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of the Russian Academy of Sciences, Novosibirsk, Russia

Politecnico di Milano, Milan, Italy

European Federation on Chemical Engineering

XXIV International Conference on Chemical Reactors
CHEMREACTOR-24

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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 Reactors and Technologies for Energy-Related Applications.

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SCIENTIFIC PROGRAM

Advances in Chemical Reactor Fundamentals

First-Principles-Based Chemical Reaction Engineering.

Chemical Reaction Kinetics.

Energy & Mass Transfer in Chemical Reactors.

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, Nature-Inspired Reactor Concepts, Modular Reactor Design for Multiproduct Purpose).

Process Intensification and Multifunctional Reactors (e.g., Microwave/Induction Heated Reactors, Ultrasonic Reactors, Unsteady-State Forcing and Sorption Enhancement in Chemical Reactors, High-gravity, High-Shear Reactors, Electricity-Driven Reactors)

Safety Considerations in Reactor Design and Operation.

Chemical Reactors and Technologies for Targeted Applications

Environmental Protection and Utilization of Waste.

Reactors for Polymers and Other Novel Materials with Targeted Properties.

Reactors for Processing of Biomass and Renewable Feedstocks into Valuable Chemicals Electrochemical and Photochemical Reaction Engineering.

CO_2 Sequestration and Utilization.

Advanced Reactors and Technologies for Energy-Related Applications

Reactors for Fuel Production from Non-Conventional and Renewable Feedstocks Advanced Reactors and Technologies for Manufacturing of Hydrogen.

Reactors and Processes for Manufacturing, Conversion and Storage of Energy Engineering of Fuel Cells.

Solar-Driven Chemical Reactors.

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PLENARY LECTURES

PL-1

Honorary Lecture devoted to the memory of Professor Mikhail Slin'ko

CHEMICAL REACTION AND REACTOR ENGINEERING: A KEY DISCIPLINE FOR PROCESS OPTIMIZATION, INNOVATION AND INTENSIFICATION

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This lecture will discuss some possible contributions of chemical reaction and reactor engineering to the transformation of the process industry imposed by global warming. This adaptation will require more than incremental optimization of existing processes. It will also create opportunities for the introduction of disruptive techniques based on process intensification and alternative energy carriers as well as alternative feedstocks.

The focus will be on the production of ethylene, one of the major building blocks for the chemical industry. As of today it is produced in large scale units with an annual production capacity of 1 million ton each consisting of about 10 gas fired furnaces operated in parallel at 850 °C and upstream of a single separation train [1]. It contributes to almost 10 % of the CO_2 emissions of the chemical industry. Hence, capture and utilization of so-called point emissions of CO_2, so-called CCU, by the chemical and other major industrial emitters like steel and cement industry, becomes very important in the context of climate change as long as no alternative carbon and energy sources have taken over. The former will, among other things, involve recycling of plastic waste [2] and renewable feedstocks [3, 4]. The latter will depend on the substitution of combustion of fossil fuels by green electricity as heat source [5] or, even better, of thermally driven processes by electrochemical ones [6].

In parallel with discussing aspects of ethylene production and CCU, i.e. the application dimension of chemical reaction and reactor engineering, attention will be paid to its methodological dimension. Chemical kinetics constitute a key discipline for the chemical engineering profession. They not only provide quantitative relations between process input and output but even more importantly insight in the reaction mechanism underlying these relations.

The tremendous progress made during the past decades in the field of computational chemistry and engineering has lead the profession away from the classical road from concept to industrial realization via the collection of a set of experimental data at increasing length scales. There is the "automated" generation of reaction networks [7] with corresponding quantum-chemical based rate coefficients [8] and of catalyst properties [9]. Computational Fluid Dynamics (CFD) codes allow to combine the chemical kinetics with the scale-dependent physical transport phenomena and to provide a proof-of-concept before engaging into an experimental program [10-12]. However, experimental verification of such computational results remains a must for the decades to come. Finally there is a caveat: any theory starts from premises and, hence colors the insights it provides. So-called Machine Learning tools should allow to avoid this pitfall and will become, if not already so, part of the toolkit of the chemical reactor engineering community [13]. Fig. 1 summarizes the field with emphasis on the multi scale aspect but also indicating the interplay between its different parts.

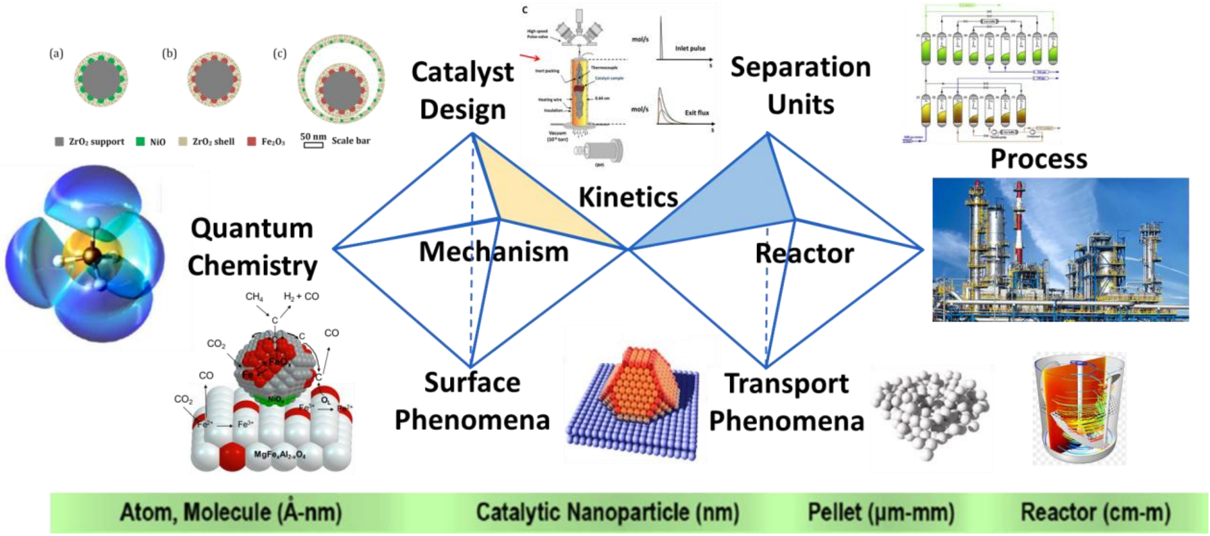

Figure 1. Chemical reaction and reactor engineering

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PL-2

PROCESS TECHNOLOGIES FOR ENERGY TRANSITION: PRODUCTION OF HYDROGEN AND CO_2 CAPTURE, STORAGE AND UTILIZATION

Roberto Zennaro

Development & Technical Activity Eni - Energy Evolution, San Donato Milanese, Italy

The European Commission through the “Green Deal” introduced new extraordinary objectives for the decarbonization of the European Union, with a target of net-zero emissions by 2050 and a midway 55 % reduction of emissions in 2030, related to 1990. Reaching net-zero emissions in the next thirty years represents a unique challenge for the global energy sector, which accounts for around three quarters of European greenhouse gas emissions today. This will involve every industrial sectors even the so-called hard-to-abate ones such as paper, ceramics, cement and concrete, and iron and steel.

To this end the European energy transition and decarbonization program needs to mobilize a wide range of technical solutions to affordably secure the energy supply. While renewables, electrification and energy efficiency are clear and recognised contributors to decarbonization, it is uncertain and questionable whether they are sufficient to fulfil the EU ambitious target.

The renewable and low-carbon hydrogen is the useful and clean energy vector mainly considered for the energy supply chain as feedstock for synthetic fuels, and industrial processes (high temperature heating). Renewable hydrogen (Green hydrogen) is produced from biomass or via electrolysis, powered by electricity from renewable sources, while low-carbon hydrogen (Blue hydrogen) is based on fossil fuels with low-emissions technologies like in the natural gas reformers integrated with carbon capture and sequestration facilities, CCS. Blue hydrogen is a flexible process likely available for large-scale production well before Green hydrogen could be and that can be the base load of the hydrogen market since Green hydrogen will not be available in substantial volumes until the power sector is fully decarbonised by renewable electricity, i.e. not before 2040, possibly 2050.

Blue hydrogen has therefore gained the interest of government and industry, particularly in the UK area while in Eni we believe that hydrogen production technologies are complementary and not competing, and there is a need for a shared classification of hydrogen production technologies according to how much they can contribute in reducing greenhouse gas emissions and there is room for developing technologies for producing sustainable hydrogen from waste products.

Eni with more than 300 kton/a of hydrogen production capacity is one of the largest producers and consumers in Italy. To date, hydrogen has been used mainly as a feedstock in traditional refining processes, as well as for producing hydrotreated vegetable oil (HVO) biofuels in our biorefineries. Hydrogen is produced mainly by steam methane reforming (SMR), a technology widely adopted in the industry.

As part of our commitment to de-carbonise our industry, Eni has recently joined the “Hydrogen Europe” association and the “European Clean Hydrogen Alliance”, being also one of 17 players from the energy sector who participated in the “Hydrogen for Europe” study, the aim of which was to assess how hydrogen can contribute to achieving climate neutrality on the continent.

As part of Eni strategy, hydrogen sector has been identified as a great transformation opportunity and it is under evaluation the feasibility and potential of projects involving Green and Blue hydrogen, as well as the use of blue and green vectors (e.g. ammonia and methanol) for the transport of hydrogen with the aim of having a tangible possibility to decarbonize hard-to-abate production processes.

As far as Blue hydrogen is concerned, the mandatory enabler for large capacity production is CCS which is a feasible and safe solution for decarbonization as it is based on consolidated technologies. As an energy company with an excellent upstream legacy, Eni has the know-how, the capabilities and the assets (in terms of depleted reservoirs and relevant infrastructures to be reused) to become an important player in this new born business which will offer CO_2 transport and storage services to third parties as a cost-effective way to decarbonize their activities.

This is what is going to happen through our CCS projects in Liverpool Bay (UK) and in Ravenna (IT) which will leverage on the competences gained in a first CCS demo plant in Ravenna expected to come in operation in 2023.

A demonstration unit of our “e-sweet” CO_2 capture technology, based on a proprietary solvent mixture, is also going to be tested in Ravenna in combination with a new demo unit of our CO_2 utilization technology, “e-CCM” (Carbon Capture and Mineralization), able to accelerate a natural process that occur spontaneously to convert large quantities of CO_2 in a mixture of stable, inert and not-toxic substances used in the cement manufacturing.

Furthermore, the proprietary natural gas catalytic partial oxidation technology to produce syngas or hydrogen called “k-Gas” is currently under development at demonstration scale in the Taranto (IT) refinery.

In terms of Green hydrogen, two ongoing initiatives at demo scale (10 to 20 MW electrolyser’s capacity) are the results of a recent collaboration between Eni and Enel aiming at evaluating the technical and economic feasibility of the renewable hydrogen production for refining. These initiatives are IPCEI (Important Project of Common European Interest) pilot projects’ candidates.

Green hydrogen is intrinsically linked to intermittent sources of renewable energy; therefore, the new green hydrogen economy requires large storage volumes of compressed gas. A chance is given by existing saline geological structures close to areas of potential production and consumption of blue and green hydrogen. An IPCEI pilot’s project has been proposed by Eni to study the entire value chain.

PL-3

PROCESS INTENSIFICATION THROUGH STRUCTURING CATALYST AND REACTOR

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After their successful introduction in emission control in the form of monoliths, due to their low pressure drop, attrition resistance, dust tolerance and selectivity control, structured catalysts and reactors have been explored the last decades for application in catalytic multiphase processes [1-3]. They facilitate following the optimal reactor selection approach of Krishna and Sie ('to mix or not to mix') [4], where conflicting design requirements can still be realized in a structured reactor.

Important industrial processes have an appreciable heat duty that have to be dealt with, exothermal [5,6] as well as endothermal processes [3]. Thermally conductive internals or internals forcing radial flow in the reactor and packed with catalyst particles, can approach nearly isothermal operation [3,7,8], facilitating operation and improving process performance.

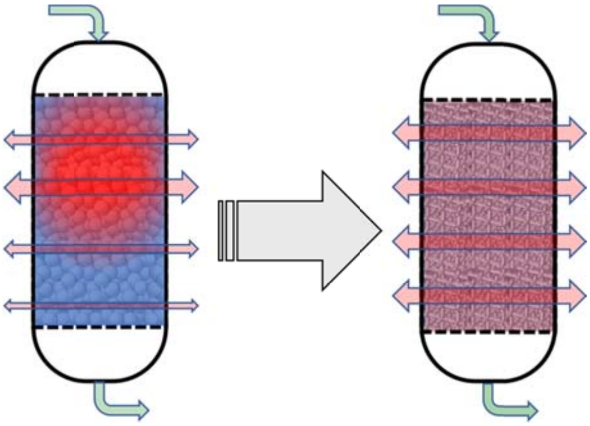

Figure 1. The schematic effect of packed structured reactor internal on changing the thermal performance of an exothermal catalytic process [3]

An interesting approach is to analyse the relative resistances of the various steps in de overall reaction acting in a multiphase catalytic reactor. Use of structured catalysts/reactor internals can eliminate or alleviate major hurdles, changing their interplay in the process [5]. The question then arises what resistance distribution is desired and what are essential guiding rules of thumb to determine the focus for the optimization of the structured catalyst-reactor internal.

The quest for process intensification has triggered new directions of improving catalysts for classical reactions. Using metal-organic frameworks as a catalyst precursor has been successful in the preparation of extremely active low- and high-temperature Fischer-Tropsch catalysts [9,10]. This changes the relative resistances in that process and new challenges arise to accommodate these systems, calling for structured reactors. Emerging technologies, like additive manufacturing/3D-printing offer new opportunities to meet these requirements.

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PL-4

MEMBRANE REACTORS AND SEPARATION ENHANCED REACTORS

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Process intensification can give a boost to the chemical industry in terms of improved energy efficiency and thus decreased emissions. Process Intensification (PI), is defined as "*any chemical engineering development that leads to a substantially smaller, cleaner, safer and more energy efficient technology*" [1], and is always referred to as the next revolution of the chemical industry.

According to several reports, the benefits on applying PI for the chemistry sector would result in a potential for energy saving of about 1000 ktoe/y using these processes.

PI is however a very broad field and, in many cases, it is just a new and nicer name for best practices that were already carried out in chemical industries. However, real PI is not just about debottlenecking processes already working at industrial level, but rather strategies that can open new process windows not available with conventional systems.

Several authors have reported reviews and books on process intensification, and an interested reader is referred to these works for more information [2–4]

The most interesting concepts can be summarized in the Figure 1 (as already reported by several authors). The strategies adopted are divided in 4 categories, where the PI will be achieved either in one or more of these domains.

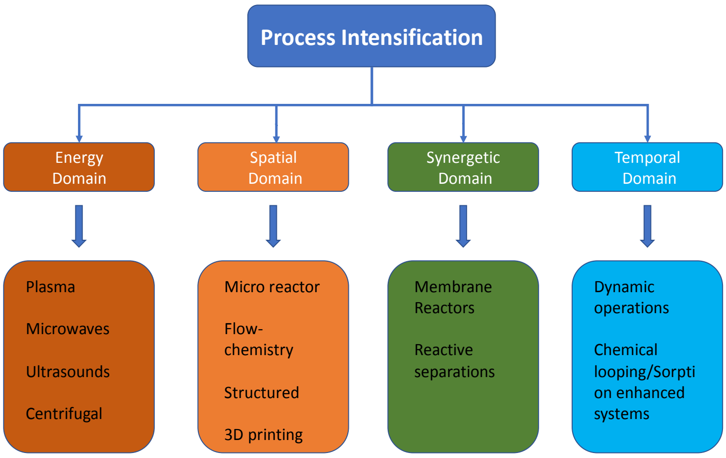

Figure 1. Summary of the process intensification strategies

One interesting strategy is achieved in the synergy domains, where functions are integrated in single units. Generally, the functions integrated are reaction and separation or reaction and heat management. The integration of functions promises to decrease the capital costs and operating costs compared to typical systems where these functions are separated.

Novel concepts are the membrane reactor concept, in which membrane separation is integrated with reaction, and separation enhanced reactors in which the separation is obtained with means different than membranes (like sorbents).

This lecture will summarize the recent advances in separation enhanced reactors, with large emphasis on membrane reactors.

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ENGINEERING OF PLASMA-ASSISTED REACTIONS

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Plasma technology is gaining increasing interest for various gas conversion applications, such as CO_2 and CH_4 conversion into value-added compounds, and N_2 fixation for fertilizer applications [1-4], i.e., more in general: green chemistry.

Plasma is a (partially) ionized gas, created by applying electricity. It consists of electrons, various ions, radicals, excited species, besides neutral gas molecules. The electrons are mainly heated by the applied electric field, due to their small mass, and they activate the gas molecules by electron impact ionization, excitation and dissociation, creating new ions, excited species and radicals. These are very reactive, so they can easily produce new products. Hence, thermodynamically or kinetically limited reactions can proceed at mild conditions of gas temperature and pressure, because the gas activation is accomplished by the electrons. Typically, plasma reactors operate at atmospheric pressure and the gas is introduced at room temperature. Plasma technology has low CAPEX costs. Finally, the plasma reactors can quickly be switched on/off, and because they operate with electricity, they are very suitable to be combined with (fluctuating) renewable electricity, for electrification of chemical reactions.

To improve this application in terms of conversion, energy efficiency and product formation, a good insight in the underlying mechanisms is desirable. We try to obtain this by computer modelling, supported by experiments.

I will first give a brief explanation about different types of plasma reactors used for gas conversion / green chemistry applications. That will be followed by an overview of the state of the art in plasma-based CO_2 and CH_4 conversion, as well as N_2 fixation, with these different types of plasma reactors, and briefly discuss the opportunities and main challenges.

Subsequently, I will present some recent results obtained in Antwerp in this domain, including experiments and modeling for a better understanding of the underlying mechanisms. This includes modeling the plasma chemistry as well as the reactor design, in the different types of plasma reactors commonly used for gas conversion, i.e., dielectric barrier discharges (DBDs), gliding arc (GA) discharges, microwave (MW) plasmas and atmospheric pressure glow discharges (APGDs). For the plasma reactor design, we use 2D or 3D computational fluid dynamics modelling [5,6]. For the plasma chemistry, we make use of zero-dimensional chemical kinetics modeling, which solves continuity equations for the various plasma species, based on production and loss terms, as defined by the chemical reactions [7]. By means of particle tracing simulations, we follow the molecule trajectories through the reactor, which allows us to define which power density and gas temperature profile they experience when travelling through the reactor. This is used as input in the chemical kinetics modelling. Indeed, the latter solves the continuity equations as a function of time, like in a batch reactor, but this can be translated to a spatial dependence, by means of the gas velocity (as obtained from the fluid dynamics simulations). Hence we describe the plasma reactors as a plug flow reactor, calling it a quasi-1D model.

Plasma is a very reactive medium, producing a lot of different species, but it is not so selective. To enhance the selectivity, a catalyst can be integrated, either inside or after the plasma (depending on the plasma type), yielding plasma catalysis [8]. This often leads to synergy, where the combined process is better that the sum of both individual processes. We also perform modelling to better understand the underlying mechanisms of plasma catalysis. This includes particle-in-cell – Monte Carlo collision simulations and computational fluid dynamics modelling to understand how plasma streamers propagate through a packed bed plasma reactor [or whether plasma can penetrate into catalyst pores [9], as well as microkinetic modelling for the chemistry at the catalyst surface [10-12]. Also these modelling results will be illustrated.

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PL-6

CONVERSION OF SUSTAINABLE ENERGY: ELECTRIFIED REACTORS

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In a future fossil free scenario our energy will come in the form of electricity mainly from windmills and photo voltaic devices. This means the energy resources are intermittent and although they can be determined a few days ahead fast adjustment to changes of energy availability will be necessary. This electrification will first of all led to a substantial energy saving as electricity is a much more efficient energy source due to its high exergy. Nevertheless, not everything can be electrified and there will be a demand for making fuels for for example long haul transport and in particular for aviation. Similarly, will there still be a demand for chemicals. Entirely new processes are now being investigated for electrifying our chemical industry like utilizing electrocatalysis. The main obstacles in electrocatalysis for first splitting water and subsequently hydrogenate CO_2 and N_2 have been identified [1], albeit far from solved. On a shorter timescale we also need to implement the electricity and replace the fossil resources for for example endothermic reactions. This has not been given much attention until recently, since generating electricity in the conventional manner inflict a 2,5 times higher energy use of fossil resources.

Two approaches shall be discussed where, in both cases, the energy source can be brought in close proximity with the catalysts avoiding strong temperature gradients. Large temperature gradients are well-known to cause long startup times and problems such as carbon deposition on the catalysts in conventional reactors as well as metal dusting.

In the first case of close proximity of heat source and catalysts we shall discuss the simple method of Ohmic heating and the advantages it may have on the size of the overall reactor and amount of catalysts for one of the most demanding endothermic reaction namely the steam reforming [2]. Here of dynamics [3] and the issues of fast startup and carbon potential shall be discussed in detail [4]. In the second approach we use inductive heating and here the challenge is to get a sufficient efficient and catalytically inert susceptor at high temperatures. Is shall be illustrated how this can be done again for the most demanding reaction, the steam reforming process using NiCo alloys nanoparticles [5]. Finally approaches for developing a generic inert susceptor for induction heating shall also be discussed if time allows.

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KEYNOTE LECTURES

KL-1

ADDITIVE MANUFACTURING OF TAILOR-MADE CATALYTIC REACTORS WITH OPTIMAL AND FLEXIBLE TRANSPORT PROPERTIES

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An intelligent matching of reaction and transport processes is key to the design and operation of optimal catalytic reactors. For the realization of optimal reaction and process conditions, the system specific requirements regarding heat and mass transport characteristics demand for suitable catalyst support materials and reactor geometries. In this regard, additive manufacturing techniques have emerged as enabling technology, which unlocks a new degree of freedom in the design of structured reactors with tailored properties. Additive manufacturing allows for the fabrication of open cellular structures of nearly arbitrary geometrical complexity, and this in a well-defined and highly reproducible manner.

In our work, we study periodic open cellular structures (POCS) that were manufactured by selective electron beam melting. POCS are promising novel catalyst supports as they offer clear advantages over conventional randomly packed fixed-bed reactors in terms of pressure drop [1-4] and heat management [5-8] as well as liquid distribution in multiphase applications [3, 9-10]. In fact, POCS combine the advantages of randomly packed beds (radial mixing, tortuosity of the flow) and honeycombs (high geometric specific surface area, low pressure drop) owing to their high porosities and their characteristic 3D cellular architecture.

Based on extensive experimental investigations as well as modeling and simulation, correlations for specific surface area, pressure drop and heat transport for POCS were established. With these models, the design and optimization of POCS that are tailor-made according to the needs of the reaction system is possible. In our work, such tailor-made POCS were manufactured, functionalized by catalytic coating, and then applied in different catalytic reaction systems with focus on the optimization of heat transport (for highly exothermic gas phase reactions) and gas-liquid distribution (in trickle-bed reactors), respectively.

To achieve even more flexibility with regard to transport characteristics, we have recently proposed a new type of interpenetrating POCS (interPOCS) which are formed by inserting a diamond unit cell based structure in the cavities of a second diamond cell structure. These interPOCS allow for in operando flow field and mass transport adjustments by shifting the (relative) position of the loose structure [4].

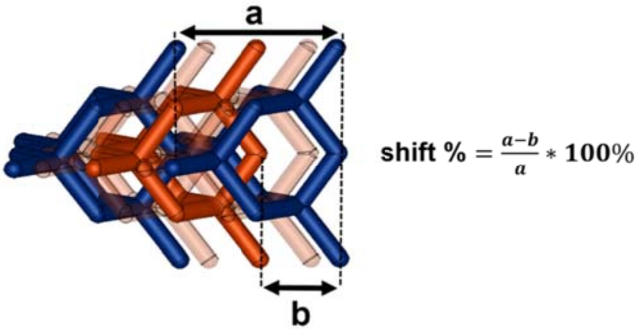

Fig. 1. Scheme of the diamond unit cell interPOCS. Blue: fix structure, Orange: loose structure

With detailed computational fluid dynamics (CFD) based simulations with an additional in-house particle-tracking algorithm implementation [11] we systematically investigated the flow field and mass transport characteristics within the interPOCS in dependency of the relative positioning of the loose structure. The highly adjustable structure allows for a broad variation of mass transport characteristics in a catalytic reactor without changing the system's periphery. This functionality enables mass transport optimization for a given system and represents a completely new application of additively manufactured catalyst support structures for highly flexible in operando tuning of flow field and mass transport characteristics.

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KL-2

DYNAMIC CATALYSTS FOR RENEWABLE ENERGY AND BIO-DERIVED CHEMICALS

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The conversion of biomass to renewable chemicals and fuels requires new approaches to catalyst and reactor design due to the complexity of molecules and pathways produced in nature [1]. In this work, we consider the breadth of hydrogenation, dehydration, and dehydrogenation chemistries common to renewable chemistry and evaluate alternative strategies for catalyst and reactor design. These important reactions have commonalities associated with their chemical energy diagrams; selection of the most active catalysts balance rate-limiting surface phenomena. Similarly, the most selective catalysts are often unique structures (e.g., phosphorous-containing zeosils [1]) that carefully inhibit undesired pathways.

The limit of catalyst/reactor design for renewable energy and bio-derived chemicals derives from the *static* nature of inorganic active site structures. Immobile active sites are designed as a compromise between both: (a) elementary steps in a single reaction, and (b) parallel and/or series competing reactions. For example, ring-opening dehydration of tetrahydrofuran to renewable butadiene balances elementary steps of ether scission and dehydration, while the active site must simultaneously suppress retro-Prins condensation to propylene [1]. These extensive demands of a single static active site result in inherent limits of catalytic performance, frequently with poor activity at the expense of improved selectivity.

In this work, we examine the catalytic potential of dynamically oscillating catalytic active sites for renewable energy and bio-derived chemicals. Active sites that vary in electronic or physical structure near the time scale of a reaction turnover can achieve overall reaction rates in excess of the Sabatier maximum [2]. Catalytic performance is dependent on design of new reactor and catalyst parameters, including the frequency at which the catalyst changes with time, the shape of the catalyst oscillation waveform, and the overall amplitude of varying in catalyst electronic and/or physical structure. Broad consideration of these dynamic parameters in combination with varied examination of the reaction chemistry parameters (e.g., BEP parameters) common to the breadth of renewable chemistry indicate that dynamic rate enhancement can be achieved for most catalytic systems [3].

In more complicated systems with parallel reaction pathways common to renewable energy systems, dynamic oscillating catalysts have the potential to more selectively suppress undesired side reactions [4]. The ability to select catalyst material & binding site in addition to dynamic parameters (e.g. frequency, amplitude), it becomes possible to radically accelerate the desired reaction over the undesired side chemistry, such that overall main pathway selectivity is significantly enhanced. In these complex reaction networks, transitions between pathway selection are demarcated by distinct changes in parameter space, making it possible to tune complex reaction networks for both activity and selectivity control. This strategy provides a new opportunity for implementing renewable energy catalysis and reactors for bio-derived chemicals.

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KL-3

NON-CATALYTIC GAS PHASE OXIDATION OF HYDROCARBONS

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The leading technological area of the twentieth century, which defined the face of modern society, was petrochemistry. The relative simplicity of destructive processes of oil refining (cracking, pyrolysis, dehydrogenation, isomerization) makes it possible to widely use equilibrium catalytic processes. But the oil resources in the earth's crust are limited. Huge resources of unconventional natural gas, especially gas hydrates, can provide the world economy with hydrocarbons for centuries. So the XXI century will inevitably become the century of natural gas and gas chemistry – petrochemistry based on methane. Gas chemistry fundamentally differs from traditional petrochemistry by "constructive" direction of its processes. Its goal is to obtain from the simplest and most stable hydrocarbon molecule CH_4 a wide variety of more complex (and less stable) products of modern petrochemistry.

Modern gas chemical technologies can be divided into two main groups: direct processes of methane conversion into chemical products and indirect processes based on its preliminary conversion into syngas. If we do not consider the relatively low-tonnage processes of halogenation and sulfidation of methane, the range of products that can be obtained directly from it is quite limited. These are hydrogen, carbon black (soot), acetylene, ethylene and simple oxygenates (methanol, formaldehyde). The conversion of methane into syngas makes it possible to obtain from it in the Fischer-Tropsch process synthetic oil, and therefore all petrochemical products. The uniqueness of syngas for gas chemistry is that it is practically the only product into which methane can be converted completely and in a thermodynamically equilibrium process. But it requires very high temperatures, up to 1000 °C, and therefore a lot of energy, making autothermal gas chemical processes particularly attractive. Existing industrial technologies of chemical conversion of natural gas are overwhelmingly based on its preliminary conversion into syngas. This complex, energy-and capital-intensive process absorb up to 70 % of the cost of the target products. Specific capital expenditures in existing gas chemistry are much higher than in petrochemistry, which hinders its development. The use of vast unconventional methane resources requires the creation of new cost-effective technologies for their extraction, transportation and chemical processing.

The report analyzes a number of fundamentally new gas chemical technologies, both direct and indirect, which have been developed recently [1-5]. Among them are such direct methods as Direct Methane To Methanol (DMTM), selective oxycracking of heavier hydrocarbons in wet natural and associated petroleum gases to obtain condition gas motor fuel, an alternative conception of GTL processes based on the partial oxidation and selective oxycracking of natural gas with subsequent catalytic carbonylation and oligomerization of products, and conjugated oxidative conversion of saturated and unsaturated hydrocarbons to light olefins. However, the most promising and universal technology of processing hydrocarbon gases of almost any composition and origin can be their non-catalytic matrix conversion into syngas [5]. It is a simple and compact technology based on the partial oxidation of hydrocarbon gases by air, enriched air or oxygen. Its specific volumetric capacity is at least an order of magnitude higher than that of steam reforming. The method allows obtaining both nitrogen-free syngas for traditional processes of methanol and Fischer-Tropsch products synthesis, and cheap nitrogen-containing syngas for low-tonnage processes of field conversion of natural gas into liquid products.

The influence of composition of hydrocarbon and hydrocarbon-hydrogen fuels on their motor characteristics, requirements to properties and composition of gas motor fuel and effective methods of converting wet natural and associated petroleum gases into conditioned fuel for power and electricity production are also considered.

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KL-4

STATUS OF WATER ELECTROLYSIS FOR GREEN HYDROGEN PRODUCTION WITHIN THE CONTEXT OF POWER-TO-X PROCESSES

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In this lecture, we will present an overview of the status of water electrolysis, the hydrogen production technology that is called to be one of the pillars of the future energy system. Reasons of the renewed interest on it include [1]:

- Continuous decline of the renewable electricity costs
- Possible integration with some of the most widely deployed renewables (mainly solar photovoltaics and wind)
- Its maturity, commercial availability, and reasonably high energy efficiency
- Its modularity and the possibility of building electrolysis plants capable of reaching the very high sizes that are expected to be required in the near future

The widespread use of electricity produced from renewable energy sources is the most effective way to decarbonize our economy. However, not all economic sectors are easily electrifiable. In addition, the intermittent nature of most of the renewable resources leads to the necessity of being able to store electricity when generation exceeds the demand. Simultaneously, time is required until the electric grid capacity and management strategies are sufficiently developed to be capable of absorbing the huge amounts of renewable electricity required to achieve our climatic neutrality objectives. Within this context, H_2 is reaching a new peak of interest to the extent of being considered a key priority by current policies aiming a clean energy transition [2]. Indeed H_2 is a good complement to batteries because, in addition to its energy storage capacity, it is also an energy carrier, a fuel, and feedstock having many possible applications in a variety of industrial and services sectors.

We should not lose sight of the fact that H_2 is being already produced in big amounts reaching 70 Mt/year that are consumed in oil refining (55 %) and ammonia synthesis (45 %). There is an additional demand of 45 Mt/year of H_2 as part of gas mixtures, such as e.g. syngas used in the synthesis of methanol and the steel industry [3]. Almost all this H_2 is being produced from fossil resources, mainly natural gas and coal. Low-carbon fossil-based production including carbon capture and storage (CCS) technologies is marginal. Water electrolysis is limited to 2 % of the global production, that is used in specific applications requiring high purities. These figures show the enormous efforts that should be devoted in order that renewable H_2 can play a relevant role in the energy mix. This challenge needs strong commitments by the public and private sectors to guarantee a favorable regulatory framework and sufficient capital investments. In this regard, the European Union has established a strategy aiming at H_2 being part of the energy system by 2030 with an installed capacity of 40 GW of water electrolysis and the production of 10 Mt of renewable H_2 [2].

One of the keystones of this strategy is that the development of a full value chain is necessary to succeed on building up a H_2 economy. It is within this value chain where the Power-to-X (P2X) processes emerge half way between the transport-distribution and end use steps. P2X processes consist is using H_2 obtained through water electrolysis fed with renewable energy to produce methane (Power-to-gas, PtG), fuel-range liquid hydrocarbons such as gasoline, kerosene, and diesel (Power-to-liquids, PtL) or methanol (Power-to-methanol, PtM). P2X products are expected to diversify H_2 applications facilitating its deployment and the penetration of renewables in sectors that are difficult to electrify such as aviation and shipping. Obviously, P2X processes require a carbon source whose origin will critically affect their environmental impact. Renewable CO_2 coming from biomass and organic wastes fermentation or gasification would lead to carbon-neutral products. CO_2 stemming from direct air capture (DAC) can become an option if the costs of the technique evolve favorably.

Water electrolysis is the chemical reaction that makes possible the production of H_2 (and O_2) from electricity. Water electrolyzers have been commercialized for long time. Currently, water electrolysis plants are available at the multi-megawatt (MW) scale. Two main technologies exist that are distinguished by the way in which ionic transport takes place [1]. The most mature technology is alkaline electrolysis in which the charge carriers are hydroxyde anions (OH^-) flowing from the cathode, where they are formed through water splitting accompanied by H_2 production, to the anode where they recombine releasing O_2. Transport takes place under the driving force of the electric field established by the external power source through an inorganic membrane impregnated with an alkaline water solution, typically of highly concentrated KOH. Proton exchange membrane (PEM) electrolyzers begun to be commercialized in the late 1970s. In this case, water decomposes at the anode surface where O_2 and protons (H^+) are formed. These positive charge carriers flow through an acid polymeric membrane from the anode to the cathode where they are reduced forming H_2. It is worth mentioning that electrolyzers operate with direct current, and that they consume deionized water to prevent electrode degradation and safety issues; therefore, the electrolysis plant should include power converters and water treatment facilities.

Both technologies have advantages and disadvantages, as will be discussed in this lecture under the perspective of a non-stationary operation and the benefits of obtaining pressurized H_2 in view of its storage and transport, and eventual use in the synthesis reactions involved in the P2X processes. Mention will be also made to two additional technologies: anion exchange membrane electrolysis and solid oxide electrolyzers. Though still not commercially available to form part of large electrolysis plants, both have good perspectives for playing an increasingly important role.

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KL-5

MICROMIXING IN MICROREACTORS: EFFECT ON NANOPARTICLES SIZES AND OTHER CHARACTERISTICS

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Reactive crystallization in a flow is one of the intensively developing areas of chemical technologies, as evidenced by the growing number of research articles and reviews. The aim of this work is to formulate, on the basis of the theory of aggregative nucleation, the concept of controlled solution synthesis.

The processes of physicochemical design and synthesis of materials have a hierarchical organization. In this case, the functional properties of materials are formed at different scale levels – from the levels of the isotopic, elemental, chemical, phase composition to the levels responsible for nano and micro scale interactions of matter in reaction media.

With the correct organization of the process, when energy is transferred from the milli or micro scale, which are the closest to the nanoscale, it is possible to form nanoparticles with high quality parameters. In this case, the micro scale should be as close as possible to the nanoscale in order to exclude unnecessary energy transformations when going from a larger scale to a smaller one (see the diagram in Fig. 1). Premixing, implemented in micro and milli scale devices, may not be too intense, and its goals are: 1) uniform distribution of ions (atoms, molecules) and their derivatives (like cation hydrates) in the volume of the solution; 2) the formation of clusters of subcritical size.

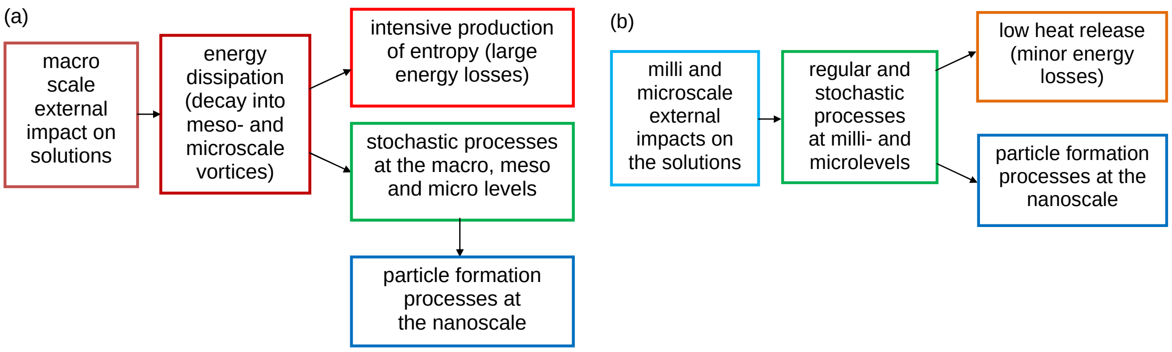

Fig. 1. Scheme of conversion of kinetic energy introduced into the solution:
a – during the transition from macro scale to nanoscale (traditional approach);
b – during the transition from milli and micro scale impacts to nanoscale (proposed approach)

A dependence of the segregation index X_s on the magnetic stirrer rotation frequency n in a laboratory reactor with a solution volume of 250 ml was found, which is constant $X_s \approx 0.52 \pm 0.03$ and quite high (at $X_s = 1$ the complete segregation takes place). The non-uniformity of concentrations is demonstrated also for the stirred tank with turbine, and even for the lab scale autoclave.

The stages of the aggregative nucleation in the frame of the energy transformation and transfer processes are distinguished as follows:

1) Uniform distribution of ions (atoms, molecules) in the volume of the solution;

2) Formation of clusters of subcritical size;

3) Formation of nuclei from clusters (aggregation);

4) Growth of nuclei;

5) Restriction of particle growth (preventing further aggregation and agglomeration).

The ideology of the effective design of microreactors, i.e. having good micromixing features and other properties listed above was developed. The advantages and limitations of various types of microreactors elaborated for the nanosized particles synthesis (Microreactor with free impinging jets, Microreactor with swirled flows, Microreactor with impinging swirled flows, Microreactor with pulsating flow type apparatus, etc.) are discussed. Several examples of successful applications of microreactors for oxides and fluorides nanoparticles synthesis are demonstrated.

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ORAL PRESENTATIONS

Section I.

Advances in Chemical Reactor Fundamentals

OP-I-1

APPARENT ACTIVATION ENERGY OF STRUCTURE SENSITIVE HETEROGENEOUS CATALYTIC REACTIONS

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Apparent activation energy is analyzed for different structure sensitive multistep heterogeneous catalytic reactions [1, 2]. In the case of kinetic coupling between catalytic cycles the activation energy in a particular route was shown to depend not only on the activation energies of the elementary steps comprising this route, but also on the frequency of the steps in a parallel route.

As an example in a mechanism

1. Z + A → ZI
2. ZI + D_2 → Z + B + W (1)
3. $\underline{\text{ZI} + \text{D}_2} \rightarrow \underline{\text{Z + C + W}}$

A + D_2 → B + W; A + D_2 → C + W

where D_2 is a reactant (e.g. dihydrogen or dioxygen), B and C are products, W is also a (optional) product (e.g. water in an oxidation reaction), the apparent activation energy along the routes are

$$\begin{aligned}E_{\text{a,app, B}} &= E_{+1} + E_{+2} - \frac{\omega_{+1}}{\omega_{+1}+\omega_{+2}+\omega_{+3}}E_{+1} - \frac{\omega_{+2}}{\omega_{+1}+\omega_{+2}+\omega_{+3}}E_{+2} = \\ &= \frac{\omega_{+2}+\omega_{+3}}{\omega_{+1}+\omega_{+2}+\omega_{+3}}E_{+1} + \frac{\omega_{+1}+\omega_{+3}}{\omega_{+1}+\omega_{+2}+\omega_{+3}}E_{+2}\end{aligned} \tag{2}$$

and

$$E_{\text{a,app, C}} = \frac{\omega_{+2}+\omega_{+3}}{\omega_{+1}+\omega_{+2}+\omega_{+3}}E_{+1} + \frac{\omega_{+1}+\omega_{+2}}{\omega_{+1}+\omega_{+2}+\omega_{+3}}E_{+3} \tag{3}$$

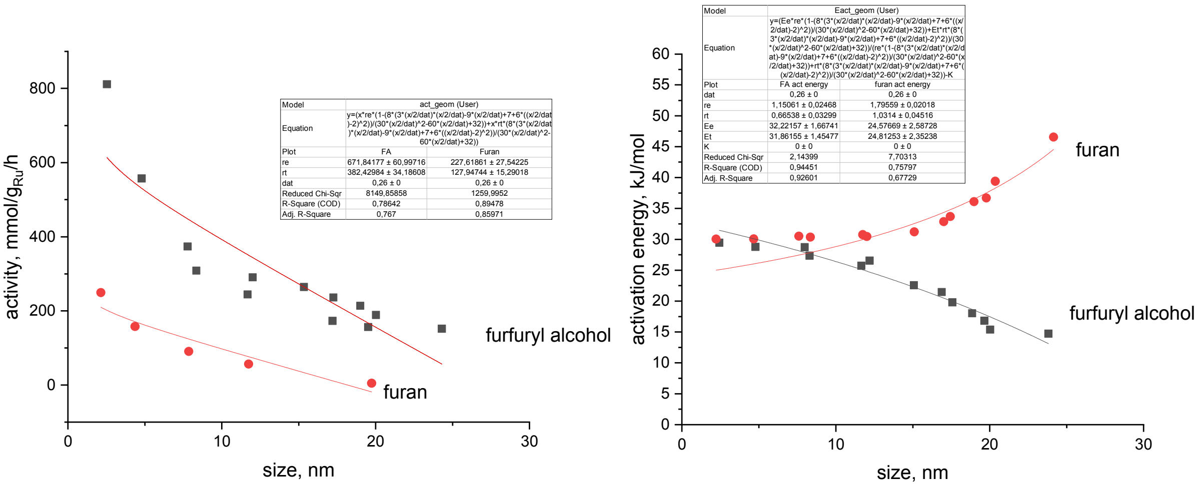
where ω_{+1}, etc. are the frequencies of steps. Eq. (2) and (3) illustrate coupling between the cycles, when the activation energy in a particular route depends on the contribution of a parallel route.

Expressions were derived for coupling between routes through irreversible adsorption of the substrate, quasi-equilibrated binding as well as different substrate adsorption modes.

Theoretical analysis of the apparent activation energy was extended for the reaction network with two routes possessing mechanistically different rate determining steps (i.e. monomolecular vs bimolecular). For structure sensitive reactions an expression for the apparent activation energy for parallel reactions was developed for cases with a continuous distribution of active centers and a cubo-octahedral representation of the metal clusters

$$E_a = \frac{k_t e^{-E_{a,t}/RT} K_t e^{-\Delta H_{a,t}/RT} C_A((E_{a,t}+\Delta H_t)+K_e e^{-\Delta H_e/RT} C_A(E_{a,t}+\Delta H_e+\Delta H_t))}{k_t e^{-E_{a,t}/RT} K_t e^{-\Delta H_{a,t}/RT} C_A f_{terraces}(1+K_e e^{-\Delta H_e/RT} C_A)+k_e e^{-E_{a,e}/RT} K_e e^{-\Delta H_e/RT} C_A(1-f_{terraces})(1+K_t e^{-\Delta H_t/RT} C_A)} f_{terraces} + \\ + \frac{k_e e^{-E_e/RT} K_e e^{-\Delta H_e/RT} C_A((E_{a,e}+\Delta H_e)+K_t e^{-\Delta H_t/RT} C_A(E_{a,e}+\Delta H_e+\Delta H_t))}{k_t e^{-E_{a,t}/RT} K_t e^{-\Delta H_t/RT} C_A f_{terraces}(1+K_e e^{-\Delta H_e/RT} C_A)+k_e e^{-E_{a,e}/RT} K_e e^{-\Delta H_e/RT} C_A(1-f_{terraces})(1+K_t e^{-\Delta H_{a,t}/RT} C_A)}(1-f_{terraces}) - \\ - \frac{k_e e^{-E_{a,e}/RT} K_e e^{-\Delta H_e/RT} C_A((E_{a,e}+\Delta H_e)+K_t e^{-\Delta H_t/RT} C_A(E_{a,e}+\Delta H_e+\Delta H_t))}{1+K_e e^{-\Delta H_e/RT} C_A+K_t e^{-\Delta H_t/RT} C_A+K_e e^{-\Delta H_e/RT} K_t e^{-\Delta H_t/RT} (C_A)^2} \quad (4)$$

A comparison between the theoretical analysis and experimental data [3] on transformations of furfural to furfuryl alcohol and furan on ruthenium clusters (Figure 1) shows applicability of the developed theoretical framework.



Model	act_geom (User)	
Equation	y=(x*re*(1-(8*(3*(x/2/dat)*(x/2/dat)-9*(x/2/dat)+7+6*((x/2/dat)-2)^2))/(30*(x/2/dat)^2-60*(x/2/dat)+32))+x*rt*(8*(3*(x/2/dat)*(x/2/dat)-9*(x/2/dat)+7+6*((x/2/dat)-2)^2))/(30*(x/2/dat)^2-60*(x/2/dat)+32))	
Plot	FA	Furan
re	671,84177 ± 60,99716	227,61861 ± 27,54225
rt	382,42984 ± 34,18608	127,94744 ± 15,29018
dat	0,26 ± 0	0,26 ± 0
Reduced Chi-Sqr	8149,85858	1259,9952
R-Square (COD)	0,78642	0,89478
Adj. R-Square	0,767	0,85971

Model	Eact_geom (User)	
Equation	y=(Ee*re*(1-(8*(3*(x/2/dat)*(x/2/dat)-9*(x/2/dat)+7+6*((x/2/dat)-2)^2))/(30*(x/2/dat)^2-60*(x/2/dat)+32))+Et*rt*(8*(3*(x/2/dat)*(x/2/dat)-9*(x/2/dat)+7+6*((x/2/dat)-2)^2))/(30*(x/2/dat)^2-60*(x/2/dat)+32))/(re*(1-(8*(3*(x/2/dat)*(x/2/dat)-9*(x/2/dat)+7+6*((x/2/dat)-2)^2))/(30*(x/2/dat)^2-60*(x/2/dat)+32))+rt*(8*(3*(x/2/dat)*(x/2/dat)-9*(x/2/dat)+7+6*((x/2/dat)-2)^2))/(30*(x/2/dat)^2-60*(x/2/dat)+32))-K	
Plot	FA act energy	furan act energy
dat	0,26 ± 0	0,26 ± 0
re	1,15061 ± 0,02468	1,79559 ± 0,02018
rt	0,66538 ± 0,03299	1,0314 ± 0,04516
Ee	32,22157 ± 1,66741	24,57669 ± 2,58728
Et	31,86155 ± 1,45477	24,81253 ± 2,35238
K	0 ± 0	0 ± 0
Reduced Chi-Sqr	2,14399	7,70313
R-Square (COD)	0,94451	0,75797
Adj. R-Square	0,92601	0,67729

Figure 1. Influence of the particle size on productivity and apparent activation energy for furfural hydrogenation to furfuryl alcohol and decarboxylation of furan. Comparison between experimental data (taken from [2] at 10 bar of hydrogen and 100-165 °C for silica supported Ru catalysts) and calculations

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OP-I-2

INCLUSION OF kMC INTO MACROSCOPIC REACTOR MODELS BY MEANS OF MACHINE LEARNING TECHNIQUES

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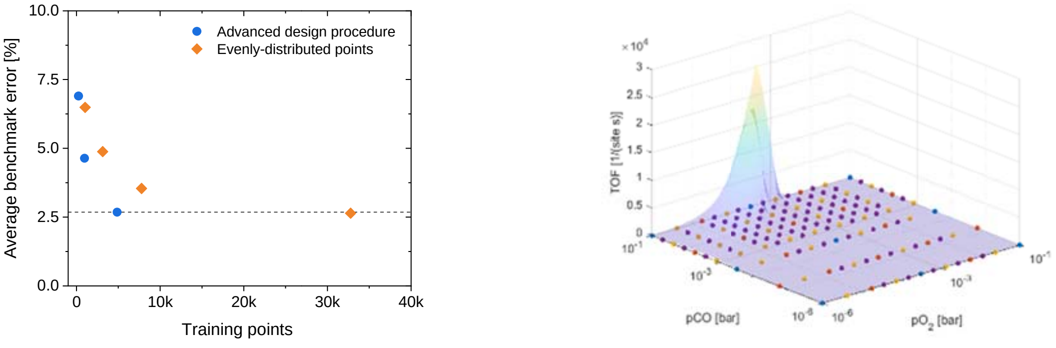
The inclusion of first-principles calculation based kinetic scheme, e.g. kinetic Monte Carlo (kMC), into numerical simulations at the reactor scale is a topic of primary importance. A direct coupling between computational fluid dynamics (CFD) and kMC simulations, required to evaluate the turnover frequency (TOF), is impractical due to the large computational cost related to the solution of the kMC system. Interpolation methods, such as spline, have been proposed to approximate the solution of the kMC models, but their applicability is confined to kinetic system characterized by a few of species [1]. To overcome such a limitation, machine learning techniques (ML), such as random forest or extremely randomized trees, are an effective method to deal with schemes of higher complexity (e.g. number of species) [2]. These methodologies enable the coupling of 1p-kinetic model within reactors model through ensemble learning and regression of an existing dataset, providing a accurate approximation of complex functions, such as the kMC-TOF. However, the generation of the training set is key to guarantee accuracy of the methodology and might become the bottleneck of the procedure due to the large number of simulations required to build the dataset. In this view, we propose an effective way to generate the training dataset by an iterative procedure aiming at the minimization of the number of data points required to achieve an accurate description of the TOF function. The procedure selectively adds data points within the multi-dimensional space in the regions where the approximation of the function is more demanding. An evenly distributed dataset is initially generated and the corresponding TOFs are calculated. In the next iterations, additional are added in the region of the composition space where the gradient of the function to be approximated is steeper. The datapoints are employed to train a ML method, such as an extra-tree regressor, which provides information on the prediction accuracy and perform internal cross-validation. The procedure terminates the target function is well approximated by the ML method.

First, the performances of the design procedure of the training data is evaluated with a Water Gas Shift (WGS) on Rh scheme [4]. The system depends from 5 variable (i.e., molecular species and temperature). An initial evenly distributed grid with 3 points for variable is employed. At each iteration, additional points are added until the approximation is sufficiently accurate. To quantitively assess the performances of the procedure 250 datapoints are randomly generated in the multi-dimensional space of the composition and the TOF in each point is computed by means of the complete solution of the kinetic model and through the RF. Figure 1a shows the mean relative error (MRE) at each iteration as a function of number of training points. The procedure converges to the target accuracy (i.e., MRE < 2.5 %) by means 3 iterations and an overall number of points around 5k. A comparison with the performances of evenly distributed grid is carried out. In this view, the same accuracy (i.e. MRE) is achieved by employing a uniform grid with 60k points, revealing the reduction of the computational cost achieved by the iterative design procedure of the training points. Then, the same analysis is carried out on a 1p-kMC CO oxidation on RuO_2(110) [5]. The kMC simulations are carried out by means of Zacros, a graph theoretical kMC framework [3]. Once again, the procedure is able to meet the target accuracy (i.e., MRE < 10%) by employing 143 points with respect to the 400 required by an evenly distributed grid. Figure 1(b) shows the final distribution of the training points along with the TOF function. It is evident that the positions of the training points follow the trend of the TOF function increasing the efficiency of the regression performances of ML technique.



