved in a reaction cycle interchanging them and whose result is $2CH_3 + O_2 = 2CH_2O + 2H$. Additionally, the direct participation of NO_2 in the $NO_2 + CH_2O = HONO + HCO$ reaction has a notable accelerating effect on methane oxidation.

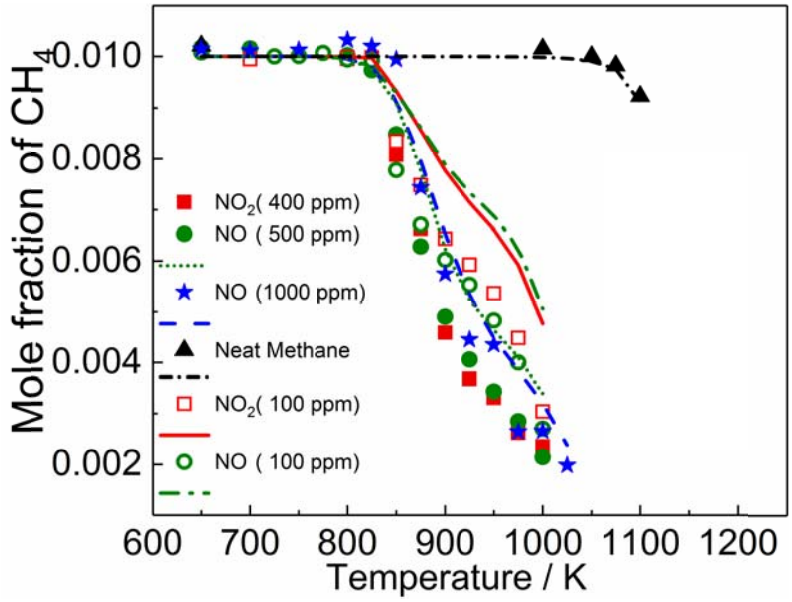

Fig. 1. Mole fractions of methane with various amount addition of NO_2 (400 and 100 ppm) and NO (1000, 500 and 100 ppm).The symbols denote experimental data and corresponding lines represent model predictions. Inlet composition: 1 % (v) CH_4, 2 % (v) O_2, various amount NO_x, balance Ar. $\Phi = 1$

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INNOVATIVE HYBRID MEMBRANE-CATALYTIC TECHNOLOGY FOR SYNGAS, HYDROGEN AND VALUABLE MONOMERS PRODUCTION

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Original porous ceramic catalytic converters have been developed. These converters can be used for high-rate dry and steam reforming processes of C_1-C_5 hydrocarbons, ethanol, dimethyl ether (DME) and fermentation products into synthesis gas as well as for steam reforming of carbon monoxide to produce purified hydrogen. The converter is the so-called ensemble of nanoreactors. It is prepared by self-spreading high-temperature synthesis (SHS) from a mixture of highly dispersed metal and oxide powders. The converter has an average pore diameter 1-3 μm and a porosity ~60 %.

It was shown that chemical reactions in channels of the converter are much more intense than in a traditional reactor with a fixed bed of the bulk catalyst. This is probably the result of improved mass and heat exchange. Thus, the synergetic effect of increasing catalytic activity was found in dry reforming of methane (DRM) on the converter with composition Ni(Al)-Co_3O_4 [45(5)-50 mas. %]. As a result the synthesis gas (H_2/CO = 1) specific productivity was 85000 $l/h \cdot dm^3$, while this value for the granular catalyst of the same composition was approximately 5 times lower [1,2].

An original hybrid membrane-catalytic reactor (HMCR) for the ultrapure hydrogen co-production has been developed. In HMCR the catalytic converter is integrated with a hydrogen-selective palladium-containing membrane [3].

It was found that during the steam reforming of dimethyl ether into synthesis gas using a porous ceramic Ni–Co-containing membrane catalytic converter, an increased hydrogen yield with H_2/CO = 15–20 is reached at T = 450–500 °C. Reforming in a hybrid membrane reactor with a Pd–containing alloy membrane integrated into the reaction volume provides recovery of ultrapure hydrogen up to 50 % at a temperature of 500–700 °C.

An original two-stage process for production of 1,3-butadiene and isoprene from n-butanol and isoamyl alcohol has been developed. The process is carried out continuously and consistently. On the first stage, dehydration of the alcohols in the corresponding olefins is carried out and on the second stage, these olefins dehydrogenate into dienes.

It was shown that complete dehydration of alcohols to olefins, with almost 100 % selectivity occurs on SHS-synthesized sample of γ-Al_2O_3 at 300 °C. It is 50 degrees lower than on industrial pellets of gamma-oxide.

It was found that the catalyst based on γ-Al_2O_3 + K, Ce, Cr (5 %) + Fe (5 %) is formed as islet coatings on the inner surface of the converter pores. It allows the production of diene hydrocarbons, such as 1,3-butadiene and isoprene with equivalent industrial yields per pass at 637 °C. At the same time, during 20 hours of the experiment, a decrease in the catalytic activity of the system was not observed, in contrast to industrial solutions where the regeneration stage is carried out every 8-15 minutes. As a result, with increased selectivity it became possible to increase the yield and productivity of butadiene and isoprene by ~2 times.

The use of the original HMCR with selective removal of hydrogen from the reaction zone made it possible to increase the productivity of 1,3-butadiene 1,6 to 2,2 $l/(h \cdot g_{act.comp.})$. The rate of ultra-pure hydrogen extraction was ~16 % in the absence of dilution with water of the initial butylene fraction. This is about 30 % compared to the traditional process with a bulk layer of catalyst. The use of the HMCR also opens the possibility for simultaneous production of ultrapure hydrogen, which is a demanded raw material for organic synthesis, as well as environmentally safe fuel for hydrogen internal combustion engines and fuel cells.

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STRUCTURE-DEPENDENT MULTISCALE MODELLING OF CATALYTIC PROCESSES: AN APPLICATION TO THE CATALYTIC PARTIAL OXIDATION OF METHANE ON RHODIUM

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Introduction. Several experimental studies clearly demonstrated the existence of strong interactions between the structure and the activity in heterogeneous catalysis [1]. Moreover, the catalyst structure is strongly dependent on the reaction environment. As a result, catalyst materials in heterogeneous catalytic reactors are intrinsically dynamic systems: they change their morphology in response to the conditions of the reaction environment, which in turn affects the reactivity [2]. Microkinetic modelling is a key tool for the investigation of the behavior of complex chemical reactions, making it suitable for the fundamental understanding of the structure-activity relations of catalytic processes. However, state-of-the-art microkinetic models in heterogeneous catalysis lack in the description of the catalyst structure by relying on an abstract and "structureless" concept of catalyst active site. This assumption enables the study of the macroscopic kinetic behavior of reacting systems [3], but it does not allow to reach an atomistic understanding of the structure-activity relations. As a consequence, the incorporation of the catalyst structure in microkinetic modelling becomes of paramount importance for the study of the structure-activity relations, which is widely recognized as one of the main progress area in modelling of catalytic processes towards the design of catalysts and reactors based on functional understanding rather than empirical testing. In this contribution we couple microkinetic modelling and *ab initio* thermodynamics to characterize the morphology of catalyst nanoparticles inside a reactor for the catalytic partial oxidation of CH_4 on Rh/Al_2O_3.

Methods. By multiscale reactor modelling we evaluate the gaseous composition profiles inside a chemical reactor and we identify the most abundant reaction intermediates (MARIs) on the catalyst surfaces. With density functional theory and *ab initio* thermodynamics we calculate the most stable bulk and surface structures of the catalyst at different conditions of the reaction environment, considering the presence of the MARIs in equilibrium with their reservoirs in the gas phase. By Wulff-Kaishew construction we calculate the shape of the catalyst and we estimate the amount of the active sites as function of the chemical environment inside the reactor.

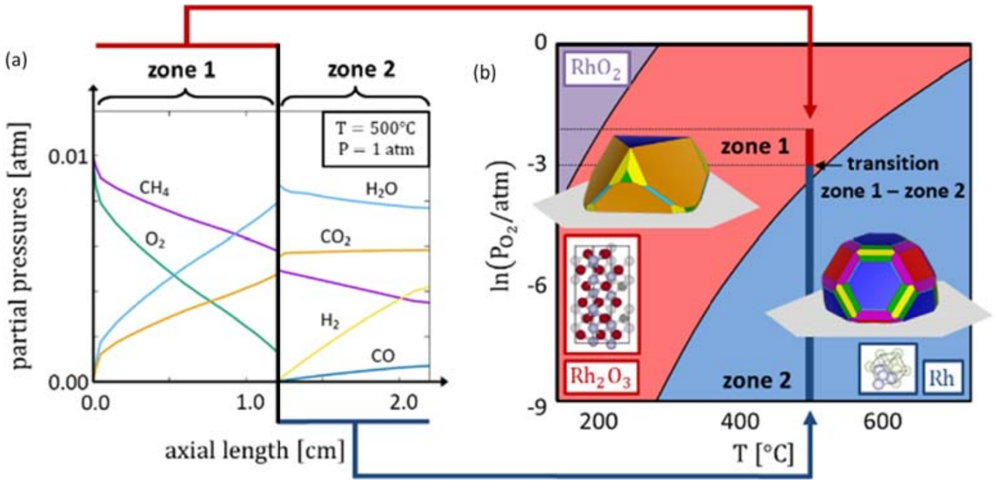

Figure 1. (a): Major species partial pressures axial profiles at the catalyst interface. T = 500°C, P = 1 atm. Inlet molar fractions: CH_4 0.01, O_2 0.01, N_2 0.98. Gas hourly space velocity: 2E6 Nl/kg_{cat}/h. Annular reactor: I.D. 4 mm, O.D. 5 mm, length 22 mm [2].
(b) Bulk phase diagram of Rh (blue), Rh_2O_3 (red) and RhO_2 (purple) and associated catalyst shapes

Results and discussion. In agreement with operando spectroscopy observations [3], we observe a sharp change in the process selectivity with residence time and temperature. When oxygen is present at the catalyst surface interface, no syngas production is observed (zone 1 in Fig. 1a). Once oxygen has been depleted, CO and H_2 start producing (zone 2 in Fig. 1a). With *ab initio* themodynamics we find that the change from zone 1 to zone 2 is accompanied by a change in the bulk structure and in the morphology of the catalyst. In the oxidizing zone of the reactor (zone 1), Rh_2O_3 is the most stable bulk structure, and the nanoparticle exposes mainly the (001), (1-12) and (113) crystal facets (Fig. 1b). In zone 2 of the reactor, metallic Rh turns out to be the most stable bulk structure. CO* and H* are the MARIs, and Rh(100) and the Rh(111) are the facets most exposed by the nanoparticle. High Miller index facets become more stable with the increase of adsorbates coverage, observed during reaction, yielding a change in shape and reactivity of the catalyst. Particle shapes are found to be in agreement with HRTEM observations and chemisorption of CO and H_2.

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OP-IV-4

PROGNOSTIC MODELLING OF DESTRUCTIVE PROCESSES OF HYDROCARBON FEEDSTOCK CONVERSION

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The process of middle distillates catalytic dewaxing, combined with hydrotreating, is currently the most up-to-date way to produce Euro-5 diesel fuel, which is capable of operating at low temperatures up to –50 °C. Hydrocracking process allows treating heavy heavy petroleum fractions into high quality components of gasoline and low-freezing low-sulfur diesel fuels along with increasing in the depth of petroleum refining. The aim of this work is modelling of hydrodewaing and hydrocracking processes using new approach taking into account intragroup distribution of hydrocarbon reactivity. According to this approach mathematical description of destructive processes of hydrodewaxing and hydrocracking, which pass in the cascade of reactors, rpresents the system of integro-differential equations as follows:

$$\frac{dC_i(x,\tau)}{d\tau}=\sum_{m=1}^{p}k_m(x)C_i(x,\tau)+\sum_{m=1}^{p}k_m(x)C_i(x,\tau)C_{H_2}+\sum_{s=1}^{n}C_{H_2}\int_{x_i}^{b}k_m(x)C_s(x',\tau)\nu_m(x,x')dx';$$

$$\frac{dT(\tau)}{d\tau}=-\frac{1}{C_p^m}\sum_{j=1}^{n}\Delta H_j\int_{x_i}^{b}k_j(x')C_j(x')\delta(x'-x_j)dx'.$$

$C_i(x,\tau)$, $k_m(x)$ – distribution functions of hydrocarbon concentrations and reaction constant rates; $\nu_m(x,x')$ – distribution functions of probability of bond breacking in paraffin hydrocracking; τ – contact time; $T(\tau)$ – temperature change in the process; C_p^m – heat capacity of the mixture; ΔH_j – average enthalpy of the certain reaction; x – number of carbon atoms in the molecule of hydrocarbon; i – number of hydrocarbon groups (parafins, iso-parafins, cycloparaffins, aromatics, etc.).

The first component in mass balance equation describes reactions wthout hydrogen; the second component describes reactions with hydrogen; the third component describes reaction of paraffin hydrocracking.

Distribution function $\nu_m(x,x')$, which characterize propability of formation with shorter chain lengh in hydrocracking of n- and iso-paraffins, is determined on the base of experimental data from industrial hydrodewaxing unit (Fig. 1).

With due take into account factors of non-stationary character of the processes, the mathematical model is written as a system of material and heat balances as follows:

$$G\cdot\frac{\partial C_i}{\partial z}=-u\cdot\frac{\partial C_i}{\partial l}+\frac{1}{l}\int_0^l W_j(l)a_j(l)dl;$$

$$\rho^m\cdot C_p^m\cdot G\cdot\frac{\partial T}{\partial z}=-u\cdot\rho^m\cdot C_p^m\cdot G\cdot\frac{\partial T}{\partial l}+\sum Q_j\cdot\frac{1}{l}\cdot\int_0^l W_j(l)a_j(l)dl.$$

Initial conditions: $z = 0$: $C_i = C_{i,0}$; $T = T_0$; $l = 0$: $C_i = C_{i,0}$; $T = T_0$.

z – volume of treated feedstock, m^3; G – feedstock flow rate, m^3/h; u – linear flow rate, m/h; l – lengh of catalyst layer, m; W_j – total reaction rate, $mol/(m^3/h)$.

The first step of the process modelling is development of a scheme of hydrocarbon conversion at the industrial conditions in the presence of catalyst; ρ^m – density of the mixture, kg/m^3; C_p^m – heat capacity of the mixture, J/(kg·K); Q_j – heat effect of chemical reaction, J/mol; T – temperature, K.

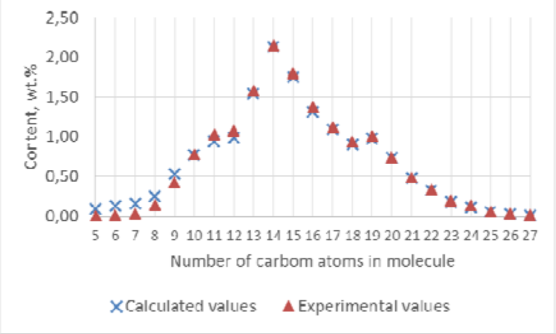

Fig. 1. Distribution of paraffins according to the number of carbon atoms in molecule

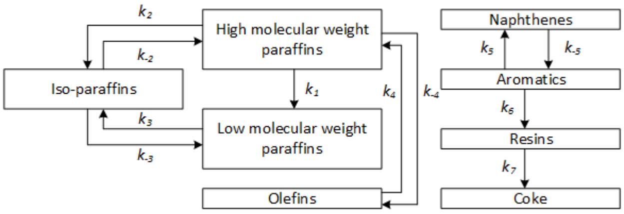

Fig. 2. Hydrocarbon conversion scheme in the process of hydrocracking

Total reaction rate (W) for hydrocracking of heavy gas oil is determined asccording to the scheme of hydrocarbon transformations presented in Fig. 2.

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INTEGRATED TECHNOLOGY OF OLEFINS SYNTHESIS FROM DYMETHYL ETHER

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At present in the world the items of natural gas conversion into petrochemical products are relevant. One of directions is gas conversion into light olefins – so called GTO-process. Current GTO-technologies via methanol/dimethyl ether (MTP – Lurgi and DTP – Japan Gas Corporation) are include three well-known in industry stages as synthesis gas production, methanol synthesis, methanol dehydration to dimethyl ether (DME). The unique (original) stage of olefins synthesis is based over using of HZSM-5 catalyst (SiO_2/Al_2O_3=150-200) which can modify by a metal [1] or non-metal [2, 3]. The main feature of current designs is dilution of feedstock – equilibrium mixture of DME/water/methanol after methanol dehydration – by a water steam at the olefins synthesis reactor inlet. This allows providing an efficient heat removal, enhancing the selectivity of light olefins synthesis and increasing the lifetime of a zeolite catalyst. In this respect the investigations of process are focused at the improving the catalyst activity, selectivity and stability on stream [4]. At the same time, the chemical engineering work is actively carried out to analyze the existing plants in order to find approaches and solutions to increase their performances [5].

One-step DME synthesis from synthesis gas is more energy efficient technology than two-step ones. However, in the case of conventional approach (with steam dilution of DME) it will required a complex system of DME recovery from gas phase [6], which in one and a half time increases the CAPEX, OPEX and prime cost. In this respect the most attractive is carrying out the DME conversion to olefins in a synthesis gas atmosphere. The investigation of gas atmosphere composition includes CO_2, CO, synthesis gas is carried out over Ca-HZSM-5 [7], but obtained results are poor. It is shown that the catalyst activity is decreasing in time on stream. The using of synthesis gas is leads to decreasing of olefins selectivity due to presence of hydrogen in the reaction system. The TIPS RAS is developed the stable state catalyst of olefins synthesis based over HZSM-5 (SiO_2/Al_2O_3=37) which modified by magnesium. The kinetic and chemistry of reaction in the nitrogen atmosphere is studied [8]. It is shown that the methanol and propylene are produced simultaneous and firstly initiate the alkene cycle mechanism. At high DME conversion the arene cycle is coming to operation and the ethylene is observed in the products. The investigation of reaction using synthesis gas as dilution agent is carrying out at unit with different catalyst loading: micro-laboratory batch (5-10 cm^3, extrudate particles 2.8x2 mm) and pilot batch (150 cm^3, extrudate particles 2.8x5 mm). It shown that catalyst has a good stability both nitrogen and synthesis gas dilution. During the scale up the results has a good agreement and the composition of atmosphere does not change the DME conversion and yield of main products (Fig. 1). Denotes synthesis gas has an improving thermal conductivity in comparison with nitrogen which allows hold the smoothed temperature profile in the reactor. The results of pilot run could be used for simulation of olefins synthesis reactor and developing the basic design of Integral Technology which include the synthesis gas production, one-step DME synthesis and DME conversion to olefins in the synthesis gas atmosphere.

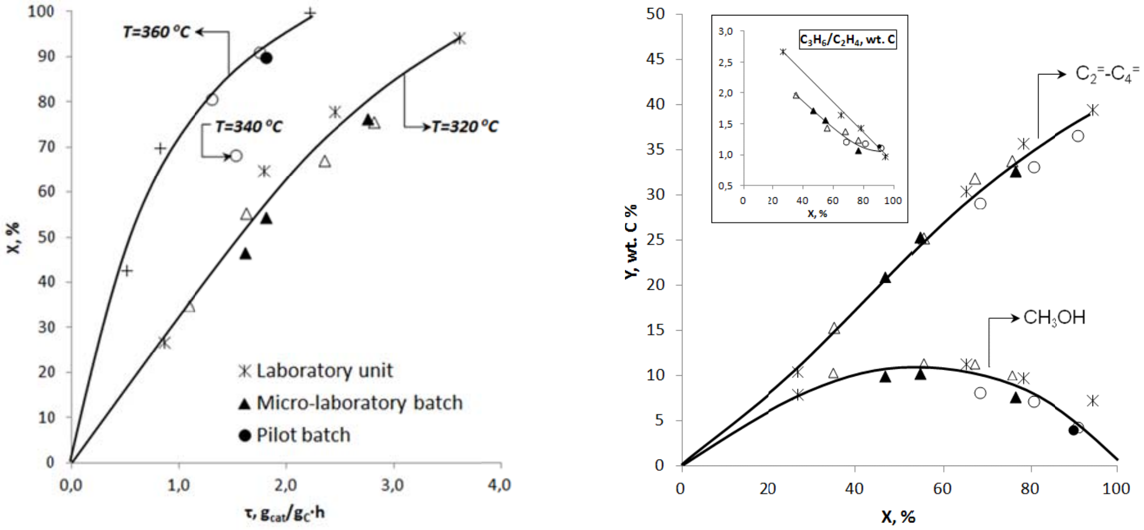

Fig. 1. Conversion (a) and yield of products (b).
Filled markers – nitrogen, empty markers – synthesis gas

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COMPARATIVE STUDY OF THE SULFUR SPECIATION BY GC AND GC×GC FOR GAS OIL CHARACTERIZATION IN HDT PROCESS SIMULATION

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The oil industry is nowadays under increasing pressure from legislators to improve the quality of diesel fuels, whereas the gas oil feedstocks tend to diversification (lesser fraction of Straight-Run), which leads to difficulties in predicting their reactivity. In order to better evaluate this reactivity, we need to properly measure the distribution of sulfur-containing compounds in the gas oils and in the hydrotreated products, thus enhancing the ability of the HDT process simulators to predict kinetics. At the moment, one of the major limitations to the use of kinetic models, is represented by the analytical uncertainties related to the sulfur speciation of feedstocks by Gas Chromatography coupled with Sulfur Chemiluminescence Detector (GC-SCD). In this respect, significant improvements have been achieved with the integration of multidimensional comprehensive chromatographic analyses such as 2D Gas Chromatography coupled with SCD (GC×GC-SCD) [1,2].

However, GCxGC-SCD is still not resoluted enough to allow its standalone use, and currently the best solution is obtained by taking the advantages and information of both techniques. The most effective way of combining the two analytical techniques still has been the subject of the present study.

On a basis of 27 Straight-Run (SR), 14 Light Cycle Oil (LCO) and 11 Coker Gas oils, three different recombination rules have been tested on the sulfur families. On the one hand, Sulfides, Thiols and Benzothiophenes families display a common reactivity for each family, and their composition has been determined from the GCxGC-SCD data, which is a more adapted method than GC-SCD for separating families of different aromaticity. On the other hand, Dibenzothiophenes (DBT) share the same aromaticity but are of very different reactivity depending on the location of the methyl substituants on alpha position of the sulfur atom (DBT, 4DBT which is more difficult to convert and 46DBT which is even more difficult) [3]. The GCxGC-SCD does not allow enough distinction among the alkylated DBT, and thus GC-SCD is also needed in order to represent the diversity of reactivity of the different types of

Gas Oils. Three combining approaches have then been considered, with variations over the role of heavy DBT.

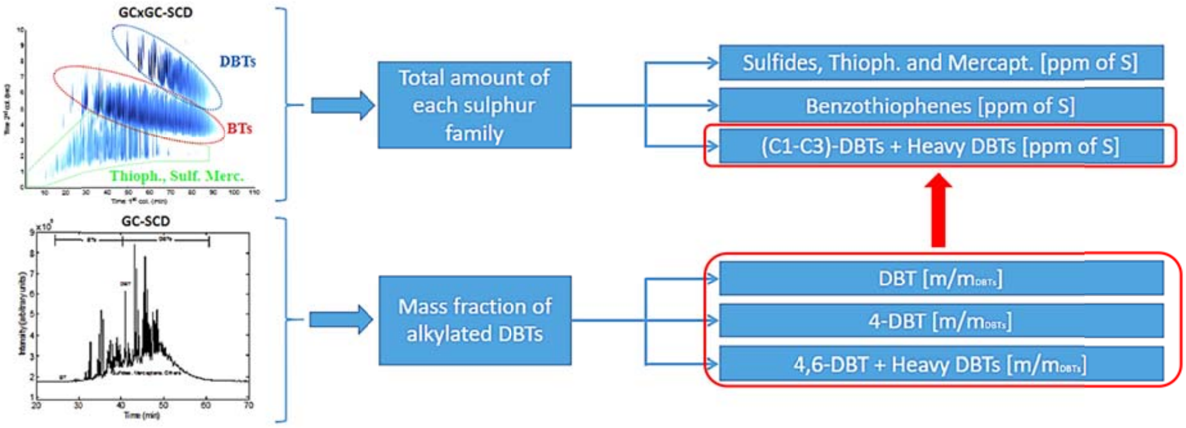

Figure 1. GC-SCD (lower chromatograph) and GCxGC-SCD (upper chromatograph) of a gas oil, and one of the sets of rule of combination for the determination of sulfur families content

The three approaches have been implemented in a gas oil hydrotreating simulator which was used for simulating 90 real pilot plant tests carried out in IFPEN on a commercial catalyst and several Gas Oils (SR, LCO, Coker and mixtures) in ULSD conditions. This simulator is based on a gas oil reconstruction algorithm developed in IFPEN [3], whose result is a matrix of 612 pseudo-compounds representative of the gas oil reactivity towards HDS, HDN and HDA.

Since the kinetic parameters have not been reoptimized for each reconstruction method, a uniform deviation can be observed between the predictions and the experimental results. Another criterion has thus been set in order to qualify these methods. For a given gas oil feedstock, the HDS predictions for various operating conditions usually tend to follow a linear trend on a parity plot (simulation vs. experimental). This originates from the kinetic formalism. Then for different gas oil natures, the predictions might end up spread along different trend lines. Thus the main criterion concerns the spreading of every gas oils prediction trends. The theta angle (θ) between the steepest and the flattest trend lines was measured to determine the most relevant way of recombining GC-SCD end GCxGC-SCD data. Indeed, when the spreading is reduced, the reactivity of the different natures of gas oils are more coherently predicted by the Gas Oil HDT simulator.

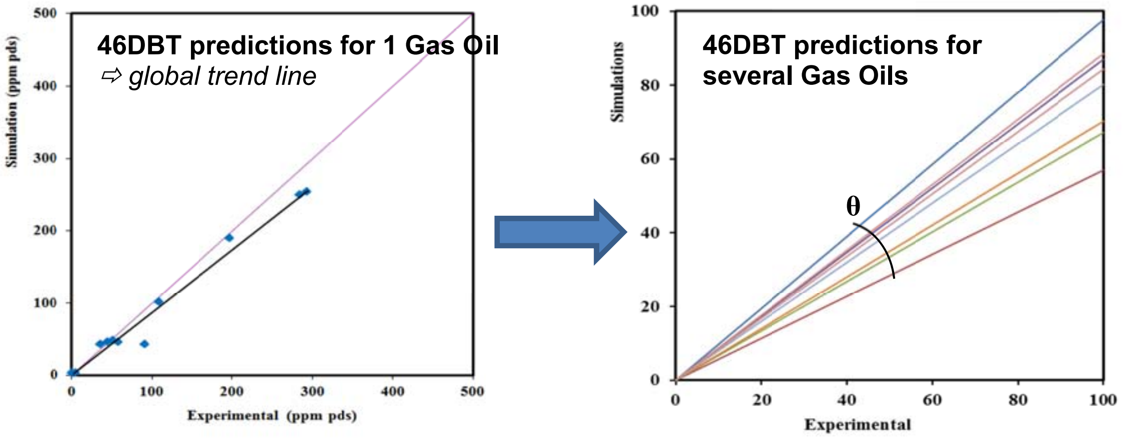

Figure 2. illustration of the trend line of predictions for a given gasoil (left scheme), and the spreading of the prediction trends (for each given Gas Oil, several operating conditions represented as a trendline), qualified by the angle θ

Finally, two out of the three methods are promising, in the way they both reduce by almost 50 % the observed spreading. The next step will consist in reoptimizing the kinetic parameters in order to quantitatively compare these two finalists.

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OP-IV-7

A THERMODYNAMICALLY CONSISTENT REACTOR MODEL FOR THE FURNACE BLACK PROCESS

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Commercial carbon black is a type of solid carbon which is manufactured in well controlled processes that process a precisely structured aggregate of carbon particles with a range of particle sizes, aggregate sizes, shapes, porosities and surface chemistry. Carbon black particles thus consists of >95 % pure carbon with minimal impurities of oxygen, nitrogen and hydrogen in a size range between 10 and 500 nm. These are then fused together into chain like aggregates with provide some of the structural characteristics of the various carbon black grades. Carbon has many diverse uses in everyday commodities and by far one of the largest market volumes is in the manufacture of car tyres.

The furnace black reactor, visualised in figure 1, is divided into two zones. The first zone combines preheated air with feed hydrocarbon to use combustion to preheat the reaction mixture. The hot mixture moves through a choke with the addition of more hydrocarbon feed to intiate the endothermic carbon black formation in the absence of oxygen. The reaction is quenched with water. In order to produce a high quality product with precise product properties it is necessary to have good control on the temperature profile, the feed compositon and water addition[1]. The aim of this project is thus to develop a pocess reactor model that is able to reproduce the mass and thermal profile of the furnace black reactor.

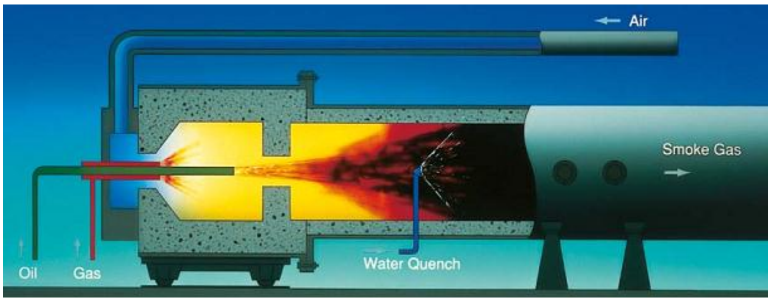

Figure 1. Illustration of the carbon black furnace

The reactor was modelled as two zones. The first zone was treated as exothermic chemical equilibrium reactor (Gibbs reactor with heat loss) carryout the combustion of the hydrocarboin feed. The second zone was treated as a tubular plug

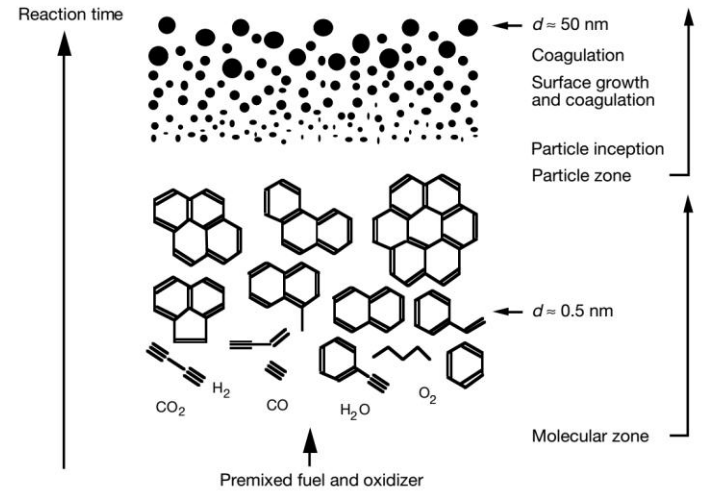

Figure 2. The conversion of gaseous carbon feed molecules to carbon black particulates [2]

flow reactor (PFR). The kinetics in zone 2 followed the two stage scheme proposed in figure 2. In order to capture the correct thermal and mass profiles in stage 1, elementary chemical reactions where developed for the fomation of the polyaromatics with associated thermo-chemical properties and kinetics. In stage to and particulate formation and agglomeration model was used. This reaction system was ingtegrated until the water was added to the the reaction mixture. Every water addition required the reactor simulation restart to account for the change in initial conditions.

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Acknowledgements

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OP-IV-8

MODELING THE REMOVAL OF SULFUR, AROMATICS AND HEAVIER COMPOUNDS OF LIGHT CYCLE OIL

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Introduction

The sustainability of the oil refining industry requires the development of intensification strategies for upgrading crude and secondary streams. The production of light cycle oil (LCO), byproduct of FCC unit, is increasing to meet with the demand of medium distillates, however, its high content in sulphur, aromatics, and low cetane index make it unsuitable as a fuel [1]. The severe hydroprocessing of LCO using bifunctional catalysts based on transition metals (Co, Mo, Ni, W) is an interesting route to reduce the high content of impurities in these feedstocks and to produce appropriate gasoline and diesel blending streams [2]. Therefore, in this work the kinetic modeling of the hydroprocessing of LCO with a $NiMo/Al_2O_3$ catalyst has been studied based on the reactions of: i) hydrodesufurization (HDS), ii) hydrodearomatization (HDA) and iii) hydrocracking (HC).

Experimental / methodology

Kinetic data have been obtained in a fixed bed reactor under the following conditions: 320-400 °C; 80 bar; space time, 0-0.5 $g_{cat}\ h\ g_{LCO}^{-1}$; and, H_2/LCO volumetric ratio of 1000. Chemical composition of LCO is: 34.3 % paraffins and isoparaffins, 3.7 % naphthenes and 62.1 % aromatics, on which 31.1 % are 1 ring aromatics and the remaining 30.9 %, 2^+ ring aromatics. The total sulfur content is of 10,212 ppm (6,603 ppm of reactive compounds in hydroprocessing and 3,609 ppm of refractory compounds). The products lumps are distributed as naphtha (T_B <216 °C, 10.9 %), diesel (T_B = 216-350 °C, 69.7 %) and gasoil (T_B >350 °C, 19.4 %).

For the hydrodesulfurization, kinetic conversion stages based on Langmuir-Hinshelwood mechanisms have been proposed, considering the H_2S formed as an inhibitor, whereas for hydrodearomatization and hydrocracking sequential kinetic schemes have been proposed considering reversible transformations from heavier lumps and chemical groups to the lighter ones.

Results and discussion

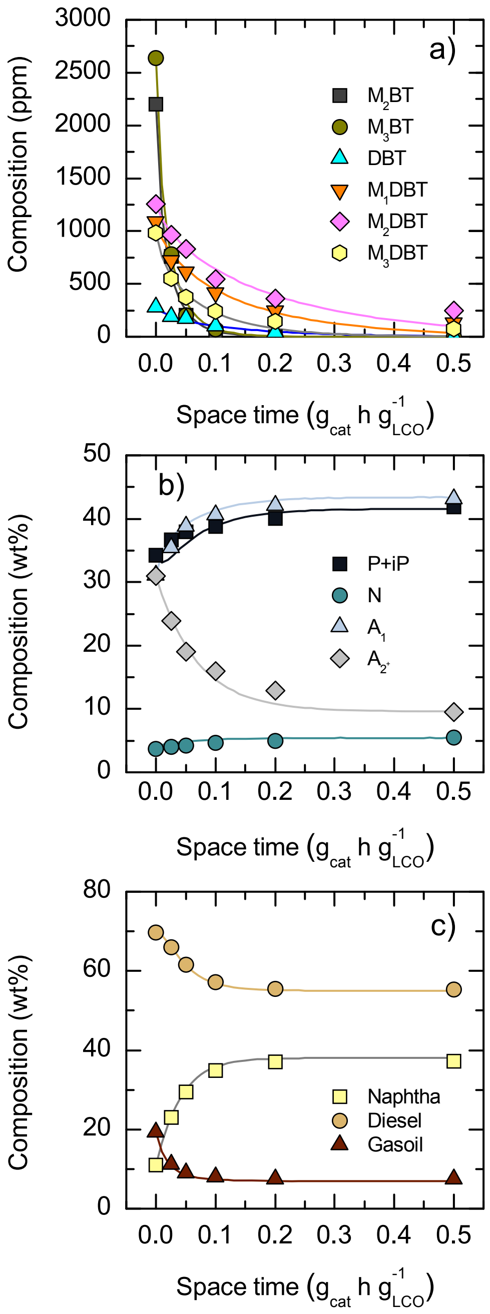

Figure 1. Comparison between the experimental data (symbols) and predicted data (lines) for the models of HDS (a), HDA (b) and HC (c)

Obtained results for the three different kinetic models at one of the studied temperatures (360 °C) and for the whole range of space time are shown in Figure 1. Focusing on the kinetic model for the HDS (Figure 1a), it can be seen that for refractory compounds (M_xDBTs) a higher conversion is predicted for the highest space time. The deviation of the fitting can be attributed to the higher internal diffusional limitations of refractory compounds on the catalyst particles at higher space time and temperatures, meaning that apparent activation energy are lower than calculated.

On the other hand, pretty good fittings of calculated values for the concentration to experimental data are obtained both for HDA and HC kinetic models (Figure 1b and c). Different kinetic models have been proposed for HDA and HC, being depicted results of the models with the best statistical significance. It should be mentioned also that kinetic model predicts the marked effect of the space time and the temperature in the concentration of chemical groups and of lumps, as well as reached steady state.

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Acknowledgements

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CHEMREACTOR-23 Special Sessions
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ON THE REACTIVITY OF MONO-LIGNOL DERIVATIVES

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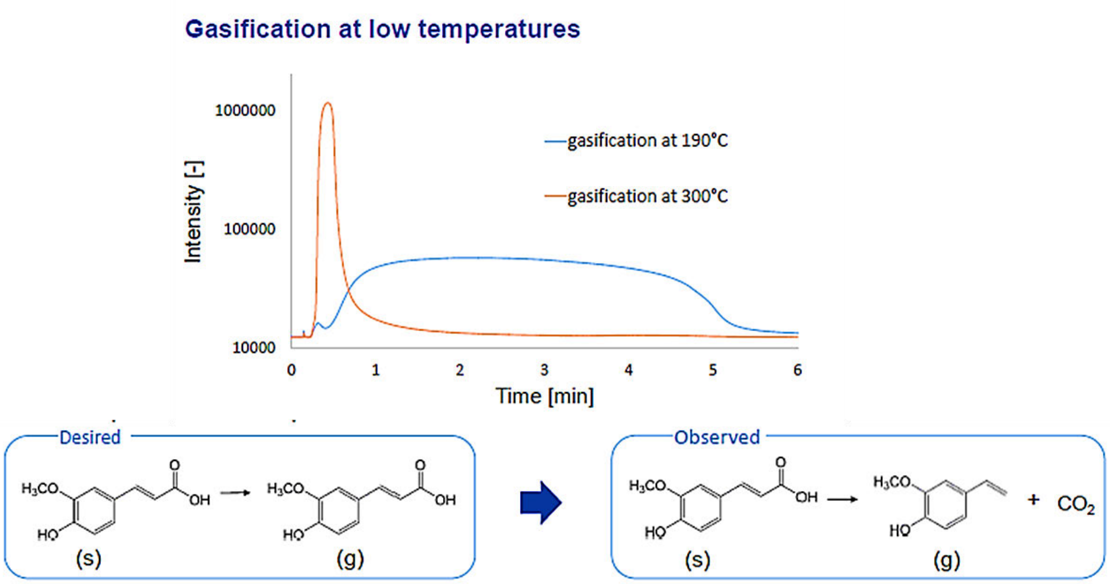
The valorization of lignin, the second most abundant component of lignocellulosic biomass, has remained a challenge for many years. Given the large concentration of phenolic groups, lignin appears to be a good potential candidate for the production of aromatic chemicals such as catechols and p-vinyl phenols. Production of such chemicals requires the ability to depolymerize lignin in a controlled manner. The thermochemical route uses fast pyrolysis to crack lignin polymers to smaller fragments. In order to be able to do so in a guided way, the thermal decomposition chemistry of lignin needs to be understood in great detail.

Lignin is mainly built from three monolignols, which are derivatives of cinnamyl alcohol and distinguish themselves through the aromatic unit, viz. p-hydroxy phenyl (H), guaiacyl (G), and syringol (S). Lignols are connected via β-O-4, α-O-4 ether and 8-8 linkages. It is assumed that both, the substitution pattern of the benzene ring and the linkage between the units have strong impacts on the product distribution. Efforts are underway to generate kinetic models able to describe these impacts and to predict pyrolysis product spectra as a function of operation condition. So far, the pyrolysis studies coupled with EPR analysis of monolignols and their derivatives provide mechanistic information of their thermal decomposition. However, very few studies focus on the intrinsic pyrolysis kinetics of these lignin model compounds.

The current work presents a comprehensive study of the fast pyrolysis kinetics of lignin model compounds such as cinnamic acid, p-coumaric acid, ferulic acid and their derivatives phenol, guaiacol and syringol. This study is performed with a two-stage micropyrolyzer setup connected on-line to the injector port of the GC. The setup also consists of an external 6-port valve to introduce a pulse of internal standard gas (neon-butane mixture) to allow easy quantification of the products. The GC x GC-FID/MS is equipped with a cold-trap cooled cryogenically for the entire duration of the reaction to refocus the product molecules. The molecules are then released based on their boiling points during the cold-trap heating. The light molecules are analyzed using a special GC with TCD and PDD detectors.

All the experimental conditions are designed in such a way that the transport effects are faster than the reaction kinetics. Sample sizes of 50-100 μg have been used in order to avoid possible mass transfer effects. In this work, one set of experiments provide intrinsic kinetics of solid-to-gas transformation of lignin model compounds obtained by connecting the 1st reactor directly to the GC x GC-MS/FID. The samples are assumed to be instantaneously heated while being dropped into the first-stage heated reactor eliminating the effects of heating rates on the product evolution.



In the second type of experiments, the first stage of the micropyrolyzer is used for vaporization of the samples and the second stage acts as an isothermal plug flow reactor, which can be operated up to 900 °C. The preliminary results show that the acids of monolignols decompose into their vinyl counterparts and CO_2 at temperatures as low as 160-190 °C. The gas-phase pyrolysis product profiles thus obtained will be interpreted with mechanistic information found in the literature and utilized in the future to construct a detailed kinetic model for lignin decomposition.

Acknowledgements

This work is supported by the 'Long Term Structural Methusalem Funding by the Flemish Government'. The SBO proposal “Bioleum” supported by the Institute for promotion of Innovation through Science and Technology in Flanders (IWT) is also acknowledged.

EXPERIMENTAL DEMONSTRATION OF BIOMASS FAST PYROLYSIS IN THE GAS-SOLID VORTEX REACTOR

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Gas-solid contacting in a centrifugal field results in denser solids beds and higher gas-solid slip velocities than those obtained in the Earth's gravitational field. This opens possibilities for substantially smaller, cleaner, safer and more energy efficient processes. The concept is realized in the Gas-Solid Vortex Reactor (GSVR) with centrifugal accelerations up to two orders of magnitude higher than the Earth's gravitational acceleration. In the GSVR, gas is injected at high velocity via tangentially oriented inlet slots in a cylindrical chamber. A rotating solids bed forms at the expense of the azimuthal momentum of the gas. In this work, the transformation of biomass via fast pyrolysis is experimentally demonstrated.

The GSVR technology can potentially benefit the biomass fast pyrolysis process in terms of both bio-oil yield and bio-oil quality. In the GSVR, convective heat transfer coefficients that are three to five times higher than those in gravitational fluidized beds can be reached [1]. The estimated residence time of the pyrolysis vapors before reaching the quenching section ranges from 50 to 110 ms. The enhanced heat transfer and bed uniformity allows to gain improved control on the pyrolysis temperature. As a consequence, it is possible to produce bio-oils with a higher selectivity towards targeted components [2].

A reactive GSVR demonstration unit has been designed, constructed and tested under cold flow conditions at the Laboratory for Chemical Technology (See Figure 1) [3]. For the demonstration unit, preheated N_2 supplies the thermal energy required by the fast pyrolysis process but a heat carrier loop of solids can also be implemented. A broad range of operation conditions can be evaluated: N_2 mass flow rates of 5-10 g s^{-1} and biomass feed mass flow rates of 0.14-1.4 g s^{-1}. Cold flow experiments with continuous feeding of biomass confirmed that the GSVR sustains a rotating fluidized bed with an average bed height of 15 mm. Additional experiments with mixture biomass-char confirmed that biomass is preferentially retained over char.

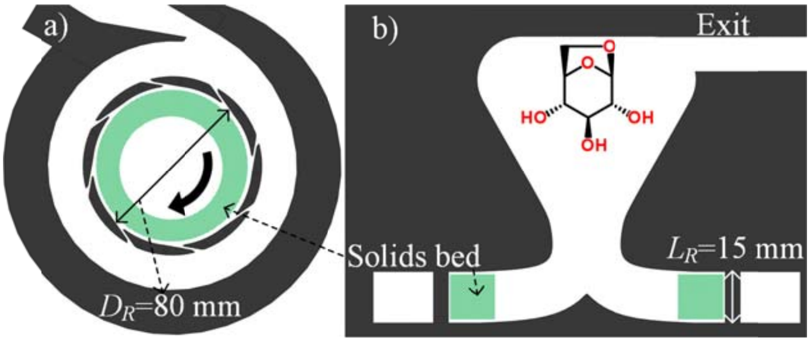

Fig. 1. Schematics of the Gas-Solid Vortex Reactor (GSVR).
a) Top view of the GSVR chamber; the circular arrow indicates the direction of rotation of the solids bed and D_R represents reactor diameter;
b) Side view of the GSVR chamber; L_R represents reactor length

Two woody biomasses of relatively low ash content (< 1 wt. % on a dry basis) will be studied: pinewood, a softwood whose lignin is predominantly type G or guaiacyl; and poplar, a hardwood whose lignin is mostly type GS or guaiacyl-syringil [4]. The yields of bio-oil, biochar and permanent gases are quantified and benchmarked with those of demonstrated fast pyrolysis technologies. Elemental and compositional characterization of the bio-oil will be carried out. The latter includes two-dimensional gas chromatography (GC × GC) coupled to time of flight mass spectrometer and different detectors to assess bio-oil quality based on feed type and operation conditions.

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Acknowledgements

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EXPERIMENTAL HEAT TRANSFER MODELLING IN A GAS-SOLID VORTEX UNIT

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Industry aims at improving processes to increase profit. This must however be done without compromising safety, environment or working environment. The combined approach is referred to as Process Intensification (PI)[1]. PI starts to become difficult in multiphase processes, like the fluidized bed catalytic cracking (FCC). Gravitational fluidized bed (FB) reactors are typically used for these multiphase processes. A key problem in FBs is their size. A conventional FCC unit is 10-20 m long, 0.2-0.6 m in diameter and is operated at high temperatures (750-850 K). Slip velocities are low, resulting in limited heat and mass transfer. The latter has a negative effect on conversion and yields. Keeping heat losses low is not an easy task. Also a further increase of the fluidizing agent flow becomes unlikely.

Using a Gas-Solid Vortex Unit (GSVU) is an option to tackle the described problem. Gas is injected through tangential inlet slots into a disk-like shaped chamber. Momentum transfer from gas to particles in the chamber makes them rotate in the form of a FB near the chamber wall. The gas flow is directed towards a central gas outlet, thus shortening the gas-solid contact time. Depending on the Swirl ratio S (the ratio of tangential to radial velocity component at the inlet slot), the total gas flow rate, the amount of solids, etc. the solids form a densely packed fluidized bed. Slip velocities in the bed are high, resulting in high heat and mass transfer. The GSVU can thus handle a very high gas throughput without compromising the bed quality. Stronger still, the bed will in general become more stable with increasing gas flow rate. This combination of properties implies that the FB in a centrifugal field can replace the conventional FBs in the gravitational field with a considerable size reduction of the equipment, coupled with more effective inter-phase transport processes. [2] [3]

At the Laboratory for Chemical Technology (LCT, Ghent University) heat transfer is studied experimentally in a GSVU (chamber diameter = 139 mm; chamber length = 25 mm; number of inlet slots = 16; slot width = 0.6-1 mm). Heated compressed air is used as a fluidizing agent to heat up alumina particles (ρ_p = 4000 kg m^{-3}; d_p ~ 0.6 mm). The experiments demonstrate the high heat transfer capabilities of GSVUs. Various temperature sensors and an Infrared (IR) Camera record the temperatures of gas and solid bed respectively. Recorded images during the experiments are shown in the added figure. The intention is to explore the heat transfer performance of this unit under various operating conditions, i.e. by changing gas and solid flows, gas temperature, solid type, etc.

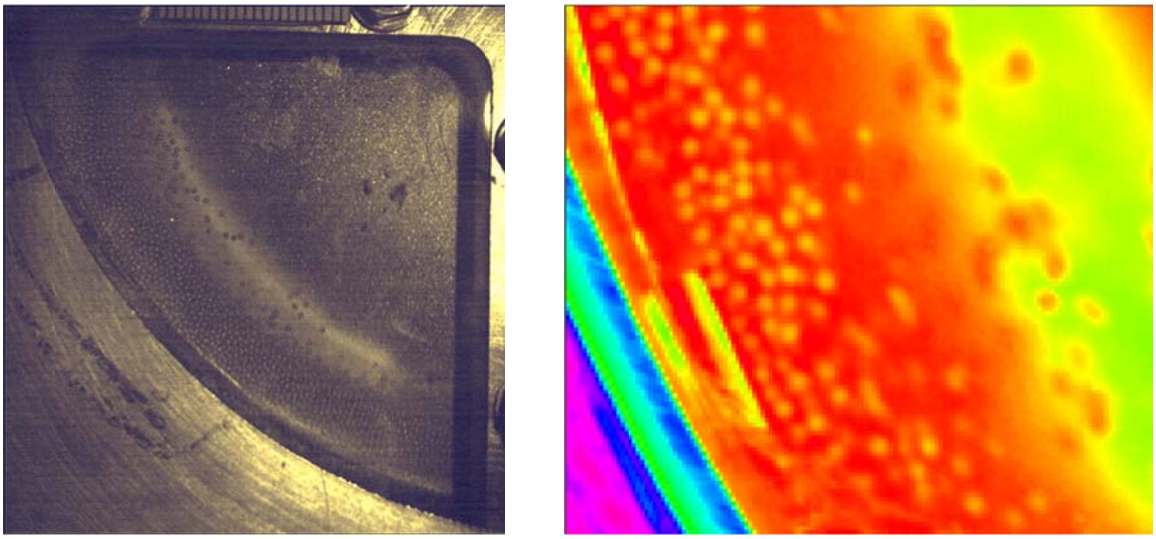
(a) (b)

Fig. (a) Image of solid bed during operation; (b) Qualitative image obtained with the IR camera showing particle bed temperatures in a background of hot gas

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ELECTROCHEMICAL UPGRADING OF FAST PYROLYSIS BIO-OIL

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Fast pyrolysis process offers a versatile platform for the production of renewable fuels and/or chemicals from biomass. The primary product of fast pyrolysis process, bio-oil, can be produced with yields of up to 75 wt. % from lignocellulosic biomass. However, utilization of bio-oil as an intermediate or final product poses challenges due to the intrinsic instability and reactivity of the bio-oil components. These adverse properties of bio-oil are simply a reflection of its complex chemical composition (comprising of aldehydes, ketones, carboxylic acids, furans, etc.). Thus, the reactive components of bio-oil should be converted preferably to more stable compounds prior to its further utilization. To achieve this goal, several processes (e.g. esterification, catalytic pyrolysis, hydrotreatment) have been investigated in literature, obtaining results with varying degrees of success. A recently proposed approach to upgrade/stabilize bio-oil components is electrochemical hydrogenation (ECH) [1]. In this attractive approach, the water present in bio-oil acts as the hydrogen source to reduce the reactive bio-oil components (aldehydes, ketones, etc.) to their corresponding alcohols at ambient temperature and pressure.

In this work, we investigated bio-oil upgrading via ECH process in a two-compartment electrochemical reactor. The anode and cathode chambers of the reactor were separated by a cation exchange membrane. The catholyte was 130 ml water soluble bio-oil (ca. 20 wt. % bio-oil in aqueous solution) and the anolyte was 1M H_2SO_4 solution. The tested cathode materials included 9 cm^2 Ti, Ru-coated Ti (Ru/Ti), and Pt-coated Ti (Pt/Ti) electrodes, with a constant projected current density of 44 mA cm^{-2}. The total reaction time was 160 hours for each test. Higher conversion of reactive bio-oil components (e.g. 84 % for glycolaldehyde conversion to ethylene glycol) was achieved with Ti electrode compared with Ru/Ti (54 %) and Pt/Ti (46 %) electrodes. In the case of Ru/Ti and Pt/Ti electrodes, hydrogen evolution reaction was the preferred pathway rather than the desired electrocatalytic hydrogenation of the organic compounds, evidenced by greater than 85 % coulombic efficiencies achieved for hydrogen production with these electrodes. This difference could be attributed to the higher overpotential of the hydrogen evolution reaction on Ti electrode. Despite the high conversions achieved for some compounds, selectivity towards desired alcohols and diols were rather low (e.g. 12-18 % ethylene glycol selectivity for glycolaldehyde conversion) for the electrodes tested in this study. High energy needs required for the conversion (due to the low faradaic efficiencies) is recognized as another challenge.

Upgrading of the water soluble fraction of bio-oil through the ECH process has potential, but further investigation is needed to understand and optimize the process, and achieve the desirable product yields and selectivities.

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ISOLATION OF PHENOLICS FROM BIO-OIL USING FLEXIBLE MIL-53 AS HIGHLY SELECTIVE ADSORBENT

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Phenolics are important compounds with applications in the food, wine, plastic, tanning, agrochemical and pharmaceutical industry. The phenolic compounds nowadays used are either synthesized from fossil feedstocks or extracted from biomass. In light of the current drive towards a sustainable chemical industry, the latter route is highly appealing, since the compounds in this feedstock are already extensively functionalized. Following pyrolysis of the lignocellulose fraction, a crude, highly complex bio-oil mixture is obtained [1]. Therefore, the development of efficient methods to harvest and purify the large number of phenolics present in this bio-oil is a key step in their production. However, the solvent extraction methods currently used involve large amounts of solvent, which poses challenges to the sustainability of the process. Alternatively, phenolics could also be recovered through adsorption. Liquid phase separation using porous materials as adsorbents is considered here as an easier and more sustainable way. The zeolite faujasite is well known as an industrial adsorbent for the selective uptake of C8 alkyl aromatics, based on the different confinement of the various isomers.

Metal Organic Frameworks (MOFs) are used here to remove phenolic compounds out of pyrolysis bio-oil. MOFs have seen exploration as adsorbent for liquid phase separations, for instance in the separation of xylenes and ethylbenzene, for fuel upgrading through desulfurisation and denitrogenation, for purification purposes by the targeted removal of organic contaminants, as well as inorganic contaminants from water, and even for the recovery of bio-based molecules from aqueous mixtures [2]. By using the flexible MOFs MIL-53(Al), as well as its commercial counterpart Basolite A100, the selective uptake of 4-methylguaiacol from a simulated bio-oil mixture was achieved, even in the presence of a huge amount of hydrogen bonding competitors such as water, methanol, propionic acid and furfuryl alcohol. As revealed by X-ray diffraction analyses, these materials transition during the adsorption process between a narrow pore form at low 4-methylguaiacol loading to a large pore form at higher 4-methylguauaicol loadings. From Fourier-transform infrared spectroscopy, we infer that the selective uptake of phenolics from the simulated bio-oil mixture mainly can be attributed to hydrogen bonding and π…π interactions between the MOF structure and the phenolic molecules. The hydroxyl groups present on the inorganic chain play a decisive role in determining the selectivity. Furthermore, we investigated the desorption and reusability of MIL-53(Al) and Basolite A100; this showed the easy desorption and stability of MOFs after four cycles. Finally, we studied the adsorption from real pyrolysis bio-oils; the desorbed bio-oil was analyzed by GC. MIL-53(Al) showed a high uptake (27 wt %) and good selectivity towards phenols, like guaiacol, 4-methylguaiacol and catechol.

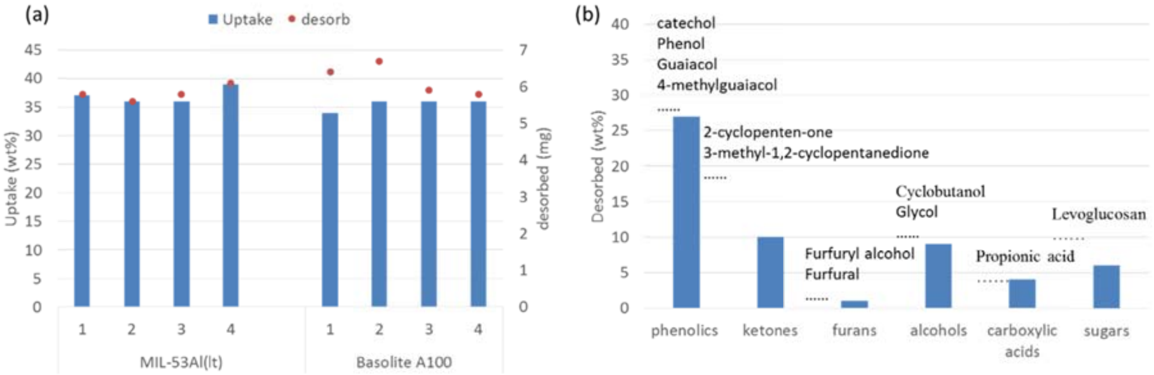

Figure 1. (a) Uptake (based on the weight percent, given as wt%) and the desorbed amount (given as mg) using the same sample of MIL-53Al and Basolite A100 for four cycles of adsorption from 0.05 M (6.9 mg in 1 mL of solution) of 4-MeG methanol water mixed solution, and desorption by using methanol solution; (b) the amount of various chemicals desorbed from MIL-53Al(lt) after adsorption from real pyrolysis bio-oil mixture

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THE OXIDATION OF LINEAR C_4-C_6 ALDEHYDES : AN EXPERIMENTAL AND KINETIC MODELLING STUDY

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Aldehydes are known as important intermediates and products of alkanes and biofuels combustion. Many studies have been performed on formaldehyde and acetaldehyde oxidation [1], [2]; however there is a lack of experimental data about heavier aldehydes oxidation and especially on C_4-C_6 aldehydes, in particular at low temperatures. In order to propose and to validate a kinetic model for the oxidation of aldehydes, the oxidations of some linear aldehydes have been carried out.

In this context, since the n-hexanal oxidation has already been studied by Rodriguez et al. [3] in a jet stirred reactor, the oxidation of n-butanal and n-pentanal has been investigated in the same reactor. These experiments have been performed over the temperature range 500-1100 K, at a residence time of 2 s, pressure of 106.7 kPa, inlet fuel mole fraction of 0.005 and at three equivalence ratios (φ=0. 5, 1 and 2). Gas chromatography analysis coupled with various detectors (Flame Ionization Detector, Thermal Conductivity Detector and Mass Spectrometer) was used to identify and quantify the oxidation products and the fuel conversion.

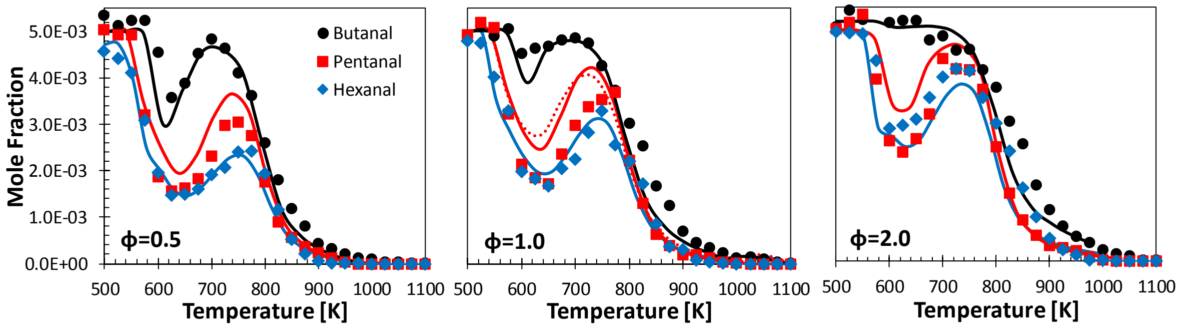

Figure 1. Comparison of experimental (symbols) and predicted (lines) mole fraction profiles of 0.5 % n-butanal, n-pentanal and n-hexanal [3] oxidation in an isothermal jet stirred reactor, φ = 0.5, 1.0, 2.0, p = 1.07 atm, τ = 2.0 s. Dotted line: example of vertical lumping, n-pentanal = 50%/50% (n-butanal/n-hexanal)

A modeling study was performed to compare the results of the experiments with the model published by Pelucchi et al. [4], extending it to describe the oxidation heavier molecular weight aldehydes. Using this model, a good agreement between experiments and model was obtained in terms of fuel conversion and for most of the detected species. This work further constrains pathways relevant to aldehyde oxidation, and highlights the influence of the carbonyl moiety on intermediate species formation.

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AN EXPERIMENTAL AND KINETIC MODELLING STUDY OF C_4-C_5 CARBOXYLIC ACIDS PYROLYSIS AND OXIDATION IN A JET STIRRED REACTOR

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Many reasons lie behind the interest in carboxylic acid oxidation chemsitry. 1) Organic acids are found in significant concentrations in the troposphere and are known to considerably affect environmental chemistry. Biomass combustion and vehicle emissions are believed to be among the most important sources that can be directly related to human activities. 2) Oxygenated species, including those carrying acid functionalities, are very abundant in the tar released from biomass pyrolysis. Acetic acid, for example, is the major acidic components of bio-oils derived from biomass fast pyrolysis [1]. 3) New fuels formulations meant to improve environmental impact and decrease energetic dependence on fossil fuels are obtained by blending increasing amounts of biofuels (e.g. alcohols) into conventional fuels. Recent studies highlighted how the combustion of such fuels might introduce new issues for human health, as their impact on pollutant formation has not been fully assessed. In fact, new unregulated pollutants such as aldehydes and organic acids may be formed in significant quantities during the combustion of these new fuels. Therefore, according to the succesive oxidation steps as alcohol → aldehyde → carboxylic acid, the description of biofuels combustion has to properly account for the formation of relevant intermediates [2]. 4) Recent experimental and modeling studies on the low temperature oxidation chemistry of hydrocarbon fuels, highlighted the importance of organic acid formation from alternative low temperature pathways of alkanes (e.g. Korcek mechanism) [3]. From a fundamental kinetic perspectives all of the above reasons share the same necessity to properly assess the influence of the carboxyl functionality on the overall reactivity of different molecular weight acids. The same systematic approach has been recently applied to linear aldehydes and alcohols [2, 4].