(a) (b)

Figure 1. Mean relative error as a function of the number of training points for the WGS on Rh (a) and distribution of the training points for CO oxidation on RuO_2(110) (b)

ML reveals to be the enabling method for the effective inclusion of 1p kinetic models in conventional and CFD reactor models [6]. Moreover, a procedure for the advanced design of the training points has been developed to increase the method accuracy and to reduce the computational cost in the generation of the dataset. The authors acknowledge the European Research Council for Grant no. 677423 (SHAPE)

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OP-I-3

UNRAVELING THE *NATURE* AND THE *IDENTITY* OF THE ACTIVE SITES IN HETEROGENEOUS CATALYSIS VIA STRUCTURE-DEPENDENT MICROKINETIC MODELING

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There is no doubt that the rational interpretation of the structure-activity relation in catalysis is a crucial task in the quest of engineering the chemical transformation at the molecular level [1]. In this respect, multiscale analyses based on structure-dependent microkinetic modeling is acknowledged to be an essential key-tool to achieve a mechanistic understanding of the catalyst functionality. However, the effect of the structure of the catalyst on reactivity and selectivity is at present neglected in state-of-the-art microkinetic modeling. As such, a “material gap” hinders the analysis of the underlying mechanisms at the atomic-scale level. To fill this gap, the modeling of the catalyst structure under reaction conditions is required [2].

Here, we present the development of a methodology for the analysis of the structure-activity relation in heterogeneous catalysis. The methodology is based on the combination of microkinetic modeling and *ab initio* thermodynamics with Wulff constructions and Boltzmann statistics at given conditions of chemical potential in the reactor [3]. First, *ab initio* thermodynamics is applied to characterize the bulk and surface structure of the catalyst. The three-dimensional shape of single-crystal nanoparticles and the corresponding distribution of active sites are calculated either with the Wulff construction method or Boltzmann statistics especially at low nanoparticle sizes, where a statistical representation of the catalyst morphology is needed. In doing so, the structure and the composition of the atoms at the surface is determined, and therefore the *nature* of the sites in reaction conditions is fully characterized. Then, microkinetic analyses are performed on the different sites in order to unravel the *identity* of the active site in reaction. Selected examples in the context of partial oxidation, CH activation, water-gas shift and reverse water-gas shift on metal catalysts will be employed as showcases.

For example, our analysis on the CH_4 catalytic partial oxidation (CPO) on Rh shows that the catalyst changes morphology drastically by undergoing a bulk phase transition from Rh_2O_3 to Rh during reaction [3]. After this modification in the *nature* of the active sites, the syngas production starts. In such conditions, we identify the Rh(311) as the crystal facet of the catalyst which gives the major contribution to the overall reaction rate and we reveal therefore the *identity* of the active sites (Figure 1).

As a whole, the proposed procedure provides an effective pathway to unraveling the *nature* and the *identity* of the active sites in reaction conditions. It represents a very important step to explicitly introduce the effect of catalyst structure in the microkinetic analysis of heterogeneous catalytic processes.

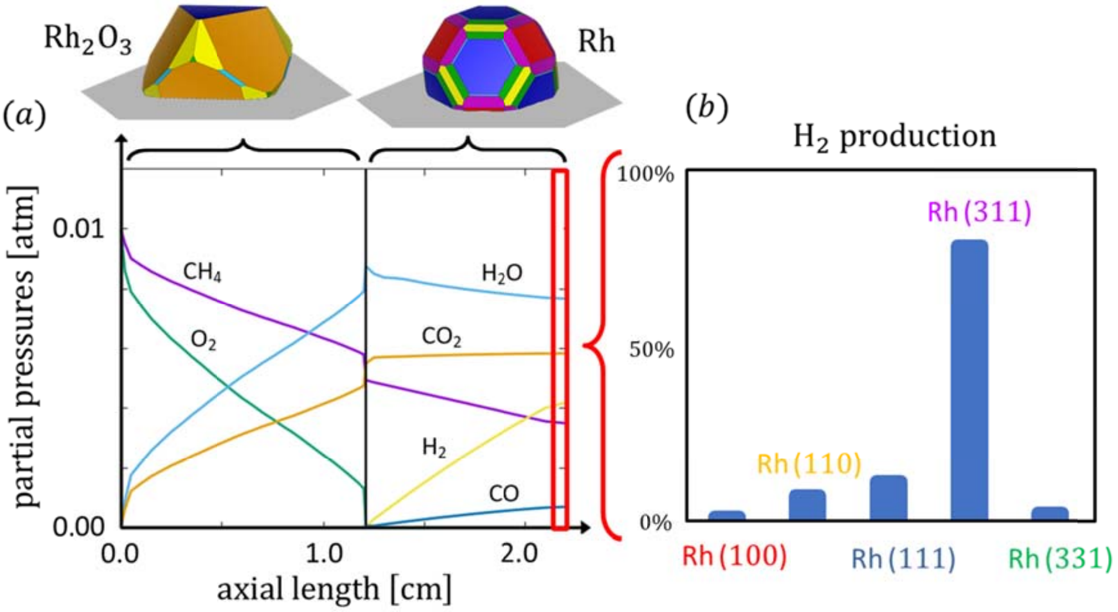

Figure 1. (a) Major species partial pressures axial profiles at the catalyst interface in an annular reactor for the CPO reaction. Temperature: 500 °C; pressure: 1 atm. On top: 3D shape model of Rh_2O_3 and Rh catalyst particles in the reactor, obtained by *ab initio* thermodynamics and Wulff-Kaishew construction. (b): Percentage net reaction rates of H_2 production on different crystal facets of Rh, calculated at the outlet of the annular reactor by structure-dependent microkinetic modeling. The Rh(311) crystal facet is the most active facet, indeed more than the 80 % of H_2 is produced on its active sites

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OP-I-4

INVARIANT EXPRESSIONS IN CHEMICAL KINETICS

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There are two well-known linear invariances that are widely used in chemistry and chemical engineering: element conservation balances, and stoichiometric relationships. The first ones are valid regardless of the properties of the reaction mechanism; the latest correspond to the detailed mechanism of a complex reaction [1, 2].

Since 2011, a new type of invariant expressions closely related to Onsager's reciprocal relations was found, arising from two symmetric experiments performed from different initial conditions (say pure A or pure B). In the simplest case of the single reversible reaction $A \rightleftarrows B$, it was found that the ratio of symmetric concentration profiles yields the equilibrium constant K_{eq} of this reaction, $B_A(t)/A_B(t) = K_{eq}$. It is valid for any value of time t>0, i.e. throughout the course of the chemical reaction. It holds not only at the equilibrium but at any moment after the start of the reaction. This equality is neither the element conservation balance nor the pseudo-equilibrium relationship for the "fast" reaction; it reflects intrinsic properties of the described reciprocal experiments [3, 4]. The similar type of invariant expression can be calculated for any linear complex mechanism, given that the pair of substances in the reciprocal experiments are connected via reversible reactions. Later, a new type of invariant expressions was found valid exclusively for linear two-step mechanisms, using two different approaches: from Scaled Incremental Conversion [2] and from Conservatively Perturbed Equilibrium [5]. This new type of invariant expressions includes non-thermodynamic ratios of kinetic coefficients of different reactions, often combined with thermodynamic ratios such as equilibrium constants.

Our most recent results are related to the generalization to more linear complex mechanisms of the invariant expressions obtained from CPE. A key concept in these new results is the concept of single-step substances, that participate exclusively in a single reaction within the linear complex mechanism. The invariant expressions are obtained from ratios of two concentration profiles of single-step substances corrected by their corresponding equilibrium concentrations, from two experiments with different initial conditions.

First, we found that the invariant expressions obtained for the two-step mechanism remain valid in two-step sub-mechanisms that occur within complex linear mechanisms. Both a two-step mechanism and a two-step sub-mechanism can be seen as single-step substances immediately connected by the same substance. The invariant expressions of the two-step mechanism are still valid if other parallel reactions occur from the substance that connects the single-step substances [6].

More generally, we found a procedure to find invariant expressions for complex linear mechanisms with at least two single-step substances, either if they are connected by a single, same substance, or by any linear sub-mechanism within the linear complex mechanism [7].

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EFFECT OF OXYGEN NONSTOICHIOMETRY ON OXYGEN PERMEABILITY PROCESS IN PEROVSKITE OXIDE

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Oxides with mixed ion-electron conductivity (MIEC) are attracted the attention due to their prospective of using as membrane materials for producing pure oxygen, catalytic conversion of methane to synthesis gas, as sorbents for oxy-fuel combustion, oxygen sensors and electrodes for solid oxides fuel cells [1-3].

Despite the practical importance of these processes, there are no universally accepted notions today about the stages that determine the course of oxygen exchange on the surface of nonstoichiometric MIEC oxides. In our opinion, this is due to the lack of a correct approach to obtaining and analyzing kinetic data necessary to form ideas about the mechanism of the reaction. As a result, there is a large scatter in the literature experimental data which prevents the development of a reliable conception of the oxygen permeability mechanism in the MIEC membranes and advance in technological aspects. Thus, understanding the factors that can ensure high oxygen permeability of perovskite oxides continues to be a challenging and actual problem. Earlier, we have developed new oxygen release techniques (QEOR and OPPR) to obtain kinetic and equilibrium parameters in grossly nonstoichimetric oxides [4, 5].

The aim of this work was to carry out a comprehensive analysis of the effect of oxygen nonstoichiometry on the kinetic parameters in the processes of oxygen transport and chemical relaxation measurements. A theoretical model has been developed for comparing the results of three independent methods. The influence of oxygen nonstoichiometry to the process of oxygen transport through gas-tight hollow fiber membranes was carried out. Stable $Ba_{0.5}Sr_{0.5}Co_{0.75}Fe_{0.2}Mo_{0.05}O_{3-\delta}$ (BSCFM5) perovskite was chosen as the object.

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OP-I-6

SPATIOTEMPORAL PATTERNS DURING CO OXIDATION ON Ni AT ATMOSPHERIC PRESSURE

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In heterogeneous catalysis two types of spatiotemporal patterns were detected, those arising on single crystal surfaces under UHV conditions [1] and non-isothermal patterns observed over polycrystalline metallic surfaces under atmospheric pressure [2]. More than 10 years ago it was found that spatiotemporal patterns in CH_4 oxidation on Ni could be monitored by the visual observation of the Ni color changes due to the oxidation/reduction processes [3]. Recently oscillatory behavior was discovered during CO oxidation on a Ni foil in CO excess at atmospheric pressure [4]. The oscillations were accompanied by propagation of the oxidation and reduction fronts which were recorded by a photo-video camera. Dark fronts of the oxidized state appear periodically in the upstream part of the catalyst and propagate downstream in the direction of the gas flow. Fronts of the bright reduced state typically move in the opposite direction. Fig. 1 (left) shows oscillations of MS signal of CO_2 along with the sequence of images displaying the propagation fronts at specific times. It can be seen that the dark oxidized state is characterized by lower activity of CO oxidation, whereas CO_2 production is much larger on the bright reduced surface.

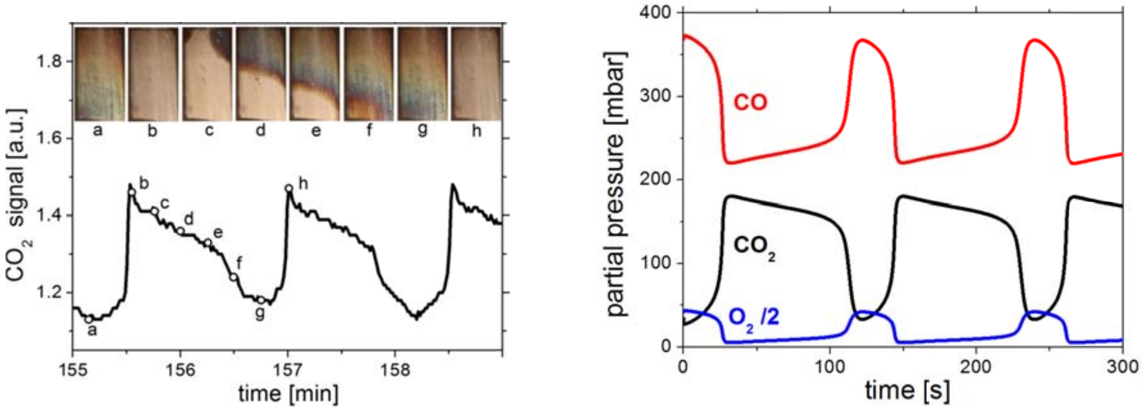

Fig. 1. Oscillations in the reaction rate at a feed rate of 30 ml/min with 40%-CO and 10%-O_2 (in He), T_{gas} = 570 °C. Left panel: experimental results. Right panel: simulations showing the oscillations of output partial pressures of O_2, CO and CO_2

A 3D convection-diffusion-reaction model was developed to describe experimental data. The model is based on the previously suggested microkinetic mechanism [5] extended to take into account the gas flow and diffusion in the reactor chamber as well as diffusion of atomic oxygen in the Ni bulk. The oscillatory mechanism involves a periodic switching between the states of low and high catalytic activity due to periodic slow variation in the surface oxide coverage. Oscillations are accompanied by propagation of oxidation front that appears under CO-rich conditions due to oxygen concentration gradient and oxygen diffusion limitations in the gas-phase. It turned out that dissolved atomic oxygen, unlike the surface oxide, has practically no influence on the surface reaction rate and the occurrence of oscillations. However, the variation in Ni color is determined by the amount of dissolved oxygen which, in turn, is regulated by the presence of empty sites on the Ni surface. When catalytic activity is high and the vacant surface sites are available, the dissolved oxygen diffuses back to the surface and reacts with CO quickly. Gradual decrease of the catalytic activity is accompanied by the accumulation of atomic oxygen in the subsurface layer. When catalytic activity and the number of vacant sites are low, oxygen atoms are locked in the Ni bulk. Oxygen species provide a slow partial oxidation of the subsurface layers and the change of the Ni color to the dark one. The simulation results are presented in Fig. 1 (right panel) and in Fig. 2. It can be seen that the local partial pressures in the reactor are strongly inhomogeneous. The oxygen pressure is higher in the left part of the catalyst, causing the dark color of Ni due to the dissolved oxygen. The right part of the catalyst is much more reduced and active than the left part. The simulations allow to explain the experimentally observed spatiotemporal behavior.

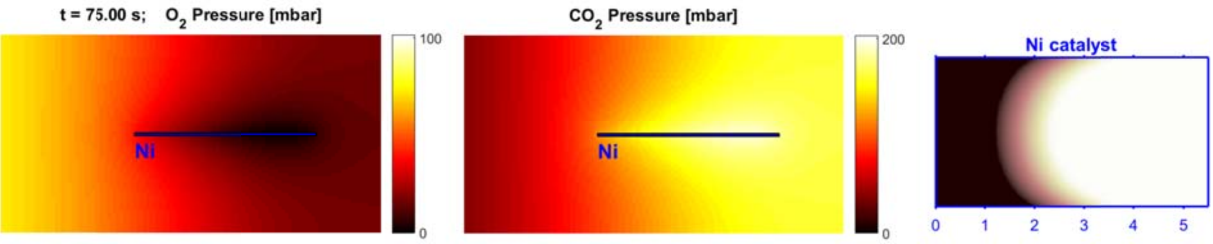

Fig. 2. Side view of spatial distributions of O_2 (left panel) and CO_2 (middle panel) corresponding to a high-activity state at t = 75 s in Fig. 1. The catalytic flow reactor is modeled as a rectangular cube of size 6×6×11.5 cm^3, the gas flows from left to right. Right panel: snapshot of Ni surface (top view); dark (white) color corresponds to a high (low) concentration of dissolved oxygen. The oxidation front moves from left to right with a velocity of about 0.07 mm/s, while the total reaction rate gradually decreases

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OP-I-7

NONSTATIONARY DYNAMICS OF CO OXIDATION DEPENDING ON THE STRUCTURE OF PALLADIUM-CERIA CATALYSTS

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Using a set of structural, spectroscopic and kinetic methods (XRD, TEM, XPS, TPR) the structural transformations in Pd/CeO_2 catalysts during their calcination over a wide temperature range were described in [1]. Depending on the temperature of calcination of the catalyst (450-800 °C) a homogeneous solid solution $Pd_xCe_{1-x}O_{2-\delta}$, PdO_x clusters or PdO nanoparticles formed.

Additionally a TPR-CO study in the flow reactor was carried out. The catalyst sample (0.2 g) preliminary was cooled in the reactor to −10 °C. Then the sample was heated to 450 °C at 10 °C/min heating rate in the reaction mixture containing 1 vol. % CO.

In order to describe the experimental TPR-CO curves, i.e. the dependences of CO_2 evolution and CO consumption on the temperature, we used the methods of mathematical modeling. The dynamics of CO oxidation in the absence of the O_2 gas phase was simulated within the model of a continuous stirred-tank reactor. We have consistently considered the underling kinetic models that take into account the presence of 1) only solid solution; 2) solid solution and clusters; 3) solid solution, clusters and palladium oxide nanoparticles. These three cases correspond to catalysts calcined at different temperatures.

Experimental dependences of both CO_2 evolution and CO consumption were described in the framework of the model, which also takes into account the diffusion of oxygen from the volume of ceria to the surface of the reduced palladium solid solution. In addition, oxygen spillover from the palladium solid solution to the reduced palladium clusters was also taken into account.

The results of the simulations are consistent with experimental data indicating that the surface of a palladium solid solution is active at sufficiently high temperatures of about 250 °C. Reduction of palladium oxide nanoparticles by CO occurs at temperatures of 100-200 °C. In the presence of PdO_x clusters, the catalyst is active in the CO oxidation reaction at the temperatures below 100 °C.

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OP-I-8

MICROKINETIC DESCRIPTION OF CO OXIDATION OVER A RHODIUM CATALYST

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Understanding the oxidation of carbon monoxide (CO) is essential for many processes, including exhaust gas after treatment and fuel cell operation. It is also important for understanding how to most effectively harness energy from hydrocarbon fuels. This work explored the catalytic oxidation of CO on a Rhodium catalyst supported on alumina (Al_2O_3) at low temperatures (175-275 °C) and at different inlet concentrations in a stagnation-flow reactor. The reactor setup allows for reducing the problem to one dimension, which enables accurate kinetic modeling and a coupling of gas and surface phase chemistry effects. Reactant species were well-mixed and flowed towards the catalyst coated onto a heated stagnation plate. Various designs of the reactor and catalyst coating methods were explored. Probe-based sampling was used to measure gaseous reactant and stable product species concentrations as a function of height above the catalyst surface. The conversion of CO to CO_2 was measured experimentally. A surface microkinetic description was developed for the catalytic oxidation of CO, which is critical for hydrocarbon-based process reactor design and optimization. State-of-the-art tools, namely pMuTT and OpenMKM, developed recently by the group of Professor Vlachos, were employed for the first time to develop and parametrize a kinetic model of CO oxidation on Rh/Al_2O_3.

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OP-I-9

MICROREACTORS AS STRONG TOOLS IN THE DETERMINATION OF INTRINSIC KINETICS FOR HETEROGENEOUSLY CATALYZED RAPID GAS-PHASE REACTIONS

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Precise determination of intrinsic kinetics for catalytic processes is important for several reasons. Kinetic data obtained under stationary and transient conditions give indication on plausible surface reaction mechanisms and adsorption behavior of the reactants, reaction intermediates and products. Based on experimental data, a mathematical model for reaction kinetics can be developed and the rate constants can be estimated with regression analysis. Such models being needed from the viewpoint of fundamental science, are also of huge importance in the design and optimization of chemical reactors in industrial scale.

Measuring the intrinsic kinetics is a challenge for rapid catalytic reactions, because the data obtained with catalyst pellets/particles are often influenced by internal diffusion limitations in the catalyst pores. Consequently, the Thiele modulus has a high value and the catalyst effectiveness factor is low. A practically applicable way to surmount this dilemma is to use very thin catalyst layers (<< 100 μm). This is, however, not possible in conventional fixed beds, which are frequently used in laboratory-scale screening of catalyst materials and measurement of reaction kinetics. Microstructured reactors enable the use of very thin catalyst layers (<< 50 μm) to suppress the diffusion resistance in the pores and to approach the conditions of intrinsic kinetics.

In this work, we illustrate the use of microreactor technology in the experimental measurement and mathematical modelling of rapid gas-phase reaction kinetics in three cases: hydrochlorination, oxidation and dehydration of alcohols. For all these processes, conventional fixed beds are not able to provide reliable data in the domain of intrinsic kinetics. The overall reaction schemes and the solid catalysts are listed below.

OP-I-9

$CH_3CH_2OH + HCl = CH_3CH_2Cl + H_2O$ Al_2O_3

$CH_3CH_2OH + ½ O_2 = CH_3CHO + H_2O$ Au on various supports

$CH_3CH_2OH = CH_2CH_2 + H_2O$ Micro and mesoporous materials

Besides the main reactions, also some side reactions take place, such as etherification of alcohols during hydrochlorination, oxidation and dehydration of alcohols. Based on kinetic data and available mechanistic information, stationary-state rate equations were derived and the numerical values of the parameters were estimated with the aid of non-linear regression analysis. Plug flow was assumed as the flow pattern in the microreactor channels. A comparison with the activation energies reported in the literature reveals that the activation energies obtained in the current work are in general higher than those reported previously; sometimes even a two-fold difference appeared. One might wonder about the origin of such discrepancy. The reason was found by developing a complete reaction-diffusion model for porous catalyst layers,

$$\frac{\partial C_{i,s}(t,z,r,r_p)}{\partial t} = \frac{D_{eff,i}}{\varepsilon_s}\left(\frac{\partial^2 C_{i,s}(t,z,r,r_p)}{\partial {r_p}^2}\right) + \frac{s}{r}\frac{\partial C_{i,G}(t,z,r,r_p)}{\partial r_p} + \rho_s \frac{\varepsilon_G}{\varepsilon_s}\sum\left(\nu_{i,j} r_{i,j}(t,z,r,r_p)\right)$$

The rate constants obtained from microreactor experiments were used in the model, along with the diffusion coefficients estimated from Fuller-Schettler-Giddings equation. Using the model equation, the concentration profiles of the components in the catalyst layers with different thicknesses were simulated numerically by using the method of lines. The simulation results revealed the reason of the discrepancy between literature data and our measurements. For these reactions, the internal diffusion resistance becomes very prominent even in rather thin catalyst layers (>>20 μm) and the effectiveness factor is diminished to 0.1 compared to intrinsic kinetics as the dimensions of the catalyst particles (< 1 mm) are approached. Evidently some previous kinetic data obtained in conventional fixed beds have been influenced by internal diffusion limitations, which in the worst case can diminish the activation energy by 50 %. It can be concluded that microreactors is a viable alternative to determine the intrinsic kinetics for very rapid catalytic gas-phase reactions along with fluidized beds, monoliths and solid foam catalysts. Microreactors have the great benefit that the flow pattern in microreactor channels is typically rather simple: either plug flow or laminar flow.

OP-I-10

KINETICS AND MECHANISM OF ISOMERIZATION REACTION OF PENTANE-HEXANE FRACTION. MATHEMATICAL MODEL OF THE REACTION

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The object of the study is the reactor unit of the catalytic isomerization unit of the pentane-hexane fraction, consisting of a cascade of three reactors. The first stage of the mathematical description of the object is the building of the scheme of hydrocarbon reactions during the process. In all known models [1–3] of the catalytic isomerization process of the pentane–hexane fraction, all the hydrocracking gases are combined into one product component, as a result of which it is impossible to predict the exact composition of hydrocarbon gases. In this work, an attempt was made to more detailed analysis of the transformation scheme based on the mechanism, including the reactions of hydrocracking products formation.

The mathematical model of the three-cascaded reactor block, adequately describing the chemical transformations within the reactors has been built and 102 kinetic parameters have been obtained [4]. Compared to the previous work, we added 3 reaction stages, this was done in order to examine the process in more detail and obtain greater accuracy of the calculations. Thus, we have obtained a refined kinetic model consisting of 108 kinetic parameters (54 activation energies and 54 preexponential factors).

The inverse problem of chemical kinetics belongs to the problems of continuous global optimization. Features of such problems are often nonlinearity, undifferentiability, multiextremality (multimodality), lack of analytical expression and high computational complexity of optimized functions, as well as high dimensionality of the search space. These features of chemical kinetics problems explain the lack of a universal algorithm for their solution. In this paper, we consider a harmony search method, which is one of the population algorithms. All population algorithms belong to the class of heuristic algorithms, that is, algorithms for which convergence to a global solution is not proven, but it is experimentally established that in most cases they give a good enough solution. Search for kinetic parameter values was performed by minimizing the deviation between the experimental and calculated concentrations:

$$F = \sum_{i=1}^{M}\sum_{j=1}^{N}\left|x_{ij}^{calc} - x_{ij}^{\exp}\right|,$$

where x_{ij}^{calc} – calculated values; x_{ij}^{exp} – experimental data; M – the number of experiment points; N – the number of substances involved in the reaction.

To solve the direct problem, the integration method ‘Radau’ was chosen; it’s an implicit Runge-Kutta method of the Radau IIA family of order 5 [6]. The error is controlled with a third-order accurate embedded formula.

In addition to solving the inverse problem, the conference will present the results of optimization of the reactor block in order to obtain dimethyl substituted components (2,2-dimethylbutane, 2,3-dimethylbutane), which affect the octane number of catalytic isomerization gasoline.

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OP-I-11

KINETIC MODEL FOR THE OLIGOMERIZATION OF 1-BUTENE TO LIQUID FUELS AT LOW- AND HIGH-PRESSURE CONDITIONS

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The oligomerization of light olefins is a versatile initiative to selectively produce hydrocarbons to be added into gasoline (C_5-C_{12}), kerosene/jet fuel (C_8-C_{16}) or diesel (C_{11}-C_{24}) pools [1] aiming to face the fluctuating fuel supply/demand of the transportation market. The increasing interest of the oligomerization is supported by the innovations for light olefin production on the conventional routes (stream cracking and fluid catalytic cracking units) and from alternative feedstocks (biomass, wastes or CO_2), via the MTO (from methanol) or DTO (from DME) processes [2]. Acid catalyzed light olefin oligomerization is highly exothermic and takes place through the classic and well-established carbocation mechanism, including oligomerization and co-oligomerization steps, as well as skeletal and double bond isomerization, hydrogen transfer, cracking and cyclization reactions [3]. Due to the complexity of the reaction system, olefin conversion and product distribution strongly depend on the properties of the catalyst (acidity and shape selectivity) and on the operating conditions (temperature, pressure and space time). The different kinetic models proposed in the literature on HZSM-5 zeolites are mainly based on single event kinetic methodology [4], without considering either the condensation phenomena of oligomer products at high pressure, or catalyst deactivation.

In this work we have established an original lump-based kinetic model for the oligomerization of 1-butene on HZSM-5 zeolite (Si/Al=15) based catalyst, able to predict the product distribution at zero time on stream and considering catalyst deactivation, as well as higher oligomer condensation in a wide range of operating conditions (150-350 °C; 1.5-40 bar; space time, 0.5-10 $g_{catalyst}$ h mol_C^{-1}).

The methodology for the kinetic model is based on the proposed in [5], which allows computing, in MATLAB, zero time on stream and deactivation kinetic parameters of best fit (kinetic constants and activation energies) simultaneously. These parameters have been calculated by fitting the experimental values of product molar fractions (obtained in a fixed bed reactor Microactivity) to the calculated ones by using multivariable nonlinear regression. We assumed gas plug flow and isothermal regime for the resolution of the conservation equations. Moreover, G-L thermodynamic equilibrium was considered for accounting for high oligomer condensation, by supposing that only gas phase compounds are reactive.

Figure 1 shows the reaction scheme, which includes 4 main lumps ($C_{4=}$, $C_{8=}$, $C_{12=}$ and $C_{16=}$ olefins), and 4 secondary lumps ($REST_1$-$REST_4$) formed by secondary reactions (oligomerization-craking and hydrogen transfer, HT). The quality of the fit is also depicted, by comparing the experimental product molar fractions (points) of evolution with time on stream, with the values calculated using the kinetic model (lines) at low (1.5 bar) and high P (30 bar) conditions.

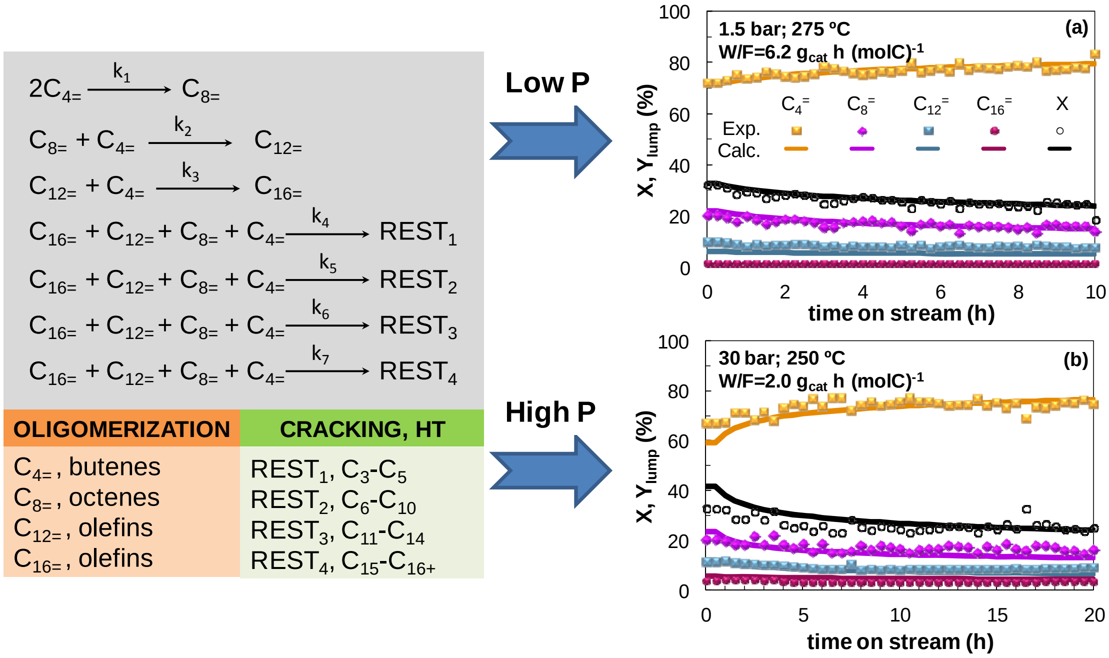

Figure 1. Simplified reaction scheme of 8 lumps (left). Fitting quality (right)

This model strikes a good balance between simplicity and acceptable fitting quality to the experimental results, which enables the subsequent optimization of the operating conditions in order to obtain fuels in the gasoline, jet fuel or diesel range.

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OP-I-12

IMPROVEMENTS IN HYDRODENITROGENATION AND HYDRODESULFURATION KINETIC MODELS OF VACCUM GAS OIL (VGO) WITH ON THE SUPPORT OF MACHINE LEARNING

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Hydrotreatment of Vacuum Gas Oil (VGO) is a critical process in refinery, preparing feedstock for hydrocracking and catalytic cracking processes. It prevents nitrogen poisoning of converting catalysts, increases hydrogen content, and enables reaching standard environmental specifications (sulfur, etc.) of downstream refinery products [1,2].

A large range of models for Hydrodesulfuration (HDS) and hydrodenitrogenation (HDN) of VGO exists [3]. However, the chemical engineer has to conciliate two antagonist constrains: (1) The need of model complexity to succeed describing the always more wider range of feedstock reactivity. Indeed, the increasing importance of heavy crude oil upgrading onto valuable products leads to a large diversification of VGO feedstock nature and composition; and (2) the scarcity of industrial data, usually limited to macroscale properties of VGO (density, Sulfur, SimDis, etc.) that not allow the use of model that requires more complex information.

Semi empirical kinetic models are relevant answers to this statement. Indeed, several works shown the good agreement of single stage power law or Langmuir-Hinshelwood type of models when applied on one or several VGO of similar profiles [4]. Though, application of such models on unalike feedstocks require addition of correlative correction terms associated to feed properties [5].

$$\frac{d[Y]}{dt} = f(feedstock\ properties) \times g\left(T, P_{H_2}, Y\right)$$

$$\text{With} \begin{cases} \text{f: empirical function based on feed properties (linear, monomial, etc.)} \\ \text{g: kinetic function (power law, Langmuir-Hinshelwood, etc.)} \end{cases}$$

The aim of this work is to associate classical methodology for kinetic model parameter estimation with machine learning methods to construct this semi-empirical kinetic model. The working process shown in Figure 1 is proposed.

OP-I-12

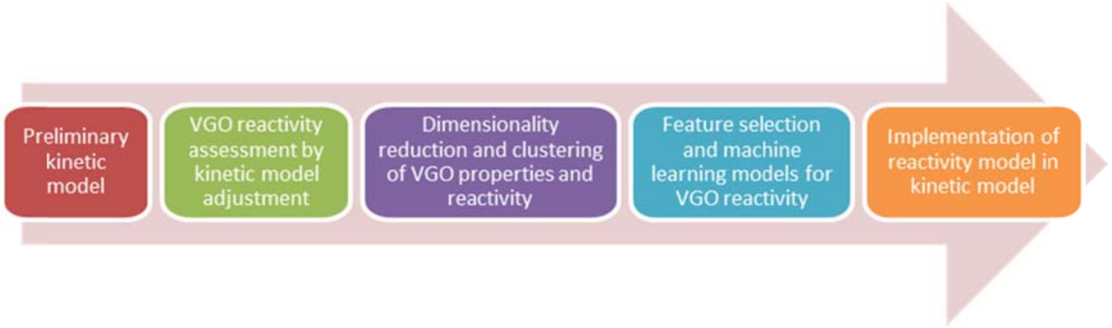

Figure 1. Workflow for rationalized construction of semi-empirical kinetic models of HDN, HDN of VGOs

This methodology has been applied on a large experimental dataset with 16 different VGO as feedstocks. The tests was performed on fixed-bed reactors packed with a commercial hydrotreatment catalyst. Machine learning methods have highlighted the key properties to take into account and most importantly, the resulting kinetic model have succeeded to show a very good accuracy for HDS as HDN for all the 16 different VGO, results barely obtained for such a diversity of feeds in the literature [5].

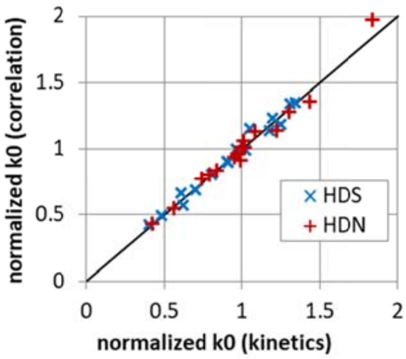

Figure 2. Parity plot of a correlation between feed reactivity (k0) and selected feed properties

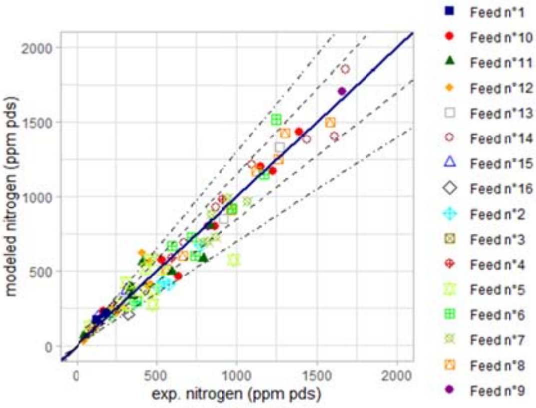

Figure 3. Parity plot of the semi-empirical kinetic model for HDN reactions

In conclusion, systematic application of the suggested strategy would be a rationalized methodology to rapidly obtain accurate semi-empirical models, particularly adapted to models for HDS and HDN of vacuum gas oils.

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OP-I-13

A KINETIC STUDY OF OXIDATIVE COUPLING OF METHANE ON La_2O_3-BASED CATALYSTS WITH Sr AND Ce DOPING

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Oxidative coupling of methane (OCM) is a process for converting methane to higher hydrocarbons in the presence of oxygen. The desired products are ethane and ethylene with some side products such as C_3, H_2O, and CO_x. La_2O_3-based catalysts, as one of the major classes of OCM catalyst in research, are considered potentially viable for commercial applications since the catalytic activity could be promoted with different metal dopants such as Sr, Ca, and Ce, etc. However, currently available catalysts still cannot satisfy the yield and selectivity of C_2+ to achieve commercial viability. Kinetic studies have been investigated to construct kinetic models to further understand and accurately describe the OCM process. Instead of performing a large amount of experiments for various operating conditions, a comprehensive kinetic model could predict the best operating conditions and screen for the most suitable catalysts by performing sensitivity analysis on target products. It is commonly accepted that both homogeneous (gas-phase) and heterogeneous (surface-catalyzed) reaction pathways occur during the OCM process [1,2]. The process starts with the chemisorption of oxygen on the catalyst surface, and one hydrogen atom from methane is abstracted by the surface active oxygen to form a methyl radical; two methyl radicals then combine in the gas phase and form one ethane molecule. Then ethylene is formed via dehydrogenation of ethane [3,4]. Many studies have considered and implemented an universal reaction mechanism for all the catalysts during OCM. However, in reality, the OCM reaction mechanism may not be the same for catalysts composed of different metals. The effect of water vapor, for example, on the kinetics for OCM has been investigated, and the results turned out to be different depending on the catalyst composition. Therefore, specific kinetic models should be developed independently for each category of catalysts [5].

In this study, the model is develped specifically for different La_2O_3-based catalysts with Sr and Ce doping based on well-validated empirical gas-phase mechanism. The surface-catalyzed mechanisms are modified based on the concept of catalytic descriptors [6] and the texture properties of the catalysts. The proposed kinetic model is validated over a wide range of operating conditions with experimental data, and provides new insights of developing a comprehensive model for La_2O_3-based catalysts.

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OP-I-14

KINETIC DATA ANALYSIS OF SUZUKI-MIYAURA COUPLING REACTIONS CATALYSED VIA MWCNT SUPPORTED Pd NANOPARTICLES

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Pd-catalysed Suzuki-Miyaura (SM) cross-coupling reactions are one of the most efficient and user friendly methods to obtain biphenyl products and their homologues. Especially milder reaction conditions around 80-100 °C, the commercial availability of boronic acids, which are easier to handle and remove when compared to other organometallic reagents, are some of the major advantages of SM coupling reaction. However, the use of homogeneous palladium complexes of phosphine based ligands as catalysts during Suzuki-Miyaura reactions limit their applications due to the toxic, air sensitive and high costs for the reusability of them. Yet the current focus is to develop heterogeneous phosphine free catalysts. Supported metal nanoparticles are promising in different heterogeneous catalyst applications. However, to have effective nanocatalysts a good control of nanoparticle properties such as size and homogenous dispersion of metals are necessary. In this manner, supercritical carbondioxide ($scCO_2$) deposition method is the matter of choice since the low viscosity, zero surface tension and easier controllable density make $scCO_2$ a practical solvent to deposit nanoparticles on especially ultrafine supports like carbon nanotubes (CNT). In this work, Pd/CNT nanocatalysts were prepared via $scCO_2$ deposition method to be applied on Suzuki-Miyaura coupling reactions conducted below conventional temperatures between 20 and 60 °C. The formation of metallic palladium, whose particle size distribution was estimated around 10.5 nm, was confirmed with XRD measurements and TEM images. The prepared Pd/CNT catalysts (0.0050 mmol) were used in Suzuki-Miyaura cross-coupling reactions of 1.0 mmol bromobenzene and 1.2 mmol phenylboronic acid at 20 °C, 40 °C and 60 °C in 2.0 ml of Ethanol:Water (1:1) solution in the presence of 2 mmol K_2CO_3 as base to obtain biphenyl. At 60 °C, the conversion reached to 98% in 30 min while at 40 °C similar conversion was recorded around 90 min. At 20 °C, in 3 hours, conversion reached to 70 %. Then, the obtained kinetic data were used to estimate the catalytic rate constants at different temperatures and the activation energy of the reaction with the help of Arrhenius equation. The kinetic data analyses were done according to batch reactor, constant volume and second order kinetics. Activation energy was estimated around 59.2 kJ for the rate constants predicted at 20 °C, 40 °C and 60 °C.

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OP-I-15

CaO-BASED SORBENTS FOR CALCIUM LOOPING APPLICATIONS: A GENERALIZED KINETIC MODEL OF CARBONATION REACTION

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Introduction

The reaction of CO_2 with CaO-based solid sorbents in cyclic mode, known also as calcium looping (CaL), has great potential for capturing CO_2 at stationary sources, storing/releasing energy in concentrated solar power plants, or even enhance thermodynamically limited reactions such as reforming and water-gas-shift [1-3]. Lime (pure CaO) suffers from severe deactivation mainly due to enhanced sintering phenomena at high temperatures. Many efforts are being put on preventing the loss of capacity of CaO through sorption/desorption cycles, by introducing an inert stabilizing phase in the CaO lattice [4]. Herein, we investigate the carbonation reaction kinetics of materials with different stabilizing agents aiming at developing a robust reaction kinetic model.

Materials and Methodology

Four materials were used in the kinetic experiments – a calcined limestone (pure CaO), a calcined dolomite (33 wt. % MgO/CaO), and two MgO- and ZrO_2-promoted synthetic sorbents, containing 15 wt % MgO and 25 wt % ZrO_2, denoted as CaMg85 and CaZr75 respectively). All the materials were sieved in the range of 45-75 μm. The kinetic experiments were carried out in a continuous-flow fixed-bed reactor apparatus connected with a mass spectrometer. The temperature and CO_2 partial pressure ranges were 670-820 °C and 0-1.2 atm respectively. For the mathematical description, the classic Random Pore Model was appropriately modified to take into account the presence of the inert phase. The developed modified model included parameters for each material related to the crystal sizes, BET surface area and dispersion of the stabilizing agent, information acquired using XRD, nitrogen physisorption and SEM characterization techniques.

Results

The fitting of the modified Random Pore Model (mRPM) on the experimental conversion-time data is shown in Figure 1A for carbonation of CaZr75 at 770 °C and under various P_{CO2} values. It can be observed that carbonation reaction is very fast, achieving a high value of material's conversion in a few seconds. The values of the specific rate *r* in terms of reaction front velocity derived from fitting of each experimental X-t curve are gathered in Figure 1B as a function of the driving force.

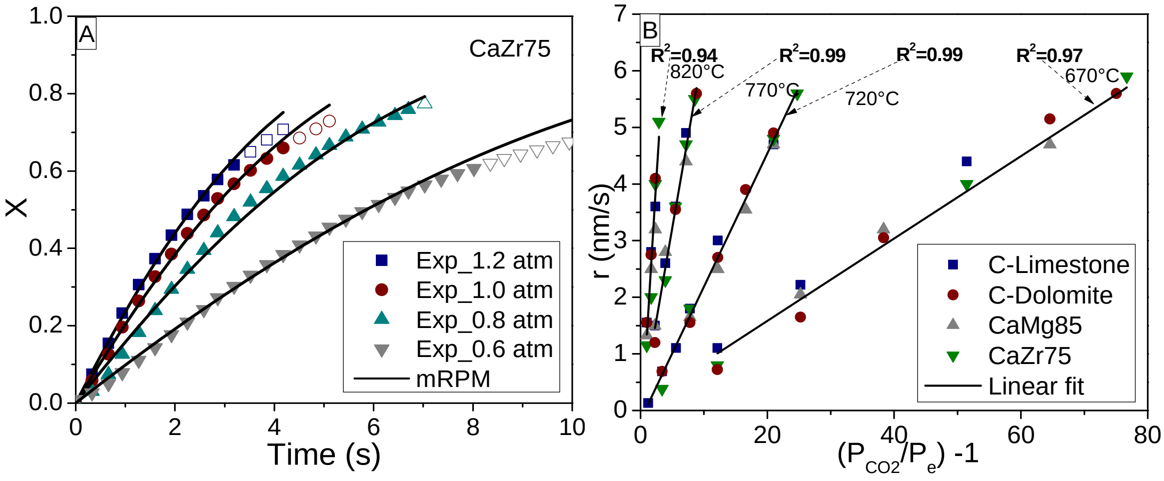

Figure 1. A) Experimental conversion-time data fitted by the mRPM for the carbonation of CaZr75 sorbent at 770 °C and for various P_{CO2}, B) rate values vs the driving force for all four tested sorbents

Carbonation is a first order reaction with respect to CO_2 (Figure 1B). Interestingly, experimental data obtained with all the examined sorbent materials can be fitted satisfactorily by the same lines despite the differences in the type and content of the stabilizing agent, further imposing that the RPM was modified correctly. A common value of activation energy for all sorbents was calculated equal to 22.1 ± 5.9 kJ/mol, which is in agreement with values reported previously for pure CaO [5].

Conclusions

Carbonation reaction of CO_2 with CaO-based sorbents exhibits fast kinetics (in the order of a few seconds), which is of great importance for real applications. Carbonation is a first order reaction with respect to CO_2 with a low activation energy of 22.1 ± 5.9 kJ/mol. A kinetic model was developed applicable for CaO-based sorbents with different type and content of stabilizing phase.

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Acknowledgments

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OP-I-16

MULTIOBJECTIVE OPTIMIZATION IN THE REACTION KINETICS OF METAL COMPLEX CATALYSIS

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The use of metal complex catalysts significantly softens the reaction conditions and allows them to implement into industrial production [1]. Metal complex catalysis is characterized by a multi-stage scheme of chemical transformations and the presence of a large number of intermediate complexes, which can be both stable and unstable. The effect of intermediate complexes and initial substrates on the reaction is reflected in the kinetic parameters of the corresponding stages.

The mathematical model of homogeneous isothermal reactions of metal complex catalysis proceeding with a change in the volume of the reaction mixture is described by the Arrhenius kinetics (1) [2]:

$$\begin{aligned}
&\frac{dy_i}{d\tau} = \Phi\kappa\sum_{j=1}^{J}\nu_{ij}w_j, i=1,\ldots I; \quad y_i(0)=y_i^0; \quad \tau\in[0,t^*];\\
&\frac{dQ}{d\tau} = \sum_{i=1}^{I}\frac{dy_i}{d\tau}; \quad Q(0)=Q^0;\\
&w_j = k_j\cdot\prod_{i=1}^{I}\left(\frac{y_i}{Q}\right)^{|\alpha_{ij}|} - k_{-j}\cdot\prod_{i=1}^{I}\left(\frac{y_i}{Q}\right)^{\beta_{ij}}; \quad k_j = k_j^0\cdot\exp\left(-\frac{E_j}{RT}\right).
\end{aligned} \tag{1}$$

Where τ – time, min; ν_{ij} – stoichiometric coefficients; J – number of stages; y_i – concentration of substances participating in the reaction, mol/L; I – number of substances; w_j – rate j-th stage, 1/min; k_j ,k_{-j} – stage speed constants (reduced), 1/min; E_j^+, E_j^- – activation energies of direct and reverse reactions, kcal/mol; R – gas constant, 2 cal/(mol*K); T – temperature, K; α_{ij} – negative elements of the matrix ν_{ij}, β_{ij} – positive elements ν_{ij}, k_j^0,k_{-j}^0 – preexponential factors, 1/min; $\Phi\kappa$ – catalyst feed function; Q – molar flow rate (mol/min).

The object of research is the catalytic hydroalumination (HA) of olefins. The process allows to obtain important cyclic and acyclic organoaluminum compounds of a given structure and is of great industrial importance. A detailed kinetic model of the reaction with diisobutylaluminium chloride (DIBAC) according to (1) is given in [3, 4]. The model describes the induction period in the reaction with DIBAC. The reaction products are higher organoaluminum compounds Bu_2AlR and $ClBuAlR$. Chemical experiments were carried out at several temperatures and with an initial amount of catalyst. Variable parameters in the multicriteria (MCO) optimization problem are reaction temperature, an initial amount of catalyst, and reaction time. The optimization problem was solved by Pareto approximation methods [5].

In fig. 1 shows the results of solving the MCO problem of the conditions for the reaction of HA olefins (octene-1) with DIBAC.

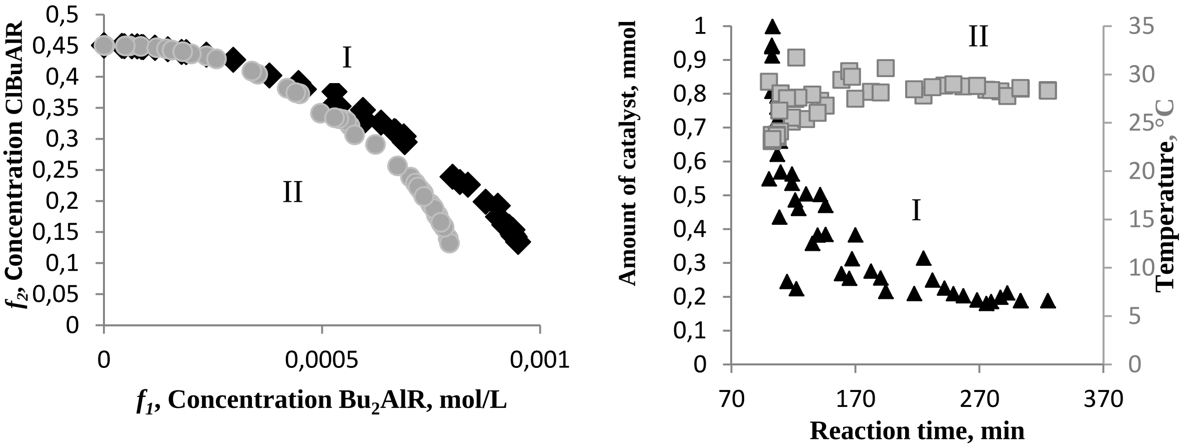

Fig. 1. Approximation of the Pareto front of the MCO-problem of the reaction of HA olefins in the presence of DIBAC

For a fixed reaction time (250 min) and varying temperature and an initial amount of catalyst, the values of product concentrations are shown in Fig. 1 a, curve II. Variation of time to achieve increased product yield Bu_2AlR, but does not affect the output of ClBuAlR – Fig. 1 a, curve I. The values of the variable parameters, i.e. the Pareto set is shown in Fig. 1 b. The increase in reaction time allows reducing the initial amount of catalyst in the reaction from 1 mmol to 0.2 mmol. The optimal temperature range is 25-30 °C. The adequacy of the solution is confirmed by experimental data.

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Acknowledgements

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OP-I-17

KINETIC MODEL FOR BIFUNCTIONAL CORE-SHELL CATALYST FOR DME SYNTHESIS

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Bifunctional catalysts for dimethyl ether (DME) synthesis from syngas + CO_2 mixtures allow shifting methanol (MeOH) synthesis equilibrium, enhancing its formation over the metallic catalyst while it dehydrates to DME over the acid catalyst. In this work, a core-shell structured bifunctional CuO-ZnO-ZrO_2@SAPO-11 catalyst has been used and a macrokinetic model has been established for this particular catalyst configuration. Catalyst synthesis, characterization and the reaction equipment, and experimental results considering deactivation have been described in previous works [1,2].

The model describes the effect of different operating conditions over product distribution with time on stream considering the confinement of each reaction in a section of the catalyst particle. Elementary reactions have been considered for CO and CO_2 hydrogenation to MeOH, its dehydration to DME, water gas shift (WGS) reaction and for the undesired side reaction of hydrocarbons formation. Besides, catalyst deactivation has also been considered. In the synthesis of MeOH a term considering the competitive adsorption of water on the metallic sites has been considered, and a term considering the competitive adsorption of both water and CO_2 on the WGS reaction. Experimental data for model fitting was obtained carrying out catalytic reactions in an isothermal fixed bed reactor under the following operating conditions: 250-320 °C; 10-50 bar; space time 1.25-15 $g_{cat}\cdot h\cdot mol_c^{-1}$, $H_2/(CO+CO_2)$ molar fraction, 2.5-4; $CO_2/(CO+CO_2)$ molar fraction, 0-1. In order to get the macrokinetic model, different assumptions are considered: i) MeOH synthesis occurs only in the metallic function; ii) its dehydration occurs only in the acid catalyst; iii) for both regions kinetics are limited by reactants internal diffusion.