Stemming from the scarcity of experimental data available in the literature for gas phase kinetics of acetic and higher molecular weight acids, this work presents new experimental data obtained in an atmospheric pressure jet stirred reactor for the pyrolysis and oxidation (φ=0.5, 1.0, 2.0) of butanoic and pentanoic acids, in the temperature range T=700-1100 K (Figure 1).

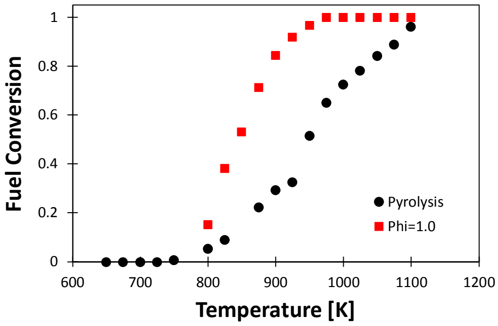

Figure 1. Experimental conversion of pentanoic acid in an atmospheric pressure Jet Stirred Reactor. Pyrolysis and stoichiometric oxidation, τ = 2.0 s

A kinetic model was derived from a recent revision of acetic acid kinetics [5] based on ab initio transition state theory calculation and from alkanes rate rules. This model was used to succesfully interpret the decomposition of the starting fuels and the formation of intermediate and product species. The insertion of an oxygenated functional group into an alkane-like molecule (e.g. n-butane → butanoic acid) strongly modifies bond dissociation energies, therefore its reactivity [6]. In addition to enhanced unimolecular initiation reactions and H-abstraction reactions, at intermediate and lower temperatures a major role si played by molecular reactions. In the case of carboxylic acids R-(C=O)-OH molecular dehydration ($R\text{-}(C{=}O)\text{-}OH \leftrightarrow H_2O + R{=}C{=}O$) and decarboxylation ($R\text{-}(C{=}O)\text{-}OH \leftrightarrow CO_2 + RH$) reactions play a key role.

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EXPERIMENTAL AERO-THERMAL INVESTIGATIONS OF SWIRLING FLOWS IN THREE-DIMENSIONAL RIBBED TUBES

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In steam cracking of hydrocarbons for the production of ethylene, the reactors operate under conditions that result in residence times of less than 1 second. In combination with the endothermic character of the process this requires high heat transfer rates. One of the most promising solutions is the use of turbulators [1, 2, 3]. Generally speaking, they disrupt the boundary layer at the wall and make the flow/temperature profile more homogeneous [4]. This does thus not only result in reduced radial gradients it also implies that lower tube wall temperatures are needed to obtain a similar process gas temperature. As a consequence, fouling phenomena that occur at the wall such as coking on the inner tube side is minimized. The latter also positively influences the tube life.

Although it has been demonstrated by several authors that the increase of the Nu number is about twice the one seen in a smooth tube at the same Reynolds and Prandtl numbers, the ribbing technique is limited by the rise in the friction losses [1]. Therefore, in an ideal world a multi-objective optimization design could be envisioned which can find out the best solution to the problem of maximum heat transfer and minimum pressure drop. Obviously this requires that the optimization tool needs a fluid dynamic solver which has to be able to well simulate the vortexes generated at the wall.

Data for the validation of Large Eddy Simulation on chemical reactors has been provided [5]. The way the code solves the Navier-Stokes and the energy equation for the small scales can be verified. The investigation has been done with Stereo-Particle Image Velocimetry [6] to measure the flow field and with Liquid Crystals Thermography to quantify the heat transfer at the pipe wall [7]. The measurements outcome shows an induced 3-dimensional separation which makes the flow to impinge on the wall (Fig. 1), providing an enhanced heat transfer. Anyway, the topology of the flow and the increased turbulence produce more skin friction at the wall. An overall efficiency of the energetic system, which takes into account both the phenomena, shows the importance of wall turbulators in enhancing heat transfer techniques.

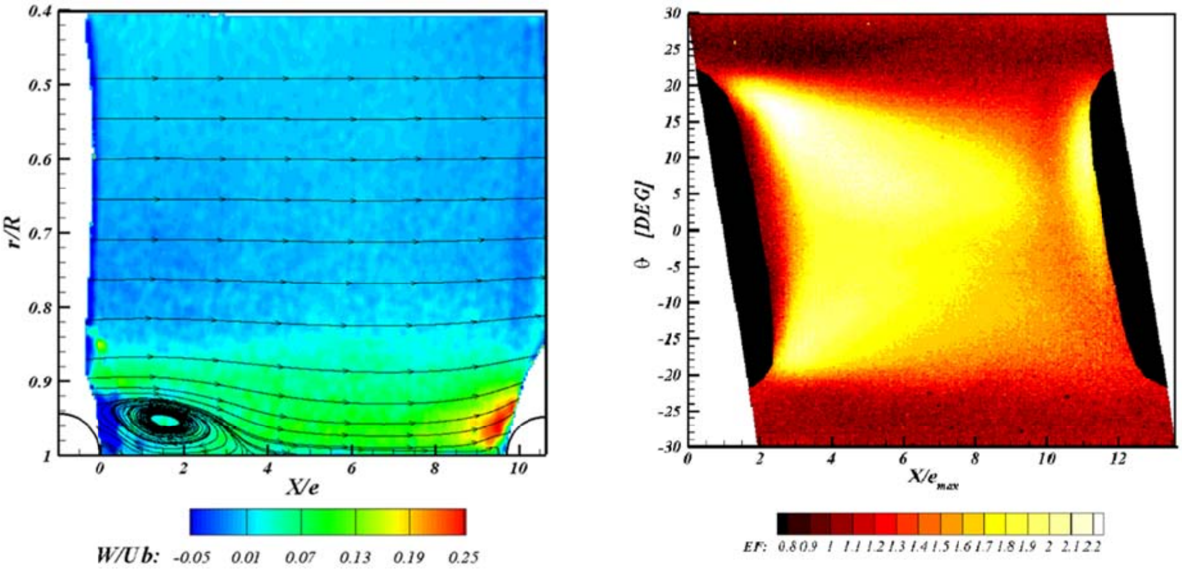

Figure 1. Left: flow field between two wall obstacles at Re = 20000; Right: enhancement of the heat transfer between two obstacles at Re = 80000

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PROCESS INTENSIFICATION IN STEAM CRACKING: FLOW CHARACTERISTICS OF SPHERICAL DIMPLES

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Olefins such as ethene and propene are key chemical components with an annual production of roughly 1.5 x 10^8 t and 8 x 10^7 t, respectively [1]. As an increase in global population and overall standard of living will further increase demand, a lot of attention was devoted in the previous years to a range of technologies for the production of light olefins [2-4].

Chemical industry however still views steam cracking as its leading technology due to its favorable process economics and significant process maturity [5]. However, industry and academia still strive to further optimize the proces, focusing on emission reduction and energy efficiency [6]. This can be done by technologies such as advanced reactor materials [7], high emissivity coatings [8] and 3D reactor technology [9-11].

For this study, computational fluid dynamics (CFD) is applied to study a novel 3D reactor technology in which spherical dimples are placed in the reactor inner wall [12]. These wall modifications imply a small additional pressure drop whilst heat transfer is enhanced significantly by an increase in radial mixing and a disruption of the boundary layer. These effects are greatly influenced by the existence of vortices inside the dimples and the interaction between neighbouring dimples.

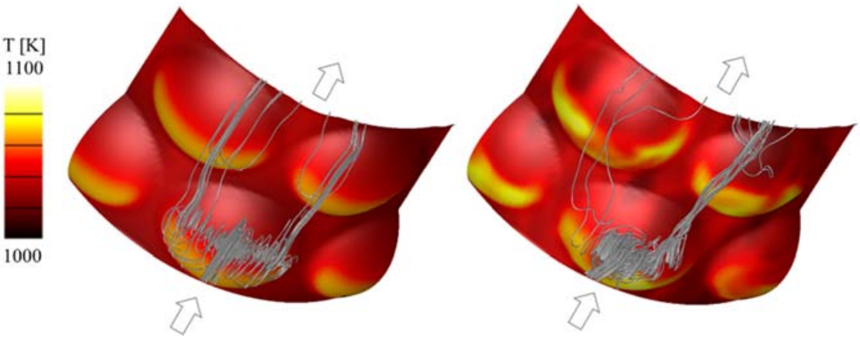

Figure 1. Time averaged (left) and instantaneous (right) wall temperature and flow behavior in a dimpled reactor

Large Eddy Simulations (LES) are performed for a range of geometries in which the position and number of neighbouring dimples are varied. Next to this, the previously reported transient behavior of vortices inside dimples [13] and the influence of reactor design and process conditions is studied.

These findings are used to propose an improved dimpled design, which is used in fluid dynamic simulations coupled with detailed kinetics to investigate the effect of the dimples and the associated enhanced heat transfer on product yields and coking rate.

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COMPUTATIONAL FLUID DYNAMIC-BASED STUDY OF THE STEAM CRACKING PROCESS USING A HYBRID 3D-1D APPROACH

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Steam cracking is the predominant process to produce light olefins which are often referred to as the building blocks of the chemical industry. As steam cracking is an energy-consuming process, improving the energy efficiency of the steam cracking process has an immediate return. The Horizon2020-funded IMPROOF project aims to reduce the energy demand of this process by implementing various novel technologies ranging from oxy-fuel combustion to augmented reactor geometries and high emissivity coatings[1]. These novel technologies are studied at a laboratory-scale and the most cost-effective technologies are to be implemented on an industrial scale.

Three dimensional computational fluid dynamics (CFD) modelling offers valuable insight in how individual or combined novel technologies contribute to the overall improvement of the energy efficiency. In the present work coupled simulations of the steam cracker radiant section, accounting for different novel technologies, are performed. The energy impact will be analyzed. Remark that a complete study of the energy balance requires that the convection section, the transfer line exchanger and the steam drum are accounted for.

A hybrid CFD-1D model is used to quantify the process improvement by implementation of a novel technology. For novel three dimensional reactor geometries, the focus is on modelling the reactor side using 3D CFD. These simulations are performed using an industrial heat flux profile or results obtained from simplified, one dimensional, furnace simulations as the radiant section boundary condition[2]. However, for novel technologies on the furnace side, e.g. high emissivity coatings and oxy-fuel combustion, highly detailed 3D CFD simulations of the furnace box are performed, iteratively combined with low cost one dimensional reactor simulations using the commercial software package COILSIM1D[3-5]. The initial objective is to optimize and validate the existing hybrid models using experimental data. The future goal is to perform fully coupled three dimensional reactor and furnace simulations.

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"PAS DE DEUX" OF HIGH-TEMPERATURE ALLOY AND 3D REACTOR TECHNOLOGY FOR STEAM CRACKING COILS: IMPACT ON PRODUCT YIELDS AND COKE FORMATION

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The production of light olefins through steam cracking is considered to be a mature technology [1]. Nevertheless, a lot of room for optimization is still available, especially in the energy consumption per ton of produced light olefins. The energy consumption of steam cracking is believed to contribute 8 % of the chemical industry's total primary energy [2]. A significant contribution to a reduced energy efficiency is the unavoidable decoking step, because coke builds up on the reactor walls, as a result of side reactions [3].

The sole purpose of the IMPROOF project is to demonstrate the latest technological innovations in the field of coke mitigation and energy efficiency during steam cracking. These innovations include the use of new advanced high temperature alloys, in combination with novel 3D reactor technologies and the application of high emissivity coatings. Two industrial reactor materials, Centralloy® ET45 micro (chromia former) and Centralloy® HT E (alumina former) [4] were compared based on their coking resistance in a pilot plant steam cracking furnace. The HT E material, in addition, was coupled with the 3D reactor technology, SCOPE® [5] (Figure 1) to benchmark it to the bare, unprocessed, coils. In total five coking cycles were performed, for which cycle four resembled high-temperature EOR industrial conditions to metallurgical age the material. The remaining cycles resemble SOR industrial conditions. After aging, only the HT E reactors proved to be stable and even improved their coking resistance. Due to the reduced radial gradients after the application of the SCOPE® technology, the TMTs decreased. This decrease resulted in a decreased coking rate in comparison with the bare tube alternative. The combination of HT E together with SCOPE® showed an exceptional coking resistance, resulting in a coke reduction of nearly a factor 3 in comparison with the bare ET45 micro and HT E reactors.

Supplementary improvements can be obtained through the application of reactive CFD simulations. In this regard, the obtained experimental results are compared with the results of the respective CFD simulations.

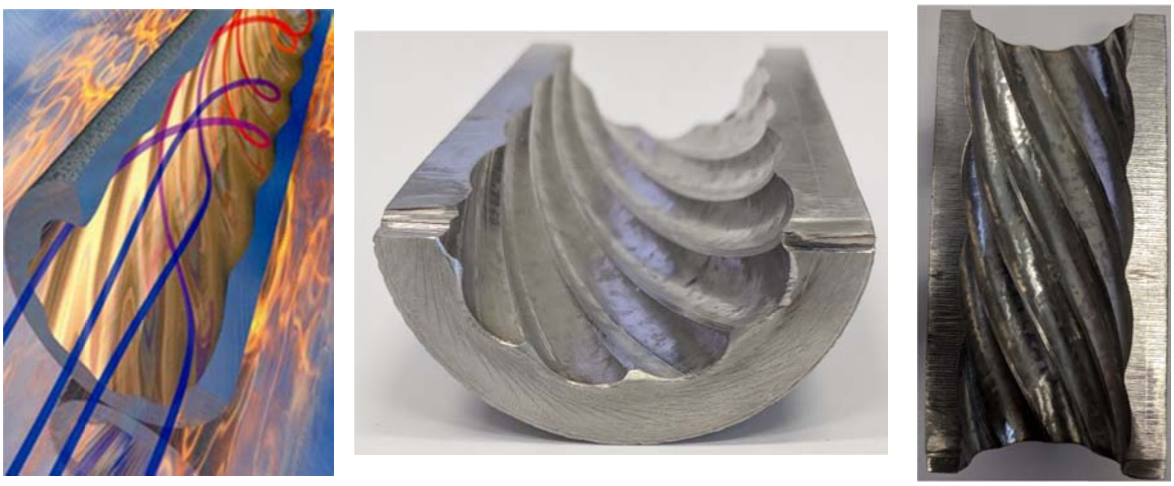

Figure 1. SCOPE® 3D reactor coil [28] technology

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POSTER PRESENTATIONS

PROCESSING OF C4 FRACTION CONTAINED IN THE WASTE GASES OF REFINERIES BY CATALYTIC ISOMERIZATION TO ISOBUTANE ON Pd/SULFATED ZIRCONIA

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Introduction

The increase in the depth of oil refining and the shift to heavier oil processing is inevitably accompanied by an increase in the formation of waste oil refinery gases. In this case, light alkanes, in particular n-butane fraction (C4 fraction), do not find an equivalent market. Processing of C4 fraction aimed at the production of high-octane oxygen-containing components of motor fuels, in particular, tert-butyl alcohol (TBA) is regarded as a promising solution to improve economic issues. The technological process to solve this problem was proposed in [1]. It includes two consecutive stages, the first is n-butane isomerization to isobutane [2], and the second is oxidation of isobutane to tert-butyl hydroperoxide (TBHP), followed by the decomposition of the formed TBHP to the targeted TBA.

Experimental

In the present work, we have performed an experimental study of the isomerization of the n-butane fraction to isobutane on a BIC proprietary Pd-SO_4/ZrO_2 catalyst (Pd load 0.5 % w/w, S_{Pd} = 1.2 m^2/g cat, D_{Pd} = 2.1 nm, Pd dispersity = 53 % of theoretical). Chromatographic analysis of industrially available C4 fractions showed that n-butane is the main component of these fractions (90-98 % w/w), other components are isobutane, 2.2-dimethylpropane, propane, butene-1, isobutene, trans-butene-2, cis-butene-2, and C_5+. The isomerization reaction was carried out in an isothermal flow reactor with an internal diameter of 10 mm, the height of the catalyst bed was up to 10 cm. The catalyst pellets were formed initially as extruded trilobes with an outer circle diameter 2 mm and a length of 3-4 mm; then they were crushed and the 0.25-0.50 mm fraction was screened. 10-14 g of this fraction diluted with quartz was loaded into the reactor. Reaction parameters were varied within the ranges as follows: temperature 120-160 °C, pressure 20-25 bar, weight hourly space velocity (WHSV) of n-butane 1.0-2.5 h^{-1}, and hydrogen/butane molar ratio 0.1-0.5.

Results

Thermodynamic equilibria for the branched paraffin isomers are generally favored by low temperatures. Efficient catalysts for n-butane isomerization should be active well below 200 °C. At 120 °C, the equilibrium conversion of n-butane to isobutane is appx. 67 %, then it drops to 60 % with an increase in temperature to 160 °C. The effect of the n-butane isomerization process conditions such as temperature, WHSV of n-butane, and hydrogen/butane molar ratio on the performance of Pd-SO_4/ZrO_2 catalyst was investigated within the ranges indicated above. It is determined that at a given temperature, conversion of n-butane strongly depends on the molar ratio H_2/C_4 and grows substantially with its decrease approaching the equilibrium values; also, it declines with the increase in WHSV of n-butane, that is, with the decrease in residence time. With the temperature increase, conversion of n-butane grows in all cases. Selectivity towards isobutane decreases slightly with the temperature rise; however, it increases with the increase in both WHSV and molar ratio H_2/C_4. The presence of relatively small isobutane impurities in the inlet reaction mixture reduces its equilibrium yield in isomerization and the observed conversion of n-butane.

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INCREASING THE EFFICIENCY OF THE HDS PROCESS BY THE MODIFICATION OF Ni/Mo/W HYDROTREATING CATALYST SUPPORTED ON MODIFIED SUPPORTS

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Deep hydrodesulfurization (HDS) of petroleum-derived fuels has attracted much attention in recent years due to environmental requirements demanding significant improvement in sulfur elimination (Stanislaus et al., 2010). Catalysts consisting of molybdenum supported on γ-alumina and promoted with Co or Ni are commonly used in the hydrotreating processes (Torielloa et al., 2015; Mendoza-Nieto 2013). Bulk unsupported trimetallic hydroprocessing catalysts has been developed for the production of ULSD, however, high metal content and low specific surface area are the principal disadvantages of bulk HDS catalysts. In general, different approaches have been followed to improve the performance of HDS catalysts. The objective of this research study was to find out the possibility of preparation of highly active supported trimetallic catalysts and to evaluate their effectiveness in hydrodesulfurization of refractory sulfur-containing compounds.

To achieve this objective, a series of Mo and W-based catalysts with Ni promoters were preparedusing modified support materials (i.e. Al_2O_3, Z-Al_2O_3 and Ti-Z-Al_2O_3) and were characterized and tested in a microreactor for their HDS performance. Differences in catalytic activities due to changes in support may arise as a result of variations in metal–support interactions which in turn, may influence the dispersion and morphology of active components (Escobar et al., 2017; Magdaleno et al., 2014).

The loading of catalytically active metals (Mo, W and Ni) into the support by wet impregnation is an important parameter that can significantly influence the activity of the catalyst and thus contribute to optimizing the productivity of the HDS process. The role of the support for the catalyst of the HDS process is also extremely important – as illustrated in Fig. 1, the catalysts on zeolite supports are the most active, and especially catalysts on Ti-Z-Al_2O_3 support.

PP-2

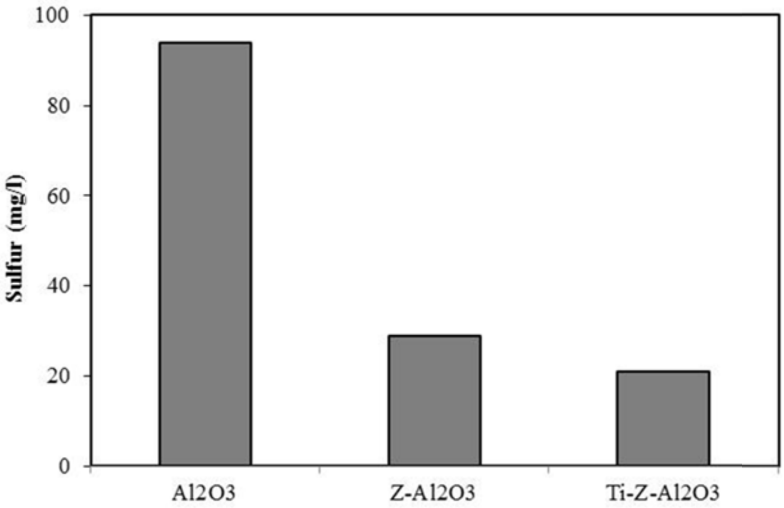

Figure1. Comparison between the HDS activities of trimetallic catalysts with different supports (Reaction Temperature 360 °C)

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MODELING CO_2 TO METHANOL CONVERSION IN A STAGNATION FLOW REACTOR

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Methanol is a critical building block for the production of many industrial chemicals. Instead of the traditional petroleum-based routes currently implemented to produce methanol, carbon dioxide presents a promising alternative as a feedstock if an appropriate catalyst is available. The catalytic conversion of carbon dioxide is, when fueled by renewable energy, a sustainable means of obtaining methanol. Typically, the ternary Cu-ZnO-Al_2O_3 catalyst is commercially used to obtain methanol from $CO:CO_2:H_2$ mixtures; however, however, when applied to the direct hydrogenation of CO_2, this catalyst displays low methanol selectivity and poor stability. An alternative to the ternary catalyst is the indium oxide (In_2O_3) system proposed by Martin et al., which scores high in selectivity, activity and stability [1].

This study presents a model developed using CHEMKIN PRO to examine the performance of an indium oxide (In_2O_3) catalytic system in the stagnation flow reactor shown in Figure 1 [2]. The key concept behind the stagnation flow reactor is that the catalyst is coated on a disk inside a chamber (to control the pressure), in which the targeted gas flows and reacts on the 0-D catalytic surface [2]. The species profiles as a function of height above the catalytic bed are quantified via mass spectroscopy, which is obtained by a sampling probe that moves in one dimension perpendicular to the catalyst surface. Reducing the problem to one dimension is key in determining the reaction mechanism, which is of critical importance for reactor design and optimization purposes.

The model developed predicts the profile of all species involved in CO_2 conversion to methanol at 573 K and 50 bar. Future work includes experimental validation, determining the mechanism of the CO_2 conversion process, and optimizing the reactor design.

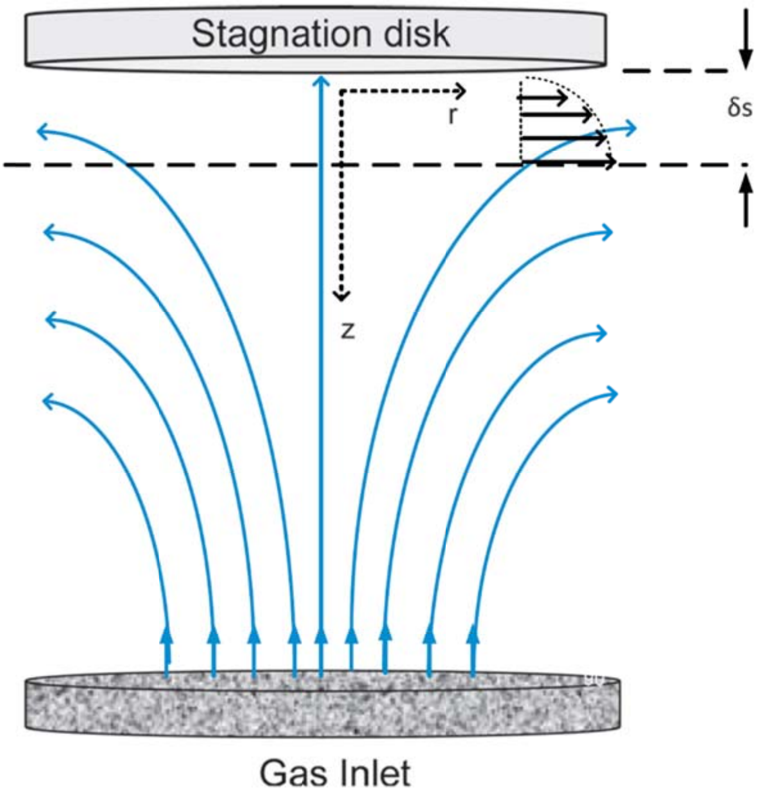

Figure 1. Stagnation-Flow Set up [2]

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MODEL BASED EVALUATION OF ALKALINE ANION EXCHANGE MEMBRANE FUEL CELLS WITH UNBALANCED PRESSURE OPERATION

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An alkaline anion exchange membrane fuel cell (AAEMFC) has been recently recognized as a promising electrochemical power generation and next generation of low temperature fuel cells [1]. It has the advantages in the terms of high electrochemical kinetics under the alkaline condition, possibility to use low cost non-noble metal catalyst at the anode, flexible fuel usage and low fuel crossover [2]. Water transport is the important issue to keep the high performance of alkaline fuel cell. In contrast with proton exchange membrane fuel cells, the water (vapor phase) and oxygen are reactants in the cathode. At the anode, liquid water is produced and also transported from the cathode to anode due to electro osmotic drag mechanism. The systematic difference leads to the new challenge of water management. Too much water at the anode may cause pore flooding in the electrodes, thus leading to a higher mass transfer resistance of reactants. The control of water transport through the membrane at suitable rate is the important transport issue. Although water transport phenomena have a significant influence on the performance of alkaline anion exchange membrane fuel cells, there are a limited number of researches focusing on the water management within alkaline anion exchange membrane fuel cells [3]. It is found that the liquid water removal from the anode is necessary to prevent the flooding problem. The encouragement of water permeation or water back diffusion from the anode to cathode is the effective way not only to mitigate flooding problem but also to increase the oxygen relative humidity with the internal humidification concept. Therefore, the aims of this work focus on the improvement of alkaline anion exchange membrane fuel cells performance with water management.

PP-4

In this work, the mathematical model of alkaline anion exchange membrane fuel cells is developed with the consideration of water transport inside the membrane and the flooding effect. The effect of operating conditions on the cell performance are analyzed when the unbalanced pressure operation are applied to enhance water back diffusion from anode side to cathode side. The direction of water transport of alkaline anion exchange membrane fuel cells at unbalanced pressure operation is present in Fig. 1. The effects of key operating parameters such as operating temperature, cathode relative humidity, anode relative humidity, cathode pressure, anode pressure on the cell performance will be analyzed. With this concept, the increasing of cathode relative humidity with the internal humidification concept and the reduction of flooding problem at the anode are observed.

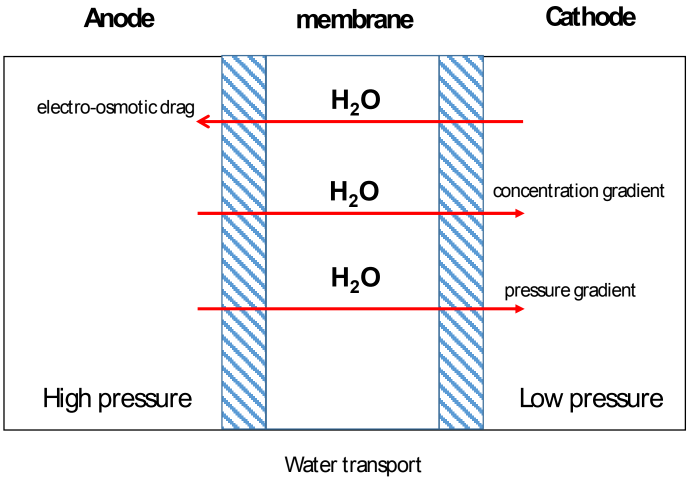

Fig. 1. Water transport of alkaline anion exchange membrane fuel cell at unbalanced pressure operation

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CO_2 REFORMING OF GLYCEROL OVER Rh-BASED CATALYSTS

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Glycerol dry reforming (GDR) offers sustainable production of syngas since it consumes glycerol which is in excess due to increased biodiesel production and greenhouse gas, CO_2. Low reactivity of CO_2 and coke formation are the major drawback of the process, calling for the need of active and stable catalysts. Owing to the lack information on the catalysis of GDR in the literature, Rh/ZrO_2 and Rh/CeO_2 are studied at GDR conditions and effects of temperature and CO_2-to-glycerol ratio (CO_2/G) on product distribution and reactant conversions are investigated.

Rh/ZrO_2 and Rh/CeO_2 containing 1 wt. % Rh are prepared by incipient-to-wetness impregnation and calcined at 800 °C for 4 h. Catalysts are reduced under H_2 flow at 800 °C prior to glycerol dry reforming tests for 2 h. Experiments are conducted in a quartz reactor involving 20 mg of catalyst. Residence time is kept constant at 0.5 mg·min/Nml. Dosing of high purity (>99.5 %) glycerol and gaseous species (CO_2 and N_2) are made by HPLC pump (Shimadzu LC-20AD) and mass flow controllers (Brooks 5850E), respectively. Glycerol conversion is calculated by elemental balance of H existing in gaseous species detected by gas chromatography. Molar inlet CO_2/G and temperature are selected in the range of 1-4 and 600-750 °C, respectively. Fresh and spent catalysts are characterized by in-situ FTIR, Raman spectroscopy and TEM-EDX techniques to provide fundamental insight into the structural changes on the catalysts and mechanisms of activity loss.

Temperature has a positive effect on the conversions of glycerol and CO_2, and on product yields. While they exhibit glycerol conversions close to those of blank tests in the 600-700 °C range, both catalysts seem to function effectively between 700 and 750 °C and are capable of converting up to ~80 % of the glycerol fed. A similar trend is observed for CO_2 conversion which is found to be 13 % and 7 % on Rh/ZrO_2 and Rh/CeO_2, respectively, at 750 °C. Yields of species, especially that of H_2, are found to increase with conversion. At a $CO_2/G = 1$, both catalysts are shown to produce syngas with H_2/CO exactly equal to 1. High temperatures also suppressed coke formation.

Glycerol conversion decreased from 91 % to 70 % on Rh/ZrO_2, and from 88 % to 64 % on Rh/CeO_2 upon increasing CO_2/G from 1 to 4. The same change in blank experiments, however, did not affect glycerol conversion that remained constant at ~47 %. Negative correlation of catalytic glycerol conversion with CO_2/G is possibly due to a competition between glycerol and CO_2. Product distribution follows a monotonic trend of decreasing H_2 and increasing CO yields at elevated CO_2/G ratios, indicating the importance of reverse water-gas shift by which H_2/CO ratio is reduced as a result of CO_2 addition into the feed. Resulting increase in H_2O is thought to trigger steam reforming CH_4, whose yields are found to decrease with CO_2/G.

Response of CO_2 conversion against change in CO_2/G is different from that of glycerol. Between CO_2/G of 1 and 2, CO_2 conversion increases from 13 % to 23 %, and from 7 % to 16 % on Rh/ZrO_2 and Rh/CeO_2, respectively, but remains almost unchanged upon further increase in CO_2/G. The trend on Rh/ZrO_2 may be associated with sintering of Rh nanoparticles whose dimensions increase from ~1.5 to 4 nm, as detected by TEM-EDX studies. Sintering is believed to offset the increase in conversion by CO_2 addition. This mechanism, however, seems not to exist on Rh/CeO_2 which involves strong metal-support interaction, as verified by the in-situ FTIR and Raman characterization. The strong interaction, together with the improved oxygen transfer properties of CeO_2, oxidizes surface carbon into CO_2, which offsets its consumption to end up with unchanged CO_2 conversions at $CO_2/G = 2\text{-}4$. The strong interaction, however, encapsulates Rh sites on CeO_2, causing CO_2 and glycerol conversions to be less than those obtained on Rh/ZrO_2.

Stability test are conducted at 750 °C and $CO_2/G = 4$ for 72 h. Despite its lower activity Rh/CeO_2 remains more stable than Rh/ZrO_2, whose activity loss is associated mainly with sintering and carbon deposition. The reduced strength of metal-support interaction in Rh/CeO_2, which is verified by the FTIR studies, is thought to be the primary cause of its particular deactivation. Composition of syngas remains almost unchanged in the range of 0.6-0.7.

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NEW MODELS FOR THE DESCRIPTION OF SORPTIVE AND TEXTURAL PROPERTIES OF CaO-BASED SORBENTS CHANGING DURING REPETITIVE SORPTION/REGENERATION CYCLES

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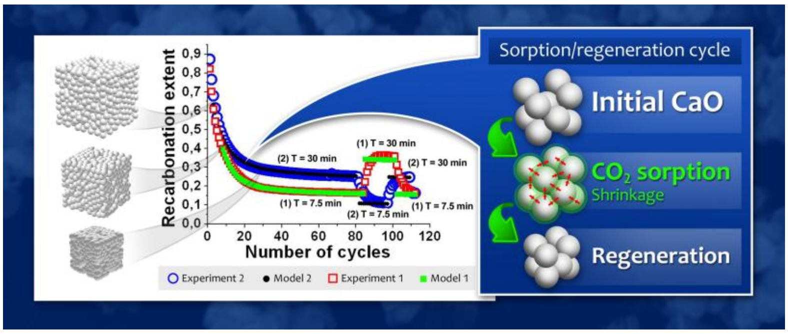
Carbon dioxide separation from gas mixtures is critical process in several emerging energy-related industries, including in hydrogen production by means of biomass utilization and exhaust gas clean up. Some studies on this topic suggest using calcium-based sorbents for effective CO_2 capture from gases because of potential advantages including: a wide range of operating temperatures; reduced energy penalties; the relatively inert nature of solid wastes.

However, the use of CaO as a regenerable CO_2 sorbent is limited by the rapid decay of the carbonation conversion with the number of carbonation/calcination cycles due sintering.

The evolution of sorptive and textural properties of CaO-based sorbents during repetitive sorption/regeneration cycles has been mathematically simulated in this study. The proposed models takes into account the morphology of nascent CaO, sorbent sintering physics and CO_2 sorption kinetics. The sintering was simulated under the assumptions: the sintering proceeds via the lattice diffusion mechanism (model a), that is characterized by the shrinkage, i.e. by reduction of the distance between the centers of sintered particles; via the surface diffusion mechanism (model b), that does not lead to shrinkage.



The results show that the volume sintering model is in good agreement with the experimental data and predicts the dependence of the recarbonation extent and the value of the sorbent specific surface area on the number and duration of the sorption/regeneration cycles well (figure 1).

Model (b) predicts the decay of the sorbent sorption capacity value from the initial to the final cycle only two times, but the real decay is more dramatic and the ratio attains the value of 4,5. Thus, computer modeling has shown that sintering of CaO sorbents occurs via the volume sintering mechanism or via a combined volume and surface sintering mechanism but not exclusively via the surface sintering mechanism.

PP-7

CALCULATION METHOD FOR PREDICTION OF THE CETANE INDEX OF BLENDED DIESEL FUELS TAKING INTO ACCOUNT NON-ADDITIVITY

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Diesel fuel is one of the main commodity products of the oil refining industry. Modern diesel fuels are not straight-run products, it are obtained by blending straight-run and hydrotreated diesel fractions and additives in the process of compounding. The need for compounding is due to the toughening of the requirements for the quality of diesel fuels. The cetane number, the most important operational characteristic of diesel fuel, is a non-additive characteristic and experimental determination of the cetane number is a multi-stage and labor-intensive process, which requires certain skills, special equipment, as well as time and money costs. According to [1], the cetane number for diesel fuel without additives can be calculated as a cetane index. For these reasons, development of a new calculation method for prediction of cetane index is relevant tasks [2-6].

In this work, the method for calculating the cetane index of blended diesel fuel taking into account the nonadditivity is presented. The cetane indices of the diesel fuels components were calculated according to the ISO 4264 "Petroleum products – Calculation of cetane index of middle-distillate fuels by the four-variable equation" [7] using the data from Russian industrial enterprise [8], the ratios of the blending components of diesel fuel (blending recipes) shows in Table 1.

Table 1. The ratios of the blending components of diesel fuel

Components	**Blends**			
	1	***2***	***3***	***4***
	v_i, **wt. %**			
Straight-run diesel fraction	0.40	0.40	0.37	0.40
Kerosene fraction	0.12	0.00	0.00	0.00
Hydrotreated diesel fraction	0.30	0.35	0.40	0.50
Dewaxed diesel fraction	0.18	0.25	0.23	0.10

To calculate the cetane index, the developed method uses the true boiling points (TBP) of the diesel fuel components obtained by recalculating the fractional composition [9]. The block diagram of the calculation procedure is shown in Figure 1.

Figure 1. Block diagram of the methodology for calculating the cetane index, taking into account nonadditivity

The results of calculations using the developed methodology are shown in Table 2. Calculated values ($CI_{mix.met.}$) were compared with experimentally determined cetane indices of blends ($CI_{mix.exp.}$), as well as with cetane indices of blends, calculated according to the rule of additivity ($CI_{mix.add.}$).

Table 2. Comparison of cetane indices calculated by different methods with experimental values

Receipt	$CI_{mix.exp.}$	$CI_{mix.add.}$	$CI_{mix.met.}$	$\Delta_{add.}$	$\Delta_{met.}$
1	47	49	47	2	0
2	49	50	48	1	1
3	48	51	50	3	2
4	50	52	49	2	1
			$\Delta_{av.}$	**2**	**1**

Thus, the developed method allows calculating the cetane index of blended diesel fuels with an average error ($\Delta_{met.}$) not exceeding 1 point, while the calculation according to the rule of additivity ($\Delta_{add.}$) has an average error of 2 points.

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PP-8

INFLUENCE OF DIESEL FUEL COMPOSITION ON THE EFFICIENCY OF THE LOW-TEMPERATURE ADDITIVES

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One of the important strategic directions for a number of countries in recent years has been the development of the Arctic and Antarctic. To overcome this challenge, it is urgent to provide technical equipment with high-quality, environmentally friendly fuels and lubricants, including diesel fuels that can be effectively operated at extremely cold temperatures typical for the Arctic regions. One of the most frequently used methods for providing low-temperature properties of diesel fuels is the use of additives to improve them. The choice of the type and necessary concentration of the additive is often empirically carried out, due to the lack of the universal technique for the use of low-temperature additives. This is justified by two factors:

1) A wide range of additives on the market, with different active substances;

2) The hydrocarbon composition of diesel fuels varies within fairly large limits, depending on the feedstock.

Three samples of straight-run diesel fuel, obtained from various fields in Western Siberia, were chosen as the object of study. For the investigated samples of straight-run diesel fuel (DF), the following characteristics were experimentally determined: fractional composition, density, viscosity, sulphur content, structural-group composition, cloud point, pour point, cold filter plugging point, and the cetane index was also calculated [1]. The results are shown in Table 1.

Table 1. Characteristics of diesel fuel samples

DF Sample	**Temperature, °C**			**Density at 15 °C, kg/m^3**	**Viscosity at 20 °C, mm^2/s**	**Sulphur content, ppm**	***CI*, points**	**Cloud point, °C**	**Cold filter plugging point, °C**	**Pour point, °C**
	V, ml									
	10	***50***	***90***							
1	189	248	338	832.0	3.8	2420	48.6	-15	-21	-35
2	190	262	332	838.0	4.2	711	49.0	-12	-22	-32
3	183	271	359	842.0	4.6	2517	48.6	-3	-4	-18

For the study, three different low-temperature additives for diesel fuels were chosen, which were assigned ciphers A, B, C. Based on the manufacturer's recommendations, using the sample 3, the mixtures of straight-run diesel fuel with low-temperature additives were prepared. The effect of additives on the cold filter plugging point (CFPP) of fuel was investigated. The results are presented in Table 2.

Table 2. Influence of additives on cold filter plugging point of sample 3

Additive	CFPP pure sample, °C	CFPP with additive, °C	CFPP change, °C
A	-7	-11	4
B		-8	1
C		-17	10

From the results presented in Table 2 it can be seen that the use of additive C is the most effective. For further research, the mixtures of the fuel samples 1 and 2 with the additive C were prepared. The cold filter plugging point was also determined for the mixtures prepared. The results are presented in Table 3.

Table 3. Influence of additive C on cold filter plugging point of diesel fuel samples

DF Sample	CFPP pure sample, °C	CFPP with additive, °C	CFPP change, °C
1	-21	-32	11
2	-22	-30	8
3	-4	-17	13

Thus, from the results presented in Table 3 it can be seen that the same additive at the same concentration has a different effect on the diesel fuel cold filter plugging point. Differences in the effectiveness of the additive can result from the effect of the composition of straight-run diesel fuel. In this study, the samples 1, 2 and 3 were investigated using the n-d-M method. The results are given in Table 4.

Table 4. Results of n-d-M analysis of diesel fuel samples

DF Sample	Carbon distribution, wt. %		
	$C_{\text{aromatic rings}}$	$C_{\text{naphthenic rings}}$	$C_{\text{paraffin chains}}$
3	8.063	25.860	66.076
4	13.229	41.242	45.529
5	12.453	35.684	51.863

The analysis showed that the greatest amount of carbon in all the samples is contained in paraffin chains, the smallest one is in aromatic rings. It cannot be unequivocally said about the effect of the distribution of carbon in hydrocarbon groups on the effectiveness of the action of the additive. However, based on the results of the studies, a direct relationship exists between the boiling point of 90 % by volume of the sample and the efficiency of the low-temperature additive, which may result from the accepted adsorption mechanism of additive action.

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METALLIC MICROREACTORS FOR THE INTENSIFICATION OF CATALYTIC HYDROGEN PRODUCTION AND PURIFICATION PROCESSES

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The development of clean and eficient energy technology solutions has been considered one of the most important challenges facing scientific and technological research since the turn of the century. In this sense, designing unconventional microreactors to facilitate catalytical processes during the production and purification of hydrogen is a significant concern in addition to the miniaturization of equipment in the feedforward system of fuel batteries [1,2]. This is mainly due to the notable increase in mass and heat transfer coefficients as compared to conventional reactors. Additionally, the use of microgrids as microreactors, characterized by dimensions in the submillimeter range, provides higher surface/volume ratio (> 40,000 m^2/m^3) and offers a configuration that allows the generation of turbulent flow.

The present work concerns with the preparation, characterisation and activity of microstructured reactors (microgrids type, Fig. 1) for the Preferential Oxidation of CO (COPROX) and the Water-Gas Shift (WGS) processes. Hydroxyapatite catalytic films will be deposited on these materials to enhance their textural and chemical properties before the impregnation of the active phase. 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 hydroxyapatite on ceramic and metallic monoliths. In the present study the deposition of hydroxyapatite film was carried out by using a modified version of the methods mentioned in the literature [1,2]. For the impregnation of the active phases (Cu, Pt, Pd) the HAP/SS316 support was dipped into a stirred aqueous solution of the corresponding salts for 2 h. Then, the samples were dried at room temperature for 2 h and at 120 °C for 12 h. Finally, the resulting samples were calcined in air at 500 °C for 4 h with temperature ramp of 1 °C min^{-1}.

Fig. 2. shows the evolution of the weight increases expressed as the HAP deposition density versus the number of the immersions in the prepared slurry. As expected, the obtained results showed that the deposition density increased linearly with the number of immersions. After 10 immersions the sample reached a deposition density of 1.2 mg$_{(HAP)}$ cm$^{-2}_{(MG)}$ (Fig. 2). Additionally, a good adherence of the deposited film was evidenced by ultrasonic tests for 1 h (wt. loss < 5 %).

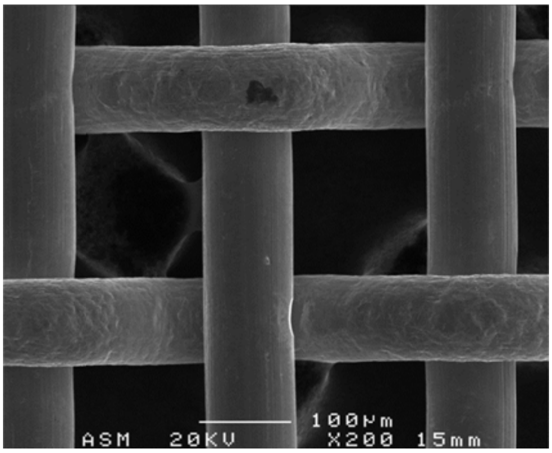

Fig. 1. SEM micrographs of the used stainless steel microgrids

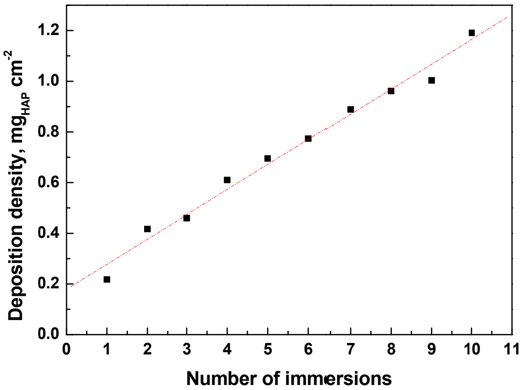

Fig. 2. Dependence of the deposition density of the HAP on the number of immersions

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Acknowledgements

The financial support for this work provided by Ministerio de Economía y Competitividad (CTQ2015-73219-JIN (AEI/FEDER/UE), ENE2013-41187-R and ENE2016-74850-R) and Gobierno Vasco (GIC IT-657-13) is gratefully acknowledged. Likewise, the technical support provided by SGIker (UPV/EHU) is gratefully acknowledged.

REACTOR SIMULATION FOR THE OPTIMAL PRODUCTION OF BIO-JET FUEL FROM THE HYDROPROCESSING OF JATROPHA OIL

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The *jatropha curcas L*. oil is a potential feedstock for the production of biofuels. Among the different types of applications of biofuels, that of bio-jet fuel has been considered to be essential to reduce the carbon footprint in the aviation industry [1]. One the standardized procedures included in the specification ASTM D7566 for the manufacture of aviation fuels is the hydroprocessing of esters and fatty acids, also known as HEFA. The main products of this process are called synthesized paraffinic kerosine (SPK) and renewable (green) diesel. This process is carried out with the use of a bifunctional catalyst, and usually two reactors are employed. The current high production cost makes the HEFA process not economically viable, and therefore it is necessary to optimize the process to maximize the yield of jet fuel and green diesel.

In this work, the optimal production of green diesel and bio-jet fuel (HEFA-SPK) from the hydrocracking of *jatropha curcas L*. oil was investigated through the simulation of the HEFA process. The simulation was carried out in ASPEN Plus®. Two reactors were considered in the process, one being the hydrotreating reactor of the triglycerides and free fatty acids contained in the jatropha oil to produce green diesel mainly, and a second one being the hydrocracking/hydroisomerization reactor to increase the production of hydrocarbons within the boiling point range of jet fuel, i.e. C_8-C_{16} paraffins, including isomers to further reduce the freezing-point of the mixture.

The first reactor was simulated by using the RYIELD model, where the yields of the different products were input according to experimental data obtained in a batch reactor, and using a jatropha oil variety from Yautepec, Mexico. The operative conditions of this reactor (pressure, temperature and type and amount of catalyst) were set from previous experience in experimental studies with jatropha oil [2-4]. On a $NiMo/Al_2O_3$ catalyst sulfided *in-situ*, the maximum yield of green diesel (C_{14}-C_{22}) was observed to be ca. 77 wt % at 80 bar and 350 °C, during three hours of residence time. This reactor was simulated using as thermodynamic method the

Non-random two-liquid (NRTL) model. The second reactor was simulated using the kinetic model reported by Calemma et al. [5] and using the Peng-Robinson equation of state as the thermodynamic method.

The simulation predicts the product flow rates and the optimal conditions for the second reactor, at which it is possible to maximize the production of isoparaffins within the boiling point range of jet fuel, trying to comply with the above mentioned specification. The simulation of the reactors has been included in a more comprehensive plant scheme of the HEFA process, including the distillation columns, which has been used to further improve the conceptual design of the plant and study alternatives for integration and intensification of the process.

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J.E. Castillo-Montiel was supported by a scholarship from CONACYT (CVU 864447).

NTP ASSISTED SINGLE STEP METHANE CONVERSION TO METHANOL OVER Cu/γ-Al_2O_3 CATALYST MODIFIED BY ZnO, ZrO_2 AND MgO AS PROMOTERS

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Partial oxidation of methane to methanol was carried out in a non-thermal DBD plasma (NTP-DBD) reactor, where air was used as the oxidizing agent. NTP condition was chosen as the reaction media to provide fast response. However, under ambient conditions, mere plasma suffers from poor energy efficiency and hence a suitable heterogeneous catalyst combination with plasma was explored to tap the synergy conditions due to catalyst action and uniform surface discharge. Moreover, plasma improves the stability of the combined system by reducing poisonig, coking and sintering of the catalysts.The influence of the reaction condition (power, CH_4/Air mole ratio) and supported metal catalysts was investigated in terms of the conversion of the feed gases, selectivity and yield of the products and the energy efficiency of the plasma process. During the present study, Cu/γ-Al_2O_3 and modified metal oxides (ZnO, ZrO_2 and MgO) catalysts were prepared by impregnation as the promoter modification leads to the high dispersion of the small metal particles over support material and hence improves the catalytic activity. The catalysts were characterized by PXRD, spectroscopy (Raman, Emission, XPS), BET, TGA, SEM and TEM to bring out the structure-function correlations and to notify the active species generated. Typical observations are as follows.

- MgO promoted catalyst (CMgA) showed the maximum CH_4 conversion of ~11 %.
- ZnO promotion yields the highest liquid product selectivity of ~50 % whereas ZrO_2 promoted the CH_3OH selectivity.
- CMgA showed the best energy efficiency of ~1.1 kJ/mmol towards the greenhouse gas (CH_4) conversion.

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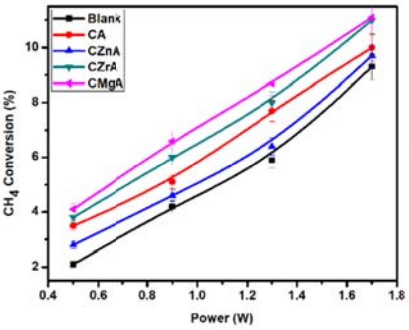

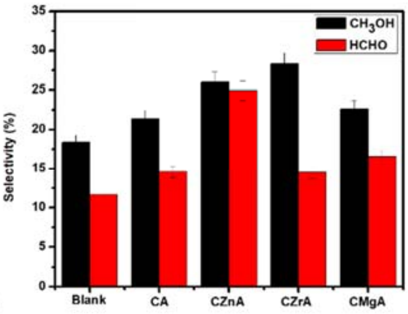

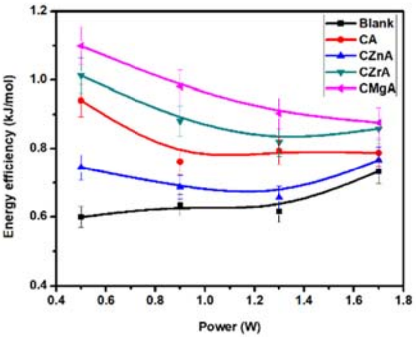

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Acknowledgements

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PP-12

PREDICTIVE MODELING OF CATALYTIC CRACKING AND FUELS BLENDING TO INCREASE OF THE GASOLINE PRODUCTION ECONOMICAL EFFICIENCY BY REDUCING THE QUALITY GIVEAWAY

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The complex research of catalytic cracking feedstock and product allowed creating the hydrocarbons conversions scheme as the mathematical model basis. Characteristics of pseudocomponents, thermodynamic and kinetic parameters of reactions at the heat equilibrium temperature between feedstock and catalyst (T = 810 K) are shown in Table 1.

Table 1. Thermodynamic and kinetic parameters of catalytic cracking reactions

Reactions		$\Delta_r H^o_{810}$	$\Delta_r G^o_{810}$	$E_{a,}$	k_d (k_{in})**
		kJ/mol			s^{-1}, $ls^{-1}mol^{-1}$
Primary	Cracking of HMW paraffins	64.7*	–70.3*	125.4	$0.14\ s^{-1}$
	Cracking of HMW paraffins to isoparaffin	65.3*	–64.5*	123	$0.25\ s^{-1}$
	Dealkylation of HMW naphthenes	100.8*	–191.5*	119	$0.15\ s^{-1}$
	Dealkylation of HMW aromatics	134.0	–143.0*	132	$0.12\ s^{-1}$
	Cracking of HMW naphthenes	267.4*	–138.5*	144	$0.19\ s^{-1}$
	Cracking of CNAH	169.5*	–119.7	132	$0.075\ s^{-1}$
	Condensation of HMW aromatics	52.1*	–32.0*	110	$0.08 ls^{-1}mol^{-1}$
Secondary	Cracking of GF paraffins	77.5	–36.6	128	$0.11\ s^{-1}$
	Isomerization of GF paraffins	–4.5	–1.5	130	$7.8 \cdot 10^{-5}\ s^{-1}$
	Cracking of GF isoparaffins	70.2	–40.2	128	$0.04\ s^{-1}$
	Cracking of GF olefins	88.2	–22.3	160.6	$0.039\ s^{-1}$
	Cracking of GF olefins to C_4H_8+C_4H_{10}	78.1	–35.3	160.6	$0.04\ s^{-1}$
	Cracking of GF olefins to C_3H_6+C_3H_8	77.8	–36.1	160.6	$0.055\ s^{-1}$
	Dealkylation of GF aromatics	80.0	–17.3	142	$0.01\ s^{-1}$
	Cyclization of GF olefins	–92.2	–25.1	132	$0.011\ s^{-1}$
	GF Diene synthesis	–72.2	–106.9	180	$0.12 ls^{-1}mol^{-1}$
	Hydrogen transfer between GF olefins and dienes	–85.2*	–40.2*	132	$2.5 ls^{-1}mol^{-1}$
	between GF olefins and naphthenes	–169.3*	–162.2*	132	$15.9 ls^{-1}mol^{-1}$
	Condensation of GF aromatics	–9.6*	–47.2*	110	$0.04 ls^{-1}mol^{-1}$
	Coke formation	26.4*	–378.5*	110	$0.2 ls^{-1}mol^{-1}$

*– quantum-chemical calculations results; HMW – paraffins C_{14}÷C_{40+}, mono- and bicyclic structures with long substituents (the average number of naphthenic and aromatic rings are 2.1÷2.3 and 2.3÷2.8 units); GF – paraffins, isoparaffins, olefins, naphthenes C_5–C_{11+}; aromatics – aromatics C_6–C_{12+}; CNAH – condensed naphthenic-aromatic hydrocarbons.
**– k_d – rate constant of the direct reaction; k_{in} – rate constant of the inverse reaction.

The differences of the catalytic cracking feedstock characteristics have a significant effect on the product yield and the coke formation degree on the catalyst, along with operating parameters [1] of the catalytic cracking (Fig. 1).

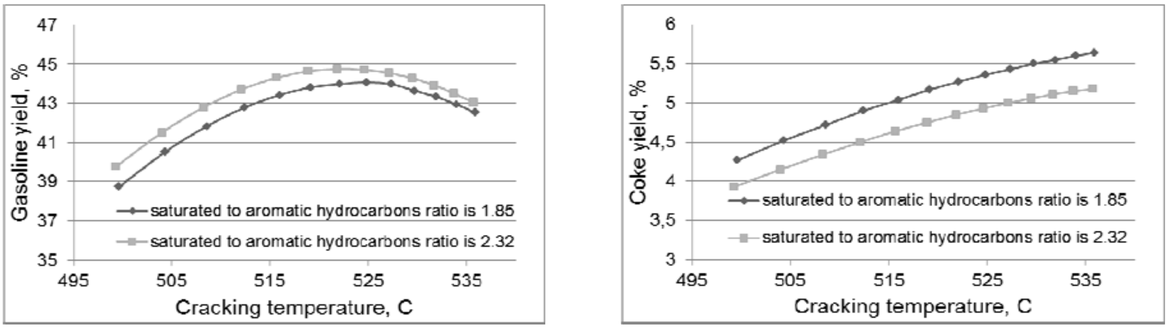

Fig. 1. Gasoline and coke yield depending on the cracking temperature

The change in the feedstock hydrocarbon composition and operating parameters of the catalytic cracking leads to the need for correction of the commercial gasoline recipes taking into account the volume and qualities changing of the catalytic cracking gasoline.

Table 2. Qualities of catalytic cracking gasoline

Parameter	Gasoline fraction 130-EBRafter overalcalinity		Gasoline fraction IBR-130	
	26.04.2017	27.04.2017	26.04.2017	27.04.2017
RON	94.40	95.41	96.17	98.19
Aromatics, %	64.44	66.09	10.61	11.07
Sulfur, wt %	0.00	0.00	0.06	0.06

The possibility of the involving a larger amount of the 70-95 °C fraction for AI-92-K-2 gasoline production is appeared (Table 3) due to increase of IBR-130 gasoline fraction RON (Table 2).

Table 3. The calculation recipe of AI-92-K-2 gasoline

Component	26.04.2017	27.04.2017	Parameter	Value
70-95 °C fraction	6.2	8.7	RON	92.01
Pentane-pentene fraction	2.9	2.8	MON	83.39
Butane-butylene fraction	2.1	2.1	Vapor pressure, kPa	81.15
C4 fraction raffinate	3.6	3.6	Density, kg/m^3	713.14
Heavy reformate	22.0	22.0	Benzene content, %	0.80
Gasoline fraction 130-EBR after overalcalinity	1.3	1.3	Aromatic HC, %	23.80
Gasoline fraction IBR-130	62.0	59.5	Sulphur content, %	0.0374
TOTALS	100.0	100.0		

Thus, the complex applying of catalytic cracking and fuels blending mathematical models allows to solve the problem of reducing the quality giveaway during the gasoline production of different grades.

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PP-13

MONOLITHIC MICROREACTORS OF DIFFERENT STRUCTURE AS AN EFFECTIVE TOOL FOR MPV REACTION

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The catalytic selective reduction of carbonyl compounds represents synthetic transformations, which are of primary importance in pharmaceutical, organics and fine-chemicals production. Meerwein-Ponndorf-Verley (MPV) reduction, traditionally carried out in slurry reactors under mild conditions, can be successfully transferred to continuous-flow system [1,2] with benefits including high productivity, better parameters control and process miniaturization. The MPV reduction via the hydrogen transfer mechanism, involves an intermediate complex, where a metal ion, acting as a Lewis acid, binds to the alkoxide and carbonyl compound. The reaction is reverse to the Oppenauer oxidation, and hence the formation of the products is favoured by optimizing process conditions, especially the catalyst loading and substrates molar ratio [3,4]. Zirconium due to its moderate acidity and reducing capabilities is often applied as a catalyst in the redox reactions [5].

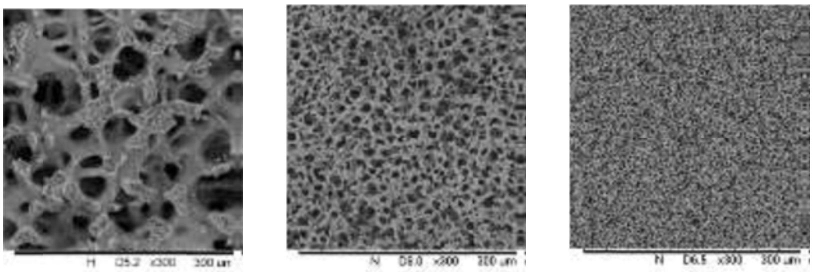

Fig. 1. SEM images of silica monoliths

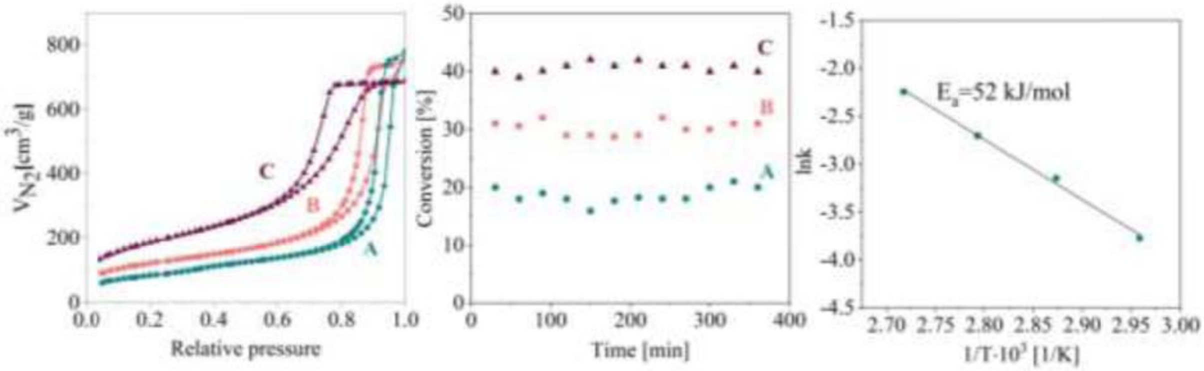

Fig. 2. Nitrogen adsorption/desorption isotherm of monoliths (a); conversion of cyclohexanone in 1 cm-long microreactors at 75 °C for constant flow rate in the reactors (b); Arrhenius plot (c)

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In this work, we compare the effectiveness of microreactors fabricated from silica monoliths functionalised with zirconium species coordinated by propoxy ligands. Three monoliths with significantly different structure and porosity were applied as reactive cores (Fig. 1, Fig. 2a). The flow-through channels of microreactors were shaped by interconnected macropores of diameters c.a. 30 μm, 10 μm and 3 μm. A large number of easily accessible catalytic centres was achieved due to the extensive network of mesopores present in the walls and struts of the silica carriers. The microreactors were studied in MPV reduction of cyclohexanone with 2-butanol. The experiments were performed in reactors of different length (1-8 cm) to obtain kinetic parameters. The significant impact of structure parameters on both, catalytic performance and flow characteristics was observed.

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CATALYTIC HEAT EXCHANGER TYPE MEMBRANE REACTOR FOR CO_2 HYDROGENATION: MODEL-BASED ANALYSIS AND FEASIBILITY ASSESSMENT

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Converting CO_2 into synthetic fuels is an attractive pathway to decrease CO_2 emissions and to reduce our dependence on fossil fuels. Thermocatalytic hydrogenation provides advantages of fast reaction rates and high conversion efficiencies, thus allowing for compact, high-throughput operation [1]. The most fundamental disadvantage is the requirement to supply a pure H_2 stream. Water electrolysis is a possibility (using renewable electricity), but this technology requires high capital and operation costs. This study assesses the feasibility of using H_2-containing renewable streams (e.g., biomass gasification gases) as a source of H_2 for the thermocatalytic CO_2 conversion into renewable natural gas via the Sabatier process ($CO_2 + 4H_2 = CH_4 + 2H_2O$). This process is highly exothermic and thermal management is a major drawback as efficient heat removal is required to drive CH_4 formation and suppress catalyst deactivation by carbon deposition [2, 3]. Herein, it is suggested to use a H_2-selective membrane to extract H_2 from a H_2-containing stream *in situ*, supplying H_2 along the catalytic bed in a distributed manner.

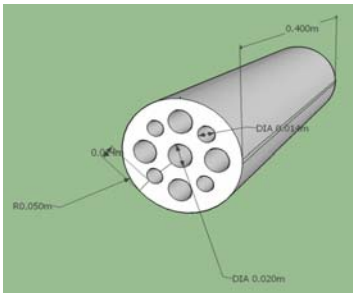

Figure 1. Schematic of the molten salt-cooled membrane Sabatier reactor

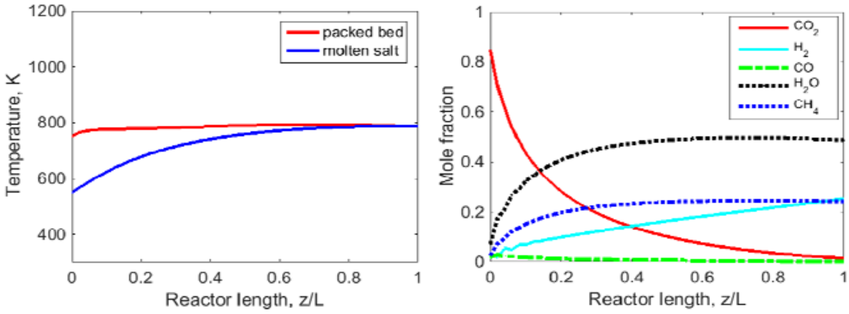

Figure 2. Simulated temperature (left) and mole fraction profiles (right) obtained after 2,000 h simulated time-on-stream ($P = 10$ bar; $T_f = 750$ K; $T_{f,MS} = 550$ K; $SV = 110$ 1/h)

A dynamic, non-isothermal model of the actively-cooled membrane reactor (**Figure 1**) was formulated and investigated via numerical simulations (**Figure 2**). The model accounts for the heat exchange between the reaction compartment and the cooling tubes, for the mass exchange through the H_2-selective membrane, as well as for catalyst deactivation.

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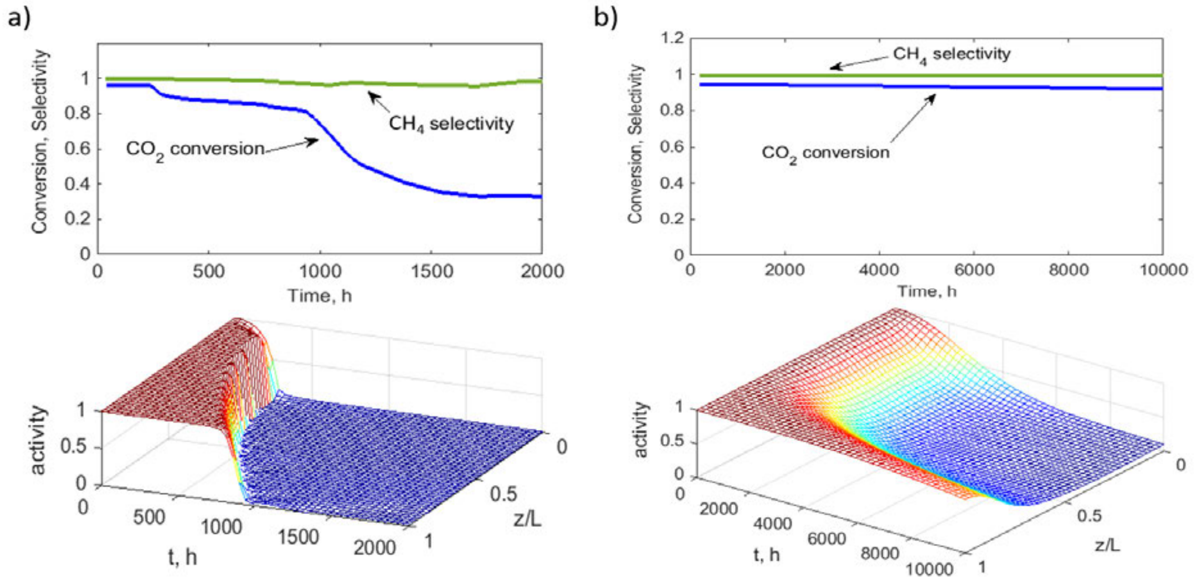

Figure 3. Simulated temporal evolution of CO_2 conversion and CH_4 selectivity (upper panels) and spatiotemporal profiles of the catalyst activity (lower panels) for the non-membrane (a) and membrane (b) operation

Typical temperature and mole fraction profiles are shown in **Figure 2**: Due to the distributed H_2 supply, CO_2 is gradually consumed, avoiding the hot spot formation in the catalytic bed and preventing CO formation. The outlet stream consists of CH_4, H_2O, and H_2. Comparison between the non-membrane and membrane cases is shown in **Figure 3**. Without the membrane (**Fig. 3a**), the model predicts severe deactivation with 70 % conversion drop after 2,000 h. When the membrane is introduced (**Fig. 3b**), no significant deactivation is observed even after 10,000 h (same CO_2 feed rate). Corresponding spatiotemporal profiles of the catalyst activity clearly demonstrate that the distributed H_2 supply suppresses the catalyst deactivation. Using the comprehensive model and numerical simulations, it has been demonstrated that the distributed H_2 supply through a membrane suppresses catalyst deactivation by coking in the Sabatier reactor.

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THE PROCESS DEVELOPMENT OF BAYERITE PREPARATION BY SELF-HYDROLYSIS OF ALUMINUM CHLORIDE HEXAHYDRATE IN BATCH REACTOR

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At present, alkaline technologies are used for the production of alumina from high-siliceous raw materials, mainly kaolinic. The proposed promising technologies based on acidic methods of processing kaolins and clays using sulfuric, hydrochloric and nitric acids are multi-stage and high-cost.

A feasibility study of aluminum chloride hydrothermal decomposition has been carried out for developing an ecologically safe integrated technology for obtaining alumina from high-silica raw materials and replacing the existing energy-consuming multi-stage high-temperature methods of aluminum chloride decomposition.

The advantages of the hydrothermal process for Al-O-H products production are:

1. One-step process;
2. Low power consumption;
3. Chemical and phase purity of the product;
4. Low level of aggregation;
5. The ability to control the size, morphology and structure;
6. The possibility of using this method for high-silica raw materials.

Our earlier studies of hydrothermal co-hydrolysis of aqueous solutions of aluminum chloride hexahydrate and carbamide showed the possibility of aluminum hydroxide (boehmite) synthesis with a yield of up to 99 % and with a chloride ion content 1.06 % in the dried up to constant mass boehmite. Carbamide was used as an additional component to accelerate the hydrolysis of aluminum chloride.

The resulting boehmite is of interest for various applications (catalysis, nanofiltration, aluminum production, etc.). However, for the creation of large tonnage processes (more than 10 million tons of alumina per year [3]), non-waste and reagent-free technologies are of particular interest.

In the present work, the process of aluminum oxyhydroxides obtaining by self-hydrolysis of aluminum chloride hexahydrate with the use of crystalline water is considered for the first time:

$$AlCl_3 \cdot 6H_2O \rightarrow Al(OH)_3 + 3HCl + 3H_2O$$

The process studies of aluminum hydroxide obtaining were conducted using a batch type autoclave at temperatures from 443 to 503 K at a pressure of 1.6-2.3 MPa with the variation of such parameters as temperature, pressure, residence time of the reaction mixture in the reactor, flow velocity of the displacing gas during hydrolysis; number of washes, time and rate of hydrothermal decomposition products centrifugation, time and temperature of aluminum hydroxide drying.

It was found that the main products of aluminum chloride hexahydrate hydrothermal decomposition are the solid phase of hydroxides (bayerite mainly) and aluminum oxychlorides with a total Cl content of not more than 4 %.

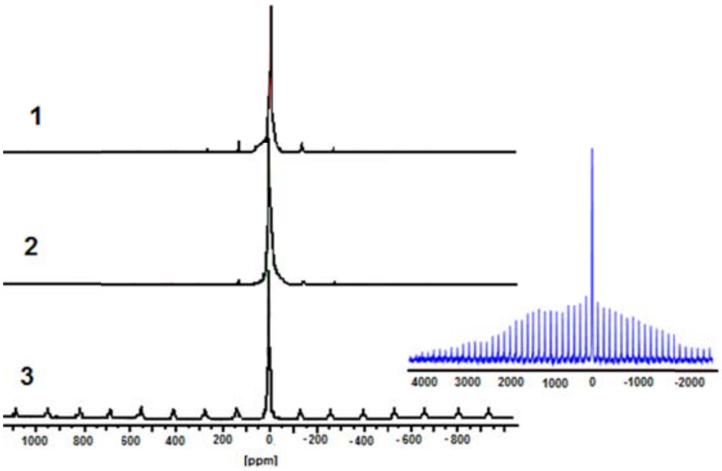

Fig. 1. The 27Al MAS NMR spectra were obtained with a Bruker Avance-400 spectrometer at 104.2 MHz.
1- all self-hydrolysis products;
2- insoluble part of self-hydrolysis products (almost pure bayerite);
3 – bayerite

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NUMERICAL SIMULATION OF BENZENE WITH ETHYLENE ALKYLATION CONSIDERING CATALYST DEACTIVATION

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Ethylbenzene is the key intermediate in styrene production, which is one of the most important industrial monomers. Despite the fact that the benzene alkylation process for ethylbenzene production has undergone significant improvements, all of them concern alkylation on zeolite catalysts. However, liquid acidic catalysts are still used and need to be improved.

In contrast to alkylation modeling and surveys on zeolite catalysts [1], there is much less information about approaches to improve and simulate the liquid acid-catalyzed units. In addition, all the existing mathematical models are steady and do not consider the catalyst deactivation. At the same time, the catalyst activity determines the product yield and quality, and its change modeling can become the instrument to its forecasting and regulation [2]. Previously, we have performed the research concerning the feasibility of mixing device reconstruction in order to intensify the reactants mixing during the $AlCl_3$ alkylation [3], without mathematical modeling of the alkylation. Now we intend to concentrate on improving the alkylation reactor performance with use of the developed computer modeling system considering the process unsteadiness

During the development of a mathematical model, the kinetic parameters [4] of the reactions found using quantum chemistry methods were refined using data from an operating industrial installation. Defined preexponential factor in the Arrhenius equation and activation energies of all the reactions were chosen in the solution of the inverse kinetic problem.

To solve the inverse kinetic problem, we used the experimental values of the substance concentrations at the inlet and outlet of the alkylator, and finally we estimated the kinetic parameters that provide minimal deviation between calculated and experimental data.

The present research investigates the possibility of obtaining this goal by developing the unsteady mathematical model considering the catalyst deactivation by heavy alkylaromatics. The reaction network is designed with due consideration of the desired and side reactions along with deactivating agents' formation and reflects the influence of the heavy hydrocarbons concentration on the catalyst activity. Decrease of the ethylbenzene concentration by 2-3 % wt. and increase of the polyalkylate outlet concentration by 1.5-2 % wt. stem from the catalyst deactivation. This can be compensated by the polyalkylate supply increasing to the reactor by 1.3 times and the temperature increasing up to 398 K. The performed calculations show that it is possible to decrease the fresh catalyst supply from 0.498 to 0.472 t/hour without losses in the ethylbenzene yield.

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INDUSTRIAL SYNTHESIS OF LINEAR ALKYLBENZENE SULFONIC ACID IN A MULTISTAGE REACTOR PROCESS UNDER NONSTATIONARY CONDITIONS

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Multistage industrial production of alkyl benzene sulfonic acid along with Pt and Ni catalysts use toxic catalysts based on aluminum chloride and HF. The object of the study is an industrial unit for synthesizing linear alkyl benzene sulphonic acid (ASA), including the stages of paraffins dehydrogenation, diolefins hydrogenation, alkylation of benzene with olefins, sulfonation of linear alkylbenzenes.

The efficiency of this industrial plant operation depends on the following factors:

- Technological regimes (dehydrogenation temperature, Pt catalyst activity, Ni catalyst activity (controlled by dimethyl disulfide DMDS consumption), HF catalyst activity)
- The composition of the feedstock – paraffins (the content of light aromatic compounds, which can be converted to unsaturated aromatic compounds during alkylation and high-viscosity homologues of tetraline during sulfonation).

To establish kinetic regularities and prognostic models of technological stages, we conducted the industrial experiment from October 7, 2017 to October 18, 2017 (Tab. 1).

Tab. 1. Industrial experiment calendar

Date	Conditions	Range	Experiment results
07.08-08.08	DMDS flow rate Hydrogenation temperature	1.5-2 ppm 191-188 °C	Output diolefins concentration: 0.1 wt. %
09.10-14.10	Temperature increase Hydrogen gaze flow rate DMDS concentration	188-194 °C 40-41,3 th. m^3/h 2-6 ppm.	The concentration of diolefins increased from to 0.2 wt. %
15.10-18.10	Temperature increase Hydrogen gaze flow rate DMDS concentration	194-197 °C 41,3-45 th. m^3/h 6-2,3 ppm.	The concentration of diolefins decreased back from 0.2 to 0.1 wt. %

The developed prognostic models of dehydrogenation hydrogenation, alkylation and sulfonation processes for the ASA synthesis considering the technological links between the devices, allow determining and changing the modes at any stage of ASA production with the changing composition of the raw materials. The results of the experiment are compared with calculations on mathematical models, Tab. 2.

Tab. 2. Adequacy of the mathematical models during the industrial experiment

	Olefines after deh. (calc.) wt. %	Olefines after deh. (exp.) wt. %	Diolefines after deh. (calc.) wt. %	Diolefines after deh. (exp.) wt. %	Diolefines after hyd. (calc.) wt. %	Diolefines after hyd. (exp.) wt. %
07.10.17	8.01	8.2	0.58	0.6	0.06	0.1
08.10.17	8.37	8.3	0.61	0.6	0.12	0.1
10.10.17	8.4	8.48	0.53	0.54	0.16	0.18
11.10.17	8.44	8.44	0.56	0.56	0.17	0.17
14.10.17	8.45	8.31	0.6	0.58	0.24	0.21
15.10.17	8.11	8.11	0.58	0.58	0.21	0.21
16.10.17	8.27	8.06	0.59	0.56	0.16	0.14

According to data presented in Tab. 2, during the industrial experiment, the calculated and experimental data on such key parameters as the content of olefins and diolefins after the dehydrogenation and hydrogenation reactors are in good agreement. This, in turn, allows using the developed mathematical models to recommend optimal regimes at the subsequent technological stages - alkylation and sulfonation, considering the heavy aromatic compounds formed (Fig. 1).

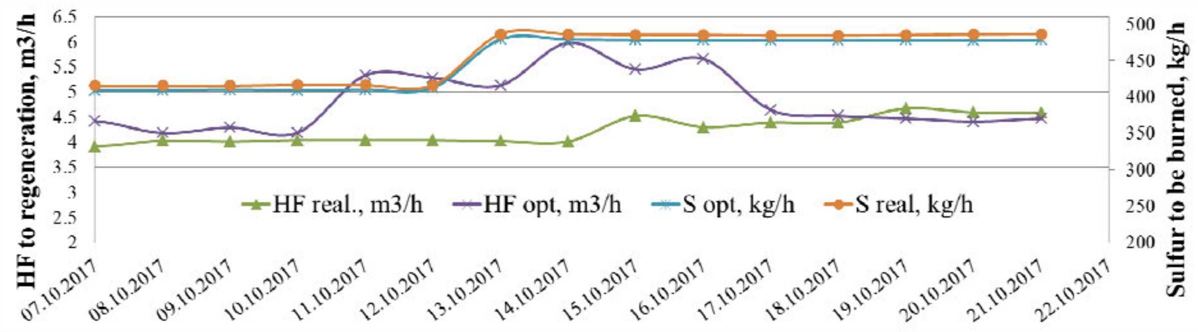

Fig. 1. Results of optimization calculations using mathematical models

From Fig. 2 it stems that in order to achieve the maximum ASA production efficiency, the alkylation and sulfonation regimes must be combined with the dehydrogenation and hydrogenation regimes. Considering the change in the concentration of diolefins after dehydrogenation and hydrogenation reactor (Tab. 2), performed with the use of the adequate mathematical models of technologically coupled stages, allows correcting the HF flow rate to regenerator and amount of sulfur to be burned.

Acknowledgements

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COMPLEX CONVERSION OF BIOMASS OVER POLYMER-BASED CATALYSTS FOR THE PRODUCTION OF SECOND-GENERATION BIODERIVED FUELS

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As the existing renewable energy sources (i.e. wind power, solar energy, hydro- and geo-energy) are suitable for the production of electricity, the problem of the proper alternative to the fossil liquid fuel remains one of the major problems. Nowadays, the use of liquid fuel accounts a half of the total energy consumption. Thus, the modern tendencies in the production of alternative ecologically clean fuels are focused on the biomass conversion processes [1]. The main vegetable biomass components are cellulose, hemicelluloses, lignin, triglycerides etc. As the biomass contains the compounds with a different structure, it can be a source to obtain different fuel components as well as various bulk materials [2]. Among the processes used for the biomass conversion, hydrogenolysis [3-5], hydrodeoxygenation [6, 7] and hydrogenation [8-10] are the most studied in last decades. In the current work, we report the use of catalysts based on the noble metals impregnated in the polymeric matrix of the hypercrosslinked polystyrene (HPS) in the processes of lignocellulosic biomass conversion into the fuel components.

HPS-based catalysts were synthesized via conventional wet-impregnation method according to the procedure described elsewhere [11] upon variation of the HPS type (MN100 or MN270). Ruthenium (IV) hydroxochloride ($Ru(OH)Cl_3$) was used as a metal precursor for the catalyst synthesis. The resulted catalysts were reduced with hydrogen at 300 °C for 2 hours. The catalysts were characterized by the TEM, XPS, XFA, TGA and low-temperature nitrogen physisorption. The processes of biomass conversion were studied using the model compounds such as alkali lignin, cellulose, levulinic acid. All the experiments were carried out in high-pressure stainless steel batch reactor (50 cm^3, Parr Instrument, USA) under the hydrogen atmosphere in a water medium. The analysis of the reaction products was performed by HPLC.

The results of the catalysts characterization are presented in Table 1. It was shown that the use of the polymeric matrix of HPS allows formation of small nanoparticles in the pores of the support. The mean particle size was found to be less than 5 nm. It is noteworthy that the presence of amino groups in the polymer structure allows decreasing particle size by 3 times.

Table 1. The results of catalyst characterization

Sample	Surface area			Ru particle size, nm	Ru content calculated by XFA, %	Ru state
	Langmuir	BET	t-plot			
	S_L,^{a} m^2/g	S_{BET},^{b} m^2/g	S_t^{c}, m^2/g			
HPS-MN-270	1500	1420	295^d 1140^e	-	-	-
HPS-MN-100	840	730	200^d, 590^e	-	-	-
3%-Ru/HPS-MN-270	1270	1180	250^d, 990^e	4.3 ± 0.7	2.8	RuO_2
3%-Ru/HPS-MN-100	890	740	195^d, 600^e	1.2 ± 0.2	2.9	RuO_2

Testing of synthesized Ru/HPS samples in the processes of cellulose hydrogenolysis, hydrogenation of levulinic acid and hydrogenolysis of lignin showed that the activity of the catalyst based on non-functionalized HPS-MN270 was in 1.5-2 times lower than the activity of the catalyst based on HPS containing amino groups HPS-MN100 in all the studied processes. The high efficiency of the catalyst is connected with the combination of the high specific surface area; narrow pore size distribution, and small monodisperse Ru nanoparticles as well as the presence of the additional acid-base active sites providing by the presence of amino groups.

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HYDROGEN PRODUCTION FROM METHANE OVER ALUMINA SUPPORTED NICKEL CATALYST

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The chemical industry is one of the main consumers of natural gas. Natural gas used for producing hydrogen, ammonia, methanol, acetylene, higher alcohols, etc. [1]. Hydrogen is the main intermediate product in the production of ammonia, methanol, synthetic fuels, with deep oil refining and the production of high-octane motor fuel. H_2 also used in the pharmaceutical, metallurgy, aviation and other industries [2]. There are several methods of catalytic methane conversion to synthesis gas and hydrogen – steam reforming [3], partial oxidation [4], carbon dioxide conversion [5], combined oxidation, etc. [6].

The concepts of combined methane oxidation for the production of hydrogen, which is a synergistic combination of steam and carbon dioxide reforming with partial oxidation of methane on one catalyst and on a single reactor, have been developed in recent years [7].

In this paper the effect of the ratio of the initial reagent (CH_4, CO_2, O_2, H_2O) was studied to produce hydrogen on a nickel-containing catalyst supported on alumina.

Experiments on testing the efficiency of catalysts were carried out on an automated flow-through catalytic unit (PKU-1). The reaction products were identified chromatographically on a "CHROMOS GX-1000" instrument using the absolute calibration method and thermal conductivity detectors.

The table gives data on the effect of the ratio CH_4: CO_2: O_2: H_2O on the process of tri-reforming of methane on a 3 % NiO – 1 % MoO_3 / γ-Al_2O_3 catalyst at a reaction temperature of 850 °C and a space velocity of 1000 h^{-1}.

From the results presented in the Table it is seen that a change in the ratio of components in the initial reaction mixture leads to a slight change in methane conversion, but it significantly affects the conversion of carbon dioxide and hydrogen concentrations.

Table 1. Influence of the ratio CH_4: CO_2: O_2: H_2O of the initial reaction mixture on the direction of the process

Ratio CH_4:CO_2:O_2:H_2O	XCH_4, %	XCO_2, %	CH_2, vol. %
2 : 2 : 1 : 0.5	98.0	81.0	52.0
2 :1 : 1 : 1	97.0	79.5	53.0
2 : 1 : 0.5 : 1	98.0	90.0	59.0
1 : 0.5 : 0.1 : 1	99.0	86.0	52.8
3 : 1 : 0.5 : 1	96.0	62.0	56.2

The optimal ratio of the initial components is the composition CH_4: CO_2: O_2: H_2O = 2 : 1 : 0.5 : 1. At this reagent ratio, the vapors of water and oxygen are converted completely, and the greatest conversions of CH_4 = 98 % and CO_2 = 90 % and the concentration of the formed H_2-59 vol. %.

Thus, under the reaction conditions ($CH_4 : CO_2 : O_2 : H_2O = 2 : 1 : 0.5 : 1$, Tr = 850 °C and W = 1000 h^{-1}) on the promoted 3 % NiO – 1 % MoO_3 / γ-Al_2O_3 catalyst the hydrogen concentration is reached up to 59 % by volume, with the conversion of methane 98 % and carbon dioxide 90 %.

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BOOSTING GASOLINE AND DIESEL PRODUCTION BY 1-BUTENE OLIGOMERIZATION ON HZSM-5 ZEOLITES

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The petrochemical industry faces the challenge to meet the growing demand of automotive fuels and the increasing environmental restrictions. In this sense, the oligomerization of light olefins (ethene, propene and butene) is becoming an attractive alternative to produce environmental friendly liquid fuels, free of sulfur and aromatics [1], since olefinic raw materials can be obtained from sources alternative to oil, such as methanol and DME, via MTO and DTO processes [2]. Furthermore, the demand of butenes has decreased due to the lower production of MtBE, which gives way to the valorization of this olefinic stream into high demanded liquid fuels.

Olefin oligomerization implies a complex reaction mechanism where catalyst properties and reaction conditions will affect the polymerization degree, levels of branched chain and the proportion of gasoline and diesel in product distribution. In order to contribute to a better understanding of this reaction mechanism, in this work HZSM-5 zeolites of different SiO_2/Al_2O_3 ratio have been studied in a wide range of operating conditions (pressure and temperature) with the aim of maximizing gasoline (C_5-C_{11}) and diesel (C_{12}-C_{20}) selectivity and yield. Special attention has been paid to the stability of the catalyst, since the attenuation of coke deactivation is a key factor for the process viability.

The catalysts studied are based on HZSM-5 zeolites (supplied by Zeolyst Int.) with different SiO_2/Al_2O_3 ratio (30-280). Zeolites have been agglomerated with pseudobohemite (30 wt. %) as binder and α-alumina (20 wt. %) as inert charge, which confers a matrix with meso-and macropore structure to the catalyst. Fresh and deactivated catalysts were characterized by N_2 adsorption-desorption, DSC-TPD of ammonia and FTIR of pyridine. The coke content deposited on the catalysts was determined by TPO.

Runs were performed in an isothermal fixed bed reactor under the following conditions: pressure, 1.5-40 bar; temperature, 250-275 °C; 1-butene partial pressure 70 %; space time 2-6 (g of catalyst h)$\cdot$(mol CH_2)$^{-1}$; time on stream, 10-20 h. Gas products were analyzed on-line in a gas chromatograph (Micro-GC Agilent 3000A), and the liquids obtained during the reaction were analyzed by GC x GC and by Simulated Distillation (SIMDIST).

As an example of the results obtained, Figure 1a shows the effect of SiO_2/Al_2O_3 ratio on 1-butene conversion and product yield at 1.5 bar and 275 °C (graph a) and at 40 bar and 250 °C (graph b). In general terms, gasoline yield is favored at low pressures, whereas jet fuel and diesel production is enhanced at high pressures and mild temperatures. It should be noted that catalyst acidity plays an important role in the oligomerization of 1-butene: an increase in SiO_2/Al_2O_3 ratio entails a decrease in 1-butene conversion and consequently a decrease in diesel and gasoline selectivity. HZ-30 shows the best performance in the wide range of operating conditions studied maintaining a high catalyts activity after 20 h of TOS.

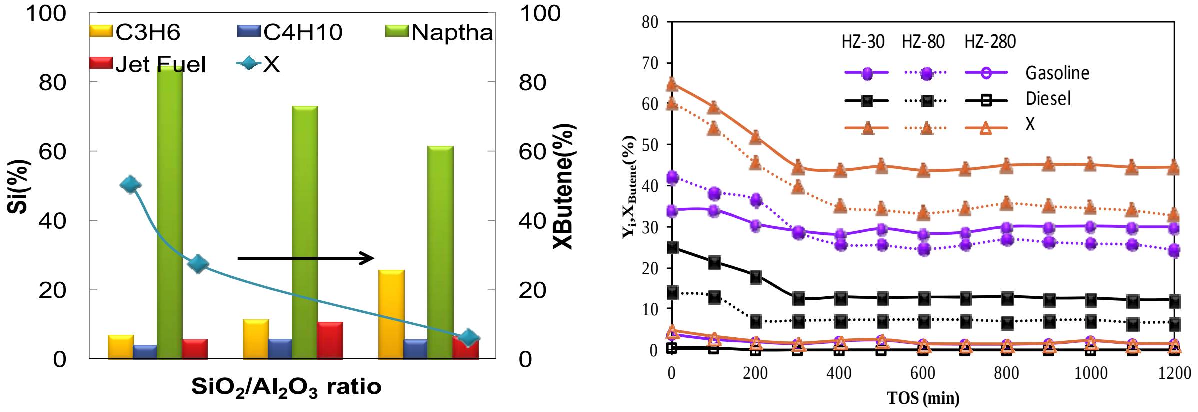

Figure 1. (a) Evolution of 1-butene conversion and product selectivity with SiO_2/Al_2O_3 ratio at zero time on stream (275 °C, 1.5 bar). (b) Evolution with time on stream of 1-butene conversion and diesel and gasoline yield on HZSM-5 catalysts (250 °C, 40 bar)

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ANALYSIS OF CORROSION PROCESSES KINETICS ON THE SURFACE OF METALS

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Among the non-destructive testing methods for corrosion monitoring [1-4] are scanning reflectometry, confocal microscopy, optical microscopy, ultrasonic inspection, laser scanning microscopy, acoustic emission, vibration analysis, etc. Due to the ease of monitoring, visual inspection is still employed Due to the ease of monitoring, visual inspection is still employed with satisfactory results because it informs about the type and extent of the corrosion. Due to the ease of monitoring, visual inspection is still employed because it informs about the type and level of the corrosion. However, visual inspection has subjective criteria.

The most part of the works connected with detection of corrosion effects by methods of computer vision analyzes cracks and pittings. Studying of pitting corrosion of stainless steel in $FeCl_3$ solution became one of the initial experience with computer vision for the metals corrosion research [5]. In [6] other method of metal corrosion identification based on a minimum distance between the recognition objects is presented.

The study of corrosion processes using computer vision methods involves four interconnected processes that create the prerequisites for the creation of data-processing system:

1. Accumulation of experimental data (corroded surface images), which require ordering, structuring and classification for correct use when solving the problem of classifier training.
2. Development of information processing methods depending on the type of problem being solved. In this case, it is the use of image processing methods, mathematical statistics and fractal analysis to evaluate and predict corrosion processes for various types of metals (steel, iron and aluminum).
3. Updating the technical means of processing information, increasing the calculations speed (using graphics processors).

4. Implementation of automatic systems of scientific research in the form of software packages and training of the end user (researcher).

These operations are specific to each problem of computer vision. Development and use of the models suitable for the effective solution of a object detection and recognition problems, substantially remains on the verge of science and art. The solution of this problem requires a special know-how or, in other words, knowledge of subject domain reflecting long-term experience of a research on the solution of specific tasks. In more detail this task is considered in work [7].

In this paper, we study the results obtained with the help of the created information-computational analytical system (ICAS) for estimating and predicting corrosion ("CorOcenka"). The main results based on the use of ICAS are listed.

The paper considers the main aspects of image processing and analysis in the studying the corrosion damage mechanism:

- The computer vision and image processing in the problem of detecting bubbles on the aluminum surface are developed;
- The general regularity of corrosion data processing on a aluminum surface is defined;
- The described algorithms are used for detection and recognition of corrosion damage for an aluminum sample by observing the intensity of hydrogen bubbles formation;
- The trained classifier was successfully applied to study several experiments of corrosion on the aluminum surface.

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KINETIC MODEL CONSIDERING CATALYST DEACTIVATION FOR THE TRANSFORMATION OF 1-BUTENE ON K/HZSM-5 ZEOLITE

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Light olefin (ethylene and butenes) interconversion is a process with a growing interest for adjusting each olefin production to the market requirements. The current increasing demand for propylene is boosting the implementation of new processes, as are propane dehydrogenation, metathesis, selective olefin cracking, and methanol to propylene (MTP), among others [1]. This work explores the transformation of 1-butene, as it is also formed in the catalytic processes for light olefin production, of lower demand than ethylene and propylene due to the decrease in methyl-tert-buthyl ether (MtBE). To improve the propylene selectivity it is helpful to develop a kinetic model for light olefin interconversion, which takes place over acid catalysts by the classical mechanism of oligomerization-cracking. In our previous work [2] a zero-time kinetic model of five lumps (ethylene, propylene, butenes, C_{1-4} paraffins and C_{5+} hydrocarbons including aromatics) was established for the transformation of 1-butene on a HZSM-5 zeolite catalyst (SiO_2/Al_2O_3 ratio of 280) modified with 1 wt % of K (of moderate acidity). The model was able to predict a product distribution that fits the experimental results in a wide range of operating conditions: 400-600 °C, space time up to 1.6 $g_{catalyst}$ (h mol_{CH2})$^{-1}$ and 1-butene partial pressure, 0.375-1.35 bar. The aim of this current work is to complement the zero-time kinetic model by proposing a kinetic equation for the catalyst deactivation by coke deposition, in order to correctly simulate the reactor and to better understand the initial stages of catalyst deactivation in the transformation of 1-butene.

The methodology for the kinetic study assumed that all the catalytic reactions of the kinetic scheme were equally affected by the decrease in catalyst activity (i.e., non-selective deactivation model). The proposed kinetic equations of deactivation and the kinetic parameters are summarized in Table 1. Discrimination of equations and the calculation of the best-fit kinetic parameters was carried out by multiple nonlinear regressions in a calculation program in MATLAB. This program solves the kinetic equations of deactivation together with the mass balances of all the compounds of the reaction scheme [3].

Table 1. Proposed kinetic equations of deactivation and best-fit kinetic parameters

Model	Deactivation equation	k_{d1}	k_{d2}	E_{a1}	E_{a2}
MD1	$-\frac{da}{dt}=k_{d1}(p_{C3=}+p_{C4=}+p_{C2=}+p_{C5+})$	0.082	-	41.88	-
MD2	$-\frac{da}{dt}=k_{d1}(p_{C3=}+p_{C4=})+k_{d2}(p_{C2=}+p_{C5+})$	0.017	0.648	44.77	53.88

where a is the activity, k_d, deactivation kinetic constant, p_i, partial pressure of compound i (atm), and, E_a, activation energy (kJ mol^{-1}).

The analysis of variances demostrated that the best-fit kinetic equation of deactivation is the one proposed in MD2, where ethylene and C_{5+} hydrocarbons have a higher contribution to catalyst deactivation in comparison to propylene and butenes. In addition, as shown in Figure 1, the proposed equations adequately predicts the influence of reaction temperature and space-time on the catalyst deactivation.

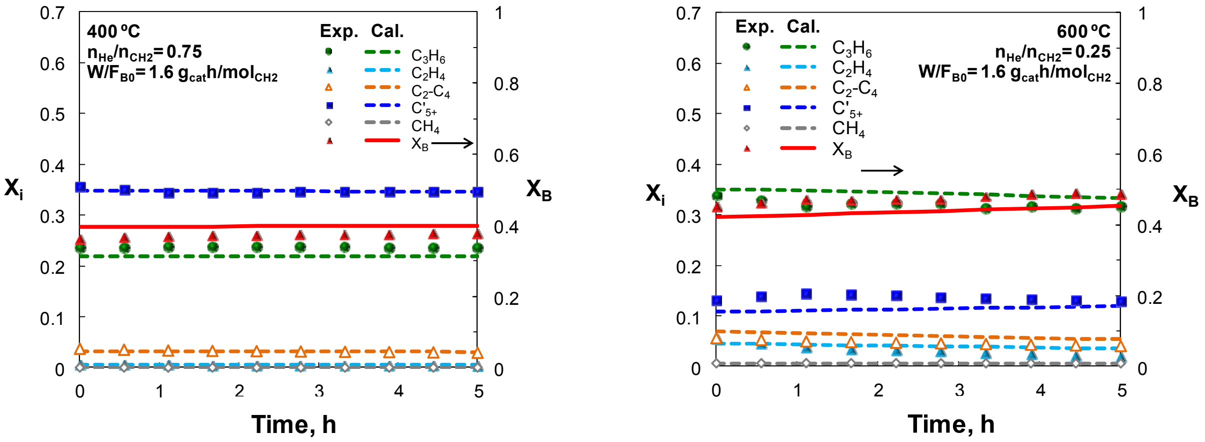

Figure 1. Comparison of experimental values (points) with those calculated using the kinetic model including catalyst deactivation (lines) at different operating conditions

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PYROLYSIS OF A MIXTURE OF MONOSILANE AND ALKANES IN A COMPRESSION REACTOR TO PRODUCE NANODISPERSED SILICON CARBIDE

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The development of new approaches to the design of electronic components with high performance characteristics is accompanied by the search for nanoscale materials with unique physicochemical properties. Silicon carbides as functional materials are interesting initially, however, despite the large number of works, the problem of obtaining nanosized silicon carbide with the required parameters in terms of purity, dispersion, productivity and other characteristics remains relevant.

There are a number of methods for obtaining nanoscale silicon carbide: sol-gel method [1], laser pyrolysis [2], self-propagating high-temperature synthesis [3], plasma chemical method [4], adiabatic compression method [5]. The disadvantage of these methods is low productivity, the difficulty of scaling and the need to use expensive unique equipment, as a result of which the cost of nanoscale powders increases.

In the proposed method for obtaining nanodispersed silicon carbide for pyrolysis of initial reagents-a mixture of gases SiH_4, Ar and light hydrocarbons, a cyclic compression method is used in the volume of a chemical reactor. The chemical compression reactor used is described quite fully in [6-7].

The composition of the reaction gas mixture was kept close to the stoichiometric, various light hydrocarbons were used – pentane, a mixture of pentane and butane, etc. The passage of the SiC synthesis reaction was monitored on-line using a universal gas analyzer UGA-200. The samples were characterized by HRTEM electron microscope JEM-2010, equipped with EDS spectrometer «QUANTAX 200-TEM» for local elemental analysis. In Fig. 1 shows typical electron-microscopic images of the morphology and structure of the obtained samples Dimensions silicon carbide particles are in the range 10-40 nm. The observed interplanar distances correspond to silicon carbide from the RFA database.

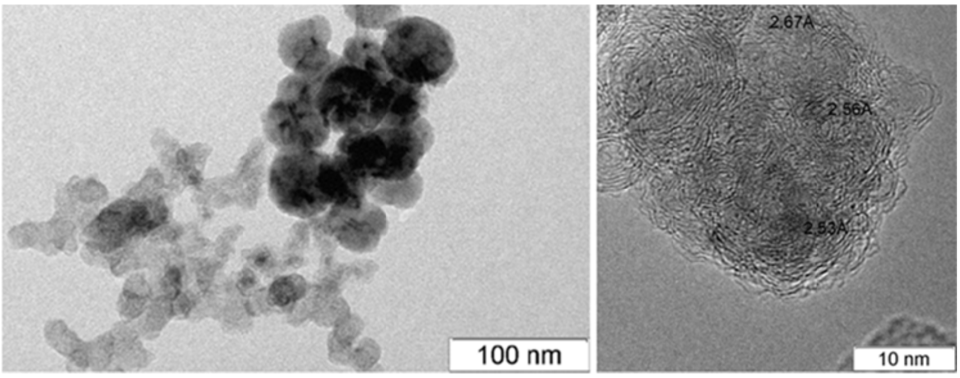

Fig. 1. Electron microscopic images of particles of a sample of nanodispersed silicon carbide

The proposed method for obtaining nanoscale silicon carbide is convenient for technological execution. The process is cyclical and fully automatic. The degree of processing of the reagents is high reaching almost complete. The product obtained during the synthesis of nanoscale SiC is chemically pure and is determined only by the degree of purification of the initial reagents, technological processes do not add additional impurities to the product. The resulting product does not require further processing, as in most of the proposed methods and is ready for use in technologies and tasks of materials science.

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THE STUDY OF COKE FORMATION IN MODELING THE DEHYDROGENATION OF HYDROCARBONS C9-C14

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The process of dehydrogenation of C9-C14 hydrocarbons allows the production of olefins used for the production of linear alkylbenzenes. One of the factors reducing the concentration of the desired product is the deactivation of the catalyst resulting from the formation of coke on its surface. The process of coke formation is affected not only by the technological parameters of the process (temperature regime, pressure, molar ratio of hydrogen / feedstock), but also by the structure of the catalyst. The aim of the work was to evaluate the influence of technological parameters and the type of dehydrogenation catalyst on the coke structure for describing the coke formation process in modeling the dehydrogenation of C9-C14 hydrocarbons. Five commodity cycles were considered (Table 1).

Table 1. Basic parameters of feed cycles

Cycle	Duration, days	Catalyst	T, C	P, MPa	I	Olefin yield, % wt.	Coke, % wt.	Water, l / h
1	32	КД-1	472-495	0,2	7/1	8,68	6,41	9,0
2	243	КД-2	468-487	0,19	7/1	8,71	2,53	9,0
3	280	КД-3	469-487	0,19	7/1	8,77	0,8	4,0-9,0
4	384	КД-3	469-487	0,18-0,20	7/1; 7,5/1; 8/1	8,65	0,89	4,0-9,0
5	432	КД-3	470-489	0,17-0,19	7/1; 6/1	8,82	1,51	4,0-14,0

The analysis of the working cycles of dehydrogenation catalysts showed that the greatest amount of coke is formed on the surface of catalysts of grades KD-1 and KD-2 in comparison with KD-3, which is caused by different catalyst structure and technological regimes. This is primarily due to a decrease in pressure in the reactor (cycles CD-2 and CD-3), as well as with a lower molar ratio (cycle 5). The decrease in pressure and the molar ratio promotes a shift in the equilibrium of the dehydrogenation reaction towards the formation of the desired product.

To determine the structure of coke formed as a result of the feedstock cycle, a thermogravimetric analysis of five catalyst samples was carried out (Table 2). From the thermograms obtained it was found that only coke of amorphous nature was formed on all catalysts (the H / C ratio should be in the range 0.2-2.0), as evidenced by the peak of the heat flux in the temperature range (450-660 °C).

Table 2. Thermal effect of combustion reactions of amorphous coke

Cycle	1	2	3	4	5
Catalyst	KD-1	KD-2	KD-3	KD-4	KD-5
Burning temperature, °C	189,6	194,31	192	392	384,5
Thermal effect, J/g	20168	10764	10140	548,5	1335

Earlier, the authors of [1] found that the ratio of H / C is 0.5 and the resulting coke has a hexagonal coronene structure, which was used in describing the coke formation in the model of the dehydrogenation of C9-C14 hydrocarbons.

To determine the H / C ratio, a thermodynamic analysis of the combustion reactions of carbon and hydrogen was carried out at the start of combustion of amorphous coke, provided that the number of carbon atoms in the coke molecule remains equal to 28 (Table 3).

Table 3. H/C ratio in the coke molecule

Cycle	1	2	3	4	5
Catalyst	KD-1	KD-2	KD-3	KD-4	KD-5
n_1 (H)	17,61	16,94	16,03	14,23	14,34
n_2 (C)	28	28	28	28	28
Molar Rate H/C (n_1/n_2)	0,63	0,61	0,60	0,51	0,51

The results of the calculation confirmed that the coke formed on the surface of the catalysts is of an amorphous nature, and the change in the H / C ratio in different cycles is related to the technological modes of operation and the composition of the catalysts of the grades.

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PP-25

TRANSPORT PHENOMENA IN RVC FOAMS

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Reticulated Vitreous Carbon (RVC) foams have many interesting properties like high thermal and electric conductivity, low density and thermal expansion, very good resistance to many corrosive media, high operating temperature (up to 3500 °C in inert environment), high porosity and specific surface area. RVC foams can be applied in numerous processes playing role of structured catalyst (biocatalyst) carrier, structure enhancing heat (mass) transfer, structured 3D electrode [1, 2]. Application to the above processes requires however knowledge of the morphological parameters (porosity, specific surface area), as well as the heat, mass and momentum transfer characteristics, which determination is the aim of this work.

The tests were done for three RVC foams (ERG Materials and Aerospace Corp.) of different pore density. The basic morphological parameters (Fig. 1A) were determined by micro-computed tomography and optical microscopy and are presented in Table 1.

Table 1. Morphological parameters of the RVC foams studied

Parameter	RVC 30 PPI	RVC 80 PPI	RVC 100 PPI
inner (skeleton) porosity, ε_{in} [%]	0.38	0.51	0.36
cell diameter, d_c [mm]	3.08	0.58	0.56
window diameter, d_w [mm]	1.16	0.23	0.22
strut diameter, d_s [mm]	0.307	0.054	0.047
open (external) porosity, ε [%]	96	96	96
specific surface area, S_v [m^2/m^3]	1223	3557	4154

Flow resistance (Fig. 1B) and heat transfer (Fig. 1C) were determined. While the flow resistance, $\Delta P/H$, increase with the PPI number (i.e. when decreasing the cell, window and strut dimensions) the Nusselt number, Nu, is almost the same for all the foams tested, i.e. independent of the foams' skeleton dimensions.

Based on the transport characteristics, the governing flow mechanism through foam samples was determined. Two possible flow mechanisms were considered, namely flow around an immersed solid body (foam struts) modelled as sphere or cylinder and developing laminar flow in a short capillary channel (foam cell). The best agreement was found for the flow around a sphere with diameter equal to the strut dimension (Fig. 1C) as was also found for metal foams [3]. A bit worse compatibility was observed for the flow through a short channel with diameter equal to the cell diameter and length equal to strut thickness [4].

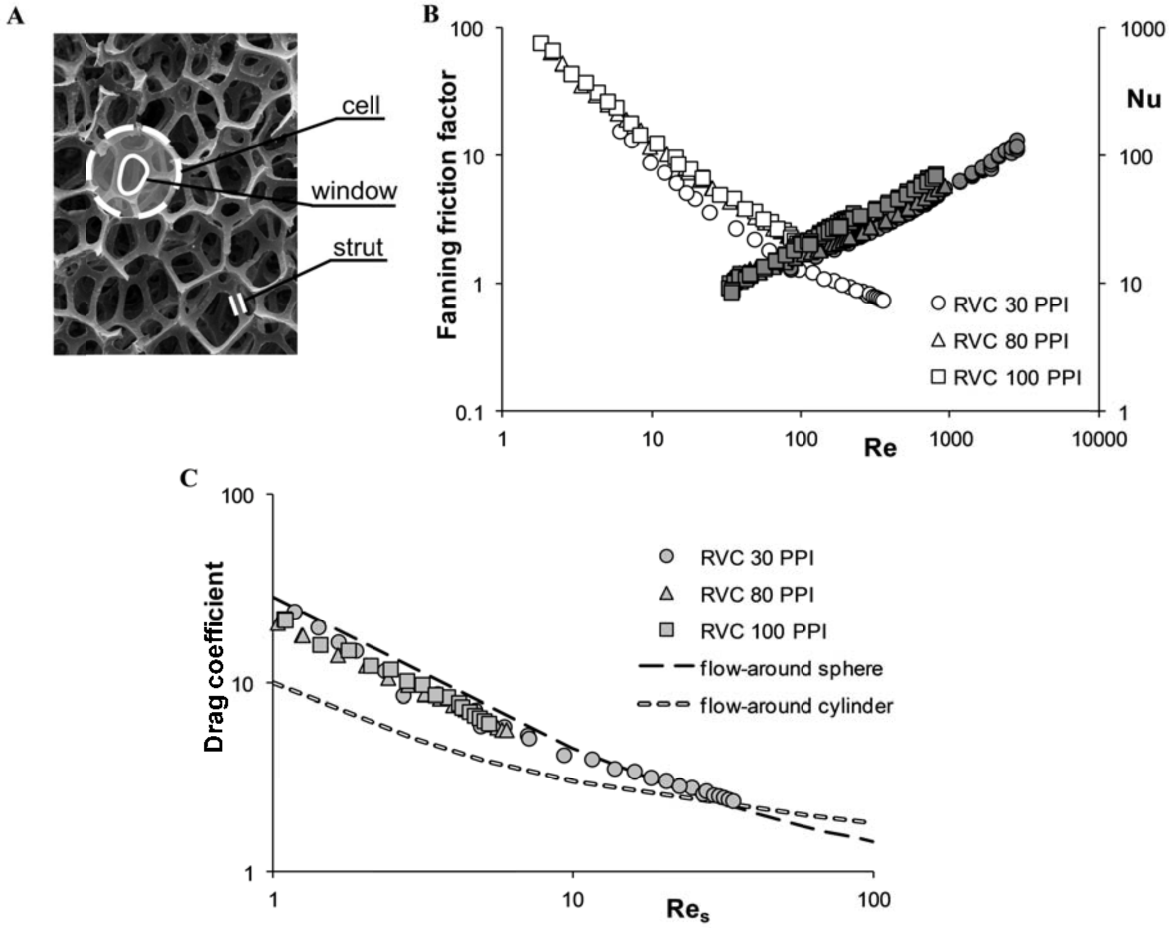

Fig. 1. A – image of RVC 100 PPI foam, B – Fanning friction factor (white points) and Nusselt number (gray points) vs Reynolds number, C – drag coefficient vs Re number (defined with strut diameter)

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A REACTION-DIFFUSION MODEL FOR BRIDGING BETWEEN ZEOLITES AND CATALYST PELLETS IN MTO PROCESS

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Methanol-to-olefins (MTO) has received considerable attention since 1970s due to its importance in the production of light olefins from resources other than oil. Despite significant progress in fundamental research in the past decades, a recent milestone is that in 2010 the world's first commercial MTO unit based on the fluidized bed reactor-regenerator configuration was successfully commissioned in north China [1]. This stimulated the rapid development of coal to chemicals industry in China.

In commercial MTO units, catalyst pellets used is exclusively based on SAPO-34 zeolites. As shown in Figure 1(A), MTO catalyst pellets are comprised of SAPO-34 zeolites (micro-pores) and agglomerate, which results in different pore sizes. In the present study, we first compared the reaction results between SAPO-34 zeolites and catalyst pellets. Notably, as can be seen from Figure 1(B), under equal acid amount conditions, the catalytic lifetime of catalyst pellets is observably longer than SAPO-34 zeolites. Considering in the catalyst pellets, agglomerate consists of meso-pores and macro-pores, where the bulk diffusion combined with Knudsen diffusion dominate [2]. Obviously, the modeling approach capable of addressing the effect of macro/meso-pores on discrepancies of reaction results between catalyst pellets and zeolites remains a non-trivial task, and is the goal of this manuscript.

In our reaction-diffusion model, the reaction kinetics was based on the dual-cycle mechanism based on SAPO-34 zeolites [3] while the diffusion was modeled by Maxwell-Stefan equation. The diffusion coefficients for methanol and major product over SAPO-34 zeolites and catalyst pellets were first measured under relatively low temperature range through sorption kinetics method by use of IGA. The MTO reaction experiments were carried out in fixed-bed quartz tubular reactor.

Figure 1(C) compared the diffusion coefficients of methanol between SAPO-34 zeolites and catalyst pellets. Due to the macro/meso-pores in catalyst pellets, the diffusion coefficients of methanol in catalyst pellets is almost 10 times faster than in SAPO-34 zeolites. Based on the diffusion coefficients and reaction results over

SAPO-34 zeolites, we first obtained kinetic parameters in zeolites level. Then based on diffusion coefficients over catalyst pellets and kinetic parameters from SAPO-34 zeolites, the reaction results of catalyst pellets could be simulated. Figure 1(D) compared the simulation results with experimental data, which shows a good aggreement. Due to the acceleration of mass transfer in catalyst pellets, which reduces the restitution time of products and retards the coke formation.

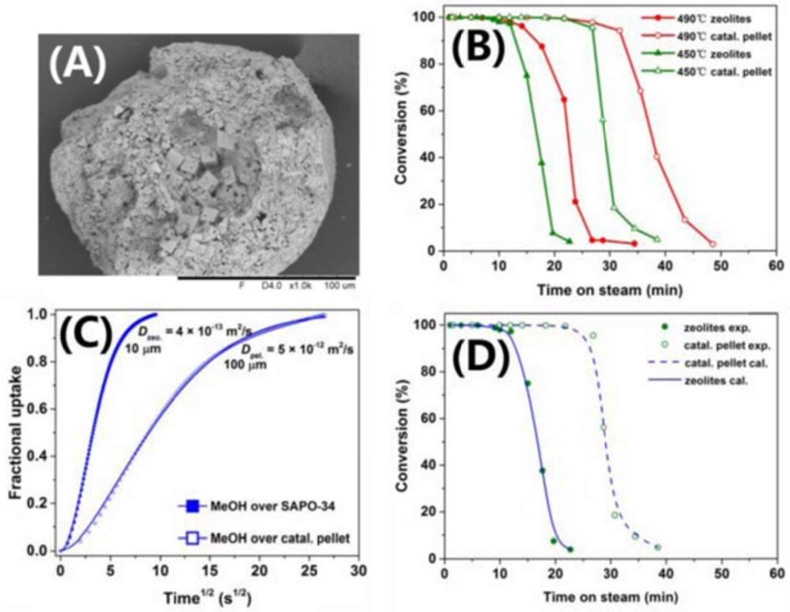

Figure 1. (A) Commercial MTO catalyst pellet; (B) Comparison between reaction results of zeolites and catalyst pellets; (C) Diffusion coefficients of methanol over zeolites and catalyst pellets; (D) Comparison between simulation results and experimental results

In the present study, a reaction-diffusion model bridging between SAPO-34 zeolites and catalyst pellets in MTO was developed, in which the reaction kinetics was based on the dual-cycle mechanism over zeolites, while the diffusion was modeled by use of Maxwell-Stefan equation. Preliminary results show that the simulation results accord well with experimental data. As the first step towards our ambition to find out the role of diffusion in product selectivity over zeolites and catalyst pellets, a detailed study on the diffusion of all major gas components is undergoing.

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SYNTHESIS OF MEMBRANE CATALYSTS BASED ON MESOPOROUS SUPPORT FOR DRY REFORMING OF METHANE

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The dry reforming of methane belongs to the most promising methods for natural gas processing. In a number of studies it was found that the implementation of this reaction in a membrane reactor with the use of porous membrane catalysts makes it possible to increase the degree of conversion, the selectivity and the rate of process.

Intensification of a number of catalytic processes in porous membrane catalysts is explained by the peculiarities of gas transport in a porous medium and, in particular, by the appearance of the Knudsen diffusion regime. The appearance of this type of mass transfer, in general, depends on the reaction conditions (temperature and pressure) and porous structure of the membrane catalyst.

The goal of this work was to obtain membrane catalysts with the required architecture and a porous structure that would ensure the emergence of Knudsen diffusion regime.

In this paper, we present the results of the sol-gel synthesis of membrane catalysts Mo_2C/Al_2O_3 and the investigation of their catalytic activity in the reaction of dry reforming of methane.

Membrane catalysts were synthesized on the basis of tubular microfiltration elements (substrate) made off electrocorundum (α-Al_2O_3). An additional layer was applied to microfiltration membranes by the filtration of a boehmite suspension; by heat treatment this layer was converted into a layer of porous Al_2O_3, which possesses a high specific surface area and a mesopore structure.

A stable dispersion of molybdenum blue was used as a dispersion system to create a catalytic layer. The catalytic layer was applied by dip-coating, then the samples were dried and heat treated.

Synthesized samples of membrane catalyst with different pore size distribution were studied in the reaction of dry reforming of methane. The reaction was carried out in a flow-through membrane catalytic reactor.

It was found that the membrane catalysts Mo_2C/Al_2O_3 exhibited catalytic activity in this reaction starting at a temperature of 800 °C. With elevating temperature, the conversion and yield of products are improved. The reaction products were hydrogen (H_2) and carbon monoxide (CO). According to the chromatographic analysis, no other reaction products, including other hydrocarbons (C_2+), were detected.

In a series of samples with a different pore size distribution, an increase in the conversion degree is observed with the elevation of the specific surface area and pore size decrease in the samples. The sample, which has the narrowest pore size distribution and the smallest mean diameter, has the greatest catalytic activity. The rate constants and the specific catalytic activity are presented in Table 1.

The probability of the Knudsen transport regime in the pores can be estimated from the value of the Knudsen number (Kn), which characterizes the ratio of the mean free path of molecules to the characteristic pore size (for example, to the mean diameter). It is generally assumed that for Kn>10 a free-molecular flow or Knudsen diffusion is observed.

The values of Knudsen numbers calculated for the test samples of supports and membrane catalysts are shown in Table 1. As can be seen the free-molecular flow should be observed in γ-Al_2O_3/α-Al_2O_3 support samples, because Knudsen numbers exceed 10. For other support samples, a transient transport mode should be expected.

Table 1. Rate constants of the methane conversion and Knudsen numbers for the membrane catalysts at a temperature of 850 °C

Sample Parameter	Mo_2C/ γ-Al_2O_3/α-Al_2O_3	Mo_2C/ δ-Al_2O_3/α-Al_2O_3	Mo_2C/ α-Al_2O_3/α-Al_2O_3
k, 1/s	1,65	0,31	0,27
k_m, 1/s·g	41,3	7,8	6,7
k_s, 1/s·m^2	0,46	0,11	0,28
Kn (support)	13	8	6
Kn (membrane catalyst)	27	25	21

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ON THE DEVELOPMENT OF HIGHLY-ACTIVE Ni-BASED CATALYSTS FOR CO_2 METHANATION: EFFECTS OF THE SUPPORT AND ACTIVATION TEMPERATURE

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Introduction

One of the most interesting alternatives to valorize CO_2 and avoid greenhouse gas emissions is catalytic hydrogenation to methane or methanation using Ni catalysts. Supported Ni catalysts having different metal-support interactions can show very distinct performances in the CO_2 methanation, thus markedly affecting their activity, stability and selectivity toward CH_4 production. Therefore, the choice of an adequate support as well as the conditions (mainly temperature) of the activation of the catalyst through reduction to obtain metallic nickel can play a crucial role on the ensuing catalytic performance. CeO_2, TiO_2 and Al_2O_3 are interesting supports of Ni to be used in the catalytic hydrogenation of CO_2 because of their different characteristics regarding textural, acid-base and redox properties. The aim of the present work is to develop Ni catalysts for CO_2 hydrogenation using CeO_2, TiO_2 and Al_2O_3 as supports and to study the effect of the catalysts' reduction temperature on their performance.

Experimental

Five Ni catalysts were prepared using the following commercial supports: γ-Al_2O_3 (Alfa Aesar), CeO_2 (Merck, CeO_2-M and Tecnan-Lurederra, CeO_2-L), and TiO_2 (Evonik P-25, TiO_2-E and Tecnan-Lurederra, TiO_2-L). The catalysts were prepared through wetness impregnation with a metal loading of 15 wt. %. All supports were calcined before the impregnation step at 500 °C for 4 h in a muffle furnace under flowing air. After the impregnation and drying, the catalysts were calcined again at the same conditions. The catalysts were characterized by N_2 adsorption/desorption, temperature programmed reduction (TPR), X-ray diffraction (XRD) and CO pulse chemisorption. The evaluation of the catalytic activity was carried out at 400 °C and atmospheric pressure in a laboratory tubular fixed-bed quartz reactor using a feed composed of N_2, CO_2 and H_2 with a H_2/CO_2 molar ratio equal to 4 and a spatial velocity of 12 L N $CO_2/(g_{cat}.h)$. Previously, the catalysts were reduced *in situ* for 3 h under H_2 flow at different temperatures between 350 and 500 °C.

Results and discussion

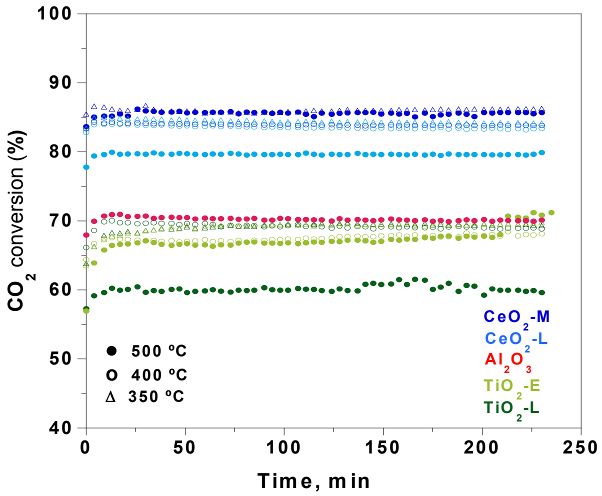

Figure 1. Evolution of the CO_2 conversion over time

Fig. 1 shows the evolution of CO_2 conversion over the reaction time in the catalytic tests carried out at 400 °C using the different catalyts previously reduced at 350, 400 and 500 °C. It can be observed that decreasing the temperature in the reduction step from 500 °C can lead to a notable increase of the activity of the catalysts supported on CeO_2 and TiO_2. The CO_2 conversions increased from values ranging between 59-65 % up to values comprised between 80 and 85 % in the following order: TiO_2-L < TiO_2-E < Al_2O_3 < CeO_2-L < CeO_2-M. Adopting Al_2O_3 as reference support, ceria allowed to obtain more active catalysts whereas the performance of the titania-supported ones was worse. It can be highlighted that both Ni/CeO_2 (M and L) catalysts yielded stable CO_2 conversions throughout at the studied reaction conditions, around 80 % or even higher regardless of the reduction temperature evaluated. Methane and CO were the only reaction products detected with selectivities to methane between 82 and 90 %.

Conclusions

The supported Ni catalysts displayed very stable performances in the hydrogenation of CO_2 at 400 °C yielding high CO_2 conversions in the case of the Ni/CeO_2 solids when the reduction temperature was lowered to 350 °C. This behaviour is being investigated and seems to be related with the reducible character of ceria an titania and the influence of the reduction temperature on the metal-support interactions.

Acknowledgements

Centro Tecnológico Lurederra and TECNAN (Los Arcos, Navarra, Spain) are greatly acknowledged for kindly supplying CeO_2 and TiO_2 supports. The Spanish Ministerio de Economía y Competitividad (MINECO) and the European Regional Development Fund (ERDF/FEDER) are acknowledged for the financial support (prj. ref. ENE2015-66975-C3). The Universidad Pública de Navarra is also thanked for the Post-doc and PhD grants awarded to I. Reyero and V.V. González-Rangulan, respectively.