The kinetic model predicts satisfactorily the performance of the core shell catalyst under a wide range of operating conditions, predicting products yield evolution with time on stream (as shown in Figure 1).

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The considered deactivation kinetics correspond to a non-selective model (it affects reactions in both phases), with a first-order expression referred to the concentration of oxygenates (MeOH and DME) and to activity, considering also the attenuation of deactivation by the competitive adsorption of water and CO_2 in the active sites of both phases. To consider components diffusion through the core-shell structure (quantified from porous structure) along with kinetic equations, spherical geometry of the particles has been assumed and the concentration profile for any particle has been defined as:

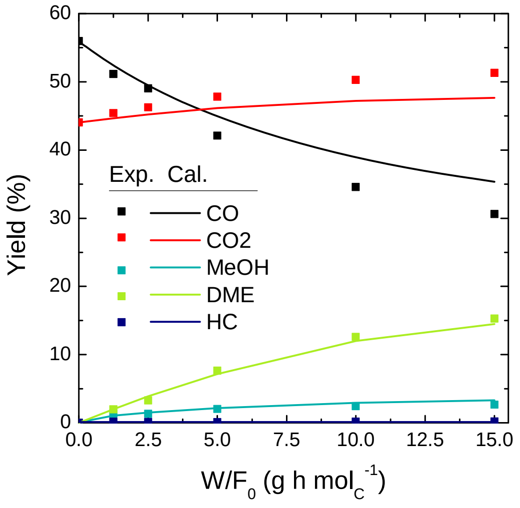

Figure 1. Fitting quality of products molar fraction

$$D_{e,i}\left(\frac{d^2y_i}{dr^2}+\frac{2}{r}\frac{dy_i}{dr}\right)=r_i\rho \qquad \text{Eq.(1)}$$

Where r_i, is formation rate of component *i*; $D_{e,I}$, its diffusion coefficient; ρ the density of the particle; and, y_i, molar fraction of component *i*.

To solve Eq. (1), diffusion on the interphase between both phases has been considered as equal. Thus, to quantify the diffusion terms, the formation term is considered null for each compound in the phase of the particle where it is not formed (DME in the metallic function, since there is no MeOH dehydration; H_2, CO, CO_2 and MeOH in the acid phase, since WGS reaction and MeOH formation occur only in the core).

This model has allowed to ascertain precisely the effect of different operating conditions in order to achieve different goals, DME yield or CO_2 valorization, as they have different optimal conditions.

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OP-I-18

EXPERIMENTAL AND NUMERICAL INVESTIGATION OF SPECIES TRANSPORT IN CATALYTIC FLUIDIZED BED REACTORS

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The conversion and selectivity of catalytic fluidized bed reactors (FBR) result from the coupling between the multiphase fluid dynamics and the catalytic reaction mechanisms at the particles' surface. In this view, a detailed multiscale modeling can provide deep insights into the coupling between physics and chemistry in the fluidized bed units. To this end, the Computational Fluid Dynamics (CFD) description of the gas flow combined with the Discrete Element Method (DEM) algorithm is crucial. Nevertheless, in reactive CFD-DEM, where DEM is used for the particle tracking, the chemistry is typically computed per computational cell, assuming the composition of each particle to be equal to the one of the hosting cell without mass transfer limitation [1]. Moreover, linearized rate equation kinetics are usually employed to sustain the computational cost. Thus, we recently proposed a reactive CFD-DEM framework [2] able to deal with the microkinetic description of chemistry and the modeling of mass transfer with gas-particle correlations in fluidized beds. Furthermore, we successfully tested the framework in lab-scale chemically limited reactors, managing the computational cost arising from microkinetic chemistry with speed-up algorithms [3].

In this work, we investigate the capability of the framework to correctly couple the description of bubble to particle transport phenomena with the interphase transport. For this purpose, we experimentally and numerically studied highly diluted (1:85 volumetric ratio of active particles) lab-scale FBR for the fast hydrogen oxidation on a Pt/Al_2O_3 powdered catalyst. In particular, a mixture of 0.5 %/0.2 % v/v hydrogen/oxygen was used as the inlet gas stream. The catalyst was manufactured by depositing Pt on porous alumina particles (300 μm mean diameter) employing Atomic Layer Deposition (ALD) [4] in an FBR. This method allowed to precisely tune the Pt nanoparticle size distribution to the optimal range of 1-3 nm for all the three investigated Pt loadings (1 %-2 %-5 % w/w). With respect to the numerical part, rate equation kinetics fitted from preliminary fixed bed tests as well as the generalized gas-particle mass transfer correlation proposed by Reichelt et al. [5] were adopted. For the catalytic test, a reactor of 1 cm diameter was filled until 2.67 cm height (Pe > 100). A broad fluid dynamic range, from 2 to 10 times the minimum fluidization velocity (U_{mf} = 4.6 cm/s), was tested. Figure 1a shows the comparison of the conversions obtained experimentally in case of the three different Pt loadings, with the CFD ones. The experimental results clearly show the presence of mass transfer limitations, being the increment in the Pt loading, between 2 % and 5 %, ineffective. The CFD results are in good agreement with the experimental ones with a maximum error of 6 percentage points of conversion (10 % and 8 % of relative error in oxygen and hydrogen molar fractions). Figure 1b reports the oxygen and void fraction maps in case of the 7.5 U_{mf} simulation. Moreover, the oxygen and solid particles distributions are reported for two cross-sections at 4.5 and 6 cm height. In case of the oxygen distribution, the catalytic particles located onto the cross-section are also shown. In particular, the oxygen map shows an oxygen gradient from the bubble until the active particle region, thus illustrating the presence of the bubble-to-particle transport limitation. Moreover, the even lower content of oxygen in the particles than the surrounding gas proves also the presence of the interphase limitation. Thus, the CFD shows that the experimentally observed limitation arises from the combination of the two oxygen transport limitations.

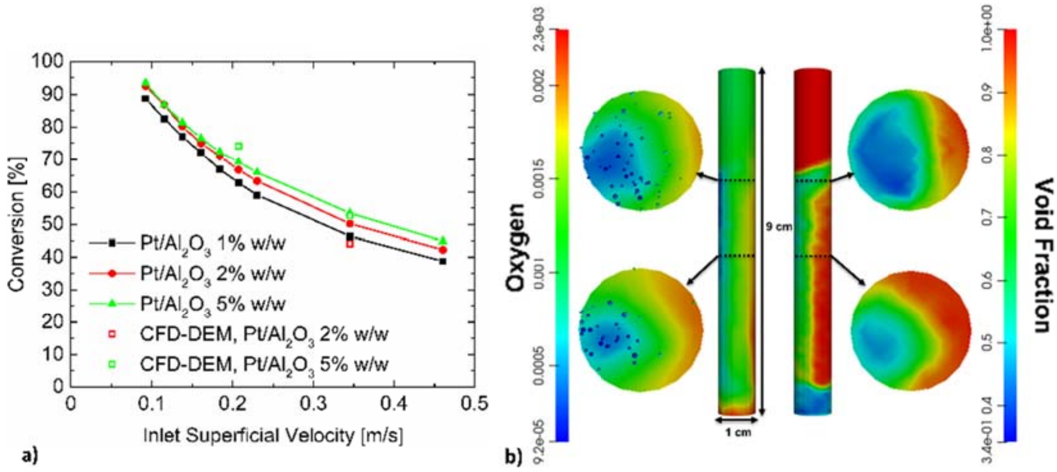

Figure 1. Species transport analysis: a) experimentally and numerically obtained conversion as a function of selectivity; b) snapshot of oxygen mass fraction map (left) and void fraction map (right) at 34 cm/s. In the oxygen map, the top limit of the scale corresponds to the feed oxygen fraction, while the bottom limit corresponds to the lowest oxygen content recorded in the particles. Active catalyst particles tracked onto the cross sections are also reported by means of the same color scale

This study demonstrates the capabilities of the developed reactive CFD-DEM framework to accurately describe the transport phenomena inside fluidized bed systems, in addition to the catalytic mechanisms proved in previous research, paving the way for a numerically optimized design of fluidized units of technical relevance.

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MICROKINETIC DEVELOPMENT FOR THE METHANATION OF CO_2 ON Ni CATALYSTS WITH RMG-CAT

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Microkinetics enable the most accurate description of a reaction on a given catalyst surface without any restrictions. If the microkinetics are elucidated by experiments or theoretical computations, it is possible to study the reaction in all possible operating conditions and to drive the process towards improvement. The development of the microkinetics and the mechanism itself is a time-consuming task, which can be significantly accelerated with the usage of an automated Reaction Mechanism Generator for heterogeneous catalyzed reactions (RMG-Cat) [1]. RMG-Cat is applied in this study to investigate the mechanism for the methanation of CO_2, which is a crucial process to produce synthetic natural gas. The microkinetics are incorporated into a reactor model and compared to experimental results.

To generate a mechanism, RMG-Cat is required to accurately predict reaction rate parameters and the thermochemistry of adsorbates on the active facets, which it achieves based on databases and scaling relations. C, O and H binding energies for the scaling relations are determined with state-of-the-art electronic structure calculations for the Ni(111) and Ni(211) facet, which are discussed to be the active sites for the methanation on Ni [2]. The algorithm considers all possible reactions and intermediates, but only those reactions and species that exceed a certain threshold are included in the microkinetic model.

Steady-state and transient CO_2 methanation experiments are conducted on a Ni/Al_2O_3 catalyst in a Berty reactor. Especially recorded temporal concentration profiles can be used for the validation of the proposed mechanism [3], which is performed in a mean-field Berty reactor model in Python within the Cantera framework. The Berty reactor is modeled as a continuously stirred tank reactor with a reactive catalyst surface. Figure 1 shows the reaction paths for both Ni facets.

OP-I-19

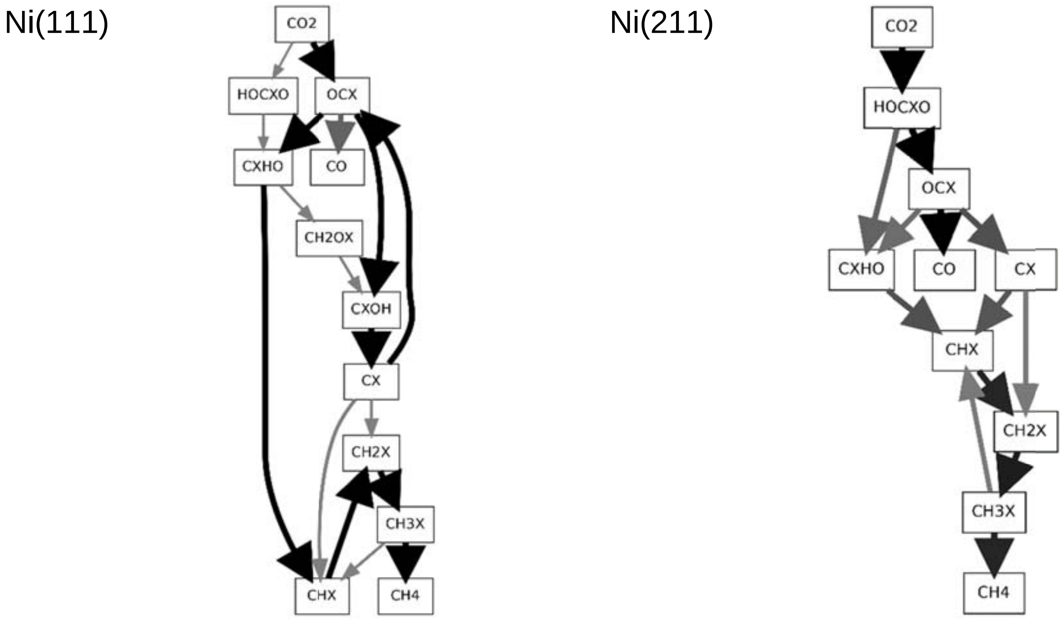

Figure 1. Reaction path analysis for the CO_2 methanation on the Ni(111) and Ni(211) surface. The thickness of the arrow illustrates the rate of reaction and the adsorption site is denoted as X. The reaction path analysis is conducted with a model of the Berty reactor. Conditions: 400 °C, 5 bar

Due to the different thermochemistry of the adsorbates on the closed-packed and stepped facet, distinct reaction networks are obtained. On the Ni(111) surface, methane is primarily produced via the H-assisted dissociation of CO*, with the formyl intermediate. CO_2 adsorbs on the (211) surface with the assistance of hydrogen and forms a carboxyl, which dissociates to CO* and is followed by both, H-assisted and unassisted dissociation and subsequent hydrogenation towards methane. While RMG-Cat can generate a reasonable microkinetic model, the comparison with experimental results clearly shows the necessity to incorporate coverage effects on the thermochemistry and reaction rates.

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OP-I-20

STOCHASTIC RECONSTRUCTION USING ENTROPY MAXIMIZATION

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Stochastic reconstruction is one of the most usable molecular reconstruction methods for heavy petroleum cuts. One of the main drawbacks of this method is the high computational time of the model parameter estimation. There already exist methods to decrease the computational time of molecular reconstruction procedure using artificial neural network [1] and reconstruction by entropy maximization with an extensive database, derived from the reconstructed reference oil fraction [2].

The key idea of the suggested algorithm (Fig. 1) is to estimate stochastic reconstruction parameters based on detailed composition after the entropy maximization step.

The reconstruction by entropy maximization after stochastic reconstruction is a well-known method [3] that usually enhances the reconstruction quality. However, it is used as a two-step reconstruction algorithm, applying the entropy maximization step after stochastic reconstruction. The suggested algorithm uses entropy maximization step instead of global optimization in order to reduce computational time.

To demonstrate this method, a vacuum gasoil sample was reconstructed with it. Fig. 2 shows simulated distillation curve of the sample, calculated distillation curves based on initial parameters and results of entropy maximization. Fig. 3 shows the resulting curves after 5 iterations.

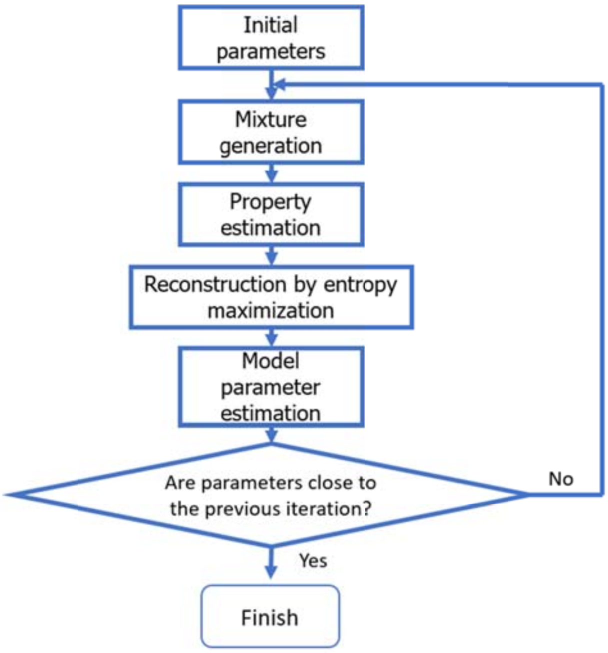

Fig. 1. The suggested algorithm

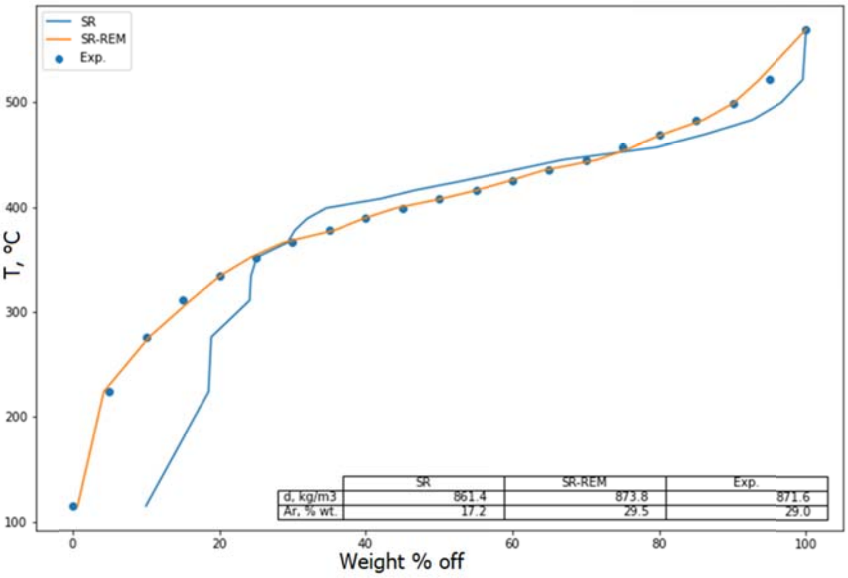

Fig. 2. Initial distillation curves

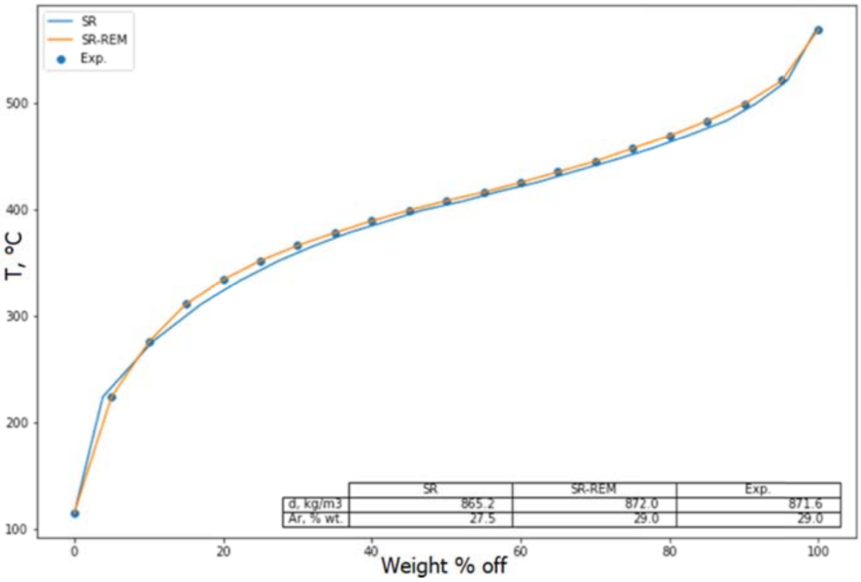

Fig. 3. Final distillation curves

Other properties (density, aromatic content) were also improved greatly (Fig. 2,3). Stochastic reconstruction with this method takes dozens of seconds in the worst-case scenario, instead of hours or even days with conventional genetic algorithm.

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OP-I-21

DEVELOPMENT OF FOUR COMPONENT REDUCED CHEMICAL KINETIC MECHANISM FOR GASOLINE SURROGATES

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For combustion systems, chemical kinetic modeling is an important tool in the analysis of fuel interactions chemistry. Many detailed kinetic models has been developed over the course of years in the field of combustion, to interpret the fundamental kinetic experiments in shock tubes, RCM, flame reactors. Researchers have reduced these detailed models using different techniques and these reduced mechanisms coupled with fluid mechanical models have become valuable in understanding complex combustion phenomena in practical combustion devices such as internal combustion engines (IC). This study proposes a new reduced model consisting of four component (Heptane/Iso-octane/Toluene/Ethanol) gasoline surrogate model containing 68 species and 310 reactions. The model has been well validated against a wide range of ignition delay time (IDT) and flame speed (FS) measurement data and compared against two characteristic literature models from Yang et al (2019) and Liu et al (2013) [1][2]. Overall excellent agreements were observed between chemical kinetic model and experimental data across the entire research octane number (RON), temperature and pressure ranges. The model well validates across entire equivalence ratios (lean and rich conditions) achieves an advantage over previous work by Yang et al (KAUST-2019). In addition, the model has been coupled with computational fluid dynamic models to simulate the heat release experimental data at homogenous charge compression ignition (HCCI) conditions for cooperative fuel research engine (CFR) of university of Michigan [3] and also constant volume spray ignition delay time and lift of length data for primary reference fuels (PRF) of various RON sweeps recommended by engine combustion network (ECN) [4]. In total, the coupled reduced model can qualitatively predict the experimental data for PRF, TPRF, TPRF-Ethanol gasoline surrogates with an improved performance.

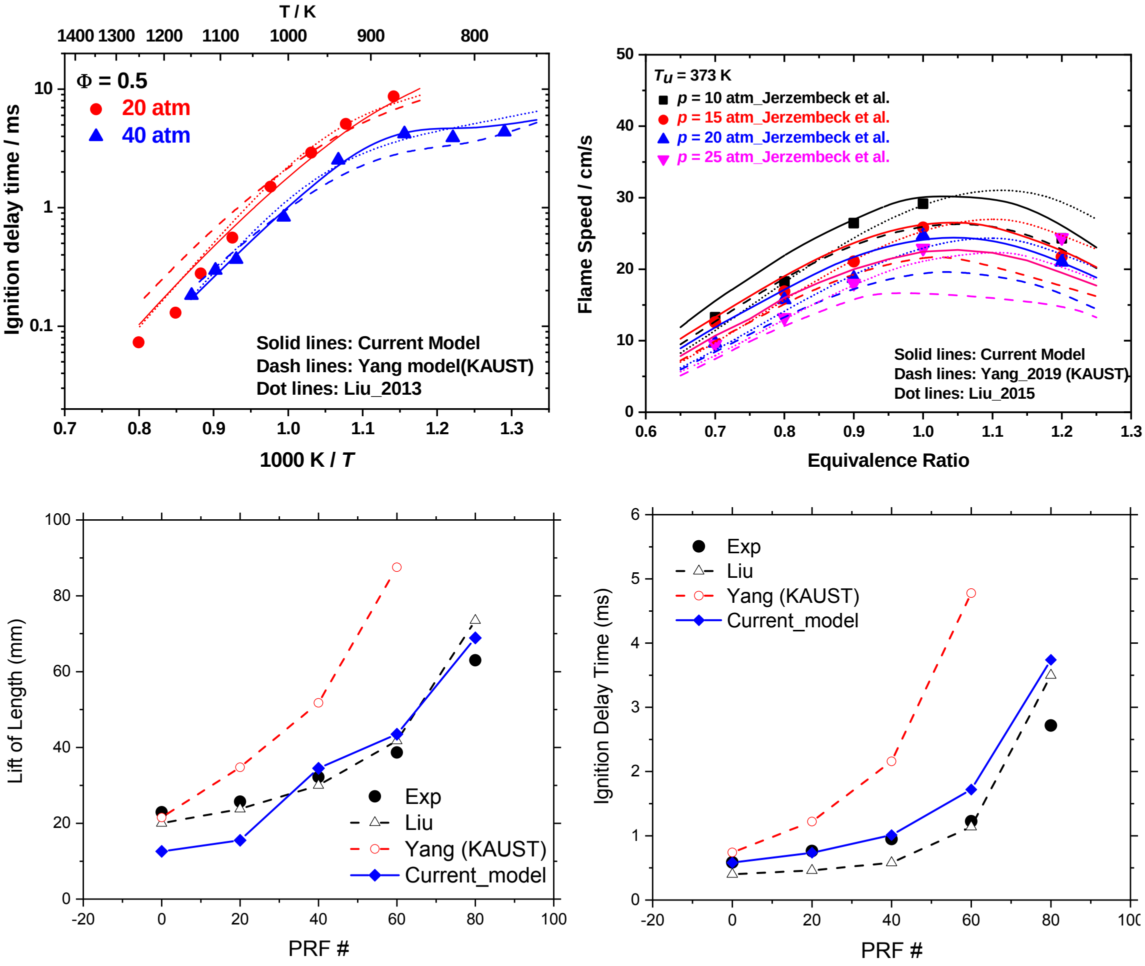

Figure. Ignition delay time (IDT) validation of PRF 91 at φ = 0.5 (top-left);
Flame speed (FS) validation of PRF 87 at various pressures (top-right);
Constant volume spray simulation IDT and Lift of length validation for various PRF RON sweeps

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OP-I-22

INVESTIGATION OF THE ROLE OF BY-PRODUCTS IN THE KINETICS OF MALEIC ANHYDRIDE SYNTHESIS USING A MILLISTRUCTURED REACTOR

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Almost the entire production of maleic anhydride (MA), one of the most important intermediate products in the chemical industry, is based on the selective catalytic oxidation of n-butane over vanadium phosphorus oxide (VPO) catalysts. Industrially, this process is typically carried out in multi-tubular fixed-bed reactors at butane contents below 2 % and temperatures in the range of 390 to 430 °C [1]. Despite these comparatively low butane concentrations, the limited heat removal can result in hotspots of up to 70 K [1], which cause a considerable potential of thermal runaway. Furthermore, the hotspot has a negative effect on the selectivity to the target product MA, so that the MA yield of industrial reactors is limited to approx. 65 % [2].

Detailed modelling and simulation of the process can help to investigate the effects of the hotspot and temperature profile on the performance of the process. An important prerequisite are profound information about the kinetics. Unfortunately, none of the published kinetics can satisfactorily describe the process, which, among other reasons, is due to the fact that the formation of the by-products acetic (AcA) and acrylic acid (AcrA) is typically neglected. Therefore, the aim of the present study is to investigate the kinetics and to clarify the role of AcA and AcrA in the formation of the undesired by-products CO and CO_2. The influence of the reaction products CO, CO_2, water and MA on the kinetics will also be investigated.

For this purpose, an enhanced version of the previously described [3] nearly isothermal salt bath-cooled millistructured fixed-bed reactor (72x44x1.65 mm) was used. To avoid mass transfer resistances, the reactor was filled with fine particles obtained by milling of an industrial catalyst provided by Clariant AG. The experiments were carried out under industry-related conditions, namely 380 to 440 °C, 1.2 to 1.5 bar and 0.9 to 2.1 % n-butane in air. Additionally, some experiments were carried out under supply of the reaction products CO, CO_2, water, MA, AcA and AcrA. The effluent gases were analyzed using a process gas analyzer for n-butane, CO, CO_2 (infrared) and O_2 (paramagnetic cell) as well as a gas chromatograph for MA and organic side products like AcA.

In the experiments, depending on the reaction conditions, selectivities of up to 4 % each were observed for the often neglected by-products AcA and AcrA. Both components seem to be formed directly from butane. Since the selectivities to both components decrease with increasing butane conversion, they have to be oxidized to CO/CO_2. Experiments under supply of AcA and AcrA show an extremely high conversion of both components. As they are nevertheless detectable under typical reaction conditions, they must play a significant role in the formation of CO/CO_2. In contrast, the direct oxidation of butane to CO/CO_2 frequently assumed in literature seems to be negligible, apart from the oxidation of the C atoms, which are abstracted during the formation of AcA and AcrA.

Furthermore, a variety of inhibitions of the different reactions by different reactants and products were found, which indicates that there have to be at least three different active sites on the catalyst surface. The results are summarized in the novel reaction network depicted in Fig. 1. and were used to derive appropriate rate equations to describe the kinetics.

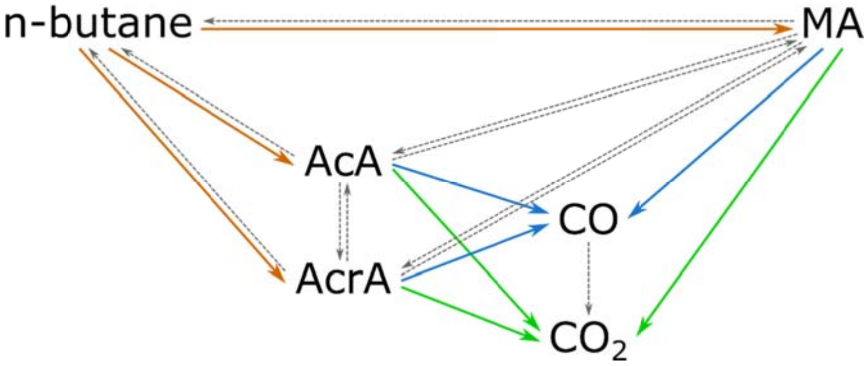

Figure 1. Reaction network with by-products. The different active sites are indicated by different colors. Dashed lines indicate observed but negligible reactions

Since the formation of CO and CO_2 is accompanied by a significant release of heat, kinetics taking into account the by-products acetic and acrylic acid can significantly improve the description of the temperature profile in the reactor.

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OP-I-23

KINETICS OF ETHYL LEVULINATE SYNTHESIS IN A CHROMATOGRAPHIC REACTOR

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Esterification of carboxylic acids with alcohols is a very actual topic of modern bio-refinery: it is normally performed to produce added-value products, such as solvents and plasticizers [1]. Ethyl levulinate has potential applications in the field of inks and paints. It is synthetized from levulinic acid and ethanol in the presence of an acid catalyst, normally a homogeneous one (e.g. H_2SO_4), but we have recently demonstrated that acid resins (e.g. Smopex-101) show a good activity in ethyl levulinate production [2]. As water is produced by the chemical reaction, and being the reaction reversible, it would be necessary to remove water onsite to improve the reaction conversion. Reactive chromatography could solve this issue, as it is an operation unit that combines chemical reaction and chromatographic separation, allowing the intensification of the esterification process. In the present work, an effort was made to investigate the kinetics of levulinic acid esterification with ethanol in the presence of Dowex 50WX-8, a non-porous gel acid catalyst used as chromarographic reactor packing material [3]. Starting from the concept, a detained kinetic investigation was conducted in an isothermal batch reactor. Advanced intraparticle models were used to verify the influence of fluid-solid and intraparticle mass transfer limitations.

The esterification experiments were carried out in a Hastelloy reactor with a capacity of 200 mL. Continuous experiments were performed packing a stainless-steel tubular reactor with Dowex 50WX-8. Ethanol was pumped continuously in the reactor, via a HPLC pump, and a solution of levulinic acid in ethanol was injected through the reactor with a fixed volume 20 uL, via a HPLC injector. The reactor was heated by electrical resistances. Data were collected at the outlet of the chromatographic reactor using an online detector (UV at 250 and 280 nm).

The kinetic investigation conducted in a batch reactor, demonstrated that the reaction follows a second order reversible mechanism referred with respect to the reactants and the products, and a linear behavior with respect to the catalyst loading

(Figure 1A), resulting in an activation energy of 75 kJ/mol (Figure **1**B). The collected data were interpreted by intraparticle mass transfer models.

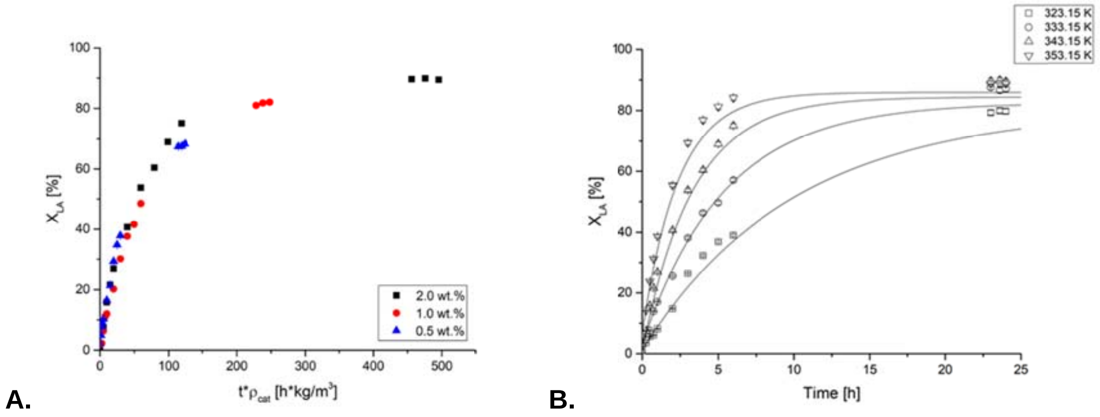

Figure 1. A. Levulinic acid conversion trend against the experimental time scaled by the catalyst bulk density. **B.** Effect of temperature on the levulinic acid esterification (ethanol/levulinic = 5:1 mol/mol, ρ_B = 20 kg/m^3, 800 RPM

The chromatographic separation method proved to work for LA esterification, as with sufficiently low flow rates the LA pulses were completely converted to EL, while with moderate flow rates the partially unconverted LA was well separated from the ester (Figure 2).

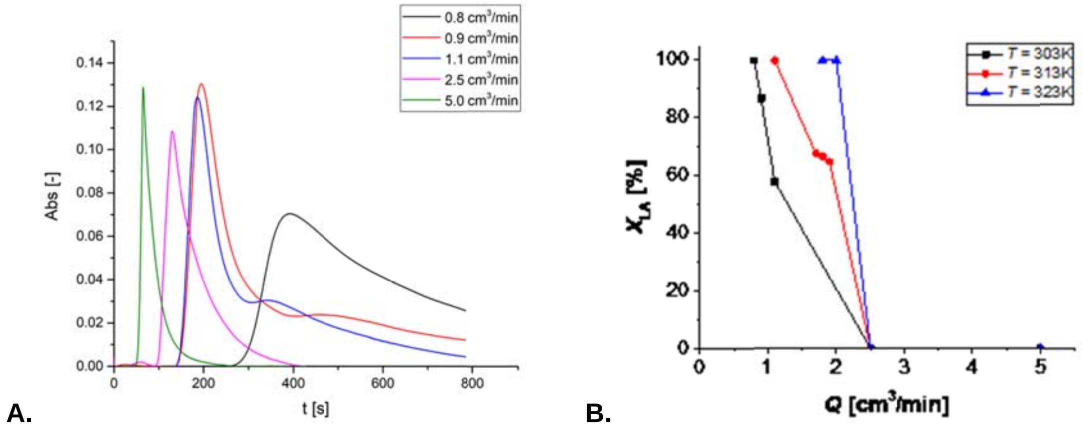

Figure 2. A. UV spectra of LA 6M injected in the chromatographic reactor working at 303 K and at different flow rates. **B.** LA conversion achieved at different operative conditions during the chromatographic reactor tests with LA 6M pulses

The results will be used for designing larger-scale reactors for scaling-up the process.

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OP-I-24

A MULTIPHASE OPERATOR SPLITTING MODEL FOR THE EULER-EULER SIMULATION OF REACTIVE FLUIDIZED SYSTEMS

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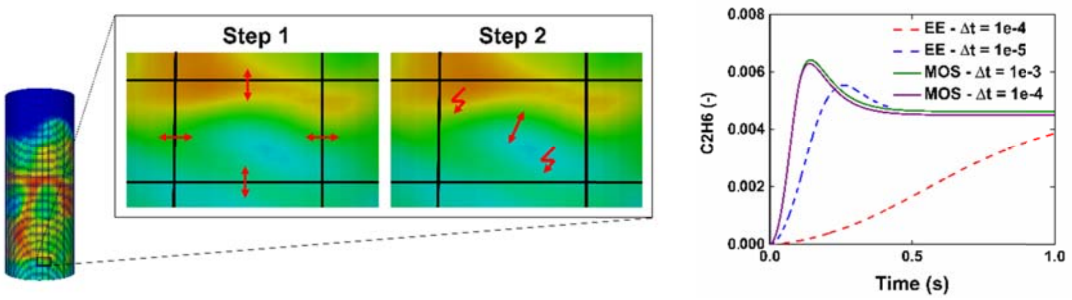
Fluidized systems are still a research challenge due to their complex multiphase fluid dynamics. In this context, Computational Fluid Dynamics (CFD) combined with a detailed description of the chemistry is a powerful tool to analyze reactive fluidized beds. In particular, a Euler-Euler (EE) approach is adopted to describe the multiphase flow in pilot/industrial scale due to the large dimension of the units. Indeed, this approach treats both gas and solid as continuum fluid phases. In doing this, the description of large-scale systems is possible at the cost of losing the tracking of each solid entity. In order to simulate reactive systems, the energy and species equations are included in the CFD framework for both the phases as reported in Eq. (1):

$$\begin{cases} \dfrac{\partial \varphi^G}{\partial t} = A^G + T^G + R^G \\ \dfrac{\partial \varphi^S}{\partial t} = A^S + T^S + R^S \end{cases} \tag{1}$$

Where φ is a generic quantity transported in the reactor, A is the advection contribution, T is the gas-transport contribution, R is the reaction contribution and the superscript G and S represent the gas and solid. Despite the coupled nature of the three contributions, a fully coupled solution of these CFD equations cannot be performed [1]. Thus, the gas and the solid phases are usually solved sequentially, and the chemistry is introduced with linearized reaction source term R [2]. Thus, the simulation time step must be carefully chosen to be smaller than the times of the physical and chemical phenomena involved in the process. On the one hand, the Courant condition ensures the correct description of the advection. On the other hand, a stricter time step condition with respect to the Courant one is necessary to describe gas-solid transport, due to high particle specific surfaces, and chemical reactions. Therefore, time steps in the order of 10^{-7}-10^{-5} s are required, especially if a detailed microkinetic description of the chemistry is adopted. In this work, a *Multiphase Operator Splitting* model (MOS) (Fig. 1(a)) is proposed to solve this issue, which would hamper the simulation of industrial units whose dynamics extend for tens of seconds. According to this model based on a Euler-Euler description of the gas-solid flow, the system is divided in several reactors, one per computational cell.

At the beginning of each time step, the advection updates the initial composition and temperature of each reactor (Step 1). Then, each computational cell is solved as a multiphase batch reactor (Step 2), where the gas-solid transport and the reactions are solved coupled through an Ordinary Differential Equation (ODE) solver. By doing so, the characteristic times of the phenomena are respected by the ODE solver sub-stepping allowing for higher simulation time steps.



(a) (b)

Fig. 1. Multiphase Operator Splitting: (a) Schematic representation; (b) Comparison of the average ethane mass fraction as a function of time obtained with EE model (dashed lines) and the MOS model (solid lines)

The MOS has been assessed by simulating the Oxidative Coupling of Methane process by means of a literature microkinetic scheme [3] in a reactor (ϕ= 2.3 cm, height 26 cm) composed by 500k cells. Fig. 1(b) shows the average ethane mass fraction obtained with EE and MOS models. EE predicts the correct pseudo-steady. Conversely, the correct dynamics is predicted only with time steps smaller than 1e-5 s. On the other hand, the MOS is able to provide accurate predictions by adopting longer time steps, leading to 1/10 the time required by the EE to reach the pseudo-steady state. It is also worth noticing that the solution of the multiphase batch reactor is more expensive with respect to the solution of the linearized kinetics, thus enabling a further optimization of the computational cost by means of speed-up algorithms [4], which is currently on going. As a whole, the work successfully proposes an optimization of reactive Euler-Euler models, paving the way for the detailed description of catalytic chemistry in fluidized systems of industrial interest.

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Acknowledgement

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OP-I-25

MICROMIXING IN A GAS-LIQUID VORTEX REACTOR: AN EXPERIMENTAL AND NUMERICAL STUDY

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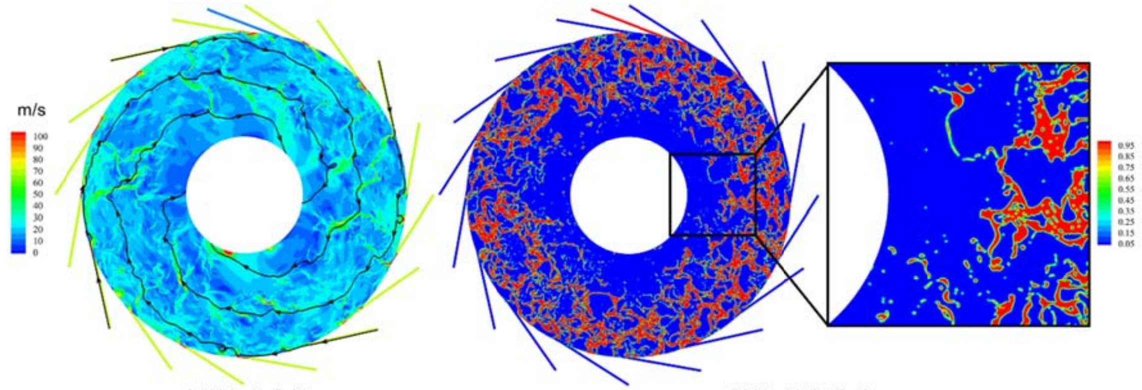
Micromixing performance of a reactor is the controlling factor for fast reactions in polymerization, pharmaceutical and crystallization applications [1,2]. To achieve process intensification in micromixing-controlled processes, a vortex-flow unit is an efficient technology that has major advantages of simple structure, low cost and easy scale-up. Ever since a gas-solid vortex reactor (GSVR) was built and operated at Laboratory for Chemical Technology (LCT, Ghent University), many successful applications have been confirmed [3,4] and patented. Our recent work showed the applicability of the vortex technology for gas-liquid flows [5], leading to the concept of a gas-liquid vortex reactor (GLVR). The micromixing efficiency of the GLVR could also be an enormous advantage for applications involving liquid-liquid mixing and fast reactions.

To investigate the micromixing process, computational fluid dynamics (CFD) is first employed as a powerful tool to reveal and understand the hydrodynamics and reactive flow in the GLVR. Figure 1 shows the velocity filed in the GLVR and the contour of the liquid (as the red colour) distribution in the reactor chamber. The gas flow (as the blue colour) generates the initial vortex flow, and the momentum transfer between the gas phase and liquid phase disperses the liquid in the reactor chamber and increases the coalescence-redispersion frequency. The gas-liquid interface is large and tiny droplets are formed, which will be validated by visualization data from high-speed camera and particle image velocimetry measurements.

The Villermaux–Dushman iodide–iodate reaction system will be used to quantify the micromixing efficiency of the GLVR [6]. Figure 2 shows the schematic diagram of the experimental setup. The acid stream and the buffer stream containing ions of iodate, iodine and borate are pumped into the GLVR and mixed. The N_2 gas flow generates the initial vortex flow, and the liquid is entrained by the gas flow. Samples are collected at the outlet and immediately analysed by an ultraviolet-visible spectrophotometer. Effects of operating conditions and different GLVR designs will be investigated and the micromixing characteristic time in GLVR is will be compared with conventional reactors. Further, by implementing the micromixing model [7] to simulate the reaction process, the CFD results will not only help to explain the experimental results but also guide the reactor design and optimization. This work will give fundamental insights in the liquid micromixing for practical GLVR applications.



(a) Velocity field

(b) Liquid distribution

Figure 1. Contour of liquid flow distribution in the GLVU

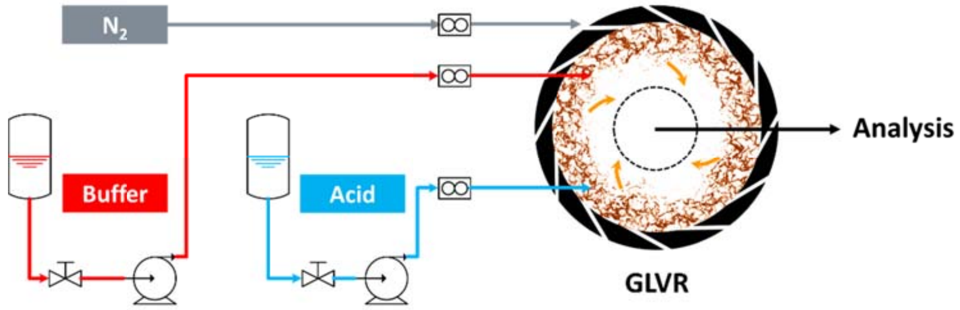


Figure 2. Schematic diagram of the experimental setup

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MODELLING INTRAGRANULAR TRANSPORT: DIGITALIZATION OF A γ-ALUMINA SUPPORT BY IMPLEMENTING COMPUTATIONAL VERSIONS OF THREE DIFFERENT CHARACTERIZATION TECHNIQUES

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1. Introduction

Understanding how transport phenomena and chemical reactions within porous catalysts are affected by the texture of the support opens the door to optimizing the catalyst performance. Explicitly accounting for the phenomena occurring at the pore scale can thus lead to novel and more rigorous heterogeneous models for chemical reactor design. To model the structure of porous catalysts, several approaches can be found in the literature [1,2]. In this work, computational tools were developed to refine the digital representation of a γ-alumina pore network [3,4] in order to match its actual textural properties and topology. Each of these tools simulates an experimental characterization technique: nitrogen porosimetry, mercury porosimetry, and Nuclear Magnetic Resonance cryo-porometry. By using theoretical and empirical models, these techniques provide quantitative textural information and qualitative topological characterization [5]. The experimental curves obtained from the characterization of an actual sample are matched by the digital characterization curves generated with the computational versions of three different characterization techniques applied to the pore network structure. Finally, a digital twin of this γ-alumina sample is recreated by using an optimization loop that manipulates the input parameters used for the pore network generation.

2. Results and discussion

The textural properties of the digital pore network were calculated both geometrically and by processing the results of the simulated characterization techniques. Compared to the direct calculation of the textural properties by simply counting the number of pores, the direct simulation of the entire characterization profiles provides a better interpretation of the experimental results by analysing the validity of the assumptions made by theoretical and/or empirical models used for the calculation of the material's textural properties from the experimental data. The pore network generation tool is based on a *O(log(n))* algorithm that allows to create a network with $6 \cdot 10^6$ pores in only 46 seconds on a Dell desktop computer with a 3.5 GHz Intel Xeon E5 CPU and 16GB of RAM. For the characterization techniques, the use of a dynamic priority list [6] to handle the exploration of the network is valid for all techniques, as the phase change and/or percolation phenomena occurring in every technique are constrained by the topology of the network. The algorithms are capable of reproducing typical hysteresis behaviour observed in the experimental results for alumina catalyst supports. By versioning the Invasion Percolation algorithm to our needs and handling the priority list using diverse versions of binary heaps, we were able to maintain a good time performance for the different algorithms created for each characterization. The execution time for the characterization techniques corresponds to an *O(nlog(n))* behaviour and takes about 25 seconds for $8 \cdot 10^6$ pores. To match the textural properties of the digital pore network with that of an actual alumina support, the input variables of the network model are modified until the differences between the output textural properties and actual values are minimized. A good agreement was observed between the properties of the digital twins and the actual aluminas.

3. Conclusions

In this work, a pore network generation algorithm was used to represent gamma-alumina supports. To obtain the textural properties of such a digital pore network, an Invasion Percolation algorithm was adapted in order to characterize this structure by means of the computer-equivalent of nitrogen porosimetry, mercury porosimetry, and NMR cryo-porometry. Using the developed algorithms, it was possible to generate digital pore networks whose properties are in good agreement with the properties experimentally measured by different characterization techniques on actual gamma-alumina supports.

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OP-I-27

DEVELOPMENT OF A MULTIPARTICLE OPTICAL TRAJECTOGRAPHY TECHNIQUE FOR HYDRODYNAMIC ANALYSIS OF A STIRRED TANK DEVOTED TO DARK FERMENTATION

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The dark fermentation process aims to produce hydrogen gas and volatile fatty acids by converting organic substrates through complex metabolic pathways. This process will play a key role in the design of biorefineries in order to respond to the growing demand for renewable energies, but it still needs to be optimized, in particular the hydrodynamic conditions that enhance mixing and mass transfer but also increase the hydromechanical stress faced by the microorganisms at the same time [1]. In addition, a low power input must be maintained to ensure economic sustainability.

To explore the influence of mixing conditions on local shear stress at low power input, optical techniques, such as planar Particle Image Velocimetry (2D-PIV), and numerical simulations based on Computational Fluid Dynamics (CFD) have been applied [2]. An alternative consists in an optical trajectography technique which gives access to the 3D Lagrangian flow field; but this remains limited to one particle as the passive tracer in the literature [3-4], implying long measurement times.

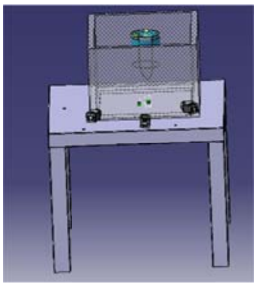


Fig. 1. Experimental set-up

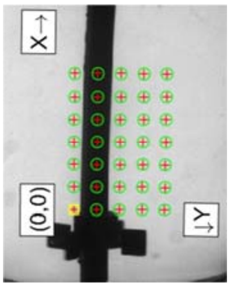
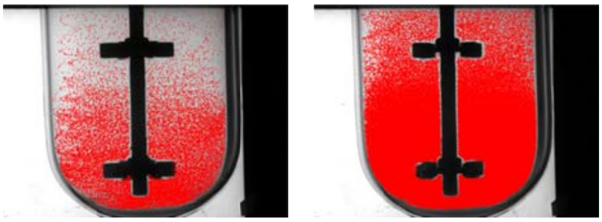


Fig. 2. Calibration by the Matlab®'s application «Stereo Camera Calibrator»

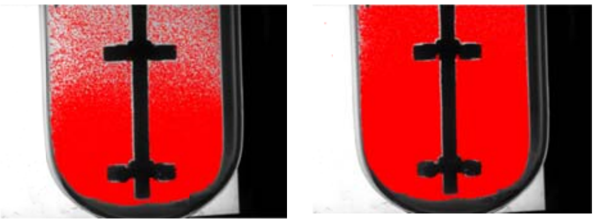
In this work, an optical trajectography technique was set up in a 2-L bioreactor, equipped with a dual-impeller (two 6-blade Rushton turbines) placed in a squared tank (Fig. 1). The purpose was to track the position and the speed of up to 15 spherical beads as passive in order to outperform the current optical trajectography technique, by reducing measurement time and enhancing the accuracy of the method. The new approach uses three cameras placed around the cylindrical reactor which must be calibrated simultaneously (Fig. 2), as well as a special data treatment that reconstructs the 3D positions of each particle over time. Experimental results were successfully compared with CFD data up to 10 spherical beads (Fig. 3-4).

Concludingly, the new multiparticle technique is able to reduce measurement time by a factor 8, while giving access to a reliable 3D flow field which agrees with CFD data.



(a) (b)

Fig. 3. Single bead detection after 30 min (a) and 360 min (b)



(a) (b)

Fig. 4. 10-bead detection after 30 min (a) and 360 min (b)

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OP-I-28

APPLICATION OF CENTRIFUGAL FORCE FOR MASS TRANSFER ENHANCEMENT IN A FALLING FILM MICROREACTOR

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Introduction

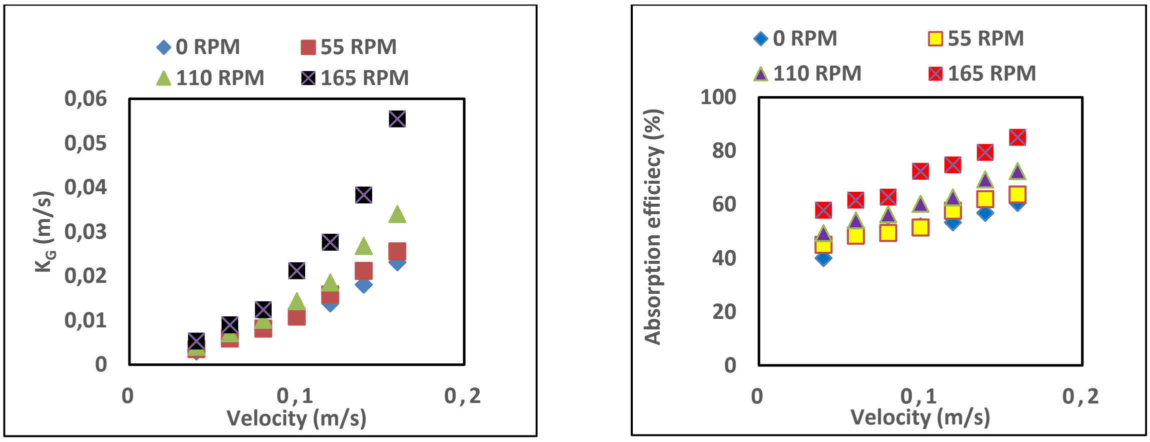
One of the most significant development in the field of process intensification is the exploitation of centrifugal acceleration for enhancement of mass transfer between phases [4]. The technique has been the basis for the intensification of many process engineering operations due to it great micro mixing ability. A simple example is the rotating packed bed (RPB) system in which mass transfer between phases are greatly enhanced due to the generation of mean acceleration that are thousands of times higher than the forces of gravity. This leads to the formation of thin liquid films and micro or even nano droplets [2]. Knowing fully well that the efficiency of the gas-liquid contact in a FFMR relies on the generation of thin liquid films, a study focus on the application of centrifugal force for mass transfer operation in this reactor was proposed. The benefit will be a reduction in diffusive/ conductive path-length, a more uniform distribution of liquid film with consequent increase in effective interfacial area for mass transfer.