AERODYNAMIC CFD SIMULATIONS OF EXPERIMENTAL AND INDUSTRIAL THERMAL FLOW REVERSAL REACTORS

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Experiments (cf. [1]) were carried out on the research & demonstration reactor at a gas apparent velocity of ca. 0.57 m_{STP}\s flowing through the honeycomb monolith packing with the square 3×3 mm channels. However, next experiments revealed, that combustion of a lean methane-air mixture as in coal mine ventillation air in this case, may be satisfactory carried out when this velocity would be even about 50 % higher. Practically, the only limiting factor is the cost and energy consumption necessary for pumping the gas through the reactor. Therefore, the flow resistance in the reactor becomes very important for the further reactor design in a larger industrial scale.

For aerodynamic analysis of such a problem the CFD simulations appear to be an appropriate tool. The ANSYS FLUENT simulations presented in the paper were divided into the two following stages:

A. Development of a simulation method which could couple simplified CFD simulations by using the results of separately performed calculations obtained from the model [1], based on partial differential equations of the mass and energy balances with own thermal combustion kinetics [2]. The aerodynamic model was verified by comparing CFD simulation results with the experimental records taken from the research & demonstration plant [1]. The simulations revealed acceptable accordance with experimental results what shows that the model may be useful in practice. This stage was aimed to get reliability of further, forecasted results for an industrial plant in a larger size scale.

B. CFD simulations for currently being designed industrial flow reversal reactor with use the flow resistance coefficients obtained and verified during simulations of the experimental reactor aerodynamic model, referred to in point A.

Thus the aim of the present study was to obtain a reliable model for a reactor which is currently going to be implemented in a coal mine. Moreover, the model was to be used to compare the designed versions of geometry from the point of view of expected pressure drop of future plant, and also from the point of view of homogeneity of the distribution of the flow velocity in cross-section of the reactor monolithic filling. The additional goal was to check whether the flow resistance will be still acceptable when the apparent flow velocity in the monolith will be raised to ca. 0.84 m_{STP}\s.

The simulations which were carried out, for ceramic monoliths with the square channels 3×3 mm and alternatively 5×5 mm too, have shown that use the wider channels significantly reduces the flow resistance and should be preferred in the reactor being designed. Moreover, these simulations enabled to conclude, that some corrections should be done in the geometry of the reactor to improve distribution of flow velocity in horizontal cross-section of the monoliths.

As an example Figures A and B illustrate velocity streamlines for both reactors simulated in the present study. The views of the streamlines were supplemented with maps of the velocities at the tops of the monolith blocks.

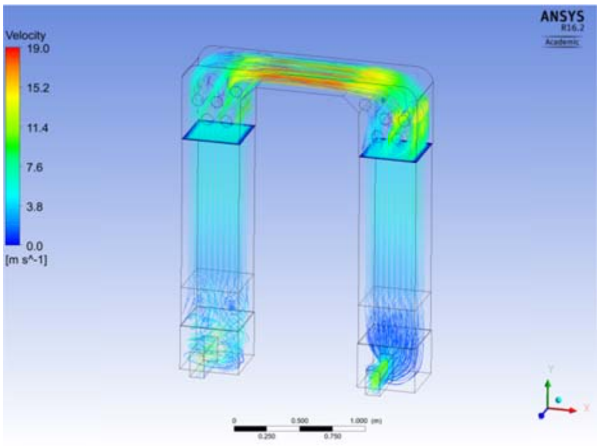

Figure A. Gas velocity streamlines in the existing research & demonstration flow reversal reactor working at apparent velocity of ca. 0.57 m_{STP}\s in the monoliths

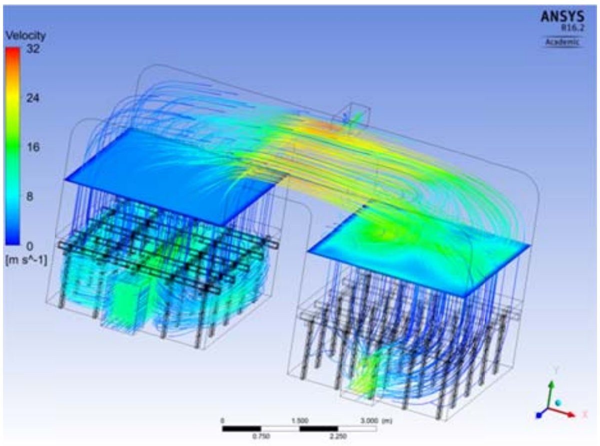

Figure B. Gas velocity streamlines in the future larger scale industrial pilot plant reactor with assumed apparent velocity of ca. 0.84 m_{STP}\s in the monoliths

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A PENALIZATION METHOD FOR THE DIRECT NUMERICAL SIMULATION OF LOW-MACH REACTING GAS-SOLID FLOWS

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Gas-solid flows are encountered in a variety of natural phenomena and industrial applications. Fluidized bed reactors are widely used in the chemical industry as they allow continuous solids processing and high mass and heat transfer rates. The simulation of industrial scale fluidized bed reactors remains challenging with billions of solid particles in motion in the reactor. In the past decades, different approaches have been developed to model complex multi-scale and multi-phase reacting flows. The Two-Fluid Model (TFM), which describes both the gas and the solid phases as continua, is currently very popular due to its relatively low computational cost. The Discrete Element Model (CFD-DEM) or its coarse-grained version in which each particle, respectively group of particles, is tracked in a Lagrangian manner has gained attention in recent years due to the increased computational power and parallel processing capabilities. However, both TFM and DEM type models depend on closure laws for interfacial mass, heat and momentum transfer. Direct Numerical Simulation (DNS) turns out to be a powerful tool for extracting closure laws starting from the fundamental principles for mass, momentum and heat transfer.

In recent years, different DNS methodologies for particle-resolved simulations have been investigated, mostly based on the Immersed Boundary Method (IBM) originally developed by Peskin [1]. The direct forcing method introduced by Mohd-Yusof [2] and later improved by Uhlmann [3] allows a better numerical treatment of rigid body problems and is therefore very popular in the fields of particulate flows. DNS-IBM was then applied by several research groups to predict fluid-particle mass, momentum and heat transfer rates [4]–[8].

Among immersed boundary methods, the penalization method developed by Arquis and Caltagirone [9] models solid obstacles as porous media with close to zero porosity. Originally used for fluid-structure interaction, this method has been scarcely investigated for the study of heat and mass transfer problems in reactive gas-solid flows.

The present study combines the penalization method to account for the presence of the solid phase with the low-Mach number assumption for the gas phase. Indeed, strong thermal effects induced by chemical reactions can induce non-negligible density gradients at the surface of solid particles and affect interfacial transfer laws. The low-Mach number assumption is of high interest for gas-solid reactive flows in that it allows density fluctuations while removing the constraint on the time step imposed by the speed of sound in fully compressible flows. Here, we extend the methodology of Lessani et al. [10] for low-Mach number flows in order to incorporate the penalization of the solid phase for momentum, heat and species transport. Different reaction scenarios are investigated: heat consumption/production and gas expansion/compression. Finally, a comparison is established with the incompressible version of the penalization method to assess the impact of density fluctuations in view of building new closure laws for gas-solid flows.

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NUMERICAL STUDY ON EFFECTS OF BUILT-IN IMPEDIMENTS IN AN ANAEROBIC FLUIDIZED BED MEMBRANE REACTOR FOR FOULING MITIGATION

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Wastewater treatment of both municipal and industrial wastewaters via anaerobic fluidized membrane bioreactors (AnFMBR) has attracted recent attention in literature [1]. The main issue of conventional membrane bioreactors is the occurring fouling and hence energy intensive removing or fouling mitigation. Cui et al. [2] showed that in conventional membrane bioreactors a non-negligible amount of fouling mitigation is due to water shear. Another approach to increase the in-situ fouling mitigation is to introduce inert particles into the membrane bioreactors and induce a fluidized bed.

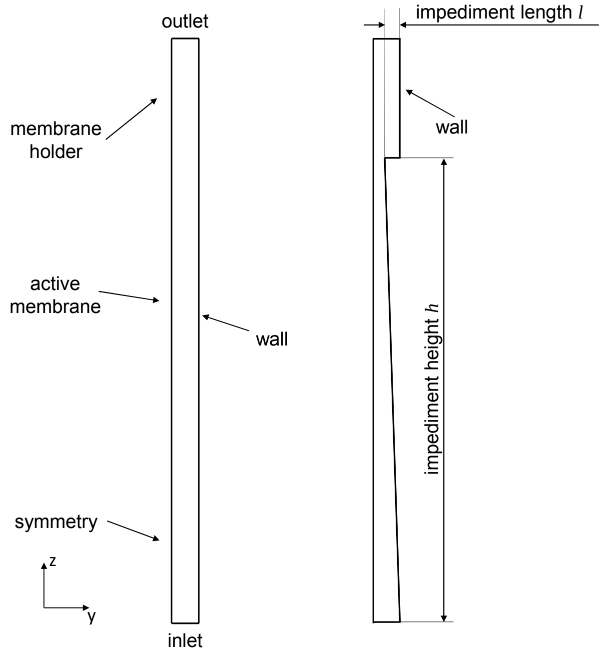

Figure 1. Schematic side view of geometry without (left) and with a built-in impediment length of 5 mm

Recent work on fouling mitigation in a fluidized membrane bioreactor with inert granular activated carbon (GAC) particles [3, 4] showed hydrodynamic correlations of different particle sizes and feed velocities towards the resulting fouling mitigation. It was apparent that increasing particle momentum has a positive effect on fouling mitigation. In the following work the AnFMBR according to [3] is simulated with a coupled CFD-DEM approach using the open-source package OpenFOAM® version 4.1. After validation of the simulations with experimental results, the geometry is modified in respect of implementing impediments. The concept of additional impediments is to modify the water velocity at certain heights of the AnFMBR due to change of the cross section and hence the particle velocities and particle concentrations change as well. As a first modification approach the impediments consist of simple prisms with different lengths *l*. The impediment height *h* is in accordance to the maximum height of the active membrane and equals to 154 mm, while the total height of the geometry is 194 mm. The impediment length *l* is varied between 1, 3, 5 and 7 mm. Figure 1 illustrates the side view of the geometry without and with an impediment length of 5 mm.

The particle diameters investigated range from 1.05 mm to 2.05 mm. The feed velocity is varied between the 3-fold and 11-fold of the minimum fluidization velocity. Figure 2 illustrates the particle momentum for selected particle diameters and impediment lengths in terms of required power input.

A maximum for the particle momentum exists for every particle size and impediment-length. The highest particle momentum in terms of all impediment heights is reached for particle diameters of 1.55 and 1.85 mm. Built-in impediments do not increase the particle momentum, but shift the maximum for the particle momentum towards a lower required power input. Therefore, built-in impediments are suitable for force sensitive or fragile membrane surfaces as the impediments lower the maximum reachable particle momentum while at the same time lowering the required power input by a higher degree than without built-in impediments.

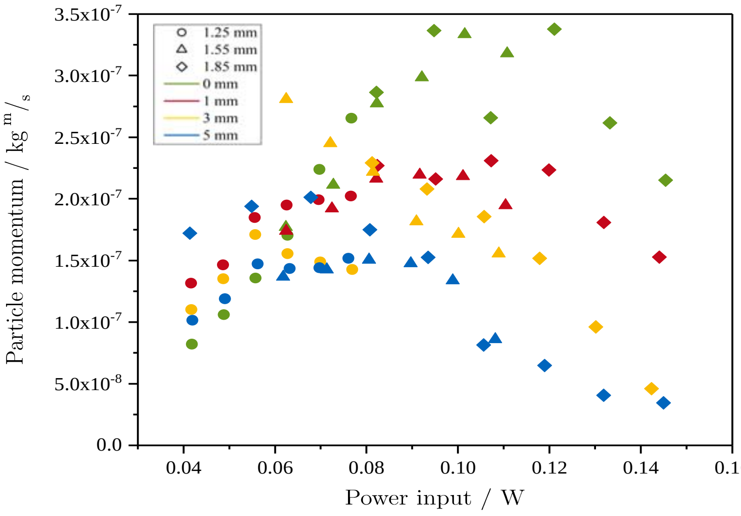

Figure 2. Particle momentum of fluidized bed with particle diameter of 1.25, 1.55 and 1.85 mm for AnFMBR's with no impediment (0 mm) and built-in impediment lengths of 1, 3, and 5 mm with required power input

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MAGNETICALLY CONTROLLED OXIDATIVE CRACKING OF FUEL OIL TO PRODUCE LIGHT PETROLEUM PRODUCTS

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The shortage of explored reserves and production of light oils observed in recent decades has caused the intensification of research and the search for new approaches in the processing of residual high-boiling fractions. Involving in processing only 10 % of oil residues, which are still used as boiler fuel, is equivalent to the production of 50-60 million tons of oil per year [1].

Fuel oil, which contains in heavy oils, is up to 50 % and higher, and a significant proportion is used to produce boiler fuel or raw materials for the production of bitumen and coke, is the main reserve for deepening oil refining [1].

The main obstacle to the processing of fuel oil in catalytic cracking (FCC) installations is the increased coking ability of raw materials and an increased content of metals, mainly nickel and vanadium [2].

The need to create low-cost technology contributed to the development under the leadership of Doctor of Chemical Sciences, Professor R.Kh. Ibrasheva innovation process of oxidative cracking of fuel oil in the presence of cheap catalysts from Kazakhstan's natural zeolites, zeolites derived from fly ash from TPPs and clays in the presence of ferromagnetic catalysts.

The activating effect of microquantities of oxygen is proved by a 20-25 wt. % decrease in the yield of the gas oil fraction during cracking on the same catalysts in an inert atmosphere. Under the influence of oxygen, only the initiation of hydrocarbon molecules occurs, and the radical chain reactions of their destruction take place on the active surface of the optimal catalysts, as evidenced by the fact that when the catalyst is removed from the reaction medium, the oxidative cracking of fuel oil ceases. These results are fundamentally new and, in contrast to previous studies, show that in the absence of a catalyst, the activation of the thermal cracking process by the oxygen in the air of residual oil fractions does not occur.

According to Chromatography-mass-spectrometry analysis, the composition of light gas oils obtained during oxidative cracking of fuel oils on optimal composites includes hydrocarbons with carbon number from C_{10} to C_{25}, with alkanes and alkenes C_{10}-C_{19} predominated, which are contained in equimolar amounts. This is evidence of their formation due to the symmetric decomposition of C_{20}-C_{38} hydrocarbons. Consequently, in the presence of ferromagnetic catalysts attached to aluminosilicates, the destruction of hydrocarbons occurs at the place with the lowest energy of the carbon–carbon bond, i.e. in the middle of the hydrocarbon chain. As a result of homolytic symmetric splitting of high molecular weight hydrocarbons in the products of cracking of fuel oil, middle distillate fractions predominate.

The effect of a constant magnetic field "fixes" a new structure of hydrocarbon systems, characterized by greater homogeneity and paramagnetic activity, lower viscosity and surface tension.

The duration of this structure is from several tens of minutes to several hours. This time is sufficient for the creation of favorable conditions for the flow of physico-chemical processes in the processing of petroleum raw materials.

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FORMATION OF THE COMPONENT COMPOSITION OF BLENDED HYDROCARBON FUELS AS THE PROBLEM OF THE MULTIOBJECT OPTIMIZATION

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The problem of energy efficiency has always been the most significant in the economy. Its solution is related to the technologies of many industries. The most significant are the reserves of energy efficiency of the use of hydrocarbon fuels, which are observed at all stages of production of high-energy hydrocarbon fuels. This is largely due to the extensive scientific search for alternative energy sources and stagnation in the conduct of search and fundamental studies of the processes of producing motor fuels from hydrocarbon raw materials.

Theoretical bases of modeling of unsteady multicomponent catalytic processes of deep refining of hydrocarbon raw materials, such as hydrotreating of diesel fractions, dewaxing of atmospheric gas oil, catalytic cracking and hydrocracking of vacuum gas oil, are developed. A new energy-efficient technology for the production of high-energy, low-freezing hydrocarbon fuels for the Arctic was created by solving the problem of multi-object optimization.

In the process of fuel production, not taking into account the chemical interaction between the individual components of the mixture (hydrocarbon streams and additives) leads to a divergence of the physicochemical properties of the calculated and experimentally determined ones. The principal consequences of this are: a) deterioration in the quality of products – commercial fuels; b) decrease in economic indicators due to over-expenditure of expensive additives used in compounding. With large volumes of commercial output, economic indicators can reach a significant level. Calculation of the recipe for motor fuels is carried out based on the parameters and properties of the mixing components that are used to produce a certain batch. This will reduce the risks of producing off-specs products, and also save expensive additives.

The resource vector of mixing components (flow rate) is limited by production capabilities, the flows ratio is determined by the the State Standard (GOST) requirements for fuels.

The following requirements are considered as the basic:

– for gasolines: density, fractional composition, sulfur content, the content of aromatic hydrocarbons, including benzene, olefins, saturated vapor pressure, motor and research octane numbers;

– for diesel fuels: density, sulfur content, fractional composition, cetane number, kinematic viscosity, cloud point, cold filter plugging point, pour point, flash point;

– for boiler fuels: density, viscosity, flash point and pour point.

To establish the correlation between the quality of the obtained mixture and the quantitative and qualitative characteristics of the mixing components, it is necessary to solve the problem of multicriteria optimization.

In the process of optimization, there are many conflicting requirements for the commercial product. The values of some indicators need to be increased, while others should be reduced at the same time. The problem is complicated by the fact that these indicators are not independent. They are interrelated, interdependent, and the increase of some indicators leads to a decrease in others. The search for the optimal solution is connected with finding a reasonable compromise in the conditions of presented contradictory requirements.

To find a compromise solution, the notion of an ideal value for all the particular components of Ψ_i is introduced. Then the efficiency criterion will be written as follows:

$$\psi = \left(1 - \frac{\psi_i}{\psi_{i,\ \text{идеал.}}}\right)^2 \rightarrow \min$$

The values of the optimized parameters X_1, X_2, … X_{12}, providing min Ψ_i, will be a compromise.

To conduct a complete qualitative and quantitative analysis of the efficiency of the blending process, it is necessary to see the interrelationship between production and operating modes of the plants, their influence on the productivity of the blending process. In this case, recommendations for changing recipes to improve the effectiveness of the mixing stage will be correct and fully justified.

To determine the volume and quality of the added streams to the off-specs volume of products in order to meet the requirements for the final product, it is required to create a software connection with databases used at the refineries.

INFLUENCE OF INPUT CONDITIONS ON A FLOW DISTRIBUTION IN TRICKLE BED REACTORS

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Trickle bed reactors with a cocurrent downward two-phase flow are widely used in industry, e.g., in the hydrotreating process of diesel fuel. In such reactors the distribution of a two-phase flow before packed catalyst bed is generally carried out by two successive steps. In the first stage the flow comes from the supply pipe to the reactor through the inlet diffuser. Then the flow is more evenly distributed over the cross section of the reactor using a basic distributor. A chimney distributor is such a device very often in practice. This is a horizontal tray fitted a set of vertical downpipes both sides open-ended.

In this study it was investigated the distribution of a two-phase flow in the inlet part of a trickle bed reactor for two designs of the input diffuser used in practical applications. Figure 1a shows a diffuser with a perforated plate [1] and Figure 1b shows a diffuser with an axial swirl chamber [2]. In addition, a study was carried out for the case without of an input diffuser.

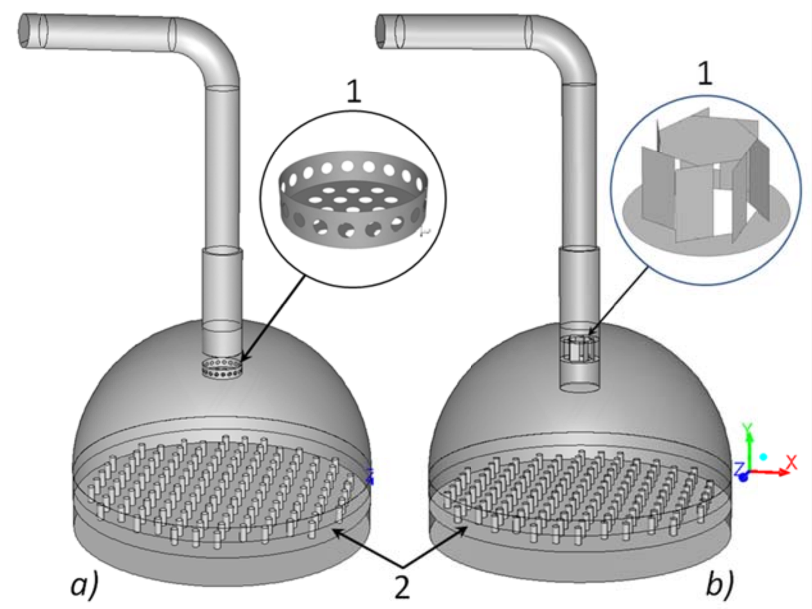

Fig. 1. An upper part of the trickle bed reactor. 1. Input diffuser, 2 - a chimney distributor. A design of diffuser: a) a perforated plate, b) an axial swirler

The study was carried out using CFD modeling. A Volume Of Fluid model (VOF) of the Euler multiphase approach was used to simulate the motion of a two-phase flow [3].

The results showed that the considered two-phase flow distribution devices may not provide an even distribution of a liquid phase to an underlying catalyst bed, if the input diffuser does not ensure a fairly even distribution of a gas phase before the basic distributor - the chimney distributor. Figure 2 shows the surface of a liquid phase in a reactor on a tray with chimneys for the case of the axial swirler diffuser. The nonuniformity of a two-phase flow after the diffuser leads to the "drying" of the upper part of the chimney pipes in the central area of the tray. This causes an uneven flow of a liquid phase onto an underlying catalyst bed.

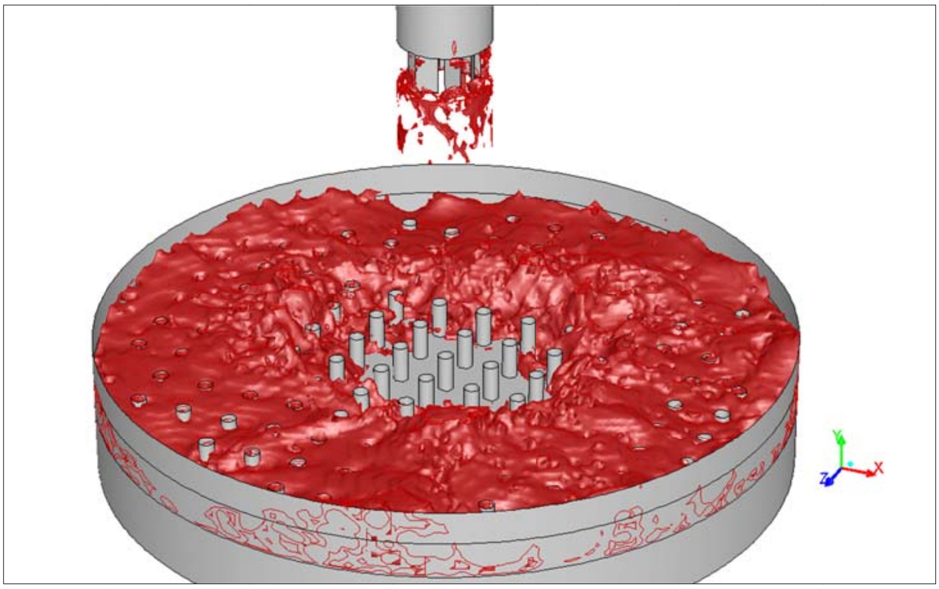

Fig. 2. The surface of a liquid phase on the tray with chimneys for the case of the axial swirler diffuser

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METAL OXIDES FORMATION ON Pt/Al_2O_3 AND Pd/Al_2O_3 CATALYSTS AND ITS IMPACT ON NO OXIDATION

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Current diesel exhaust aftertreatment systems consist of a diesel oxidation catalyst (DOC) for CO and hydrocarbon oxidation, a deNOx catalyst for reduction of nitrogen oxides (either lean NO_x trap – LNT, or selective catalytic reduction – SCR), and a diesel particulate filter (DPF). The NO_x reduction efficiency depends on NO_2/NO_x ratio in the exhaust gas. NO_2 adsorbs in a significantly greater extent than NO in LNT, and the NO_2/NO_x ratio of 1/2 enables the fast SCR reaction. NO oxidation in DOC located in front of the deNOx catalysts therefore significantly affects the overall function of the combined aftertreatment system.

Diesel oxidation catalysts are based on Pt or Pt-Pd nanoparticles supported by Al_2O_3 and/or CeO_2. However, in highly oxidative atmosphere of the diesel exhaust gas, noble metal oxides formation is thermodynamically favored and the metal oxides show a lower catalytic activity for NO oxidation. Optimum design and control of the combined DOC–deNOx aftertreatment system therefore relies on the understanding and quantification of metal oxides formation and its impact on NO oxidation rate, depending on both actual operating conditions and history of the catalyst [1,2].

In this contribution we aim on the elucidation of metal oxides formation effects on Pt/Al_2O_3 and Pd/Al_2O_3 catalysts, focusing on similarities and differences between the two catalyst formulations. Series of isothermal deactivation experiments was performed as well as heat-up and cool-down temperature ramps showing inverse hysteresis of NO_2 yield due to metal oxide formation on the catalyst surface (Figure **1**). Prior to each experiment, the catalyst was reduced in hydrogen to obtain fully reduced initial state of the catalyst. A global kinetic model of DOC is developed, considering NO oxidation rate dependence on the fraction of Pt or Pd sites in the form of metal oxides [1]. The model includes gradual oxidation of metal sites by NO_2 and O_2, thermal decomposition of metal oxides, and their reduction by NO, CO and C_3H_6 under overall lean conditions. The kinetic parameters are evaluated from the measured evolution of outlet concentrations.

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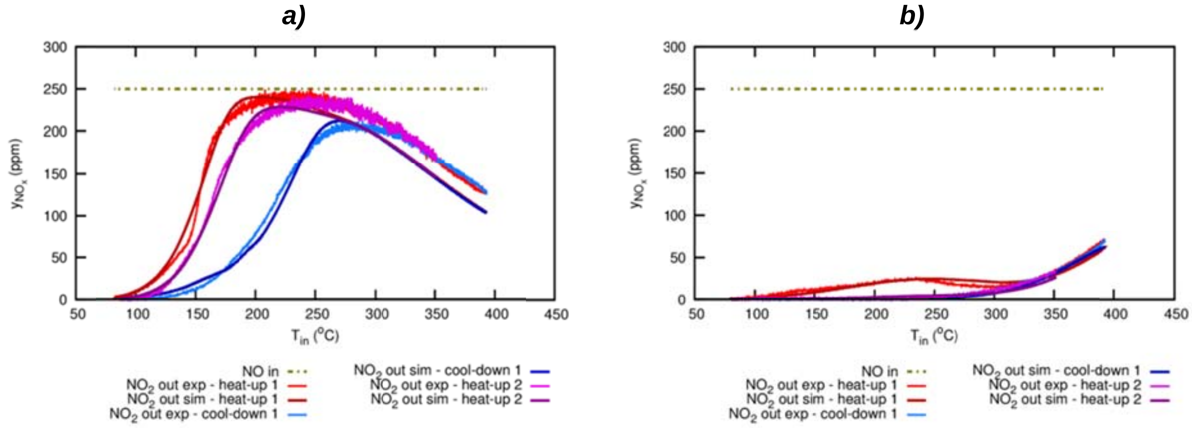

Figure 1. Experimental and simulated NO_2 concentration in NO oxidation during subsequent heat-up and cool-down temperature ramps on a) Pt/Al_2O_3 catalyst, and b) Pd/Al_2O_3 catalyst. Initial state: reduced. Feed: 250 ppm NO, 8 % O_2, 8 % CO_2, 8 % H_2O

The results in Figure **1** demonstrate that for both catalyst types the highest NO_2 yield is obtained in the first heat-up ramp after the catalyst reduction. Both catalysts exhibit significantly lower activity during the subsequent cool-down ramp, due to transformation of the metal sites into a less active oxidized state. The NO_2 yield on Pd/Al_2O_3 is generally lower than on Pt/Al_2O_3, where it reaches maximum values and becomes limited by reaction equilibrium above 250°C.

It is also easier to partially recover the NO oxidation activity on platinum-based catalyst – the formed PtO_x can be reduced back to Pt at lower operating temperature by NO in the feed. The second Pt/Al_2O_3 heat-up ramp in Figure **1**a shows a higher NO_2 yield compared to the cool-down ramp. No such reactivation is observed with Pd/Al_2O_3 (Figure **1**b). This indicates a significantly higher stability of PdO_x compared to PtO_x. Reducibility of the metal oxides and recovery of NO oxidation activity under practical operating conditions is further examined in experiments with lean CO and C_3H_6 pulses [1]. The developed kinetic model of DOC captures well the observed phenomena. It is able to predict metal oxides coverage on the catalyst surface as well as NO oxidation rate depending on history of the operating conditions [2].

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Acknowledgements

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HARDWARE COMPLEX FOR CONDUCTING EDUCATIONAL AND SCIENTIFIC WORKS ON COKING HYDROCARBON AND CARBON-CONTAINING RAW MATERIALS

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An increasing number of oil companies in worldwide and Russia equip their oil refineries with delayed coking unites for heavy residua feedstocks, since this process allows to deepen processing to 95 %, expand resources for obtaining commercial fuels and start production of special petroleum coke. Over the past 10 years, the delayed coking capacity in Russia has increased almost 3 times and at the beginning of 2018 amounted to 15.8 million tons per year for processed raw materials [1,2].

Conducting pilot runs directly on industrial installations may not always be economically or technologically justified, and in some cases leads to additional capital costs. To avoid this, the authors propose to conduct experimental studies on coking hydrocarbon and carbon-containing raw materials on the experimental setup.

The experimental coking unit for educational and scientific works includes: 1) a coking reactor with a charge of up to 0.5-1.0 kg, which is a cylindrical vessel for operation under pressure up to 0.10 MPa; 2) a "tube-in-pipe" heat exchanger for cooling the withdrawn gas-liquid product mixture; 3) a receptacle for collecting liquid distillate products for subsequent rectification; 4) gas flow meter; 5) scales (raw and food) for mass flow control; 6) electric control unit, including PID regulators and measuring regulators for monitoring the temperatures of the bottom, middle and top of the coking bed of the reactor; 7) PC with a mnemonic circuit connected to the electrical control unit and the ability to control the process from the SCADA system.

This experimental unit will allow us to carry out studies related to the assessment of the quality of petroleum coke, the kinetics of process, the effect of modifying additives.

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MIXTURE EFFECT ON ALKANE AND CYCLOALKANE HYDROCONVERSION OVER Pt/USY CATALYST

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Hydroconversion over bifunctional catalysts is one of the most common ways to convert both oil cuts and alternative feedstocks into more valuable products. For instance, naphtha streams are converted into high-octane gasoline fuel by hydroisomerization, because of its capability to convert n-alkanes to i-alkanes [1]. The reaction mechanism comprises metal-catalyzed (de)hydrogenation and acid-catalyzed reactions of isomerization and cracking [1-3]. These reactions occur on a bifunctional catalyst, which usually consists of Pt deposited on a zeolite. The isomer yield is maximized when the reactions on the acid sites are rate determining, i.e. when so-called ideal hydrocracking occurs [1].

Hydroisomerization and -cracking of pure alkanes or cycloalkanes has already been investigated in detail, often employing model compounds (mixtures). [1-3] Realistic feeds are typically complex mixtures of such compounds. For instance, cycloalkanes have been observed to have negative impact on conversion and isomer selectivity in n-alkane hydrocracking [4,5]. This effect has qualitatively been attributed to physisorption, dehydrogenation, [4,5] or/and protonation steps, [6] however, quantification of reaction kinetics has not been performed yet. The Single-Event MicroKinetic (SEMK) methodology has been proved to be a particularly convenient tool for modelling hydroisomerization and hydrocracking reactions as it accounts for all elementary steps employing parameters with a precise physico-chemical meaning [2,3]. Using the SEMK method will enable us to assess literature reported experimental results complemented by own measurements and identify which phenomena are impacted when feeding mixtures. Due to its fundamental character, extrapolation to different ranges of industrially-relevant n-alkanes, cycloalkanes, and reaction conditions is possible.

More specifically, the experiments and simulations with SEMK model for pure alkane and cycloalkane and for their mixture are in progress. The first experimental campaign is being carried out to obtain preliminary information about the alkane-cycloalkane mixture effect during hydroconversion. The alkanes to be tested are linear alkane between C6 and C8, while methyl-cyclohexane is used to represent cycloalkane. There are carried out experiments with pure hydrocarbon feeds and with equimolar mixtures of alkane and cycloalkane. The experiment conditions were set with the goal to be close to the transition from ideal to non-ideal hydrocracking. The experiment operating conditions are listed in Table 1.

Table 1. The operating conditions for hydroconversion tests

Variable	Value
Temperature	220 °C
Total pressure	0.5 MPa; 1 MPa
H_2/HC	50
Catalyst	Pt/USY (CBV712)
Pt loading	0.1 wt % 0.5 wt %

The simulations of SEMK model for ideal hydrocracking of pure alkane and cycloalkane, as well as their mixtures, are in progress. By comparing the experimental results and simulations we expect to get the first insight in the hydrocracking of mixtures and determine the occurrence of either antagonistic or synergetic effects. We expect to obtain sufficient understanding of the fundamental features after accounting of competitive adsorption, and dehydrogenation and protonation as rate determining steps in the SEMK model.

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THERMAL MODES OF PLUG FLOW REACTOR WITH HETEROGENEOUS REACTION

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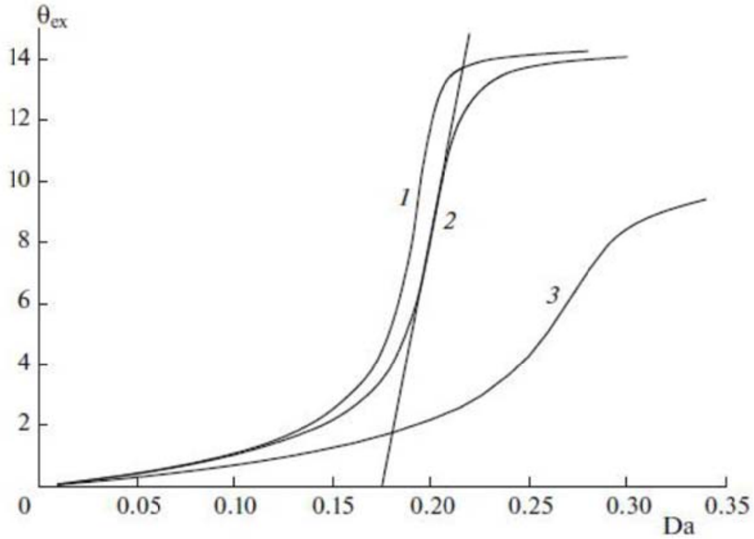
The thermal modes of a flow plug reactor with an exothermal chemical reaction are numerically simulated. A heterogeneous reaction system consisting of two immiscible liquids is studied: one of the liquids (dispersed phase) in the form of droplets is distributed in the other (dispersion phase). The characteristics of the thermal modes of the reactor at various values of two governing parameters, the Damkohler number and the rate of extraction of the dissolved substance from the dispersed phase into the dispersion phase is examined. Two modes of chemical reaction in the reactor are demonstrated to be possible: low-temperature and hightemperature. Critical criteria of thermal ignition are formulated. The dependence of the structure of the thermal wave on the governing parameters is investigated.



Dependence of the temperature at the reactor outlet θ_{ex} on the parameter Damkohler Da at Pe = 1000 and *P* = (*1*) 100, (*2*) 10, and (*3*). Pe is a Peclet parameter and P is a parameter that determines the relationship between feeding the reactant mixture to the reactor and extracting the reagent B into the dispersion phase.

SYNTHESIS OF BUTYLLACTATE FROM FERMENTATION BROTH BY ESTERIFICATION IN A CONTINUOUS FLOW COLUMN-TYPE REACTOR

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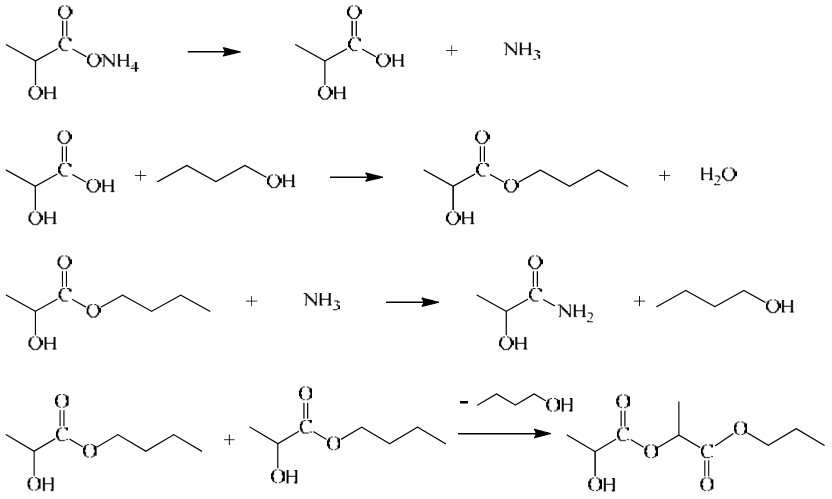
Nowadays, great variety of chemical products is producing by biotechnology methods from vegetable renewable sources. One of the most in-demand products from them is lactic acid, which is the basic substance for producing of wide variety of valuable organic chemicals, such as lactic acid esters, lactide, polylactide, propylene glycol.

Most resent bio-lactic acid technologies have a stage of separation lactic acid from fermentation broth by sedimentation insoluble salt – calcium lactate. Next step is calcium lactate acidifying with conversion to lactic acid. This stage results to production of great amount of calcium sulphate (gypsum) wastes, about 1 ton of wastes on 1 ton of lactic acid. Thus, the costs for the purification of lactic acid and waste disposal reach 50 % of the product total cost price.

To avoid this problem, new method of lactic acid separation in butyllactate form was developed, which includes esterification of ammonium lactate with butanol-1, and then purification of obtained ester by vacuum rectification. In addition, it is possible to recycle the evolved ammonia to fermentation step.

Main (1,2) and side (3,4) reactions:



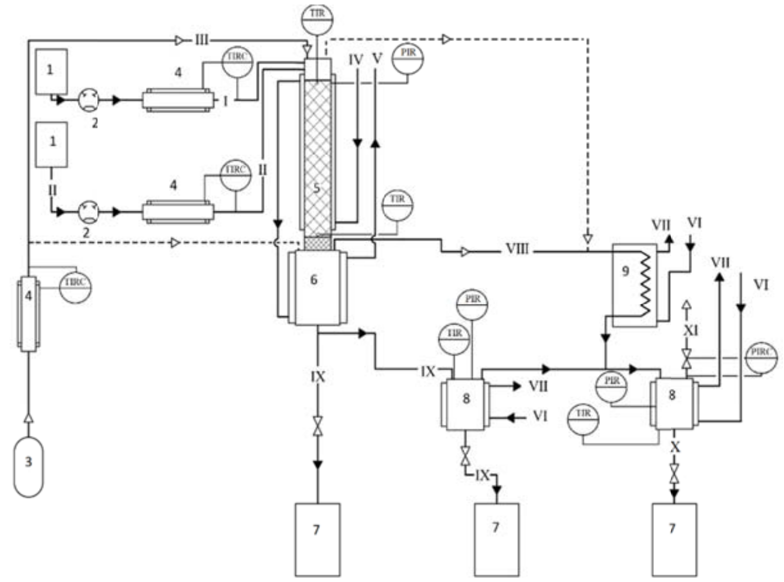
(1)

(2)

(3)

(4)

In the present work, esterification was carried out in a packed column flow reactor (Fig. 1).



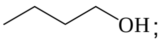
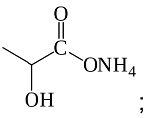
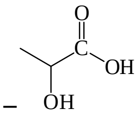
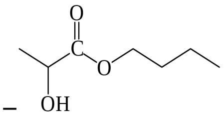
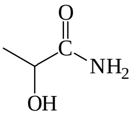
1 - bin;
2 - dosing pump;
3 - flask with nitrogen;
4 - electric heater;
5 - reactor;
6 - hot separator;
7 - sampler;
8 - storage bin;
9 - condenser;
I - mixture of ammonium lactate and n-butanol; **II** - n-butanol;
III - nitrogen; **IV** - hot heat carrier;
V - waste heat carrier;
VI - circulating water (supply);
VII - circulating water (reverse);
VIII - vapor-like synthesis products;
IX - liquid synthesis products (cube);
X - aqueous solution of butanol (condensate);
XI - ammonia-nitrogen mixture

Fig. 1. Esterification column flow reactor

The uncatalyzed reaction was carried out in molar ratio of [Ammonium Lactate]: [n-Butanol] = 1: 4-7. The reaction temperature is 140-180 °C, pressure is 4-8 atm, mass flow of feedstock is 5-10 g/min, N_2 volume flow is 100-500 ml/min. Reactor diameter is 33 mm, high is 1500 mm.

Series of experiments were carried out to find parameters, which allows to achieve a high conversion of ammonium lactate.

T column top, °C	T column bottom, °C	N_2, ml/min	n BuOH/ n $LaNH_4$	Conversion ($LaNH_4$), %	Conversion ($LaNH_4$+LA), %	Yield BL, %	Selectivity (BL), %	Selectivity (LAmid), %
182	172	100	7	99	43	43	97,5	2,5

BuOH –  ; **LaNH4** –  ; **LA** –  ; **BL** –  ; **LAmid** – 

Producibility 3.12 g BL/min*L.

The next rapid catalyzed step with strong acid catalyst also possible to provide in this flow reactor to obtain the full conversion of lactic acid and the high yield of butyllactate.

Thus, this method gives an ability to carry out the process of lactic acid separation from fermentation broth in a form of butyllactate in continues mode, and to avoid the formation of gypsum wastes.

MODELING OF THE DIESEL FUEL HYDRAULIC CLEANER REACTOR WITH THE ACCOUNT OF THE CATALYST DEACTIVATION

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Analysis of the current state of research in the field of modeling the process of hydrotreating diesel fuel is reduced to finding the kinetic patterns of transformation and describing the observed reaction rates. To describe the actual process of operation of catalysts and hydrotreating reactors, simplified kinetic equations for the total sulfur content are used. However, such models do not take into account the interactions of reagents-products, that is, do not take into account the different hydrogenation rates of various sulfur-containing compounds in the feedstock.

The aim of this work is to develop mathematical model of diesel fuel desulphurization process using experimental data, obtained both from laboratory and industrial scale desulpurization units, using real feedstock (diesel fraction), and taking into account transformations of sulphur-containing compounds presented in diesel fractions.

The first stage of modeling is the calculation of thermodynamic parameters for creating a formalized scheme, based on which a mathematical model of the process is constructed in the future.

The calculation of the thermodynamic parameters was carried out under the conditions of the hydrotreating process: a temperature of 400 °C and a pressure of 2.0 MPa. Thermodynamic analysis showed that the hydrogenolysis rate of sulfur compounds decreases in the series: sulfides> thiophenes> benzothiophenes> dibenzothiophenes, which corresponds to an increase in their stability.

The average Gibbs energy of the reactions of hydrogenolysis of sulfides, thiophenes, benzothiophenes to cycloparaffins and dibenzothiophenes to diaromatic hydrocarbons was "-146.8"; "-137.7"; "-71.4" and "-37.8", respectively. In addition, hydrogenation reactions of mono- and polyaromatic compounds, olefins, also take place during hydrotreatment. The obtained results were taken into account in the preparation of a formalized scheme for the conversion of hydrocarbons in the process of hydrotreating diesel fractions (Figure 1).

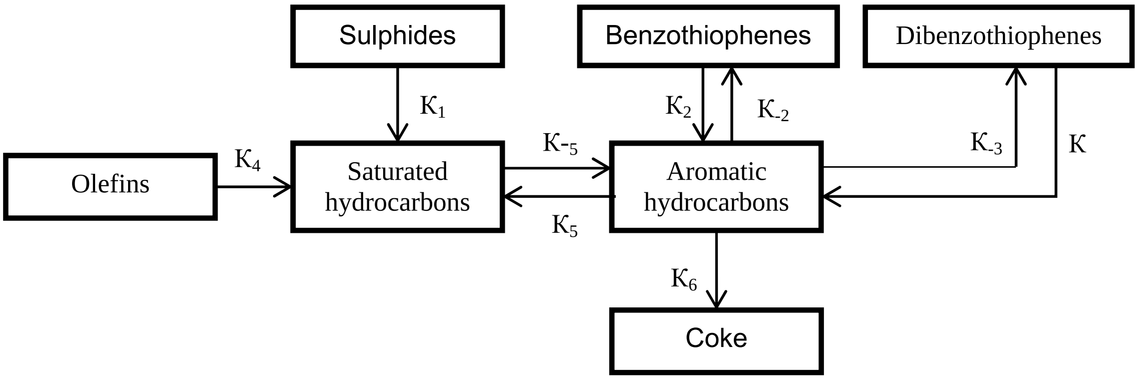

Figure 1. The formalized scheme of reactions of the hydrotreating process of diesel fuel

Based on the formalized scheme of hydrocarbon transformations (Fig. 1), a kinetic model of the hydrofining process of diesel fractions was compiled (Table 1).

Table 1. Kinetic model of the hydrotreating process of diesel fractions taking into account deactivation of the catalyst

Compound	Dependence of the concentration of substances on time
Sulphides	$\frac{dC_{\text{Sulphides}}}{dt} = -A_1 * W_1$, where $W_1 = k_1 C_{\text{Sulphides}} C_{\text{H}_2}^{\nu}$
Benzothiophenes (BT)	$\frac{dC_{\text{BT}}}{dt} = -A_2 * W_2 + A_{-2} * W_{-2}$, where $W_2 = k_2 C_{\text{BT}} C_{\text{H}_2}^{\nu}$, $W_{-2} = k_{-2} C_{\text{Arens}} C_{\text{H}_2}^{\nu}$
Dibenzothiophenes (DBT)	$\frac{dC_{\text{DBT}}}{dt} = -A_3 * W_3 + A_{-3} * W_{-3}$, where $W_3 = k_3 C_{\text{DBT}} C_{\text{H}_2}^{\nu}$, $W_{-3} = k_{-3} C_{\text{Arens}} C_{\text{H}_2}^{\nu}$
Saturated hydrocarbons (SH)	$\frac{dC_{\text{SH}}}{dt} = A_4 * W_4 + A_1 * W_1 - A_5 * W_5 + A_{-5} * W_{-5}$, where $W_4 = k_4 C_{\text{Олефины}} C_{\text{H}_2}^{\nu}$, $W_5 = k_5 C_{\text{SH}} C_{\text{H}_2}^{\nu}$, $W_{-5} = k_{-5} C_{\text{Arens}} C_{\text{H}_2}^{\nu}$
Aromatic hydrocarbons (Arens)	$\frac{dC_{\text{Olefins}}}{dt} = A_2 * W_2 + A_3 * W_3 + A_5 * W_5 - A_6 * W_6 - A_{-2} * W_{-2} - A_{-3} * W_{-3} - A_{-5} * W_{-5}$
Olefins	$\frac{dC_{\text{Olefins}}}{dt} = -A_4 * W_4$
Hydrogen	$\frac{dC_{\text{Hydrogen}}}{dt} = -A_1 * W_1 - A_2 * W_2 - A_3 * W_3 - A_4 * W_4 + A_5 * W_5 - A_6 * W_6 - A_{-2} * W_{-2} - A_{-3} * W_{-3} + A_{-5} * W_{-5}$
Coke	$\frac{dC_{\text{Coke}}}{dt} = A_6 * W_6$, where $W_6 = k_6 C_{\text{Arens}} C_{\text{H}_2}^{\nu}$

The Initial conditions: t = 0: $C_i = C_{i0}$, where *i* is the corresponding hydrocarbon or hydrogen, k_i – rate constant of chemical reaction; C_i is the current concentration of substance i; v is the stoichiometric coefficient; A_i is the relative activity of the catalyst with respect to route i; t is the reaction time; W_i – speed of chemical reaction, *i* is the number of hydrocarbon groups.

CO_2 UTILIZATION VIA TRI-REFORMING OF METHANE: EFFECT OF CATALYST SUPPORT

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1. Introduction

Methane is an important feedstock for fuels and chemicals [1]. Dry reforming of methane utilizes greenhouse gas CO_2 to reform methane and thereby has environmental implication [2]. However, it requires CO_2 pre-separation from its concentrated source. CO_2 pre-separation from flue gas of electricity power generation plants is highly energy intensive step and it alone reduces plant's net electricity output by as much as 20 %. A novel process called "Tri-reforming of methane (TRM)" does away with pre-separation as it employs CO_2, H_2O and O_2 of flue gas to reform methane in a single reforming reactor [3]. However, large scale implementation of TRM has been impeded by lack of highly active and stable catalyst. It remains a challenge to develop a catalyst which is able to adsorb and activate all the reactant species CH_4, CO_2, H_2O and O_2 efficiently. Therefore, the present work aims to study the catalytic behavior of low cost Ni-based catalysts for TRM process. For this purpose, various Ni-based catalysts by employing different metal oxides Al_2O_3, MgO and CeO_2-ZrO_2 as catalyst support were synthesized and tested for TRM reaction at 800 °C under atmospheric pressure. A detailed characterization of calcined, reduced and spent forms of each catalyst has been carried out and finally correlation between catalyst physicochemical properties and catalyst activity has been established.

2. Results and discussion

Fig. 1 shows XRD pattern of calcined form of catalysts. NiO/Al_2O_3 displayed a set of diffraction peaks centered at 19.5^o, 31.8^o, 37.2^o, 45.3^o, 60.1^o and 66.2^o which can be assigned to $NiAl_2O_4$ cubic spinel-type structure (JCPDS 78-1601). No separate reflection corresponding to either NiO or MgO is observed in XRD pattern of NiO/MgO. It can be attributed to the formation of NiO-MgO solid solution. However, NiO/CeO_2-ZrO_2 showed cubic NiO peaks corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) crystal planes centered at 37.2^o, 43.3^o, 62.8^o, 75.4^o and 79.2^o respectively (JCPDS 78-0643). H_2 – TPR profile showed in Fig. 2 indicates reduction peak of calcined form of Ni/Al_2O_3, Ni/MgO and Ni/CeO_2-ZrO_2 positioned at 850 °C, 743 °C and 489 °C with 35, 2 and 40 ml/g @ STP hydrogen uptake respectively. The Ni particle size of Ni/Al_2O_3, Ni/MgO and Ni/CeO_2-ZrO_2 determined by TEM images (not shown here) was 13, 23 and 55 nm respectively.

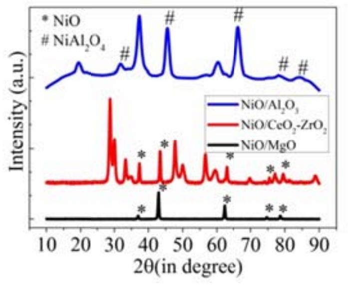

Figure 1. XRD pattern

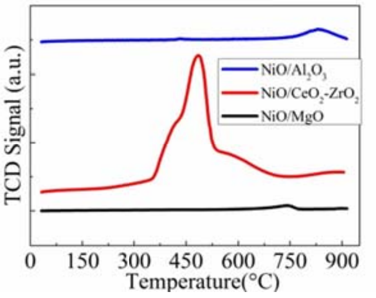

Figure 2. TPR profile

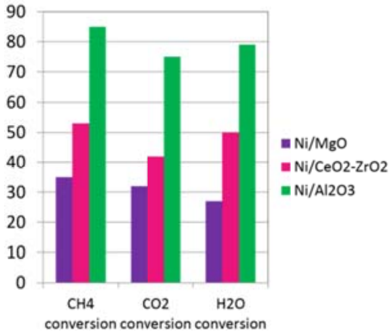

Figure 3. Catalyst activity

The performance of these catalysts for tri-reforming reaction has been compared in fixed bed tubular reactor at identical condition of 800 °C temperature, 1 atm pressure and 11180 ml/g/h @ STP GHSV and their activity results are shown in Fig. 3. Ni/Al_2O_3 demonstrated higher activity with 85 %, 75 % and 79 % CH_4, CO_2 and H_2O conversion respectively. The TPR results indicate strong metal-support interaction and high degree of reducibility for Ni/Al_2O_3. Also, Ni particle size of Ni/Al_2O_3 was relatively smaller. On the other hand, degree of reducibility of Ni/MgO was lower, while, metal-support interaction of Ni/CeO_2-ZrO_2 was weaker as evident from TPR results.

3. Conclusions

Ni/Al_2O_3 derived from spinel $NiAl_2O_4$ displayed superior activity than Ni/MgO and Ni/CeO_2-ZrO_2. Detailed catalyst characterization reveals that both strong metal-support interaction and high degree of reducibility are essential for high catalyst's activity.

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STUDY OF FLUID FLOW PATTERN IN STATIC LIQUID-LIQUID VORTEX CONTACTOR. EFFECT OF LIQUIDS SEPARATION

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Liquid-liquid contacting for solute extraction or chemical reactions is widely employed in chemical industry. The choice of a liquid-liquid extractor depends on the field of application and special process requirements. To reach high intensity of mass-exchange between liquid phases the efficient blending and dispersing of liquids with intense interphase surface renovation are needed. These can be met in confined swirled flows where a spatially uniform field of shear stresses is present as well as a high level of turbulence.

Liquid-liquid vortex contactor (LLVC) for efficient contacting immiscible liquids with moderate viscosities was developed [1]. It was kept in mind the extraction of sour impurities, such as mercaptans, from liquid hydrocarbon stream to an aqueous caustic solution with their subsequent partitioning to serve in the MEROX process. Current industry practice is to use a sieve-tray column with its large mass and overall dimensions. Fluid enters the static liquid-liquid vortex chamber (Fig. 1) via multiple tangential speeding up slots providing efficient conversion of initial pressure energy to vortex motion with almost total dissipation of incoming energy inside the flow due to reduction of incoming angular momentum by the flow friction stress on the end wall surfaces providing also shear stresses field within totally turbulent vortex flow. LLVC is designed for effective dissipation of incoming pressure energy inside the flow while keeping the sufficient level of centrifugal gravity to sustain the vortex motion. Liquid-liquid vortex contactor has some attractive characteristics: sufficient yet not excessive mixing; absence of any moving or spinning parts; functioning under rocking condition. The simplest theoretical description of the flow in a such type contactor is presented based on an axis-symmetrical flow assumption. It is shown, that for mainly one phase flow, introducing the dimensionless radius $r* = (r_0 - 1)/(r_0 - r_\alpha)$ and relative height $h* = h_0/(r_0 - r_\alpha)$ of the vortex chamber, as well as the swirl number S_0 at radius r_0 for a flat VC from angular momentum balance equation the circulation reduction in the flow may expressed as:

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$\Gamma/\Gamma_0 = r\mathrm{v}_\varphi/r_0\mathrm{v}_{\varphi\,0} = (1 + fS_0 r^*/h^*)^{-1}$. And the criterion of sufficient flow deceleration can be expressed as: $X = fS_0/(h^*)^2 \geq 1$. Summarized data on the various configurations tested at swirl numbers $S_0 > 10$ give for energy dissipation rates 5÷15 W/L at contact times 3÷10 s in a L-L vortex layer and $Re_\varphi = 1 \div 5 \cdot 10^5$. Calculated ratio of flow energy dissipated in the vortex flow to outgoing kinetic energy was in the range 93÷98 %.

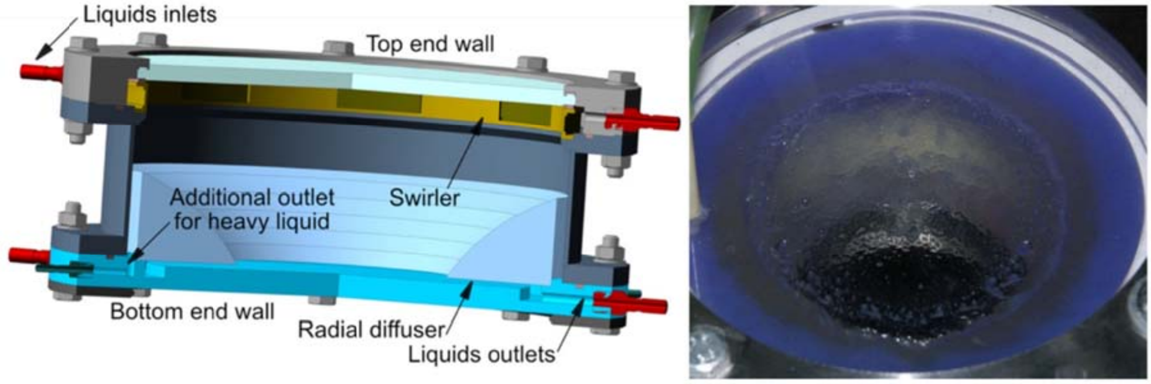

Figure 1. The design of static vortex chamber of LLVC (left) and the effect of liquids separation appearing under certain conditions and demonstrated for colored water-hexane system (right)

At certain swirler numbers the “high g” forces promote the formation of two distinct layers of liquid (Fig. 1). The formation of a distinct heavy phase layer theoretically permits bulk phase separation and removal of the heavier fluid from of the chamber periphery. Explanation of thus phenomena is discussed based on developed theory. Laser-Doppler anemometry data on flow pattern in such type vortex chamber are analyzed, which indicate the presence of reverse flow formation inside vortex layer. Some theoretical description of this effect is also provided.

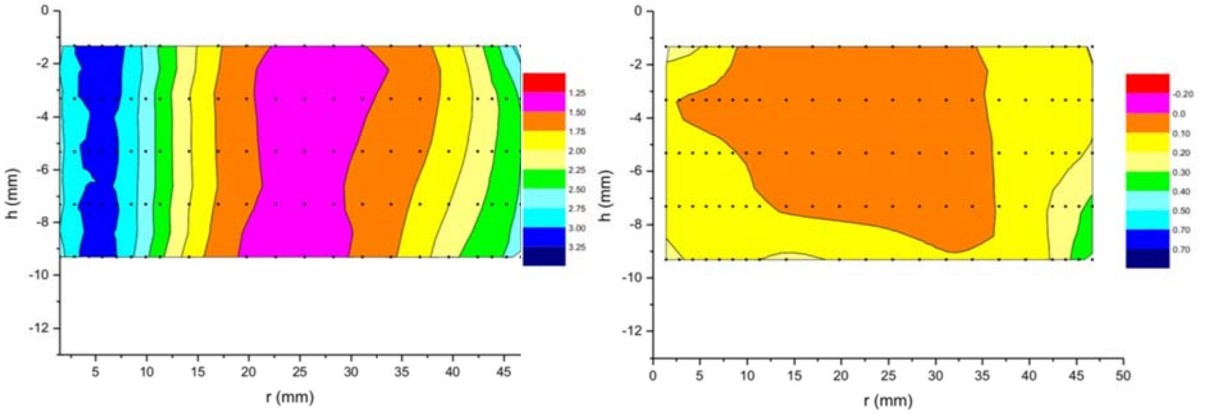

Figure 2. Typical contour plots of v_r and v_φ vs r distribution inside vortex chamber

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CATALYTIC DEVICE ON THE BASE OF GLASS-FIBER CATALYST FOR ENVIRONMENTALLY SAFE COMBUSTION OF FUELS AND UTILIZATION OF TOXIC WASTES

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Catalytic combustion of fuels and various organic substances create the environmentally efficient basis for novel technologies in the area of energy production and utilization of harmful wastes. The glass-fiber catalysts (GFCs) which are under active development during last two decades are very promising for such applications due to their low pressure drop, intensive mass transfer and high thermal stability [1-3].

The flow-sheet of the catalytic combustor is presented in Fig. 1.

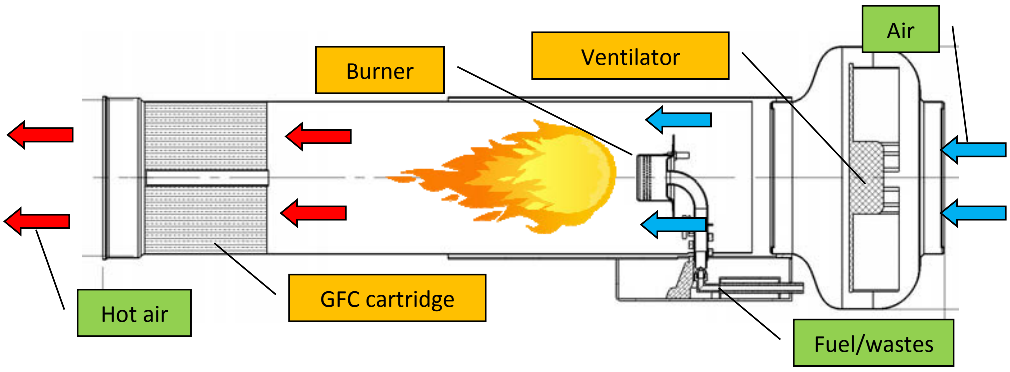

Fig. 1. The flow-sheet of the catalytic combustor

The initial fuel is oxidized in the burner under limited amount of air supply to the flame zone. The oxygen deficiency in this zone gives the way to minimize or completely exclude the formation nitrogen oxides. Then the combustion products are mixed with air and fed to GFC-based cartridge, where CO and unburned hydrocarbons and organic substances are catalytically oxidized to harmless products: CO_2 and water.

The combustor may be used for direct air heating in various rooms and buildings. If the initial air contains some organic compounds, then they will be also oxidized, so the combustor may clear the atmosphere in the room instead of polluting it. The air may be supplied from the outside, so the combustor may combine the functions of air heating and ventilation systems.

The device uses the thermostable Pt-containing GFC IC-12-S111 [1] within the spiral cartridge structured with metal meshes. Such cartridges are characterized with high efficiency of mass transfer and low pressure drop.

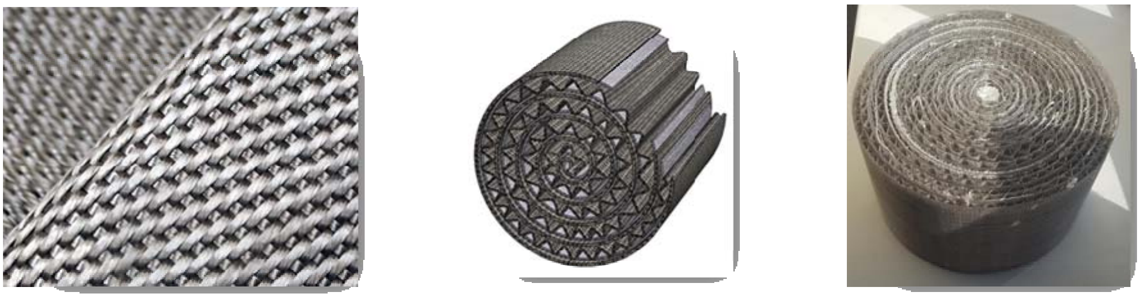

Fig. 2. The IC-12-S111 catalyst (left), structure and view of spiral catalytic cartridge (center and right)

The pilot tests of the 15 kW combustor were performed using the LPG (propane-butane) as a fuel. The test demonstrated the achievement of the designed heat power. The outlet gases contained less than 5 mg/m^3 CO, less than 11 mg/m^3 hydrocarbons and less than 1 ppm NOx. The obtained environmental efficiency of the proposed device is higher than one for all known analogs.

Except conventional gaseous fuels (LPG, natural gas) the GFC combustor may be adapted for the use of liquid fuels, both the conditional ones and the liquid wastes, containing the significant amounts of toxic organic compounds. In the latter case, the device may be mostly used, except energy production, for utilization of hazardous wastes.

The GFCs are known as efficient catalysts for oxidation of chlorinated hydrocarbons [4], so the application areas may include the utilization of liquid toxic chlor-organic wastes without formation of toxic secondary wastes like phosgene or dioxins.

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ACTIVATION OF ALUMINUM OXIDE AIRGEL FOR IMPROVEMENT OF CATALYTIC CAPACITY IN THE REACTION OF PROPANE DEHYDROGENATION

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Recently, the monolithic aerogels of aluminum oxyhydroxide nanofilaments were obtained of by oxidation of pure aluminum, which possessed a high specific surface area of 300 m^2/g and a low density – 0.004 g/cm^3, which is significantly less than the values (0.01-0.05 g/cm^3) [1].

Investigations of catalytic activity were conducted at atmospheric pressure in catalytic fluid cracking unit with a quartz reactor, loading of the catalyst was equal to 0.05 g. As initial raw materials propane of high purity (99.98 mass %) was used. Flow velocity was equal to 1.25 ml/s.Analysis of the reaction products was carried out by means of a chromatograph Crystal 2000M.

Electron microscopic investigations showed that the NFOA microstructure consists of the intertangled aluminum oxide fibers with a diameter of about 5-6 nanometers. Investigations were conducted by means of an electronic translucent microscope of JEM 2120, the sample was placed on a substrate moistened with alcohol without preliminary treatment.

The parameters of the porous structure of the samples were determined from nitrogen vapors adsorption isotherms at 77 K, measured by means of a high-vacuum volumetric equipment ASAP-2020 MP Micromeritics USA. Comparative plots showed that the NFOA filaments are nonporous, that is coincides with the TEM microscopy data (Table 1).

Table 1. Pore structure characteristic of catalyst

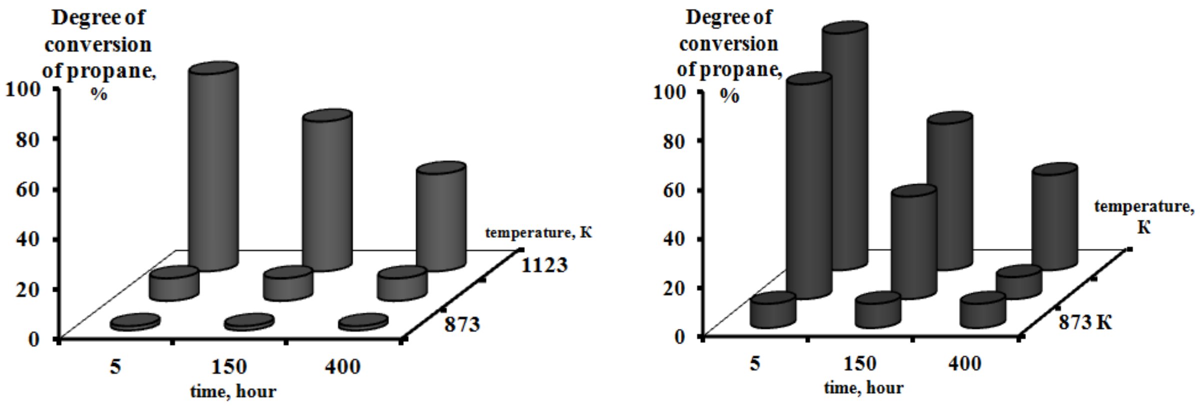
sample	S_{BET}, m^2/g	S_{Mp}, m^2/g	W_{BJH}, cm^3/g	2_{xoBET}, nm
NFOA	320	320	0.58/0.56	10
$NFOA_{act}$	219	184	0.48/0.50	35

Freshly prepared NFOA was used as a catalyst in the cracking of pure propane, but it has not shown any catalytic activity. Therefore, freshly prepared NFOA sample was activated in hydrogen flow at 1123 K for 1 hour, and the catalytic activity of the activated catalyst was investigated in the same model reaction.

The temperature dependence of ethylene selectivity of reaction shows that the $NFOA_{act}$ aerogels have a high selectivity in relation to ethylene formation at the yield of ethylene of about 50 % in the catalytic temperature range 773-1123 K, with a maximum of 63 % at 730 K (before resinification starts).

Temperature dependence of the yield of ethylene for the $NFOA_{act}$ catalyst increases more sharply than that observed for the commercial Pt/Al_2O_3 catalyst [2] displaying almost linear growth of yield with temperature. At that, starting from 923 K using the $NFOA_{act}$ gives the yield of ethylene higher than in the case of using of commercial catalyst. It should be noted that the commercial catalyst contains active metal – platinum which determines its activity.

The catalytic activity of the activated Al_2O_3 catalyst was quite stable. Namely, at temperatures up to 873 K, the catalyst exhibited the activity during ~ 400 hours. In the temperature range of 873-1023 K, the complete loss of activity occurred after 150 hours; above 1023 K the activity disappeared after 5 hours.



a b

Figure 1. The catalytic activity of the catalyst: a - free Al_2O_3; b - activated Al_2O_3

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HYDROGEN SOLUBILITY IN ANILINE/NITROBENZENE REACTION MIXTURES

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Mass transfer generally plays an important role in designing efficient gas-liquid-solid reactors. The achievable mass transfer rates of the gaseous compound significantly depend on its solubility in the liquid phase. For the catalytic hydrogenation of nitrobenzene to aniline, reaction scheme see Figure 1, solubility data at industrial conditions are rather unknown which hinders to model and to design corresponding multiphase reactors.

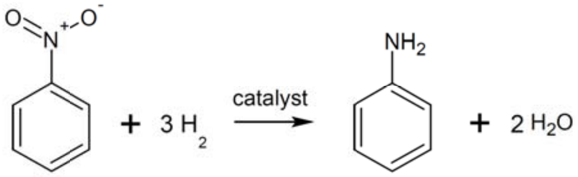

Figure 1. Reaction scheme for the hydrogenation of nitrobenzene to aniline

This work experimentally determines hydrogen solubility in reaction mixtures at different degrees of the nitrobenzene conversion, U_{NB}, by performing absorption experiments in a stirred-tank reactor under industrial conditions. The reaction mixtures either contained only the reactant nitrobenzene and the products aniline and water or contained additionally the solvent ethanol. As shown in Table 1, there is a miscibility gap at lower ethanol contents which eminently affects solubility. To avoid this miscibility gap, occuring under atmospheric conditions, it was essential to conduct the experiments for determining the solubility at elevated pressure and under constant stirring.

Table 1. Miscibility of the reaction mixture at different ethanol mole fractions, x_{ETH}, and different conversions of nitrobenzene, U_{NB}.

U_{NB} \ x_{ETH}	99.4 %	94.0 %	40.0 %	0 %
0 %	✓	✓	✓	✓
30 %	✓	✓	O	O
50 %	✓	✓	O	O
70 %	✓	✓	O	O
100 %	✓	✓	O	O

O - miscibility gap, ✓ - completely miscible

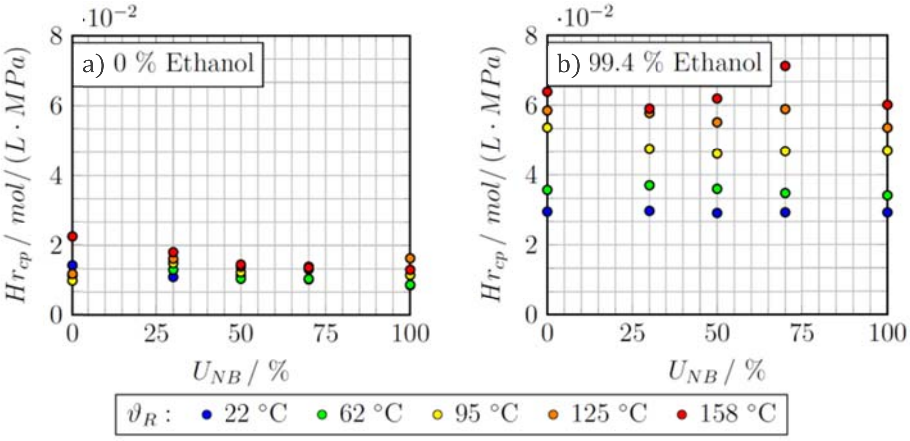

Figure 2. Hydrogen solubility, Hr_{cp}, in dependence on the reaction temperature, ϑ_R, and the nitrobenzene conversion, U_{NB}, for different diluted reaction mixtures [1]

From the amount of absorbed hydrogen, Henry coefficients at equal initial pressure, Hr_{cp}, were computed. Selected coefficients are depicted in Figure 2. It is obvious that the strongly diluted mixture provides significantly larger Henry coefficients. Furthermore, the impact of reaction temperature is more pronounced in comparison with the mixture exclusive of any ethanol.

The obtained Henry coefficients for hydrogen in the reaction mixture, Hr_{cp_M}, were well described by the following model (cf. [2]):

$$\ln Hr_{cp_M} = \sum_{i=1}^{N} [x_i \cdot \ln(Hr_{cp_i})] + \sum_{i=1}^{N} \left[\frac{K_i}{R \cdot T} \ln(1 + p_{s_i}(T)\, x_i Hr_{cp_i}(T)) \right] \tag{1}$$

containing the Henry coefficients of the pure liquids, Hr_{cp_i}, their mole fractions, x_i, their vapour pressures, p_{s_i}, as well as empiric model parameters, K_i. In the full paper further experimental solubility data and more details on the model parameters will be given.

It can be concluded that this work provides a reliable model to predict hydrogen solubility for a broad range of typically employed reaction mixtures at industrial conditions which forms the basis for a future model-based reactor optimization.

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EFFECT OF THE EXPERIMENTAL CONDITIONS ON THE HYDROCRACKING OF HYDROTREATED LIGHT CYCLE OIL

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The regular use of light cycle oil (LCO) for diesel fuel production by hydrotreatment (HDT) procedures is facing difficulties due to the currently stricter environmental regulations [1]. LCO present high sulfur, nitrogen and aromatic contents [2]. Most of the aromatic compounds are di-aromatic type hydrocarbons, i.e. naphthalene derivatives. One upgrading alternative may be to carry out hidrotreating (HDT) which involves hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and a controlled hydrodearomatization (HDA) for obtaining a 1,2,3,4-tetrahydronaphthalene (tetralin) enriched fraction followed by an hydrocraking (HCK) procedure to get benzene, toluene and xylene (BTX) [3]. A summary of the reactions involved is shown in Figure 1.

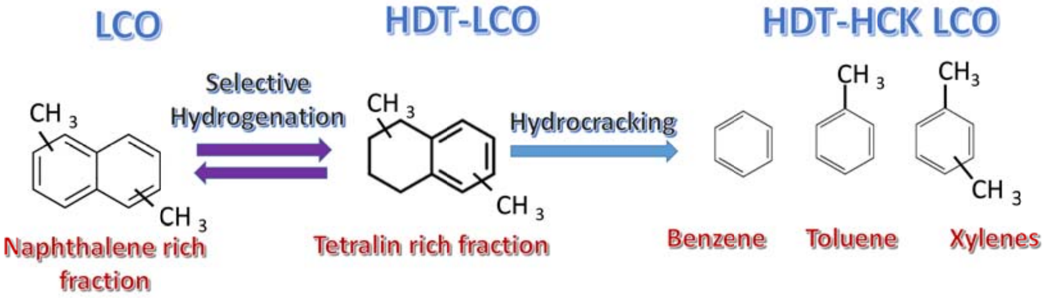

Figure 1. Reaction scheme for obtaining BTX, LPG and naphtha from naphthalene derivatives in the LCO

The main objective was to study the experimental conditions required for the HCK process for obtaining the higher amount of BTX from tetralin derivatives present in the hydrotreated LCO (HDT-LCO).

The experiments were carried out in a bench-scale unit equipped with a fixed-bed trickle reactor (Catalyst volume = 6.62 mL; internal diameter = 1.0 cm; down-flow mode). A commercial HCK catalyst was used. The experimental conditions were: 350-450 °C, 1.2. 1.7, 1.9 and 2.7 h^{-1} (WHSV), 7.4 MPa, and H_2/Hc ratio of 442 m^3/m^3. The liquid products were weighted and characterized by the FID-GC, according their retention times as follows: Light fraction (LF), BTX, middle fraction (MF) and heavy fraction (HF). The following equations were used:

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Hydrocracking yield (HCK)	$HCK,\% = 100\left[\frac{MF_{feed} - MF_{\mathrm{Prod}}}{MF_{feed}}\right]$
BTX selectivity	$BTX,\% = 100\left[\frac{BTX}{TOTAL}\right]$

HDT-LCO as feed presented 0, 0, 98.7 and 1.3 wt. % of LF, BTX, MF and HF, respectively. The results are shown in Figure 2.

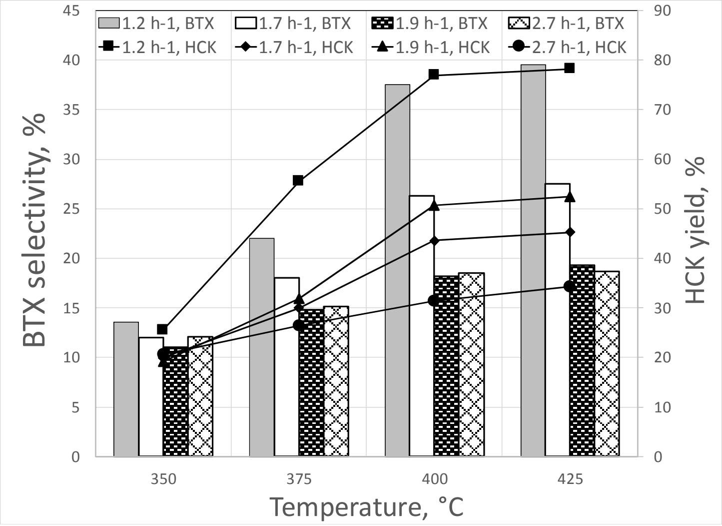

Figure 2. Effect of the experimental conditions on the BTX selectivity from HDT-LCO

The WHSV did not show to have an impact neither on the HCK yield nor in the BTX selectivity at 350 °C. Up to 400 °C as the temperature increased, the effect of the WHSV became more important. It is noteworthy that, at 400 °C, the HCK yield decreased from 77 to 31 % and the BTX selectivity went from 37 to 19 % by increasing the WHSV from 1.2 to 2.7 h^{-1}. The increment in the temperature at a 2.7 h^{-1} did not show notable effects neither in the HCK yield nor in the BTX selectivity.

Optimal experimental conditions for attaining higher HCK yields and BTX selectivity were: 1.2-1.7 h^{-1} (WHSV), 375 to 400 °C and 7.4 MPa.

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EFFECT OF THE CATALYST ON THE HYDROGENATION OF LIGHT CYCLE OIL

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The regular use of light cycle oil (LCO) for diesel fuel production by hydrotreatment (HDT) procedures is facing difficulties due to the currently stricter environmental regulations [1]. LCO present high sulfur, nitrogen and aromatic contents [2]. Most of the aromatic compounds are di-aromatic type hydrocarbons, i.e. naphthalene derivatives. One upgrading alternative may be to carry out hidrotreating (HDT) which involves hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and a controlled hydrodearomatization (HDA) for obtaining a 1,2,3,4-tetrahydronaphthalene (tetralin) enriched fraction followed by an hydrocraking (HCK) procedure to get benzene, toluene and xylene (BTX) [3].

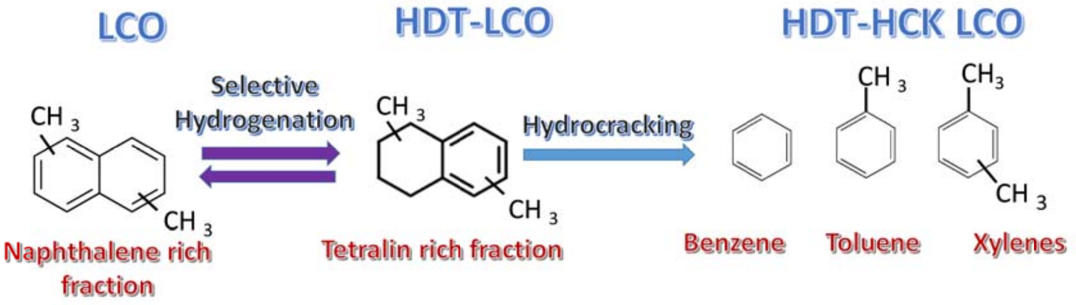

Figure 1. Reaction scheme for obtaining BTX, LPG and naphtha from naphthalene derivatives in the LCO

The main objective was to study the effect of the catalyst: Cobalt-moolybdenum (CoMo, HT-1) or Nickel molybdenum (NiMo, HT-2) on alumina (Al_2O_3) for reaching the higher conversions to tetralin derivatives.

The experiments were carried out in a bench-scale unit equipped with a fixed-bed trickle reactor (Catalyst volume = 6.62 mL; internal diameter = 1.0 cm; down-flow mode). Two commercial HDT catalyst were used. The experimental conditions were: 330-370 °C, 1.2 and 2.5 h^{-1} (LHSV), 5.5 and 7.54 MPa, and H_2/Hc ratio of 360 and 800 m^3/m^3. The liquid products were weighted and characterized using the following standard procedures: ASTM D-4294 (sulfur conent, wt. %), ASTM D-4629 (nitrogen content mg/kg), and aromatic content (D-5186, wt. %). Results are shown in Figure 2.

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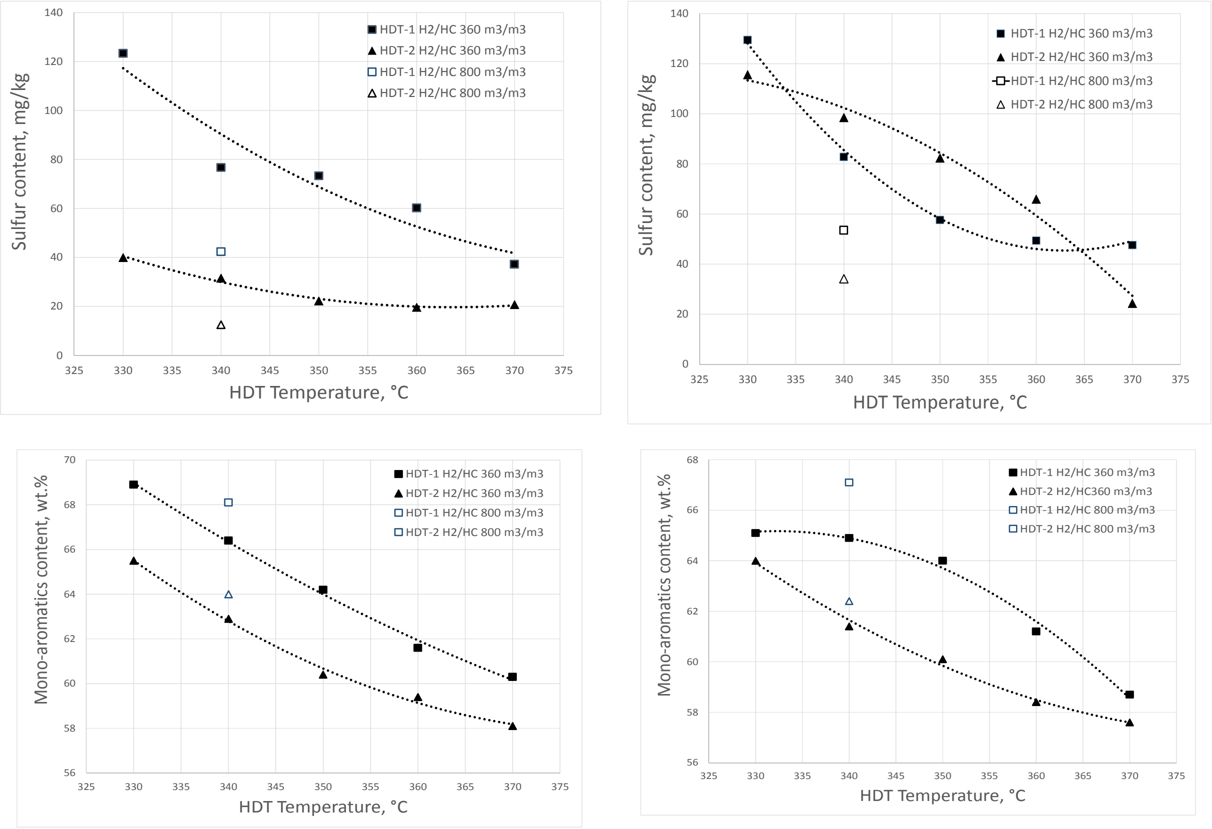
Sulfur content decreased as the temperature increased at both 5.5 and 7.5 MPa for both catalyst, HDT-1 and HDT-2. However, at 5.5 MPa, the HDT-2 presented a better performance reducing the sulfur content to less than 40 mg/kg at temperatures as low as 330 °C. The higher LHSV from 1.0 to 2.5 h^{-1} did not seem to have an adverse effect.



5.5 MPa   7.5 MPa

Figure 2. Effect of the experimental conditions on the hydrogenation of LCO

The increment in temperature using both catalyst (HDT-1 and HDT-2), and pressures (5.5 and 7.5 MPa) presented a detrimental impact in the mono-aromatic presence for all the hydrotreated products. The higher amount of mono-aromatics were obtained when using HDT-1, 330 °C, 5.5 MPa, and a H_2/HC of 360 m^3/m^3. A faster LHSV from 1.0 to 2.5 h^{-1} seemed to have also a good influence (Figure 2).

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NUMERICAL STUDY ON FLUIDIZED BED METHANATION BY USING OpenFOAM

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Methanation from syngas or coke oven gas for the production of synthetic natural gas (SNG) is a feasible way to alleviate the problems due to sharply-increasing energy demands [1]. Quite a few researchers have investigated the fixed bed methanation process which has been successfully utilized in the commercial plants [2, 3]. Compared with fixed bed, bubbling fluidized bed methanation is promising technology due to its advantages in mass and heat transfer, especially for the highly exothermic methanation reactions [4]. However, the multiphysics including gas-solid two-phase flow, mass and heat transfer and the chemical reactions in the bubbling fluidized bed are complex due to the multi-scale phenomenon [5].

In this work, a numerical model is developed by accounting for the multi-scale phenomenon. For the micro-scale, a modified chemical kinetic model is proposed based on the kinetics of Kopyscinski et al. [6] by taking account the chemical equilibrium of CO methanation. The modified chemcial kinetics can be extended to higher temperature and can also be utilized to dynamic simulations. For the meso-scale structure, the local-structure-dependent drag model in our previous study is employed to calculate the gas-solid interactions [7]. In the macro-scale, the continuity equations, momentum equations and the species transport equations are solved by using the *reactingTwoPhaseEulerFoam* solver in the open source package OpenFOAM. Isothermal flow is assumed in the bubbling fluidized bed and thus the energy equations are not solved [8]. Then the simulation results were validated by some experiments in a lab-scale bubbling fluidized bed with the inner diameter of 15mm and the initial bed height of 12 mm. The product gases were dried and the compositions were quantitatively determined by mass spectrometry.

The effects of operating temperature, inlet gas composition and superficial inlet gas velocity are investigated and verified. Figure 1 shows the comparison of the experimental and simulated outlet gas compositions at different operating temperatures. It can be found from the figure that, in general, the model predictions are in agreement with the experimental data. The accurate predictions at higher temperature (>400 °C) demonstrate that the modified kinetic model can capture the reaction behaviours in a fluidized bed methanation process. In addition, the numerical predictions at different inlet gas compositions and superficial inlet gas velocities are also in agreement with the experimental results.

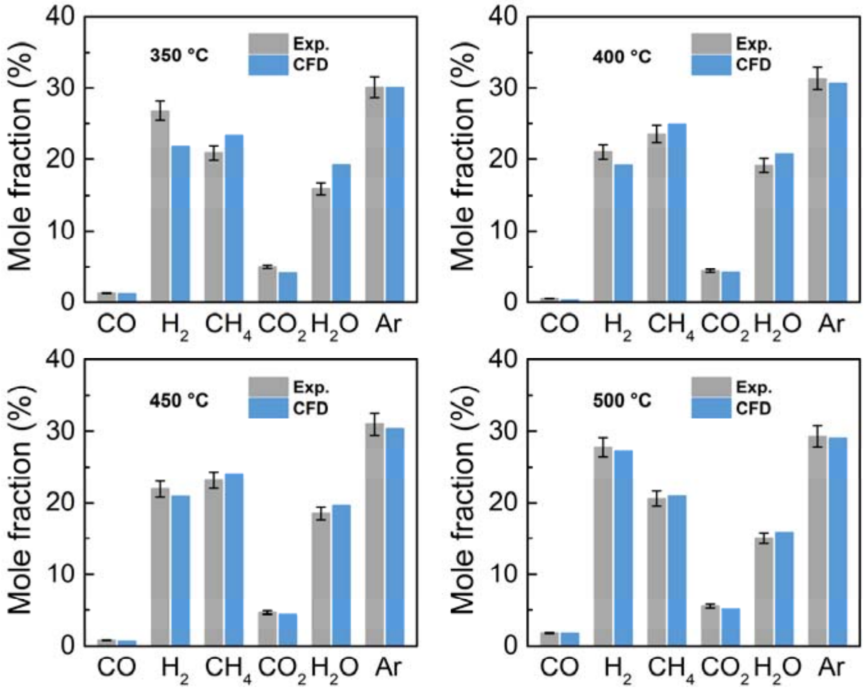

Figure 1. Comparison of the experimental outlet gas compositions and CFD simulations at different operating temperatures

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PREPARATION OF Mo-BASED CATALYSTS IN A T-SHAPED MICROMIXER AND ITS OXIDATIVE DESULFURIZATION PERFORMANCE

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MoO_3/SiO_2, a supported transitional metal oxide, has proved to be an efficient catalyst for oxidative desulfurization (ODS) [1]. The ODS performance of MoO_3/SiO_2 is significantly influenced by its particle size uniformity. Traditional synthetic methods in tank reactors always lack precise control over the mixing, nucleation and growth processes, thus the sizes and size distribution of the particles are not in uniform. Therefore, the obtained catalyst shows low activity and stability for ODS [2]. Due to the excellent properties of heat and mass transfer and continuous processing, micro-mixer offers a variety of advantages over batch synthesis of nanoparticles and has already been widely applied in synthesizing nanomaterials and catalysts [3,4].

Herein, a facile controllable route for preparing 10 % MoO_3/SiO_2 in the T-shaped micro-mixer was reported. The effects of the preparation conditions, such as flow rate, temperature and reactant concentration were investigated so as to obtain the optimal synthesis condition. In order to contrast, a sample synthesized through batch reactor was prepared. The X-ray diffraction (XRD) patterns of the samples are presented in Figure 1. All diffraction peaks can be indexed to the pure MoO_3 without the presence of any impurities and the sample prepared through micro-mixer shows an enhanced dispersion of MoO_3 over SiO_2. The catalyst shows higher activity and stability in the oxidation of dibenzothiophene (DBT) with tert-butyl hydroperoxide (TBHP) as the oxidant than the catalyst prepared by traditional synthesis method (sol-gel) in tank reactors, as shown in Figure 2. It should be noted that, 10 % MoO_3/SiO_2 prepared via the T-shaped micro-mixer also shows remarkable stability in a fixed-bed reactor with high ODS activity (96 %) and negligible leaching of Mo in 300 h.

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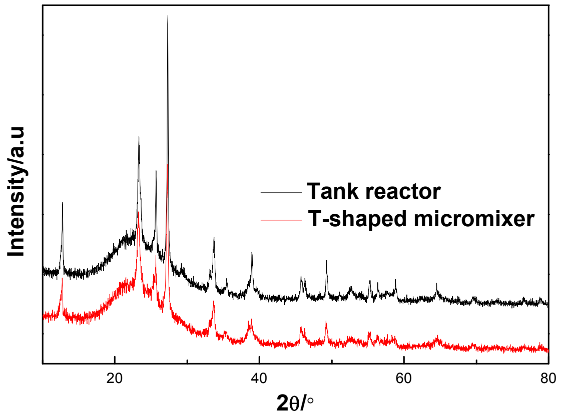

Fig. 1. XRD patterns of MoO_3/SiO_2 prepared by different reactor types

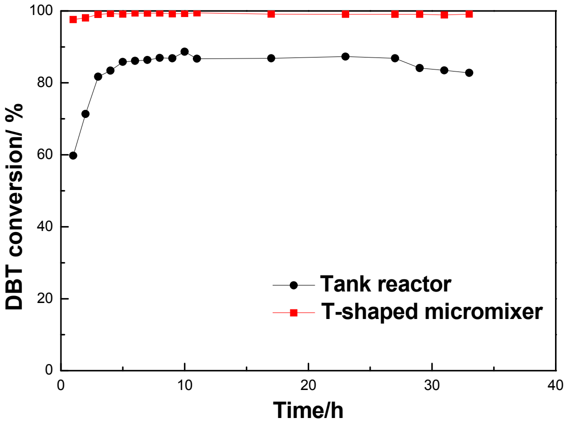

Fig. 2. DBT conversion on MoO_3/SiO_2 catalysts with different reactor types

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METHANOL-TO-OLEFINS: A DETAILED DESCRIPTION FOR THE AROMATIC HYDROCARBON POOL

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In recent years, research on sustainable alternatives to crude oil has increased due to fluctuating oil prices and gain in environmental awareness. Among commercially relevant olefins, particularly the interest in propylene has risen due to significantly increased demands. Currently, the established methanol-to-olefins (MTO) process over an H-ZSM-5 or H-SAPO-34 zeolite provides an alternative route towards light olefin as compared to steam cracking [1].

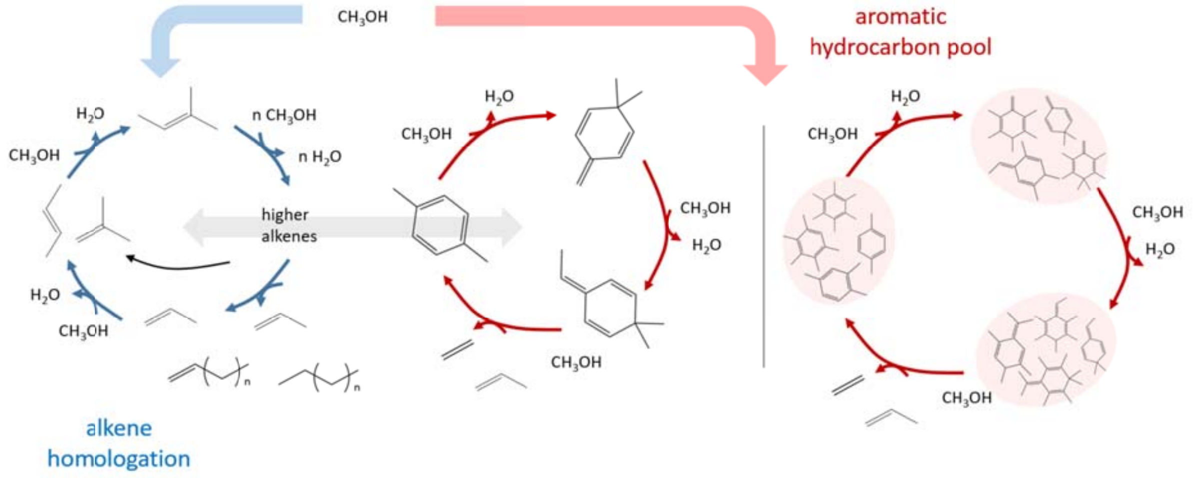

Figure 1. Dual cycle mechanism consisting of the alkene homologation cycle (left) and the aromatic hydrocarbon pool as considered in the state-of-the-art (middle) and molecularly detailed (right) kinetic model on a zeolite catalyst, adapted from [1]

Over the years, many different reaction mechanisms have been proposed for the zeolite-catalyzed MTO reaction. At present, it is generally accepted that conversion within the zeolite occurs according to a dual cycle mechanism [2, 3], comprising two catalytic cycles, as schematically represented in Figure 1. The first one corresponds to *'alkene homologation'* and mainly ensures the formation of higher, i.e., C_3^+, olefins through carbenium ion intermediates. The second one, denoted as the *'aromatic hydrocarbon pool'*, is responsible for C_2-C_3 olefin formation. In H-ZSM-5, highly-methyl-substituted benzenes, rapidly interconverting among each other, have been identified as the catalytically active centers transforming methanol into olefins [4].

The propylene selectivity can be steered by manipulating the extent to which both catalytic cycles contribute to the product distribution. A fundamental model, capable of quantifying these contributions would, hence, be an invaluable asset.

In the current state-of-the-art, the aromatic hydrocarbon pool species is considered as a separate catalytic site distinct from the acid sites in the zeolite framework [5]. The present work aims at more accurately describing the MTO reaction by including a detailed molecular description of the aromatic hydrocarbon pool species as indicated in Figure 1 (right). Accounting for the chemical dynamics of the formation and consumption of the species belonging to both the alkene homologation and aromatic hydrocarbon pool cycle will allow to well described the balance between both catalytic cycles. The application of (de)-protonation, (de)-methylation, (de)-alkylation and rearrangement reaction families to the methylated benzene species results in the complete reaction network comprising 4443 aromatic hydrocarbon pool species being interconverted in 13694 reactions. This implementation was performed with the in-house developed Reaction Network Generation Program (ReNGeP) [6] for acid-catalyzed conversion of fossil resources.

Current work in progress is the implementation of this detailed network in the in-house developed kinetic model for methanol-to-olefins [5]. The newly developed model is expected to accurately represent the balance between the two catalytic cycles and the experimentally observed product distribution [7] as compared to the state-of-the-art model [5].

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STUDY OF KINETIC ASPECTS OF THE WATER VAPOR ADSORPTION ON ALUMINUM OXIDE MATERIALS DOPED WITH ALKALI METAL IONS

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Water removal is an important step in air conditioning and industrial gas drying. Water is removed from air to avoid undesirable influence caused by liquid and ice formation and corrosion. The adsorbents based on aluminum oxide have found wide application just owing to their high efficiency in drying of gases with relative humidity and to their high mechanical strength [1, 2]. To ascertain the role played by the chemical modification in changing the adsorption characteristics and acid properties of the surface [3], it is necessary to have data on the adsorption dynamics (kinetics), obtained with the fine fraction of the sorbent in the absence of the internal diffusion.

In this work, we studied the kinetics (dynamics) of the water vapor adsorption on aluminum oxide materials modified with alkali metal ions.

In this study, the used several same pseudoboehmite-based samples synthesized by the method of centrifugal thermalactivation of hydrargillite [4]. Sample A-2 was produced by peptization with nitric acid, and samples modified with alkali ions of sodium (A-2–Na) and potassium (A-2–K) were formed by peptization with alkali solutions (NaOH and KOH).

The adsorbents were characterized by physicochemical analysis: an *X-ray diffraction* (XRD) analysis was made on a Rigaku Miniflex 600 diffractometer; *thermogravimetric studies* of the samples were carried out on a NETZSCH STA 409 instrument for synchronous thermal analysis in the oxidizing atmosphere; the *texture characteristics* were determined from nitrogen adsorption isotherms measured at 77 K; the *mesopore volume* was calculated by analysis of the curve of the integral pore volume distribution as a function of the pore radius; the *content of* sodium and potassium in the samples was determined by the method of mass spectrometry with inductively coupled plasma (ICP-MS) on an Agilent 7500cx instrument.

According to the XRD results, the samples of aluminum oxide drying agents had the form of a mixture of low-temperature modifications of aluminum oxide,

($\gamma + \eta + \chi$)–Al_2O_3. The phase ratio remained nearly unchanged upon. The content of sodium ions in the modified samples A-2–Na and A-2–K, the content of the corresponding modifying cation is ~2 wt %.

The determination of the dynamic of water vapor adsorption on adsorbent samples were determined by the weighing method on a McBain–Bakr quartz balance. The sensitivity of the balance was 2.9 × 10^{-3} g mm^{-1}. The results of the measurements are shown in Figure.

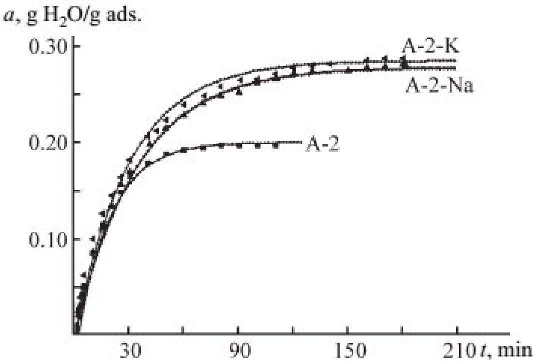

Fig. Dynamic curves of water vapor adsorption on the different adsorbent samples (the 0.5-1.0-mm fraction). The points represent the experimental data, and the lines are calculated by the equation (1)

For the vapor adsorption under isothermal conditions at a constant partial pressure, the kinetic absorption process is described by the equation:

$$da/dt = \beta(a^* - a), \quad t=0: a = 0.$$

Thus, it was found that the alkaline modification of the surface of aluminum oxide adsorbents results in that absorption equilibrium (a^*) increases (by ~40 %) as compared with the unmodified drying agent.

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SIMULATION OF THE RECOVERY AND STORAGE OF RESIDUAL THERMAL ENERGY IN SOLIDS OF THE INDUSTRY OF NORTHERN MEXICO

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Thermal energy is a type of energy widely used in industrial processes and due to its inherent characteristics, its use has not been maximized. In this project, a packed bed equipment is simulated, to analyze regional, natural and waste solids, for you take advantage of its transport properties and take advantage of the thermal energy of process waste streams and preheat the supply currents, in this way the heating service requirement will decrease and the emissions to the environment will have lower temperatures than the current ones. This project focuses on proposing the resolution of a mathematical model based on transport phenomena with experimental validation [1,2,3] that allows the adequate design of a thermal energy recovery and storage system.

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EVALUATION OF THE EFFICIENCY OF THE DEWAXING UNIT UNDER OPTIMAL CONDITIONS

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The study of properties and prediction of the behavior of complex systems, both natural and artificial, is impossible without constructing models of these systems. Depending on the nature of the system under investigation, physical or mathematical models can be used. As a rule, mathematical models are more often used to study complex systems than physical models, since they have a number of advantages.

The necessity of applying the method of mathematical modeling for chemical industry systems is dictated by the urgency of the problem of the efficiency of production processes. Especially this problem is relevant for catalytic processes, since the possibilities of the physical modeling method are limited when applied for the purpose of optimizing processes and predicting the catalyst regeneration cycle.

In this study, calculations were performed using a mathematical model of the dewaxing process. The mathematical model was supplemented with the function of searching for the optimal temperature regime of the process, depending on other input parameters (raw material quality, raw material consumption, hydrogen-containing gas flow) [1].

The controlled parameters of the dewaxing process are the raw material consumption, the hydrogen-containing gas flow rate and the reactor temperature. Since the consumption of raw materials is determined by the need for the product, the optimization of the process was carried out according to the temperature and flow rate of the hydrogen-containing gas.

In the study [1] on the effect of hydrogen-containing gas on product yield, cold filter plugging point, and relative activity of catalyst activity, recommendations were proposed on the values of raw material consumption, depending on the density of raw materials, which were taken into account in the calculations.

The purpose of temperature optimization is to determine the value of such a process temperature at which the temperature of the cold filter plugging point of the product (diesel fraction) is reached minus 26, as a rule, this temperature corresponds to the maximum yield of the diesel fraction, because the overestimated process temperature leads to an increase in the yield of gasoline and gas fractions and reduction of the yield of the diesel fraction.

The calculation shows that with an optimal consumption of the hydrogen-containing gas and the process temperature, it is possible to obtain a larger yield of the product on average by 2.6 % per year, it is permissible to conduct the process at a temperature somewhat lower (on average 5-7 °C) without loss quality of the product, in addition, the coke accumulation is significantly reduced and the activity of the catalyst remains (Fig. 1, Table 1).

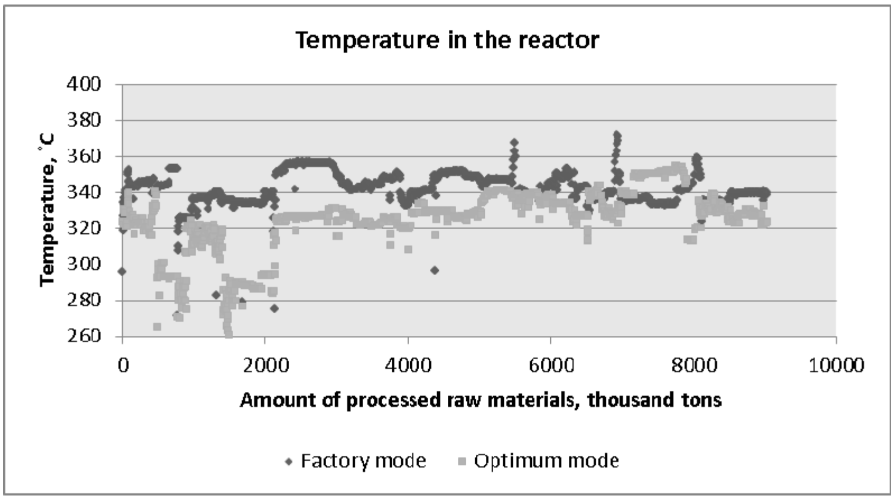

Fig. 1. Optimum and factory temperature modes

Table 1. Operating parameters of the dewaxing unit

Yield of diesel fraction, thousand tons							
Year	2012	2013	2014	2015	2016	2017	Amount
Factory mode	921	1125	1954	1752	1538	397	7687
Optimum mode	940	1179	2013	1756	1605	401	7894
Increase in yield of diesel fraction in operation at the optimal temperature regime, %	2,0	4,6	2,9	0,2	4,2	1,0	2,6
Relative activity of the catalyst at the end of the period, rel. units							
Factory mode	0,55						
Optimum mode	0,96						
The average temperature in the reactor, °C							
Factory mode, °C	341						
Factory mode, °C	334						

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KINETICS OF DEHYDRATION OF LINEAR PRIMARY ALCOHOLS OVER H-ZSM-5 ZEOLITE CATALYST UNDER HIGH PRESSURE

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Alcohols/bio-alcohols conversion to distillates as an alternative feedstock for energy is receiving considerable attention the world over since the discovery of methanol to gasoline and distillates (MTGD) process by ExxonMobil. Information regarding the conversion of primary alcohols to distillates remains limited on the open literature. The purpose of this study was to investigate reaction mechanisms and kinetic constants of linear primary alcohols dehydration over HZSM-5 zeolite catalyst under conditions used in the conversion of olefins to distillates (COD) reaction system viz. 40 bar; 220 °C. The ethanol kinetics were developed via the hydrocarbon pool mechanisms in which the alkylation of dietyhyl ether formed was dominant. The kinetic constants for ethanol dehydration when co-fed with propylene were determined by regression of experimental data at 220-260 °C. Whilst, the dehydration kinetic constants of n-propanol and n-butanol were determined at 140-185 °C. The results obtained for all alcohols dehydration showed a reasonable agreement between experimental data and the proposed kinetic model. The results found depicts that ethanol dehydrates to ethylene, diethyl ether and water, while diethyl ether formed further reacts with the co-fed propylene as well as generated C4 and C5 olefins to form higher olefins. Minor oligomerization of propylene and butene to C6 and C7 olefins was also observed. n-Propanol was found to have dehydrated to propylene, di-n-propyl ether and water. Whereas, the dehydration of n-butanol led to the formation of butene, di-n-butyl ether and water. In both instances, no occurrence of oligomerization reactions was observed. Lower temperatures favoured ethers formation (via Lnk_2) rather than olefins (via Lnk_1) due to the predominance of the forward exothermic reactions where ethanol, n-propanol and n-butanol dehydrated to diethyl ether, di-n-propyl ether and di-n-butyl ether respectively, as shown in Figure 1. The apparent rate constants further showed that olefins are formed firstly through the decomposition of ethers (Lnk_3) especially at low temperatures compared to the dehydration of alcohols to olefins (Lnk$_1$), as can be seen in Figure 1a, 1b and 1c. With regards to ethanol dehydration, the alkylation of diethyl ether (Lnk$_4$) occured at the faster rate compared to dehydration (Lnk$_1$, Lnk$_2$ and Lnk$_3$) and oligomerization (Lnk$_5$) rates, as shown in Figure 1a.

The apparent activation energies of -104±3.76 kJ mol^{-1} and -116±7.27 kJ mol^{-1} were determined for the dehydration of ethanol to ethylene and the decomposition of diethyl ether to ethylene reactions respectively. Whilst, the apparent activation energy for the alkylation of diethyl ether with olefins was determined as -70±2.7 kJ mol^{-1}. For the dehydration of n-propanol to propylene and the decomposition of di-n-propyl ether to propylene the determined apparent activation energies were -80±1.5 kJ mol^{-1} and -10±0.23 kJ mol^{-1} respectively. While, the apparent activation energies of -102±1.0 kJ mol^{-1} and -5.6±1.1 kJ mol^{-1} were determined for the dehydration of n-butanol to butene and the decomposition of di-n-butyl ether to butene reactions respectively. In overall, the reaction temperature was the main driving force for the dehydration of alcohols mainly owing to endothermic nature of these reactions.

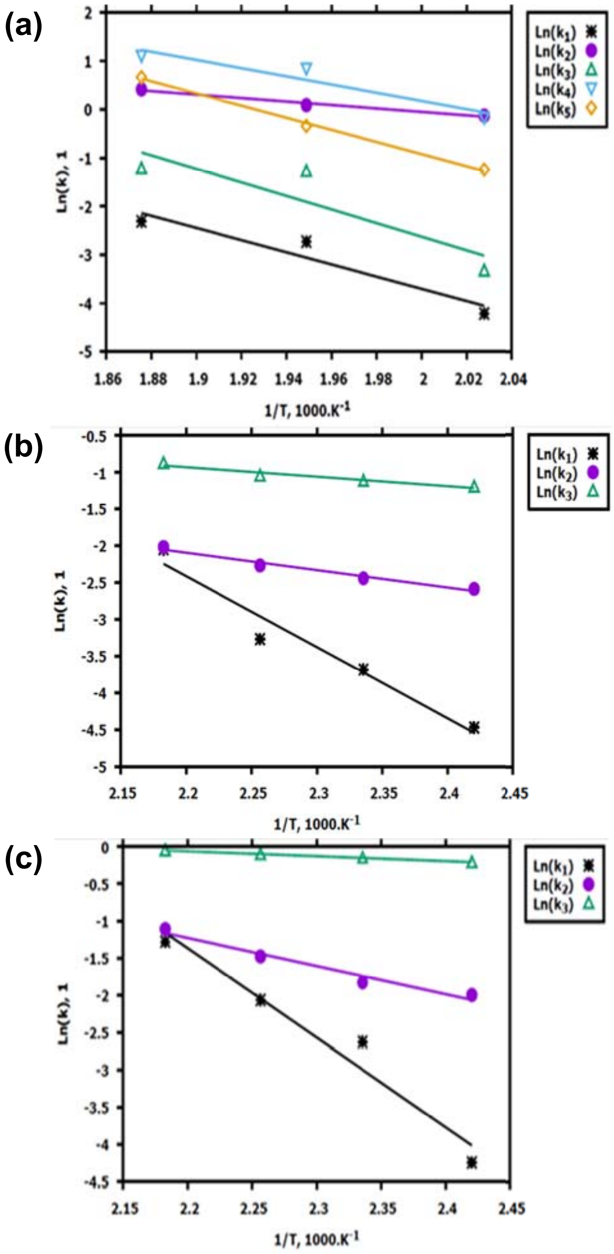

Figure 1. Arrhenius plots of alcohols dehydration reactions over HZSM-5 catalyst at 40 bar. **(a)** ethanol, **(b)** n-propanol and **(c)** n-butanol. Points: kinetic model reaction rate constants. Lines: fitted gradient line (Ea/R)

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THREE-STAGE HEAVY OIL HYDROPROCESSING OVER MACROPOROUS CATALYSTS

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Effect of catalyst pore size on heavy oil hydroprocessing has been a matter of discussion for several decades. It is widely known that a developed pore structure is needed for high molecular heavy oil components to access catalytic sites, however, exceedingly high pore volume and size should inevitably lead to the drop in specific surface area and mechanical strength of the catalyst pellet. Therefore, the optimum in the pore size for this particular process is considered to be in the range of 30-50 nm [1]. Nevertheless, more and more decreasing quality of heavy feed encourages researchers to extend the range of the pore size to a macroporous region. A theoretical contribution [2] reports on the superior lifetime and lower deactivation rate of the hierarchically structured catalyst with a meso-macropore network compared with the optimized purely mesoporous structure. The present work is aimed at studying the effect of hierarchical macro-mesoporous structure on the catalyst activity in heavy oil hydroprocessing. A facile "hard" template method using polymeric microbeads has been proposed for the preparation of alumina-supported catalysts with the desired textural parameters. Multistage catalytic experiments have been carried out under conditions close to the industrial ones (350-420 °C, 7 MPa, LHSV 1 h^{-1}, vol. H_2/feed = 1000, 200-800 h on stream), with the I stage providing metal and asphaltene removal, II stage capable of S removal, and III stage designed for hydrocracking of large molecules.

The proposed "hard" template method consists in creation of the additional macropore structure by the removal of polymeric microbeads from the precursor-template composite [3, 4]. Monodispersity and tunable size make these microbeads good templates for the preparation of hierarchical Al_2O_3 with bimodal porosity (10 and ~200 nm) and exceedingly narrow pore size distribution. Therefore, specific surface area (100-150 m^2/g) and mechanical strength (2-5 MPa) values lay in the range

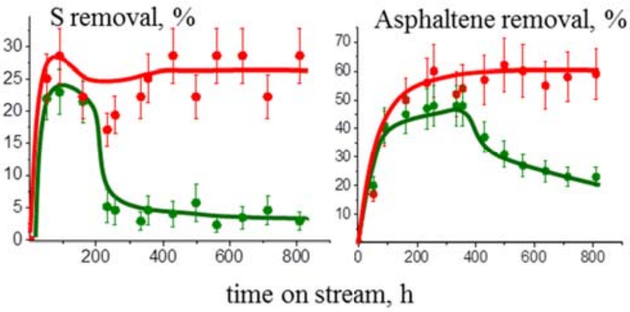

Figure 1. Sulfur and asphaltene removal over hierarchical (red) and mesoporous (green) catalyst

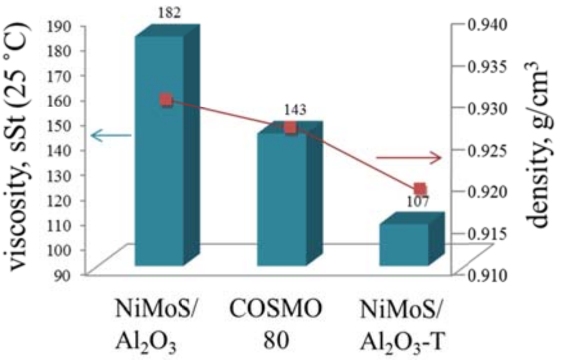

Figure 2. Viscosity and density of the products over the reference (NiMoS/Al_2O_3), commercial (COSMO-80) and hierarchical (NiMoS/Al_2O_3-T) catalyst

typical for purely mesoporous structures, whereas pore volume reaches 0.75-1.20 cm^3/g with 30-75 % of macropore volume fraction. The catalysts supported on hierarchical Al_2O_3 were tested in the consecutive three-stage hydroprocessing of heavy Tatar oil in the following order: I stage – metal and asphaltene removal over a “guard-type” catalyst Al_2O_3, II stage – S removal over a hydrotreating NiMoS/Al_2O_3 catalyst, III stage – hydrocracking and isomerization over NiMoS/Al_2O_3-ZSM-5 catalyst modified with zeolite as an acidic additive. The samples based on the reference mesoporous Al_2O_3 and a commercial catalyst COSMO-80 were also investigated for comparison. The experiments over the “guard-type” catalysts clearly revealed a rapid deactivation for the mesoporous sample: it showed a continuous decrease in asphaltene removal and significant drop in S/metal removal after 400 h on stream, while the macro-mesoporous catalyst still had five-fold S removal and three-fold asphaltene conversion, as well as 5-10 times higher demetallization after 800 h on stream. The second stage hydrotreating test demonstrated that the hierarchical NiMoS/Al_2O_3 only had a slightly better S conversion after 200 h on stream when compared to the reference and commercial samples (54 % vs. 47 and 50 %, respectively). Nevertheless, the viscosity of the oil products was substantially lower (by 40-80 %) that indicates the decrease in diffusion restraints in this process. The third stage experiments were carried out with the similar catalysts modified with 15 wt. % of zeolite. In the case of the mesoporous NiMoS/Al_2O_3-ZSM-5, no significant changes were observed in the catalyst activity and stability in comparison with the non-modified sample. The hierarchical structure, otherwise, makes zeolite crystals accessible for high-molecular reagents. So, the templated NiMoS/Al_2O_3-

ZSM-5 catalysts showed an extremely high hydrocracking rate leading to the rapid deactivation. A theoretical modeling of asphaltene diffusion in the hierarchically porous catalyst is also being in progress. The preliminary results do confirm the hypothesis of superior stability of the catalysts with bimodal pore size distribution.

A facile "hard" template method has been applied to the preparation of the hierarchical macro-mesoporous catalyst for heavy oil hydroprocessing. The technique allows one to obtain a narrow bimodal pore size distribution, that imply the specific surface area and mechanical strength values lay in the range typical for purely mesoporous structures, whereas the pore volume reaches 0.75-1.20 cm^3/g with 30-75 vol. % of macropores. The results on the consecutive three-stage hydroprocessing of heavy oil clearly indicate that the developed hierarchical texture improves the catalyst stability against metal and asphaltene deposition by several times, as well as increases hydrocracking activity of $NiMoS/Al_2O_3$ catalysts, especially those modified with zeolite as an acidic additive.

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EXPLORING PULSED LASER POLYMERIZATION IN VIEW OF REACTOR DESIGN AND CONTROL

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Many polymer products in everyday life are produced via free radical polymerization (FRP), which is characterized by a chain-growth mechanism with initiation, propagation, and termination as the basic reactions. The design of industrial scale radical polymerization reactors is complicated as many competitive phenomena are simultaneously occurring, including diffusional limitations due to viscosity changes along the polymerization [1]. A model-based design strategy is recommendable, as it allows a fast screening of a broad range of polymerization conditions. The success of model-based design strategies is however determined by the availability of accurate kinetic parameters. For many reaction steps, the Arrhenius parameters are still uncertain, which hampers the design of radical polymerization processes.

Moreover, in view of reactor control, accurate knowledge of the polymerization rate is crucial taking into account the high amount of heat generated during monomer incorporation. A key parameter controlling the polymerization rate is the propagation rate coefficient k_p. The preferred technique for the determination of k_p is pulsed laser polymerization (PLP) [2-5]. In PLP, photoinitiated radical pulses are generated with a frequency v (or dark time $\Delta t = v^{-1}$), which, after a limited monomer conversion (< 5 mol %), leads to a molar mass distribution (MMD) possessing repetitive inflection points L_j (j = 1, 2, …). For systems with one dominant macroradical type, k_p can be directly determined via:

$$k_\mathrm{p} = L_\mathrm{j}\,(j\,\Delta t)^{-1}\,[M]_0^{-1} \qquad (1)$$

in which $[M]_0$ is the initial monomer concentration.

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In acrylate radical polymerization, more than one dominant macroradical type can be present. Depending on the laser pulse frequency and polymerization temperature, secondary end-chain radicals (ECRs) can be converted into tertiary mid-chain radicals (MCRs) via backbiting. MCRs can in turn undergo β-scission leading to smaller ECRs and macromonomer. In this work, regression analysis to low frequency inflection point data is proposed as a novel methodology to determine the backbiting and β-scission rate coefficients k_{bb} [6] and $k_{\beta s}$ [7]. Due to the high activation energy of β-scission, Arrhenius parameters for backbiting can first be determined from low temperature PLP experiments (Figure 1) for which β-scission is kinetically insignificant. In a next step, the Arrhenius parameters for β-scission can be determined from high temperature experiments.

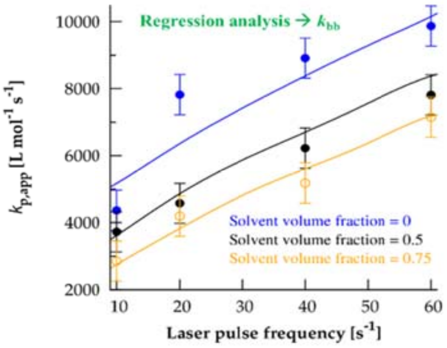

Figure 1. Application of the new method for the determination of k_{bb} to *n*-butyl acrylate radical polymerization at 303 K

The PLP technique can also be used to study radical copolymerization. Regression analysis to inflection point data obtained via PLP experiments with different initial comonomer volume fractions, allows the determination of cross-propagation rate coefficients and also allows to evaluate the importance of penultimate unit effects.

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THERMAL EXPLOSION IN A BATCH REACTOR WITH HETEROGENEOUS REACTION

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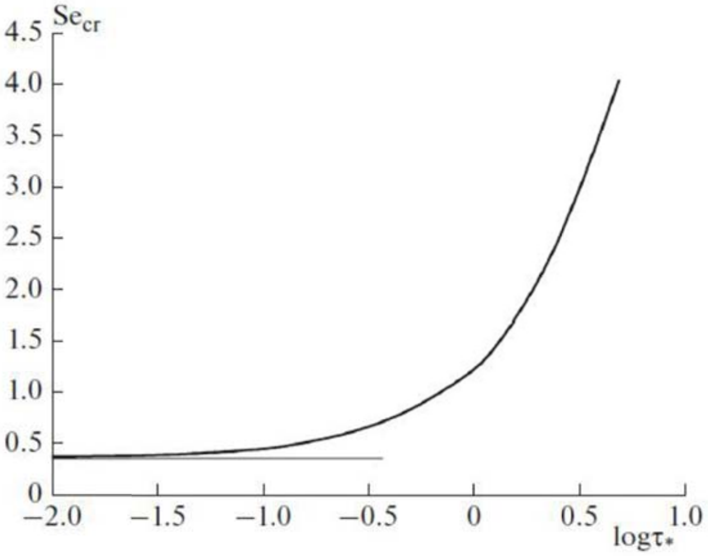
The characteristics of a thermal explosion in an ideal mixing batch reactor charged with a liquid–solid heterogeneous system are studied. The reactor initially contains both phases. The solid reagent dissolves and reacts in the liquid phase. A strong dependence of the critical value of the Semenov parameter on the dimensionless time of complete dissolution of the solid reagent is established. It is shown that, at short times of complete dissolution, the critical value of the Semenov parameter is practically independent on this time, and the thermal explosion occurs as in a homogeneous system, according to Semenov theory. The heterogeneous properties of the reaction system manifest themselves only at long times of complete dissolution.



Dependence of the parameter Se_{cr} of the dimensionless time τ_*. The line parallel to the abscissa corresponds to the value Se_{cr} of in the Semenov theory.

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POWER-TO-GAS: BIMETALLIC CATALYSTS SUPPORTED ON Al_2O_3 FROM A SULPHUR CONTAING BIOGAS

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Energy storage from alternatives sources (solar, wind,…) is possible by chemical way. The full process, Power-to-gas, uses the energy for the water electrolysis to produce hydrogen and oxygen in a first step. Secondly, carbon dioxide – from a biogas for example – reacts with hydrogen in order to produce methane that can be stored, burned or injected into the existing natural gas grid.