Method

The effect of centrifugal field on mass transfer in a FFMR in terms of the gas-phase mass transfer coefficient (K_G), was assessed through a series of experimental tests involving the absorption and reaction of SO_2 with aqueous solution of NaOH. The operating parameters used were modified from the study reported by [1] to account for improvement in process efficiency and hence the K_G. Similarly, the liquid phase mass transfer coefficient was investigated using the reaction between absorbed CO_2 in water with NaOH. The amount of CO_2 absorbed was determined using Warder's method of double indicator titration. The method reported by [3] was modified and adopted. Investigations were conducted with the system operated at 0, 55, 110 and165 RPM.

Result

In this study the effect of key operating parameters on gas phase mass transfer coefficient was investigated. Focus was on the effect of rotating speed of the system on the absorption efficiency of the process with consequent impact on gas-phase mass transfer coefficient (K_G). It could be seen from figure 1(a) that in addition to increase in gas velocity, increase in the rotating speed of the system from 0-165 RPM was observed to have enhanced the K_G values from 0.003 to 0.055 m/s. Similarly, in figure 1(b) the peak values in absorption efficiency of the process has increased by about 25 %. The outcome of the liquid phase study also yielded a similar trend.



(a) **(b)**

Figure 1. (a) and (b) Average gas-phase mass transfer coefficient and absorption efficiency as a function of velocity at different rotating speed of 1.25ml/min liquid volumetric flowrate

Conclusion

The effect of centrifugal force on gas-liquid contact operation in an FFMR was studied. Increase in rotating speed of the system was found to have favored the absorption efficiency of the process with consequent increase in mass transfer coefficients. At the highest rotating speed of 165 RPM investigated for the gas phase, up to 85 % absorption efficiency was attained.

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Acknowledgment

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OP-I-29

EXPERIMENTAL AND NUMERICAL ANALYSIS OF TRANSPORT PROPERTIES OF CELLULAR MEDIA TO ENABLE REACTOR-SCALE SIMULATIONS

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Process intensification (PI) is a topic of high significance in academic and industrial research aiming at the development of more compact, energy-efficient processes [1]. In this view, structured catalysts have been widely investigated to overcome conventional limitations of packed-bed reactors. In particular, cellular materials (foams, Periodic Open Cellular Structures - POCS) are envisioned as potential candidates for enhanced catalyst substrates due to their flexibility in design [2], as their manufacture by means of 3D printing provides plenty of possibilities for design and optimization. To pursue this goal, it is necessary to understand the coupling between transport and geometrical properties of the substrates aiming at the derivation of engineering correlations which enable the catalytic reactor design. Herein we propose a combined experimental and numerical investigation of the transport properties of the cellular substrates as shown in Figure 1. On one hand, Computational Fluid Dynamics (CFD) allows for the analysis of the transport properties providing also detailed insight in the transport mechanism. However, the significant computational burden of such simulations hinders their application to the reactor scale. In this view, a hierarchical approach following the procedure proposed by Rebughini et al. [3,4] is employed to investigate representative structures volumes by means of CFD.

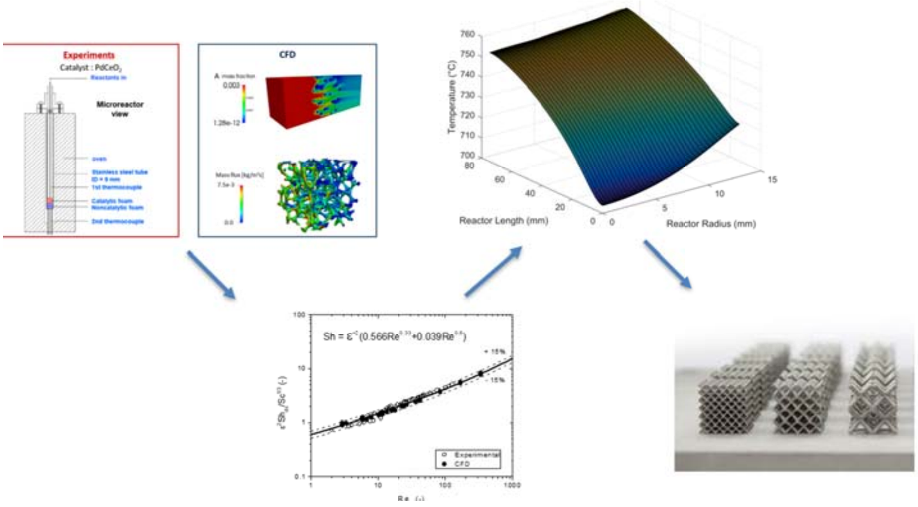

Figure 1. Approach for process intensification: 1) experimental and numerical analysis, 2) derivation of correlations, 3) reactor-scale simulations, 4) optimization of geometrical parameters

On the other hand, experiments are employed to extensively validate the numerical models guaranteeing the accuracy of the simulations and their accuracy in reproducing the behaviour of the structures. According to such approach, the numerical simulations enable the parametric analysis of the effect of a single morphological parameter (e.g. cell shape, porosity, cell diameter) on the selected transport properties without any cross influence [5]. Consequently, the simulation results along with the collected experimental data are employed aiming at the derivation of engineering correlations which are then employed in conventional models for reactor design.

In this work, we show the potential of the proposed approach for the fundamental investigation of the mass and heat transport properties of POCS along with the analysis of the pressure drops. In Figure 2 first the cross validation of experiments and CFD is shown by comparing the pressure drops of TKKD unit cells. A gas/solid mass transfer correlation for the same cells is then reported, showing the functional dependencies to the porosity and the flow field.

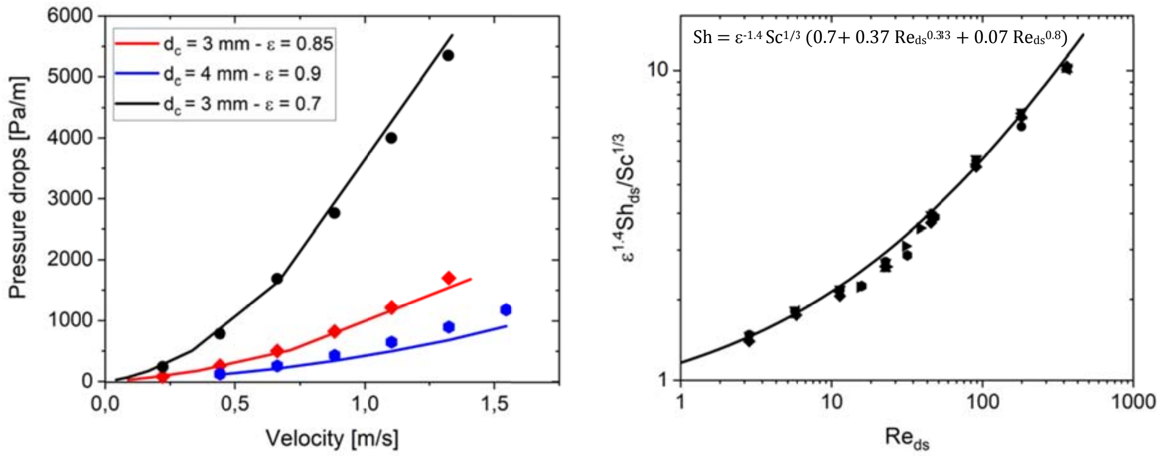

Figure 2. Left – Pressure drops of TKKD cells evaluated with experiments (points) and CFD (lines); right: correlation for Sh number of TKKD unit cells (line) derived from CFD simulations (points)

In this work, we presented a work-flow methodology for the fundamental investigation of transport properties in cellular substrates by performing experiments and CFD, deriving engineering correlations for the design of intensified catalytic reactors.

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Acknowledgements

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OP-I-30

ENABLING THE EVALUATION OF MASS TRANSFER PROPERTIES OF 3D PRINTED CATALYST SUBSTRATES WITH RICH H_2 OXIDATION

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In recent years, the need to comply with more and more stringent environmental legislations is pushing towards the development of new, high performing catalytic solutions. The freedom in catalyst supports design associated with the development of 3D printing technologies may enable the manufacture of substrates that exhibit better performances than state of the art honeycomb monoliths in terms the tradeoff between gas/solid mass transfer and pressure drops [1]. In view of the large number of structures that can be manufactured by 3D printing, an efficient screening methodology for the evaluation of these properties is required. Among 3D printing techniques, stereolithography apparatus (SLA) shows the highest precision and accuracy, being able to print samples with geometrical details below 0.2 mm in size. The technique is used to print polymeric materials, that are characterized by moderate resistance to temperature. In previous works [2-4], CO oxidation over noble metal catalysts was used to drive the system to the diffusion limited regime in order to evaluate external mass transfer performances. However, the external mass transfer regime is usually reached for temperatures above 300 °C which are not compatible with the resin substrate. To meet the temperature limits of the resin samples, H_2 oxidation under rich conditions is a good candidate. SLA 3D printed samples have been used for other process intensification devices (e.g. static mixers), however, no catalytic applications have been yet reported in the literature. In this work, we propose the use of catalytically active 3D printed resin samples for the investigation of external mass transfer properties by running rich H_2 oxidation catalytic tests.

POCS samples (cylinders, id = 9 mm, length = 15 mm) are printed using FLHTAM01 high-temperature (HT) resin ($HDT_{@0.45MPa}$ = 289 °C) and a Form2 SLA 3D printer. The finished samples are coated with a 3 % Pd/CeO_2 slurry and the excess slurry is removed by spin-coating. Samples are flash dried in air at 200 °C for 3 min and the procedure is repeated until the target loading of 15 g_{cat}/L is obtained.

Samples are then reduced in situ at 200 °C using a $N_2/H_2/O_2$ 95/4/1 % v/v feed mixture. Catalytic activation with Pd/CeO_2 slurry via spin-coating resulted in a homogeneous and well controlled washcoat loading. Over the Pd catalyst, the reaction starts just above room temperature and reaches the diffusional regime at temperatures lower than 200 °C, as shown in Fig. 1a). Operation with H_2 excess allows to avoid eventual polymer oxidation; furthermore, in these conditions O_2 is the limiting reactant which controls the mass transfer rate. For validation purposes, a resin POCS is directly compared with an identical FeCrAlloy sample tested in mass transfer limited CO oxidation tests (1.5 % CO in Air). Mass transfer coefficients, expressed as $ShSc^{-1/3}$, are calculated from O_2 conversions in the external mass transfer regime assuming a PFR behavior. Fig. 1b) shows that the dimensionless mass transfer coefficients evaluated from the conventional and the novel testing methodology results are very well aligned. A parametric investigation of mass transfer properties in POCS structures is currently ongoing.

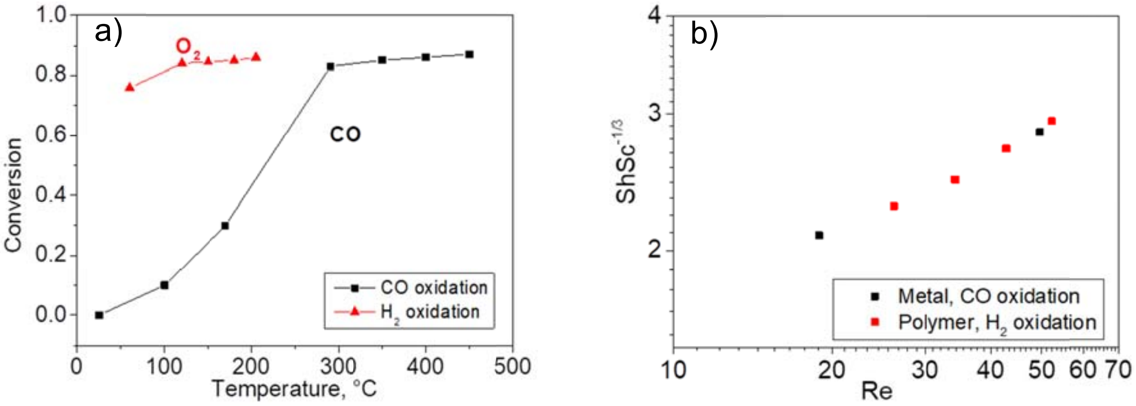

Figure 1. Limiting reactant conversion for CO and H_2 oxidation. Q = 3 L/min (STP), cubic POCS (a) and $ShSc^{-1/3}$ vs Re for cubic POCS: cell diameter = 2.5mm, ε = 0.92 (b)

A new experimental protocol has been developed to allow accurate, fast and low-cost screening of complex 3D cellular substrates through the use of: i) HT resin for the manufacturing of 3D printed catalyst supports, and ii) rich H_2 oxidation as the test reaction.

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OP-I-31

HEAT TRANSPORT CHARACTERIZATION AND GEOMETRIC OPTIMIZATION OF PERIODIC OPEN CELLULAR STRUCTURES

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Periodic Open Cellular Structures (POCS) produced by additive manufacturing are a promising alternative to conventional fixed bed reactors with random particle packings. POCS consist of a unit cell (*Fig. 1, left and middle*) which is repeated in all three spatial directions, thereby forming an interconnected network of struts (*Fig. 1, right*). This geometrical structure features high porosity, high specific surface area and consequently low pressure drop [1] as well as a uniform liquid distribution for two-phase flow [2] and high thermal conductivities [3] inside the structures. The latter aspect is especially important for strongly exo- or endothermic reactions and offers great potential for process intensification. Most of the heat transport is attributed to heat conduction rather than convection. This makes it also possible to operate at lower gas velocities in comparison to particle packed beds. As a result, longer residence times and/or more compact reactors can be realized, thereby unlocking an extended operation range in contrast to conventional reactors with particle packings.

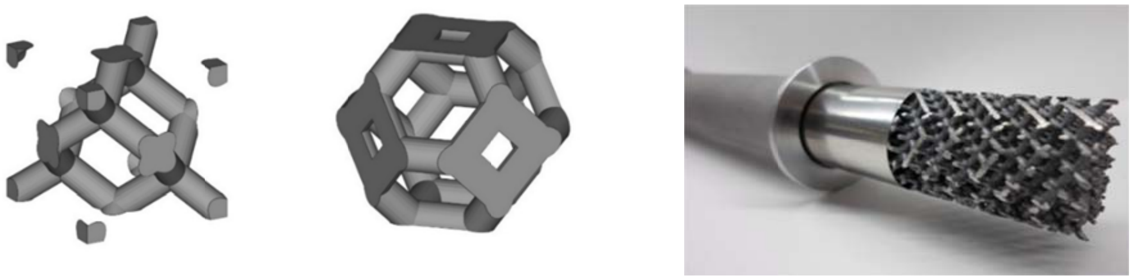

Fig. 1. Investigated unit cells and resulting full geometrical structure
(left: Diamond, middle: Kelvin, right: POCS with Diamond unit cell in tube)

By additive manufacturing, there are almost no limitations for the geometrical design of the structures, which also enables the optimization of the geometry depending on the targeted application. To perform the design and optimization of POCS as novel catalyst supports the accuracy of the underlying models used to describe the hydrodynamics and heat transport characteristics as well as the kinetics of the reaction system is crucial. As a consequence, reliable correlations for the description of the hydrodynamics and heat transport characteristics in POCS are necessary. The present contribution focuses on the heat transport characteristics of

POCS with different geometric parameters in order to develop a correlation for the a priori calculation of heat transport coefficients in POCS.

In this regard, the heat transport characteristics of different POCS were investigated experimentally. The structures were produced via Selective Electron Beam Melting (SEBM) out of different materials and for the two different unit cells shown in *Fig. 1*. For the investigations, a double pipe heat exchanger lab setup was used and the POCS were placed inside the tube. Axial and radial temperature profiles in the heated structures were measured using three multipoint thermocouples. Based on the use of the so-called α_W-model, the heat transfer model coefficients (α_W and λ_r specifically) were determined from the measured temperature profiles. These values could then be correlated using a Nusselt-Reynolds approach [3] in order to allow for generalization and enable the transfer to other structures. Different behavior depending on the unit cell and geometric properties could be observed. Structures based on the Diamond unit cell show better heat transport performance compared to Kelvin cell structures (see *Fig. 2*). To further enhance the heat transport, additionally tilted Diamond cell structures were investigated.

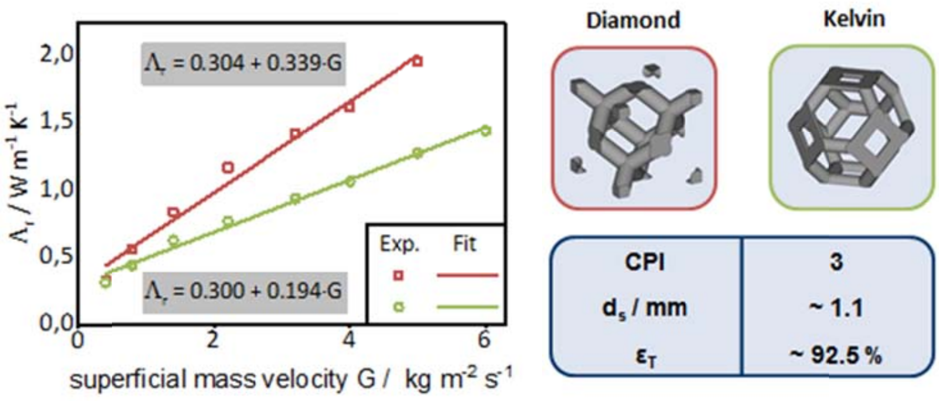

Fig. 2. Effective radial thermal conductivity in dependence of the mass velocity for a Diamond and a Kelvin cell structure

Furthermore, first rigorous optimization studies were performed, which show the possibility of the geometric optimization of the structures according to the needs of the reaction system using the determined heat transport model.

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OP-I-32

INFLUENCE OF THE GAS PHASE ON HYDRODYNAMICS AND GAS TRANSFER IN A STIRRED TANK UNDER ANAEROBIC DARK FERMENTATION CONDITIONS

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Fontaine J.-P.[1], **Vial Ch.**[1]

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Dark fermentation (DF) is an anaerobic process similar to anaerobic digestion (AD) in which methanogenesis has been suppressed. Thus, it is able to convert organic waste into a biogas enriched in hydrogen, and a liquid digestate rich in volatile fatty acids. This process is environment friendly, but economic sustainability can be reached only if power input for pumping and mixing is low, below 8−10 W/m^3 [1].

Mixing has already been shown to play a key role on the performance of DF, but the effect of the gas phase remains unknown in mechanically-stirred fermenters up to now. Even though biogas production rate remains low in DF, usually below 2.5 10^{-2} VVM [2,3], far below than in aerobic reactors usually operated at 1 VVM or more, this value is, however, far higher than in AD which is around 15 10^{-3} VVM. The objective is, therefore, to investigate the effect of the gas phase on hydrodynamics and mixing in a mechanically-stirred anaerobic fermenters under the conditions of DF.

In this study, the respective effects of fluid rheology, rotation speed (N) and gas flow rate (G) were analyzed using Newtonian and non-Newtonian shear-thinning model fluids, covering flow conditions from laminar to turbulent in a 2-L cylindrical baffled bioreactor equipped with dual Rushton turbines. Image analysis was used to determine bubble size and the spatial distribution of the gas phase; the velocity and turbulence local flow fields were measured using PIV, fluorescent tracer particles with a specific treatment to distinguish both phases; PLIF was applied to derive mixing time; also, the volumetric gas liquid-mass transfer (k_La) was estimated locally using a Clark electrode. Experimental results were also compared to available data on single-phase flows measured in the same bioreactor under the same conditions.

Experimental data highlighted that rheology plays a key role on bubble size, as coalescence phenomena were prevented by shear-thinning fluids. Conversely, the shear-thinning behavior enhanced spatial heterogeneity which emerged not only from PIV data by the generation of caverns when the flow index decreased, but also by a spatial distribution of k_La values which fell close to the tank walls. This effect could be partially counterbalanced when *N* was increased. Experimental results also demonstrated that if *G* did not strongly affect the liquid velocity and turbulence flow fields close to the impellers, these were more significantly altered between the Rushton turbines where bubbles more significantly contributed to mixing. This effect was, however, dampened when the shear-thinning behavior of the fluid increased.

Finally, contrary to mechanically-stirred anaerobic digesters in which the biogas produced in situ plays a negligible role on hydrodynamics and mixing, this cannot be disregarded in DF. While the Reynolds number (Re) still remains the key parameter to describe univocally global features, such as mixing time and k_La (Fig. 1), CFD simulations must either involve multiphase flow models, or include an additional mixing process accounting for the gas phase in single-phase simulations.

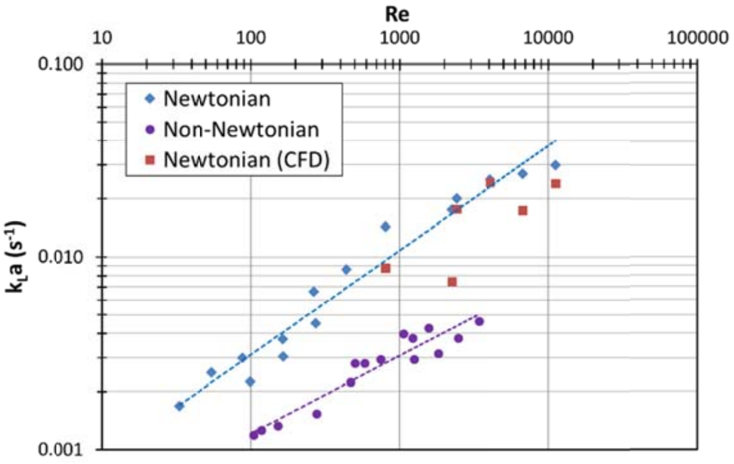

Fig. 1. Evolution of k_La vs. Re at 0.04 VVM for Newtonian and non-Newtonian shear-thinning fluids, and comparison with CFD simulations

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MODELING OF INTERNAL TRANSPORT LIMITATIONS IN CATALYTIC PARTICULATE FILTERS

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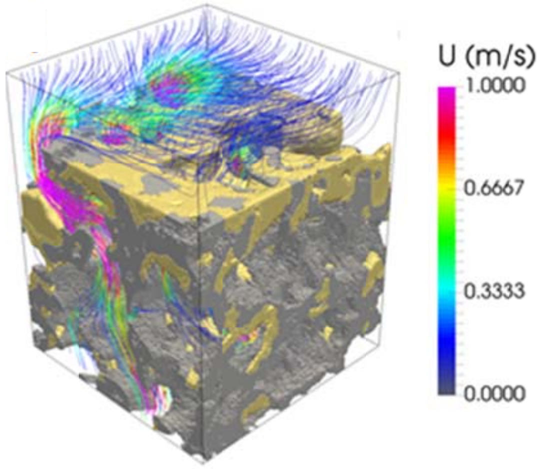
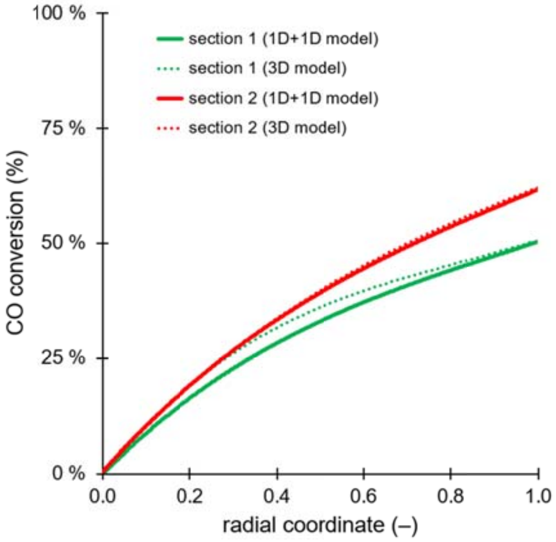
A catalytic particulate filter used for automotive exhaust gas aftertreatment is traditionally described by so-called 1D+1D model that uses 1D plug flow inside the channels and 1D transport and reactions across the filter wall [1]. A recently developed 3D model may be utilized for micro-scale simulations of gas flow, diffusion and reactions inside the catalytic filter wall [2]. The detailed model works with a 3D reconstructed porous medium which represents the realistic morphology of pores and catalytic coating obtained from X-ray microtomography. The effective properties of the wall, such as permeability and filtration efficiency, are received by spatial averaging of the computed 3D profiles. These effective values are applied as input parameters for the overall 1D+1D model [1].

The reactions occur only in the zones coated with catalytic material, which is located inside large macropores of the filter wall. Despite the convective transport of reactants through the wall, part of the active sites inside the coated domains is still accessible only by slow diffusion through small internal pores in the coating, because gas flows predominantly through large open pores. In this paper we present a methodology and comparative study for the prediction of internal limitations in catalytic filters with various spatial distribution of the catalyst inside and/or on top of the filter wall.

To describe the extent of this diffusion limitation in the 1D+1D model, we use a modified concept of the effectiveness factor $\eta = r^{\mathrm{obs}}/r$, where r^{obs} is the observed reaction rate and r is the reaction rate without any diffusion limitation. The effectiveness factor can be calculated from Thiele modulus which involves characteristic diffusion length, reaction rate constant and diffusivity [3]. In order to obtain the estimate of the diffusion length that characterizes the coating distribution in the wall, we first perform detailed 3D pore-scale simulation in the reconstructed filter wall and calculate spatially averaged 1D concentration profile over the wall [2], and then fit the value of the characteristic diffusion length in the 1D model to match this profile [4]. The value of the diffusion length characterizes accessibility of the catalytic coating inside the filter wall (the larger is the diffusion length, the less accessible the catalytic sites are).



Flow profile through the wall structure obtained from detailed 3D model



CO conversion profiles in wall – spatially averaged profiles from the 3D model and profiles from the improved 1D+1D model

To demonstrate and validate this approach, Thiele moduli and effectiveness factors of catalytic CO oxidation are calculated for several different structures of real catalytic filter samples under various operating conditions (stoichiometric mixture or lean mixture with oxygen excess, high or low CO concentration) and the corresponding characteristic diffusion lengths are evaluated. We further apply and compare the analytical relations of Thiele modulus for different types of reaction kinetics: pseudo-first order, pseudo-second order and Langmuir-Hinshelwood [5]. Light-off curves for catalytic filters with varying distribution of catalytic coating are predicted and the impact of internal diffusion limitations on the conversion under realistic operating conditions is discussed.

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OP-I-34

HEAT TRANSFER ANALYSIS ON α-Al_2O_3 AND TiO_2 AS SUPPORT MATERIALS FOR THE OXIDATIVE DEHYDROGENATION OF ETHANE (ODH-C_2) IN AN INDUSTRIAL WALL-COOLED PACKED BED REACTOR

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Packed bed reactors with low tube to particle diameter ratio ($d_t/d_p < 10$) are, on the one hand, industrially used to carry out highly exothermic reactions, such as the selective oxidation of o-xylene to produce phthalic anhydride [1], selective oxidation of ethylene to ethylene oxide [2], among others selective oxidations [3]. On the other hand, this type of reactors are of great interest for carrying out promising reactions such as the oxidative dehydrogenation of ethane (ODH-C_2) to produce ethylene [4], due to its low environmental, energetic and economic impact compared to the conventional process to produce this olefin, i. e., thermal cracking.

Due to the exothermicity of this type of reactions, mainly the total oxidations, the geometrical configuration, low d_t/d_p, and non-porous support, i. e., α-Al_2O_3 [5] and TiO_2 [1], favors the dissipation of the reaction heat. Otherwise, higher hot spots can be obtained in the bed, which could lead to a runaway situation as well as an irreversible deactivation of the catalyst. Although there are many works in literature trying to characterize the heat transfer mechanisms within this type of packed reactors with low d_t/d_p [4], a lot of uncertainties remain about their modeling. This limits both the design of new processes and the optimization of the existing ones. Some of the main drawbacks are: high statistical correlation between the estimated effective heat transfer parameters, plug flow velocity profile rather than a velocity field which influence on local temperatures. Secondly, the description of steady state rather than transient state observations. Thirdly, there is no clarity on the role of the radial velocity component on heat transfer mechanisms. Yet among other concerns remain [6].

This work focuses on the analysis of heat transfer with and without reaction in a wall-cooled packed bed reactor with low d_t/d_p, aimed to carry out the ODH-C_2 over a Ni-based material externally deposited on two types of supports, i. e., α-Al_2O_3 and TiO_2

(anatase). This analysis accounts for the design of heat transfer experiments in absence of reaction, their modeling by evaluating different approaches to overcome some heat transfer drawbacks and, finally, the evaluation of these approaches by describing the performance of an industrial scale reactor where the ODH-C_2 takes place.

To reach this aim, a design of heat transfer experiments in absence of reaction is performed on a bench-scale bed which is operated in either quasi-adiabatic or non-isothermal and non-adiabatic mode, see Figure 1. On the other hand, pressure drop experiments were carried out to characterize the hydrodynamics in the bed, see Figure 2. Hydrodynamic and heat transfer studies used spherical pellets of TiO_2 (anatase) with a particle diameter of 8.2 mm, and cylindrical pellets of α-Al_2O_3 with a particle diameter of 6.667 mm and 7.43 mm of length. Particle Reynolds numbers (Re_p) similar to those found in industrial processes, i. e., Re_p 0 – 1400 were achieved. Finally, the industrial reactor performance was modeled using the estimated effective heat transfer parameters, and a kinetic model developed within the research group for the ODH-C_2 on two materials: MoVTeNbO [7] and a NiSnO [3].

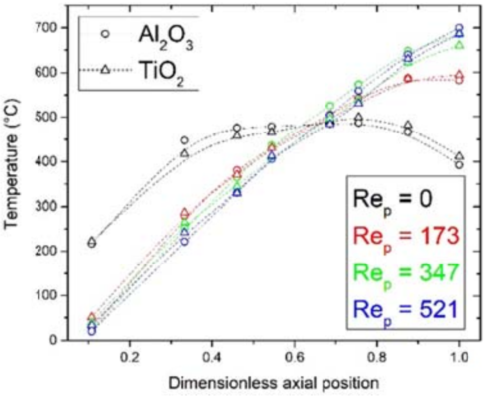

Figure 1. Experimental axial steady state measurements

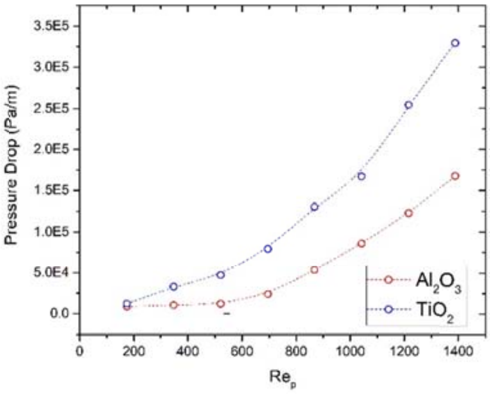

Figure 2. Experimental pressure drop measurements

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OP-I-35

CO_2 METHANATION AND REVERSE WATER GAS SHIFT REACTION. KINETIC STUDY BASED ON *IN-SITU* SPATIALLY-RESOLVED MEASUREMENTS

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Introduction

The design of CO_2 methanation reactors for the Power-to-Gas process requires a detailed understanding of the reaction mechanism and its corresponding kinetic description. In-situ spatially-resolved measurements of the gas composition profile and catalyst surface temperature enable the collection of a much larger set of kinetic data compared to the traditional steady-state packed bed reactors with end-of-pipe measurements as they combine differential and integral methods.

Experimental and Modeling

Ordered mesoporous nickel-alumina [1] (~30 wt % Ni/Al_2O_3) catalysts were synthesized, coated onto a metal plate, and placed in the bottom of a new optically accessible channel reactor with spatially resolved capabilities for kinetic data acquisition [2,3]. Kinetic experiments were conducted from 320 to 420 °C, 1.2 to 7.3 bar_{abs}, with different reactants (CO_2, H_2) and products (CH_4, H_2O, CO) partial pressures. The catalyst surface temperature with a resolution of 9 data points per mm^2 was determined via IR thermography, while the gas composition was determined via a movable sample capillary (0.5 mm diameter). A one dimensional reactor model in combination with the Bayesian approach was used to estimate kinetic parameters of 20 proposed Langmuir-Hinshelwood rate expressions for the CO_2 methanation and reverse water gas shift reaction (RWGS) assuming different rate-determining steps. Model discrimination was based on posterior probability share as well as on Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) experiments to identify adsorbed surface species.

Results and Discussion

More than 21,000 data (gas composition profiles) were collected, which allowed for a detailed kinetic analysis. The model with the highest probability share follows a hybrid mechanism in which the first C–O bond dissociation of the adsorbed CO_2^* to CO* is rather fast, while the second C–O bond cleavage is hydrogen assisted (COH* complex) and the slowest step (COH* + H* ↔ CH* + OH*). Water was assumed to be adsorbed as a hydroxyl species (OH*), while methane did not influence the reaction. The best fit model could correctly predict the behavior over the complete range of temperature, pressure (Fig. 1 left) as well as for direct biogas methanation. The addition of the RWGS and the use of spatially-resolved kinetic data represents nicely the CO formation via RWGS at the beginning and after 20 mm the subsequent CO conversion. Time-resolved DRIFTS measurements validated the assumed reaction mechanism by confirming the presence of COH*, OH* as well as surface formates as depicted in Fig. 1 right.

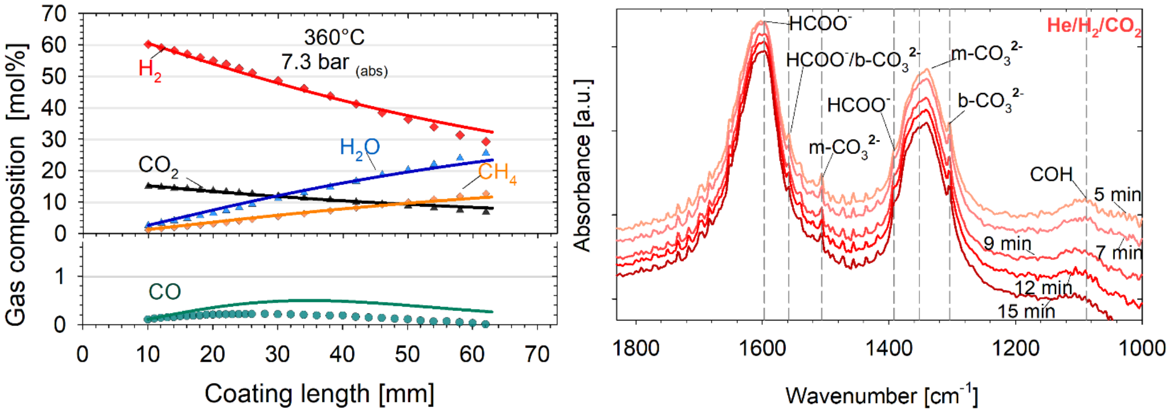

Fig. 1. Left: Measured (symbols) and calculated (solid line) gas species concentrations. Right: Time-resolved DRIFTS collected at 350 °C

The activation energy of the CO_2 methanation and RWGS reactions are 79.7 kJ mol^{-1} and 194.7 kJ mol^{-1}, respectively. The value for the CO_2 methanation is similar to literature [4], whereas the RWGS differs.

Conclusions

In this work, a comprehensive set of kinetic data was collected in an optical catalytic plate reactor with spatially resolved measurement capabilities. By applying a one-dimensional reactor model, the kinetic parameters of the CO_2 methanation and RWGS were estimated, and the assumptions on the RDS were validated via spectroscopy.

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OP-I-36

IMPROVED CATALYTIC PLATE REACTOR (CPR) DESIGN FOR HIGH QUALITY KINETIC DATA GENERATION USING EXPERIMENTS AND CFD MODELING

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Introduction

Kinetic experiments commonly use small laboratory packed bed reactors with end-of-pipe measurements. Utilizing an integral reactor like our recently developed optically accessible catalytic plate reactor (CPR) (40 x 100 x 5 mm) with spatially resolved measurement capability allows for collecting high-resolution gas composition and catalyst surface temperature profiles along the reactor axis via a small movable sampling capillary and short-wave infrared camera, respectively [1]. The CPR represents a reactive flow between two parallel plates (i.e., catalyst coated bottom plate and quartz glass top plate). The goal of this work is to understand the hydrodynamic, and mass and heat transfer effects on the kinetic data generated and use it to develop design guidelines for the next generation CPR.

Experimental and Modeling

Inlet manifold, sampling capillary design and reactor aspect ratio (Width/Height) have a significant impact on the internal flow phenomena. The effect of each is independently investigated using the catalyticFOAM [2] framework; a CFD numerical solver based on OpenFOAM able to couple the solution of Navier Stokes with mass and energy balance coupled with detailed modeling of heterogeneous chemistry. A 3D reactive CFD model of the CPR reactor with CO_2 methanation kinetics is developed and validated against a comprehensive set of experimental data collected over a broad range of operational conditions (280-420 °C, 1.2-7.3 bar_{abs}, 50-150 ml (STP)/min). Two inlet manifold configurations (i.e. centrally located inlet and side inlet) are compared.

Results and Discussion

The mesh independent CFD model predictions for the final CO_2 conversion compare against experimental data with <1 % error and species molar concentration shows good agreement along the length of the reactor (Fig. 1 (a)). The validated

CPR model is used to perform sensitivity study over a range of temperature (300-400 °C) and pressure of (1.2-7 bar_{abs}).

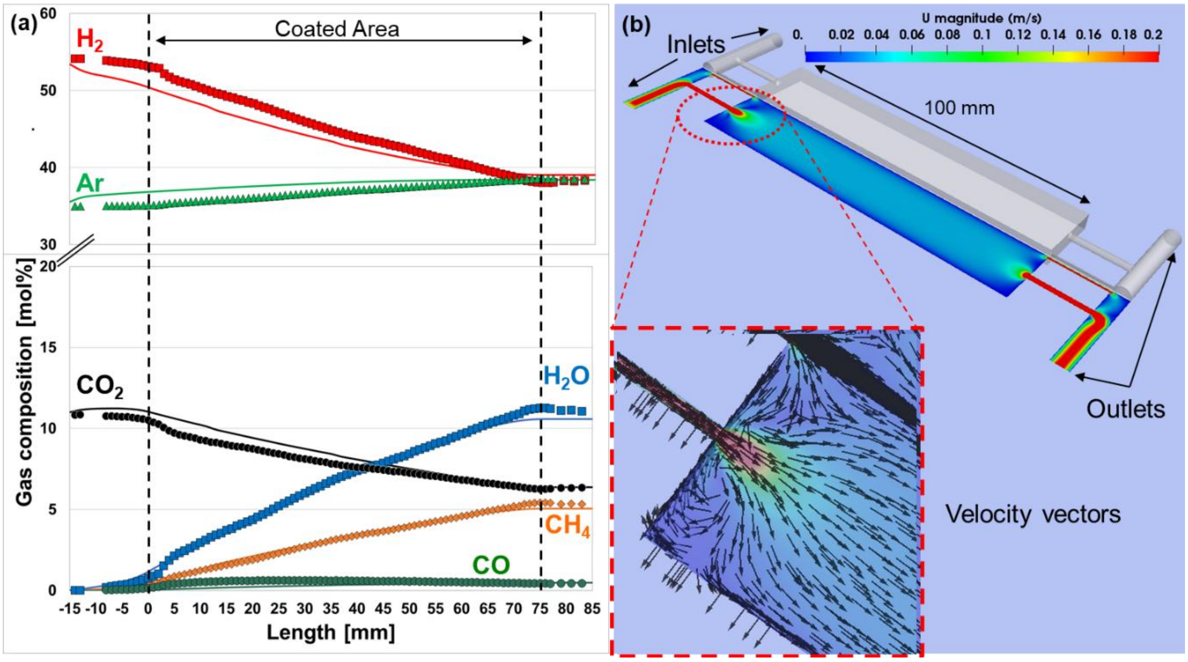

Fig. 1. (a) Measured vs CFD model values for axial gas composition profiles. (CPR experiments:150 ml_N/min, 360 °C, 1.2 bar and $H_2/C = 5$) (b) velocity contours and local velocity vectors on a horizontal plane in the CPR reactor. (reactive CFD model:150 ml_N/min)

Among the three channels present in the inlet manifold, the central channel has the least flow due to the reduction in flow area by the passing capillary. The rapid increase in area at the end of the inlet manifold results in recirculation of flow in this region (Fig. 1 (b)). This secondary flow is present at all the investigated flowrates and it dissipates in the initial 20 mm into the reactor for the 150 ml (STP)/min case. This recirculation is minimized by reduction in aspect ratio of geometry and better flow distribution in the inlet manifold.

Conclusions

In this work, a set of design guidelines were developed for the next generation CPR including the optimal width to length ratio for studying fast reactions, inlet manifold design and sampling capillary design. These insights were developed using CFD modeling studies of the CPR reactor that were validated with the data collected in an optical catalytic plate reactor with spatially resolved measurement capabilities.

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OP-I-37

KINETICS COUPLED WITH RADIATIVE TRANSFER UNDER VISIBLE LIGHT OPERATION REACTIONS ON GRAPHENE OXIDE

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Introduction

The design of a photocatalytic reactor requires a model accounting for the interaction among kinetics, mass transport and radiative transfer. The key variable relating them is the Local Volumetric Rate of Energy Absorption (LVREA) [1]. However, its reliability depends on the adequate determination of the suspended catalyst optical properties, such as: the specific extinction coefficient, β^*; the scattering ratio, γ; the Henyey-Greenstein phase function form parameter, g [2]. A study that allows the determination of the optical properties grants, in turn, the possibility to relate and understand the interaction among kinetics and radiative transfer. It is in this sense, that the kinetic evaluation of the production of hydroxyl radicals ($OH^\bullet$) and holes (h^+), species that appear when the catalyst is excited, allows the connection between the amount of light absorbed locally and the production of these species. By understanding this relation it is possible to assess a reaction and with the obtained information, aid the elucidation of a possible reaction mechanism and the determination of the reaction rates. In this regard, in this work we present a theoretical and experimental methodology that allows the kinetic evaluation of the production of photocatalytic intermediate species such as h^+ and $^\bullet OH$, coupled with the radiative transfer for graphene oxide (GO) as a promising material for visible light absorption. Results are compared to those obtained for the state-of-the-art photocatalyst reference, TiO_2 Degussa P25.

Materials and Methods

Degussa P25 TiO_2 is used as reference material while graphene oxide (GO) is prepared through the oxidation of graphite powder (nanoparticles) via a modified Hummers method [3] that removes the usage of sodium nitrate ($NaNO_3$). An in-house developed methodology, where macroscopic light measurements are utilized for independent optical properties determination, is used. While the kinetic evaluation of the $^{\bullet}$OH is carried out qualitatively through photoluminescence (PL) and quantitatively via HPLC [4]. As for the h$^+$, ammonium oxalate is used as hole scavenger [5].

Results and discussion

The optical parameters herein presented show that the Degussa P25 catalyst has less than 1 interaction with light per meter and per unit of concentration, under the visible range, while it disperses 81 % of the light it interacts with mainly in a forward fashion as described by the g value. It is worth noting that for the sake of this abstract only Degussa P25 TiO_2 results are shown.

Table 1. Degussa P25 TiO_2 Optical Properties

β^*	γ	g
0.78 $ppm^{-1}m^{-1}$	0.81	0.76

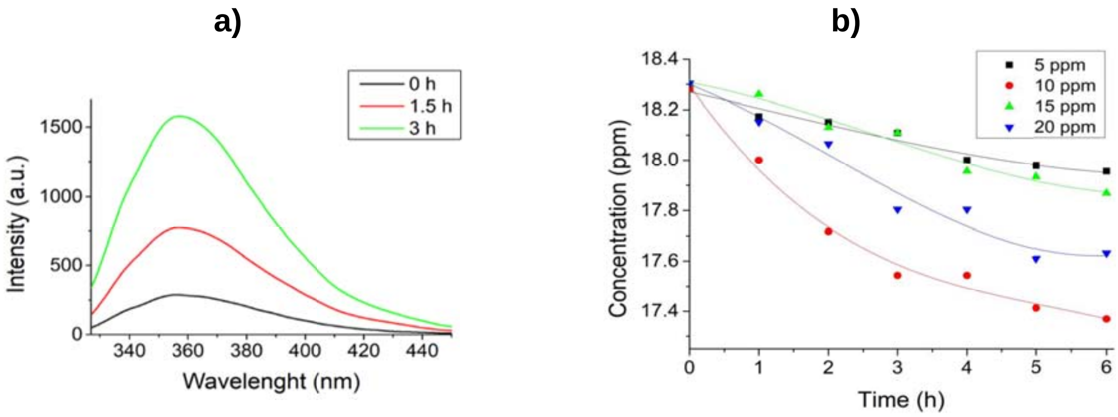

Figure 1. a) Hydroxyl radical assessment via PL and b) IC photodegradation

Fig. 1a shows the increase of $^{\bullet}$OH radicals over time for 10 ppm of Degussa P25 while Fig. 1b displays the degradation of Indigo Carmine (IC) as model molecule, achieving the highest yield for 10 ppm.

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OP-I-38

DEVELOPMENT OF A MACROSCOPIC MODEL FOR HYDRODYNAMICS IN FIXED BED REACTORS WITH LOW d_t/d_p RATIO

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Industrial wall-cooled fixed bed reactors (FBR) with low tube-to-particle diameter ratio (d_t/d_p<10) have been widely studied in academia and industry as their application for carrying out highly exothermic reactions of interest for the petrochemical industry [2,3]. Due to the high computational costs of the local scale description, modeling of this type of reactor uses effective medium equations or pseudo-homogenous equations expressed in terms of effective medium coefficients. In particular, for momentum transfer, these models are based on the semi-deterministic Darcy-Brinkman-Forchheimer (DBF) equation, in which the effective coefficients are determined out of a parameter estimation strategy based on a proper experimental design and regression analysis [4]. Nevertheless, the experimental cost, regression limitations, and the limited operational range where the effective coefficients present confidence lead to the proposal of alternative strategies to determine these effective coefficients.

This work aims at developing effective medium equations by using the volume averaging method (VAM) [1], for describing momentum transfer in a FBR presenting a low d_t/d_p ratio and accounting for the incompressible single-phase flow. The resulting average equations contain terms of position-dependent effective medium coefficients, i.e., a total inertial tensor ($\mathbf{J}_\beta$) and an apparent permeability tensor ($\mathbf{H}_\beta$). These coefficients are herein obtained by solving the associated local closure problems. In addition, it is worth mentioning that the average equations account for the second Brinkman's correction that arises by considering the spatial variations of the void fraction.

Macroscopic equations are applied during the hydrodynamic description of an industrial-scale FBR packed with an arrangement of spherical pellets, presenting a

d_t/d_p = 3.09, and operated at a particle Reynolds number (Re_p) from 700 to 1400. The effective coefficients involved in the equations were computed by solving the associated local closure problem and from direct numerical simulations (DNS) in a representative element of volume of the FBR. For the sake of brevity, herein, we only present results at Re_p = 1400. Fig. 1 displays the radial variation of the apparent permeability and the void fraction determined out of DNS. The inclusion of these coefficients in the effective medium equations allowed the prediction of the average velocity profile in the FBR, vide Fig. 2; this velocity profile was, to this end, compared to that profile obtained out of DNS and the conventional model (DFB). It is worth noting that the developed average equations led to better results than the DBF model when comparing their predictions with those of obtained out of DNS. Similar results were obtained at others Re_p. As conclusion, we developed a hydrodynamic model, without the need of estimating effective transport parameters, able to capture the physical phenomena involved in a FBR with low d_t/d_p ratio.

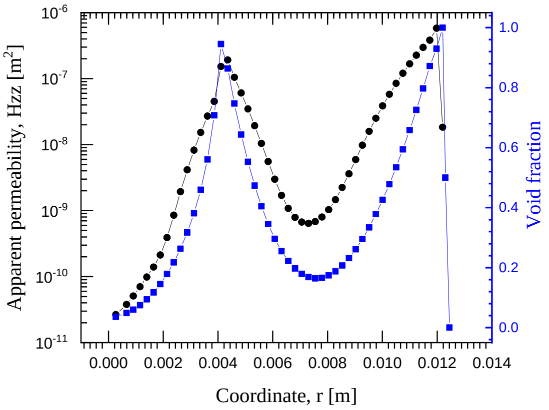

Fig. 1. Radial variations of the permeability and void fraction in the FBR obtained from DNS and volume integration of the geometry, respectively

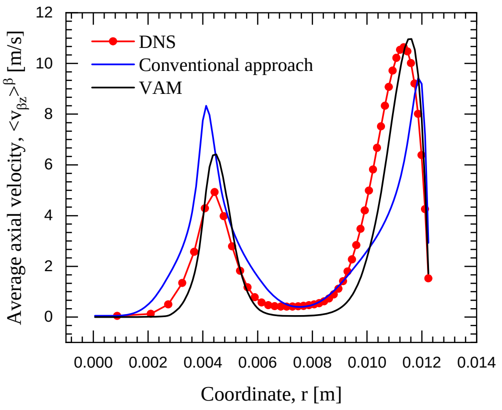

Fig. 2. Comparison of the axial average velocity profile in the FBR obtained from DNS, conventional DBF equation, and VAM

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OP-I-39

A DNS BASED EFFECTIVE MEDIUM MODEL FOR COMPRESSIBLE FLOW IN A FIXED BED REACTOR WITH LOW d_t/d_p

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Fixed bed reactors (FBR) are normally used in ca. 70 % of industrial applications. The wall-cooled FBR with low tube to particle diameter ratio ($d_t/d_p<10$) is used to carry out highly exothermic reactions of interest for the petrochemical industry. The low d_t/d_p ratio favors heat dissipation along the radial coordinate of the bed; however, it also generates prolongate changes in void fraction and local velocity, which in turn influences local mass and heat transport, and hence, kinetics and catalyst deactivation [1,2]. Computational Fluid Dynamics (CFD) has been employed as a tool to investigate the fluid flow and heat transfer in fixed beds with low d_t/d_p ratio. Nevertheless, when coupled to the other transport phenomena, reaction, and catalyst deactivation, there is a significative increase in the computational time; in fact, to best of our knowledge, CFD has only be applied to model a FBR with lower dimensions than those involved in an industrial system [3,4]. On the other hand, effective medium models are used in the description of FBR, nevertheless, all mechanistic information is captured through effective descriptors, or effective parameters, accounting for the magnitude of the different associated transport phenomena. In most of publications related to hydrodynamics in FBR, incompressibility of the fluid is neglected, and effective parameters are determined out of experiments. This work is aimed at developing an effective hydrodynamic model accounting for fluid compressibility in a FBR with a $d_t/d_p = 3.1$. The development of this model makes use of local average information derived from direct numerical simulation (DNS). The packed bed consists of a tube of 10 cm with an internal tube diameter of 2.46 cm. This tube is packed with spherical pellets of 0.8 cm of diameter. Compressible Navier-Stokes equations used during DNS. On the other hand, the effective medium model developed in this work is given by the following equations:

$$\nabla \cdot \left(\rho_f \langle \mathbf{u} \rangle \right) = 0 \qquad (1)$$

$$\frac{\rho_f}{\phi(\mathbf{r})}\left(\langle\mathbf{u}\rangle\cdot\nabla\left(\frac{\langle\mathbf{u}\rangle}{\phi(\mathbf{r})}\right)\right)=\nabla\cdot\left[-\langle p\rangle^f\mathbf{I}+\frac{\mu_f}{\phi(\mathbf{r})}\left(\nabla\langle\mathbf{u}\rangle+\nabla\langle\mathbf{u}\rangle^T\right)-\frac{2}{3}\frac{\mu_f}{\phi(\mathbf{r})}\left(\nabla\cdot\langle\mathbf{u}\rangle\right)\mathbf{I}\right]-\mu_f\mathbf{D}(\mathbf{r})^{-1}\cdot\langle\mathbf{u}\rangle+\rho_f\mathbf{g} \qquad (2)$$

Where $\phi(\mathbf{r})$ is the fluid void fraction profile, $\langle\mathbf{u}\rangle$ is the superficial velocity vector, $\langle p\rangle^f$ is the intrinsic pressure which relates to its superficial form as $\langle p\rangle=\phi(\mathbf{r})\langle p\rangle^f$, $\mathbf{D}(\mathbf{r})$ is a term taking into account the contribution of those forces acting on the solid-fluid interphase. $\mathbf{D}(\mathbf{r})$ is obtained out of DNS. Figure 1 presents a first evaluation of the effective medium model. Figure 1a displays the radial apparent permeability profile obtained from DNS. Two maximum values are observed in the apparent permeability profile, these maximums are consistent with those values obtained for the local void fraction. Figure 1b compares the averaged velocity profile obtained by DNS and that one predicted by the developed effective medium model. The proposed model describes velocity profile better than the conventional Navier-Stokes-Darcy-Forchheimer (NSDF) model, in fact, our model describes successfully the velocity profile near to wall region, what is a challenge when developing the conventional hydrodynamic model. The hydrodynamic model developed herein will be implemented to describe heat and mass transfer with and in absence of reaction in future works.