In this work, carbon dioxide methanation was studied from an effluent with sulphur, taking into account deactivation of the catalysts and a regeneration process. Because of that, different catalysts supported on alumina [1] were prepared, using nickel (13 %) as main active metal and with the addition of small amounts of transition metals like Mo, Fe, Co or Cr, in different proportion (from 4 to 8 wt. %), in order to increase their catalytic activity and deactivation resistance [2]. Addition of noble metals increased the dispersion and the reducibility of the nickel species [3]; while the addition of transition metals has the same effect than noble metals, increasing the dispersion and reducibility of nickel species with lower prices, thus reducing the prices of the catalyst. The nickel catalytic activity, between 300 and 500 °C, at 10 bar, was increased when transition metals were added. These bimetallic catalysts present a higher deactivation resistance than nickel monometallic catalyst. Although after several hours hydrogen sulfide also deactivates the bimetallic catalysts. Afterwards H_2S is removed followed by a regeneration with oxygen [4]. For the catalytic systems tested a different behavior was measured. Second metal addition proves that catalysts stability increased maintaining the high yield of monometallic catalyst.

The catalysts are studied employing different characterization techniques in order to analyze the main physicochemical properties. The techniques employed are: ICP-OES, N_2 adsorption-desorption isotherms at 77 K, TPR, XRD and XPS, between others. Physicochemical characterization of catalytic samples shows differences in chemical state, metal-support interactions, average crystallite sizes and redox properties of nickel metal particles.

The activity tests were performed in a bench-scale plant using temperatures ranging between 523 and 723 K at 10 bar, feeding a mixture of H_2 and CO_2 in a 4:1 ratio (275 mL/min of mass flow with 0,2 g of catalyst). The yield obtained for the different catalyst prepared is summarized in figure 1.

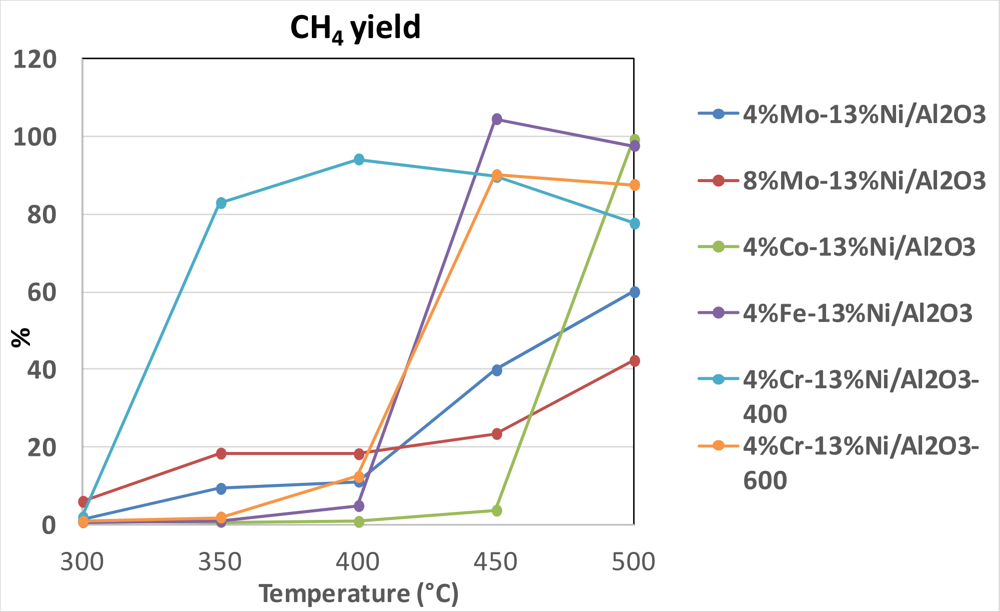

Figure 1. Methane yield obtained for the tested catalysts supported on γ-alumina

High initial activity is achieved for the Cr promoted Ni catalyst. On the contrary, for the Fe promoted catalyst high activity is achieved but only at high temperature.

The main goal of this work is the valorization of CO_2 which contains sulphur for the generation of methane and by the development of promising catalysts doped with Cr, Fe and Co.

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CONTINUOUS PRODUCTION PROCESS OF PHARMACEUTICAL ESTERS OF PLANT ORIGIN BY DIRECT ESTERIFICATION

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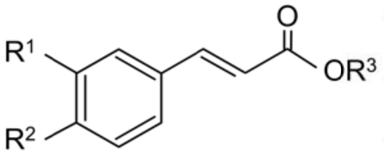
Cinnamic acid esters of plant origin consist of various cinnamic acids, a group of aromatic carboxylic acids, and alcohols (Fig. 1). The esters have been reported to show high pharmaceutical activities such as anti-inflammation and anti-cancer [1]. They are mainly extracted from the natural products [2]. However, they are expensive because of low content in the natural products. On the other hand, the cinnamic acids are widely found in the cell wall of herbaceous plants, and play a role in linking to hemicellulose and lignin by ester or ether bonds as shown in Fig. 2 [3]. Recently, it has been reported that when lignocellulosic biomass is degraded under mild condition the cinamic acids is recovered at a relatively high concentration [4]. Thus, many researchers have attempted to chemically synthesize the cinnamic acid esters from the degradation products of lignocellulosic biomass. However, the direct esterification of cinamic acids and alcohols using the conventional homogeneous acid catalyst hardly proceeded and the yields were low (about 40 %). There are no feasible catalysts for the esterification of cinnamic acids so far. On the other hand, we reported that the commercially available porous type ion-exchange resin, conventionally used for water treatment, has a high catalytic activity for the esterification of free fatty acids in solvent free system [5]. In this research, first, the direct esterification of various cinnamic acids and alcohols was performed using the porous type strongly acidic cation exchange resin in order to investigate the effect of structure of the reactants. Next, the continous production process was constructed using the column reactor packed with the resin by optimizing operating conditions to obtain complete comversion.



	ferulic acid	caffeic acid	cinnamic acid
R^1	OCH_3	OH	H
R^2	OH	OH	H

R^3-OH = alcohols

Fig. 1. Structural formula of cinnamic acid esters

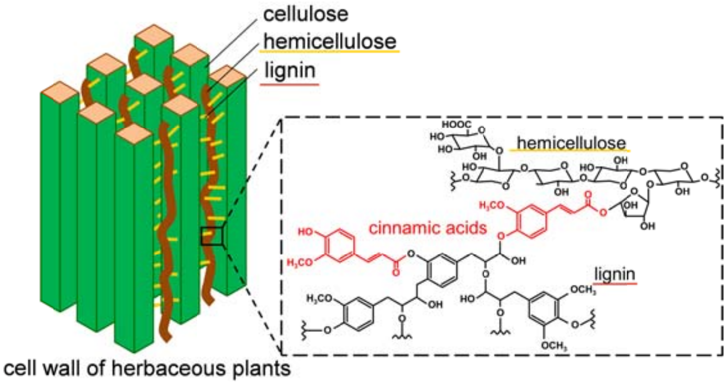


Fig. 2. Conceptual structure of cell wall of harbaceous plants

Table 1 shows the equilibrium conversion and the required time to reach the equilibrium in the batch esterification using various cinnamic acids and alcohols at 50 °C. For reference, the pharmaceutical activities of each ester are also listed. In all cases, high conversion of cinnamic acids were achieved. In addtion, the resin catalyst was able to be repeatedly used without any loss in the catalytic activity.

Table 1. Equilibrium conversion and required time in batch esterification of various cinnamic acids and alcohols

reactants		pharmaceutical activities of products	experiment results	
cinnamic acids	alcohols		equilibrium conversion [%]	required time [h]
caffeic acid	methanol	anti-diabetes	99.4	24
ferulic acid	methanol	anti-inflammation	99.3	24
cinnamic acid	methanol	anti-oxidation	98.7	24
caffeic acid	ethanol	anti-inflammation	99.0	48
ferulic acid	ethylene glycol	ultraviolet absorber	94.3	96
caffeic acid	phenyl ethanol	anti-cancer	98.1	120

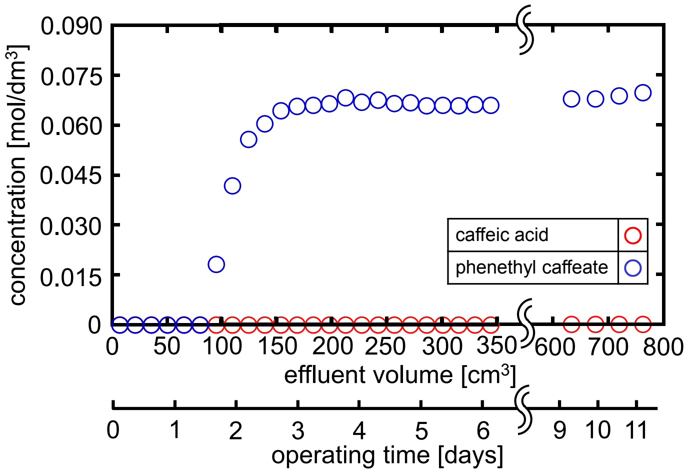


Fig. 3. Concentration profiles in effluent from column in continuous esterification of cafferic acid and phenethyl alcohol

Figure 3 shows the concentration profiles in the effluent from the column packed with the resin, kept at 60 °C, in the continuous esterification of caffeic acid and phenethyl alcohol. The abscissa shows the total effluent volume. For reference, operating time is also shown as a co-abscissa. The phenethyl caffeate concentration in the effluent became constant after the effluent volume reached about 150 cm^3 and the steady state was cnsidered to be reached. The concentration of caffeic acid was almost zero until the end of the operation, so that the complete conversion was obtained. Furthermore, the target pharmaceutical ester was continuously produced for about two weeks without any loss in the catalytic activity. Therefore, the method using the porous type resin catalyst in the solvent free system would provide an industrially feasible process to simply and efiiciently produce various cinnamic acid esters.

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PP-60

Rh/Al_2O_3 STRUCTURED CATALYSTS FOR SYNGAS PRODUCTION VIA DRY REFORMING AND PARTIAL OXIDATION OF BIOGAS

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Introduction

At present there is a great interest in biogas valorization by means of its transformation into syngas (CO + H_2). Methane dry reforming processes for syngas production using Ni catalysts have been widely studied in the literature. However, due to severe deactivation of Ni catalysts by carbon deposition, the development of noble metal-based catalysts such as Rh is an interesting alternative with very promising results recently reported. Moreover, by combining methane dry reforming with the partial oxidation of methane reaction (using O_2), the difficulties associated to dry reforming processes could be overcome. Such approach is known as combined reforming or oxy-CO_2 reforming. In addition, the use of structured catalysts is advantageous in these processes because mass and heat transfer are improved and high methane conversion levels can be attained at very short contact times. Within this context, the general objective of this work is the development of suitable structured catalysts for syngas production from biogas through the combination of dry reforming and partial oxidation processes using Rh/Al_2O_3 catalysts.

Experimental

0.5 % Rh/Al_2O_3 catalysts were prepared by the incipient wetness impregnation technique (catalysts named as 'reference'). The structured catalysts were prepared by washcoating with several suspensions using 2 types of Fecralloy® monoliths (2360 and 289 cpsi) and foams (60 and 40 ppi) having diferent cell densities or porosities. The suspensions were prepared using additives (colloidal alumina and polyvinyl alcohol, PVA) by two different methods: i) preformed catalyst, that is, using previously prepared powder Rh/Al_2O_3 catalysts together with the additives, ii) and all-in-one, by adding the Rh precursor, alumina support and the additives at the same time. Part of the suspensions were dried and calcined for 2 h at 400 °C (slurried cataysts) to compare them with the reference catalyst. The catalysts were tested in a tubular fixed bed quartz reactor operating at atmospheric pressure. The tests were carried out at 700 °C and 150 N L $CH_4/(g_{cat}\cdot h)$, using different O_2/CH_4 molar ratios in the feed, between 0 and 0.45. A synthetic gas mixture composed of 54 % CH_4, 40 % CO_2 and 6 % N_2 was fed into the reactor in all experiments, and high-purity synthetic air (21 % O_2) was added to the gas feeding line in the oxy-CO_2 reforming runs.

Results and Discussion

Firstly, the influence of the suspension preparation method was studied by testing the suspensions under dry reforming (O_2/CH_4 = 0) and oxy-CO_2 reforming (O_2/CH_4 = 0.45) conditions. Figure 1 shows the evolution of methane conversion over the reaction time. Adding O_2 in the gas feed results in a notable increase in methane conversions. It can also be observed that suspensions from both preparation methods presented similar performances in comparison with the reference, both under dry and oxy-CO_2 reforming conditions. Nevertheless, the all-in-one suspension had slightly better activity, greater H_2 and CO yields and superior stability. Therefore, this method was selected for preparing the structured catalysts. Figure 2 shows two of the structured catalysts prepared, a monolith (2.a) and a foam (2.b), after several coating steps carried out to deposit around 160 mg of total solid, of which 0.25 mg are Rh. These structured catalysts present an average thickness layer between 4 and 10 μm with an excelent adherence. In view of these results, further work is ongoing testing these structured catalysts both under dry and oxy-CO_2 reforming conditions.

Figure 1

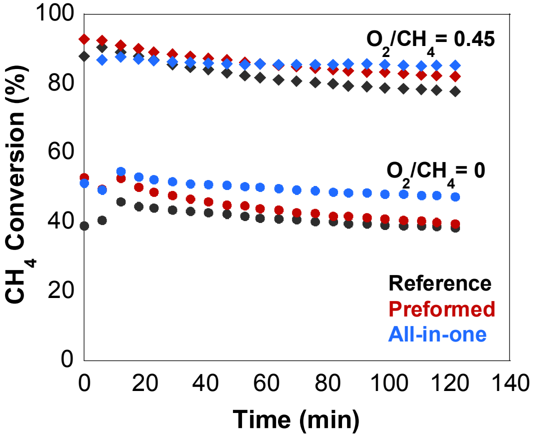
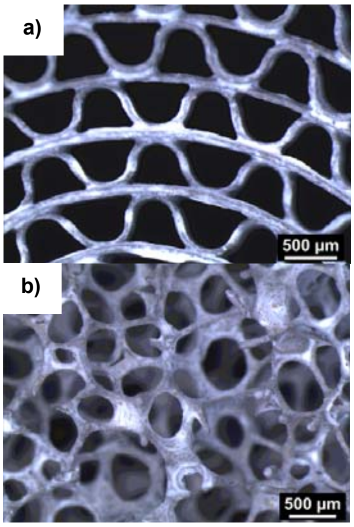


Figure 2



Acknowledgements

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MODELLING OF CATALYTIC CRACKING TAKING INTO ACCOUNT THE CATALYST DEACTIVATION BY COKE AND HEAVY METALS

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The zeolite-containing cracking catalyst deactivation is one of the most important problems for oil refineries [1]. The activity loss of the catalyst under the heavy metals effect is an irreversible process alternatively to catalyst deactivation by coke. The catalytic cracking model taking into account the catalyst activity changing under the influence of deactivating factors (Ni, V, coke) and the coke formation intensity accounting for the structure-selective properties of the catalyst is proposed in this research (Fig. 1).

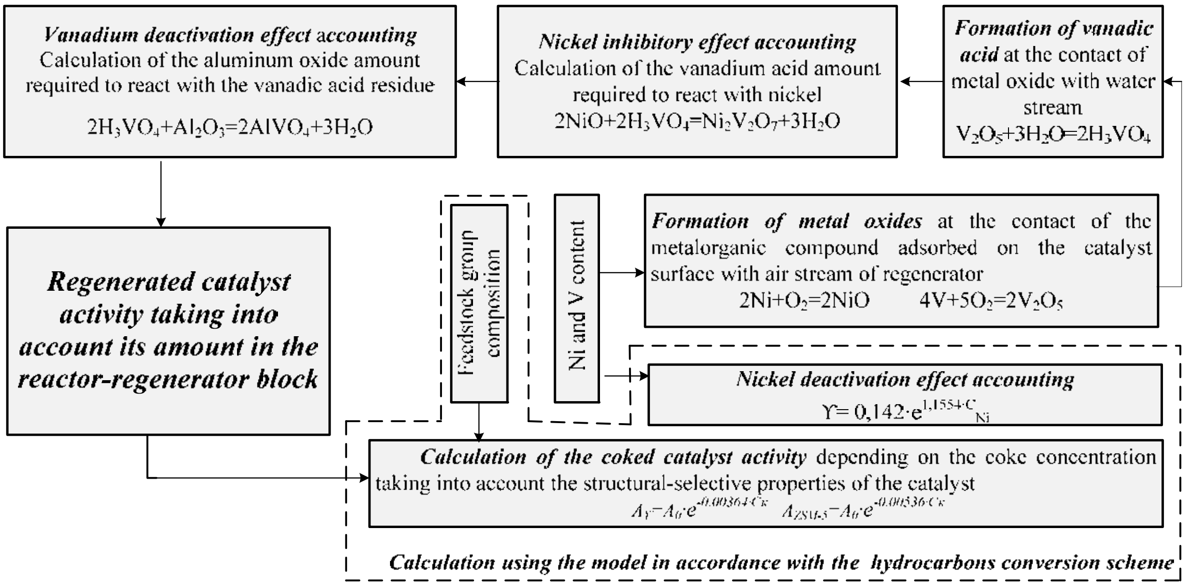

Figure1. Accounting scheme of the reversible and irreversible catalyst deactivation during the catalytic cracking

The dependence of the catalyst dehydrogenation ability on the metal content in the feedstock has been revealed to account for the Ni deactivation effect on the catalyst. This effect leads to increase of the coke formation degree on the catalyst and decrease of the main products yield [2]. The deactivation scheme in accordance with [3] has been chosen for V deactivation effect accounting. The scheme takes into account that the dealumination occurs due to the reaction of catalyst with vanadium acid formed from the contact of the vanadium oxide with water vapor. The formation of metal oxides occurs in the air stream during the regeneration. Along with, the nickel inhibitory effect, which reduces the V destructive effect at the contact of Ni with vanadic acid, is taken into account. The current relative catalyst activities for the primary and secondary reactions occurring with Y (AY) and ZSM-5 (AZSM-5) zeolites are described by an exponential dependence in accordance with experimental data taking into account the acid and structural properties of the catalyst.

The object of research is catalytic cracking industrial unit of vacuum distillate (fr. 350-550 °C). The cracking temperature is 495-542 °C, the pressure is 78000-160000 Pa, the feedstock flowrate is 160-425 m^3/h, the feedstock temperature 240.0-350.0 °C, the catalyst flow temperature after regeneration, 630-730 °C.

Forecasted calculations using the model show that the catalyst activity decreases by 3.5 % due to dealumination with increasing the feedstock volume from daily (6500 th) to annual (2.4 mln ·th) taking into account the amount of the catalyst in the reactor-regenerator unit. Also, the V destructive effect decreases with a simultaneous increasing the Ni content in the catalytic cracking feedstock by 0.2 ppm. As a result, the regenerated catalyst activity is restored by 0.32 %.

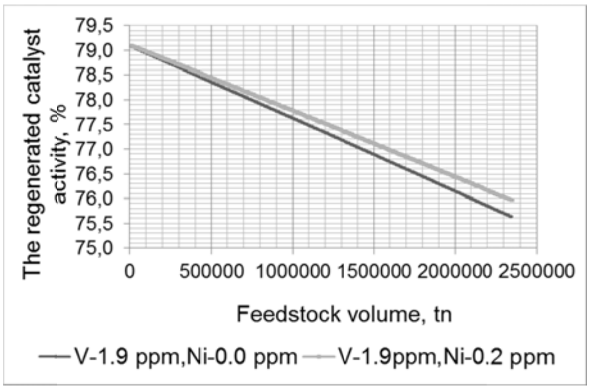

Figure 2. The effect of Ni и V on the regenerated catalyst activity

It is important to take into account that the catalyst dehydrogenation ability rises with increasing the Ni content by 0.2 ppm. It leads to increase of the coke content on the catalyst from 0.78 to 0.873 % and decrease of the gasoline yield of by 0.6 wt %.

The amount of the fresh catalyst feed at the processing of the feedstock with different concentration of heavy metals can be estimated using the forecasted mathematical model of the catalytic cracking. It will improve the use of the feedstock and catalyst resource.

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MICROTUBULAR SOLID OXIDE ELECTROLYZER CELL FOR HYDROGEN PRODUCTION

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Alternative methods of power generation attract more attention in recent years. This interest is caused, from one side, by reduction of mineral fuels, from other - by economic efficiency of the innovative approaches in the production of electric power and strict ecological requirements for new technologies.

One of directions of alternative energy development are the high temperature electrochemical devices (ECD). Such devices allows to a) effectively (efficiency 60-70 %) transform an organic fuel and hydrogen, in electric power with the use of solid-oxide fuel cells (SOFC) and b) process carbon dioxide and aquatic steam in a synthesis gas ($CO + 2H_2$), utilizing the extrass of greenhouse gases, effectively stocking energy of cheap energy sources, with the use of high temperature solid-oxide electrolyzers (SOE). As known, hydrogen is not only basis of ecofriendly hydrogen energy but also feedstock for the various hydroprocessing technologies, multi-tonnage production of ammonia and methanol and subsequent chemical products.

Structurally SOE/SOFC can be divided into planar and tubular shape. A planar design is widely used in stationary devices, by power from a megawatt and higher, as provides good heat and mass transfer, compactness of assembling and allows to use the standard methods of ceramic treatment. The substantial lack of planar configuration is high requirements to absence of considerable temperature gradients along a membrane, that can result in device destruction during thermal cycling and dramatic changes of temperature. This results in a slow startup speed.

The problem can be solved using microtubular membranes, the advantages of which are improved thermal and mechanical stability, ease of sealing. The rapid launch of high-temperature ECD opens the possibility of developing a promising niche of compact, mobile devices in transport, in the military field and in household appliances.

In this paper, the results of studying the functional properties of microtubular SOEC with new cathode materials are presented. The obtained data indicate the promise of these cathode compositions.

Acknowledgements

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PP-63

ACCELERATION OF GAS ABSORPTION RATE USING LIQUID FILM FORMED ON ROTATING HORIZONTAL CYLINDER

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Gas absoption processes can be seen in various industrial processes. Improvement of their rates is one of the important issues becasue they are sometimes limiting steps of the whole process. In this study, a new process of gas absroption to a liquid is developed to enhance the gas absorption rate. When a rotating cylinder is halfway immersed into a liquid bath, a liquid film is formed on the cicumferential surface of the cylinder. To this liquid film, fresh absorbent (liquid) is always supplied and the concentration difference can be kept large. Additionally, it is considered that the fast motion of the liquid film can be enhance the mass transfer rate around the gas-liquid interface. Thus the gas absorption rate is expected to be improved by this new process. This study experimentally discusses the effectiveness of this new process and the gas absorption characteristics.

The gas absoption rates were measured through the experiments. First, the rotating horizontal cylinder is settled in the rectangular vessel. This vessel is put into the airthight container. The atmosphere in the container is replaced with CO_2 and the CO_2 is kept to flow at certain flow rate. The absorbent liquid is poured into the vessel upto the axis of the cylinder. Distilled water or aqueous solusion of NaOH is used as the absorbent. A pH sensor is inserted into the bath and start to rotate the cylinder. The concentration of CO_2 in the absorbent is obtained from the pH of the absorbent.

Figure 1 shows the variation of CO_2 concentration in the absorbent of NaOH aqueous solusion. While the CO_2 concentration changes little under the condition without cylinder rotation, it quickly increases when the cylinder rotates. The variation of CO_2 concentration becomes faster with increase in the cylinder rotation rate.

In this exeperimental condition, the gas phase consists of only CO_2 and the mass transfer resistance can be neglected. Thus it is considered that the increase in the CO_2 absorption rate with cylinder rotation is caused by the enhancement of mass transfer rate in the liquid film. Thus the mass transfer coefficient in the liquid film is estimated by the following equation.

$$\dot{N}_{\mathrm{CO_2}} = Ak_{\mathrm{L}}(C^{*}_{\mathrm{CO_2}} - C_{\mathrm{CO_2}}) \qquad (1)$$

where k_{L} is mass transfer coefficient, $C_{\mathrm{CO_2}}$ and $C^{*}_{\mathrm{CO_2}}$ are concentrations of CO_2 in the bath and at the gas-liquid film interface, respectively. Variation of the mass transfer coefficient with cylinder rotation rate is shown in Fig. 2. The mass transfer rate in the liquid film linearly increases with rotation rate.

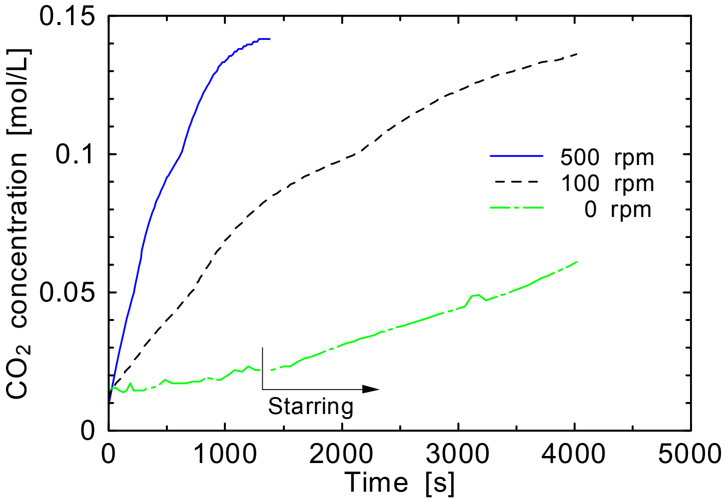

Fig. 1. Variations of CO_2 concentration in the bath

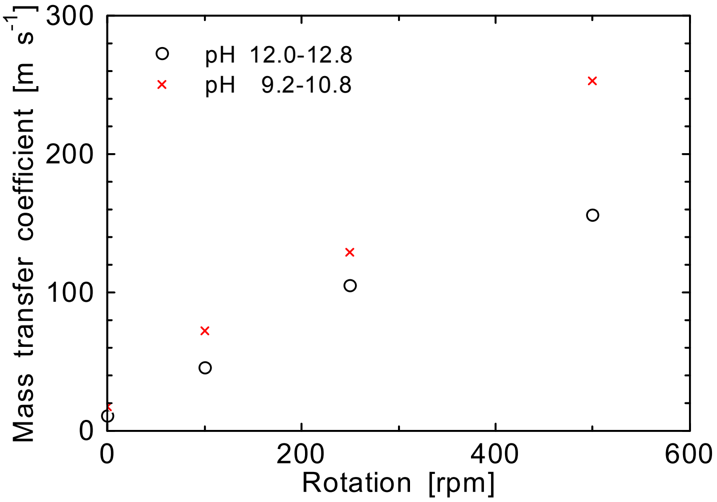

Fig. 2. Effect of cylinder rotatin rate on mass transfer coefficient

Acknowledgements

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PP-64

MONITORING IONIC LIQUID SYNTHESES WITH IN SITU IR-SPECTROSCOPY – THE INTRICACY OF SOLVENT EFFECTS

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Ionic liquids (ILs) are often synthesized by the alkylation of tertiary amines, especially imidazoles, and phosphines. Two neutral substrates form the ionic product by the transfer of an alkyl cation following an S_N2-mechanism. The Hughes-Ingold-rules [1] predict that the reaction is accelerated in more polar solvents. Therefore, it is expected that the synthesis of ILs is autocatalytic since the product is more polar than the substrates.

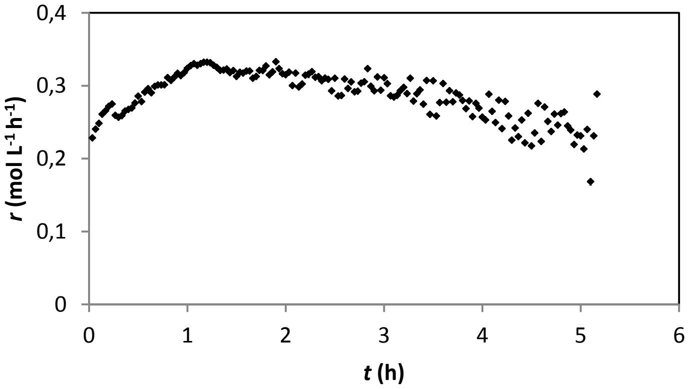

Figure 1. Reaction rate profile of the reaction between triethylamine and dimethyl carbonate at 125 °C [2]. An increasing section can be observed in the beginning which indicates an autocatalytic behavior. Furthermore, a bend at ca. one hour reaction time can be observed

The kinetics of the IL syntheses starting from dimethyl carbonate and either triethylamine [2] or N-ethylimidazole are compared in this work. The reaction progress is monitored using ATR-IR immersion probes in an autoclave. The evaluation of the reaction rate *r* shows an increasing part in the beginning, followed by an decreasing part. The analysis of the reaction rate constant *k* reveals that the autocatalytic behaviour is based on a kinetic salt effect. Furthermore, the reaction rate of triethylamine and dimethyl carbonate shows a bend after certain time. The bend can be attributed to a phase change from solvated ion clusters at small product concentration to a phase separation of the ionic liquid at elevated concentrations. The effect of the phase separation takes place on a microscopic scale, while the reaction mixture appears homogeneous. The autocatalytic effect of the ion clusters is more pronounced than the effect of the separated IL phase, which results in a bend in the reaction rate.

Dimethyl carbonate can be used as a green reagent in methylations and methoxycarbonylation reactions and is a substitute for phosgene and methyl halogenides [3]. The synthesis of halogen-free ILs by the methylation of tertiary amines with dimethyl carbonate is patented as the CBILS®-process from the Austrian company proionic GmbH (**C**arbonate **B**ased **I**onic **L**iquid**S**) [4].

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PP-65

APPLIED ASPECTS OF PROCESSING THE OAT-HULLS-ETHANOL TO BIOETHYLENE: EFFECT OF IMPURITIES

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The processing of non-food lignocellulosic raw materials to bioethanol is a promising solution both from economic and ethical points of view. The process of bioethylene production from bioethanol origined from renewable bioresources has been widely studied as an innovative technology and commercialized in several countries. This process has many advantages over the conventional one, such as independence from the petrochemical sources of raw materials, and the possibility to launch the plants of low capacity. Technology is rather simple and environmentally benign, thus ensuring much less impurities in the ethylene produced. Assessment of economic indicators allows us to conclude that low-tonnage production of bioethylene and its high-margin derivatives would have the best market [1,2]. The diversity of bioresources, which are potentially applicable to bioethylene production, is growing constantly, and the areas to apply the chemicals produced thereof expand. In this regard, the bioethanol impurities issue and their impact on the bioproducts becomes of particular concern. The influence of typical impurities in biotechnological products on their downstream processing should be thoroughly investigated in the course of the optimal development of new biotechnologies.

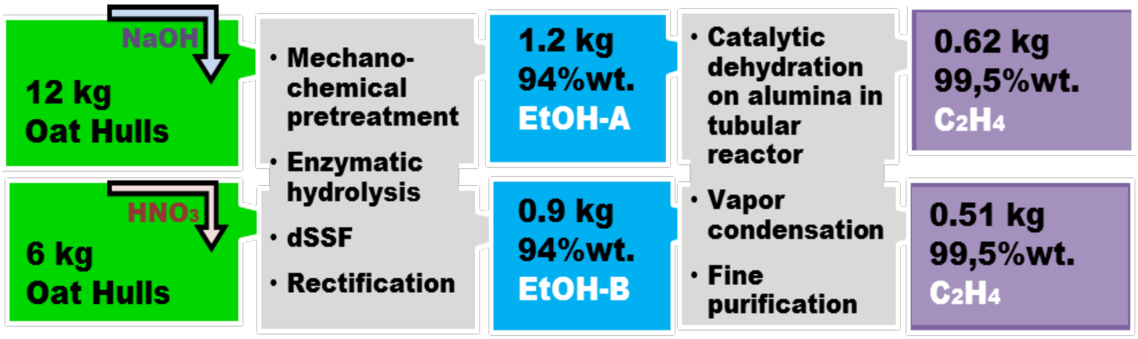

Figure.

In the present work, the influence of impurities in bioethanol produced from oat hulls on the process of its catalytic dehydration into ethylene has been studied. The study was carried out using an alumina catalyst [3-4] which was found to be sufficiently stable in undiluted feedstocks and sufficiently active at 370-450°C [3]. Samples of bioethanol were manufactured at the IPCET SB RAS; they were prepared using either NaOH, or HNO_3 at the stage of oat hulls pretreatment [5]. After rectification to 94%wt., the bioethanol samples differed in the content of organic and inorganic microimpurities. In turn, this had a different effect on ethylene yield and ethanol conversion (Fig.). Taking into account the ethanol consumption factor per 1 ton of ethylene, a comparative estimation of the necessary mass of plant bioresources for obtaining from 1 to 20,000 t of bioethylene was made. Technical and economic indicators of the bioethylene production process were obtained from the results of pilot-scale testing [4]; based on it, the prospects for commercial production of ethylene have been analyzed.

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FEATURES OF ORGANIC SYNTHESIS PROCESSES WITH USE OF BIFUNCTIONAL CATALYSTS ON THE BASIS OF PEROXO POLYOXO TUNGSTATES

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The studies deal with phosphorus stabilized catalytic systems based on tungsten complexes and combined with the quaternary ammonium cations (Q^+) acting as phase-transfer catalysts. It is known that *in situ* synthesis of the catalysts using such precursors as ($H_3PW_{12}O_{40}$ + H_2O_2) or (H_2WO_4 + H_3PO_4 + H_2O_2), or (Na_2WO_4 + $NH_2CH_2PO_3H_2$) leads to the formation of a mixture of peroxo complexes with different structures, for example: $Q_3\{PO_4[WO(O_2)_2]_4\}$, $Q_2[W_2O_3(O_2)_4(H_2O)_2]$, $Q_2\{HPO_4[WO(O_2)_2]_2\}$ [1-3]. These complexes were isolated and characterized using IR, Raman and EXAFS techniques. The complexes comprising the tetranuclear anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$ was the most active catalyst for oxidation of organic compounds with aqueous hydrogen peroxide [3-4].

The results of complex studies of one-stage catalytic syntheses of important organic compounds (epoxides, N-oxides of amines, mono- and di-carboxylic acids and their derivatives) from petrochemical products and renewable raw materials are reported. The catalytic oxidation reactions of organic substrates (cycloalkenes, α-alkenes, alcohols, bicyclic ketones, tertiary amines, unsaturated fatty acids and their esters, terpenes, coumarins) proceed under mild conditions at temperatures not higher than 100 °C and atmospheric pressure.

The studies of the synthesis conditions and structural characteristics of tetranuclear tungsten porero xopolyoxo complexes $Q_3\{PO_4[WO(O_2)_2]_4\}$ using EXAFS, Raman and IR spectroscopic techniques led to establish that the cation nature influences the strength of bonding between tungsten atoms with the cation. With the cations containing at least one aryl substituent along with alkyl one, a specific interaction between protons of pyridine and benzene rings with the anion was revealed [5]. In view of this fact it is reasonable to suppose that these are the factors (the presence of four peroxo groups in the anion and of the pyridine ring in the cation) which are responsible to the high activity of complex $[C_5H_5N(CH_2)_{15}Me]_3\{PO_4[WO(O_2)_2]_4\}$ to most of the substrates under study. It is not improbable that both of the said factors are of key importance for predicting the catalytic activity of tungsten peroxo polyoxo complexes to oxidation of organic substrates [6].

The results obtained open the way for creation of new generation technologies for fine organic synthesis with good economic parameters to meet the modern ecological requirements of a low E-factor (kg waste/kg product).

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Acknowledgements

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PP-67

ANALYSIS OF PRESSURE REDUCING EFFECTIVENESS IN THE REFORMING INDUSTRIAL UNIT WITH MATHEMATICAL MODELLING METHOD USING

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Catalytic naphtha reforming process is a vital process for refineries due to the production of high-octane components, which is intensely demanded in our modern life [1]. Hydrogen and lighter hydrocarbons are also obtained as side products. Catalyst is the most important constituent of the reforming process, and many researchers have been inventing and investigating new catalysts with better quality, as well as lower deactivation. Nowadays the process of catalytic properties improving has almost reached its limit: industrial modern polymetallic reforming catalysts contain minor quantities of platinum providing high product yield with high octane numbers. The effectiveness of the reforming process is providing by its technological conditions. Thermodynamically favorable conditions of the target reactions occurring is in area of low pressures and high temperatures. Depending on the technology used the pressure in reactors could vary from 0.35 to 2.0 MPa. The strategy of reforming technology improving goes hand in hand with a pressure reduction. However, with the pressure decreasing the coke deposition on the catalyst and the catalyst deactivation rate increase. For this reason, the reforming process with a fixed bed catalyst is not carried out at a pressure lower than 1.4 - 1.5 MPa. With mathematical modelling method using the research of physio-chemical regularities of catalytic reforming process under reduced pressure has been done. Industrial catalytic reforming unit with catalyst was used as an object of study. The results of chromatographic analysis of the hydrocarbon feedstock composition, technological modes of production unit operation were used as source data [2]. With mathematical model using the pressure effect on the product yield and quality was analyzed [3]. Table 1, 2 shows the results obtained with two reforming catalysts using: PR-9 and PR-81.

Table 1. Pressure effect on the product yield and quality with catalyst PR-9 using

Pressure, MPa	**P=1,6**	**P=1,5**	**P=1,4**	**P=1,3**	**P=1,2**
Octane number	93,2	93,4	93,6	93,7	93,8
Aromatics, % mass.	60,66	61,01	61,32	61,56	61,81
Hydrogen output, %	1,94	1,97	2,0	2,04	2,07
Coke, % mass.	3,63	3,62	3,64	3,67	3,69
Product yield, % mass.	89,92	90,05	90,19	90,36	90,53

Table 2. Pressure effect on the product yield and quality with catalyst PR-81 using

Pressure, MPa	**P=1,6**	**P=1,5**	**P=1,4**	**P=1,3**	**P=1,2**
Octane number	93,7	94,1	93,9	94,5	94,5
Aromatics, % mass.	60,61	61,23	61,39	61,58	61,88
Hydrogen output, %	1,94	1,98	2,0	2,04	2,07
Coke, % mass.	3,56	3,59	3,60	3,62	3,65
Product yield, % mass.	90,25	90,52	90,76	91,01	91,16

It could be concluded that the operating pressure deacreasing of the reforming process favors the target reactions and promotes process selectivity. Wherein pressure decreasing increases coke formation in the reactor according to the Le Chatelier's principle, and it could be recommended do not reduce pressure lower than 1.4 MPa.

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PP-68

KINETIC STUDY OF OXIDATIVE COUPLING OF METHANE OVER Sr/La_2O_3 CATALYST

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Oxidation coupling of methane (OCM) is one of the promising ways for producing ethane-ethylene mixture directly from natural gas, without the stage of synthesis gas production. For this purpose, a large amount of research has been carried out over the last 30 years. In the OCM process methane at high temperatures (> 550 °C) is oxidized on a catalysts to produce the C_2 hydrocarbons: ethane and ethylene, and by-products - carbon oxides [1, 2]. The target products are also involved in oxidation processes to form carbon monoxide and carbon dioxide. Since the OCM is a homogeneous-heterogeneous process, the experimental studies of kinetic regularities and identification of the scheme of process on various heterogeneous catalysts is an urgent task.

In this work, we studied the influence of temperature and contact time on the regularities of the process of OCM on the catalyst Sr/La_2O_3.

The catalyst 5 % Sr/La_2O_3 was prepared by method of wet impregnation, the calcination time is 4 hours at 700 °C; carrier the La_2O_3 was prepared by decomposition of La nitrate, calcined for 10 hours at 700 °C. The catalyst was characterized by physicochemical analysis: an X-ray diffraction (XRD) analysis was performed on a Bruker D8 diffractometer using Anton Paar high-temperature X-ray chamber; the texture characteristics were determined from nitrogen adsorption isotherms measured at 77 K; the mesopore volume was calculated by analysis of the curve of the integral pore volume distribution as a function of the pore radius.

The catalytic activity in oxidative methane coupling (OCM) was measured in a fixed-bed quartz tube reactor (5 mm i.d.) at 850-900 °C and ambient pressure [3]. The temperature of the catalyst was measured with chromel–alumel thermocouple adjusting the outer surface of the reactor at the middle of the catalyst bed. Reactant and product concentrations were analyzed by on-line gas chromatograph with Porapack Q. The ratio CH_4/O_2 at reactor inlet is equals 4.

From the experimental data it follows that with increasing temperature, selectivity towards ethane and ethylene increases, and selectivity for carbon monoxide decreases. The ethane selectivity begins to increase at a lower temperature than the ethylene selectivity (Figure). Experiments carried out at a low conversion of methane shows that C_2 hydrocarbons and CO_x are formed in the process of OCM in parallel routes.

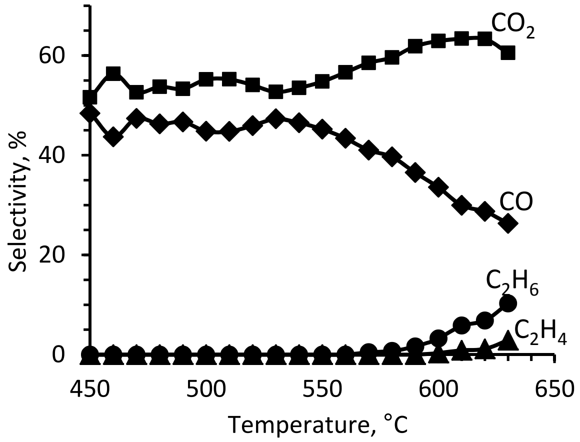

Figure. Dependence of products selectivity vs. temperature

To estimate the equilibrium concentration of reagents thermodynamic analysis of reactions occurring in the process of OCM was performed. It is shown that the equilibrium content of C_2 hydrocarbons (ethane, ethylene) in the studied range of temperature and concentrations of methane and oxygen in the sum was insignificant value < 0.1 %. During catalytic oxidation of methane experimental concentration C_2 is higher than the equilibrium value.

Thus, on the basis of experimental data obtained at a low conversions, it was found that the primary products of methane oxidation are ethane and carbon oxides, and ethylene is formed as a result of ethane dehydrogenation in various reactions. It is shown that the use of the catalyst, in particular Sr/La_2O_3, allows for more selective oxidation of methane to C_2 hydrocarbons compared to their equilibrium concentrations.

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PP-69

CONVERSION OF HYDROCARBONS TO SYNTHESIS GAS IN A COUNTERFLOW MOVING BED FILTRATION COMBUSTION REACTOR: A THERMODYNAMIC ASSESSMENT

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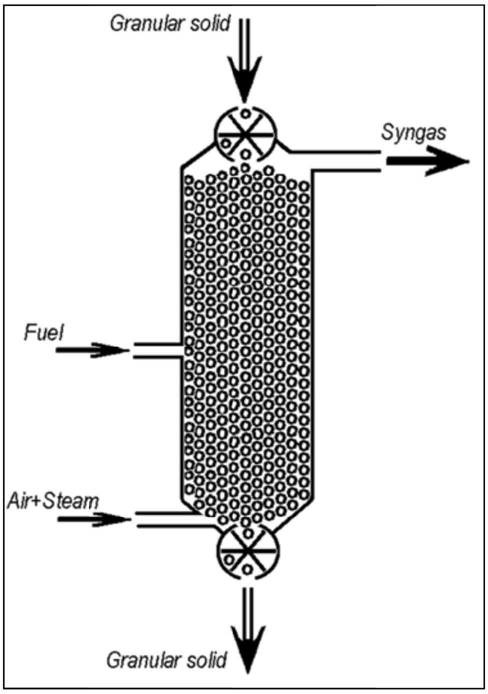


The conversion of hydrocarbons to synthesis gases via partial oxidation in a non-premixed filtration combustion is considered in a continuous reactor wherein filtration medium/inert solid matrix comprises a moving bed of a granular material flowing countercurrently to the gas flow. Similar to the previously considered [1, 2] conversion in a reversed-flow reactor, such embodiment provides a possibility of attaining high combustion temperature due to efficient heat recuperation, while performing the process continuously without transients associated with the flow reverse. The reactor is schematically shown in Fig. 1.

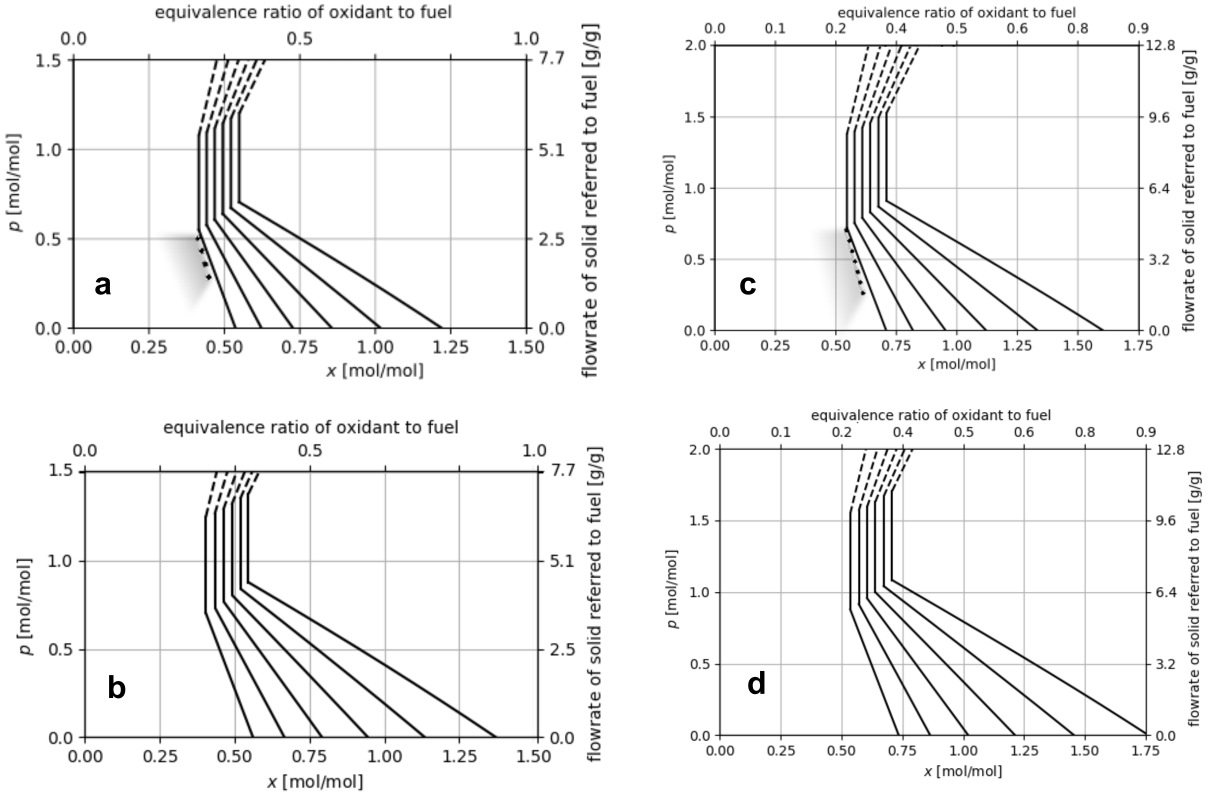
In the moving bed process, the flowrate of the granular material becomes an independent control parameter. We provide calculations for preliminary assessment of the optimal conditions for the process, i.e., control parameters providing a highest efficiency of fuel conversion to syngas. A fuel having gross formula CH_yO_z is converted to syngas by the supplied air and steam according to the following gross reaction:

$$CH_yO_z + xO_2 + w_0H_2O + n_0N_2 \rightarrow dCO_2 + mCO + hH_2 + w_sH_2O + nN_2 \qquad (1)$$

Thus, for a given fuel flowrate one should optimize the flowrates of air (x and n_0), steam (w_0), and flowrate of granular solid (p). The model proposed is based on the following basic assumptions. First, we suppose that composition of syngas attains thermodynamic equilibrium at the combustion temperature and contains no other gases except those in (1) RHS. Second, reactor is sufficiently heat-insulated to disregard the heat loss. Third, we suppose that the reactor is large enough to contain all gas-solid heat exchange zones. With the assumptions made the conversion regime is described by elementwise conservation equations, directly following from (1), and equation of thermodynamic equilibrium $d*h = m*w_s*\kappa_1(T_s)$, where $\kappa_1(T_s)$ is the equilibrium constant for water-gas reaction at the combustion temperature T_s.

The equations set is closed with the energy conservation condition, which has three forms depending on the flowrate of granular solid. For a low flowrate, when the heat capacity of the solid flow is lower than that of air-steam mixture, the sensible heat of sold heated to the combustion temperature is recovered with the flow of air-steam mixture. For higher flowrate of solid, the regime is equivalent to [1]. Still higher flowrate when the heat capacity of the solid flow is higher than that of syngas results in an unstable regime.

Example calculations for the methane/air-steam and 2-propanol/air-steam conversion.



Isotherms (left to right) T_s = 1100,1300,1500,1700,1900, 2100 K for 2-propanol (a,b) and methane (c,d); w_0 = 0 (a,c), 0.5 (b,d). Soot formation in shaded area left to the dotted line (a,c).

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Acknowledgement

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PP-70

KINETIC CONJUGATION EFFECTS IN OXIDATION OF C_1-C_2 HYDROCARBONS

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Investigation of the kinetics of oxidative methane coupling (OKM) is of particular interest since it is considered as a convenient model for the study of the processes operating via heterogeneous-homogeneous mechanism and includes the steps typical of oxidation of any hydrocarbon. Another feature of the OCM is that this process starts with the activation of chemically stable methane molecule, the reactivity of which is substantially lower in comparison with that of the target products (ethene, ethylene). This can bring to the competetiveness of the reactant and product molecules at the activation over any active sites present in the system – both surface species and active particles in gas. Herewith, the formation of various products proceeds through the same intermediates, i.e., free radicals, which present in the reaction mixture and affect gas phase reaction rates. Therefore, such complex interdependences of possible reactions define the apparent kinetics of OKM. The current study has a purpose to reveal a reciprocal influence of the components of the reaction mixture on their conversion routes and rates under conditions of catalytic oxidation of methane to ethane and ethylene. The mixed NaWMn/SiO_2 oxide was used as a model catalyst.

It was shown that homogeneous oxidation of C_2 hydrocarbons occures at a high rate in an empty reactor at temperatures above 750 °C. However, when quartz or catalyst are loaded into the reactor, the conversion rate of both ethane and ethylene reduces significantly (see Fig. 1).

Experiments on the oxidation of ethane and ethylene in excess of nitrogen or methane showed that:

- methane decreases the rate of ethane oxidation (see Fig. 2A), but also a strong reciprocal effect of these hydrocarbons on the rate and direction of their transformations is observed in the presence of NaWMn/SiO_2 catalyst;
- methane also inhibits gas phase oxidation of ethylene by reducing the contribution of chain reactions to the total process rate (see Fig. 2B); in the presence of NaWMn/SiO_2 catalyst when the rate of CH_3 radicals formation

from methane is high, their efficient trapping by ethylene takes place leading to propylene formation.

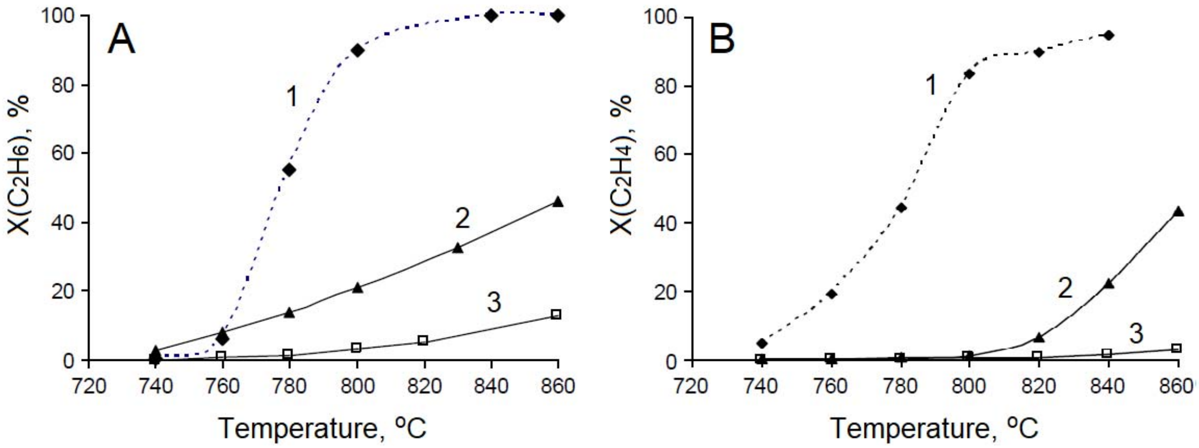

Fig. 1. Ethane (A) and ethylene (B) conversion at different reactor loadings:
1 – empty reactor; 2 – reactor with quartz; 3 – reactor with NaWMn/SiO_2 catalyst

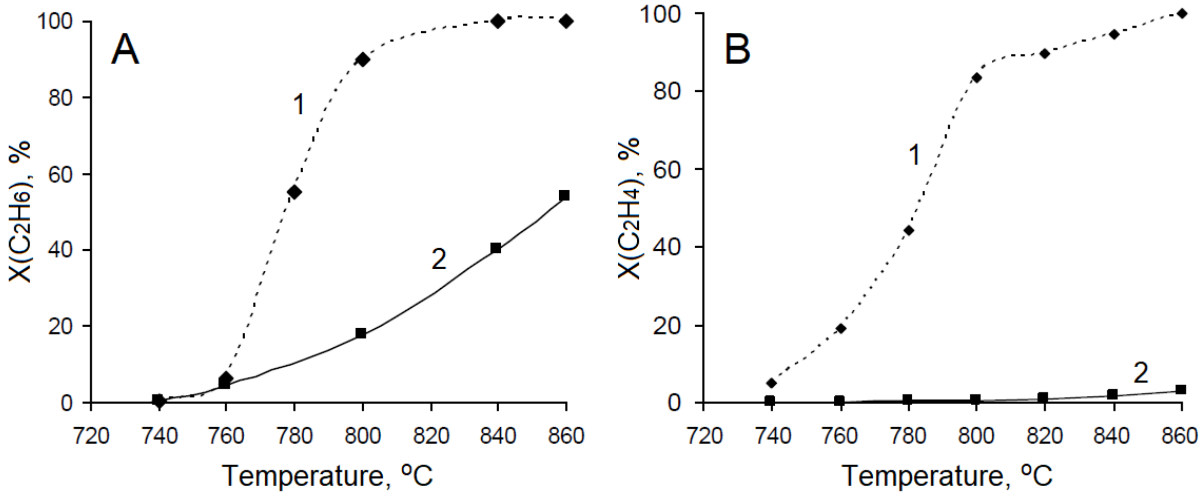

Fig. 2. Ethane (A) and ethylene (B) conversion in empty reactor at different gas dilutions:
1 – C_2H_6 (C_2H_4) : O_2 : N_2 = 5.5 : 11 : 83.5; 2 – C_2H_6 (C_2H_4) : O_2 : CH_4 = 5.5 : 11 : 83.5

Thus, the presence of complex kinetic conjugation and the apperarance of new reaction routes during the joint oxidation of C_1-C_2 hydrocarbons has been demonstrated.

The experimentally observed effectes are discussed in the framework of the detailed kinetic model that accounts elementary reactions of molecule and free-radical species both in the gas phase and over surface active sites.

Acknowledgements

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PP-71

HOW TO DESIGN AN EFFECTIVE CO PROX CATALYST AND REACTOR?

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CO preferential oxidation (CO PROX) as an important reaction for CO removal from H_2-rich reformate for low temperature polymer electrolyte membrane fuel cells feeding applications. Designing a CO PROX catalyst is a challenging problem in terms of substrate-selective catalysis: the catalyst requires to oxidize only ca. 1 vol. % CO in the huge excess of H_2 (60-70 vol. %). In the present report, we would like to summarize literature data and our experience in catalyst designing and determination of key factors affecting the CO PROX reaction.

CuO-CeO_2 and bimetallic Au-Cu and Pt-Co catalytic were approved to be selective and able to provide stable CO removal to level below 10 ppm. The simple and effective preparation methods were proposed. Thin catalytic coatings onto supports with high thermal conductivity (metal plates and gauzes) were successfully applied to extend catalysts temperature operational window and provide stable operation.

According to our and literature data (Fig. 1) conventional Pt-, Pd-, Rh-, Ru-based catalysts are not enough selective. This is due to the dense coverage of metal surface by adsorbed CO at low temperatures, that inhibits both CO and H_2 oxidation. The H_2 and CO oxidation start together at elevated temperatures when equilibrium CO coverage decreases and empty metal appears.

There are two main strategies to design a selective CO PROX catalyst:

1) Utilize the CO inhibition effect on H_2 oxidation reaction and provide a low-temperature CO oxidation reaction pathway. It could be done by application of bimetallic Pt-M (M = Fe, Co, Ni, Cu, etc.) systems, where second metal is responsible for oxygen activation (Fig. 2). Pt-Co was concluded to be the most promising one.
2) Apply metal sites, which are not "very good" in hydrogen adsorption but are able to activate CO and O_2. Cu and Au were considered as promising candidates. Copper-ceria system appeared to be the most interesting.

An approach based on double complex salts single-source precursors decomposition inside the supports pore space was applied to prepare bimetallic Pt-Co nanoalloy and Pt-Co_3O_4 metal-oxide composite catalysts. Comparison of their properties revealed the key role of interface between Pt and Co atoms on the catalyst surface. Working temperature interval of Pt-Co catalysts is 60-120 °C, which is close to the working temperature of “Nafion” membrane. So, PROX reactor could be easily integrated with fuel cell.

For CuO-CeO_2 catalysts copper-ceria interface was identified as a key factor of high performance. Most likely oxygen atoms from ceria surface take part in CO oxidation, which is activated on Cu sites. Working temperature of CuO-CeO_2 catalysts is 200-240 °C, which is close the outlet of low-temperature WGS reaction. So, in this case PROX reactor could be easily integrated with WGS reactor.

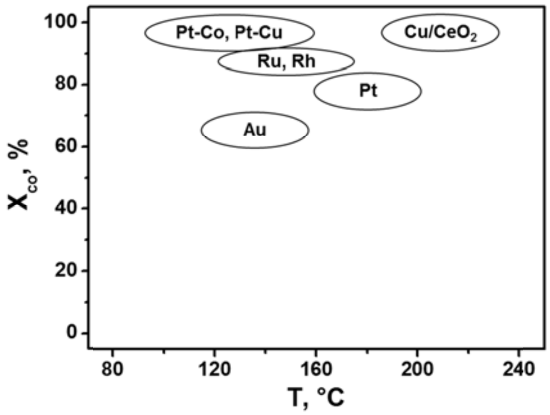

Fig. 1. Schematic view of CO PROX working temperature windows for different catalytic systems

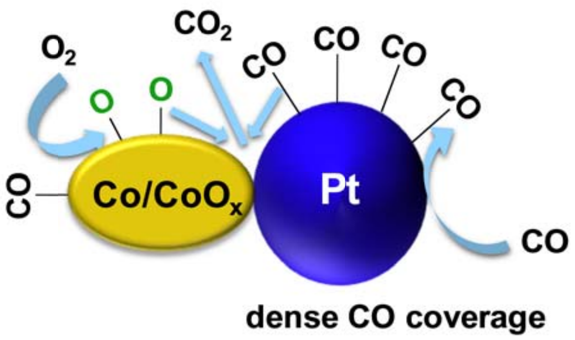

Fig. 2. The scheme of low-temperature CO oxidation reaction route over bimetallic Pt-Co catalysts

It is seen that for all catalytic systems PROX reaction is very sensitive for reaction temperature. Hot spots formation is expectable for conventional catalyst pellets due to high heat effect of the reactions. This could lead to CO clean up failure due to acceleration of H_2 oxidation reaction. So, heat management is of great importance for PROX reactors. Wall-coated stainless steel microreactors were recognized as a great tool to provide stable PROX catalyst operation, reaction controllability and to pave a way to modular compact hydrogen generators.

Summarizing, two strategies for CO PROX were proposed. The origin of catalysts high selectivity was clarified. Microreactors were demonstrated to be great choice for PROX reaction.

Acknowledgements

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MATEMATICAL MODELING OF REGENERATION OF COKED Cr-Mg CATALYST IN FIXED BED REACTORS

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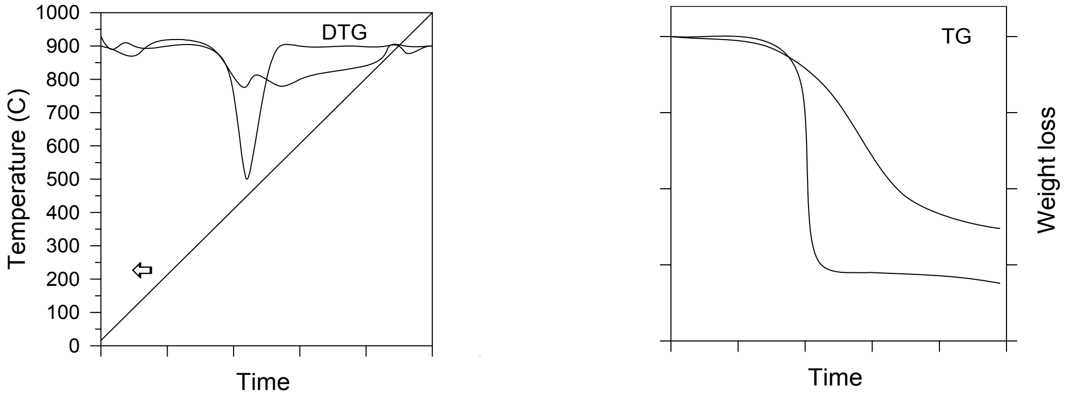
Catalyst deactivation leads to the loss of its activity and selectivity during catalytic reaction. The activity decline can be reversible (phase transition of active component, coking) or irreversible (sintering, poisoning, thermal or chemical degradation). A reversible deactivation enables catalysts to be partially or completely regenerated by heating or changing the composition of reaction mixture. In production of ozone-safe chladones (R-134a, R-125 etc.) by gas-phase hydrofluorination of chloroethylenes the catalysts, are used containing chromium (+3) and fluorides of metals of Group II. Catalyst deactivation in these processes is caused by coking. During its regeneration by oxygen it is important to prevent the catalyst overheating, which can lead to sintering of active component, and as a result, irreversible loosing its activity. In industrial processes, the knowledge of the regeneration kinetics specific type of catalyst and catalyst bed dynamics are necessary for optimal design of the reaction-regeneration cycles.