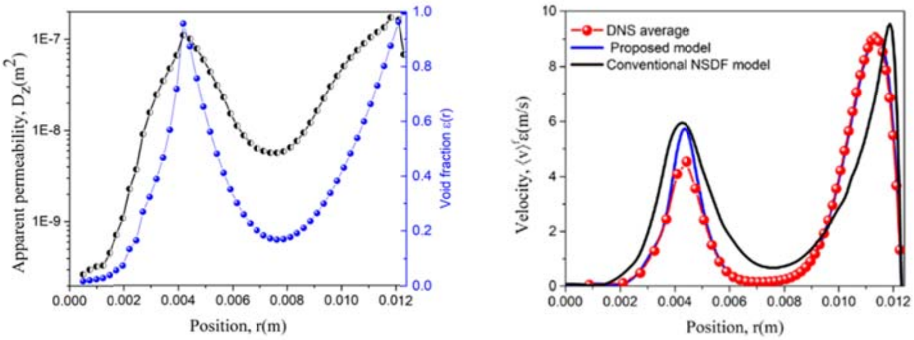

Figure 1. a) Radial apparent permeability profile determined from DNS and radial void fraction profile, b) Comparation between radial velocity profile from DNS, proposed effective model and conventional NSDF model

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ORAL PRESENTATIONS
Section II.
Chemical Reaction Engineering and Reactor Design – Novel Experimental Approaches, Modeling, Scale-Up and Optimization

OP-II-1

CONVERSION OF METHANE INTO HYDROGEN OR OLEFINS: A STUDY EVALUATING DIFFERENT REACTORS

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In this presentation I will discuss two investigations concerning the conversion of methane: i) reaction over α-Al_2O_3 surfaces, ii) reaction in a pulsed compression reactor (PCR). In these reactors essentially the same reaction proceeds. Though, in the PCR the reaction is terminated at C_2H_4 while over the α-Al_2O_3 it is driven to completion.

Reaction over α-Al_2O_3 surfaces

The pyrolytic conversion of methane for the production of hydrogen and carbon was investigated over nonporous α-Al_2O_3 surfaces in the range of 900-1300 °C. Two devices were used: i) a single particle reactor to determine the carbon deposition rate at various temperatures and ii) a fixed bed in which both methane conversion and carbon deposition were measured. It was observed that at 1000 °C and below, the selectivity towards carbon (and hydrogen) was initially low over fresh α-Al_2O_3 (e.g. 38 % at 250 s reaction time), increasing to 100 % over time. Methane conversion was constant at 20 % during this period. These observations point towards the presence of an activation process for the formation of carbon and hydrogen from the intermediates products (e.g. benzene) of methane pyrolysis. A temperature dependent maximum in carbon loading was observed. When this maximum carbon loading was reached, methane conversion also stopped completely, indicating 100 % selectivity towards carbon and hydrogen. Two kinetic models for carbon deposition were derived and applied. After parameterization of these models using single particle data, they were able to predict carbon growth and CH_4 conversion as function of temperature, specific bed area, carbon loading and gas composition in the new data set from the fixed bed.

Pulsed compression

Pulsed compression is introduced for the conversion of methane, by pyrolysis, into ethylene. At the point of maximal compression temperatures of 900 to 1620 K were reached, while the initial and final temperature of the gas did not exceed 523 K. By the use of a free piston reactor concept pressures of up to 460 bar were measured with nitrogen as a diluting gas. From 1100 K onwards methane conversion was measured. By increasing the temperature, the mechanism of pyrolytic methane conversion, being subsequent production of ethane, ethylene, acetylene, ..., benzene, and ultimately tar/soot, was clearly observed. Without hydrogen in the feed, the attainable operating window (C2-selectivity vs. methane conversion) observed was similar to other catalytic oxidative and non-oxidative coupling processes. With hydrogen, in a first attempt to optimize the product yield, 24 % C2-yield (62 % ethylene selectivity, 93 % C2-selectivity) at 26 % conversion was reached without producing observable soot. It is worthwhile to explore pulsed compression further because it does not require a catalyst and therefore, does not deactivate over time and it operates at low reactor temperature.

OP-II-2

KINETIC INSIGHTS INTO CO_2 ACTIVATION VIA REVERSE WATER - GAS SHIFT ON Rh CATALYSTS

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Nowadays, the CO_2 in the atmosphere is the major factor causing global warming. The concentration of carbon dioxide highly increased in the last decades due to anthropogenic emissions, causing an imbalance of the natural carbon cycle [1]. Hence, governments are adopting strict policies to lower CO_2 emissions. A promising route is the reduction of the emitted carbon dioxide using green hydrogen, as a co-reactant, getting rid of the emissions caused by processes that are difficult to replace. In this context, the reverse water-gas shift (RWGS) reaction is a valid alternative for the consumption of carbon dioxide, producing CO, a fundamental building block of the chemical industry. Moreover, the RWGS reaction is involved in all the systems where the feed is composed of high concentrations of CO_2 and H_2 (e.g. CO_2 to methanol, CO_2 to methane). The RWGS reaction can occur through 3 main reaction mechanisms: (i) CO_2 dissociation pathway, (ii) COOH* pathway, (iii) HCOO* pathway. This reaction has been and is widely studied by researchers, but there is still debate concerning the actual reaction mechanism and how the operating conditions affect the prevalent mechanism [2].

The kinetic mechanism of the reverse water-gas shift reaction on 4 wt % Rh/ α-Al_2O_3 catalyst was investigated, in a wide range of operating conditions at ambient pressure. The catalytic tests were performed in an annular reactor with proper design to be in a chemical regime. The effects of the reactants (CO_2 and H_2) and products (CO and H_2O) concentrations were studied (Figure 1) and experiments were performed at different temperatures to calculate the apparent activation energy (T = 600-750 °C). The reaction rate was calculated according to the differential method. RWGS reaction rate was strongly influenced by CO_2 partial pressure with a linear dependence on CO_2 until the approach to the stoichiometric ratio of the RWGS reaction $CO_2 / H_2 = 1$, after which the dependence is still linear but with a smaller slope (Figure 1a). The rate was mildly influenced by H_2 partial pressure, with a linear dependence on CO_2 until the approach to the stoichiometric ratio of the RWGS reaction CO_2 / H_2 = 1, after which the dependence started to have a smaller slope, becoming almost negligible (Figure 1b). Moreover, H_2O did not affect the reaction rate (Figure 1c), while there was a small inhibition effect of CO (Figure 1d), which was more prominent at the highest CO_2 / H_2 ratio investigated. How the reactants affect the reaction rate depended on the CO_2 / H_2 ratio. The RWGS reaction was found to occur via two parallel pathways whose kinetic relevance was found to change as a function of the CO_2/H_2 ratio. The two mechanisms could be identified as the CO_2 dissociation to CO* and O* pathway and the CO_2 activation through COOH* formation pathway. At increasing CO_2 / H_2 ratio the rate depends more on CO_2 and H_2 concentrations (COOH* path), while at decreasing CO_2 / H_2 ratio the rate depends less on H_2 concentrations but keeping the dependence on CO_2 (CO_2 dissociation path). The derived mechanism was used to propose a kinetic law considering the observed duality of the reaction pathways and to shed light on the identity of the elementary steps that mediate the reaction at the different operating conditions.

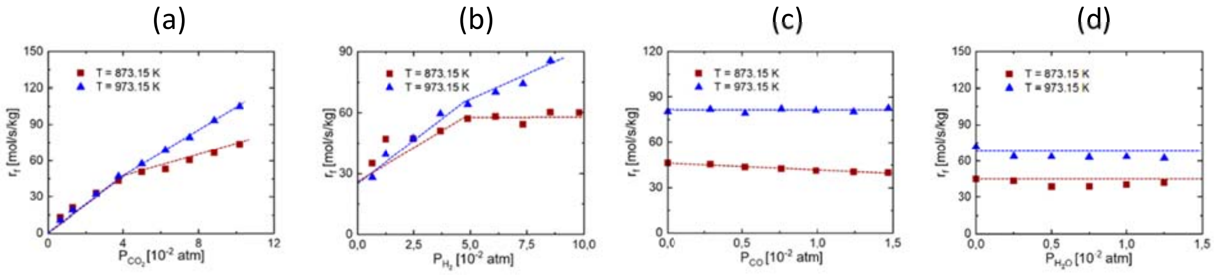

Figure 1. Effect of CO_2 (a), H_2 (b), CO (c) and H_2O (d) partial pressure on forward RWGS reaction rate on 4 wt % Rh/Al_2O_3. ((a) H_2 = 5 %, (b) CO_2 = 5 %, (c, d) H_2 = 5 %, CO_2 = 5 %, balance N_2)

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OP-II-3

COMPUTATIONAL FLUID DYNAMICS SIMULATION OF DECOKING IN STEAM CRACKING REACTORS

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Steam cracking of hydrocarbons is and will continue to be the main industrial process to produce light olefins in the coming decades. A major factor for the process efficiency is the formation of a coke layer on the inner surface of the tubular shaped cracking reactors. Due to this insulating carbonaceous layer, heat transfer to the process gas is hampered, leading to excessively high tube metal temperatures. Additionally, the cross sectional area for flow is reduced and the reactor pressure drop increases, resulting in a loss of olefin selectivity. Decoking of industrial reactors, which is accompanied by CO_2 emissions that don't result in production of light olefins, is thus inevitable. In consideration of this energetic and economic drawback, many efforts have been made towards the development of technologies to reduce coke formation. Three-dimensional (3D) coil geometries are often introduced to enhance radial mixing resulting in lower coking rates and longer run lengths. In previous work [1], we developed a methodology to simulate coke layer growth in these 3D coil geometries, and more specifically we compared a bare tube with ribbed and finned reactor designs. In this work, a similar methodology is used to investigate the decoking process in these coils.

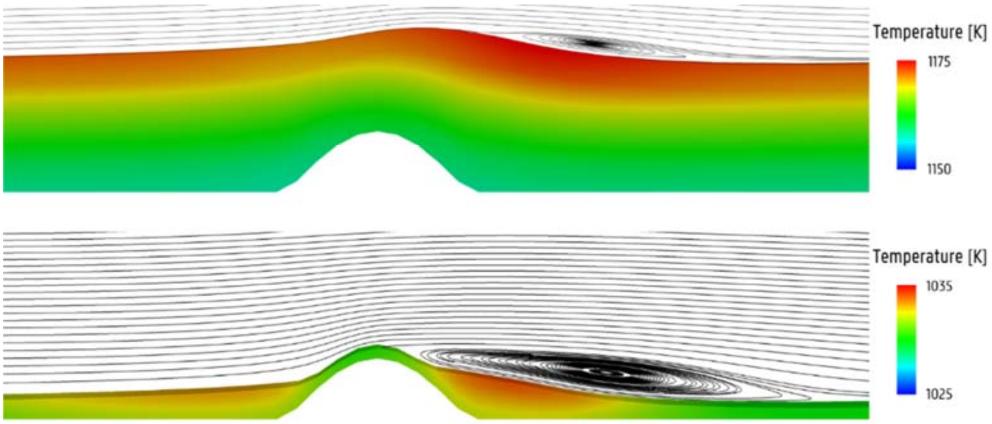

Figure 1. Representation of coke layer thickness around a rib at start of decoking (top) and after 4hr of decoking (bottom)

Accurate modeling of the decoking process can help to limit the duration of this procedure, as well as to assess the influences of 3D reactor geometries. A computational framework is presented which includes decoking surface reactions and dynamic mesh generation. As a proof-of-concept, a comparison of decoking of a bare, ribbed and finned reactor in a single-pass furnace is presented, for an industrial inlet mixture as well as for pure air. The ribbed geometry requires significantly less heating compared to the bare and finned geometries due to the enhanced heat transfer induced by the ribs. However, the risk of spalling is increased and due to lower process gas-coke interface temperatures, the decoking rate is reduced, resulting in an overall longer decoking time. The finned reactor requires a longer decoking time compared to the bare tube as well, due to the non-uniform coke thickness around the circumference, resulting in a lower average decoking rate. Additionally, due to significantly altered thermal gradients at the start of decoking compared to the end of cracking, the potential to induce cracks in the reactor tubes is increased. Simulations of pure air decoking resulted in a temperature peak exceeding the maximal allowable TMT of all currently available reactor materials and a 30K higher temperature at the inside of the reactor metal compared to the outside, relatively unaffected by the decoking time and axial coordinate. This poses risks for decoking procedures incorporating a pure air step because the TMT overshoot might not be observed in industrial practice, resulting in a deterioration of the reactor material. The insights obtained in this work can be used to further optimize decoking procedures in industrial steam cracking reactors.

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MATHEMATICAL MODELING OF AMMONIA OXIDATION TO NITROUS OXIDE IN MICROCHANNEL REACTOR

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The best-known uses of nitrous oxide are as a medical anesthetic and analgetic. In the food industry, nitrous oxide is a highly effective propellant for dispensing fatty liquids. Another popular use of nitrous oxide is a fuel additive which improves engine performance. Due to its high reactivity, nitrous oxide is also used in the synthesis of important chemicals, phenol in particular [1]. For on-purpose production of nitrous oxide, a method of catalytic oxidation of ammonia over highly selective catalyst was developed [2]. Reaction proceeds with a considerable heat release; thus, to ensure the process safety and the catalyst thermal stability, an efficient heat removal from the reaction zone is necessary. Turbulent fluidized bed reactor [3] and fixed-bed tubular reactor [4,5] proved its efficiency but were limited in the unit productivity.

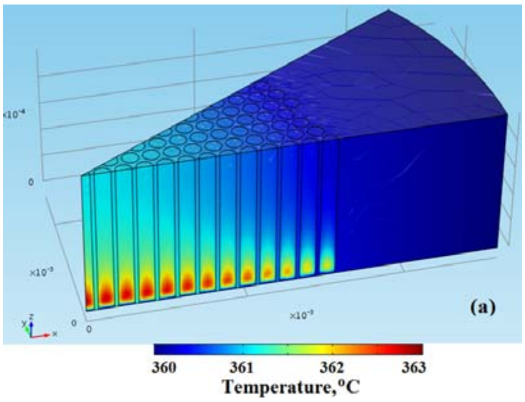
In recent years, a number of scholar studies was devoted to microchannel reactors (MCR). Since MCRs are well suited for highly exothermal heterogeneous catalytic processes [6,7], these devices would be the right choice when it comes to a small-scale production of nitrous oxide. This work presents a theoretical study of selective ammonia oxidation in a MCR over Mn/Bi/Al mixed oxides catalyst [2]. This catalyst provides a high conversion of ammonia mainly to nitrous oxide, with an almost complete absence of nitrogen oxides NO, NO_2.

MCR under study comprises a metal disc 10mm in height, 52 mm in diameter with parallel straight-through channels 1mm in diameter filled with catalyst. The mathematical model takes into account thermal conductivity of the bulk disk, axial and radial heat and mass transfer inside the reactor channels, heat transfer between the disk and the channels, catalytic reactions accompanied by a change in reaction volume inside the channels. Kinetic equations describing both the rate of nitrous oxide formation and the total rate of by-products formation, as well as the corresponding kinetic parameters, were taken from [5].

In mathematical modeling, we varied the thermal conductivity of the bulk disk λ = 70…205 J/(m s K), temperature at the edge of the disk T_{edge} = 340…370 °C and at the inlet of channels T_{in} = 280…370 °C, linear velocity u = 0.005…0.02 m/s, pressure P = 0.1…0.3 MPa, inlet concentration of ammonia C_{NH3} = 4…20 vol. %, and water C_{H2O} = 10…40 vol. %, C_{NH3}/C_{O2} = 1. The effect of the parameters on ammonia conversion (X_{NH3}) and nitrous oxide selectivity (S_{N2O}) at the outlet of reactor, on the maximum temperatures in the central (T^{c}_{max}) and peripheral (T^{p}_{max}) channels was studied. The set of differential equations was solved using COMSOL Multiphysics.

The adequacy of the MCR model was checked in [6] by fitting the experimental data on methanol to formaldehyde oxidation with simulation. The predicted data on ammonia oxidation to nitrous oxide were compared in [8] with the experimental results. Those data were obtained in a tubular reactor which can be considered as an analogue of the separate MCR channel.

The temperature distribution in the MCR shows (Fig. 1a) that the difference between T^{c}_{max} and T^{p}_{max} is no more than 1 °C, which indicates a highly efficient heat removal from the reaction zone. Due to a small temperature difference, the outlet X_{NH3} changes negligibly as well (Fig. 1b). S_{N2O} is almost constant at the channels outlet and is equal to 90.6 %. A set of parameters has been determined that allows achieving S_{N2O} > 90 % at X_{NH3} > 99 %. In this case, the difference in T_{max} between channels does not exceed 2 °C, while the difference in T_{max} and T_{edge} is no more than 5.5 °C. The values of parameters are as follows: λ = 100…170 J/(m s K), T_{in} = T_{edge} = 360…370 °C, u = 0.005 m/s, P = 0.2 MPa, C_{NH3} = 4…20 vol. %, C_{H2O} = 10 vol. %.



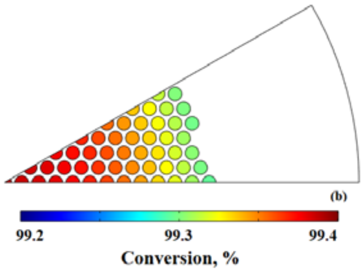


Fig. 1. Temperature distribution in the MCR (a); NH_3 conversion at the outlet of channels (b). λ = 140 J/(m s K), T_{in} = T_{edge} = 360 °C, u = 0.005 m/s, P = 0.2 MPa, C_{NH3} = 12 vol. %, C_{H2O} = 10 vol. %.

Mathematical modeling of ammonia oxidation to nitrous oxide in MCR used the model that takes into account processes both in the bulk disk and inside the reactor channels. Within the range of parameters found, the MCR operates in almost isothermal conditions; ammonia conversion and nitrous oxide selectivity are higher than 99 and 90 %, respectively. MCR can be operated at the inlet C_{NH3} as high as

20 vol. % with no catalyst overheating; herewith the yield of nitrous oxide per unit volume of catalyst shall be 5 times greater than in a conventional tubular reactor.

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OP-II-5

CFD MODELING OF THE EVAPORATION, AUTO-IGNITION AND COMBUSTION OF DROPLETS OF FPBO SURROGATE COMPONENTS

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Fast pyrolysis bio-oils (FPBO) are black-brownish liquids obtained from the fast pyrolysis of vegetable biomass [1,2]. The vapors are condensed, obtaining a fuel which is inherently different from petroleum-based fuels, both in terms of physical and chemical properties. It is a mixture of hundreds of components, for which a surrogate mixture is therefore necessary to efficiently describe its reactivity. Mimicking both the physical and chemical properties of bio-oils, a nine components mixture has been defined (water, acetic acid, ethylene glycol, glycol aldehyde, vanillin, HMW-lignin, levoglucosan, 2,5-dimethylfuran and oleic acid) as a part of the European project Residue2Heat [3]. The surrogate mixture and the real bio-oil have been experimentally compared in terms of evaporation rate and combustion characteristics: the experimental analyses concerned the evaporation and subsequent combustion of a single isolated droplet suspended on a thin thermocouple in a controlled combustion chamber [4]. Recently, in our previous work we successfully simulated this experimental device: focusing on the sole vaporization process, we used the DropletSMOKE++ code [5] to numerically describe the evaporation of a suspended droplet of acetic acid, ethylene glycol as well as their mixture, including a non-ideal description of the thermodynamic properties [6].

The aim of this work is to proceed a step further in order to include the combustion phenomena. The DropletSMOKE++ code has been extended to include:

- An operator splitting approach to efficiently manage the combustion chemistry, characterized by tens of different species. The same concept is adopted by the laminarSMOKE solver [7], already extensively validated;
- An optically thin model for the description of radiative heat transfer;
- The possibility for boiling to occur, especially close to the suspending fiber.

The final model is then applied to the evaporation, auto-ignition and combustion of suspended fuel droplets (acetic acid, ethylene glycol and their mixture), heated by an electrical coil placed below the thermocouple. As already described in our previous work, the solid phase is modeled as well to describe the preferential heat transfer from the fiber to the droplet. DropletSMOKE++ shows a reasonable agreement with the experimental data, adopting a kinetic mechanism for the acetic acid-ethylene glycol mixture that comprehends tens of species and hundreds of reactions. It is obtained via a previous skeletal reduction [8] to reduce the computational cost.

The importance of this work is two-fold: on one side it allows to have a better insight on the vaporization and combustion phenomena (e.g. ignition time) occuring when a droplet burns in convective conditions. On the other side it paves the way for the analysis of more complex fuels, from multicomponent mixtures to the real bio oil surrogate. In particular, in this latter case the combustion chemistry is not only limited to the gas-phase, but also includes the liquid phase, with the formation of solid carbonaceous residues (cenospheres).

The detailed modeling of these aspects will be the main focus of future works.

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OP-II-6

NUMERICAL MODELING OF CHEMICAL VAPOR INFILTRATION (CVI) WITH DETAILED HOMOGENEOUS AND HETEROGENEOUS KINETICS

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The Chemical Vapor Infiltration (CVI) is one of the leading manufacturing processes for production of Carbon/Carbon (C/C) composites, such as brakes. The CVI is a complex process, in which multi-physical and multi-chemical phenomena are involved: homogeneous gas phase reactions, heterogeneous surface-deposition reactions, molecular diffusion, mixed convection gas flow, radiative heat transfer, etc. A wide range of length and temporal scales associated to the transport and chemical phenomena occurring along the reactor and inside the porous preforms can be observed. In particular, time scales vary from those associated with pyrolytic reactions (order of microseconds) to the deposition process time scales (of the order of dozens of hours). Other time scales exist between these two disparate scales, including the fast and slow chemical reactions rates, and conduction and convection time scales. In principle, a complete mathematical model has to account for most of these scales [1,2]. However, in practice, this cannot be realized since the span between the different scales is too large. Thus, alternative approaches have to be accounted for.

In this work we present a modeling strategy based on the partial decoupling between the evolution of gaseous phase in CVI reactors and densification process occurring over the porous substrates. The proposed methodology allows to overcome the issues mentioned above, without reducing the level of detailed in the description of homogeneous and heterogeneous reactions.

In particular, the following two steps are carried out in series: 1) a steady-state CFD simulation of the whole reactor is performed, in which only the gaseous phase is modeled, by solving the transport equations of mass, momentum, gaseous species and energy. No heterogeneous (i.e. deposition) reactions are accounted for and no equations are solved inside the porous preforms; 2) the CFD solution (Step 1) is used to provide the proper boundary conditions for modeling the densification process in each porous preform. In other words, once the CFD solution is available, the densification is modeled by solving the transport equations of mass, species and energy in each preform, accounting both for homogeneous and heterogeneous (i.e. deposition) reactions. This 2-step strategy is based on the assumption that the gaseous reactions occurring inside the reactor are much faster than the densification process, which is usually limited by porous diffusion, even when low temperatures are adopted. This means that the homogeneous gaseous phase can be treated as quasi-steady with respect to the densification.

Two different tools were developed to carry out the 2 steps. The CFD step (Step 1) is carried out with a customized version of laminarSMOKE code [3], a CFD code based on the OpenFOAM® framework, specifically conceived for laminar reacting flows with detailed kinetic mechanisms. The solver is able to model reactors of arbitrarily complex geometry and size, both in steady state and unsteady conditions. No limitations on the size and complexity of kinetic mechanisms are present. The densification step (Step 2) is carried out with the CVISMOKE++ solver. In its current implementation, CVISMOKE++ is able to model the densification in 2D porous preforms (planar or axisymmetric geometries), by solving the unsteady transport equations of mass, species and energy. Both homogeneous and heterogeneous kinetic mechanisms are accounted for, without limitations on their size and complexity.

The proposed algorithm was validated in comparison with experimental data available in the literature [4]. The agreement with experimental data is more than satisfactory. The model is able to capture, also on a quantitative basis, that bulk density slightly decreases from the outside to the inside of the felt, which is an indication of the inception of a diffusion limitation. Sensitivity analyses, carried out by adding different amounts of hydrogen to the inlet stream, revealed that hydrogen addition is helpful in avoiding premature formation of crusts along the external surface of preforms.

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MICREOREACTOR MODELLING FOR ETHOXYLATION REACTIONS

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The ethoxylation of fatty alcohol is an important process to produce non-ionic surfactants. Ethylene oxide reacts rapidly with long chain alcohols, reaction promoted by strong base catalyst, reaching almost full selectivity to the desired products, as no-side reactions are favored in the presence of base catalysts. The reaction occurs via anionic polymerization, where ethylene oxide molecules are added to a growing ether chain, leading to a statistical distribution of the products. The alkoxylation reactions are generally performed in semibatch reactors [1], also in series, in which the catalyst and the substrate (alkyl phenols, fatty alcohols or acids) are initially charged while epoxide (ethylene or propylene oxide) is added during the reaction course. This synthesis strategy is due to the high reactivity of alkoxides and also to the high heat involved in alkoxylation reaction. The use of semibatch reactors, however, have some drawbacks that can be summarized in the following points: (i) the reactor volume is relatively high; this aspect could represent a serious problem for safety issues due to the high quantity of alkoxide present in the reactor at a certain time; (ii) the productivity of the system is quite low for the various steps involved in a semibatch process; (iii) the safety of the overall process is not optimal, fact due to possible epoxide accumulations that could lead easily to runaways reactions.

A possible solution that could allow overcoming the mentioned drawbacks is the adoption of a continuous reactor that can be properly designed for the achievement of the desired alkoxylation degree. In the scientific and patent literature both traditional tubular reactors and more innovative reactor configurations, like microreactors, have been proposed for the alkoxylation reactions. These last are particularly suitable for exothermic and multiphase reactions, thanks to the high heat and mass transfer exchange. Such reactors were tested in the literature, showing good performances in terms of reaction conversion and thermal control, allowing to work at relatively high temperatures (240 °C) [2-3]. Even though in the adopted experimental conditions it was demonstrated that the flow-pattern is laminar [4], the collected data are normally simulated with a plug-flow model approach [2]. This approximation certainly leads to a non-rigorous determination of the parameters related to the intrinsic kinetics of the reaction. At this purpose, in the present work a laminar-flow model was applied to the description of the experimental data collected in the literature.

The partial differential equation (PDE) system describing the single liquid phase reactor was solved with the method of lines already implemented in gPROMS Model Builder v. 4.0. The reaction occurs in a liquid system, considered non-isothermal [4] hence it is necessary to write both mass and energy balance equations. The model was written in a time-dependent form, to simulate the evolution of the concentration and temperature profiles along the reactor length and reactor radius.

$$\frac{\partial c_i}{\partial t} = -u(r)\frac{\partial c_i}{\partial z} + D_i\left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r}\frac{\partial c_i}{\partial r}\right) + \sum_j \nu_{ij} r_j \tag{1}$$

$$\frac{\partial T}{\partial t} = -u(r)\frac{\partial T}{\partial z} + \left(\frac{\lambda}{\overline{c}_p \overline{\rho}} + D_i\right)\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \frac{\sum_j \nu_{ij} r_j \left(-\Delta H_j\right)}{\overline{c}_p \overline{\rho}} \tag{2}$$

The developed model was firstly applied to conduct a sensitivity study, showing high flexibility of the model, simulating for a very exothermic reaction temperature gradients along the radial coordinate. Them, the model was applied to describe the experiments conducted at different temperatures (from 180 to 240 °C) taken from the literature [2-3]. All the required physical properties were taken from the literature [2]. In every case, a good fit was obtained (Figure 1).

The kinetic parameters shown a deviation from the ones obtained using a plug flow-approach (30 % deviation). The model showed a high flexibility in interpreting the experimental data and a good prediction power that will allow the design of a continuous equipment intensifying ethoxylation processes.

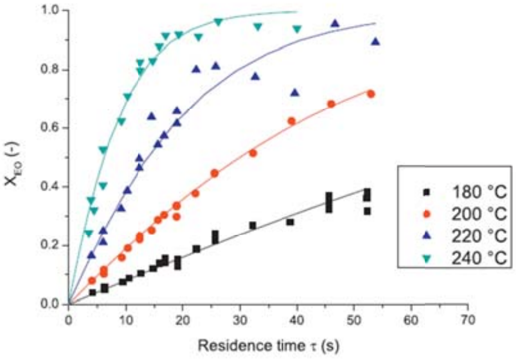

Figure 1. Ethylene oxide conversion along the residence time of the microreactor. Experiments conducted at different temperatures, taken from the literature [2-3]

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OP-II-8

APPRAISAL AND MODELLING OF INTERNAL MASS TRANSFER LIMITATIONS IN LIGHT OLEFINS SYNTHESIS USING BIFUNCTIONAL CATALYSTS (OX-ZEO PROCESS)

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The key challenge in improving the performance of bifunctional systems is linked with the control and adjustment of the distance (or intimacy) between the two functions to maximize their cooperation [1]. Traditionally, Weisz-Prater and related intimacy criteria are employed [2]. Notwithstanding, those does not seem suitable for micro/meso scale intimacy of various functions involved in catalytic processes [1,3].

Herein, we focus on the conversion of syngas to light olefins (OX-ZEO process) assuming methanol intermediate [4] over bi-functional oxide/zeolite-type catalysts. Besides, we aim at describing the effect of spatial organization of functions (Figure 1) within reactor bed (macro-scale intimacy), catalyst pellet (micro-scale intimacy) and core-shells (meso-scale intimacy) altogether with the impact of internal gradients on catalyst activity and product selectivity. Thus, we establish a transient 1D pseudo homogeneous plug-flow reactor model and couple DFT-inspired micro-kinetic network with a 1D spherical diffusion inside solid catalyst particles. The former is extended to account for distinctive reactor (mechanical mixture, double-bed, n-multi-bed) and catalyst grain configurations (uniform solid pellets and core-shells) represented in Figure 1, allowing a thorough analysis of various inter-functions intimacy scales. Hence, our approach covers a several intimacy scales discussed in the literature providing some new insights into intimacy criteria from the chemical engineering perspective. Moreover, in-house experimental data is used for microkinetic model fitting, yielding the most important trends regarding products selectivity and catalyst activity as well. In conclusion, the approach used herein shed some light on the internal diffusion limitations in a bifunctional system and provides some new insights into its impact on product selectivity and catalyst activity.

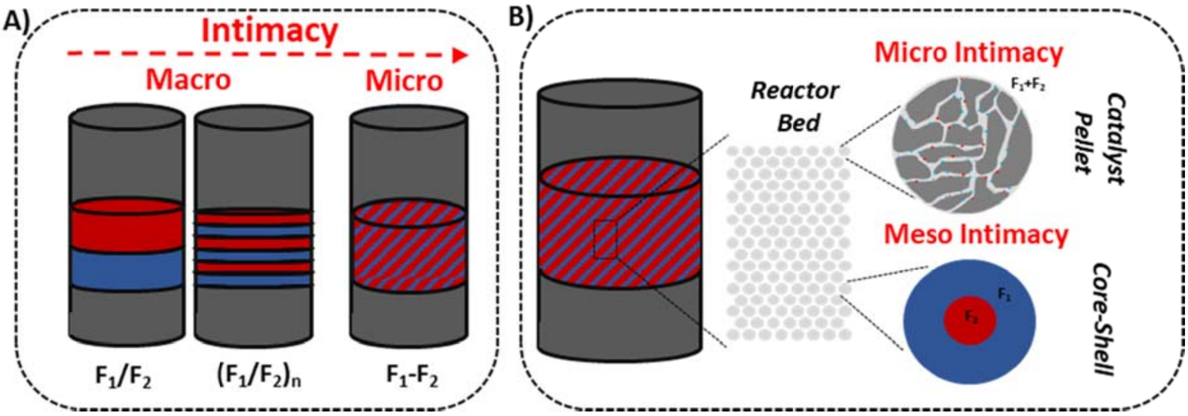

Figure 1. Different Scales of Inter-function Intimacy within A) Reactor-bed-scale and B) Catalyst-pellet-scale; F_1/F_2 double-bed, F_1/F_2 n-multi-bed configurations and F_1-F_2 mechanical mixture

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OP-II-9

TOWARDS THE OPTIMIZATION OF THE INTERNALS DESIGN TO BOOST THE HEAT TRANSFER PERFORMANCES OF COMPACT FISCHER-TROPSCH REACTORS

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In the last decades, several intensified structured reactors based on highly conductive inserts were proposed to manage the strong exothermicity of the low temperature Fischer-Tropsch synthesis ($\Delta H_R^0 \approx -165$ kJ/mol_{CO}) [1,2].

In our recent papers [3,4], we showed that heat transfer limitations can be overcome by adopting aluminum open-cell foam and periodic open cellular structures (POCS) as reactor internals. In this regard, our tests revealed that the packed-POCS reactor reached extreme performances (CO Conversion ≈ 80 %) that could not be accessed even with the packed-foam reactor technology [4]. The strengths of the packed-POCS reactor configuration are the regular geometry of the POCS ($R = d_{node}d_{strut}/{\approx}1$) that intensifies the internal thermal conductivity, and the improved contact of the ordered structure with the reactor wall that governs the wall heat transfer coefficient [4].

In order to gain more insight in the role of the wall/structure contact on the heat transfer performances of a packed-POCS reactor, we have tested in the FTS a POCS with a 0.5 mm thick outer metallic skin. The POCS was manufactured by 3D printing using AlSi7Mg0.6 alloy. The POCS with the skin was printed with the same cylindrical shape (O.D = 2.78 cm and L = 4.2 cm) and geometrical properties (d_{cell} = 3 mm and ε_{POCS} = 0.890) of the bare POCS reported in [4]. Two axial through holes of 3.2 mm diameter were located at the centerline and at half of the radius of the structure for the insertion of the two sliding J-type thermocouples.

Once the POCS was loaded in the tubular reactor, the system was packed like the bare POCS reported in [4] (catalyst ≈ 7.2 g). The performances of the catalyst packed into the POCS with the skin were assessed at industrially relevant process conditions (180-240 °C, 25 bar, H_2/CO = 2 mol/mol, 6410 cm^3(STP)/h/g_{cat}). The packed-POCS with the skin reached outstanding performances (CO conversion ≈ 80 %; volumetric heat duty (Q) ≈ 1833 kW/m^3) with a remarkable temperature control.

Fig. 1 compares the thermal behavior of the two packed-POCS reactors configurations (with and without the skin) by plotting the volumetric heat duty (Q) measured at different reaction temperatures against internal radial ($T_{\text{half radius}}$-$T_{\text{centerline}}$) and the overall radial (T_{wall}-$T_{\text{centerline}}$), respectively. In this regard, the slope of the data in Fig. 1a reflects the internal effective heat conductivity, while the slope of the data in Fig. 1b is representative of an overall heat transfer coefficient including also the wall heat transfer resistance. Data for a packed foam are also included in Fig.1 [3].

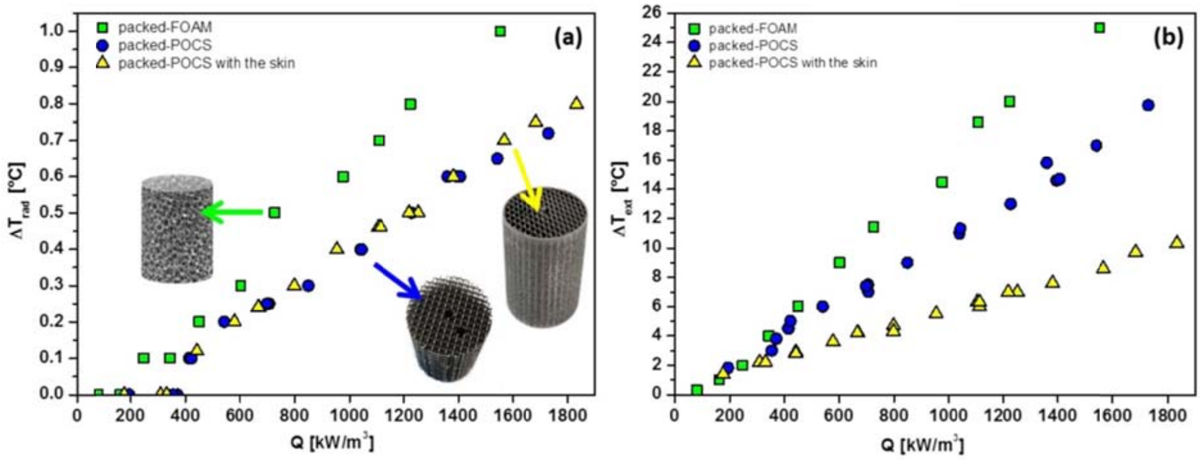

Fig. 1. (a) radial and (b) external T-difference as a function of Q measured in the packed-foam (green square), packed-POCS (blue circle) and packed-POCS with the skin (yellow triangle) reactors

The internal radial temperature differences measured over the two configurations are very similar (Fig. 1a), in line with the fact that the POCS with and without the skin have the same geometrical properties and R ≈ 1. Strong differences are apparent in Fig. 1b: the POCS with the skin strongly outperforms both the bare POCS and the foam. Indeed, the slope of the ΔT_{ext} vs Q plot of the POCS with the skin is about 2 and 3 times lower than the bare POCS and the foam, respectively. Such differences are reasonably explained by the maximized contact of the POCS with the reactor wall thanks to the presence of the skin. This also confirms that the internal conductive heat transfer resistance provides only a minor contribution to the overall heat transfer resistance in the reactor, which is dominated by the wall heat transfer resistance.

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OP-II-10

CATALYTIC WALL PLATE MICROREACTOR STRUCTURALIZED FOR REACTANTS' ADVECTIVE TRANSPORT IMPROVEMENT IN DRY REFORMING OF METHANE

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Dry reforming of methane (DRM, $CH_4+CO_2 \rightleftarrows 2CO + 2H_2$, $\Delta Hr^\circ = 247$ kJ/mol) with CO_2 have taken an attention of its energy saving and the green house reduction effect. On the other hand, its large endotherm is leadig to emerging the cold spot, which causes to low methane conversion with slowing down of the reaction rate and/or the equilibrium carbon deposit (mainly, $CH_4 \rightleftarrows C+2H_2$) with the channel blockage.

Micro-reactor technology is one of the suitable approaches to the above problems, i.e. the contribution for the process intensification in such a fast gaseous reaction as syngas production process. The catalyst coating technique on the reactor wall is a good way to prevent the cold spot problem because of the promotion of the thermal transport in the catalyst fixed domain and keeping low pressure drop. However, currently-available washcoated microreactors face constrained catalyst loading (less than ca. 20 % of total volume of the reactor) and high manufacturing cost.

To address these conventional drawbacks, the authors have tried to developed a high-performance, versatile, less coking-prone, and highly-reusable assembly-type microreactor for fast gaseous reactions. The main feature of the catalytic wall plate microreactor (CWPMR) is that packed bed of powdered catalyst is employed as the catalytic layer instead of a catalyst washcoat (Fig. 1). The usage of highly-porous packed layer allows increase of catalyst loading to desired capacity and still-intensified transport properties. CWPMR takes about 10 times better heat-transfer performance than a micro-packed bed reactor with ca. φ4 mm-inner diameter.

Now the authors tackle to intensify the mass transport in the flow channel of the original CWPMR. In the case of straight blow-through channel, the contact between the reacting molecules and the catalyst bed almost relies on the molecular diffusion (Fig. 2a). There is a problem that molecular diffusive transport cannot catch up appropriate supply of the reactants to the catalyst bed due to very fast reaction rate in the high temperature range of 650 °C to 900 °C or higher in such as methane reforming. It is expected as an approach of the problem to install a structured channel in which the advection of the reaction fluid is induced to the catalyst for direct encoutering.

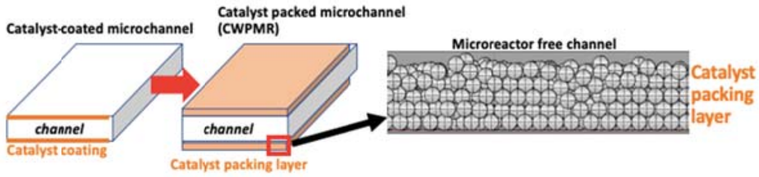

Figure 1. A concept of the CWPMR

The appropriate structure was selected by the computational fluid dynamics (CFD) simulation. Since it is necessary to predict the flow stream through the gap of inter-particles, the catalyst packed domain was reproduced by the Particle Resolved (PR) model (catalyst packing layer in Fig. 1), and the structure inside the CWPMR was examined. It was visualized and clarified that the provision of the baffle in the straight blow-through channel was effective for reactants gas to contact the catalyst.

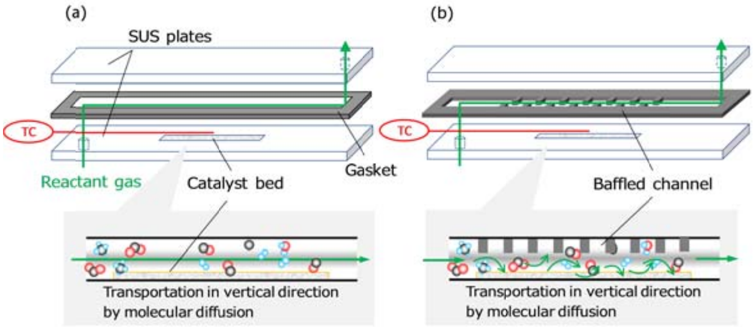

Figure 2. A geometry of the CWPMR with (a) straight blow-through channel, and (b) baffled channel

A proto-type CWPMR with the baffle channel was fabricated (Fig. 2b) and verified in DRM reaction test. As a result, it was demonstrated that the conversion of methane was significantly improved at 500-600 °C compared to a CWPMR without the baffle and a micro-packed bed reactor. It is considered that the heat- and the mass-transfer resistance were greatly reduced and reached to reaction kinetics controlled. On the other hand, the CWPMR with the baffle was not showing the outperformance at 650 °C, because reaction rate was accelerated comparable to the mass transport rate. The authors reached an expanded region of reaction kinetics controlled even in a higher temperature region (at least, at 700 °C) by optimizing the dimensions, and also reached another effect of reducing carbon formation.

OP-II-11

PORE THROUGH REACTORS, DEVELOPMENT, CHARACTERIZATION AND ACTIVITY TESTS

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Introduction

Nowadays almost 50 % of word production of hydrogen is generated via Steam Methane Reforming (SMR) that uses natural gas as feedstock [1]. However this industrial process is only efficient at large scales and it still has a great deal of thermodynamically limitations and it also emits greenhouse gases [2]. Therefore, it is essential to ensure an efficient way to produce hydrogen al small-medium scales. A new reactor concept is presented in this paper, a pore-through reactor (PTR). This type of reactor consists of a α-Al_2O_3 porous ceramic tube (top layer of 100 or 200 nm) were the catalyst (Pd) has been incorporated by means of seeding [3]. Thus, the reactants are passed though tiny pores were catalyst is placed as it is shown in Fig 1.

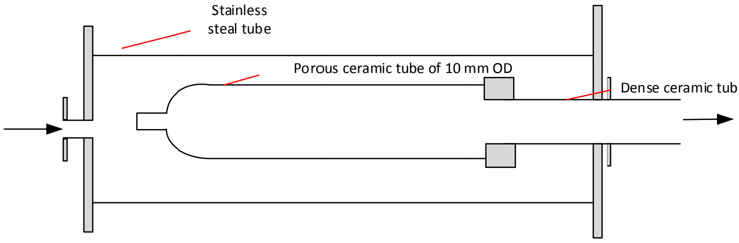

Fig. 1. Scheme of the Pore Through reactor

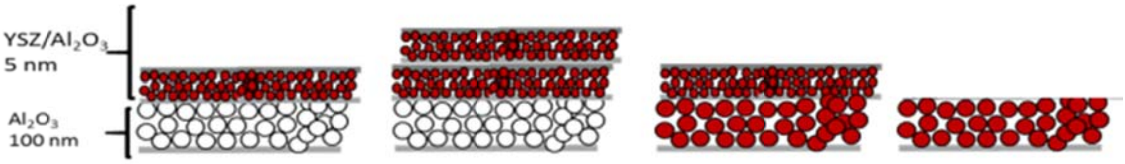

Fig. 2. Ceramic porous tubes with a) one YSZ/Al_2O_3 layer and one seeding, b) one YSZ/Al_2O_3 layer and two seeding, c) one YSZ/Al_2O_3 layer and two seeding (one in the support) d) seeding in the support of the tube

Additionally, in some tubes different layers of γ-Al_2O_3-YSZ prepared by a "dip coating technique" were placed before placing the catalyst in order to have an additional layer with smaller pore sizes to deposit the catalyst (from 3 to 5 nm) (see Fig 2).

OP-II-11

Experimental

Different PTR configurations were tested in a lab scale plant .The SMR tests were carried out between 500 °C to 900 °C at 10 bar. During the tests, the methane was fed at a rate of 100 mL/min and the steam to carbon ratio (S/C) was maintained at 5. The effect of different tube configurations was studied and then these results were compared to the results obtained in a conventional fixed bed reactor tested under the same conditions. Finally, all the tubes were characterized by Scanning Electron Microscope (SEM) and the amount of Pd in each tube was determined by ICP-OES.

Result and discussion

All the tubes exhibited an increase of the hydrogen yield while the reaction temperature increased, as it was expected. The tubes with the palladium seeding in the support have revealed a higher H_2 yield than the same tubes but without the support seeding. The γ-Al_2O_3-YSZ layers did not involve an improvement to the activity to the tubes. Besides, this γ-Al_2O_3-YSZ layer was extremely fragile and SEM images showed that it husked due to the exposure to high temperatures. All tubes showed higher methane conversion as well as higher H_2 yield than the values achieved in the fixed bed reactor. Moreover, PTR show activity at 500 and 600 °C while conventional fixed bed reactor did not show any.

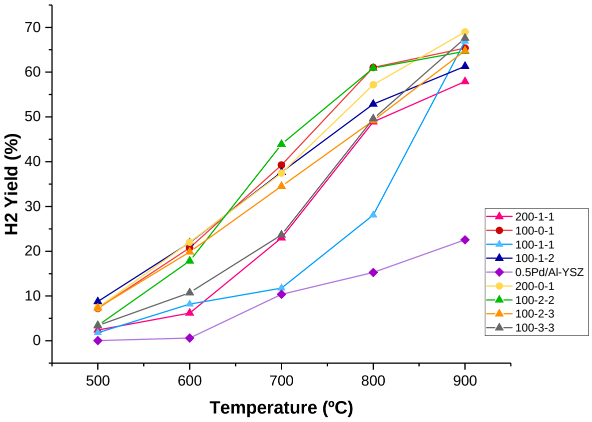

Fig. 3. Hydrogen yield at different temperatures (Code “Pore size (nm) - α-Al_2O_3-YSZ layer – nr of Pd seedings”)

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CONTINUOUS-FLOW REACTOR FOR ONE-STEP PRODUCING TETRAMETHYL ORTHOSILICATES FROM SILICA MATERIALS IN SUPERCRITICAL METHANOL

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Alkyl esters of orthosilicic acid are multi-purpose products for different applications, firstly for sol-gel synthesis of pure or silica composite materials – sorbents, catalyst supports, aerogels, ceramics, *etc*. Conventional methods for producing tetraalkyl orthosilicates (TAOS) usually compose of some steps including a high energy-consuming process. For example, one of the widely used methods is three-step synthesis *via*: 1) a silica reduction by activated carbon at high temperature to obtain metallic silicon; 2) eco-dangerous reaction of metallic silicon oxidation by molecular chlorine Cl_2 to give $SiCl_4$ (with producing highly toxic waste); 3) alcoholysis of $SiCl_4$ to give target TAOS together with "highly undesired" HCl. In 1949, E.G. Rochow patented a method [1] that is up to now the most popular commercial one: metallic silicon is directly oxidized by methanol at high temperature into tetramethyl orthosilicate (TMOS). This reaction needs to be catalyzed by metallic copper. Another popular process was known since 1992–1993 [2,3]: TMOS is obtained by the reaction of silica and dimethyl carbonate (DMC) also at high temperature. This direct method requires one more step – production of DMC from methanol.

Earlier, we have reported that TMOS together with its oligomers can be produce by one-step method from silica-based materials (Pyrex glass, quartz, silica gel) and methanol at 350 °C in a batch reactor: $SiO_2 + 4MeOH \rightarrow Si(OMe)_4 + 2H_2O$ [4,5]. The process is known to be reversible. The accumulation of water formed in the reaction negatively affects the process shifting the thermodynamic equilibrium towards the starting reagents. A new approach is in the use of desiccant to extract water from the reaction mixture during the reaction. For the experimental study, two continuous-flow reactors are made containing a flow-through cartridge with a fixed-bed dryer (molecular sieves): 1) fixed-bed continuous circulation-flow reactor (***A***), and 2) continuous-flow cascade reactor system (***B***) (see Figure) [6,7].

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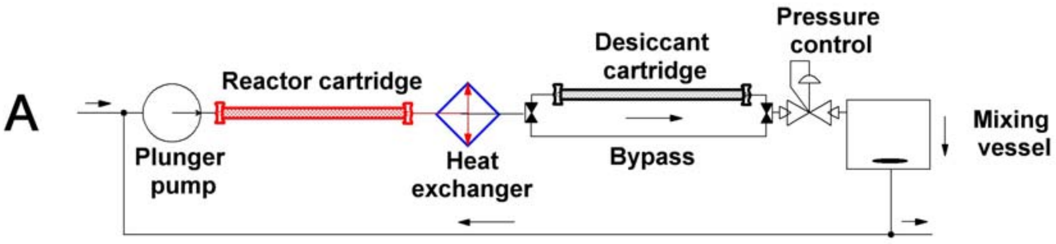

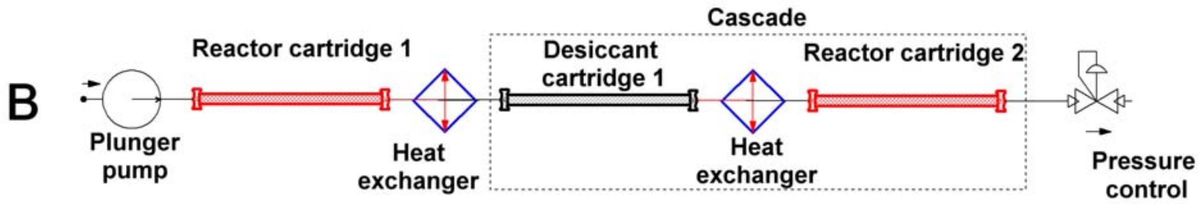

The use of plug-in dryer cartridge allows producing the reaction mixtures with chemical composition close to thermodynamically equilibrium mixtures at 270 °C, with maximum product concentrations. So, TMOS content was only 12.8 g/L in a mode without desiccant, while 20.2 g/L was in the reaction with desiccant. The moisture capacity of the desiccant was evaluated at these conditions. For circulation-flow reactor (***A***), kinetic curves of product accumulation were obtain for the reaction of some silica materials (quartz sand, perlite, silica gel and vermiculite) of different SiO_2 content and specific surface area. For industrial production of TMOS, in our opinion, the most suitable set-up is a cascade continuous-flow system (***B***). Optimization of the cascade version of the continuous flow set-up will allow achieving the highest concentration (highest yield) of the product depending on type of desiccant used.

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INFLUENCE OF CATALYST CHARACTERISTICS ON THE FORMATION OF MWCNT - AGGLOMERATES DURING SYNTHESIS IN A FLUIDIZED BED REACTOR

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An important scientific and technological problem is the development of continuous high-performance processes that make it possible to obtain multi-walled carbon nanotubes (MWCNTs), which, due to their unique properties, are one of the key components of rapidly developing nanotechnology. Analysis of various options for the design of such a process allows us to identify the most promising fluidized bed (FB) technology. Despite some progress in understanding the patterns of individual nanotubes catalytic growth and their synthesis in FB under conditions of a significant increase in its volume [1,2], a number of problems related to the design of a continuous technological process remain unresolved.

One of the most serious hydrodynamic problems is the creation of a uniform fluidization of the nanoparticle powder. The cause of this problem is the strong influence of the cohesion of nanotubes and their agglomerates on the hydrodynamics of FB. Due to the small size of nanoparticles, they are characterized by very large values of the ratio of surface area to volume. This leads to the significant predominance of cohesion forces between nanoparticles over the forces of gravity and hydrodynamic resistance in the gas flow [3]. The consequence is the formation of agglomerates of nanoparticles. The formation and destruction of agglomerates is a dynamic process. As the nanotube agglomerates grow, the role of the surface interaction of the agglomerates decreases, and their final size and the behavior of the FB consisting of them depend on the conditions under which the hydrodynamic forces destroying the agglomerates balance the cohesion forces [4]. Under unfavorable conditions, a global violation of the homogeneity of FB and formation of stagnant zones and jets can occur, leading to the defluidization and loss of main technological advantages.

Here, the relationship between the type and morphology of dispersed powders of catalysts for the synthesis of MWCNTs and cohesive properties of primary nanotube agglomerates growing on a separate catalyst particle are investigated. Three main types of catalysts were studied: 30 % Fe-Co/Al_2O_3; 40 % Fe-Co/Al_2O_3 and 40 % Fe-Co/CaO, which provide MWCNTs with varying average diameters (7, 10, and 20 nm, respectively). The morphology of the initial catalysts and the MWCNTs obtained with their use in reactors with fixed and fluidized beds (at T = 660-680 °C, C_2H_4:Ar = 1:1) was investigated by microscopy methods. In addition, bulk density of the powders and their specific surface were measured, and the analysis of the particle size distribution and fractality was carried out. The fluidity of MWCNT powders was evaluated using a drum-type powder rheometer.

Data were obtained on the fractality of catalysts and MWCNTs produced, and their influence on the size distribution of primary and secondary agglomerates of MWCNTs formed at different stages of the growth process was analyzed. The study of the fluidity of powders by the dynamic method made it possible to establish the dependence of the cumulative energy of avalanches on the time between them, as well as to measure the fractality of the dynamic and stationary layer of powders. These data were used to assess the cohesive properties of catalyst powders and MWCNTs. The cohesive properties obtained on various types of catalysts are compared with the stability of the FB pilot reactor with internal diameter of 12 cm and a capacity of up to 10-12 kg MCNTs per day. The requirements for ensuring this FB-reactor stable operation are determined.

The numerical simulation of the hydrodynamic behavior of the MWCNT powder in the drum rheometer and directly in a fluidized bed was also performed. The method of discrete elements coupled with continuous gas flow simulation, CFD-DEM, was used. The established correspondence between the mechanical characteristics of model particles and experimental data on the properties of MWCNT agglomerates made it possible to close the causal chain "catalyst properties – properties of nanotube agglomerates – fluidization regimes of MWCNTs". Together with the experimental results, this allows to formulate requirements for catalysts that provide conditions for uniform fluidization of MWCNTs.

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OP-II-14

A NOVEL RADIAL-FLOW REACTOR BASED ON CELLULAR SUBSTRATES FOR AFTER-TREATMENT APPLICATIONS

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The reduction of the vehicular emission limits imposed by legislations requires the intensification of the exhaust gas aftertreatment systems (ATS). The abatement performances depend on the trade-off between the chemistry, the gas-to-solid transport properties and the pressure drops. The state-of-the-art honeycomb monolith catalyst substrates suffer from some limitations in the external mass transfer regime. In this context, the development of innovative catalyst supports is pivotal to improve the ATS performances. Open cell foams and Periodic Ordered Cellular Structures (POCS) are characterized by high specific surface areas (>2000 m^{-1}) and void fractions (>0.9). Previous work from our group [1,2] revealed that these supports guarantee high volumetric gas-solid mass transfer coefficients along with relatively low pressure drops. Hence, such structures are potential candidates as enhanced catalyst supports for these applications. In this work, we employ Computational Fluid Dynamics (CFD) numerical simulations to quantify their performances in realistic ATS applications and to compare abatement efficiencies to those of honeycombs.

The numerical simulations are based on a Volume-Averaging Technique (VAT) for porous media implemented in the catalyticFoam framework [3]. Two distinct phases, i.e. the gas and the cellular material, characterized by averaged and homogeneous properties are employed to describe the system whose tri-dimensional and complex geometry is reduced to two pseudo-continuous media. Dedicated closure models are employed to account for the inter-phase transport [1,2]. As an example of the methodology, a NH_3-SCR system has been considered assuming simple first order kinetics in NO. A catalyst effectiveness factor based on the Thiele modulus is used to account for internal transport limitations.

Initially, the performances of open-cell foams and honeycomb monoliths have been compared in a conventional ATS device (diameter 19.05 cm - length 30.5 cm). A 400/5 honeycomb monolith loaded with 140 g/L of Cu-zeolite catalyst is assumed as reference. An open-cell foam with 40 pore per inch (ppi) and 0.9 bare porosity has been selected such that, after that the catalyst load was consider, shows similar surface area of the monolith. Figure 1a compares pressure drop and NO conversion in the two systems. The conversions in kinetic and internal mass transfer limited regimes are almost superimposed. In contrast, the open-cell foam significantly outperforms the honeycomb monolith in external mass transfer conditions ($k_{m,foam}$ ≈

10 $k_{m,HC}$). However, foams are characterized by one order of magnitude higher pressure drops, hindering their application to ATS.

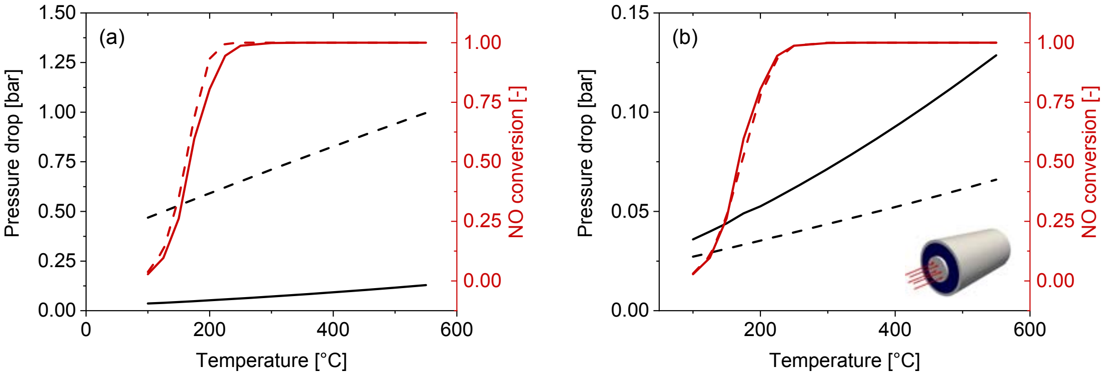

Figure 1. Conversion and pressure drop for honeycomb (continuous line) and open-cell foams (dashed line) in conventional (axial) (a) and innovative (radial) configuration (b) at a gas-hourly-space velocity (GHSV) of 87000 h^{-1}

To overcome such a limitation, we propose a different geometry of the device. A radial flow configuration, widely adopted in conventional chemical process applications when pressure drops are key, is considered. It is evident that such a solution is possible only with open-cell foams and POCS, since their geometry is isotropic and permeable to the fluid in all the spatial directions. The inset in Figure 1b shows an alternative configuration which consists of an internal inlet channel surrounded by an annulus of foam and by an external exit channel. To accommodate the same amount of catalyst, the device diameter is kept constant while the length is increased (+20 %) to compensate for the void volume of the inlet and outlet channels. An open-cell foams with 60 ppi is considered in this case. Despite the radial flow configuration reduces the volumetric mass transfer coefficients, still an advantage of a factor 7 respect to the honeycomb is present. The NO conversions are similar for both the supports in the entire regime considered, as shown in Figure 1b. Besides, radial flow is able to drastically reduce the pressure drop which is even lower than in the conventional honeycomb. Advantages are also expected thanks to faster heat-up of the device. Further optimization of both the structures and the geometry is expected to provide additional improvements of the performances, paving the way towards the intensification of aftertreatment systems.

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OP-II-15

FLAT CATALYST AS A HEATING ELEMENT OF A REACTOR

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The research work deals with developing a prototype of reactor in which a catalyst serves also as a heating element of the reactor. This reactor comprises mainly of two disc-like plates, the flat catalyst inserted between them, and wide O-ring seals made of electroinsulating material and placed on the inner edges of the disc-like plates. The heating of the internal space of the reactor is accomplished by clamping the catalyst's opposite ends with copper connectors which are connected to an external power source. When the electrical current flows through the catalytic it encounters resistance, resulting in heating of the catalyst and the reaction gas mixture flowing through it (i.e. Joule heating). The use of O-ring seals with non-conductive properties ensures the isolation of catalyst, therefore no current flows through the disc-like plates. The heating element of the reactor is based on stainless steel wire mesh with deposited metal nanoparticles (such as Cu, Ni). The advantages of such reaction design are: simplicity of the construction and ease of replacement of catalyst; and energy efficiency as only one element of the reactor is heated.

The reactor was used to evaluate the influence of the passage of electric current through the catalyst on the course of catalytic processes in the presence or absence of externally applied electromagnetic field. This field was generated by application of an insulated porous electrode in close proximity to a catalyst's surface. The effect of electromagnetic effect was investigated in the model reaction of gas-phase oxidation of volatile organic compounds. The copper and nickel catalysts were prepared by electrochemical deposition from corresponding nitrate salts. The analysis of the reaction products was carried out by using two on-line gas chromatographs equipped with a FID and TCD.

OP-II-16

UNVEILING THE ROLE OF SURFACE BARRIERS IN THE CATALYST DEACTIVATION BY COKING BY USE OF A REACTION-DIFFUSION MODEL

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Intracrystalline diffusion of guest molecules in nanoporous materials has been long time recognized as the dominance of mass transport. With the advent of microimaging, surface barriers of guest molecules has been shown to be an appealing challenge in applying nanoporous materials in catalysis and separation[1,2]. Deciphering the role of surface barriers in catalysis is often nontrivial owning to the intertwinement of mass transport and complex reactions observed from overall measurements.

In this work, we aimed at developing a reaction-diffusion model to account for the surface barriers inside porous materials. The propylene oligomerization, which composes of step of methanol-to-olefins reaction, was considered as model reaction. The explicit function of surface barriers on coke deactivation was unveiled.

To emphasize the effect of surface barriers on reaction, the boundary conditions (*i.e.* Neumann boundary condition) was considered for a 3D reaction-diffusion model[3]

$$D_i(\mathrm{d}q_i/\mathrm{d}x)_{x=l} = \alpha(f_iC_i - q_i)_{x=l}$$

where D is the intracrystalline diffusivity (m^2/s), α the surface permeability (m/s), q the loading of component i (mol/m^3), f the adsorption constant, C the concentration in gas phase (mol/m^3) and l the half of material length (m). In Figure 1a, the 3D reaction-diffusion model was developed for cubic porous materials.

By use of post-synthetic method[1], the external surfaces of SAPO-34 zeolites were modified to finely alter the surface permeability of guest molecules. The uptake measurements of propylene were performed on these two samples to obtain transport coefficients. In Figure 1b, compared with the results of SAPO-34-surf sample, the α of propylene in modified SAPO-34 zeolites (SAPO-34-int) is significantly improved while the intracrystalline diffusivity D remains almost constant. Reaction-diffusion simulations indicate that the retention of propylene at the external surface imposed by surface barriers results in the decreased conversion of propylene and acceleration of catalyst deactivation as shown in Figure 1d. These results are verified by *in-situ* IR spectroscopy in Figure 1c, for the SAPO-34-int sample, both formation rate and amount of propylene oligomers (PO) are larger than that of SAPO-34-surf sample. In Figure 1e, combining with the SIM techniques, the profound insights of impact of surface barriers on evolutions of ‘coke’ inside zeolites are visualized.

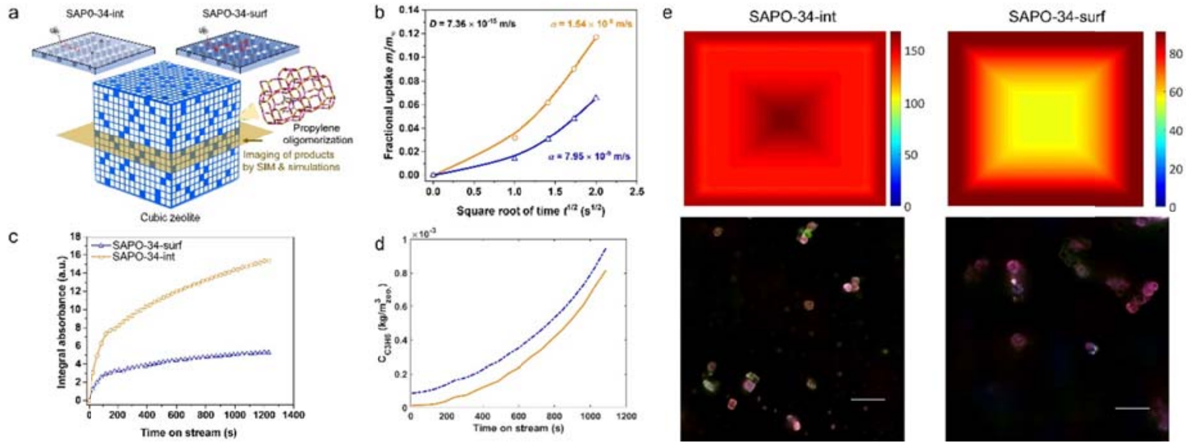

Figure 1. (a) Reaction-diffusion modelling developed based on 3D cubic porous materials. (b) Initial uptake rate of propylene in SAPO-34-int and SAPO-34-surf samples at 298 K. (c) In-situ IR spectroscopy of the effect of surface barriers on the formation of PO in SAPO-34 zeolites. (d) The effect of surface barriers on propylene conversion by simulations. (e) Simulations and SIM imaging results of spatial distribution of PO inside SAPO-34 zeolites affected by surface barriers

In this work, a 3D reaction-diffusion model was developed for porous materials, which accounts for both the impacts of surface barriers and intracrystalline diffusion. The impact of surface barriers on propylene oligomerization, was studied. The results were first validated by advanced spectroscopy. We showed the governing role of surface barriers in coke deactivation inside zeolites.

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Acknowledgements

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OP-II-17

PARTICLE-RESOLVED CFD SIMULATIONS OF CO_2 METHANATION IN FIXED-BED REACTORS

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The transition in the energy sector from fossil fuels to renewable sources leads to the search for a suitable energy storage. Surplus energy can be used for the electrolysis of water to hydrogen and oxygen. However, the storage of hydrogen as an energy carrier is challenging due to its reactivity, diffusivity and corrosion affinity. Further conversion to methane is an alternative where the existing storage and infrastructure of natural gas, containing methane as a key component, can be used. The reaction will take place in a fixed-bed reactor containing a nickel catalyst to convert hydrogen and carbon dioxide to methane. For the development of further prediction models, a thorough understanding of the underlying kinetics is important.

In this investigation, a profile reactor, see Figure 1(a), sheds light on the local interactions between chemical reactions and transport phenomena inside the reactor. It provides axial temperature and concentration profile by using a capillary in the central axis of the fixed bed. The setup is shown in Figure 1(a), while the dimensions of the fixed bed and capillary are shown in Figure 1(b).

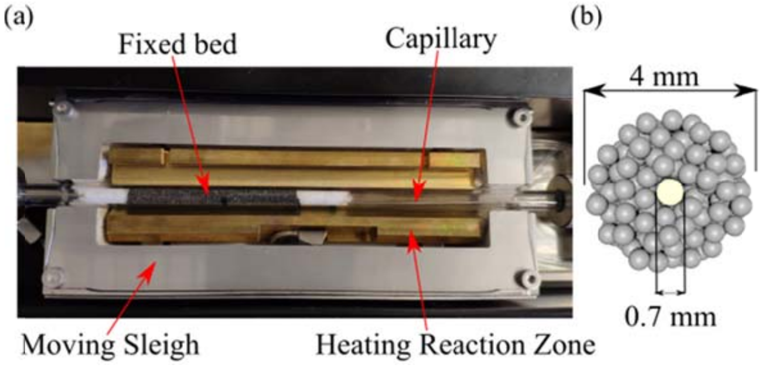

Figure 1. (a) Experimental setup of the profile reactor. (b) Dimensions of tube and capillary and relation to the particle diameter (in this case $d_p = 0.5$ mm)

A ceramic carrier impregnated with Ni catalyst is used for the reaction. The diameter of these particles is about 500 micrometers, which, due to the small reactor diameter, results in a tube to particle diameter ratio D/d_p of less than 10. In addition, the capillary in the center also affects the bed structure, since it forms an additional wall. This leads to particle-resolved CFD simulations in which each particle is mapped three-dimensionally (cf. [1]). The reaction in the pellet is resolved with a detailed three-dimensional model and the species and heat exchange between solid and fluid phase is realized by a tabular approach. In this method, no velocity is transferred into the particle, so that only diffusion takes place inside the particle [2]. The methanation reaction is included in the model using a Langmuir-Hinshelwood-Hougen-Watson kinetics from [3]. First results for the reaction are shown in Figure (a) and the velocity in reactor and particles in Figure (b).

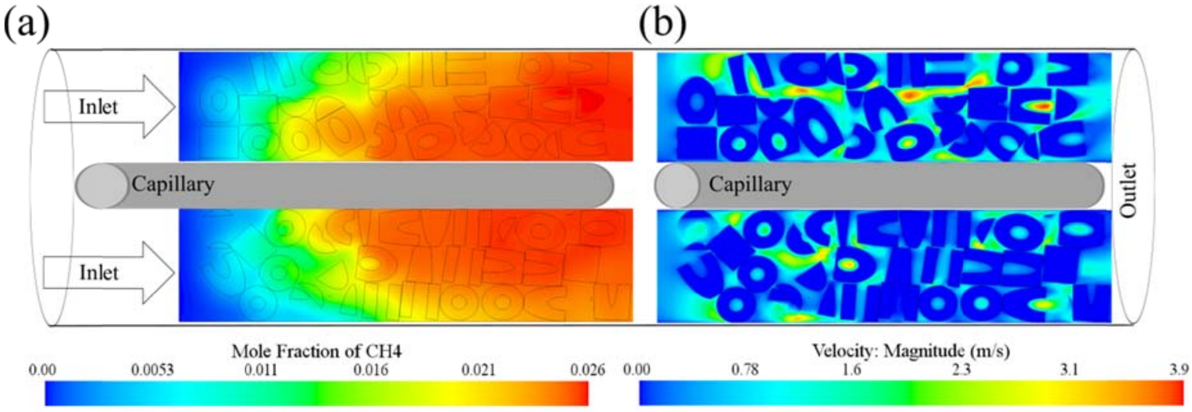

Figure 2. (a) Methanation reaction in the profile reactor with ring particle shape. (b) Velocity in the reactor and the pellet. The volume flow is $\dot{V}_{Inlet} = 250\ mL_N/min$ and the wall temperature $T_{wall} = 550\ K$.

A comparison of this particle-resolved model with a heterogeneous 1D model will show under which circumstances spatial simplifications are appropriate.

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OP-II-18

MODELLING AND SIMULATION OF NON-ISOTHERMAL CATALYST PELLETS FOR UNSTEADY-STATE METHANATION OF CO/CO$_2$ MIXTURES

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The methanation process is a promising part of a sustainable energy supply and infrastructure via the power-to-gas (PtG) process. However, since the availability of renewable energy and carbon sources is fluctuating, the methanation has to be operated under unsteady-state conditions as well, depending on the upstream storage capacities [1]. One of the main challenges arising from this situation is the dynamic behavior of the porous catalyst pellets used for methanation, where heat and mass transfer as well as the chemical reaction occur simultaneously. Thus, dynamically changing spatial profiles of temperature and concentrations develop, which are coupled non-linearly. Among methanation of pure CO$_2$ and CO, a mixture of both carbon oxides is of interest, especially when considering process gases as a carbon source, for example blast furnace gas. However, when switching from CO$_2$ to CO-methanation or between various mixtures of both, the dynamic profiles change in an unpredictable way. Thus, the present contribution analyses the dynamic behavior at particle scale based on modelling and simulation.

The model equations for heat and mass balance arising from the unsteady-state reaction-diffusion problem are implemented in Aspen Custom Modeler for simulation. The binary friction diffusion models are used in accordance to Kerkhof [2], while the reaction kinetics are taken from Klose [3] and Koschany [4]. For simulation typical methanation conditions are chosen with respect to temperature, pressure and reactant composition. Since the external heat transfer resistance is expected to predominate the internal, the external resistances are calculated as well. Based on the dynamic profiles developing upon switching between CO$_2$- and CO-rich periods the core temperature and the surface methane flux are used as indicators for the pellet performance. These indicators are used to study the influence of structural parameters, such as diffusion length or pore size, on the dynamic behavior.

Figure 1 exemplarily shows the simulated spatial profiles of the involved components under isothermal conditions and negligible external mass transfer

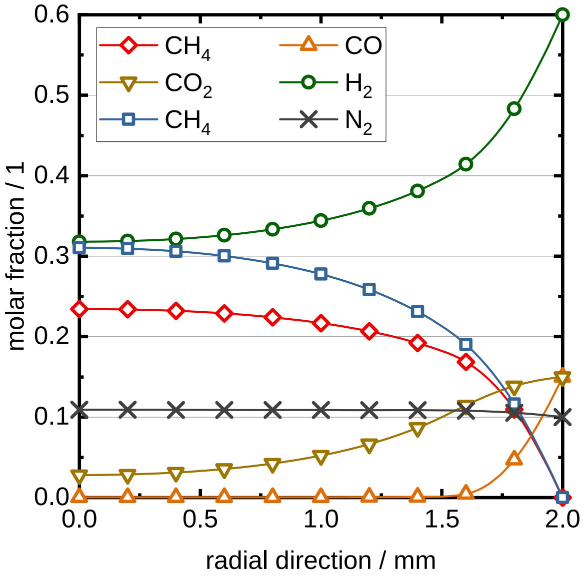

Figure 1. Steady-state mole fraction profiles for simultaneous CO/CO_2-methantion

resistances for the methanation of a mixture of CO and CO_2. It becomes obvious that CO_2 diffuses deeper into the particle, since it is less reactive than CO. The inflection point in the CO_2 profile also indicates that it is converted to CH_4 once CO is already converted to a high extent. Although H_2 is provided at the surface below the stoichiometrically required fraction, it is not consumed completely along the radial direction because of its high diffusion coefficient. The profile of the N_2 molar fraction represents the effect of volume contraction during reaction, which induces viscous flow in addition to a pure diffusive transport mechanism.

The dynamic behavior is studied for the isothermal and non-isothermal case and aperiodic and periodic step changes of the gas composition are simulated. The mass flux across the external catalyst was evaluated for different Knudsen numbers. The isothermal results show the impact of different characteristic times for diffusion and reaction for the species considered in the simulation. These exemplarily leads to a non-monotonic mass flux for H_2 upon switching from CO to CO_2 rich feed gas. Those findings are also reported experimentally for methane. The simulation results for the non-isothermal case will be reported in the contribution, with emphasis on deducing the effect of the non-linear coupling between heat and mass balance on the obtained fluxes for the reactive species.

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OP-II-19

A WIDE-RANGE EXPERIMENTAL AND MODELING STUDY OF H_2S PYROLYSIS AND OXIDATION IN JET-STIRRED AND FLOW REACTORS

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In recent times, the increasing interest in bio-gas and bio-oil as possible replacement of fossil energy sources has opened further environmental issues, due to the presence of contaminant species, often harmful for the human health [1]. Among them, the presence of hydrogen sulfide (H_2S) is particularly critical: although being present in traces (< 10^4 ppm [2]) it might be letal for human health even in such amounts. Moreover, from a chemical point of view, both experiments and kinetic modeling [3] showed that small amounts of H_2S can modify hydrocarbon reactivity, promoting an early oxidation. As a result, obtaining a comprehensive characterization of the underlying chemistry behind H_2S and its mutual interactions with other species has become of major importance for a gradual energy transition to renewable resources.

As a first step, this work aims at characterizing the pyrolysis and oxidation of H_2S in a wide range of operating conditions. To address this, new experimental measurements were obtained at CNRS Nancy in a Jet-Stirred and Flow-Reactor configurations, in such a way to cover low-, intermediate- and high-temperature operating conditions, with high dilution levels and H_2S as fuel in trace amounts.

Table **1** summarizes the investigated experimental conditions, for both pyrolysis and oxidation cases.

Table 1. Experimental compositions investigated in this work

Type	P	T	τ	X_{H_2S}	X_{He}	X_{O_2}
JSR	1.07 bar	600-1200 K	2 s	500 ppm	balance	-
JSR	1.07 bar	400-1200 K	2 s	500 ppm	balance	0.003-0.0204 0.0408-0.0816
FR	1.20 bar	1000-2000 K	0.25 s	500 ppm	balance	-
FR	1.27 bar	600-1300 K	0.25 s	500 ppm	balance	0.0075

At the same time, a detailed kinetic model for the pyrolysis and the oxidation of H_2S was developed by leveraging the most updated experimental and theoretical estimations of the rate constants available in literature. Specifically, the works by Zhou et al. [4] and Glarborg et al. [5] were used as reference points.

Figure 1 shows the pyrolysis results and related predictions, as obtained in Jet-Stirred and Flow Reactors. It can be observed that the kinetic model underestimates JSR reactivity at lower temperatures, while a reasonable agreement is obtained in FR conditions.

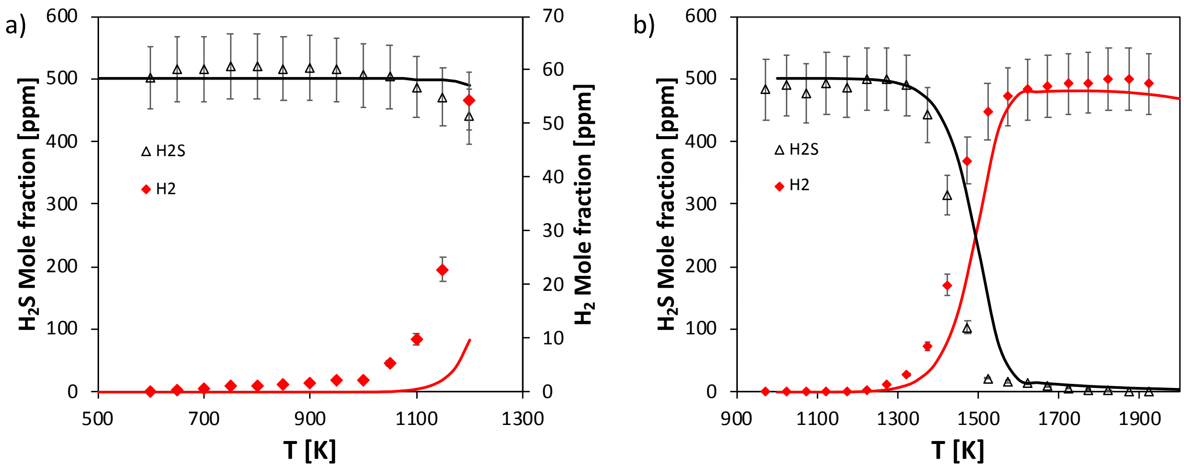

Figure 1. H_2S pyrolysis in a) Jet-Stirred Reactor and b) flow reactor, respectively. Experiments vs kinetic modeling

Further study will involve the extension of the kinetic mechanism in oxidation conditions, and validation against the experimental results obtained in parallel during the experimental campaign.

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OP-II-20

PRODUCTION OF ELEMENTAL SULFUR AND HYDROGEN FROM HYDROGEN SULFIDE IN THE CYCLIC CHEMISORPTION-CATALYTIC REGIME

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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 is 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 hydrogen-containing compounds met in nature.

Unfortunately, the reaction of hydrogen sulfide decomposition

$$H_2S \Leftrightarrow 1/n\ S_n + H_2 \qquad (1)$$

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 **Ошибка! Источник ссылки не найден.** 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:

$$H_2S + MeS_n \Rightarrow H_2 + MeS_{n+1} \qquad (2)$$

$$MeS_{n+1} \Rightarrow MeS_n + 1/n\ S_n \qquad (3)$$

As shown by thermodynamic calculations [1], the reaction (2) is exothermic and the corresponding equilibrium conversion of H_2S may reach 100 % at ambient temperature. The regeneration reaction (2) require higher temperatures, but the backward formation of H_2S is completely excluded by hydrogen absence in the reaction media during the regeneration stage.

The earlier work [2]stated the possibility of hydrogen sulfide decomposition at ambient temperatures, but it contained no quantitative data on hydrogen yield. The aim of the current study was experimental check of this possibility.

The performed experiments showed that under cyclic alteration of chemisorption and regeneration stages, the formation of hydrogen at ambient temperatures is negligible at all tested sulfides, most probably, due to kinetic limitations. The conversion of H_2S with emission of hydrogen at the chemisorption stage becomes visible starting from 200 °C and it rises with temperature increase reaching maximum at 350 °C (see Fig. 1), this rise caused by kinetic factors. With further temperature rise the influence of backward reaction of H_2S formation becomes significant and the observed conversion decreases. At the same time, it is seen that H_2S conversion in all presented temperature range significantly exceeds the equilibrium value, this is caused by the chemisorption enhancement of the H_2S decomposition reaction.

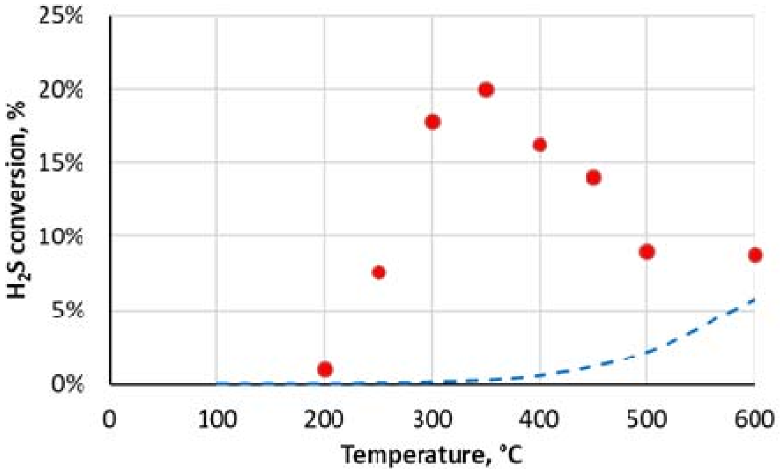

Fig. 1. Conversion of H_2S at the chemisorption stage under the chemisorption-regeneration cycling. Points – experimental data, dashed line equilibrium for reaction (1). Chemisorbent – FeS, reaction media – 5% H_2S in nitrogen

High-temperature (600 °C) regeneration completely restores the chemisorbent properties, showing no degradation of this material during 20 cycles.

Though the received results appeared to be less optimistic than it was expected in respect to reaction temperatures, the propose process approach is still feasible for practical application in hydrogen manufacturing purposes. The presentation discusses the possible process flow sheets.

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OP-II-21

SORPTION ENHANCED DIMETHYL ETHER SYNTHESIS: MAXIMISING CARBON EFFICIENCY

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Introduction

Utilisation of CO_2 is expected to play a crucial role to enable sustainable industrial production of carbon-based products, the large-scale storage and transport of renewable energy, and the production of renewable fuels [1]. Conversion of CO_2 with H_2 produces H_2O as by-product, and the reactions are generally equilibrium limited. By the principle of Le Chatelier, the in situ removal of H_2O from the reaction mixture results in a shift of the equilibrium to the product side and enhance the conversion [2]. Very high carbon efficiencies, an important criterion for the value chain for converting the available CO_2, have been demonstrated for the conversion of synthesis gas and CO_2 to DME (fuel and platform chemical) by sorption enhanced DME synthesis (SEDMES) [3,4], in which water is removed in situ by the use of a solid adsorbent. Experimental proof-of-principle has shown increased DME yield, improved selectivity towards DME over methanol, and reduced CO_2 content in the product [3,5]. This contribution will present a combined approach of experimental scale-up and model development, which has been proven successful in the development and scale-up of the SEDMES process [2,6].

Methods

Both a 1D dynamic cycle model (Matlab) was developed, verified and validated, and transient experiments in a packed-bed reactor were performed for various stoichiometric feed compositions and inert N_2, Ar. Various copper/zinc oxide/alumina catalysts and commercial zeolite LTA steam adsorbent (mixed in different ratios) were used experimentally. Adsorption was conducted at 250-300 °C, 25-40 bar(a) and with different feed gas compositions. Regeneration was done by switching to dry gas, depressurisation and eventual heating to 400 °C. Transient analysis was done by a combination of mass spectrometry and micro GC.

Results and discussion

A representative breakthrough experiment of sorption enhanced DME synthesis is shown in Figure 1. Prior to steam breakthrough, DME and unconverted CO are the primary products. After steam breakthrough (inset Figure 1) the concentration of DME drops, accompanied with the breakthrough of CO_2 and methanol indicating saturation of the adsorbent. Full feed flexibility is obtained since the sorption enhancement is similar for all CO/CO_2 compositions of the feed (Figure 2).

As can be seen in Figure 1 the dynamic cycle model, using literature reaction kinetics and water adsorption isotherm, describes the experimental results reasonably well. With the model, a window of operation has been explored for the SEDMES process. Key parameter for process performance is the working capacity. Improving this capacity can be done by tuning the reactive adsorption and the regeneration conditions. Reverting to pressure swing regeneration (without temperature swing) appears as a promising option.

Experimentally, different catalysts (commercial and novel) and steam adsorbents have been tested and have shown to be promising for further development of the process to industrially relevant conditions. Stability of the different catalytic functions depends on operating conditions throughout the cycle [5,7,8]. Experimental campaigns of more than 100 cycles without observed degradation support the model study indicating high carbon efficiency to DME and reduced CO_2 content in the product for a typical SEDMES operation. The testing under industrially relevant conditions also proves increasingly high performance with pressure swing regeneration and gives relevant data as input for validation and tuning of the SEDMES model. The improved model in its turn is used for the cycle design optimization of the SEDMES process, for which full cyclic continuous DME production in a multicolumn setup will be demonstrated early 2020.

Given the potential of the SEDMES technology to convert CO_2 to DME with high single-pass yield, a containerized and transportable Power-to-DME demonstration unit has been designed. Combining water electrolysis and SEDMES, the Power-to-DME concept will be demonstrated at 3 kg/h DME scale.

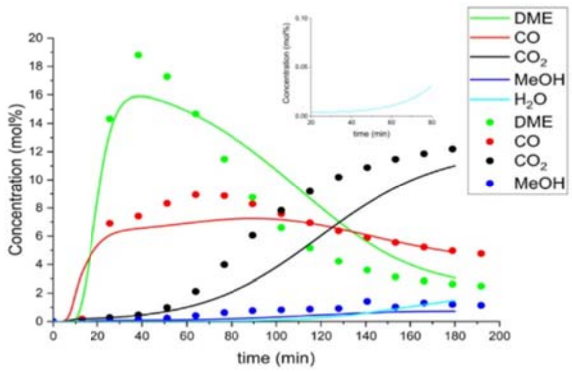

Figure 1. Breakthrough experiment (points) and model prediction (lines) at 40 bar(a), 275 °C, feed $H_2:CO:CO_2 = 8:1:2$ (regeneration to 400 °C)

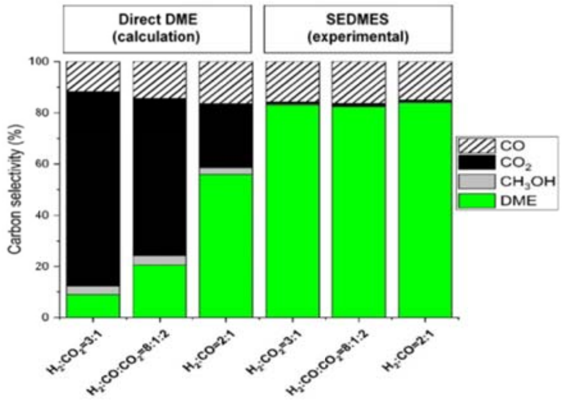

Figure 2. Thermodynamic carbon distribution (left) versus experimentally obtained results for sorption enhanced DME synthesis (right). Conditions: stoichiometric H_2 to CO_x feed, CO_x feed is CO_2, CO_2:CO 2:1 and CO, including 30 % inert, 275 °C & 40 bar(a)

Conclusions

The SEDMES process is a promising process intensification, achieving over 80 % single-pass CO_2 conversion, thus requiring less downstream separation, and smaller recycle streams especially for a CO_2-rich feed. Within EU Horizon 2020 project Fledged SEDMES cycle design has been explored and continuous DME production will be demonstrated in a multicolumn test rig. Further development of the SEDMES process is pursued within the Interreg E2C project by the design, construction and operation of a dedicated Power-to-DME demonstration unit.

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OP-II-22

SORPTION ENHANCED DIMETHYL ETHER SYNTHESIS: REACTOR MODELLING AND DESIGN

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Introduction

Dimethyl ether (DME), a promising alternative fuel [1], can be synthetized from syngas via a one-step process (direct synthesis) based on a single reactor loaded with both methanol synthesis and dehydration catalysts. Two of the main issues of the direct DME synthesis are the thermodynamic equilibrium limitations and the thermal management of the reactor [2]. The thermodynamic limitations are more stringent when CO_2-rich feed is used (e.g. syngas obtained from biomass gasification) due to the larger production of water associated to the DME synthesis from CO_2. Sorption Enhanced DiMethyl Ether Synthesis (SEDMES) process with in-situ water removal is a potential solution to overcome such limitation allowing for once through process configurations [3].

Methods

A 2D+1D dynamic model of a single tube of an externally cooled multitubular fixed bed SEDMES reactor has been developed and implemented in gPROMS for the numerical solution. The model includes 2D mass, enthalpy and momentum balances for the gas phase and 1D mass balances for the catalysts and adsorbent solid phases, for an accurate description of thermal effects and internal diffusion limitations. Transport coefficients and H_2O adsorption isotherm correlations are taken from the literature. The kinetics is based on a literature model [4,5] refitted on the basis of experimental data.

Results and Discussion

The model has been successfully used to reproduce the dynamic behavior of a bench scale SEDMES tubular reactor operated in the TNO test facilities in Petten. The calculated outlet molar concentrations and centerline gas temperature have been used for the validation. In *Figure 1* model predictions are compared with experimental data obtained at 25 bar, 523 K of inlet and wall temperature, space velocity of 100 h^{-1}, syngas feed composition with CO/CO_2 ratio 2 and

M = $(H_2 – CO_2)/CO_x = 2$. In *Figure 1a* the molar fractions at the reactor outlet are reported versus time: both the reactants (CO and CO_2) and the products (MeOH and DME) are not detected in the first minutes of the process since the reactor is initially full of inert N_2, which is progressively displaced by reactants and products. Starting at about 400 s the DME concentration rapidly increases, passes through a maximum and then gradually decreases due to the progressive adsorbent saturation with time. The temperature profile (*Figure 1b*) has a similar behavior: a sharp increase, though smoother than that observed in the experiment, is predicted when the reactant wave reaches the monitored bed position, starting the exothermic process. Then, after reaching a maximum, the temperature gradually declines because: i) heat release by water adsorption decreases due to progressive sorbent saturation; ii) reaction rates slow down due to the local shift of the thermodynamic equilibria and the inhibiting effect of increasing water concentration. The validated SEDMES reactor model is currently used for the design of multitubular reactors able to cope with the observed thermal effects.

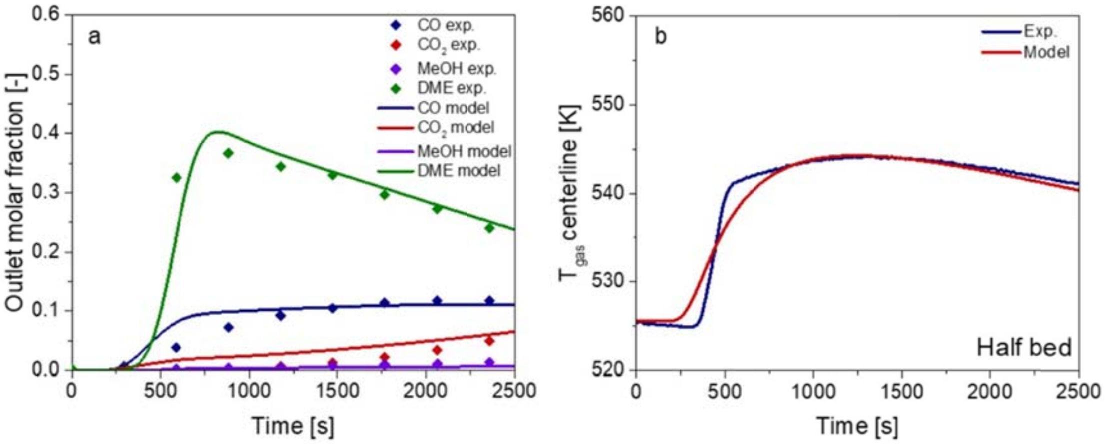

Figure 1. Evolution with time of a) Outlet molar fractions of reactants (CO and CO_2) and products (MeOH and DME), experimental data vs. model results; b) gas centerline temperature at half bed

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OP-II-23

MATHEMATICAL MODELING OF VOLATILE ORGANIC COMPOUNDS OXIDATION PROCESS IN REVERSE-FLOW REACTOR WITH SIDE GAS INLET

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In the environmental protection field an important direction is the purification of waste gases from volatile organic compounds (VOCs) impurities. Currently, for low-concentrated emissions processing, the catalytic reverse-flow processes [1, 2] possess the best economic and environmental indicators and are capable to treat gases with VOC content higher than 1 g/m^3 in autothermal regime (not requiring additional energy supply).

The reverse-flow reactor considered in the present study has non-standard inlet/outlet arrangement as gas enters and leaves the bed not in axially-oriented direction, but from the cylindrical apparatus side. The process was examined by means of mathematical modeling in 3D geometry (COMSOL Multiphysics) for toluene oxidation reaction [3]:

$$C_7H_8 + 9O_2 \Rightarrow 7CO_2 + 4H_2O \qquad (1)$$

The catalyst bed was considered as porous medium and model took into account gas velocity and pressure (Brinkman equations), mixture compounds and medium temperature distributions. The calculations were carried out until the stabilization of forward-reverse cycles was reached.

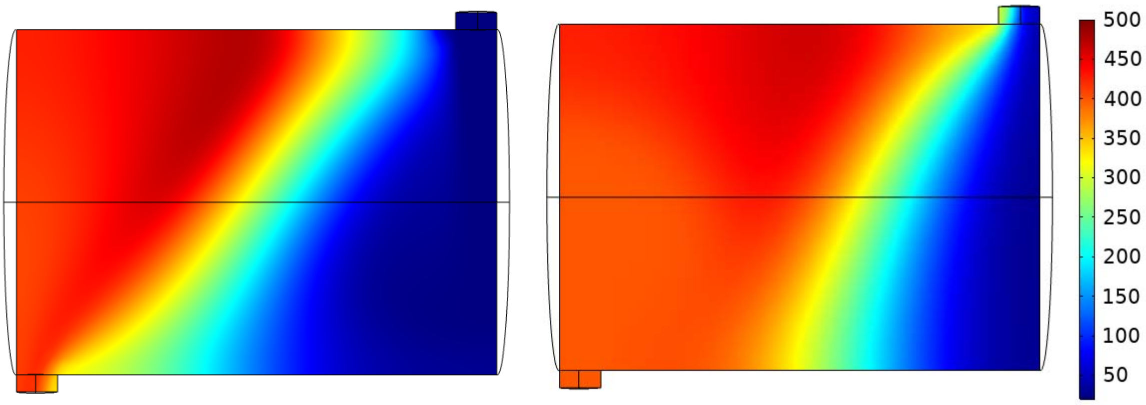

Fig. 1. Temperature distribution at the end of forward and reverse cycles (°C)

Fig. 1 shows the temperature distribution at the end of forward (left) and reverse (right) cycles in the central reactor plane. The model showed that heat wave, that formed in the reactor provides strongly nonuniform temperature distribution near the apparatus walls.

During the model calculations the geometric and inlet gas parameters were varied to explore the process behavior in different conditions. It was discovered that process passes in asymmetric nonstationary modes that do not possess such a good stability as symmetric ones. Thus, the management and arrangement of the flow inlet/outlet significantly affects on the reverse-flow process stability and efficiency.

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OP-II-24

ROOM-TEMPERATURE TOLUENE DECOMPOSITION BY CATALYTIC NON-THERMAL PLASMA REACTOR

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The present work deals with the decomposition of low concentrations of a volatile organic compound, toluene, in a packed-bed dielectric barrier discharge (DBD) plasma reactor. 2.5 % $MO_x/\gamma\text{-}Al_2O_3$ (M = Mn, Co) catalysts prepared by wet impregnation method and characterised by PXRD, BET, TPR, TPD (CO_2 and NH_3), TEM, and XPS to understand the metal-support interaction. Toluene vapour blended with atmospheric air (@ 100 lph) is fed into the reactor. The influence of varying input toluene concentration between 50 and 200 ppm on the conversion is studied for different packing conditions. The effect of surface modifications of $\gamma\text{-}Al_2O_3$ with transition metal oxides is found to have a significant impact on product selectivity and ozone formation. The plasma reactor that employed surface-modified $\gamma\text{-}Al_2O_3$ with transition metal oxides indicated improvement in CO_2 selectivity besides suppressing the formation of ozone, compared to $\gamma\text{-}Al_2O_3$ and DVD reactor plasma reactor. $Co_3O_4/\gamma\text{-}Al_2O_3$ effectively decomposed toluene (95 % at 3.3 W) at lower concentrations with about 70 % CO_2 selectivity. $MnO_2/\gamma\text{-}Al_2O_3$ and $Co_3O_4/\gamma\text{-}Al_2O_3$ displayed the same conversion effect at higher toluene input. Almost 98% of the carbon balance was obtained while using $MnO_2/\gamma\text{-}Al_2O_3$ and $Co_3O_4/\gamma\text{-}Al_2O_3$, which signifies the necessity of integration of metal oxide to get the effective conversion as well as maximum selectivity towards the desired products. The mean electron energies and energy electron distribution function were also calculated using BOLSIG+ software. The high-performance packed-bed DBD with 2.5 % $MO_x/\gamma\text{-}Al_2O_3$ packing offers a promising approach for removing dilute VOCs. To optimise the reaction conditions and to obtain 100 % conversion, the input power and airflow rate were varied.

OP-II-24

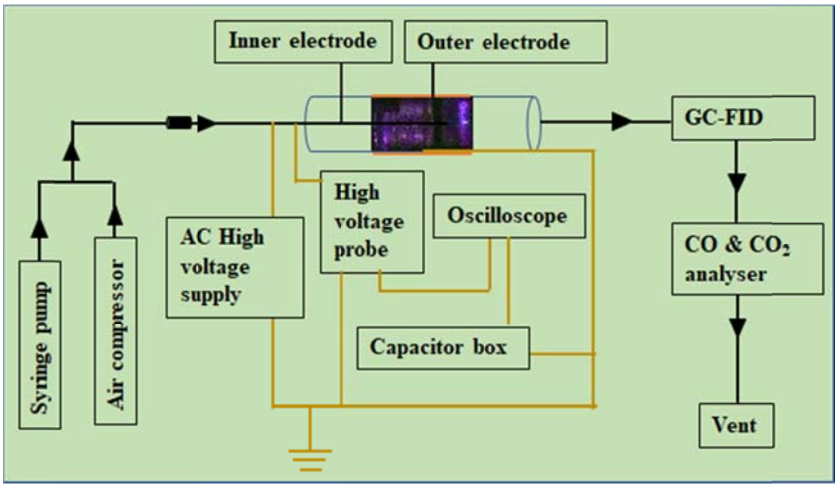

Figure 1. Experimental set-up

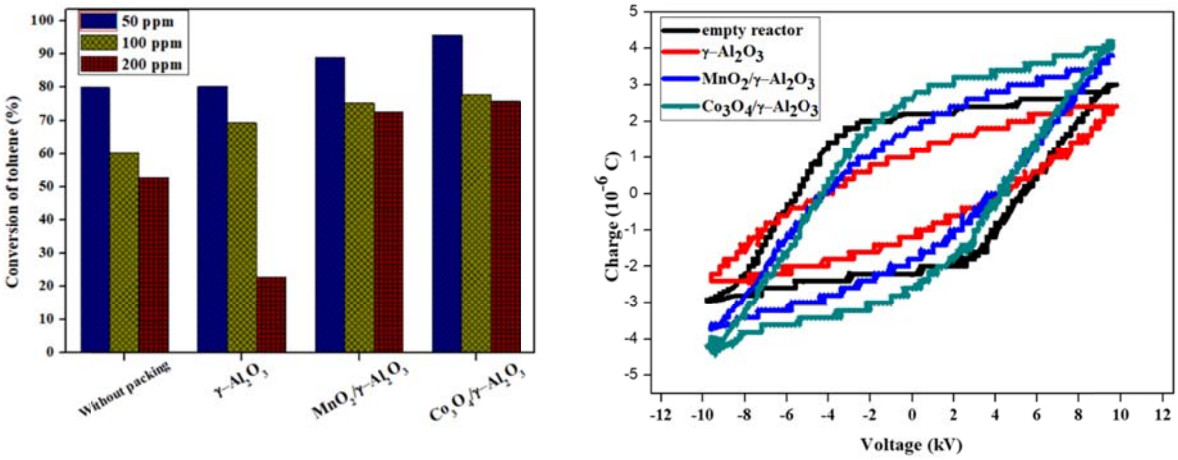

Figure 2. (a) Influence of γ-Al_2O_3 metal oxide supported catalysts on the conversion of toluene. (b) Lissajous figures with different catalyst packing

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OP-II-25

HEAT TRANSFER IN BUBBLING FLUIDISED BED REACTORS WITH IMMERSED VERTICAL HEAT EXCHANGERS

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Conversion of chemical energy carriers often involves strongly exo- or endothermic chemical reactions such as methanation, Fischer Tropsch, gasification, hydrogenation/ dehydrogenation of liquid organic hydrogen carriers (LOHC). The challenge for these reactors is to ensure high conversion while not compromising the selectivity or, in many cases, the catalyst stability. Although technical solutions exist for large scale processes running continuously such as in the oil/gas industry, these cannot be directly transferred to an energy system that needs to integrate a large share of volatile renewable energy resources. Here, compact and flexible reactors at smaller scale are necessary. Bubbling fluidised bed reactors allow for fast start-up and load changes; they offer very high heat transfer rates to the immersed heat exchanger tubes even in part load, and have proven to be a robust and flexible technology for several investigated methanation processes.