The aims of the present work were the following: (i) the determination of kinetic parameters of coke burning for Cr-Mg catalyst and parameters of diffusion or mass-transfer limitation; (ii) the investigation of the influence of technological parameters on coke burning and regeneration time in a fixed bed reactor.

The simulation of the process was performed using the detailed mathematical model that takes into account the reaction and adsorption processes in the catalyst pellet, heat and mass transfer between gas flow and catalyst surface, oxygen diffusion inside the pellet pores, heat release during reactions [1]. The reaction rate constant, activation energy, and mass transfer parameters were defined by the two independent methods: (i) from experimental data of the coked catalyst regeneration in a lab-scale reactor; (ii) from the simulation of experiments of thermal analysis.

The reaction rate constant of coke regeneration ($k=k_0e^{-E/RT}$) were determined by the experiments: the activation energy E_A = 31 kcal/mol and k_0 = $1.5 \cdot 10^9$ 1/min. Analysis of the process occurring in the catalyst bed shows that coke burning proceeds in the region of strong diffusion limitations. This is confirmed by DTG and TG analysis data (Fig. 1).



(a) **(b)**

Fig. 1. DTG – (a) and TGA – (b) curves for different size of catalyst pellet: catalyst powder (dashed line) and catalyst pellet (solid line)

The mathematical modeling of catalyst regeneration was performed at following conditions: initial coke concentrations are 5 wt % and 15 wt %; the inlet gas temperature is 400 °C, and inlet oxygen concentration is 0.98 vol %.

Thus, the influence of process parameters, e.g. oxygen and coke concentration, inlet gas temperatures (T_{in}), gas flow rate, and pellet size has been studied. It was determined that if T_{in} is higher than catalyst temperature, burning front heats the catalyst bed from T_{in} up to maximal adiabatic temperature $T_{max}=T_{in} + \Delta T_{ad}$ which should not exceed the 500 °C. If the inlet gas temperature is lower than initial catalyst temperature the coke burning occurs only near the surface of catalyst pellet, because the bed is cooled by the inlet gas flow. This leads to the catalyst overheating $T_{max}>T_{in} + \Delta T_{ad}$, and can cause active component crystallization and catalyst sintering. Optimal conditions were determined in order to prevent the catalyst overheating during regeneration.

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STUDY OF DIFFERENT KINETIC EXPRESSIONS ON THE ACETYLENE HYDROGENATION

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In this work a dynamic model was developed to describe a reactor system for the hydrogenation of acetylene in an ethylene stream by selective hydrogenation over Pd/Al_2O_3. The system consists of three adiabatic fixed-bed catalytic reactors, in series, with cooling between them. This system is integrated with a Steam-Cracker unit at the Repsol plant in Portugal and is front-end configuration.

In order to improve the ethylene selectivity, i.e. to decrease the ethane formation from both acetylene and ethylene, the amount of CO is controlled in the process. However, the presence of CO decreases the acetylene conversion and influences the oligomer formation [1] whose typical composition includes C4–C20 reactive oligomers of varying composition, with boiling point range from 120 to 400 °C [2].

A pseudo-homogeneous model approximation was used under adiabatic operation and assuming that the kinetics can be described by kinetics laws found in the literature. In this work, a careful choice was made of the kinetic expressions that were studied by Schbib et al. and which ones are best suited to our experimental data. After choosing the kinetic expressions, several hypotheses have been considered such as: if the reagents, hydrogen and hydrocarbons, will adsorb at different active sites (Schbib 1) or in the same active sites (Schbib 2) or if hydrogen reacts directly with adsorbed C_2H_2 and C_2H_4 (Schbib 3). The kinetics expressions used for the acetylene hydrogenation were of the Langmuir-Hinshelwood type or Rideal–Eley type, based on the one proposed by Schbib et al. [3]:

Table 1. Kinetic rate equations for the selective hydrogenation of C_2H_2 and C_2H_4 proposed by Schbib et al.

$r_{C_2H_2} = \frac{k_A P_{C_2H_2} P_{H_2}}{(1+K_{C_2H_2}P_{C_2H_2}+K_{C_2H_4}P_{C_2H_4}+K_{C_2H_6}P_{C_2H_6}+K_{CO}P_{CO})\left(1+K_{H_2}^{\frac{1}{2}}P_{H_2}^{\frac{1}{2}}\right)^2}$ $r_{C_2H_6} = \frac{k_E P_{C_2H_4} P_{H_2}}{(1+K_{C_2H_2}P_{C_2H_2}+K_{C_2H_4}P_{C_2H_4}+K_{C_2H_6}P_{C_2H_6}+K_{CO}P_{CO})\left(1+K_{H_2}^{\frac{1}{2}}P_{H_2}^{\frac{1}{2}}\right)^2}$	*Schbib 1*
$r_{C_2H_2} = \frac{k_A P_{C_2H_2} P_{H_2}}{(1+K_{C_2H_2}P_{C_2H_2}+K_{C_2H_4}P_{C_2H_4}+K_{C_2H_6}P_{C_2H_6}+\left(K_{H_2}P_{H_2}\right)^{\frac{1}{2}}+K_{CO}P_{CO})^3}$ $r_{C_2H_6} = \frac{k_E P_{C_2H_4} P_{H_2}}{(1+K_{C_2H_2}P_{C_2H_2}+K_{C_2H_4}P_{C_2H_4}+K_{C_2H_6}P_{C_2H_6}+\left(K_{H_2}P_{H_2}\right)^{\frac{1}{2}}+K_{CO}P_{CO})^3}$	*Schbib 2*
$r_{C_2H_2} = \frac{k_A P_{C_2H_2} P_{H_2}}{1+K_{C_2H_2}P_{C_2H_2}+K_{C_2H_4}P_{C_2H_4}+K_{C_2H_6}P_{C_2H_6}+K_{CO}P_{CO}}$ $r_{C_2H_6} = \frac{k_E P_{C_2H_4} P_{H_2}}{1+K_{C_2H_2}P_{C_2H_2}+K_{C_2H_4}P_{C_2H_4}+K_{C_2H_6}P_{C_2H_6}+K_{CO}P_{CO}}$	*Schbib 3*

The temperature profiles in each of the reactors in the industrial hydrogenation unit and concentration of acetylene in last reactor were computed and compared to the actual industrial reactor data, using the kinetic expressions presented previously. However, only one of these expressions was able to describe our system, but was necessary to fit the kinetics parameters in the equations proposed to Schbib et al. [3].

The final model was able to describe the temperature profile and conversion inside the reactor not only in steady state and but also when there are disturbances on input flow rate, carbon monoxide concentration and inlet temperature in the first reactor in the time operation range studied.

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PP-74

FISCHER-TROPSCH SYNTHESIS INTENSIFICATION IN METALLIC FOAM STRUCTURES

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Introduction

Fischer-Tropsch synthesis (FTS) is a well-known process which transforms syngas to liquid hydrocarbons for transportation or further production of more add-value products. This is a highly exothermic reaction, and its products distribution is extremely affected by temperature changes and diffusion limitations of reactants and products through the catalyst pores. With the development of contemporary catalysts, the possibilities for intensification of the FTS have emerged, motivating investigations for potential use of structured reactors, for which the negative effects of diffusion limitations and heat removal would be suppressed. Parallel channel monoliths offer a narrow channel structure inside which laminar flow takes place, and this fact implies external mass-transfer limitation. To increase the mass transfer, as well as the radial temperature and composition homogeneity, metallic foams of open porosity (85-90 %) are very interesting option. However, the problem linked with the effective catalyst weight per foam volume unit to achieve intensification limit in FTS has not been studied. Therefore, the main goal of this work is to study the FTS intensification in a foam structure to enhance the fuel production.

Experimental

Aluminum foams (40 ppi, DUOCEL®, D = 16 mm, L = 30 mm) were loaded by washcoating with different catalyst coating thickness from 50 to 90 μm (500-1400 mg). FTS catalysts of this work were prepared by a special wet impregnation method developed in our group to produce in a single step the catalyst preparation (Co and Re impregnation on the alumina) and the washcoating of metallic structured substrates [1]. In a typical synthesis of a catalyst slurry, an aqueous suspension of 20 % (w/w) of total solids (the active phase precursors $Co(NO_3)_3$ and Re_2O_7, Al_2O_3 support and colloidal alumina) is prepared. The nominal weight composition of all catalysts is 20 % Co – 0.5 % Re/Al_2O_3. The structured catalysts were tested in a commercial micro-reactior unit (Microactivity Reference® from PID Eng&Tech) at 220 °C and 20 bar and a spatial velocity of 6 L/h·gcat of syngas with a $H_2/CO=2$ molar ratio.

Results and Discussion

Figure 1 shows the catalytic results of coated aluminum foam structures (40 ppi, $V_{reactor}$ = 6 cm^3) as a function of catalyst layer thickness. For thicknesses of 50-70 μm, the CO conversion remained constant. However, for thicker catalyst layer the CO conversion and hydrocarbon productivity decreased. In addition, the selectivity to methane linearly increased in all cases. In washcoated structured reactors, increasing the catalyst loading results in thicker layers. Long pores filled with hydrocarbons limit the diffusion of CO and heavy products, favoring that of lighter ones, especially hydrogen and methane [2]. The internal diffusional limitations result in lower reaction rate (decrease in catalyst effectiveness) and decrease in selectivity to liquid hydrocarbons [3].

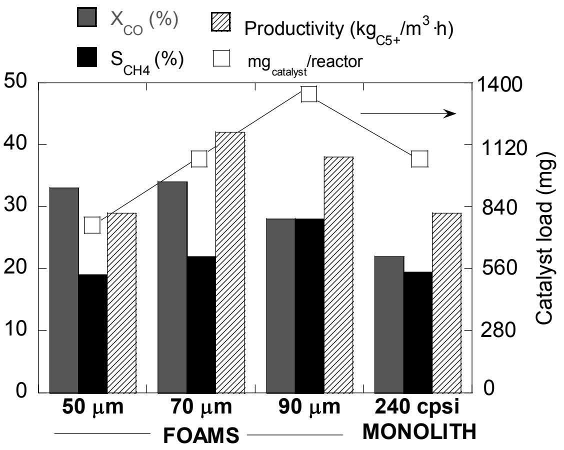

Figure 1

On the other hand, the catalyst activity of foam structures were compared with parallel channel monoliths coated with the same catalyst amount [1], showing an improvement in activity of 45 % (Figure 1). The better properties of the foam structure as compared with the monoliths could be related to a better mixing of reactants due to the tortuosity of the narrow porous substrate structure.

Considering the promising results obtained for washcoated foam structure, the effect of reaction temperature was studied. The almost isothermal behavior of aluminum foams allowed the C_{5+} productivity to be increased up to 87 $Kg_{C5+}/m^3 \cdot h$ at 250 °C.

It can be concluded that foam structures are very interesting for FTS intensification.

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Acknowledgements

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AN EFFICIENT APPROACH TO KINETIC PARAMETER ESTIMATION THROUGH DYNAMIC-MODEL-BASED DESIGN OF EXPERIMENT

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Keywords: design of experiment, kinetics, dynamic model, three phases

The conventional kinetic study is time consuming mainly due to two reasons: (1) data is typically recorded after a certain duration when the reactor reaches steady-state conditions; sufficient data is required to achieve an acceptable precision because a part of data provides limited information. By contrast, a dynamic model can fit the data at any time. There is significant body of literature in process chemistry on the use of dynamical reaction data for identification of reaction mechanisms and generation of kinetic models, see e.g., [1]. Design of experiment (DoE) can further enhance the methodology by identifying the best experiments to improve the effective use of experimental data [2].

The kinetics of CO_2 hydrogenation to methanol in a three-phase reactor is used as a case study. The gas phase is continuous, while catalysts (solid phase) are well dispersed in the liquid phase operated in a batch mode. The solvent is selected based on two criteria – low volatility and high methanol solubility. High stirring rate guarantees a fast distribution of components between the gas and the liquid phases. The mathematical model is formulated in ModelBuilder of gPROMS, describing the dynamic behavior of methanol concentration in the liquid phase and carbon species in the gas phase. Graaf's kinetic model [3] is inserted for the reaction, and the relevant kinetic parameter is explored using the "DoE – experiment execution – parameter estimation" cyclic strategy. The DoE can recommend optimal operational conditions (temperature, pressure, space velocity, sampling time points) for experiment execution, followed by parameter estimation. With several cyclic iterations, an acceptable parameter precision is expected to be achieved with much less effort in the experiment compared to conventional methods.

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PP-76

ANALYSIS OF THERMAL TRANSPORT IN OPEN-CELL METAL FOAMS

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Solid foams as porous materials have been successful thanks to their specific thermal, mechanical, electrical and acoustic properties, such as high void volume (porosity), up to 97 %, resulting in low specific weight, large geometric surface area, intensive heat and mass transport, increased flexibility when comparing with cast material [1-3]. Their important advantage is possibility to be made of almost any material, such as metal (aluminum, chromium-nickel, nickel, copper), ceramics (alumina, cordierite, mullite), polymer (polystyrene, PVC, polyethylene), as well as glass and carbon. Therefore, solid foams have been tested as a catalyst carrier for many chemical reactions, e.g. oxidation of carbon monoxide, Fischer-Tropsch synthesis or selective catalytic reduction of nitrogen oxides (NOx) [1-3].

Growing interest in open-cell metal foams considered as catalytic support is related to continuous search of alternative for monolithic and packed-bed reactors. Previous studies indicated that in terms of mass transfer and flow resistance, foams are placed between the packed bed and monoliths of similar geometric surface area [1]. In practice, this means that the reactor filled with foam catalyst can be much shorter than the monolithic one achieving identical conversion. [4].

The experimental procedure was the same as presented in [5, 6]. Six open-cell metal foams considered as possible catalyst support were tested: Al-10, Al-20, Al-40, Ni0610, NC0610 and NC2733. The experiments were carried out for single-phase gas flow. The foam was heated by strong electric current (up to 150 A) flowing directly through the metal foam skeleton. Several thermocouples measured temperatures of the foam surface and flowing air. Foam morpgology was rigorously studied using computer microtomography (μCT; SkyScan 1172) and optical microscopy. Detailed description of the research can be found in our previous works [7, 8].

It was proved that heat transfer of metal foams is much higher than that of monolithic structure and even comparable with packed-bed. Despite the geometric complexity and material type of foams, their thermal characteristics lie close together. Therefore, heat transfer can be described by single equation displaying satisfactory accuracy (17 %) for all the foams studied:

$$Nu=1.16Re^{0.56}Pr^{1/3} \tag{1}$$

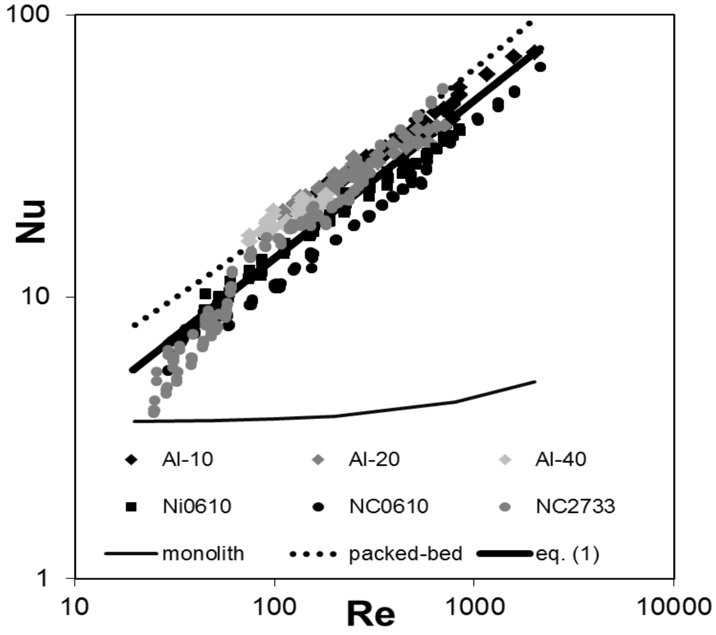

Fig. 1. Comparison of heat transfer for catalytic reactor carriers (foams, monolith, packed-bed)

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PP-77

PRODUCTION TECHNOLOGY OF BACTERIAL CELLULOSE FROM OAT HULLS

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The quest for new cost-effective carbon and nitrogen sources from cellulosic raw materials such as agricultural residues of no food value to produce bacterial cellulose (BC) in high yield is a key challenge to cut down the cost of expensive BC [1]. Here we utilize a globally abundant, industrially available, renewable and sustainable feedstock, the oat hulls. Oat hulls account for 28 % of the grain weight and contain up to 35 % cellulose [2]. We have developed a production technology for BC from oat hulls, involving four basic unit operations: (1) chemical pretreatment; (2) enzymatic saccharification; (3) mixed-culture fermentation; (4) BC purification (Fig. 1). The pretreatment was run in 250-L standard vessel equipment under atmospheric pressure, sequentially with 4 wt % HNO_3 and NaOH solutions. The pulp yield was 24 %, the pulp comprising 93.2 % α-cellulose. The pulp was fermented in a 100-L fermentor. The concentration of reducing sugars in the enzymatic hydrolyzate thus obtained from the pulp was 32.2 g/L, as measured by spectrophotometry. The mixed-culture fermentation was performed with *Medusomyces gisevii* that exhibits an adaptive potential, which is crucial for the sustainable production at an industrial scale [3]. The BC yield was 10 % of the reducing sugar concentration on a dry matter basis. The BC was purified sequentially with 2 wt % NaOH solution, water, dilute HCl (pH 3) solution, and water again. An optimistic yield of BC was obtained: 0,95 ton of 98 % wet product per 1 metric ton of oats hulls. In this case, BC features a high quality: 90 % crystallinity index and 100 % Iα-phase, suggesting a superior quality of the resultant BC and successful engineering solutions at each technological stage of the BC production from oat hulls.

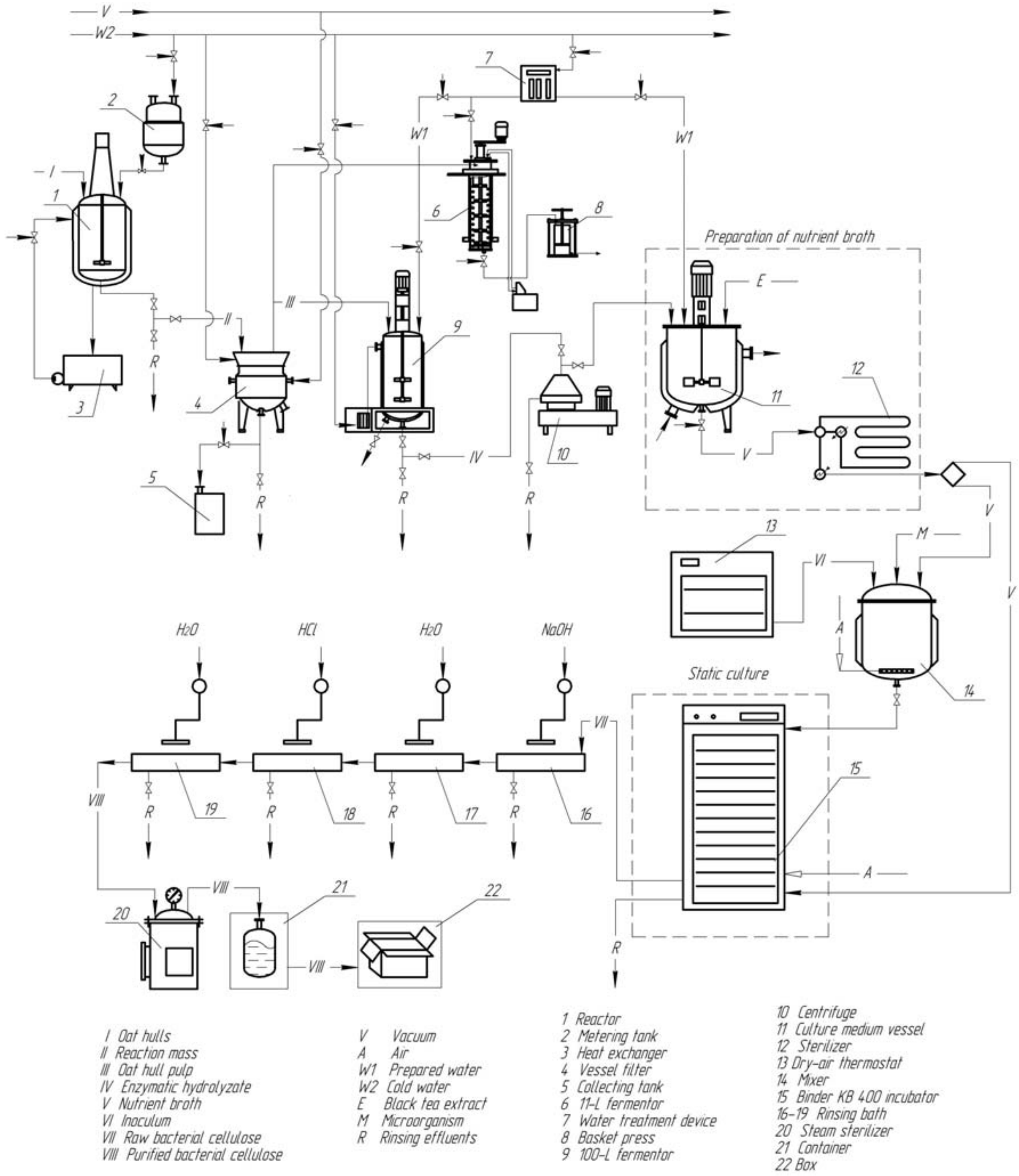

Fig. 1. Process flow diagram for producing bacterial cellulose from oat hulls

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LIGANDLESS CATALYSTS OF SUZUKI REACTION BASED ON HYPERCROSSLINKED POLYSTYRENE: INFLUENCE OF REACTION CONDITIONS, PRECURSOR NATURE AND SECOND METAL ADDITION

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Suzuki cross-coupling is an important reaction of C-C bond formation that uses aryl halides and aryl boronic acids as starting compounds. Suzuki reaction is often used in the synthesis of APIs and new functional materials [1]. Homogeneous Pd complexes are traditionally used as catalysts for the Suzuki reaction with high yields of desired products [2]. Last decades the development of new ligandless palladium catalysts is of high importance, since they can be easily separated from the reaction mixture and reused [3]. In order to improve the efficiency of cross-coupling processes, bimetallic ligandless catalysts can be used since they allow increasing the lifetime of catalysts due to the decrease of palladium leaching, carrying out cross-coupling at milder reaction conditions, increasing activity and selectivity in comparison with monometallic analogues.

In this work we investigated the hypercrosslinked polystyrene (HPS)-supported mono- (Pd, Au) and bimetallic (Pd-Au) catalysts of Suzuki cross-coupling of 4-bromoanisole and phenylboronic acid. HPS is a polymer network in which "pores" are formed spontaneously during polymer synthesis. A unique property of HPS is its ability to swell in various solvents, which facilitates the incorporation of organometallic compounds into the HPS matrix. Due to its high degree of cross-linking, which can exceed 100 %, the HPS consists of rigid nanopores ("nanopores") that create interfaces between the pore volume and polymer walls – nanostructures serving as nanoreactors for particle growth [4, 5]. Recently, we have shown HPS to be a promising support for Pd nanoparticles for different catalytic applications including the Suzuki reaction [6-8].

The Suzuki cross-coupling reaction was carried out at ambient pressure while using low-molecular weight alcohols and water as solvents. Kinetic study was carried out at variation of type and concentration of base, solvent nature and composition, reaction temperature and gas phase composition. During the variation of solvent nature, in the case of Pd-containing HPS-based catalysts, it was found that the use of mixture of low-molecular weight alcohols (e.g. EtOH, i-PrOH) with water allows relatively high activity at mild temperatures (60-70 °C). Moreover, best results were obtained for the catalyst synthesized while using $PdCl_2(CH_3CN)_2$ as the precursor. In this case, the use of HPS as a support allowed achieving more than 98 % conversion of aryl halide for less than one hour of reaction duration at mild reaction conditions (60 °C, NaOH, solvent EtOH/water mixture) and at the absence of phase-transfer agents.

However, independently of the precursor nature, Pd(II) was assumed to be the direct source of the main catalytically active form of Pd (Pd_n clusters formed *in situ*) in the case of unreduced Pd-containing samples. For the samples, which were preliminarily reduced in hydrogen flow, the use of HPS as a support allowed formation of a large number of Pd nanoparticles as well as of Pd_n clusters (shown by the XPS method), and the latter were found to be responsible for the observed high activity of reduced Pd/HPS catalysts.

In the case of reduced Pd-containing catalysts, the influence of the second metal (gold) addition was studied. More than 2.5-fold higher activity among the preliminarily reduced catalysts was achieved in the case of bimetallic Pd-Au catalysts in comparison with monometallic ones. Besides, the possibility of catalyst separation and multiple reuses was also investigated. It was revealed that synthesized bimetallic HPS-based catalysts can be reused four times without essential loss in activity.

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PP-79

INCREASING HIGH OCTANE GASOLINE PRODUCTION VOLUME USING COMPLEX MODELING SYSTEM “COMPOUNDING”

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In the last years in Russia tendency to high-octane and high-quality gasoline (octane number – 95 and 98) production is occurred. Producers have to modify the fuel mixing blend recipes, redistribute raw materials between the units in secondary oil refinery, optimize the management process and gasoline production, as well as to upgrade existing refineries for the gasoline production.

The most efficient way for solution of multi-factor problems of optimization and forecasting of gasoline production can be to apply the method of mathematical modeling and the use of computer modeling system on a physico-chemical basis [1].

During the research with the use of computer modeling system “Compounding”, planned and actual gasoline blending recipes for 2015-2016 were analyzed, according to this recipes gasoline production was realized at one of the refineries of the European part of Russia. Two gasoline brands: AI-92 and AI-95 were produced at the refinery.

For further research 4 months of gasoline production were chosen: the analysis of planned and actual blending formulations was made, as well as a comparison of the main properties of the produced gasoline was made (RON – octane number, research method; MON – octane number, motor method; SVP – saturated vapor pressure). For gasoline of all brands (actual results) octane number satisfies the requirements of state standard No.°32513-2013 “Motor fuel. Gasoline unleaded. Technical conditions”, and the content of aromatic hydrocarbons (HC) and benzene satisfy the requirements of Technical regulations of the customs Union No.°013/2011, but for AI-95 the value of octane number higher than the required (95 points) on 1.6-2.4 points. Thus, we can see that there is a significant overruns of high-octane and expensive raw flows. For larger production of high-octane gasoline in a more resource-efficient way, it is necessary to correct the gasoline blending recipes.

Correction of gasoline blending recipes was realized in the direction of increasing the production of high-octane, high-quality gasoline AI-95 and AI-98.

During the blending recipes correction, the following difficulties, which are associated with the features of gasoline production at this oil refinery, arose:

- During the correction there was frequent problem of excessive unacceptable content of aromatic hydrocarbons in gasoline because of high amount of high-aromatic raw streams.
- For both brands there is a significant excess of the required octane number with large volumes of production.

In connection with the above difficulties, during correction of gasoline recipes AI-95 reformate 1 flow has been replaced by raw materials of this process.

The results of the correction are presented in tables 1.

Table 1. Gasoline volume production before and after recipes correction

Flows	Before correction		After correction		
	AI-92	**AI-95**	**AI-92**	**AI-95**	**AI-98**
	wt. %				
Reformate	53.9	61.9	51.4	62.1	64.2
Fluid cracking gasoline	16.5	4.6	19.3	7.1	–
Light isomerizate	10.2	5.4	8.5	0.8	16.2
Isomerizate	11.7	14.2	13.7	16.0	6.6
Reformate 1	6.1	2.7	7.1	–	–
Raw reformate 1 flow	–	–	–	4.2	–
TAME	1.7	11.3	–	9.7	13.0

As can be seen from tables 1, after recipes correction the feedstock flows are redistributed in such a way that 22.7 wt. % of the total gasoline is of high octane brand of AI-98 at the initial lack of the brand in production. The change in production for brands AI-92 and AI-95 was 14.68 wt. % and 35.76 wt. % respectively.

As a result of the correction, the initial overruns of expensive raw materials was eliminated; 22 215 tons of high-quality gasoline of the AI-98 brand were produced from this raw material. All the basic properties of gasoline after correction comply with all norms and requirements. Reserve of octane number is around 0.2 points, it will allow in case of change of the raw material to produce a conditional gasoline.

With the using of the developed complex modeling system, the necessary correction of gasoline blending recipes was carried out. The developed recipes in each case conform to the concept of the most efficient use of raw materials, depending on their quality and available quantity.

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PP-80

STUDY OF KINETIC PARTICULARITIES OF LOW-TEMPERATURE WGSR OVER CERAMOMETAL CATALYSTS: EFFECT OF CATALYST SIZE

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Water-gas shift (WGS) reaction is one of the primary industrial steps of hydrogen production. Many works devoted to kinetics and properties of catalysts for this process were summarized in a series of reviews [1-4]. Most of the catalysts are usually comprised of Cu, Zn and Al oxide composites prepared by coprecipitation or impregnation. One of the problems of the low temperature WGSR reaction is a low activity of the conventional granulated CuZnAl catalyst per unit volume of the catalyst bed [3,4] explained by a low loading density and a poor access of reagents into the bulk of granules due to internal diffusion [5]. One of the possible way to increase catalyst activity is the use of ceramometal catalysts. Such catalysts could decrease diffusion limitation due to specific system of transport macropores and mesopores.

In this work, we studied the influence of the temperature reaction, contact time and catalyst size on kinetic particularities of low-temperature WGSR over development CuAlO/CuALceramometal and commercial Cu-Zn-Al-O (CZA) catalysts.

Catalytic properties in WGSR were studied in a laboratory flow setup with the gas chromatographic analysis. The catalysts were activated in the mixture of 5 % H_2 in He at 3000-4000 h^{-1} with a temperature ramp of 2°/min up to 270 °C for 2 h. Activity was measured at a pressure of 1 bar in the mixture of $CO:H_2O:H_2$ = 8:42:50 at a steam/gas ratio of 0.6–0.7; a catalyst (0.14–0.25 mm fraction and 3,2×3,2×5 мм) mixed with quartz sand. The height of the catalyst bed diluted with quartz was 3 cm, and the reactor diameter was 20 mm.

The total pore volume of the monolith was calculated from the values of true and apparent densities. True density was measured using a helium pycnometer – Autopycnometer 1320 (Micromeritics). The fraction of micropores and mesopores (called for brevity the “mesopores) as well as the specific surface area (SSA) were determined from adsorption isotherms of nitrogen recorded at 77 K using an ASAP-2400 Micromeritics instrument. The macropore volume was estimated from the difference of the total and mesopore volume.

Table 1. Textural properties different samples of CuAl cermets and commercial Cu-Zn-Al-O (CZA) catalysts

Sample (time MA, min)	SSA, m^2/g	V_{meso}, cm^3/g	V_{macro}, cm^3/g	δ_{gran}, g/cm^3	$\delta_{cat.bed}$, g/cm^3
CuAl(3)	14.4	0.02	0.05	4.24	~2.3
CuAl(6)	9.9	0.01	0.06	4.22	~2.2
CuAl(9)	9.0	0.02	0.07	4.00	~2.1
CuAl(12)	15.7	0.04	0.04	3.87	~2.0
CuZnAl	122	0.25	<0.001	2.00	~1.0

Catalyst was characterized by the apparent rate constant of the first order with respect to CO, which was determined taking into account the reversibility of the reaction. The reaction rate constant was calculated under the assumption that the reactor operated in the plug flow regime. All catalytic data are given for the catalysts that reached a steady state activity (after continuous operation for at least 25 h). The bulk density of the fraction of catalysts without quartz varied from 1 to 2.3 g/cm^3 (Table 1). Activity of granules having a prismatic shape and dimensions $3.2\times3.2\times5$ mm^3 was also studied in the special Temkin single-row reactor [6]. Due to a considerable variation of the bulk density at close weights, contact time also changed significantly, from 0.02 to 0.05 s. It was shown, that ceramometal catalyst more active in comparison with commercial Cu-Zn-Al-O catalyst at the all range of temperatures (150-240 °C).

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IMPROVEMENT OF CATALYTIC STABILITY IN THE PROCESS OF DRY REFORMING OF METHANE BY CoAl-HDL AND CoFe-HDL: PRIORITIZING THE ROLE OF CARBON RESISTANCE WHILE MAINTAINING ELEVATED CATALYST ACTIVITY

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CO_2 reforming of methane, also named dry reforming of methane, is a method of producing hydrogen from the reaction of carbon dioxide with methane (DRM) ($CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$). The major problem associated with this reaction is the sintering of the active phase and carbon formation [1]. The carbon generated during this reaction can be the result of direct decomposition of methane ($CH_4 \leftrightarrow C + 2H_2$) or the Boudouard reaction ($2CO \leftrightarrow CO_2 + C$) [1, 2]. Many ideas were put forward by scientists to develop catalysts bearing both high activity and high resistance to coke. The activity of a catalyst is related to the metal surface area [2, 3]. This implies that the catalytic activity is proportional with the high dispersion of metal particles. The aim of the present work is to investigate the use of NiAl-HDL and NiFe-HDL, previously prepared by co-precipitation method with $Ni^{2+}/Al^{3+}=2$ and pH=12. The products obtained after heat treatment at 800 °C were characterized by XRD, ICP, TPR, BET, SEM-EDX and TEM. After reduction, the catalysts were evaluated in the reforming of methane reaction under continuous flow with CH_4/CO_2 ratio equal to 1, at atmospheric pressure and a temperature range [400-700 °C]. At 700 °C, the catalysts showed significant CH_4 conversions, i.e, 87 % and 79 % respectively for both NiAl-HDL and NiFe-HDL respectively; this was compared to 91 %, and 84 % for CO_2 conversions. Despite NiAl-HDL catalyst exhibiting rather high catalytic activity compared to NiFe-HDL, this latter showed a good resistance to metal sintering and carbon deposition.

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REACTORS DEVELOPMENT AND PROTOTYPING AT ICI CALDAIE

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The activity of ICI Caldaie started 60 years ago in the business of high temperature and high pressure boilers (up to 850 °C and 30 bar). Nowadays ICI Caldaie is recognized as a world leading industry in this business.

In the early 2000' ICI Caldaie became aware that chemical reactors were the proper and natural way to exploit the high level reached by its R&D department and started a dedicated laboratory called “ICI LAB”.

Since the beginning of the activity “ICI LAB” created synergies between its academic partners and the industrial department of ICI CALDAIE, becoming a player able to have an holistic approach to the reactors business, starting from joint design solutions, through feasibility studies and up to the manufacturing and industrialization of the reactors. Partnerships with universities, research centers and other industries all over the world have led to many projects (Internal [1], National [2],[3], European [4],[5]) focused on the realization of chemical reactors.

Thanks to its fully-equipped laboratory and a rapid setup manufacturing unit, provided with data acquisition and analyzing tools, the implementation and testing of new developed solutions is now a routine at ICI Caldaie.

The normal course leading to the development of a new reactor foresees the following steps: Identification and evaluation of a potential product and its applications – Market analysis – Feasibility study – Consortium creation – Project preparation – Sharing technology and knowhow – Joint development – Patent application – Design and Prototyping – Lab testing – Integration and Installation – Field test – Production and Commercialization.

The first field of application was identified in the onsite hydrogen production from natural gas and Bio gas. Different reactors for hydrogen production were developed according to different sizes (from 3 to 50 Nm^3/h) and different grades of purity for different hydrogen applications.

The more traditional designs based on fixed bed catalyst with temperature up to 850 °C and pressure up to 2 bar are now running alongside with innovative designs based on membrane reactors with fluidized bed catalyst, with temperature up to 600 °C and pressure up to 12 bar.

Together with hydrogen production and purification, the experience and knowhow acquired so far range from “CO_2 capture and sequestration”, “gas to liquid reactors” to several other systems.

Figure 1. Different phases in the prototype of chemical reactors at ICI Caldaie

Thanks to ICI manufacturing capability and proven ability of good knowledge transfer between industry and university, ICI is now well ready for the development and joint prototyping of the reactors.

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PP-83

EVALUATION OF Au/Fe_3O_4 CORE-SHELL NANOPARTICLES FUNCIONALIZED WITH DOX-FOLATE IN THE TREATMENT OF AN AGGRESSIVE LUNG CANCER

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Lung cancer is, worldwide, the leading cause of cancer deaths, i.e., every year, lung cancer causes more than 1.6 million of deaths [1]. The poor prognosis of this type of cancer gives rise to a five-year survival of the patients [2]. Ineffective methods for early detection and lack of curative treatment for advanced disease are the primary reasons of this cause of death, and hence are the main challenges to overcome for the academy and pharmaceutical industry [3]. Nanoparticles have, nowadays, gained attention because of their potential during different drug delivery applications, especially in cancer theranostics (therapy and diagnosis) [4]. Nevertheless, there are yet challenges to overcome before their use at the human level: namely, there is not a clear understanding of their biocatalytic and kinetic performance when interacting with the cancer tumor during *in vivo* experiments.

This work aims at giving information on the effect of Au coated on Fe_3O_4 nanoparticles (NPs), functionalizing them with doxorubicin to treat an aggressive lung cancer cell line. It is worth mentioning that during the functionalization of NPs there was used folate to give them more affinity to be sorbed on cancer cells rather than on healthy cells.

The co-precipitation method is used to synthesize the NPs. Besides, the Au precursor used to coat Fe_3O_4 was a gold (III) salt. Au layers on Fe_3O_4 were added by using a seed-mediated approach. The core-shell nanoparticles (CSNPs) of Au/Fe_3O_4 were, then, characterized by ultraviolet-visible (UV-vis) absorption spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Before the evaluation of these CSNPs during the treatment of a lung cancer cell line, they were transferred into an aqueous solution to be bio-functionalized with doxorubicin, an effectively cytotoxic against small cell lung cancer (SCLC) cell lines. Therapeutic effect of these functionalized CSNPs was evaluated by using an MTT assay for assessing metabolic activity of the lung cancer cell line H69. Then, preliminary *in vivo* studies are considered to understand the performance of this nanomaterial system in nude mice. First, subcutaneous tumors of Small Cell Lung Cancer (SCLC) were generated in nude mice (Foxn1nu: Nu/Nu). The human cell line was identified as NCI-H69 [H69] (ATCC® HTB119™). Second, the distribution of gold based core-shell nanoparticles in the studied mice model was visualized by Magnetic Resonance Imaging (MRI).

As primary results, characterization indicated the presence and favorable dispersion of Au on the surface of Fe_3O_4 nanoparticles, which could be related to their efficient functionalizing with doxorubicin-folate. MTT assays showed the capability of the nanoparticles decreasing the metabolic activity of lung cancer cells. Related to *in vivo* results, the subcutaneous tumors of a SCLC formed as expected in the nude mice. MRI elucidated how the NPs were distributed, giving inferences on their residence time in the mouse model. In control mouse model, NPs were mainly located at the kidney; at 8 hours, there was observed the largest concentration of NPs, and at 24 hours, NPs left out the mouse model by urine. In the mouse model with the subcutaneous tumor, the NPs were mainly concentrated in the tumor area, which was attributed to the enhanced permeability and retention (EPR) phenomenon. EPR is considered to be the driving force for NPs to reach and accumulate in the tumor, through either passive or active targeting [5].

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MODELING THE TRANSITION FROM OXIDATIVE COUPLING TO PARTIAL OXIDATION OF METHANE BY Ir-DOPING ON La_2O_3/CeO_2 NANOFIBER CATALYST

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Oxidative coupling of methane (OCM) is an important process to directly convert methane to higher hydrocarbons in the presence of oxygen. OCM mainly produces the desired product ethylene with some side products such as acetylene, propene, and CO_x. La-based catalysts are considered potentially viable to commericalize the OCM process and nanostructured La_2O_3/CeO_2 catalysts showed superior performance over traditional La-based catalysts. However, the latter nanostructured catalysts still could not satisfy the yield and selectivity of C_{2+} to achieve commercial viability. Noon et al. [1] synthesized La_2O_3/CeO_2 nanofibers which could achieve C_{2+} selectivities and yields of up to 70 % and 18 %. However, by doping increasing amounts of Ir up to 1 wt %, the products shifted from OCM, mainly C_2, to partial oxidative of methane (CPO), which is synthesis gas [2]. This demonstrated the possiblity of a new CPO mechanism correlated with OCM, which was different from previous literature. The present study investigates the chemical kinetics and mechanisms for both OCM and CPO in order to further understand this transition process. This work proposes a detailed reaction mechanism describing this transition process dependent on the amount of Ir doping.

The model is developed by combining OCM and CPO mechanisms from various literature. Each reaction is analyzed to validate the mechanism based on the experimental results of spatial concentration and temperature profiles with different amount of Ir doping. The results could provide new insights correlating both OCM and CPO under their complex reaction chemistry.

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PP-85

PROCESS DESIGN FOR SEPARATION AND PURIFICATION OF NATURAL VITAMIN E BASED ON COMPETITIVE ADSORPTION MODEL

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Natural vitamin E ($V_{E}H$) has been used as a bioactive compound because of their strong anti-oxidation activities [1]. $V_{E}H$ is industrially recovered from distillate, byproduct of vegetable oil refining, by multi-stage molecular distillation at high temperature (100-250 °C) [2]. However, $V_{E}H$ recovery yield is low (about 50 %), and several impurities with similar separation properties remain (about 65 wt %). We proposed a new recovery method by adsorption/desorption of $V_{E}H$ using porous type strongly basic resin at low temperature (50 °C) [3]. In this method, $V_{E}H$ recovery yield was improved to be 84 %, and impurity was reduced to 22 wt %. Impurity was only free fatty acid (FaH) which competitively adsorbed on the resin with $V_{E}H$. In addition, a kinetic model considering the competitive adsorption of $V_{E}H$ and FaH was constructed and described that each adsorption zone of $V_{E}H$ and FaH was found to be separately formed in the column [4].

In this research, in order to improve $V_{E}H$ purity, we have designed a multistage column system based on the simulation by the kinetic model. Figure 1 shows the simulated concentration profiles along the length of the column using model feeds assumed to be distillate from soybean(a) or palm(b). FaH was localized upstream of the column, and $V_{E}H$ was localized downstream of the column. The model well simulated each adsorption zone under various feed compositions. If the column was separated by the dashed line, high purity $V_{E}H$ can be obtained from the downstrean of the column. Based on these calculation results, we have designed multistage column systems packed with the resin (Diaion PA306S, total amount of 20 g-wet) as shown in Fig. 2. In the adsorption process, the model feed solution was fed from the bottom until the top of the multistage column. In the desorption process, the acetic acid solution was supplied to the top of the column A in each system. The

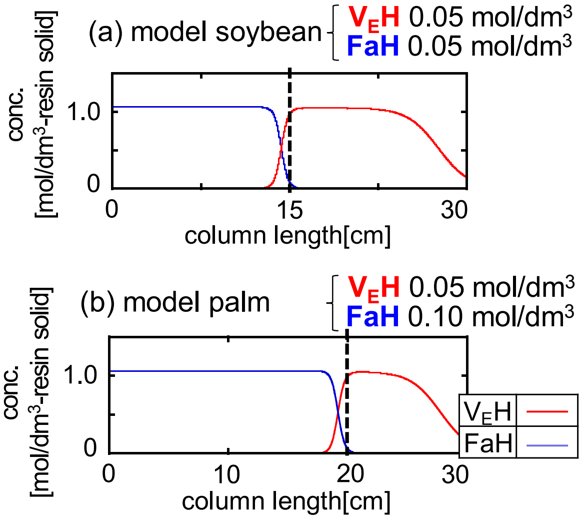

Fig. 1. Concentration profiles of each component in solid

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effluent from the bottom of the column A was obtained and the concentrations of each component were measured by HPLC. The same desorption operation was performed to the other columns (B or B+C).

Figure 3 shows the concentration profiles in the effluent from each column during the desorption using the model soybean. V_EH was confirmed to be selectively recovered only from the column A. Table 1 shows the experimental and calculated results for recovery amounts and V_EH purity. The experimental V_EH purity was increased (94.0 wt %) compared with the case without partition (50.9 wt %). The calculated results are in good agreement with the experimental ones. Table 2 shows the experimental and calculated results using the model palm. V_EH purity was increased by changing the partition position according to the feed compositon. The multistage column system enables the simple and effficient production of high purity V_EH.

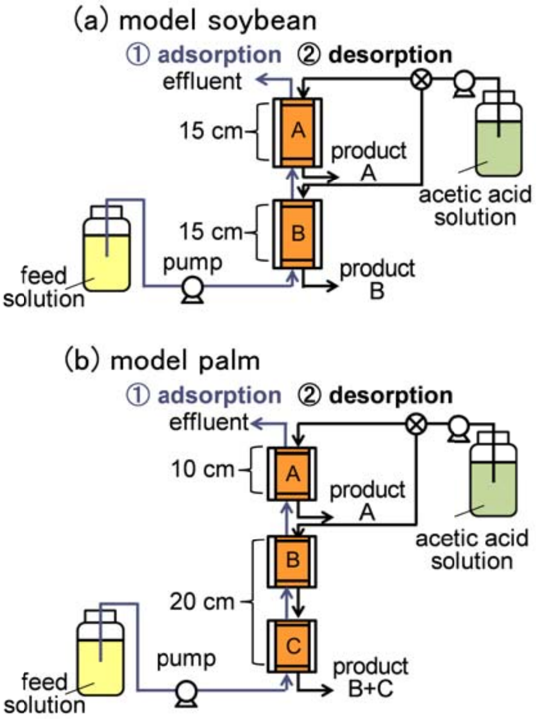

Fig. 2. Schematic diagram of multistage column system for recovey of V_EH

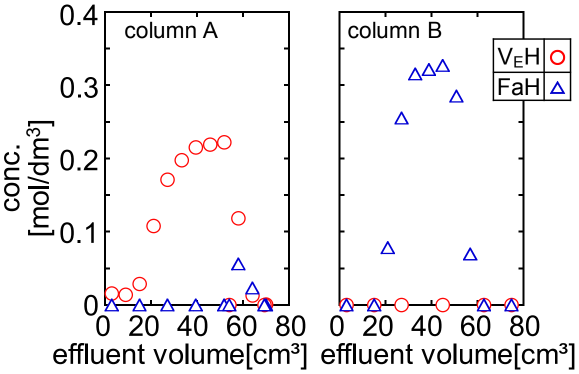

Fig. 3. Concentration profile in the effluent during desorption (model soybean)

Table 1. Desorbed amounts and V_EH purity (model soybean)

	exp.			calc.		
column	A	B	A+B	A	B	A+B
V_EH[mmol]	6.48	–	6.48	7.22	0.50	7.72
FaH[mmol]	0.63	8.90	9.53	0.02	9.26	9.27
V_EH purity[wt%]	94.0	0	50.9	99.8	7.10	54.3

Table 2. Desorbed amounts and V_EH purity (model palm)

	exp.			calc.		
column	A	B+C	A+B+C	A	B+C	A+B+C
V_EH[mmol]	3.42	0.20	3.62	4.30	0.46	4.76
FaH[mmol]	0.08	12.0	12.1	0.02	14.6	14.7
V_EH purity[wt%]	98.4	2.33	30.0	99.7	4.27	31.6

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REACTION RATE ENHANCEMENT IN GAS-LIQUID-LIQUID-SOLID FOUR-PHASE CONTINUOUS FLOW REACTOR

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The reactant (carbobenzoxy phenylalanine) is soluble in an organic solvent and hydrogenated to the product (phenylalanine) using solid catalyst. Phenylalanine is not soluble in the organic solvent, so it needed to be dissolved in an aqueous phase. This was the gas-liquid-liquid-solid four-phase system. Mass transfer becomes more complicated in comparison to three-phase reactors as the catalyst needs to efficiently contact a gas phase as well as two immiscible liquid phases. The catalyst surface properties (hydrophilic versus hydrophobic) also play an important role in the reaction related to the wetting efficiency of the liquids at the solid interface [1]. Gas-liquid-liquid cocurrent upflow reator was used. When hydrophobic catalyst support was used, the catalyst surface was preferentially contacted by the organic solvent phase. Contact with the aqueous phase was poor. The efficient removal of the reaction product was prevented. This led to deactivation of the catalyst due to the product being deposited on the catalyst surface. When hydrophilic catalyst, Pd/Al_2O_3, was used, stable performance with no observed degradation in conversion was observed. However, the hydrophilic catalyst, Pd/Al_2O_3, was found to have a lower conversion than the hydrophobic catalyst, Pd/C, in early usage.

Fig. 1. Catalyst bed

To improve Pd/Al_2O_3 (3 mm in diameter, 3.2 mm inlength) reaction rate, inert partice was inserted to the catalyst bed. Object of

Inert particle was calming the gas and liquid flow patern and incresing the gas and liquid velocity. Four kinds of glass beads were used as inert particle. There diameter were 5.0 mm, 1.0 mm and 0.3 mm. Figure 1 shows the catalyst bed diluted with 0.3 mm glass beads. 3 mm glass beads was settled at the bottom of the catalyst bed. Column inner diameter was 2.0 cm. Gas flow rate was 1.7×10^{-6} m3/s. Liqud flow rate ratio of water to organic solution was 3. 1-octanol was used as organic solvent. Reaction temperature was 323 K.

Gas and liquids hold up was measured to determined the residence time. Water was the continuous phase in this reaction system. Liquid hold ups were increased with increse of liquids flow rate. Each liquid residence time was calculated from holdup and flow rate. Total liquids flow rate were varied and conversion was measured in each liquid flow rate. Figure 2 shows the effects of the organic solvent residence time on the conversion. Two type of catalyst bed were used. Diluted bed is shown in green mark and catalyst only bed is shown in blue mark. Conversions were linealy increased with increase of the residence time. Slopes of the lines show the reaction rate. The reaction rate has 0th order dependence to the reactant concentration. The raction rate was increased 1.6 times by using glass beads.

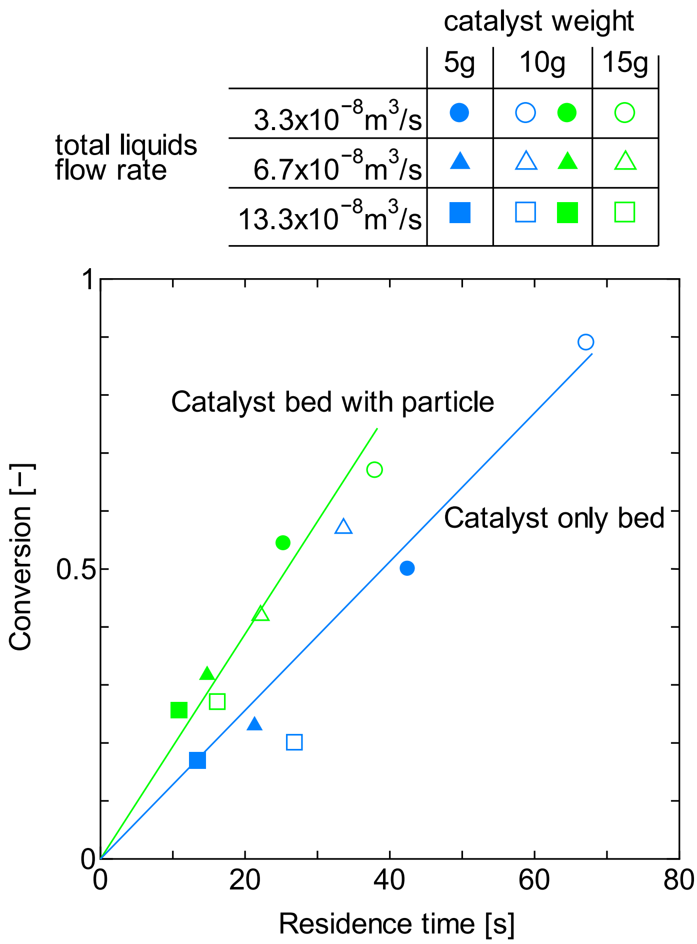

Fig.2 Reaction rate in the upflow reactor

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ELECTROPHYSICAL METHODS OF PRE-TREATMENT OF SEEDS

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Currently, the ecological situation is characterized by a high level of anthropogenic impact on agroecosystems, which brings with it a number of negative consequences for the environment, leads to an increase in the number of phytophages and the prevalence of pathogens.

Therefore, in recent decades, the search for biophysical techniques and technologies aimed at realizing the genetic potential, increasing non-specific resistance to abiotic and biotic stresses, increasing the adaptive potential of plants for the purpose of growth and stabilization of the harvest has been increasingly being pursued.

Currently, one of the priority areas in science and technology is the study and practical development of new, increasingly short-wave (EHF) ranges of electromagnetic radiation. This trend, above all, refers to the waves of the EHF-range.

For the first time we studied the reaction of plants of different varieties and species of spring cereal crops to presowing seed treatment by electrophysical methods – electromagnetic waves of the EHF-range in the presence of nanosized magnetic composites stabilized by humates. Optimal regimes of the electrophysical effect on the stability of seeds of cereal grains to the diseases of fungal etiology depending on the radiation parameters and exposure time are determined.

The obtained results showed that EHF-irradiation of seeds improves the seeding qualities, increasing the germination energy depending on culture and variety up to 12 %, and laboratory germination up to 9.6 % in comparison with the control variant for a batch of seeds with reduced seeding qualities. The positive effect of seeds irradiation on their sowing qualities, the growth and development of plants, and the resistance of seedlings and plants to damage by root rot increases their safety, contributing to an increase in this indicator by the harvesting period in wheat in the epiphytoty of up to 15 % and barley to 11 %.

The water retention capacity of wheat and barley plants increases with respect to control in the variants with EHF-irradiation by 7-15 %, which indicates an increase in the level of drought resistance of experimental plants.

The effect of electrophysical methods in the presence of magnetic composites and humates on the seeds of grain crops, unlike chemical protectants, had a prolonged effect and increased the resistance to airborne pathogens.

The effect of physical methods on seeds before sowing, namely irradiation of seeds with electromagnetic waves of the EHF-range in the presence of magnetic composites and humates, with a pulsed magnetic field in the presence of magnetic composites and humates contributed to an increase in the yield of spring wheat by 15.4 and 10.1 %, and barley – by 14.3 and 10.8 %, respectively, relative to control, which was higher (by 8-13 %) or at the level of variants with the use of growth regulators and protectants. With the germination of seeds, there is an acceleration of metabolic processes, especially in the early stages of development. Such a directed magnetic field is the force that awakens the dormant biological forces of grain or seeds, awakens even before the grain enters the earth. This is precisely the active effect of magnetic fields on the vital functions of seeds.

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MAGNETIC ENRICHMENT OF SLUDGE WASTE FROM TPP TO OBTAIN A CONCENTRATE OF RARE AND SCATTERED ELEMENTS

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Rare metals determine the level of modern materials science and are used in the production of materials for microelectronics, radio engineering, electrical engineering, nuclear energy, etc. Sufficiently promising raw materials for these purposes are coal ash. The paper presents the results of studies on the possibility of extracting rare and rare-earth elements from ash of Ekibastuz coal containing from 40 to 63 % of mineral components. When burning dusty fuel at 1200-1700 °C, solid wastes of two types are formed: fly ash and slag. Approximately 80 % of the mineral part of the coal passes into fly ash, trapped in cyclones and electrostatic precipitators, and up to 20 % passes into slag, which accumulates in slag bins under the furnace. Then, the ash and slags are transferred to ash dumps by the hydraulic removal method, where they are stored in the open air or under a layer of water [1]. Ashes of 95-99 % consist of Al, Fe, O, Ca, Ti, Mg, S, K, Na. When coal burns, a part of trace elements (Sc, Sr, Y, La, Ti, Zr) are concentrated in the slag. Other elements (Ga, In, Tl, Ge, Sn, Pb, etc.) at a temperature above 100 °C are removed from the high-temperature zone and condense in electrostatic precipitators at 110-120 °C, fly ash is enriched by these metals.

In practice, enrichment can be carried out by various methods: gravity, flotation, magnetic and electrical separation, chemical enrichment, etc. Magnetic enrichment of mineral raw materials is one of the most environmentally friendly methods of processing raw materials. Ash-slag materials of TPPs containing rare-earth elements are mostly weakly magnetic.

We have shown that, when vortex electromagnetic reactors are used, the initial materials (ash and slag) are grinded to particle sizes from 10 to 1 μm in the presence of an extractant and paramagnetic particles in an oxygen or air medium, a complete transition of non-ferrous metals to the extractant takes place within 5-10 min, and in the slag there are only oxides of calcium, aluminum and silicon. In an electromagnetic vortex reactor, the raw material undergoes a triple action: 1. Variable electromagnetic field; 2. Constant magnetic field of working bodies from 1 to 10 mm; 3. Mechanical impacts of many working magnetic bodies in the working chamber of the reactor. As a result of the triple action in the reactor, the activation of substances at the electronic level takes place. In the presence of paramagnetic particles, the process is carried out in a resonant regime. Non-ferrous metals are extracted with a solvent, and after the addition of water, in addition to the iron compounds, it is extracted into an aqueous solution, the evaporation of which produces a concentrate of rare and scattered elements.

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CONVERSION OF HYDROCARBON LIQUIDS TO SYNTHESIS GAS BY PARTIAL OXIDATION IN A MOVING BED REACTOR

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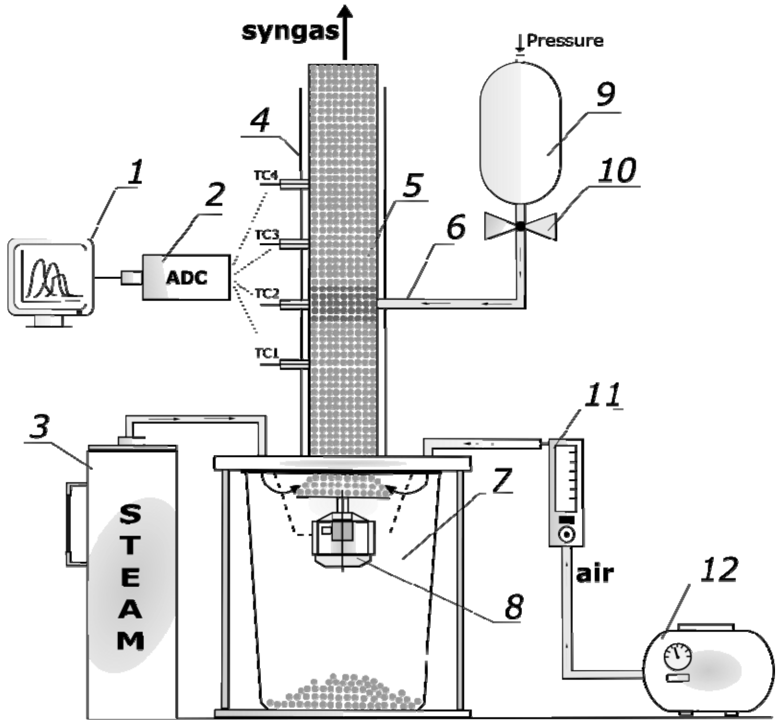
Conversion of hydrocarbon liquids by means of partial oxidation in superadiabatic regime of filtration combustion (FC) was studied experimentally using 2-propanol as a model. Superadiabatic heating is achieved in a counterflow reactor with a moving bed of granular solid with non-premixed supply of air-steam mixture and fuel [1]. The experimental setup is schematically presented in Fig. 1.



1 – data acquisition,
2 – ADC,
3 – steam supply,
4 – mirror screen,
5 – quartz reactor,
6 – fuel supply,
7 – ash bin,
8 – rotary grate,
9 – fuel storage,
10 – control valve,
11 – air flowrate meter,
12 – compressor

The 66-mm-id vertical shaft kiln reactor (5) made of quartz covered with an aluminum foil mirror screen (12) was filled with a granular inert solid, 7...10-mm chamotte crumbs. The inert material was controllably discharged from the lower part of the reactor with the rotary grating; the level of the granular bed was maintained constant by charging atop the same volume of fresh solid. After an initial heat pulse, air and steam were supplied from the lower part and fuel, 2-propanol, supplied at the rector center. The fuel supply rate was measured prior to an experiment and checked as the average consumption. The temperature in the reactor was measured using Type K thermocouples. Syngas was sampled from the upper part of the reactor and further analyzed using a GC-CRYSTAL 5000 chromatograph. C2-C5 hydrocarbons can be detected with an accuracy of 0.01 % vol. Similar embodiment was used for conversion (gasification of a pulverized coal [2].

The ignition was achieved by charging a preheated mixture of granular solid with charcoal and started air supply. Fig. 2 shows a typical time dependence of the temperature on thermocouples 1 to 6 up from the grating. Fuel supply was started on the level of TC3 from 10 min. The oscillations reveal discharging and charging of solid.