For safe scale-up and reactor optimization, correct prediction of the reactor performance is necessary not only with respect to reaction kinetics and mass transfer, but also to the energy balance. The latter is dominated by the heat transfer to the immersed heat exchanger tubes, which in turn is influenced by rising bubbles that cause intense mixing of the solids.

A pilot scale pressurized set-up (inner diameter 22 cm, up to 2 m bed height, 36 heat exchanger tubes, up to 10 barg operation) was built and is used for measuring bubble sizes, their rise velocities [1] and overall heat transfer for Geldart A and B material and several linear velocities. The main reactor has horizontal ports for devices that allow radial movement of the optical sensors under pressure and temperature. From top, an axially movable sampling tube is introduced to measure.

To better understand the impact of rising bubbles on the heat transfer, a heat flux sensor (HFX) is used in the Perspex flow model, see Figure 1. One of the mock-ups of the heat exchanger tubes is heated with hot water, while a flat sensor on its surface

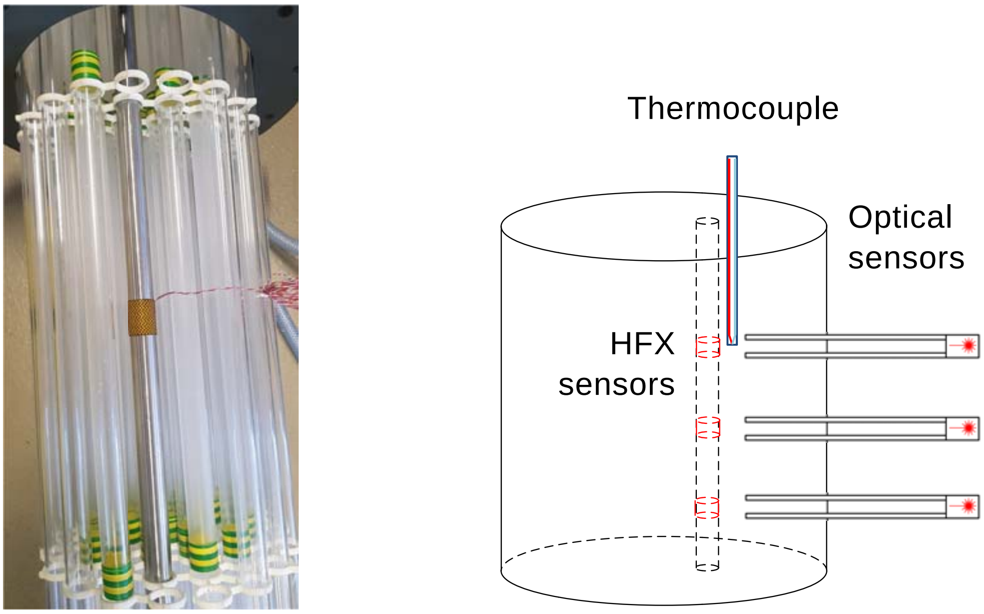

Figure 1. Cold flow model auf bubbling fluididised bed with optical and heat flux sensors

measures the heat flux to the fluidised particle bed, whose temperature is measured by an immersed thermocouple. Using optical probes at the same time will allow investigation of the influence of rising bubbles on the local heat transfer. As shown in the figure below (Figure 2), passing bubbles lead to an increase in local heat flux. Knowledge of the local heat flux will help to better understand the overall heat transfer data from the pilot scale experiments and to find the optimal operation conditions.

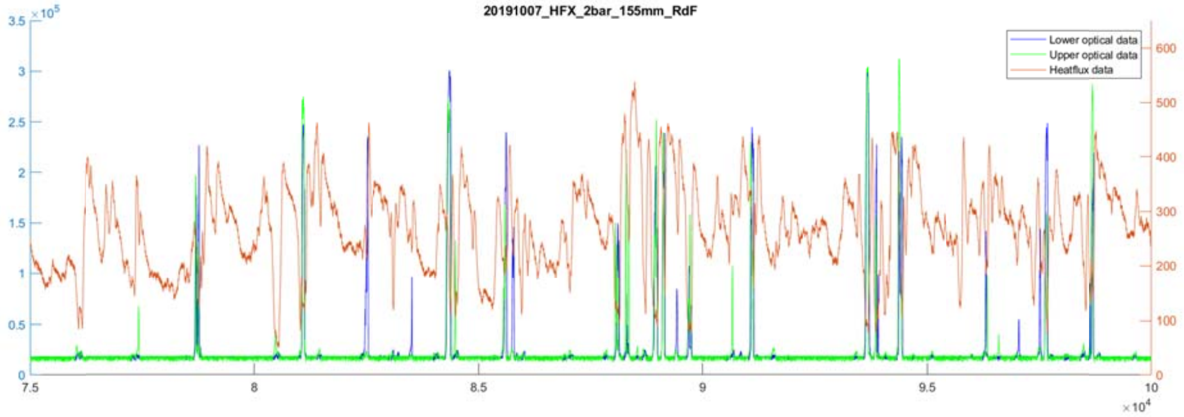

Figure 2. Results from cold flow model auf bubbling fluididised bed with optical and heat flux sensor

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OP-II-26

MICROREACTORS PAVE THE WAY FOR CONTROLLED REACTION, IN-DEPTH STUDY AND ENHANCED PROCESSING OF MATERIALS

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Self-assembly refers to the autonomous organization of molecules and/or artificial components into patterned/ordered structures without human or machine intervention. Among the self-assembled structures, crystalline materials are an appealing category owing to their high order of organization at the molecular level. However, the majority of the investigations on crystalline materials study their self-assembly process under equilibrium conditions, where only the thermodynamically stable species can be obtained [1]. This limitation not only hampers the proper understanding of the process, but it is a drawback for the effective formation of materials with desired properties.

To tackle this challenge, we developed a continuous flow microfluidic-based platform with four input flows (Q_1-Q_4) capable of obtaining out-of-equilibrium crystal structures (Fig. 1). Employing this approach, we successfully isolated the crystalline structures of a coordination polymer (CP) that are not achievable through conventional approaches. In such a system, altering primary parameters such as input flow rates, the self-assembly process and reaction conditions can be fine-tuned, and thus, advanced materials with desired properties, e.g. morphology, can be obtained [2].

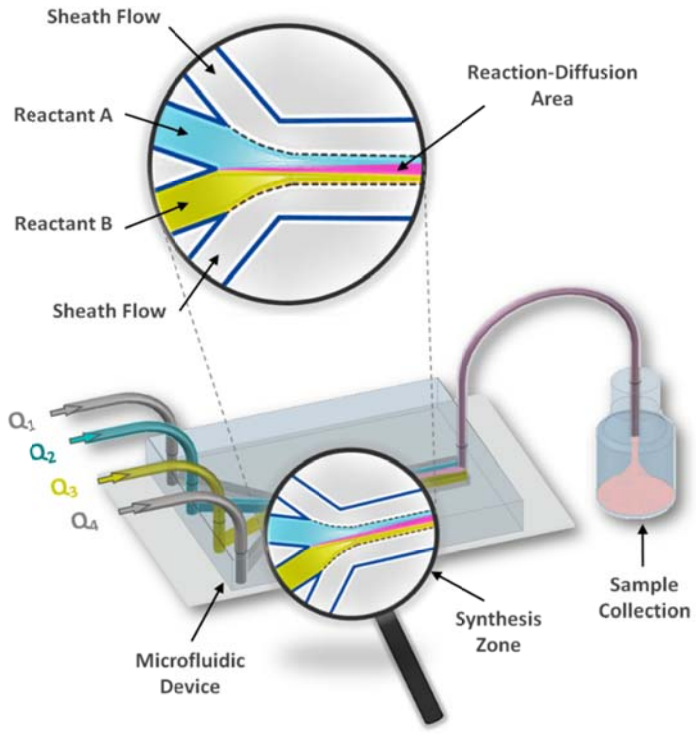

Fig. 1. Microfluidic set-up used as a microreactor for synthesis, collection and processing of materials

Subsequently, controlling the reaction-diffusion area and concentration gradient of the reagents, and hence, the kinetics of the reaction, we performed the controlled synthesis of a spin crossover (SCO) material, i.e. a material capable of exhibiting bistability. Obtained SCO materials possess suitable chemical and physical properties that bring promises for their use in different applications, notably as sensors or molecular switches [3]. Moreover, preparation of a SCO in a microreactor (such as Fig. 1) under controlled synthetic conditions revealed the interesting unprecedented growing pathways, which cannot be explored using conventional methods.

Furthermore, crystalline materials are typically insoluble and unprocessable crystalline powders, which poses issues in their handling and application. To overcome this drawback, we demonstrated the ability of this microfluidic-based method (Figure 1) to produce processable fibers of crystalline materials. Surprisingly, this microfluidic approach also allowed the controlled deposition and conformal printing of the produced fibers of crystalline materials on various surfaces, enabling the application of these materials in advanced patterning technologies [4-5].

In summary, microreactors provided by microfluidic approaches give rise to useful and promising platforms for controlled synthesis, in-depth study, and enhanced processing of materials, particularly crystalline materials. These features are not attainable through conventional methods currently used for synthesis of these materials.

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OP-II-27

PARAMETRIC SENSITIVITY AND DESIGN OF REACTORS FOR CHEMICAL PROCESSES IN WATER FLUIDS

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Water fluids at temperatures approaching the critical point (647 K) and above are used as an environmentally benign ("green") media and reactants for various chemical processes, including syntheses of organic compounds and inorganic materials, processing of natural raw materials, waste treatment, etc. [1]. In some of the most important chemical and physical properties, including reactivity and dissolution ability, degree of dissociation and dielectric properties, they differ significantly from liquid water and water vapor at relatively low temperatures and pressures. It is these differences that often determine the technological advantages of water fluids in the considered temperature range. However, in this case, the properties of water can vary sharply and non-monotonously with changing state parameters. This determines the high parametric sensitivity of chemical processes and makes special demands on the equipment used for their implementation.

In this work, we studied the structuring and crystallization of amorphous silicon oxide (high-purity amorphous silica and Sigma-Aldrich silica gel Davisil grade 646) in batch reactors of various designs. The influence of state parameters on the formation of materials of a target structure and morphology, as well as on side processes caused by uncontrolled phase transitions and mass transfer in the reactor, is considered.

It is shown that during the processing of amorphous silica in a water fluid medium at 600-700 K, a sharp decrease in the value of its specific surface area occurs over time; in the presence of alkali metal ions (Na^+) in a concentration above 10^{-2} %, crystalline phases are formed, the amount and ratio of which are governed by temperature, fluid density and processing time. Figure 1 shows the dependence of the specific surface area and the intensity of the main reflexes in the diffraction patterns of silica gel on the fluid density (ρ). It is worth noting that even at ρ as low as 10^{-3} g cm^{-3} (that is created in the closed autoclave by water adsorbed in the material) a significant structuring ("cold sintering") of the material occurs, whereas after a similar treatment in a crucible in the open air no changes were noticed.

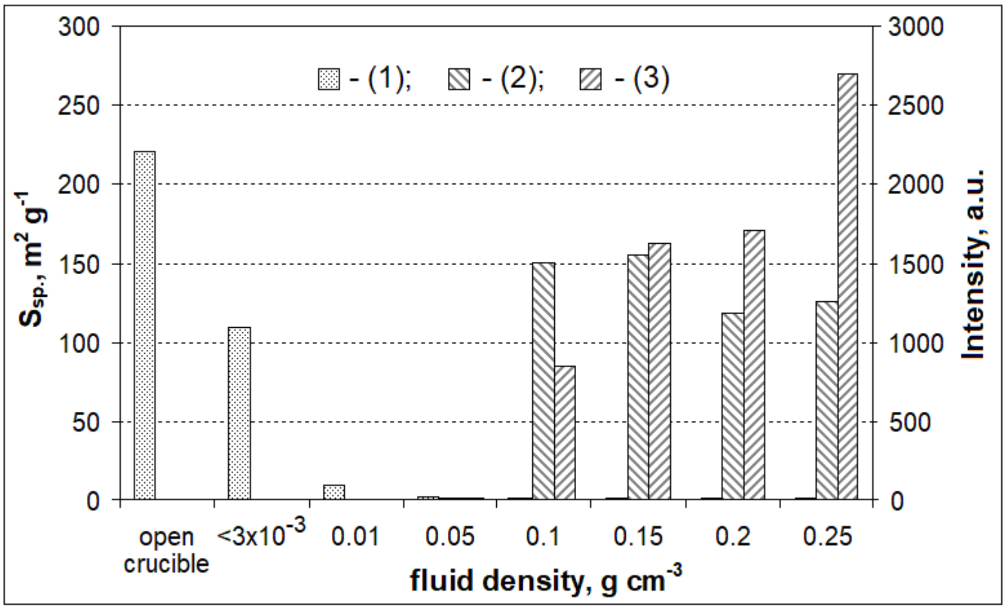

Fig. 1. Effect of fluid density on specific surface area (1) and intensity of main reflexes of cristobalite (2) and keatite (3) phases; silica gel treated at 653 K for 3 h

In addition to the duration of the treatment, temperature and pressure (or fluid density), the physical state of water (liquid vs. vapor) below the critical point significantly affects the intensity of the process and the phase composition of the resulting material. One of the reasons for the uncontrolled appearance of liquid water in the reaction space and its side effect on the target process is the presence of relatively cold zones in the reactor where condensation can occur.

Several solutions for the design of reactors of various sizes have been considered, which make it possible to achieve a constant temperature in the reaction zone and to avoid the influence of liquid water on the morphology and phase composition of silica during its processing in water fluids. In particular, for experimental small-volume autoclaves with individual heating, it is optimal to use an additional inner cell of heat-conducting material with a loose fitting lid.

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Acknowledgements

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OP-II-28

THE RELATIONSHIP BETWEEN THE MODES OF THE CONTACTOR AND THE EXTRACTOR IN THE REACTOR WITH A MEMBRANE CATALYST

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The main reactor modes with a membrane catalyst (contactor, distributor and extractor) differ from each other in the way the reactants are fed into the reactor and the reaction products are removed from it. In the extractor mode, the reagents are fed into the reactor as a mixture of the appropriate composition, and the products are separated into two streams (permeate (P) and retentate (R)) with different chemical compositions on both sides of the membrane catalyst.

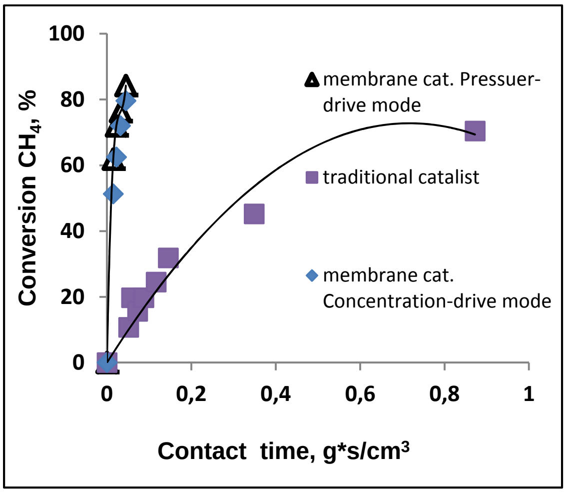

Fig. 1. Conversion CH_4 in DRM on Mo_2C membrane and tradition (powder) catalysts from contact time at 850 C, CH_4:CO_2 = 1

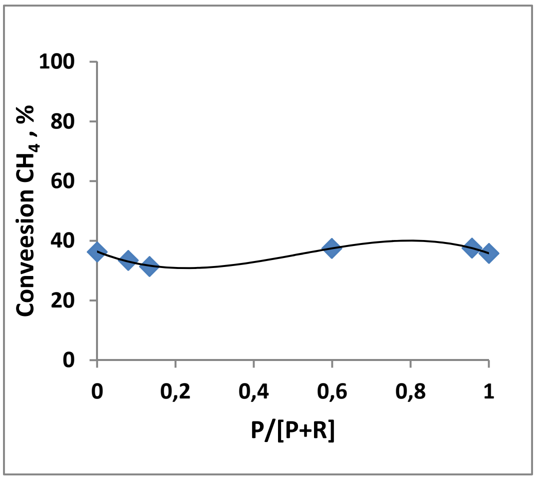

Fig. 2. Conversion CH_4 in DRM at extractor mode on Mo_2C membrane catalysts from ratio P/[P+R] at 850 °C, CH_4:CO_2 = 1, contact time – 0,007 s

The technological boundaries of the extractor's mode are two that with forced (pressure-drive) and diffusion (concentration-drive) transport of contactor. At the forced transport contactor mode reagent mixture passes through the pore structure of the membrane catalyst due to pressure difference. In the of diffusion transport mode, the entire mixture of reagents enters and exits from shell-side of reactor and penetrates into the membran catalyst as a result of concentration difference.

Figure 1 shows the change in the degree of conversion of methane in DRM as function of the contact time for powdered Mo_2C (traditional catalyst) and for molybdenum carbide deposited on the corundum microfiltration membrane

(membrane catalyst). Already at contact time a value of 0.045 g·s/cm^3, the methane conversion on the membrane catalyst reaches 80 %. On a traditional catalyst such a conversion value was not achieved at all under conditions of our experiment. This can undoubtedly be considered as a demonstration of the catalytic process intensification on membrane molybdenum-carbide catalyst for forced and diffusion mode of contactor.

Figure 2 shows the change in conversion of methane in the extractor mode in the reactor with a membrane catalyst. At P/[P+R] = 0, the entire CH_4:CO_2 mixture passes only through the shell side of the reactor (diffusion mode). At P/[P+R] = 1, the entire reagents mixture passes through the pores of the membrane catalyst and removed out from tube side (forced mode). It turns out that results of these modes DRM are almost the same - 36.3 % and 35.8 %, respectively. Moreover, the forced transport of the reagents into the pores of the membrane catalyst (penetrated flow) reduces the conversion of methane.

Both results presented in the graphs cannot be explained from the standpoint of classical catalysis and mass transfer in a continuous viscous medium. To understand the essence of the presented results, one should use the hypothesis that was proposed to explain the intensification of DRM on a tungsten-carbide membrane catalyst [1].

The essence of the proposed hypothesis is analogy with the phenomena observed in the Knudsen compressor. When a temperature gradient is applied in the channels of a porous material, the dimensions of which are less than 1 μm, two oppositely directed flows are arisen. One is thermal slip at the surface of the channel wall. Another flow of opposite direction along the axis of the channel is controlled by Darcy's law. If conditions in the porous medium are established then the circulation of gases is appeared. In our DRM experiments, the temperature difference reached 30 K and reagent mixture can contact catalytic layer more than eight times because of circulation for the stay time in reactor.

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ELECTRIFIED STEAM REFORMING: RESISTIVE WASHCOATED SiC FOAMS AS INTERNAL HEATING ELEMENTS FOR HYDROGEN PRODUCTION

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In the last decade, a substantial increase of electric energy production with renewable intermittent sources was observed. The large availability of relatively low-cost renewable electric energy represents a significant opportunity to decrease the carbon footprint of endothermic chemical processes. In particular, the application of this concept to the steam reforming of natural gas would provide a twofold beneficial effect: first, the electrically-heated reformer would prevent the combustion of methane (which is burnt in traditional reformers to fulfill the endothermic process demand), playing a crucial role in the quest for reducing CO_2 emissions. Moreover, electric current could be used to directly convert methane into hydrogen rich streams, while still relying on a well-established industrial process.

Based on this approach, electrically heated washcoated tubes (Ø 5 mm) were recently proposed as an innovative reactor layout for steam reforming [1]. One of the main drawbacks of the proposed system, however, is the scale-up of the concept. If bigger tubes are employed, larger negative radial T-gradients are expected, and the catalyst inventory per volume is reduced, as well as the hydrogen generated.

In this work we propose a reactor concept in which electric current is forced to flow through the solid matrix of a SiC open cell foam, which heats up due to Joule effect. The reagent feed is directly heated by the silicon carbide foam and catalytic activity is obtained by packing egg-shell catalyst particles in the open cavities of the foam, as reported in [2,3]. In the first portion of the foam the gas is heated up to a temperature where the highly active Rh catalyst is reported to be active. As typically occurs in noble-metal catalyzed systems for steam reforming, at T > 550 °C the conversion is limited by chemical equilibrium [2,3], thus, by the heat transfer rate. This approach aims at obtaining a local and distributed heat generation, capable of sustaining effectively the heat demand of the process.

To assess the feasibility of the concept, first the electric resistance of a SiC foam support (L = 10 cm, d = 3.2 cm, $\varepsilon = 0.9$) was measured by means of a multimeter. The resistance was found to decrease with growing temperature up to an almost constant value over 300 °C. Extrapolation of the results at higher temperatures was considered for thermodynamic calculations.

A thermodynamic analysis of the process was performed considering Joule heating of the SiC foam, and assuming both Steam Reforming and Water Gas Shift reactions at chemical equilibrium under adiabatic conditions. A GHSV = 5400 h^{-1} referred to the total reactor volume was assumed, with a feed S/C ratio of 3.5 and an inlet temperature of 500 °C and 1 atm. Thermodynamic calculations show that the methane conversion and the equilibrium temperature of the system depend on the current density: with values in the range of 2-2.1 A/cm^2, corresponding to a specific power generation of 4 W/cm^3, it is possible to reach significant methane conversions. Experimental tests and detailed numerical simulations are ongoing to validate the potential of the proposed concept.

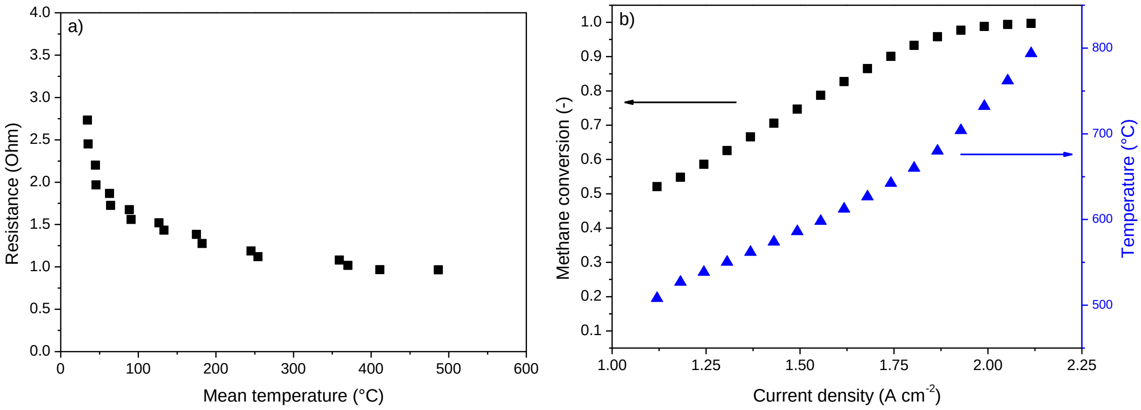

Figure 1. Measurements of the electric resistance as a function of temperature (a) and thermodynamic simulations of equilibrium conversion and temperature vs input current (b)

In this contribution we propose the adoption of packed SiC foams for electrified steam reforming of natural gas. The use Joule heating to sustain the endothermic Methane Steam Reforming over pelletized catalysts embedded in the SiC foam allows for a remarkable process intensification.

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HEAT TRANSFER IN SLENDER PACKED BED REACTORS: EFFECT OF RADIATION

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Radial heat transfer is one of the most challenging aspects of a safe, stable, and economic operation of packed bed reactors [1]. However, the comprehensive description of heat transfer is far from trivial. During the last two decades, particle resolved computational fluid dynamics (PRCFD) has enabled researchers to gain insights into transport phenomena in packed beds that are nearly impossible with experiments [2]. This approach takes the actual packed bed structure into account and calculate momentum, heat, and mass transport within the finite volume method. With PRCFD, we showed in previous studies that thermal radiation significantly contributes to the overall heat transfer mechanism [3] in slender packed beds and can therefore also influence the local reaction rate [4]. Since PRCFD is still too computationally demanding for daily engineering problems, simplified engineering models are widely applied. In this contribution, we compare heat transfer in packed beds calculated from PRCFD simulations and from a classical 2D plug flow model with and without thermal radiation conditions.

We followed our PRCFD approach and generated one packed of spheres and one packed bed of rings, for which heat transfer simulations were carried out over a wide range of inlet/wall temperatures and particle Reynolds numbers. In order to compare the classical 2D plug flow heat transfer model [1], the wall Nusselt number Nu_W and the effective thermal conductivity of the bed were governed from the axial temperature profile of the CFD simulations. This is described in very detail elsewhere [5]. The obtained parameters are compared to well established correlations by Martin & Nilles for Nu_W and Zehner-Bauer-Schlünder (ZBS) for $\Lambda_{r,\mathrm{eff}}$ [1]. Lastly, radial temperature profiles are calculated with the obtained parameters of the CFD simulations.

Figure 1 (A) and (B) show impressively the intensified surface temperature of the spheres in the near-wall region. Due to the extra heat transfer mechanism of thermal radiation, the particles in the near-wall region show in general higher temperatures than for the simulation neglecting thermal radiation. This effect is reflected by Nu_W, which increases with the temperature level. However, the correlations from Martin & Nilles underpredict this near-wall phenomenon, see Figure 1 (C). Contrarily, the effective thermal conductivity of the bed is well predicted by the ZBS correlation, which indicates minor thermal radiation effects in the bulk region of the bed. The results of the bed of Raschig rings do not show this pronounced near-wall radiation effect, probably due to the enhanced lateral mixing by convection.

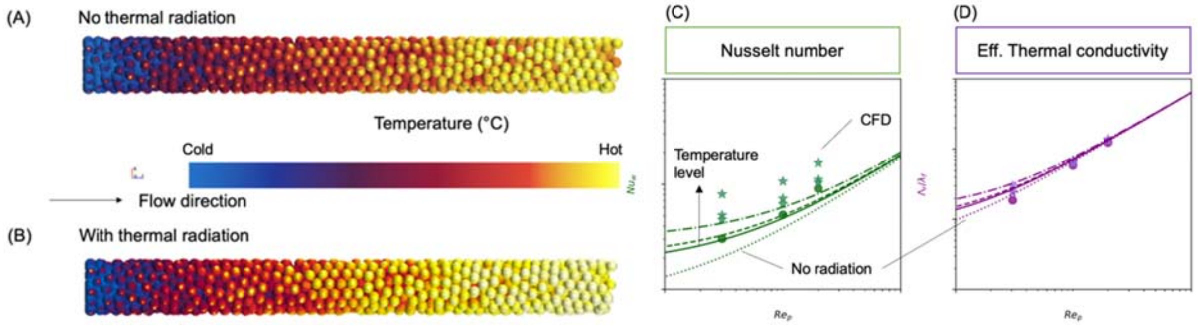

Figure 1. Surface temperatures of packed bed of spheres: (A) no thermal radiation and (B) with thermal radiation. (C) Wall Nusselt number, (D) effective thermal conductivity over Particle Reynolds number

Figure 2 shows the comparison of radial temperature profiles at different axial positions between the CFD simulations and the 2D model without and with thermal radiation in the bed of spheres. In general, the largest differences occur close to the wall and in the entrance and exit region of the packed bed. With the parameters governed by the CFD simulations, the thermal radiation case can also be predicted.

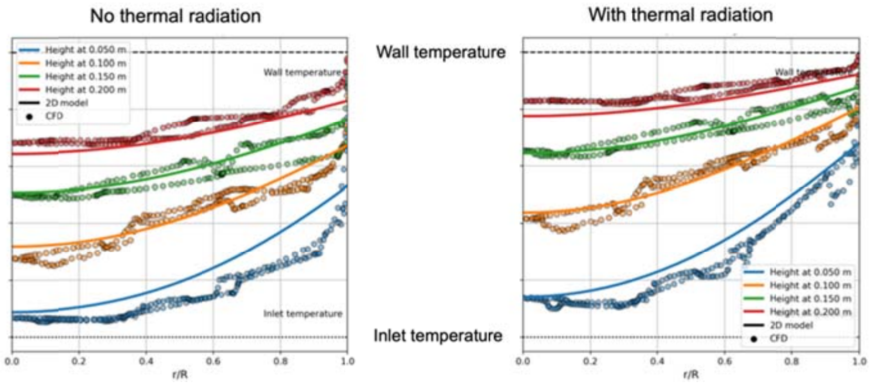

Figure 2. Radial temperature profiles at different axial positions. CFD vs. 2D model

PRCFD helps to understand fundamental aspects of heat transfer phenomena inside packed bed reactors, especially where thermal radiation occurs. Furthermore, we showed how to effectively use CFD data to improve 2D reaction engineering models.

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OP-II-31

FILTER PRESS REACTOR FOR THE CONTINUOUS ELECTROCATALYTIC REDUCTION OF CO_2 TO FORMATE USING Bi-BASED ELECTRODES

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The electrocatalytic reduction of CO_2 to value-added products has been considered as a fascinating option in order to mitigate climate change and, at the same time, to store energy from intermittent and renewable sources of energy [1]. Among these potential products, formate ($HCOO^-$) is used in a wide range of industries and it has been suggested as a suitable fuel for fuel-cells and as a promising renewable energy hydrogen carrier [2].

Bismuth (Bi) catalysts have recently been suggested as interesting materials for the electrocatalytic reduction of CO_2 to $HCOO^-$ due to the lower overpotential compared with other electrocatalysts [3]. The aim of this work is to analyse the performance of Bi-based electrodes with the configuration so-called “Catalyst Coated Membrane Electrodes”, in which the catalyst is deposited directly over the membrane [4-5] for the electrocatalytic reduction of CO_2 to $HCOO^-$. As illustrated in Fig. 1, the Bi Catalyst Coated Membrane Electrode (Bi-CCME) acts as a cathode and at the same time, as a separator between the compartments of the filter press reactor: cathode and anode compartments.

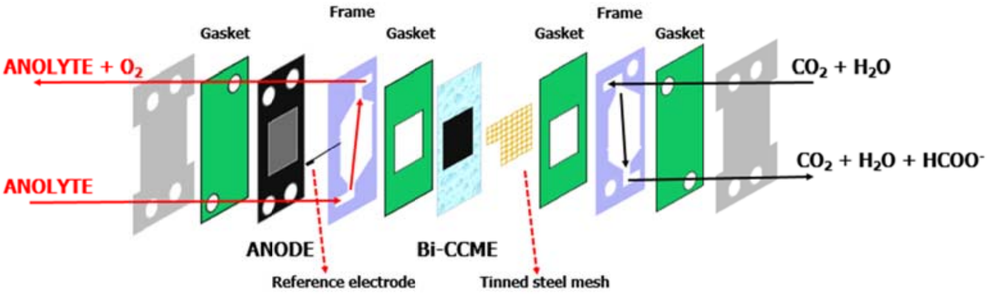

Fig. 1. Electrochemical filter-press reactor configuration for the continuous electroreduction of CO_2 to obtain $HCOO^-$ using Bi-CCMEs

Moreover, the influence of relevant variables, such as the temperature and the water flow of the CO_2 input stream, has been studied. The performance of the process has been assessed considering as figures of merit: the faradaic efficiency (FE) towards reaction products, $HCOO^{-}$ concentration ($[HCOO^{-}]$), $HCOO^{-}$ rate and the consumption of energy per kmol of $HCOO^{-}$. Promising results were obtained operating at ambient condition of temperature and with a water flow in the CO_2 stream of 0.5 $g{\cdot}h^{-1}$, obtaining $[HCOO^{-}]$ up to 26 $g{\cdot}L^{-1}$ with a FE towards $HCOO^{-}$, a $HCOO^{-}$ rate and a consumption of energy per kmol of $HCOO^{-}$ of 55 %, 1.28 $mmol{\cdot}m^{-2}{\cdot}s^{-1}$ and 266 $kWh{\cdot}kmol^{-1}$, respectively. These results were achieved operating with a Bi catalyst load of 0.75 $mg{\cdot}cm^{-2}$ and with a current density of 45 $mA{\cdot}cm^{-2}$.

Further tests were carried out with the aim of improving the performance of the electrocatalytic reduction of CO_2 to $HCOO^{-}$, analysing the influence of the catalyst loading in the CCME and the current density supplied to the electrochemical filter press reactor. When the catalyst load and the current density were raised from 0.75 to 1.5 $mg{\cdot}cm^{-2}$ and from 45 to 200 $mA{\cdot}cm^{-2}$, respectively, $[HCOO^{-}]$ up to 46.5 $g{\cdot}L^{-1}$ was obtained but at expenses of an important decrease in the Faraday Efficiency towards $HCOO^{-}$. Further research is still required to improve the performance of the electrocatalytic conversion of CO_2 to $HCOO^{-}$ using Bi-CCMEs for a future implementation of the electrochemical process at industrial scale.

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OP-II-32

THE WAY TO VALIDATE A NEW AMMONIA SYNTHESIS CATALYST: A COLLABORATION BETWEEN CASALE AND CLARIANT

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Catalytic ammonia synthesis from H_2 and N_2 represents one of the most important industrial reactions today. The catalyst used in this reaction is made from iron oxide with small amounts of other oxides added as promoters to enhance activity and stability. Despite the Haber-Bosch process being more than 100 years old [1-3], only incremental improvements have been achieved until recently. Combining the catalyst expertise of CLARIANT and the engineering knowledge of CASALE, a breakthrough has been realized leading to the new ammonia synthesis catalyst AmoMax®-Casale. The catalyst is a customized design by CLARIANT for CASALE reactors (patent pending) with significantly improved activity compared to state-of-the-art iron-based catalysts. When introducing a new catalyst into the market, performance evaluation is of utmost importance, but simple tests of the catalyst in powder form are not representative enough for industrial applications and only suitable for screening purposes. Therefore, a precise and rigorous methodology must be applied. In our paper, we report on the general guidelines that must be taken into account, exemplified by the development of the AmoMax®-Casale catalyst.

To reliably validate a new catalyst, laboratory-scale tests should be representative of the industrial catalyst. Thus, catalytic and mechanical tests are performed with the final form and shape of the catalyst. During catalytic tests, the temperature profile in the catalyst bed is measured and correlated with the heat exchange between oven and reactor. Subsequently, a systematic modelling of the obtained data is applied in order to understand the performance of the catalyst under industrial conditions. The information acquired is used to compare the new catalyst with the best available state-of-the-art catalyst technology. In case of superior activity of the new catalyst, as next step in-depth mechanical stability characterizations are performed to confirm the robustness of the catalyst. This includes simulations and experiments of friction between the catalyst pellets/granules and the walls of the reactor, crush strength and simulations of start-up/shut-down of industrial reactors. If the catalyst passes all the mechanical tests, proof of concept is achieved, and it is considered ready for scale-up. Transferring the catalyst recipe from lab to production scale is a highly complex process with numerous important parameters, which must be considered by the catalyst manufacturer. After a successful scale-up, the catalyst is prepared for shipment. To ensure it maintains its mechanical integrity and activity after transport from production site to plant, samples are taken during transportation, sent to different analytical laboratories and precisely analyzed. The catalyst is then validated with the same catalytic and mechanical tests applied during the proof of concept phase. If all the parameters are confirmed, the catalyst is finally ready for the market.

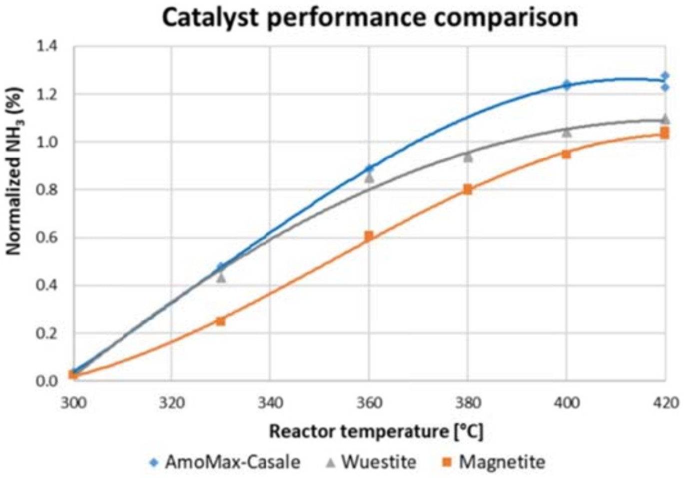

Figure 1. Comparison between state-of-the art magnetite-based catalyst, wuestite based catalyst and AmoMax®-Casale

Laboratory results for the catalytic activity are reported in the Figure 1. The results show how the new AmoMax®-Casale outperforms the state-of-the-art catalysts for ammonia synthesis. Results from field validation will be reported during the presentation. In a joint multidisciplinary effort involving process engineers, scientists, modelling engineers, and fluid dynamic engineers, CASALE and CLARIANT created a new ammonia synthesis catalyst that was ready for the market in less than three years.

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ORAL PRESENTATIONS
Section III.
Chemical Reactors and Technologies for Targeted Applications

OP-III-1

EFFECTS OF FLY ASH DEPOSITION ON THE PERFORMANCE OF SCR MONOLITHS: DEVELOPMENT OF A MICRO-SLAB REACTOR FOR KINETIC AND MASS TRANSFER STUDIES

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Introduction

Vanadium-based catalysts are used worldwide in the SCR-DeNO$_x$ units of coal-fired power plants in the form of honeycomb monoliths or corrugated plates [1]. Three main chemical processes are catalyzed: the reduction of NO$_x$ by NH$_3$, the oxidation of Hg^0 into HgCl$_2$ [2], the oxidation of SO$_2$ to SO$_3$ [3]. It is well known that NO$_x$ reduction suffers from strong mass transfer limitations but it is less known that also Hg^0 oxychlorination (highly desired, due to the easier removal of Hg^{2+} rather than elemental Hg) is also mass-transfer limited. Both processes are thus largely affected by the catalyst morphology and by changes of it due to the deposition of inorganics from the flue gas. Indeed, fly ash deposition is a known major factor of deactivation that periodically causes the replacement of catalyst layers; this is a tremendous economical factor, considering the huge catalyst inventory of SCR reactors (roughly 1 m^3 catalyst/MW of generated power). Thus, it is of keen interest to understand if the loss of catalytic performances is mainly due to chemical or morphological effects, which may support the identification of optimal strategies for catalyst re-juvenation. In this work, samples of a commercial monolith unloaded from full scale SCR reactors at different time on stream (1500 and 35000 h) were studied and compared with the reference fresh formulation. Kinetic studies are traditionally carried out at the lab-scale by using powdered catalysts, where the contribution of diffusion is negligible; however, an objective of this study was to preserve the wall integrity and study the role of intra-porous mass transfer limitations. At this scope, a simple micro-slab reactor was developed, where the reactor temperature is the “tuning” parameter through which the catalyst operating regime can be turned from fully chemical to mass-transfer controlled. The well defined flow pattern of the micro-slab reactor allowed for a simple modelling analysis that, together with an extensive catalyst characterisation, supported the identification of the factors responsible for the decay of activity.

Results

A 3.5 cm long and 6 mm wide micro-slab was cut from each monolith and inserted along the axial coordinate in a 6-mm wide quartz reactor. Two identical semicircular channels were thus obtained, each with an active face. NH_3-SCR tests were performed at 200 Ncc/min, NO and NH_3 = 900 ppm, 8 % O_2. Figure 1 compares the activity of the fresh catalyst and the activity of catalysts with 1500 h and 35000 h of service in a high-dust plant. All catalysts had comparable performance up to 225°C (where a kinetic regime prevailed), but at higher temperatures the 35000 h-slab showed a dramatics deactivation. XRD showed no important structural crystalline changes of the support nor agglomeration of V. NH_3-TPD experiments showed that NH_3-adsorption capacity was comparable in the three catalysts. Moderate loss of surface area and pore volume were found by BET and Hg-intrusion for the 35000 h sample, which could not explain the important change of NO_x conversion. However, SEM-EDX measurements evidenced the presence of a 10 µm deposit of ashes over the surface of 35000 h aged catalyst; the micro-slab was scratched and the test repeated. Surprisingly, the catalytic activity was largely recovered (green symbols). A 1D modelling analysis (accounting for the intrinsic kinetics estimated from powders and the impact of intraporous diffusion) was performed and confirmed that the presence of an inactive layer with the same effective diffusivity as the bulk of the wall, acting as external diffusion barrier, could entirely explain the loss of conversion as well as its recovery.

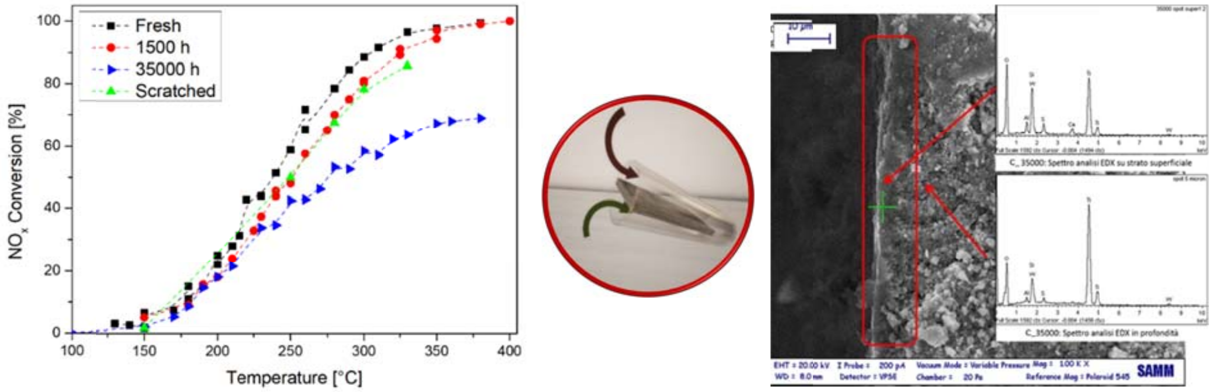

Figure 1. NO_x conversion of the micro-slab catalysts; micro-slab reactor; SEM-EDX and XRD analysis of 35000 h aged sample

This study demonstrated a simple and powerful technique to analyze the combined effect of kinetics and transport phenomena in the wall of the SCR catalyst, which has a general relevance; herein, this turned out to be very informative on the nature of the activity loss due to aging (largely explained by the formation of a diffusion barrier).

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OP-III-2

FACILE COATING OF Co_3O_4 ON OPEN-CELL METALLIC FOAMS FOR N_2O CATALYTIC DECOMPOSITION

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Open-cell foams, a special member of the 3D structured supports family with high porosity (void fraction of 90-95 %) and geometrical surface area (e.g., 7800 m^2 m^{-3} for 450 μm cell-size with 85 % porosity), are commercially available made by single metals or alloys [1, 2]. These materials offer extra-advantages in heterogeneous catalysis such as enhanced mass and heat transfer as well as low pressure-drop in comparison to pelletized catalysts. A lot of efforts have been made to homogenously coat the complex shape of the foams with catalytic films. For instance, spin-coating rather than conventional dip-coating is preferred when dealing with small-pore metallic foams [3]. Moreover, we proposed an electrochemical route to prepare structured catalysts [1]. It consists in the electro-generation of a basic media in the vicinity of the foam immersed in an aqueous solution of metal nitrates, hence it is possible to selectively precipitate hydroxides/oxides directly on the structured support. The main challenges to overcome, due to strict requirements of heterogeneous catalysts, are electrodeposit enough coating with controlled composition and high stability under reaction conditions.

In view of the above challenges, this study focuses on the electrodeposition of $Co(OH)_2$ on FeCralloy open-cell foams of relatively high pore density (80 ppi) to prepare, after calcination at 600 °C, Co_3O_4 spinel coatings active in the N_2O decomposition. The properties of the catalytic films (morphology, surface area, and redox behavior) are compared with those of a Co_3O_4 precipitated sample. To our best knowledge, the use of structured catalysts made by Co_3O_4 coated on open cell metallic foams is rare, including N_2O decomposition. Otherwise, it is an important process to eliminate N_2O, which is a strong greenhouse gas coming mainly from nitric acid or adipic acid production plants.

Electrobase-generation method allows to prepare a stable layer of Co_3O_4 up to 15-18 μm, with ca. ~22 $m^2\ g^{-1}$ surface area (Fig. 1a). Interestingly, the catalyst loading can be adjusted by tailoring synthesis parameters such as time and concentration, but without altering the catalytic activity. For instance, two catalysts with similar loadings of Co_3O_4 (ca. 18 wt. %) show a T_{50} around 490 °C and a reaction rate of 39 nmol $N_2O\ m^{-2}\ s^{-1}$ at 450 °C (Fig. 1b). Moreover, the structured catalysts show higher reaction rates than those of powder Co_3O_4 reported in the scientific literature [4,5]), e.g., 24.3-30 nmol $N_2O\ m^{-2}\ s^{-1}$ at 500-550 °C. The research is in progress to further optimize activity over coated foams (e.g., through incorporation of alkali promoters).

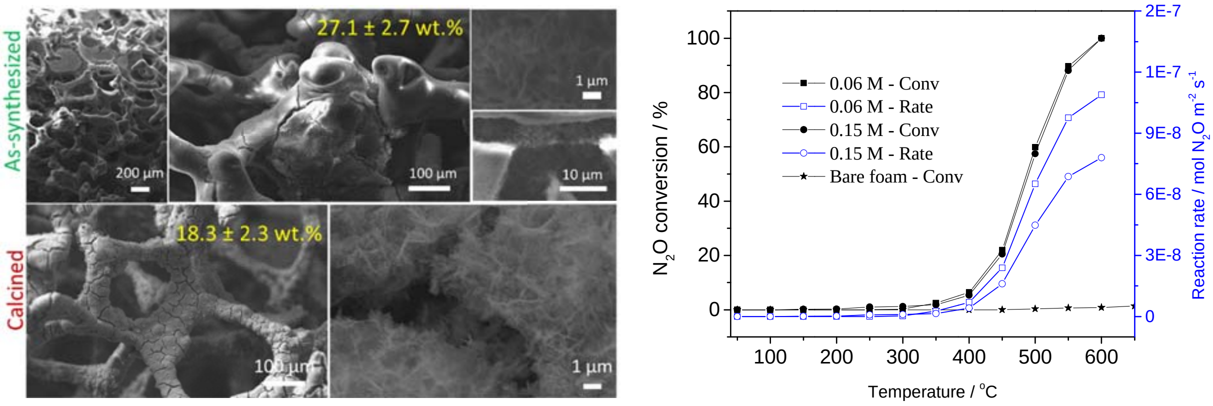
(a) **(b)**

Fig. 1. SEM images of cobalt-based structured catalyst prepared by electrodeposition at -1.2 V vs SCE (saturated calomel electrode) for 500 s in a 0.15 M aqueous solution of $Co(NO_3)_2$ (a) and results of catalytic tests of N_2O decomposition over catalysts prepared with 0.06 and 0.15 M aqueous solutions of $Co(NO_3)_2$ (1b). Reaction conditions: two coated foams (ID 0.8 cm), GHSV = 6,800 h^{-1}, under 80 mL min^{-1} of 1000 ppm N_2O/N_2.

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OP-III-3

EXPERIENCE IN OPERATIONG A PILOT PLANT FOR THE SEWAGE SLUDGE UTILIZATION IN A FLUIDIZED BED OF CATALYST

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Today, one of the acute problems facing humanity is the formation of a huge amount of waste. Among them are the wastes from sewage treatment facilities and communal services – sewage sludge. Effective utilization of such materials is in itself an urgent task, attracting the attention of the world scientific community. In turn, the possibility of obtaining additional benefits in the form of, for example, thermal energy makes work in this area extremely attractive.

Most of the currently existing methods for such types of waste processing have a number of significant drawbacks, such as low efficiency, the formation of significant amounts of pollutants, the high operating cost of the process, etc. Moreover, in some countries, the main part of such waste is sent to landfill, which creates even more environmental problems and limits the use of land allocated for storage.

In the Boreskov institute of catalysis has been developed and successfully applied the technology for the processing of fuels and wastes, which consists in combustion of raw materials in a fluidized bed of catalyst. The implementation of this technology makes it possible to avoid most of the drawbacks characteristic of traditional combustion methods (layered, flare, and in a fluidized bed of inert material). Moreover, the technology is universal and can be used for solid, liquid and gaseous materials, including those with high ash content, humidity and volatile content.

At the moment, a pilot plant for the utilization of sewage sludge in a fluidized bed of catalyst has been commissioned. The installation was built on the territory of the Omsk water treatment facilities (JSC “Omskvodokanal”) and covers 30 % of the need for sludge combustion. The plans include the construction of two more reactors, which will provide 100 % combustion of the sludge formed in the city of Omsk, and will also allow the restoration of already filled dumps.

This work demonstrates the description and capabilities of the created pilot plant, its technological features and advantages in comparison with existing analogues. In addition, the first experience of operating the plant is also described.

Acknowledgements

This work was supported by the Russian Science Foundation, project № 17-73-30032.

OP-III-4

ADVANCED FLUE-GAS CLEANING BY WET OXIDATIVE SCRUBBING USING $NaClO_2$ AQUEOUS SOLUTIONS

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Introduction

Nowadays, the SO_x and NO_x emission control from flue-gas still represents one of the most critical issues in the field of energy generation, municipal waste incineration, internal combustion engines and industrial production and manufacturing processes.

It is widely known that SO_x emissions can be limited and almost eliminated by using fuels with low-sulphur content, which are typically more expensive. Differently, NO_x emissions can be partially controlled by improving the combustion technologies. For several applications, after-treatment processes are the only available options to comply with regulations. These technologies include dry and semi-dry (dry-scrubbers and spray dryer) or wet scrubbing columns (wet-scrubbers) for SO_x capture, and Selective Catalytic Reduction (SCR) or thermal Selective Non-Catalytic Reduction (SNCR) units for NO_x control. Despite the efforts to improve these technologies and their integration, the combined use of these units requires high capital (*CAPEX*) and operation and maintenance (*O&M*) costs, and they have a large footprint for the plant installation. These constraints are even more relevant in the case of retrofitting of existing systems and for the treatment of exhaust gases from heavy-duty diesel engines, including those used for the propulsion and for auxiliary systems in the marine and train applications.

In this work, we developed a promising technology for the simultaneous SO_x and NO_x emissions control as an alternative to traditional after-treatment systems adopted, which involve the combined use of de-SO_x and de-NO_x units. The process consists in a wet scrubbing of SO_x and NO_x by an aqueous solution doped with sodium chlorite ($NaClO_2$) that allows the optimized capture and subsequent oxidation of SO_x and NO_x to sulfates and nitrates, respectively [1-4]. This work is an upgrade of our previous works [3,4], where de-SO_x and de-NO_x treatment systems have been studied separately by applying wet oxidative technology.

The de-SO_x and de-NO_x scrubbing experiments were performed in a fully instrumented pilot-scale scrubber [3,4], having a DN 100, and equipped with

Mellapak 250.X structured packing with height of 892 mm. A simulated flue-gas stream with a constant gas flow rate of 32 m^3/h (1.15 m/s) containing 500 ppm_v of SO_2 and 1030 ppm_v of NO_x at 60 °C was used as a reference case. The scrubbing liquid was an aqueous solution containing a concentration of $NaClO_2$ ranging from 0 to 1 % w/w, fed with liquid-to-gas ratios between 1.25-4.06 L/m^3 at 25 °C.