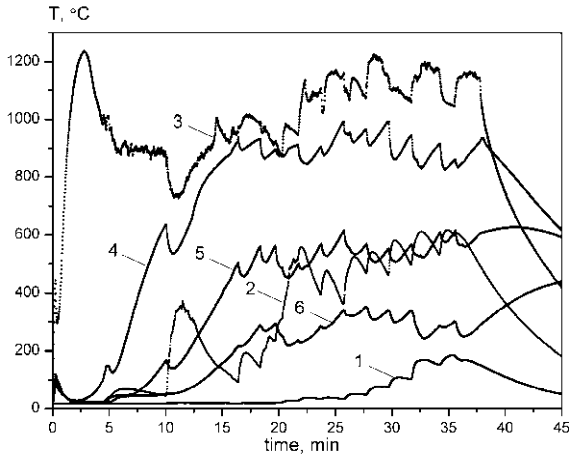
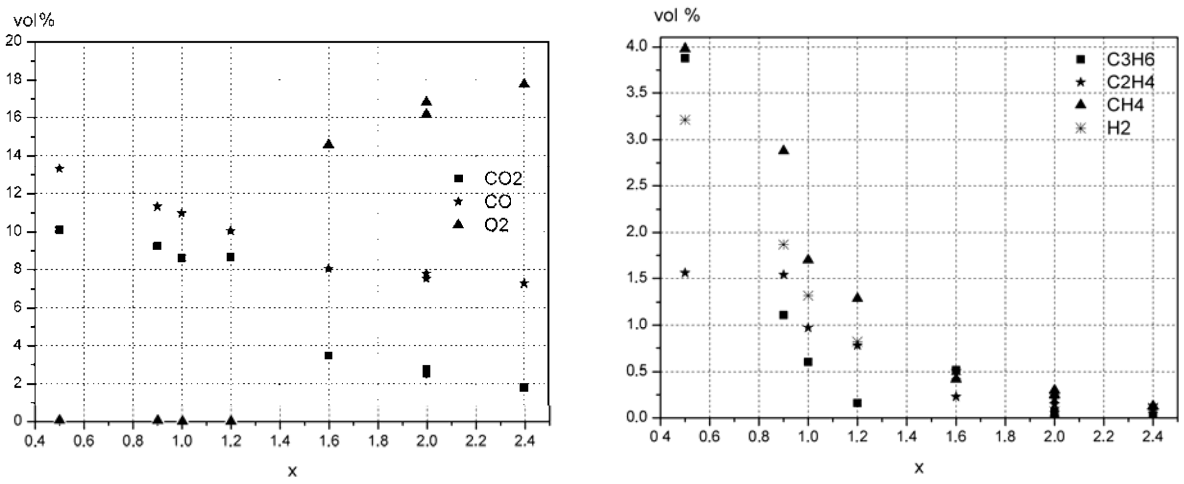


Fig. 3 presents preliminary results for gaseous products of 2-propanol conversion as dependent of air flowrate varied while propanol supply was maintained constant.



Here $x = [O_2]/([C_3H_8O]*3)$ is oxygen to carbon molar ratio [1]. In the regime presented in Fig. 3 the conversion yields substantial concentrations of hydrocarbon gases.

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Acknowledgement

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EFFICIENT TWO-PHASE PROCESSES OF OXIDIZING SUBSTITUTED ALKYLPHENOLS INTO THE CORRESPONDING *PARA*-QUINONES IN THE PRESENCE OF HETEROPOLY ACID SOLUTIONS

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Substituted alkyl-1,4-benzoquinones are valuable chemicals used, for example, in chemical organic and pharmaceutical synthesis, catalysis, and chemical physics, which nowadays are produced from the corresponding phenols by diverse oxidizing methods with moderate selectivity and efficiency [1]. Search for novel approaches to convert various phenols, such as 2,3- and 2,6-dimethylphenols (Me_2Ps), as well as 2,6-di-*tert*-butylphenol (2,6-*t*BuP), stays a popular task. The aim of the study was to develop an efficient method for oxidizing aforesaid phenols into valuable benzoquinones in the presence of modified P–Mo-V heteropoly acid solutions (P–Mo-V HPAs) that are good oxidants with the property of reversible oxidability.

The modified-type P–Mo-V HPA solutions of $H_aP_zMo_yV_xO_b$ gross-composition with different vanadium content (x) were prepared in two stages by H_2O_2-based activation of V_2O_5 and subsequent addition of obtained $H_6V_{10}O_{28}$ solution stabilized with H_3PO_4 into boiling aqueous suspension of MoO_3 and H_3PO_4 [2]. The catalysts were characterized by ^{31}P and ^{51}V NMR spectroscopy, potentiometry, titrimetry, and pH measurements and tested in two-phase oxidation of 2,3- and 2,6-Me_2Ps, as well 2,6-*t*BuP at various reaction parameters. ^{31}P and ^{51}V NMR spectra showed that the obtained HPAs are complex mixtures of heteropoly anions $H_{x-1}PMo_{12-x}V_xO_{40}^{4-}$ (with different number of vanadium atoms x) surrounded by cations VO_2^+ and H_3O^+ and anions $H_zPO_4^{(3-z)-}$. All solutions were found to be strong Brønsted acids with pH below 0 and possess oxidation potential values above 1 V. The content of vanadium(IV) obtained by potentiometric titration was less than 6% that is explained by the partial reduction of vanadium(V) with H_2O_2 to vanadium(IV) during synthesis.

The synthesized P–Mo-V HPA solutions were tested as catalysts for two-phase oxidizing the above phenols into the corresponding benzoquinones, varying an organic solvent type and its volume, temperature (25-70 °C), atmosphere (N_2, O_2, CO_2), and molar ratio of vanadium (V) to substrate (in the range of 4-21) (Eq. (1)).

$$H_2Su + O_2 \xrightarrow{HPA} SuO + H_2O \quad (1)$$

The performed optimization of reaction conditions allowed achieving benzoquinones selectivity above 95 % with a total process time of about 1 h [3,4]. To realize the process 1 with high product selectivity, it was performed in two different reactors according Eqns. (2) and (3).

$$ {}^{m}/_{4}\,H_2Su + {}^{m}/_{4}\,H_2O + HPA \rightarrow {}^{m}/_{4}\,SuO + H_mHPA \quad (2) $$

$$ H_mHPA + {}^{m}/_{4}\,O_2 \rightarrow HPA + {}^{m}/_{2}\,H_2O \quad (3) $$

At the first stage, solutions of catalyst and substrate reacted in a jacketed glass reactor equipped with a reflux condenser in the absence of oxygen. The high oxidative potential of optimal HPAs provided a high rate of the reaction (20-30 min). After reaction completion, the obtained mixture was transferred to a separating system where the catalyst was detached from the products by simple and efficient phase disengagement. Isolated catalyst solution was submitted to a unique plug-flow air reactor (Figure 1 [5]) and regenerated for 30 min at 160-170 °C and 20 bar (P_{O_2} = 4 bar) according to Eq. (3). The regenerated catalyst was fed again to reaction 2 for the next catalytic cycle. Reaction 2 was found to have a first order in substrate and a variable order in HPA depending on the catalyst reduction degree.

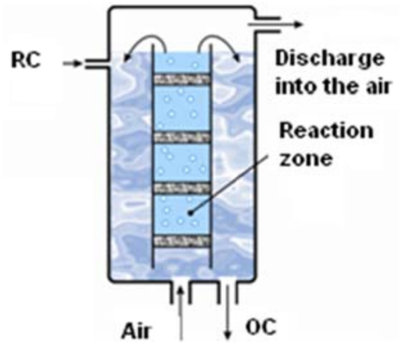

Figure 1. Air reactor scheme. RC – reduced catalyst; OC – oxidized catalyst

Two-phase oxidation of substituted phenols into valuable quinones in the presence of P–Mo-V HPA solutions realizing in two technological stages by using different reactors is a convenient and efficient method that provides high selectivities of target products, efficient regenerating spent HPA solutions, as well a process safety and simplicity of product separating. The described process can be realized in the form of a closed cycle.

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SO_2 OXIDATION IN STRUCTURED CATALYTIC CARTRIDGES WITH GLASS-FIBER CATALYST FOR CONDITIONING OF FLUE GASES FROM COAL-FIRED POWERPLANTS

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Abatement of ash particulates emissions into atmosphere with flue gases of coal-fired powerplants is an important environmental protection problem. The ash particles are usually removed in electrostatic precipitators, but their efficiency may be decsreased by high electric resistivity of ash, produced in result of combustion of some types of coal.

This problem may be resolved by application of flue gas conditioning technologies, based, in particular, on addition of amounts of SO_3. Sulfur trioxide forms the microdroplets of sulfuric acid, which are adsorbed at the surface of ash particles thus decreasing their electric resistivity and improving the operation of precipitators.

Application of pure SO_3 as an external conditioning agent is not feasible due to problems with its tranporation, storage and injection into the flow of flue gases. Oxidation of sulfur trioxide present in the flue gases is much more attractive alternative.

All existing catalysts are not suitable for this purpose. The very strong limitations of the pressure drop, very high fluid velocity and significant content of ash particles in the flue gases makes impossible to apply conventional granulated vanadia catalysts due to their very high pressure drop and high risk of clogging by particulates. These catalysts are not manufactured in a form of structured monoliths characterized with low hydraulic resistance and high permeability.

The breakthrough in this area may be provided by application of glass-fiber catalysts (GFCs) [1]. It was demonstrated that such catalysts show high operation stability and lower ignition temperature, compared to conventional vanadia catalysts [2]. At the same time, such catalysts use zirconia-promoted glass-fiber supports, which are expensive and have limited availability at the open market.

In our current work we have proposed new type of Pt-based GFC which shows high activity and even more lower ignition temperature: ~250 °C compared to 300-330 °C in case of previous GFC and 360-400 °C for vanadia catalysts (see Fig.1).

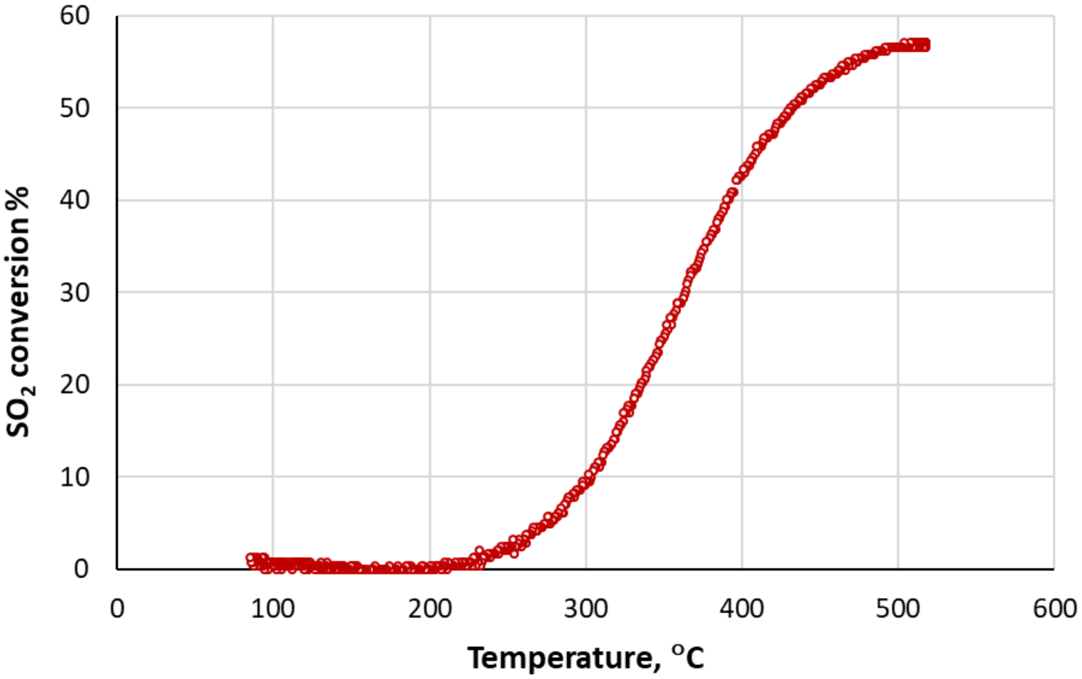

Fig. 1. SO_2 conversion vs temperature in oxidation of SO_2.
Conditions: inlet SO_2 concentration – 200 ppm, GFC loading – 9 g, gas flow rate – 22 l/min

This catalyst may be applied for oxidation sulfur dioxide in form of structured catalytic cartridges, which are characterized with excellent ratio between mass transfer efficiency and pressure drop [3]. These cartridges are also characterized with increased permeability, making possible to use them in a flow with high content of ash particles.

The presentation also discusses the synthesis and experimental testing of vanadia-based GFCs, which may be considered as an alternative to Pt-containing catalyst within the given approach.

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PP-92

FUTURE DEVELOPMENT OF UPGRADING PROCESSES FOR HEAVY OIL FEEDSTOCKS

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Nowadays, the development of new effective technologies for the extraction and processing of heavy hydrocarbon feedstocks, such as heavy and superheavy oils, natural bitumen, bitumen-saturated rocks and asphaltites, is actively researched [1-3]. This fact is due to the steady decline in the share of light oil produced in the world and the annual increase in the number of heavy oils involved in processing. These types of feedstock have not been practically used in the petrochemical industry before.

Heavy oil feedstocks are characterized by a high content of tar-asphaltene substances and heteroatom compounds. These features determine the main processing options. Having no scientific information on the composition of these components, it is impossible to solve the problems of using such non-standard feedstock in an effective way [4-6]. A very important aspect of this problem is the structural and mechanical properties of heavy oil feedstock, which also determine the way of oil extraction and processing. At the moment, the mechanism of interaction between resin and asphaltene molecules with reagents used to change the structural properties of heavy petroleum feedstocks has not been studied in practice, as well as the regularities of resin and asphaltene molecule transformation in various types of oil processing.

Therefore, the urgent issue is the question of studying the transformation mechanisms of heavy oil high-molecular compounds while processing and interaction with reagents that improve the rheological, structural and mechanical properties of heavy oils, as well as the search for new, alternative methods of extraction and processing of heavy oil.

One of the most promising methods in the field of heavy hydrocarbon feedstock processing is the conversion in a water vapor medium under critical and supercritical conditions. Water under supercritical conditions has the properties of a proton-donor nonpolar solvent, which in turn increases the efficiency of thermal destruction processes and produces hydrocarbon mixtures with a low content of heteroatomic compounds [7].

Consequently, the main purpose of this work is to identify the principal directions of changing in resin and asphaltene structures of heavy oil in the process of aquathermolysis under various conditions, as well as the development of methods for regulating the rheological and structural-mechanical characteristics of heavy oils.

The following tasks are planned:

1. To consider the possibility of using aquathermolysis as one of the most promising processes for upgrading heavy oil feedstocks.
2. To study the interaction process of resin and asphaltene molecules with reagents that improve the rheological and structural-mechanical properties of heavy oil feedstocks.
3. To determine a transformation mechanism for the conversion of resin and asphaltene molecules when interacting with reagents that improve the rheological, structural and mechanical properties of heavy oil.

The solution of these problems will enable not only to simplify heavy oil feedstock refining, transporting and processing without changing the configuration of oil refineries, but will also facilitate the extraction of heavy oils and natural bitumen.

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VIRTUAL PRESENTATIONS

VP-1

MODELING OF ISOTHERMAL ADSORPTION OF SULPHANOL ON THE QUARTZ SAND

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Many of the tasks associated with the use of surfactants in the field of oil recovery remain unresolved. These include the management of the injection operation in the formation of a surfactant solution, which depends significantly on the complexity of the approach to process modeling. Adsorption of a surfactant in a porous medium leads to the fact that at the front of oil displacement, water does not contain surfactants or contains them in very small, inefficient concentrations. The front of the surfactant moves 10-20 times slower in the formation than the displacement front. The well placement system for the application of aqueous surfactant solutions can be the same as for conventional water flooding.

The main objective of the study was to give an experimental and theoretical estimate of the effect of sulfonol adsorption on quartz sand.

Discussion of the experimental results shows that the given process is characterized by a nonequilibrium dynamics of adsorption and can be described by a system of equations: the balance of sulfonol (1), the kinetics of its adsorption on quartz sand (2), the adsorption isotherm (3), the initial and boundary conditions (4).

$$\frac{\partial C}{\partial t} + \upsilon \frac{\partial C}{\partial x} + \frac{(1\text{-}m')}{m'} + \frac{\partial a}{\partial t} = D_{\text{э}} \frac{\partial^2 C}{\partial x^2}\ , \qquad (1)$$

$$\frac{(1-m')}{m'} \frac{\partial a}{\partial t} = \beta_0 (C - a/\Gamma)\ , \qquad (2)$$

$$a = f(C)\ , \qquad (3)$$

$$C(0,t) = C_0;\ \ C(\infty,t) = 0;\ \ C(x,0) = 0;\ \ a(x,0) = 0\ . \qquad (4)$$

Here C – adsorption concentration, C_0 – initial concentration of adsorbent at the inlet of the adsorber, a – adsorbate concentration, υ – linear velocity, t – time, x – height coordinate of adsorbent bed, $D_{\text{э}}$ – effective diffusion coefficient, β_0 – coefficient of kinetics, Γ – Henry's coefficient, $m = (1 - m')/m'$, m' – porosity.

MATHEMATICAL MODELING OF PYROLYSIS IN TUBULAR REACTORS OF VARIOUS TYPES

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Pyrolysis of carbonaceous feedstock is an important essential part of the actual problem of recycling. Experiments show that the implementation of pyrolysis process in an oscillating temperature field leads to a noticeable increase of productivity of the pyrolysis equipment.

Kinetic model of the process, corresponding to the set of consecutive-parallel reactions has been proposed [1]. It is shown that in a certain temperature the oscillating regimes allow to increase the efficiency of the pyrolysis process. On the kinetic stage of the technology design an important role of the branched chain reaction mechanisms of the pyrolysis has been revealed [2].

Macrokinetic model of pyrolysis is proposed. It allows to obtain qualitative and quantitative characteristics of transport processes during the implementation of the pyrolysis of carbonaceous feedstock in equipments of a tubular reactor type [3]. It is shown that the kinetic regime is retained in a tubular reactor with a radius of less than 1.5-2 cm.

The problem of optimal temperature control of the pyrolysis process in a plug-flow reactor is formulated and solved. It is shown that the optimal temperature regime of the pyrolysis reactor control with screw feed of carbonaceous feedstock significantly depends on character of the main stages of kinetic scheme of reactions [4].

Mathematical modeling of pyrolysis in a tubular reactors of a multichannel type, a countercurrent and a variable cross-section was carried out [5–7]. For example, a thermokinetic model for consecutive-parallel scheme of transformations has the form of the material balance equations [6]

$$\begin{aligned}
&\frac{\partial c_1}{\partial t} + \vec{v}(\ell)\frac{\partial c_1}{\partial \ell} = -k_1(\vec{T})c_1, \\
&\frac{\partial c_i}{\partial t} + \vec{v}(\ell)\frac{\partial c_i}{\partial \ell} = k_i(\vec{T})c_2, \qquad i = 3,4,5
\end{aligned} \tag{1}$$

where c_i are the dimensionless concentrations of the substances. The heat balance equation of the condensed phase is

$$\frac{\partial \vec{T}}{\partial t} + \vec{v}(\ell)\frac{\partial \vec{T}}{\partial \ell} = \lambda \frac{\partial^2 \vec{T}}{\partial \ell^2} + \sum \Delta H_j k_j(c,\, \vec{T}) + \alpha(T_* - \vec{T}) + \beta(\overleftarrow{T} - \vec{T}), \tag{2}$$

ΔH_j are the heats of reactions; α is the heat-transfer coefficient from the reactor wall to the biomass; β is the heat-transfer coefficient from the countercurrent gas flow to the feedstock being pyrolyzed; T_* and is the reactor wall temperature. The heat balance equation of the gas phase is

$$\frac{\partial \overleftarrow{T}}{\partial t} + \overleftarrow{v}(\ell)\frac{\partial \overleftarrow{T}}{\partial \ell} = \mu \frac{\partial^2 \overleftarrow{T}}{\partial \ell^2} + F + \gamma(T_* - \overleftarrow{T}) + \beta(\vec{T} - \overleftarrow{T}), \tag{3}$$

where μ is the thermal conductivity of the gas fed countercurrent to the moving biomass, γ is the heat-transfer coefficient from the gas to the reactor wall, $\overleftarrow{v}$ and is the gas velocity in the countercurrent flow.

Calculations (1)–(3) show that the implementation of pyrolysis in a tubular reactor, in which the heating of porous carbonaceous feedstock occurs in the countercurrent flow of heated gas, can provide significant productivity of process.

The proposed stages of modeling of pyrolytic processes allows to speak about the development of the theoretical foundations of designing of pyrolysis processes of carbonaceous feedstock, which is carried out in the regime of oscillating temperature fields.

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INVESTIGATION OF THE CATALYTIC EFFICIENCY OF COBALT AND NICKEL PYROPHOSPHATES IN THE PROCESS OF DEHYDRATION OF METHYL LACTATE

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Introduction

The growing demand for acrylic acid (AA) and its derivatives are set the task of developing new efficient and environmentally friendly methods for producing acrylic acid and acrylates. One of the most promising and environmentally friendly direction of their synthesis is currently the dehydration of lactic acid and its esters derived from renewable feedstocks. The main problem for the implementation of this area is the lack of efficient catalyst systems. At presentthe best results are shown by salt catalysts, especially a catalytic system containing magnesium and barium pyrophosphates, structured by silicon dioxide.

The purpose of this study is to study the activity and selectivity of catalytic systems containing cobalt and nickel pyrophosphates in ML dehydration reaction. The pyrophosphates of cobalt and nickel was added to catalytic system based on barium and magnesium pyrophosphates with silica, this catalytic system was studied in our previously [1]. The activity of following catalytic systems were investigated: $Ba_2P_2O_7/Mg_2P_2O_7/Ni_2P_2O_7/SiO_2$ (1/1/1/1 mol),$Ba_2P_2O_7/Mg_2P_2O_7/Ni_2P_2O_7$ (1/1/1 mol), $Ba_2P_2O_7/Mg_2P_2O_7/Co_2P_2O_7/SiO_2$ (1/1/1/1 mol),$Ba_2P_2O_7/Mg_2P_2O_7/Co_2P_2O_7$(1/1/1 mol).

Experimental part

Investigation of the catalyst systems were carried out in a vertical tubular reactor with a fixed catalyst bed 10 ml volume at atmospheric pressure in a nitrogen stream, at temperatures ranging 350-390 °C and a contact time of 0.5 to 1 second, ML mixture was fed to the reactor with water in a weight ratio of input 20/80.

Experiment duration was 4 hours, with an interval analysis of the reaction mixture in 1 hour. The product composition was determined using GC and HPLC. Activity of catalysts were evaluated for ML conversion (X_{ML}, wt. %) and the selectivity to AA (S_{AA}, wt. %), which was determined by the amount of acrylic acid formed by the dehydration reaction.

After each experiment, the catalyst was regenerated by feeding air at 480 °C temperature for 40 min. During regeneration, all samples recovery their initial catalytic properties.

Results

The following table shows the best results achieved for each of the investigated catalyst systems.

Among theinvestigated catalytic systems containing cobalt and nickel pyrophosphates, the most effective is the $Ba_2P_2O_7/Mg_2P_2O_7/Co_2P_2O_7$.The ML conversion is equal to 87.5 % that very close to ML conversion over $Ba_2P_2O_7/Mg_2P_2O_7/SiO_2$ (94.5 %), also AA selectivity is equal to 53.7 % a little bit higher that over $Ba_2P_2O_7/Mg_2P_2O_7/SiO_2$ (51.1 %).

Catalyst	Contact time, s	Temperature,°C	X_{ML}, wt. %	S_{AA}, wt. %
$Ba_2P_2O_7/Mg_2P_2O_7/SiO_2$	1	370	**94.5**	**50.8**
$Ba_2P_2O_7/Mg_2P_2O_7/Ni_2P_2O_7/SiO_2$			64,6	44,4
$Ba_2P_2O_7/Mg_2P_2O_7/Ni_2P_2O_7$			70,6	43,6
$Ba_2P_2O_7/Mg_2P_2O_7/Co_2P_2O_7/SiO_2$			76,9	52,7
$Ba_2P_2O_7/Mg_2P_2O_7/Co_2P_2O_7$			**87,5**	**53,7**

However, the catalytic system $Ba_2P_2O_7/Mg_2P_2O_7/Co_2P_2O_7$is more stable: when it used for 4 hours, the ML conversion reduced by 5-7 %, whereas when using $Ba_2P_2O_7/Mg_2P_2O_7/SiO_2$ – by 10-13 %.

Conclusions

The effect of addition of nickel and cobalt pyrophosphates to ML dehydration catalysts was studied. It established that the addition of cobalt pyrophosphate ($Co_2P_2O_7$) leads to an increase in the stability of the catalyst without reducing its efficiency.

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CATALYSIS OF TRANSFORMATION OF BIOETHANOL TO ACETALDEHYDE AND HYDROGEN

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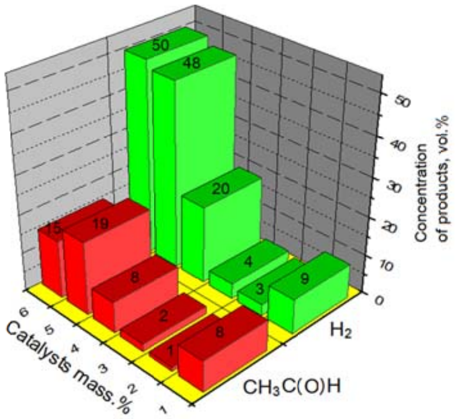
Oil reserves – the main raw material for the synthesis of most valuable commodity products, are deemed exhausted by many analysts [1-3]. The most promising renewable raw material with practically unlimited reserves meeting modern ecological requirements is bioethanol. Using catalytic methods from bioethanol can be synthesized industrially significant chemical compounds such as acetaldehyde, hydrogen, etc. Acetaldehyde – one of the most important multi-tonnage products and it is on the first place among aldehydes as an intermediate product of organic synthesis for producing acetic acid, acetic anhydride, ethyl acetate, 2-ethylhexanol etc. [4]. H_2 is used in low-tonnage, science-intensive industries: electronic, pharmaceutical, food, metallurgy, the synthesis of chemicals and in organic chemistry, petrochemistry, oil and gas processing [5]. H_2 is one of the attractive universal energy carriers with high ecological purity, flexibility and efficiency of energy conversion with its participation. It ranks first among energy carriers by the heat of combustion. The purpose of this work is to develop and study the activity of oxide catalysts in the conversion of bioethanol to acetaldehyde and hydrogen and to determine the dependence of their efficiency on the physical-chemical characteristics. As the active phase, oxides of transition elements Cu, Cr and Zn deposited on γ-Al_2O_3 were studied. The choice of the active phase was justified by the fact that these oxides are active in a number of works in the conversion of ethanol. It is known [6] that for transition metal oxides a broader set of degrees of oxidation, acid-base and oxidation-reduction properties are characteristic. The catalysts CuO/γ-Al_2O_3, ZnO/γ-Al_2O_3, Cr_2O_3/γ-Al_2O_3, CuO-Cr_2O_3/γ-Al_2O_3 and CuO-ZnO/γ-Al_2O_3 were prepared by impregnating the carrier on the moisture capacity. The activity of catalysts was tested on an automated flow-through catalytic unit (PCU-2). The reaction products were identified on the "CHROMOS GC-1000" instrument using the absolute calibration method. The catalysts were investigated in the temperature range of 150-350 °C and a space velocity of 0.5-1 h^{-1}. The optimum temperature is 300 °C, the space velocity $W = 1\ h^{-1}$.



1 – 1 % $CuO/\gamma\text{-}Al_2O_3$;
2 – 1 % $ZnO/\gamma\text{-}Al_2O_3$;
3 – 1 % $Cr_2O_3/\gamma\text{-}Al_2O_3$;
4 – 3 % $CuO/\gamma\text{-}Al_2O_3$;
5 – 3 % CuO-2 % $Cr_2O_3/\gamma\text{-}Al_2O_3$;
6 – 3 % CuO-2 % $ZnO/\gamma\text{-}Al_2O_3$

Figure. Concentration of acetaldehyde and hydrogen in the conversion of bioethanol on various catalysts (Tr = 300 °C, W = 1 h^{-1})

The figure shows that on 3 % CuO-2 % $Cr_2O_3/\gamma\text{-}Al_2O_3$ catalyst, the acetaldehyde concentration increases from 1 to 19 vol. %, on the 3 % CuO-2 % $ZnO/\gamma\text{-}Al_2O_3$ the hydrogen concentration rises from 3 to 50 vol. %. Physical chemical characteristics of the catalysts were investigated by SEM, TEM, IRS, etc. The SEM data showed that the catalysts have particles of different sizes and shapes, as well as amorphous particles, i.e. in this state, ultrafine particles with dimensions less than 5 nm can be found. TEM microphotographs of the Cu-Cr-catalysts revealed nanophase particles with dimensions ≈ 5-7 nm. These characteristics have a positive effect on the catalyst activity in the ethanol conversion. The acid properties of the Cu-containing catalysts were investigated by the IRS with a pyridine as the probe molecule and showed that the synthesized catalysts contain only Lewis acid sites (LAS). The highest amount of LAS (171 μmol / gKt) is observed on the catalyst 3 % CuO-2 % $Cr_2O_3/\gamma\text{-}Al_2O_3$. These changes help to increase its activity in the conversion of bioethanol to acetaldehyde.

Thus, the obtained results showed that among the developed catalysts, Cu-Cr oxide catalyst systems on alumina (3 % CuO-2 % $Cr_2O_3/\gamma\text{-}Al_2O_3$) are characterized by sufficiently high activity in the reaction of conversion of bioethanol to acetaldehyde. 3 % CuO-2 % $ZnO/\gamma\text{-}Al_2O_3$ oxide catalyst is active for the production of H_2.

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MATHEMATICAL MODELING OF INTRAMOLECULAR TRANSFORMATIONS OF *ORTHO*-SUBSTITUTED AROMATIC NITROSO OXIDES

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This work is focused on study of ortho-substituted aromatic nitroso oxides. Nitroso oxides have unique properties due to the *cis-trans* isomerism phenomenon and one-and-a-half N-O bond order in the nitroso oxide fragment. The chemistry of nitroso oxides is discussed in reviews [1-5]. This paper considers the decay reaction of aromatic nitroso oxides. Considering the complexity of aromatic nitroso oxides, conformational transformations development of a new comprehensive approach using experimental and theoretical tools alongside with mathematical methods and informational technologies is particularly relevant. The main objective of the paper is to develop an algorithm for numerical modeling of aromatic ortho-substituted nitroso oxides decay process. Mathematical model for decay reactions of 2,4-dimethoxyphenyl nitroso oxide is suggested. The kinetic modeling allowed us not only to get an agreement between quantum-chemical and experimental data, but also to estimate previously unknown rate constants including the constants for the recombination stages. An algorithm for calculating the effective constants of niroso oxide isomers consumption, based on quantum chemical data, is developed alongside with an algorithm for searching for optimal values of the formation enthalpies and free Gibbs energies.

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THE STUDIED OF ALTERNATIVE METHOD FOR PRODUCTION OF ACRYLIC ACID BY DEHYDRATION OF BUTYL LACTATE

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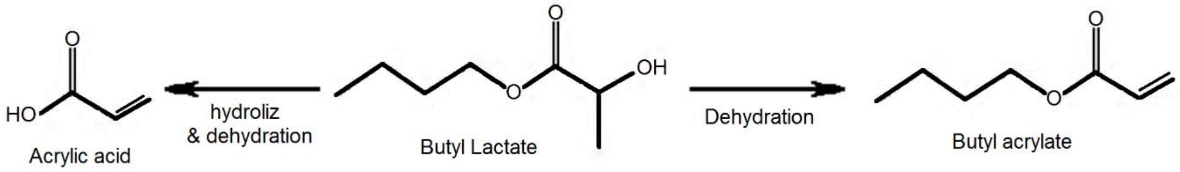
The acrylic acid (AA) is an important chemical intermediate, the consumption and production of which is growing steadily. This push the academic community to research a new technologies for the production of AA from renewable raw materials. This direction is most interesting for countries that do not has extensive hydrocarbons reserves of has limited access to them (gas, oil, etc.).

In view of this, the potential direction is the production of AA by the dehydration of not only lactic acid (LA). Currently produced by the microbiological method from raw materials, but also by the dehydration of LA esters in particular butyl lactate (BL), obtained directly from the enzymatic substance without stage of purification of LA, by esterification of ammonium lactate with n-butanol.

Development of such a hybrid technology, including the production of butyl ester of lactic acid by fermentation of plant material and it's further catalytic dehydration into acrylic acid.



From the available scientific and technical literature on the dehydration of LA on zeolites [1] and dehydration of MLour previously studies over the phosphate catalysts [2], it follows that zeolites catalysts show high selectivity for the main products (AA/MA), but too quickly lose their catalytic activity. In turn, phosphate catalysts are much slower deactivate with average selectivity for the main products. The aim of this paper is to study the behavior of these two different catalytic systems using BL with n-butanol as initial mixture.

Based on results achieved for dehydration of ML over mixed phosphates catalysts (pyrophosphates alkali-earth metals structured by silica gel), a sample: BaPP/MgPP/SiO_2 (mole ration 1/1/1) was synthesized to study the dehydration of BL. In comparison was choose a zeolite of the NaY type.

The studies were in the vertical tube reactor with a fixed catalyst bed of 5 ml at atmospheric pressure in a nitrogen flow at 370-390 °C and a contact time is equal to 1 sec. The BL was feed into reactor in a mixture with n-butanol a weight ratio of 20/80.

The composition of the products was determined by using GC, GC combined with mass spectroscopy and HPLC. In addition to AA, butyl acrylate (BA) also taken into account as the main product. The activity and selectivity of the catalysts were evaluated by the conversion of BL (X_{BL}, %) and the selectivity of formation of AA (S_{AA}, %) and BA (S_{BA}, %) (table. 1).

Time, min	**NaY**			**BaPP/MgPP/SiO_2**		
	X(BL), %	**S(AA), %**	**S(BA), %**	**X(BL), %**	**S(AA), %**	**S(BA), %**
60	90.9	43.5	4.2	53.5	19.3	11.4
120	96.3	44.3	5.3	35.2	33.2	19.5
180	57.5	42.6	6.9	30.9	34.5	19.1
240	14.0	40.9	12.1	30.3	37.8	20.9

The experiments showed that zeolite NaY rapidly deactivated in the course of experiments. The conversion of BL decreased from 91 % to 14 % in 4 hours. For the BaPP/MgPP/SiO_2 phosphate catalyst, the BL conversion decrease from 54 % to 30 % in 3 hours and then remain stable.

The average total selectivity for the main products (AA and BA) on the NaY was 49.5 % and on the phosphate catalyst 53.5 %. Thus, further studies of the dehydration reaction of BL in AA and BA need continued using phosphate catalysts.

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RESEARCH OF DIESEL FUEL CLEANING ON THE ALUMINOSILICATE ADSORBENT

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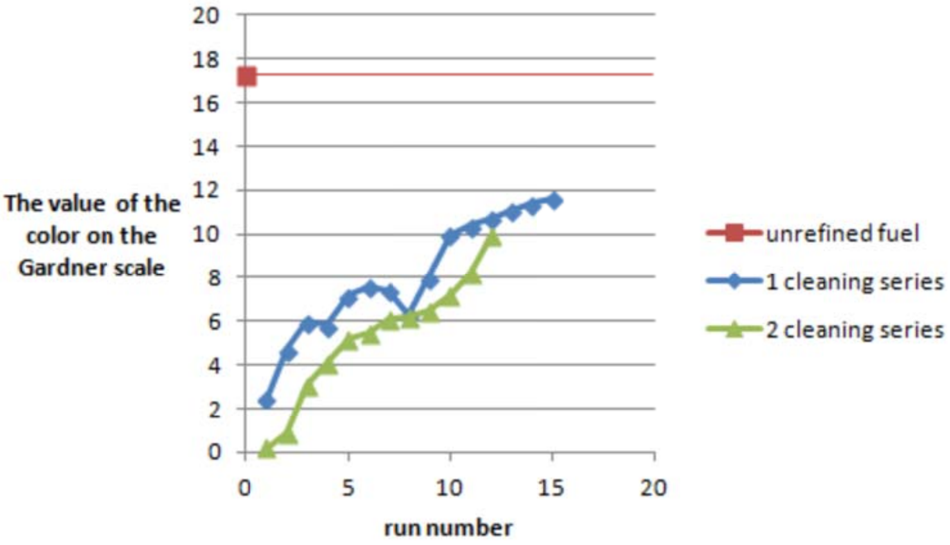
With the tightening of environmental and operational requirements for diesel fuels, the load on hydrotreating processes has increased, due to the increase in hydrogen consumption and the search for new catalytic systems, which entails an increase in operating costs. In addition, diesel fractions of secondary origin containing a large amount of tar-asphaltene substances (TAS) are increasingly involved in processing. The use of processes based on the adsorption of TAS and sulfur compounds, will allow for hydrotreating in milder conditions, with obtaining products of required quality. The advantage of adsorption cleaning, in comparison with other methods, lies in its high efficiency, the possibility of carrying out the process under mild conditions, the simplicity of technology, and the safety of production [1,2].

Practical implementation of the process includes two stages: adsorption and regeneration of the spent adsorbent. The efficiency of the process is determined by the high capacity and selectivity of the adsorbent with respect to the TAS, as well as the completeness of recovery of its activity after regeneration. Based on the literature review for this work was selected aluminosilicate adsorbent brand AS-230Sh of two types: type "B" (fraction size 0.0-0.2 mm) and type "C" (fraction size 0.2-1.6 mm), which has the greatest adsorbability with respect to the TAS and capacity in comparison with other adsorbents [3,4]. For regeneration, no additional reagents are required, during use, the adsorbent is practically not consumed [5].

The first stage of the process – adsorption – is carried out in a column with a height of 900 mm and an inner diameter of 29 mm filled with an aluminosilicate sorbent. The process is carried out at a temperature of 20-25 °C and atmospheric pressure. After completion of the first stage, nitrogen is blown through the filled adsorbent for a while (nitrogen flow rate 1.4 l / min, column pressure 0.5 atm) to desorb the adsorbed substances. The complete regeneration of the adsorbent from tar-asphaltene substances was carried out in an oven at 500 °C for 15-20 hours.

The first series of experiments is carried out on a column packed with an adsorbent column, in a mass ratio: type "C": type "B": type "C" = 15:70:15. Volume of column filling adsorbent 500 ml. In the course of the process, 15 samples weighing 200 g (the mass of the first sample – 400 g) are consistently loaded, followed by a regeneration step and similarly loaded with 12 more samples. The outflow parameters sufficient to determine the degree of purification were measured. The color of petroleum products is an external visual indicator of their chemical composition. Thus, TAS have strong coloring properties, the presence of even a small amount of TAS in the oil product has a significant effect on the color of the product [6]. As a result, the change in chromaticity in Fig. 1:



Based on the literature review and the data obtained, it can be concluded that this purification method is an attractive method of refining fuels from impurities that can be used alone or in combination with other methods. By selecting certain process conditions, types and sizes of adsorbents, it is possible to achieve high selectivity and purification degree.

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PREDICTIONS OF CHEMICAL REACTIVITY BY THEORETICAL CALCULATIONS

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What determines the catalytic activity for a given chemical reaction? For reactions with more than one possible product the presence of a surface can change the catalytic selectivity [1]. The quantum-chemical calculation has been provided to illustrate the possibilities of theoretical interpretation and prediction of catalytic reaction pathway.

In this paper, the theory of the transition state is used for a detailed study of the kinetics of one of the most important reaction stages in the inhibition of a hydrogen flame by phosphorus-containing substances. There remain open questions about way of the suppression of fire: a molecule of a combustion inhibitor substance, or the destruction products. An analysis of the sensitivity of the rate constants of reactions containing organophosphorus components has shown [2] that the rate of free flame propagation depends most strongly on the rate constants of reactions:

$PO_2^{\bullet} + H^{\bullet} + M \rightarrow HOPO^{\bullet} + M$ (1),

$HOPO + H \rightarrow H_2 + PO_2$ (2),

$PO + O \rightarrow OH + PO_2$ (3),

entering into the catalytic recombination cycle [1]. In this case, reactions (1) and (2) are most effective. Quantum-chemical methods that are used in this paper to clarify the mechanism of one of the most important stages (2) in the cycle of hydrogen flame inhibition by phosphorus-containing substances. Thermodynamic characteristics of molecules are an important element of many chemical studies and are used in the development of technologies for the industrial synthesis of new materials, processes for processing oil and solid fuels, modeling and solving environmental problems. In this work, we calculated the thermodynamic characteristics of elementary reactions according to the Twarowsky mechanism [1], which proposed an inhibitory cycle involving small phosphorus-containing radicals. For the first time in this work, the inhibitory cycle of phosphorus containing substances is supplemented by one more reaction $PO^{\bullet} + O^{\bullet\bullet} \rightarrow PO_2^{\bullet}$, as a result of which both atomic oxygen captured and the regenerated of the most important inhibiting particle $PO_2^{\bullet}$ occur simultaneously. In Table 1 shows the calculated thermodynamic characteristics of elementary reactions in the Twarowsky cycle.

Table 1. Gibbs energies of elementary stages of transformation of particles PO• and PO_2• at the flame suppression

№	Stages of inhibition cycle	Gibbs energies ΔG, kcal/mole at the temperature, T, K								
		298	500	700	900	1100	1300	1500	1700	1900
1	PO• + O••→PO_2•	7,5	12,3	17,1	21,8	26,6	31,6	36,3	41,1	46,4
2	PO•+•OH→HOPO	-10,9	-16,9	-22,7	-28,4	-34,1	-39,8	-45,3	-50,9	-56,4
3	PO• + •H→ HPO	-9,0	-13,3	-17,7	-22,3	-26,9	-31,7	-36,3	-41,0	-45,8
4	PO_2• +•OH → $HOPO_2$	-13,4	-20,5	-27,3	-34,3	-40,7	-47,3	-53,8	-60,3	-66,6
5	PO_2• + H•→HOPO	-13,1	-18,2	-23,5	-27,9	-34,3	-39,7	-45,2	-50,7	-56,1
6	HOPO+H•→PO_2•+H_2	-1,9	-2,6	-3,3	-3,9	-4,4	-4,8	-5,3	-5,6	-5,7
7	HOPO+OH•→PO_2•+H_2O	-2,7	-0,9	-1,5	-2,0	-2,9	-2,8	-3,3	-3,5	-3,8

Thus, for the first time in the work, the transition state of one of the leading elementary reactions in the cycle of hydrogen flame inhibition by phosphorus containing substances was calculated. The predominant role of small phosphorus-containing radicals in suppressing the flame by organic phosphates has been proved. The new reaction stage has been added to the well known inhibition cyrcle.

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PRODUCTION OF PLASTICIZERS BASED ON SUCCINIC ACID AND 2-ETHYLHEXANOL AND CYCLOHEXANOL

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Today most of the manufactured worldwide plasticizers are esters of phthalic acids. Researches of their physicochemical and consumer properties have shown that they are easily released from polymer compositions and are pollutants on a global scale [1].

Therefore an important problem is development of the ways of receiving phthalate-free plasticizers, which will have good plasticizing properties, high speed of biological degradation and hypotoxicity of products of their decomposition. According to the literature data, it is known that succinic acid esters (succinates) can be used as such plasticizers for PVC, which, in terms of their bacterial biodegradation, significantly exceed phthalates. [2]

To study the plasticizing ability of succinates, samples of dicyclohexylsuccinate (DCHS) and di-2-ethylhexyl succinate (DEHS) were obtained. The tests of the obtained individual samples of succinates and comparison of their properties with the properties of dioctyl phthalate (DOP) showed that none of them in pure form is suitable for use as a plasticizer.

To obtain a sample, that meets the requirements for plasticizers, several compositions were prepared, which are a mixture of DCHS and DEHS in different proportions, and their plasticizing properties were studied. It turned out that the blended sample with a ratio of DCHS to DEHS as 0.68 : 1 (mole/mole) has properties, which close to DOP.

Another way for the preparation of plasticizer can be by direct synthesis by reacting of dimethyl ester of succinic acid with a mixture of cyclohexanol and 2-ethylhexanol of various compositions. In this case, besides individual DCHS and DEHS, obtained plasticizer sample will contain an unsymmetrical ester cyclohexyl-2-ethylhexylsuccinate (CHEHS).

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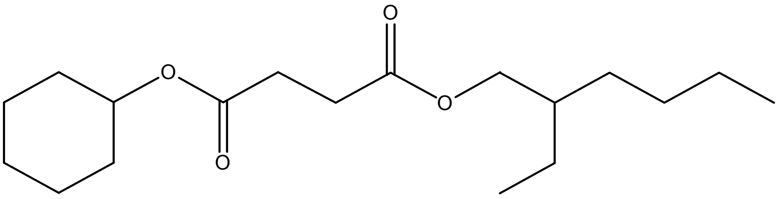

Alcoholysis of dimethyl succinate with a mixture of alcohols of cyclohexanol and 2-ethylhexanol at different ratios, catalyzed by the sodium hydroxide, was carried out with distillation of the concomitant methanol. The process was carried out under vacuum until the methanol evolution ceased, and the final product was purified from excess alcohols by distillation with steam, and from the intermediate products (methylcyclohexyl succinate and methyl 2-ethylhexylsuccinate) by vacuum rectification. The reaction mixture was analyzed by gas chromatography.

The obtained samples of plasticizers were a mixture of unsymmetrical CHEHS and symmetric DCHSs and DEHSs in different ratios. The distribution of the reaction products as a function of the molar ratio of alcohols was investigated. The distribution coefficients for DCHS, CHEHS and DEHS for the range of ratio cyclohexanol/ 2-ethylhexanol (1.1-1.5 ÷ 1 mol/mol) were calculated (Table 1).

Table 1. Properties of unsymmetric succinic acid esters

Name of index	CHEHS Samples 1	CHEHS Samples 2	CHEHS Samples 3
The initial ratio of cyclohexanol to 2-ethylhexanol, mole	1.1:1	1.3:1	1.5:1
The ratio of the alkyl groups C6 / C8 in the sample	0.53:1	0.69:1	0.9:1

The tests of the obtained samples on their plasticizing properties have shown the possibility of using a mixture sample and sample No. 2 as a plasticizer on a par with DOP.

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XYLENES OXIDATION IN THE PRESENCE OF TRANSITION METALS SALTS MIXTURE

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Oxidation of individual ortho- and para-xylenes in the presence of transition metal salts has been studied for a long time. We believe the process mechanism looks like the following: peroxide radicals first involve hydrocarbons into chain oxidation process, then the same radicals are responsible for quaternary breakage of those hydrocarbons. In the case, metal proves to act as the initiator of intermediate peroxides or similar products decomposition, with further radicals release into the reaction space [1]. This technology is much appreciated within industrial processed, dedicated to production of aromatic acids from corresponding pure xylenes. Initial substances are separated by means of rectification, because the products of oil fractions reforming contain an isomer mixture of those substances [2].

This investigation is aimed on isomer mixture oxidation, without their separation, to obtain a mixture of o- and p-toluic acids. The oxidation rates of ortho-xylene and para-xylene without solvent over cobalt catalyst are comparable. We can expect those oxidation rates are kept within a mixture, or they may take closer or similar values, because any of original hydrocarbons may be involved to chain by both radicals, each with its own chain propagation rate constant. However, setting up the experiment with an equimolar mixture of xylenes resulted in dramatic oxidation rate decrease of para-xylene in the presence of ortho-isomer. The same speed ratio kept in the presence of a manganese-promoted cobalt catalyst.

The inhibitory effect of ortho-xylene in the oxidation of para-isomer can be explained by the fact that probably hydroperoxide radical o-xylene, o-ROO● is more stable than an equivalent p-ROO●, and the latter is more active. Then, ROO● is capable of attracting only less oxidation-resistant o-xylene and incapable of interacting with p-xylene. Active ROO● radicals react with both hydrocarbons. In this case, the concentration of ROO● in the reaction mass will increase, resulting in formation of o-toluic acid, and suppressing the oxidation of p-xylene. Thus, o-xylene acts as a gradually expended inhibitor of the reaction. Meanwhile, kinetic curves of the para-isomer oxidation show it’s accelerated comsumption at high conversion rates of o-xylene.

Varying concentrations of the initial substances within the mixture makes it possible to estimate the relative activity of para-ROO● and ortho-ROO● radicals. The changes are observed, according to chain propagation rate constants. The observed phenomenon may prove valuable, because it first allows to oxidize ortho-isomer, then to separate o-toluic acid by means of filtering, and then to oxidize the remaining p-xylene to p-toluic and terephthalic acids.

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SYNTHESIS AND EXTRUSION MOLDING OF Fe-Mo CATALYST FOR OXIDATIVE DEHYDROGENATION OF METHANOL TO FORMALDEHYDE

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Modern industrial technology of Fe-Mo catalyst for oxidative dehydration of methanol includes deposition of iron (III) molibdate from aqueous solutions of ammonia molibdate and iron (III) nitrate, rinsing, drying, and pelletization of grains (or ring-shaped tablets) [1]. The principal disadvantages of the said technology are abundance of waste water, as well as non-optimal pore structure of the catalyst (including low mesopore content). The present study reports low-waste "dry" and "combined" technologies for catalyst preparation; extrusion molding as an alternative to pelletization was also assessed.

"Dry" technology includes oxidative sintering of ammonia molibdate and iron (III) oxide requires extensive heating along with periodic stirring of the mixture. Introduction of organic acids, i.e. citric, into the mixture, allows for obtaining sintered (550 °C) product containing no free iron (III) oxide (as per XRD data). In our prospective, "combined" technology seems very promising. It is based on combustion of concentrated solutions of ammonia molibdate and iron (III) oxide at 500-550 °C in the presence of complexing agents such as tartaric or citric acid, which allows a one-step synthesis of $Fe_2(MoO_4)_3$ and MoO_3 mixture with desired phase ratio (as demonstrated via XRD) at quantitative yield.

Improving heat- and mass-transfer along with decreasing of pressure drop of catalytic layers in cylindrical reactors requires the use of special "energy-effective" catalytic particles (size under 5 mm) with increased outer surface, i.e. grooved cylindrical granules. We used extrusion molding of water-bonded pastes with appropriate additives. Obtained granules (see fig. 1) had far better mechanical strength as compared to industrial pellets which might significantly increase catalytic layer lifetime.

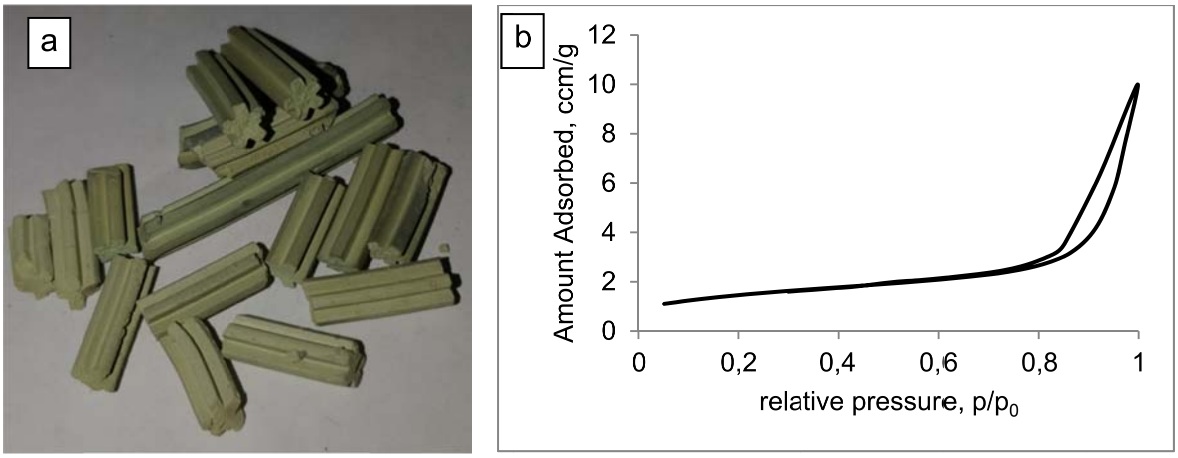

Figure 1. Image of extrusion-molded Fe-Mo catalyst granules (a) and typical adsorption-desorption isotherm of extrusion-molded granules

Another important advantage of extrusion-molded catalysts is increased (up to about 3 times) volume of optimal-sized size (ca.80 Å) pores. Obtained catalysts were markedly mesoporous with pronounced adsoption-desorption isotherm hysteresis (type IV isotherm [2]) (see fig. 1b) which is also suggestive of mainly mesopore-type adsorption.

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INFLUENCE OF PALLADIUM CONTENT ON THE ACTIVITY AND STABILITY OF THE CATALYST OF THE BENZYL ALCOHOL AQUEOUS ALKALINE OXIDATION

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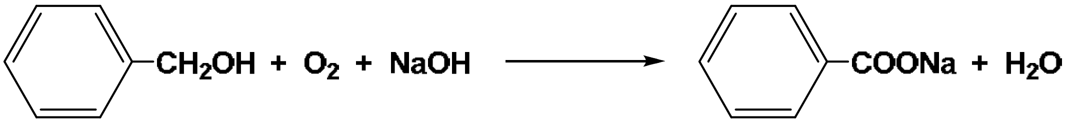
Benzyl alcohol is widely used as one of the model substrates for investigation of liquid-phase oxidation (oxidative dehydrogenation) of alcohols over platinum-group and gold catalysts.

The kinetics of aqueous-alkaline oxidation of benzyl alcohol with oxygen



in the presence of 0.5 % palladium-on-carbon was studied by a volumetric method.

The alcohol concentration did not exceed the limits of its solubility in the aqueous phase. The hydrodynamicы ensured the absence of limiting difficulties for mass transfer at the gas/liquid and liquid/solid boundaries and in the bulk liquid phase. The degree of dispersion of the catalyst ensured the absence of internal diffusion resistance.

In each test conversion was low enough to provide ‘isolation’ conditions for liquid phase reagents. The reaction order with respect to these reagents (alcohol and alkali) were determined from the relationship of the initial reaction rate vs varying initial concentrations: zero order in alkali and first order in alcohol.

It is experimentally shown that there is no effect of sodium benzoate on the reaction rate in the range studied. Nevertheless, during each experiment, a significant decrease in the rate of oxidation was observed (Fig. 1, typical kinetic curves, a catalysts series).

It was concluded this result is due to catalyst deactivation with oxygen, known as ‘over-oxidation’. A mathematical model is proposed that adequately describes the results obtained:

$$dC^*(O_2)/d\tau = kAC_{BzOH}C_{cat}, \qquad -dA/d\tau = k_D A,$$

where $C^*(O_2) = \Delta N(O_2)$ is effective absorbed oxygen concentration; C_{BzOH} and C_{cat} are benzyl alcohol and catalyst concentrations; τ is reaction time; A is current relative catalyst activity ($A_0 = 1$).

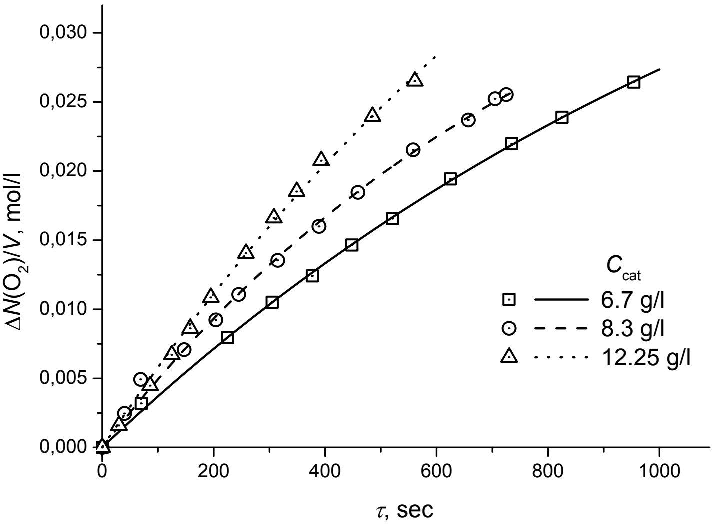


Fig. 1.

Oxidation (k) and deactivation (k_D) constants are quasi, since the model does not take into account the effect of oxygen concentration.

Using the technique and the mathematical model described above, the relationship of the catalyst activity and resistance to deactivation with palladium content was studied. It was found that palladium content increasing from 0.25 to 2 % causes a moderate monotonic growth of initial catalyst activity. At the same time, a sharp, almost step-like, drop of the deactivation rate, i.e., an increasing of the catalyst stability, is occured in the region between 0.25 and 0.5 % palladium content (Fig. 2).

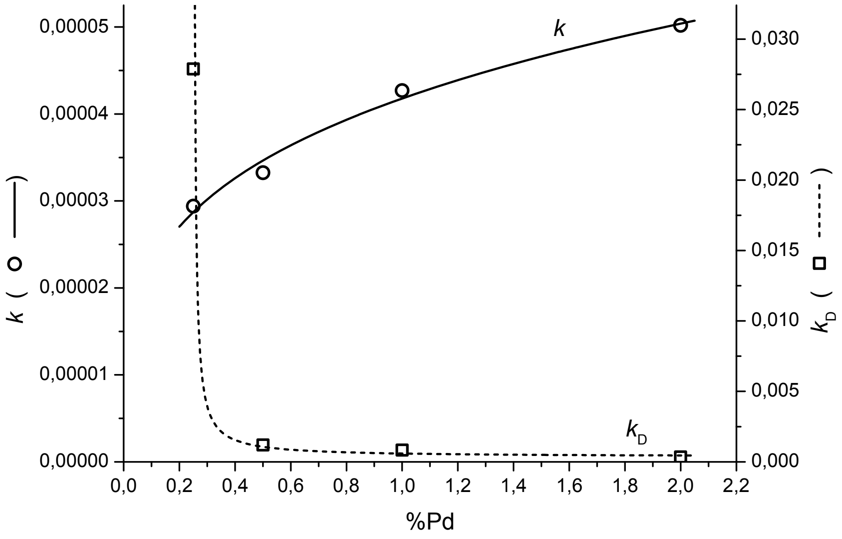


Fig. 2

MODIFIED FATTY ACID METHYL ESTERS DISTILLATION BOTTOMS AS A NOVEL STABILIZER FOR POLYMER COMPOSITIONS

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Nowadays, due to the growth of world production of the biodiesel, there is a problem of waste conversion, which don't find adequate market outlet in raw condition. So, during the purification of fatty acid methyl esters (FAME) distillation bottoms remain, which basically contain of unreacted vegetable oil. Vegetable oils are products consisting of triglycerides of fatty acids. In turn, derivatives of vegetable oils have found application in many industrial areas [1].

Epoxidized vegetable oils and their derivatives have the greatest industrial interest, since they possess high reactivity and they are universal intermediates for the production of various materials widely used in everyday life (lubricants, epoxy and alkyd resins, etc.) [2].

In present work, the raw material for the epoxidation reaction was the distillation bottoms of FAME from vacuum distillation stage. O-xylene was used as a solvent, since the distillation bottoms represent materials of viscous consistency. 37 % hydrogen peroxide and 85 % formic acid (both obtained from «Labtech») were used to prepare the epoxidizing agent.

Epoxidation procedure was carried out in a round bottom three necked flask of 150 mL capacity, placed in thermostated oil bath, equipped with a thermometer, reflux condenser and overhead stirrer (500-600 rpm). The reaction was carried out in molar ratio of [HCOOH]: [Double bonds] = 1.5: 1; [H_2O_2]: [Double bonds] = 1: 1. The mixture was heated to the reaction temperature (40 °C). Then, the calculated amount of 37 % hydrogen peroxide was added drop-wise for 20 min. Upon completion of the epoxidation prior to analysis the epoxidated bottoms were washed repeatedly with distilled water until they were acid free (water extraction). Finally rotary evaporator was used to remove solvent and trace water. The obtained samples were analyzed for oxirane content and iodine value.

In the course of the experiments, it was found that in order to achieve maximum yield, it is necessary to carry out the process in several stages. After five stages of the reaction the yield of epoxides was 87 %.

Also, tests of the epoxidized bottoms as the viscosity stabilizer for PVC paste were carried out (Table 1). The viscosity of the resulting mixture was measured on a Viscometer BROOKFIELD DV-II + Pro.

Table 1. Determination of the viscosity of the composition

Measuring time	Paste 1 (without epoxidized product)					Paste 2 (with epoxidized product)				
	t, °C	Viscosity, cP				t, °C	Viscosity, cP			
		10, sec^{-1}	**20, sec^{-1}**	50, sec^{-1}	100, sec^{-1}		10, sec^{-1}	**20, sec^{-1}**	50, sec^{-1}	100, sec^{-1}
Initial	24,2	3479	**3419**	2879	2807	25,1	3959	**3539**	3143	3011
In 2 h	23,5	4199	**3899**	3719	3575	23,8	4079	**3599**	3359	3263
In 24 h	22,4	4919	**4559**	4391	4271	23,0	4679	**4079**	3935	3875
In 48 h	21,8	5759	**5159**	4871	4727	22,4	5039	**4559**	4103	3879
In 72 h	20,7	6239	**5579**	5303	5111	20,8	5039	**4799**	4511	4379

It turned out that the sample with the epoxidized distillation bottoms introduced into the composition gave the PVC paste viscosity stability in time. So, epoxidized FAME distillation bottoms may be used as alternative, cheep and environmentally friendly stabilizers.

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ELECTROMAGNETIC INSTALLATION FOR NEUTRALIZATION OF WASTEWATER PRODUCTION OF OLIVE OILS

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The majority of known processes of clearing of water environments from oil pollution is based on use the methods of oxidation, flotation, absorbtion, and also methods of biological clearing. 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.

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
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);

3) Standartization 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 reactor.

Installation has passed industrial tests in a zone: 1) Caspian pool: Russia, Republic Dagestan, 2006-2010; 2) Germany, Wesendorf and Hanover in 2015; 3) Greece, the Coast of the Ionian sea (Ligya) and the island of Corfu, 2015.

PHOTOS AND VIDEOS

Greece, the Ionian Coast. 2015. Test and presentation of the installation of water treatment of olive production to the technical quality of recycled water

Pilot Plant – Photo
Greece, the Coast of the Ionian sea (Ligya) and the island of Corfu, 2015

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