Key Results

The experimental results showed that the scrubber was able to completely remove the SO_2 and to reduce NO_x emissions up to 65%. Moreover, the experiments allowed determining the establishment of acidic conditions as the main oxidation pathway and removal mechanism, which enhanced the oxidation rates of NO_x. Indeed, the wash water pH resulted to be lower than 7 in all the experiments, thanks to the presence of SO_2 in the flue-gas. The operating dosage of $NaClO_2$ that allowed the maximum NO_x removal tested (65 %) was equal to about 12 times the moles of NO_x in the fed gas, while for SO_2 was about 1.1 for a complete removal according to Flagiello et al. [3]. Although an excess of $NaClO_2$ was necessary, the data suggested that higher removals for NO_x could be achieved by increasing the $NaClO_2$ loading or liquid flow rate compared to the de-NO_x experiments by Flagiello et al. [4].

This process can be used to design absorption towers in which de-SO_x and de-NO_x operation are combined in one device, allowing the compliance with the most stringent emissions regulations in force so far and simultaneously assuring lower *CAPEX* and *O&M* costs and easier installation than conventional after-treatment systems.

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THERMAL DEGRADATION OF NYLON-6 AND REAL MIXTURES OF SOLID PLASTIC WASTE. AN EXPERIMENTAL AND KINETIC MODELLING STUDY

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The current challenges related to plastic waste disposal motivates the renewed interest in understanding the chemical and physical phenomena involved in the thermal treatments of plastic polymers, such as pyrolysis and gasification [1]. Embracing the current trends and incentives towards the implementation of circular economy strategies for the production of energy and goods, *chemical recycle* of solid plastic waste (SPW) is attracting the interest of petrochemical and oil and gas industries.

Pyrolysis is a promising technology for SPW that are difficult to recycle mechanically and today are disposed in landfills. This is the case of complex mixtures, typically containing polyethylene (PE, ~40 % wt.), polypropylene (PP, ~25 % wt.), polystyrene (PS, ~15 % wt.), polyethylene terephtalate (PET, ~8 % wt.), polyvinylchloride (PVC, ~7 % wt.), and polyamide (PA, ~5 % wt.). Pyrolysis processes have the advantage of being feedstock flexible, thus capable of treating heterogeneous mixtures.

A fundamental understanding of polymer decomposition chemistry and yields of products formation can be achieved by coupling laboratory experiments such as thermogravimetric analyses and gas cromatography-mass spectrometry measurements (GC-MS) to semi-detailed kinetic models. As reported in Figure 1, plastic polymers decomposition occurs in a quite tight temperature window (~50 °C), with the exception of PVC whose dechlorination starts ~100-150 °C earlier compared to PS and PE, respectively. Detailed kinetic models allow to investigate the effect of different parameters (e.g. temperature, residence times, feedstock variations, etc.) thus allowing improved design of pyrolysis reactors and downstream separation and purification units. Developing upon existing kinetic subsets for PE, PP, PS, PVC and PET [2-7], this work presents and discusses the first semi-detailed kinetic model for PA.

OP-III-5

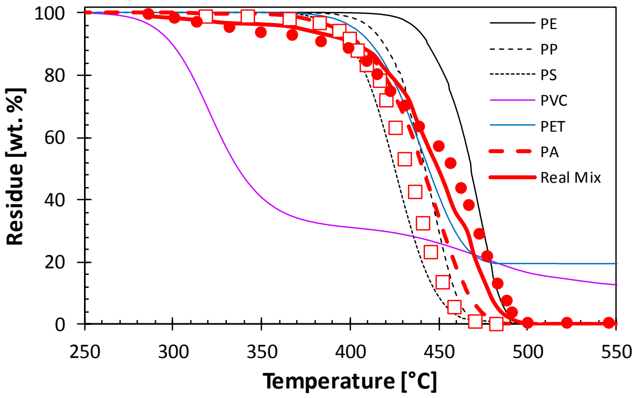

Figure 1. TGA analysis of single plastic polymers and of a real mixture. Symbols: experimental measurements performed at POLIMI for PA (open squares) and for the mixture (full circles), lines: results from model simulations

The scarce amount of information available in the literature mostly focuses on the most abundant polyamide, Nylon-6. Taking advantage of this limited but useful amount of information, Nylon-6 has been selected as the representative of the polyamide fraction of SPW (~5 % wt.). The model has been developed based upon reference reaction classes and kinetic parameters, and is validated by comparison with the limited number of TGA/GC-MS data. Additional measurements have been performed at Politecnico di Milano for single polymers, including PA, and mixtures of increasing complexity (i.e. from binary to real SPW samples), allowing to test the predictive capabilities of the model.

The model correctly reproduces the loss of mass and the distribution of the main products: Nylon-6 monomer (2-azacycloheptanone, up to 90 % wt) and its dimer (1,8-diazacyclotetradecan-2,9-dione, up to 10 % wt.). Other minor products are mentioned in literature (e.g. cyclohexanone, cyclohexenone, hexanenitrile, hexenenitrile) but, based on the current state of the art, quantitative comparisons are not conclusive. As a further proof of the reliability of the POLIMI kinetic model for thermal degradation of plastic polymers, results for real SPW samples are also presented and discussed.

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OP-III-6

PYROLYSIS OF PLASTIC FROM WEEE IN A REACTIVE DISTILLATION APPROACH

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In recent years, there has been an increased growth in waste from electrical and electronic equipment (WEEE). With the evolution of technology, innovation cycles are becoming shorter and, consequently, the production of new electronic equipment increases along with their replacement with more innovative equipment, making electrical and electronic equipment (EEE) a fast growing source of waste [1]. About 20-25 % of WEEE is composed of plastic. Part of the selected plastic can be directed to mechanical recycling, while the remaining part of the plastic will be discarded for landfill or incineration. A possible alternative to recover the material is pyrolysis, where the waste is heated in the absence of oxygen; the products of this degradation can be used as feedstock for the petrochemistry, including fuels [1,2]. The polymers most commonly found in WEEE are: acrylonitrile butadiene styrene (ABS) 30 %, high impact polystyrene (HIPS) 25 % and polycarbonate (PC) 10 % [2]. Pyrolysis of styrene-based polymers such as ABS, HIPS, PS and mixtures has been reported to produce mostly aromatic products [2-3]. In this work, pyrolysis of a WEEE plastic mixtures (originated from the casings from a TV and a Mixer Stand), in varied proportions, were carried out in a reactive distillation reactor.

The WEEE plastics were provided by Ambigroup. The samples were washed and crushed. The thermal pyrolysis experiments were carried out using an unstirred glass reactor in reactive distillation system at atmospheric pressure [4]. The reactor was loaded with 10 g of the plastic waste material and before the experiments start, the reactor was purged with nitrogen to ensure an inert atmosphere. After that, the oven is heated to the required temperature with a heating rate of 10 °C/min. This final temperature was maintained during 90 min. On top of the reactor there is a liquid collector to store the liquid formed. On top of this collector, there is a cooling system, where the temperature of cooling water is 20 °C to control the outflow of lighter products. The yield of the products obtained for thermal pyrolysis of a WEEE plastic mixtures (ABS and PS), with different compositions, are shown in Figure 1, for the set point temperature of 500 °C with a reaction time of 90 min.

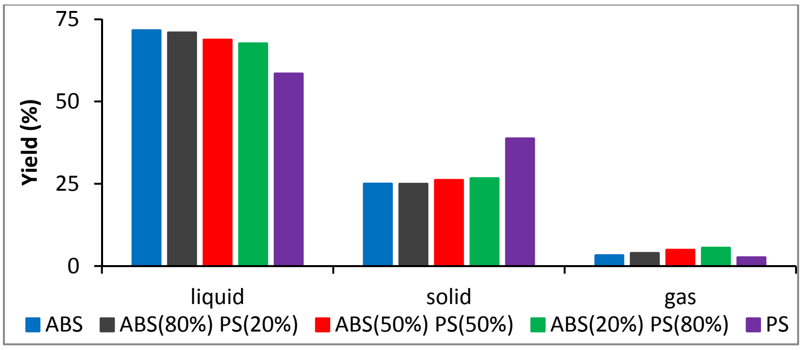

Figure 1. Pyrolysis yields (wt %) for different mixtures of plastics, at 500 °C and 90 min

From Figure 1 it is clear that the largest amount of products formed are in the liquid phase. The conversion with 100 % of waste PS showed the highest yield of solid products (39 %). ABS showed the least yield of solids, but it is important to note that even a small proportion of ABS causes a very significant decrease in solid yield, in comparison to the expected weighted average of the two individual plastics.

The internal temperature of the reactor was also measured during the experiments and it is possible to observe (see Figure 2) that there is a significant difference between the measured temperature and the Set Point temperature (SP), and that this difference is partially related to the reaction taking place. Moreover, it can be seen that there is a difference in the profile when there is a single type of plastic when compared to the co-processing of different types of plastic.

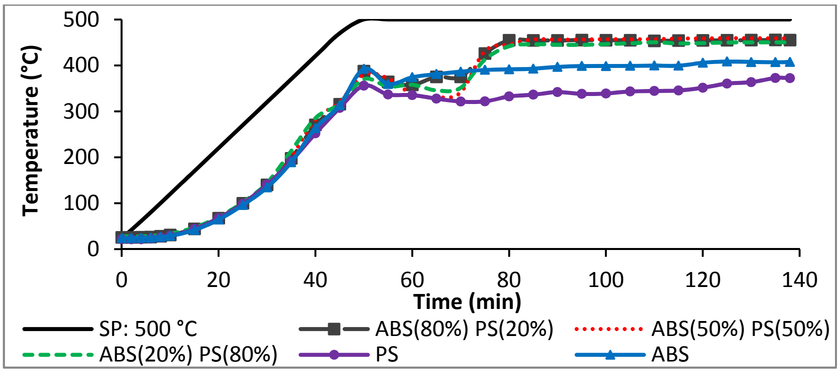

Figure 2. Internal temperature of the reactor with different mixtures of plastics

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THERMAL AND CATALYTIC PYROLYSIS OF WASTE POLYSTYRENE IN A SEMI-BATCH REACTOR

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Polystyrene (PS) is one of the most common plastics found in the waste of electric and electronic equipment (WEEE) [1]. Mechanical recycling of plastic from WEEE is difficult due to the complicated recycling processes required to achieve pure polymer separation [1]. Chemical recycling is an alternative to treat this kind of waste since it provides a way to convert the waste plastic, even when it is composed of mixed components, into valuable products for the chemical industry [2]. This work focuses on the comparison of thermal and catalytic pyrolysis of both virgin PS and waste PS from WEEE. Preliminary experiments were conducted in a simultaneous TG/DSC apparatus to study the kinetics for both the thermal and catalytic degradation processes. The pyrolysis reactions were performed in a bench-scale reactor that works as a reactive distillation system, operating in semi-batch mode, under atmospheric pressure [3]. In the beginning the feedstock is loaded to the reactor and constant removal of the products is possible when the compounds achieve a sufficiently low molecular weight to exit the reactor. The reactor operates under reflux conditions, which permits further cracking of heavier compounds. Different temperatures were used for thermal and catalytic pyrolysis (400, 450 and 500 °C) using a reaction time of 90 minutes.

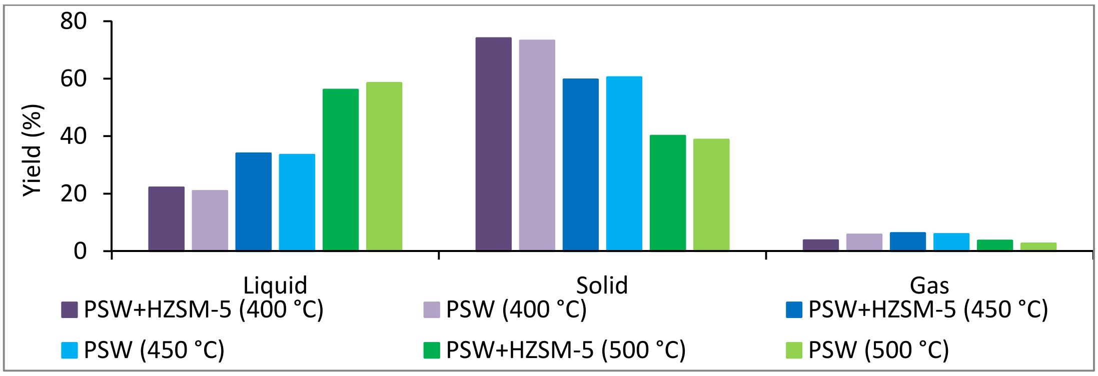

Figure 1. Yield of products for thermal and catalytic pyrolysis at different set-point temperatures

From Figure 1 it is possible to see the yield of liquid, solid and gas products for the pyrolysis of waste PS with HZSM-5. It is observed that the catalyst tested (HZSM-5) has only a slight effect on the overall behaviour. At 500 °C the liquid yield obtained for the thermal pyrolysis is 58 % and for the catalytic pyrolysis 56 %. The gas and liquid products were analysed using gas chromatography. The analysis of the liquid products (Fig. 2) shows that, for both thermal and catalytic pyrolysis, the products obtained with higher amounts were aromatics in the range between C_7 to C_9. The C_7 hydrocarbons probably correspond to toluene and C_8 hydrocarbons correspond mostly to styrene. The C_9 hydrocarbons might correspond to alpha-methylstyrene. In case of catalytic pyrolysis there is also some C_6 formation, which corresponds to benzene.

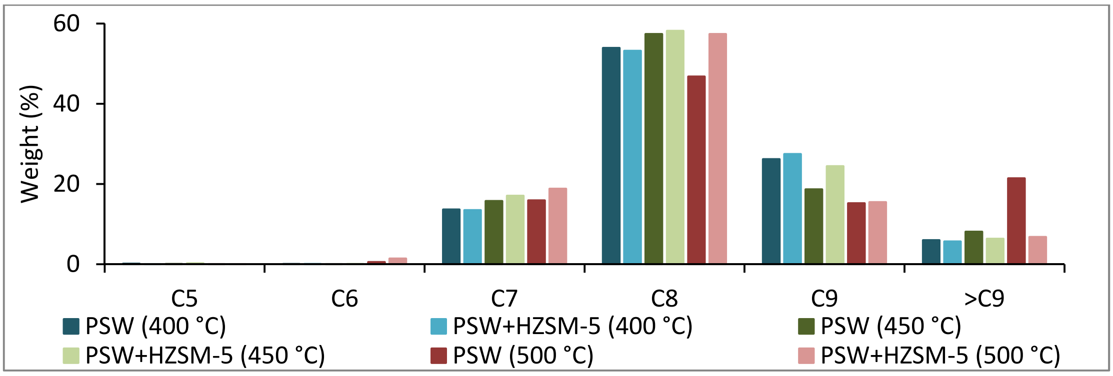

Figure 2. Liquid composition for thermal and catalytic pyrolysis in the reactor of waste PS

Thus, the pyrolysis of waste PS produces hydrocarbons that may be reused in the chemical industry, as feedstock to produce new plastics with the Circular Economy approach in mind.

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OP-III-8

3D-PRINTING OF ADSORBENTS FOR INCREASED PRODUCTIVITY IN CARBON CAPTURE APPLICATIONS (3D-CAPS)

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Developing energy efficient carbon capture technologies is of great importance to combat climate change. Currently, the commercialization of adsorbent based capture technologies is hampered by both the size of equipment and the energy associated with the carbon abatement. The 3D-CAPS project aims to solve these challenges associated with removing and recovering CO_2 from industrial gases by significantly increasing the productivity (kg CO_2/m^3hr) of two adsorbent based technologies by structuring through 3D-printing: a) potassium-promoted hydrotalcite (K-HTC) for sorption-enhanced water-gas shift (SEWGS) [1] and b) amine functionalized silica (ImmoAmmo) [2].

Structured adsorbents and catalysts have recently gained significant interest owing to the advantages of lower pressure drop and faster mass transfer over conventional shaped materials [3,4]. The required adsorbents for these technologies are prepared using the latest innovations in additive manufacturing (3D-printing). This technology allows to prepare bespoke materials, with tailored channel sizes and wall thickness, having improved heat and mass-transfer characteristics, that are not available through traditional material preparation routes. The 3D-technology used to develop the structured adsorbents is Digital Light Processing (DLP; Figure 1).

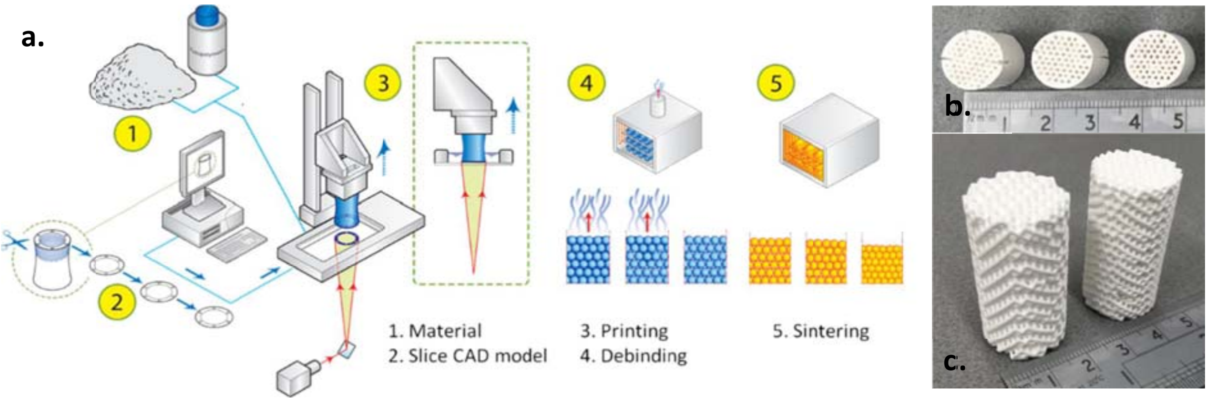

Figure 1. a) Schematic representation of DLP technology. The printer (3) illuminates the paste (1) layer-by-layer as a projected cross-section (2). After each layer, the structure is moved up, and the layer of paste is restored. After printing, delamination (4) and sintering (5) lead to the final structured material. b) several K-HTC monolith structures and c) 3D-printed silica based isoreticular foam (ImmoAmmo)

The DLP technology consists of an indirect slurry-based process that uses a photo-active material to initiate binding. After printing the structure layer by layer by illuminating cross-sections of the design, a debinding and sintering step is required to obtain the final structured adsorbents. For the ImmoAmmo adsorbent, the silica support will be printed after which various amines are impregnated or grafted on the structured material.

Pastes for 3D printing are developed for both the K-HTC and ImmoAmmo sorbents. Several 3D-structures, designed with the aid of mathematical modelling (CFD), have been printed and post-processed (Figure 1, b & c). For the ImmoAmmo sorbents a recipe to graft amino silanes onto the 3D-structured silica support is developed. The resulting sorbent shows similar capacities to the grafted silica beads. Also the printed and post-processed K-HTC materials keep their original CO_2 capture capacity compared to the starting sorbents.

The 3D printed adsorbents are evaluated against traditional packed bed of pellets in Pressure Swing Adsorption (PSA) and Vacuum PSA processes for CO_2 capture in Natural gas combined cycle (NGCC) and decarbonized H_2 production. The adsorption characteristics (equilibrium isotherms and kinetic parameters) for the relevant gaseous components (CO_2, N_2, H_2O) as well as pressure drop for different structures are measured. Single and multi-column models for the performance of the SEWGS and ImmoAmmo 3D-printed solution for the selected applications have been set up. The models are calibrated for operation at the high-flow rates to obtain high productivity rates, capture rate and efficient utility use. The experimental data are used to validate the multi-cycle models that determine the potential of the structures for productivity increase.

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OP-III-9

A NEW FAMILY OF SINGLE-ATOM CATALYSTS FOR THE DEGRADATION OF PHARMACEUTICAL WATER POLLUTANTS

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Highly-efficient catalytic technologies are urgently needed to remove pharmaceutical pollutants from water [1]. Today's contaminants are, in fact, more challenging to degrade than in the past because of their stable and complex structure. In this contribution, we report the preparation, characterization, and photocatalytic performance of a series of heterogeneous catalysts featuring single-atom transition metals over graphitic carbon nitride. In line with previous reports on single-atom catalysis from our group [2-3], the atomic character was confirmed by spectrometric analyses. By combining advanced characterizations with kinetic investigations under batch and flow conditions, we demonstrate that these newly-formed isolated single atom catalysts act as a bridge, facilitating the faster electron transfer, increasing the local charge density, and reducing the photocarrier transfer barrier. This improves the degradation of Gemfibrozil, a model pharmaceutical pollutant found in wastewater, reducing the formation of toxic byproducts during photooxidation (**Figure 1**). This effect is not observed over the conventional nanoparticle-based catalytic counterparts. The work thus opens new avenues in the design of selective photocatalysts for advanced oxidation processes, showing the importance of atom coordination to control the surface and catalytic properties of single-atom materials.

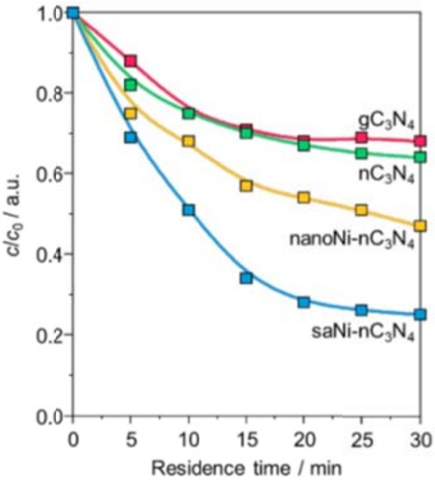

Figure 1. Degradation of Gemfibrozil over a catalyst selection. The figure illustrates the outstanding performance of single-atom saNinC$_3$N$_4$.

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OP-III-10

COUPLING ELECTROSTATIC CLASSIFIER WITH SPARK DISCHARGE GENERATOR FOR GENERATION OF MONODISPERSE CATALYST FOR SINGLE-WALLED CARBON NANOTUBE GROWTH

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Single-walled carbon nanotubes (SWCNTs) are one of the most promising materials for various applications owing to the set unique physical, structural, and electronic characteristics. Optoelectronic and biomedical applications (*e.g.* transparent electrodes, single-photon emitters, thin film transistors, drug delivery agents) require precise control of SWCNT morphology and electronic properties corresponding to the structural aspects of an individual nanotube.

Nowadays, one of the most promising methods addressing the fine tuning of individual SWCNT characteristics is the aerosol chemical vapor deposition (CVD) technique – a specific case of floating catalyst CVD. While the structural aspects of SWCNTs are mainly affected by the growth conditions and the catalyst nature (composition, diameter distribution, preparation technique, *etc.*), the methods for the catalyst formation during the aerosol CVD show a complex mutual dependence of SWCNT characteristics on growth parameters enhanced by the lack in control number size distribution and stability in nanoparticle generation. Recently, we have shown the spark discharge generator of aerosol nanoparticles to provide a spatial separation of the nanoparticle formation and carbon nanotube nucleation processes: the systematic study has shown the generator to provide a facile and repeatable route to precisely control the size of the catalyst particle and, consequently, SWCNT growth [1,2].

In this work, we enhance aerosol CVD synthesis based on a spark discharge generator of nanoparticles with an electrostatic classifier to provide monodisperse catalyst particles for single-walled carbon nanotube growth. In a simple way, electrostatic classifier “cuts” the polydisperse flow basing on a principle that the velocity of a charged aerosol particle in an electric field is directly related to its diameter (via mobility). Generally, catalytic nanoparticles produced by spark discharge generator are transferred by carrier gas (N_2) into the electrostatic classifier with following introduction to the reactor zone to form (or not to form depending on size and reaction conditions) SWCNTs. The resulting aerosol is transferred to the second DMA for monitoring the possible process of carbon nanotube synthesis.

By variation of the operating voltage, aerosol particles with a particular diameter are segregated and carried into aerosol reactor. Using a mobility-based separation technique of aerosol particles, we not only define the diameter range of the Fe particles active in SWCNT growth but also directly track the influence of the catalyst composition on the SWCNT growth parameters. The method opens a new avenue for precise catalytic experiments as well as fine synthesis processes. In this we work we show, the advances of the method examining the SWCNT-based thin conductive films.

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OP-III-11

COUPLING OF HYDROTHERMAL LIQUEFACTION AND AQUEOUS PHASE REFORMING FOR LIGNIN RICH STREAM VALORIZATION

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Hydrothermal liquefaction (HTL) of biomass is a strategic process to convert renewable feedstocks into a sustainable biofuel (i.e. biocrude) [1]. Despite their importance, the research has not deeply investigated the aqueous side-streams, that may contain up to 30 % of the carbon present in the feed [2] and whose disposal cost is second only to the feedstock one [3]. Aqueous phase reforming (APR) may be a key process to convert the organics into a gas phase rich in hydrogen which may be used to perform the upgrade of the biocrude, reducing its oxygen content [4]. Moreover, the cleaned water can be recirculated to the HTL reducing the need of fresh water (Figure 1). In the current work, HTL and APR were studied looking at the process integration between the two technologies. A particular attention was put on minimizing the impact on the environment thanks to the reduction of external hydrogen need for bio-crude upgrade and fresh water via a recycle loop.

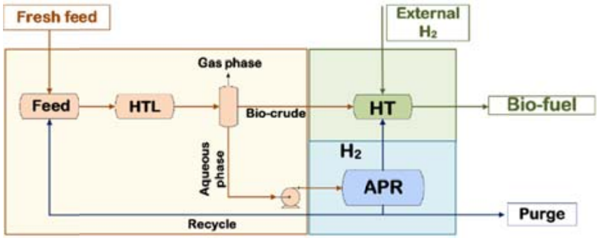

Figure 1. Block flow diagram of a HTL-APR integrated plant from [5]

The HTL and APR test were performed in the experimental set up described in [5]. The influence of different solvents to recover part of the organic content, dissolved in the aqueous phase (HTL-AP), was studied on the APR performance. First, it was observed that the composition of the HTL-AP was affected by the used solvent, such as diethyl ether (DEE), ethyl acetate and others. The washing with DEE recovered the aromatics content from the aqueous phase (Figure 2, a). Interestingly, removing the aromatics increased the hydrogen production in the APR step, moving from 1.3 mmoles at the highest concentration of phenolics (0.12 %) to about

20 mmoles when they were not detected by HPLC analysis (Figure 2, b). Finally, the water coming from APR (APR-AP) was used as dilution water to reach the required grade of humidity of the hydrothermal liquefaction (e.g. about 90 % of water). The HTL-APR experimental campaign allowed to study the possibility of improving the integration of the two reactions in terms of hydrogen production and water need. In Figure 2, c the results of a test conduct with 80 % of APR-AP and 20 % of fresh water showed no major difference compared with the reference test (100 % of fresh water, 350 °C, 10 min, 10 wt. % lignin-rich).

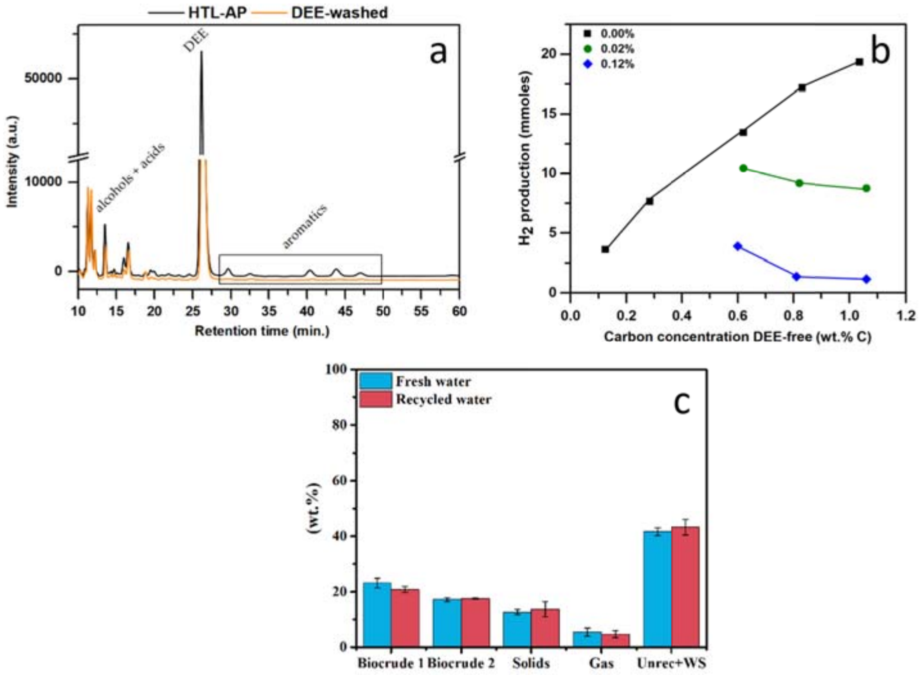

Figure 2. Influence of used solvent on the aqueous phase composition (a); Influence of phenolics content on hydrogen production (b); Effect of the APR-AP as dilution water for the HTL reaction (c)

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Acknowledgment

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OP-III-12

AQUEOUS PHASE REFORMING OF LIGNIN-RICH LIQUEFACTION WASTE FOR HYDROGEN PRODUCTION

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Hydrothermal processes of biomass can lead to alternative and renewable fuels. For example, the hydrothermal liquefaction (HTL) of lignocellulosic biomass is able to produce an organic phase (biocrude) with higher heating value and stability then the bio-oil obtained by pyrolysis, thanks to the lower oxygen content. However, the management of the waste-water stream derived from HTL can be an important bottleneck in the development of such technologies. It has been estimated that the cost of aqueous by-products disposal comes right after the cost of the feedstock. For this reason, in order to increase the environmental and economic sustainability of the HTL process, the water fraction should be valorized. In this work, the aqueous phase reforming (APR) process has been investigated with a double goal. First, it can convert the carbon-laden aqueous phase into a hydrogen-rich gas mixture, in order to reduce the amount of hydrogen necessary for the upgrade of the bio-crude (Figure 1) [1]; second, it can clean the aqueous phase that can be recycled to the liquefaction step, reducing the need for water make-up.

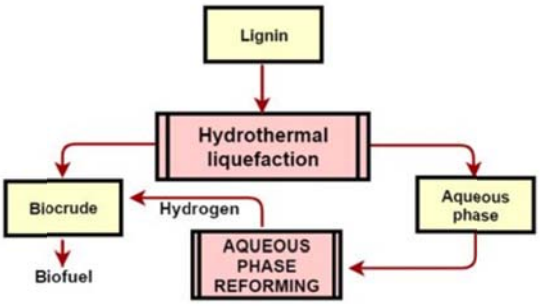

Figure 1. Block flow diagram of an HTL-APR integrated plant

Aqueous phase reforming has been traditionally studied with simple model compounds, such as alcohols and poly-alcohols [2]. In the present work, also a real aqueous-phase derived from lignin-rich hydrothermal liquefaction was used as a feedstock. The tests were performed in a continuous fixed-bed reactor (Microactivity Effi), 9.1 mm internal diameter, using a developmental 5 % Pt/C catalyst by a commercial supplier. The influence of several reaction conditions was investigated, such as temperature, weight-hourly space velocity, co-feeding of an inert weeping gas. Beside the use of a real aqueous phase, a synthetic representative mixture was used to highlight differences in the reactive behaviour. Among the obtained results, in the next Figure 2, a comparison between the synthetic and real mixtures is reported. It is highlighted that the synthetic mixture showed a stable conversion of the reactants (glycolic and lactic acid, glycerol, methanol), while acetic acid was indeed produced by side-reactions, not being consumed. On the other hand, the real mixture reported deactivation phenomena after 250 min. The study of the textural properties of the catalyst reported that the surface area decreased, suggesting a deactivation by fouling/coking mechanism.

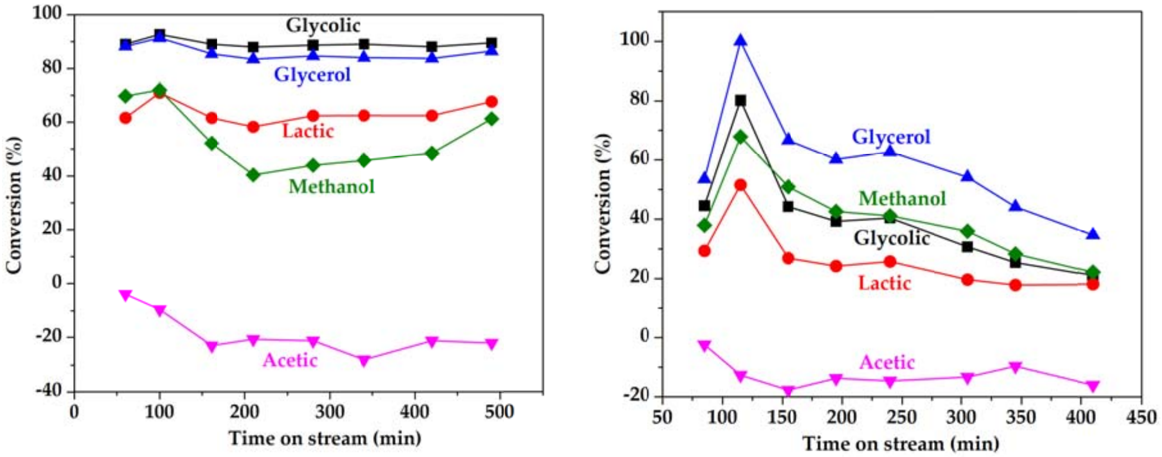

Figure 2. APR of synthetic (left) and real (right) mixtures.
Reaction conditions: 0.8 mL/min feed flowrate, 1 g Pt/C, 270 °C

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Rh- AND Pt-DOPED g-C_3N_4 FOR THE PHOTOCATALYTIC HYDROGEN EVOLUTION FROM AQUEOUS SOLUTIONS OF TRIETHANOLAMINE UNDER VISIBLE LIGHT

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One of the most urgent areas of sustainable energy development is the development of solar energy. This process is constrained by the fact that there are few catalysts that are activated under visible light and are capable of water splitting [1]. One of the promising photocatalysts attracting attention is graphitic carbon nitride (g-C_3N_4), which has a number of important advantages such as simple synthesis, suitable bandgap for water reduction and oxidation, as well as chemical and thermal stability. A factor limiting its high catalytic activity in the photocatalytic hydrogen evolution is the small surface area of g-C_3N_4 since strong agglomeration of particles always occurs in g-C_3N_4 due to high-temperature calcination. In this regard, it is important to study new processes for the synthesize of g-C_3N_4 with a large surface area. Increasing the surface area of g-C_3N_4 is considered to be an effective way to increase its photocatalytic activity. The aim of this work was to synthesize highly active photocatalysts based on g-C_3N_4 with a low content of noble metals such as Pt and Rh.

The suspension containing melamine and glucose was placed in autoclave and heated at 180 °C for 12 hours. Thereafter, the obtained precursor was calcined at 550 °C for 3 hours with a heating rate of 0.5 °C min^{-1}. The photocatalysts $Pt_{0.5}$/g-C_3N_4 and $Rh_{0.5}$/g-C_3N_4 were prepared by chemisorption using the precursors of binuclear complexes $(Me_4N)_2[Pt_2(OH)_2(NO_3)_8]$ and $[Rh_2(OH)_2(H_2O)_8](NO_3)_4$, based on the method described earlier [2]. Subsequent samples reduction was carried out in H_2. The photocatalytic hydrogen evolution was measured in an aqueous-alkaline solution of triethanolamine (TEOA – 10 vol. %, 0.1 M NaOH) under visible light irradiation (λ = 425 nm).

An increase in the temperature at which $Pt_{0.5}$/g-C_3N_4 photocatalyst was reduced in H_2 led to an increase in the photocatalytic activity due to the complete reduction of Pt^{2+} to Pt^0. In the case of $Rh_{0.5}$/g-C_3N_4, it was observed that an increase in the reduction temperature in H_2 to 400 °C leads to an increase in the hydrogen evolution rate ≈ 2 times compared with the sample not reduced in H_2, while the reduction of photocatalysts at temperatures from 100 up to 300 °C had no positive effect on the hydrogen evolution rate. Probably, this may be due to the fact that Rh on the g-C_3N_4 surface is already in the reduced form. The results of the study of activity are presented in Figure 1.

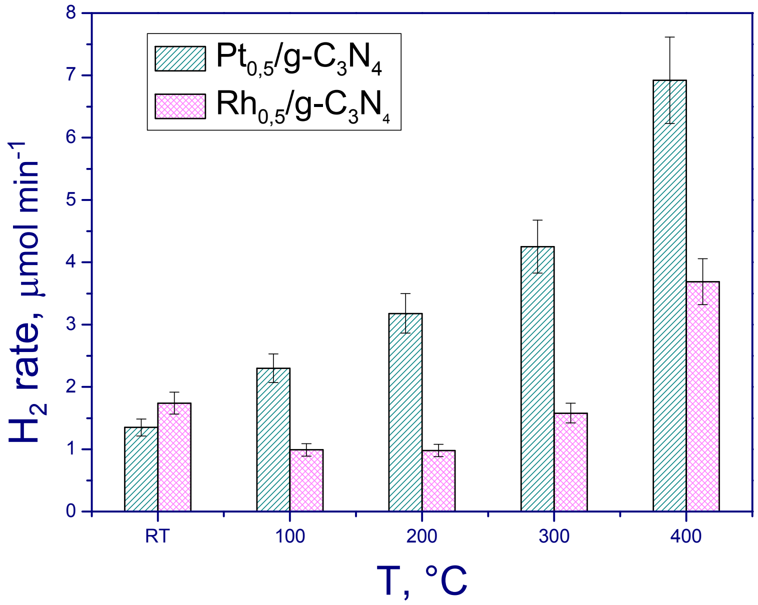

Figure 1. The influence of photocatalysts temperature synthesis on the activity in the hydrogen evolution

As a result of optimization of the catalyst preparation procedure, the most active sample was $Pt_{0.5}$/g-C_3N_4 – 8300 μmol g_{cat}^{-1} h^{-1} reduced in H_2 at 400 °C for 1 h with apparent quantum efficiency at a wavelength of 425 nm equal to 4.9 %. The catalytic activity of $Rh_{0.5}$/g-C_3N_4 sample (H_2, 400 °C, 1 h) was 4430 μmol g_{cat}^{-1} h^{-1}, and apparent quantum efficiency was 2.6 %.

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Acknowledgements

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OP-III-14

UREA-PERSULFATE FUEL CELL COMBINED WITH FORWARD OSMOSIS FOR A CONTINUOUS GENERATION OF POWER AND WATER FROM URINE

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The wastewater fuel cell system has been investigated in the water-energy nexus framework, by simultaneously achieving power generation and water treatment. In particular, the direct urea fuel cell (DUFC) can recover chemical energy from waste urea in toilet wastewater using the urea oxidation reaction (UOR). Nickel-based catalysts have been up-to-date the most widely investigated electrocatalysts to reduce the overpotential and kinetic barrier for the UOR, while combination with the secondary elements (Co, Fe) has been reported to enhance the UOR activity. This study explored the UOR on Ni-based anodes prepared by electro-deposition of mixed metal (oxy)hydroxide ($NiFeO_x$ or $NiCoO_x$ with variable mixing ratios) on three-dimensional foam base (e.g., Ni foam). Compared to monometallic Ni (hydr)oxide, additions of the secondary elements (Fe and Co) were found to accelerate the formation of NiOOH (the active intermediate for UOR), by partial charge transfer among the mixed metals. The highest UOR activity was marked by $NiCoO_x$ (Ni:Co = 9:1) electrodeposited on Ni foam to be employed as an anode in the DUFC. In addition, this study utilized persulfate ion (stronger oxidant than molecular oxygen) as the electron acceptor. A comprehensive chemical reactor engineering was performed to maximize the power generation from urea solutions, by altering the carbon-based cathode materials (e.g. carbon paper, Pd/graphite felt, activated carbon/graphite), pH of anolyte/catholyte, and urea concentrations. The maximum power density of DUFC was observed to be 1.37 mW cm^{-2} with N-doped activated carbon/graphite cathode, anolyte with 0.33 M urea at pH 13, and catholyte with 1 M persulfate at pH 2.25. The anolyte pH was found to be the principal parameter. The DUFC was further combined with an alkaline-resistant forward osmosis (FO) membrane for a continuous production of clean water under steady urea concentration in the anolyte and power generation. The novel FO-DUFC system achieved nearly constant power density (1.2 - 1.55 mW cm^{-2}) for 5 h during a constant load discharge. The current efficiency of urea degradation was estimated to be 15.2 %. Operation with an artificial urine

indicated moderately reduced power density (~ 0.7 mW cm^{-2}) due to side reactions in the complex ionic matrix.

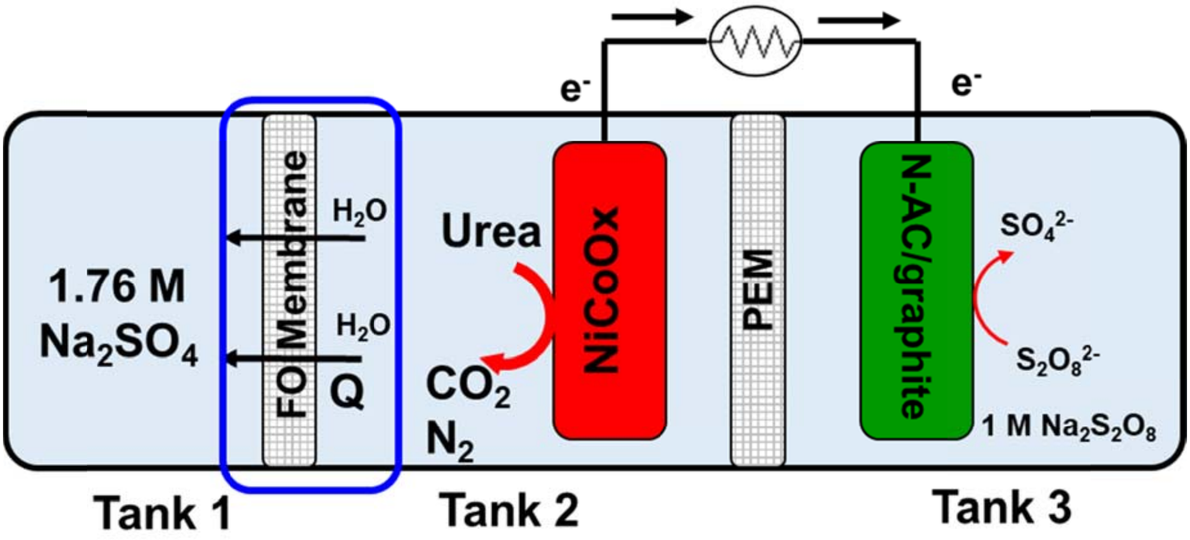

Figure 1. Schematic representation of FO-DUFC system

OP-III-15

WATER TREATMENT BY A TUBULAR PHOTOELECTROCATALYTIC REACTOR WITH ELECTROCHEMICALLY SELF-DOPED TiO_2 NANOTUBE ARRAYS

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Electrochemical self-doping has been evinced to be a plausible way to enhance the electrochemical (EC) and photo-electrochemical (PEC) activities of TiO_2 nano-structures in mild conditions (room temperature and atmospheric pressure) for water splitting and purification among other purposes [1]. The cathodic polarization would affect the level of self-dopants (Ti^{3+} and oxygen vacancy) to reduce the bandgap by introducing additional energy levels in forbidden band gap, which could improve light absorbance, electrical conductivity, capacitance, and charge transfer depending on the doping level [2]. We herein report the effects of primary doping conditions on the physico-chemical properties and photocurrent generation for the self-doped TiO_2 nanotube arrays (TNA) for potential applications in PEC water treatment within a novel batch tubular PEC reactor. A systematical interrogation was performed for the TNA prepared by anodization of Ti plate that were subject to variable regimes of applied potential bias, duration and pH of electrolyte during the cathodic polarization. Diffuse reflectance spectroscopy (DRS), Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) were utilized to estimate the band alignment and surface oxidation state of Ti. Incident photon-to-current conversion efficiency (IPCE) was assessed under illumination of UV and visible light, while the rates of a model organic compound (Polyacrylic acid, PAA) degradation were evaluated within the tubular PEC reactor. A cylindrical UV lamp was inserted into the pipe-shaped self-doped TNA to irradiate in inner TNA surface as a light source, while Ti rods were utilized for the PEC application (Figure 1). The anatase crystal formation in TNA during pre-treatment of atmospheric annealing at 450 °C sharply deteriorated the faradaic efficiency of subsequent self-doping so that the cathodization current and duration effectively altered the rate of PAA degradation. The pH of the cathodization electrolyte was found to switch the relative level of Ti^{3+} on surface of TNA and IPCE from 300 to 400 nm. DRS spectra shows comparable UV absorbance for UVA range, whereas substantial increases in visible light absorptivity were noted by self-doping along with the formation of mid-gap states. The optimized self-doped TNA in the batch tubular reactor enabled a successful degradation of the non-biodegradable organic compound (PAA), while maintaining the activity upon a long-term sequential batch cycles. The findings of this study would broaden the applicability of cathodized TNA, by tuning the physico-chemical characteristics. In addition, the proposed tubular TNA reactor can be an effective option for a practical PEC water purification.

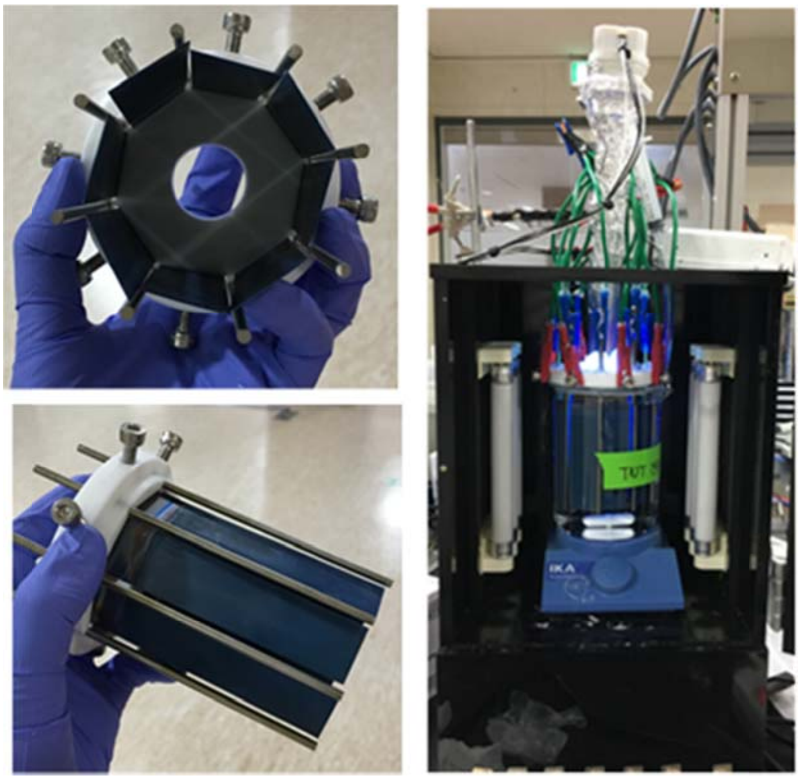

Figure 1. Pictures of tubular photoelectrocatalytic reactor equipped with electrochemically self-doped TiO_2 nanotube arrays

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OP-III-16

MACHINE LEARNING FOR OPTIMIZATION OF SINGLE-WALLED CARBON NANOTUBE SYNTHESIS BY AEROSOL CVD REACTOR

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Unique properties of single-walled carbon nanotubes (SWCNTs) make them prospective material to be implemented in different areas from biomedicine to nanoelectronics [1]. A key step in the successful promotion of this outstanding material in the industry is the development of cost-effective and robust technology for the controllable production of the material with tunable characteristics. Among different approaches to SWCNT synthesis, aerosol (floating-catalyst) chemical vapor deposition (CVD) [2] method is considered to be the most promising one, fulfilling most of the industrial requirements, namely scalability [3], high purity of the material, potential for tuning nanotube properties directly during the synthesis process, and a simple way of film fabrication as well as deposition of individual species on any desired substrate [4].

Despite all the advantages and advances already achieved in the field, the production of nanotubes with precisely tuned and even defined properties on an industrial scale is still challenging. The main factor inhibiting the progress is usually attributed to the complexity of mechanisms for the nanotube nucleation, growth, and termination burdened by the lack of the general model, providing a quantitative relationship between the synthesis conditions and SWCNT parameters. Though the main aspects of the SWCNT growth are deduced, the multiparametric nature of the chemical processes associated with the inconsistency of the results among reactors worldwide inhibits the progress towards the precise control over nanotube properties and actualizes the development of novel approaches to govern synthesis process [5].

In this work, we combine the problem with another vastly developing field which shows its best with multiparametric complex tasks – Machine Learning (ML). We report the utilization of ML numerical models for processing of experimental data, obtained using a single aerosol CVD reactor, based on thermal decomposition of ferrocene and the Boudouard reaction on the surface of iron catalyst. We demonstrate the prediction of the reactor output (yield, diameter, and quality of producing carbon nanotubes) with an accuracy of as low as 4 %, using temperature and gas mixture compound as input parameters. We developed a predictive model based on an artificial neural network (ANN) and trained it on a pre-processed experimental data adjusting hyperparameters for the best performance [6]. For optimization of reactor operation and further development of approach employed, we also solve regression tasks and refine synthesis conditions to enhance the performance of SWCNT films as a transparent and conductive material. The strategy employed allowed us to fabricate films with equivalent sheet resistance (at 90 % transmittance) of 39 Ω/□ – one of the lowest values achieved so far [7]. Collected dataset accompanied by proof-of-the-concept experiments formed a basis for fine optimization of reactor performance, governed by ML algorithm.

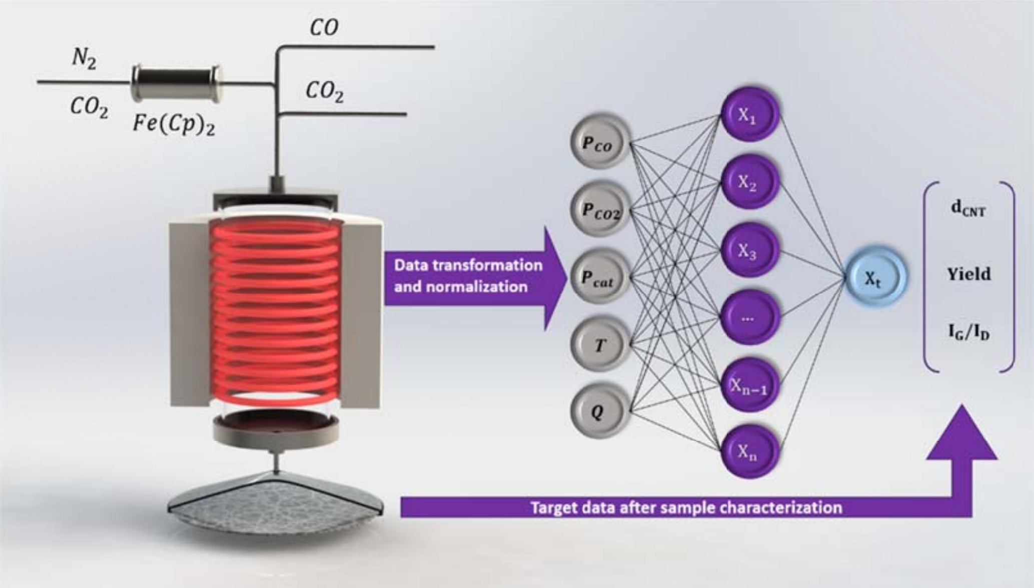

Figure 1. ANN implementation to nanotube production [6]

Thus, our results justify Machine Learning implementation in chemical engineering, especially in the nanomaterial production field, requiring high precision control over chemical processes for advanced implementation. The demonstration of highly conductive and transparent films obtained using a simple laboratory-scale reactor is valuable for SWCNT thin-film technology and we believe that these results could be significantly improved by designing a more-sophisticated industrial-scale system with feedback and using reinforcement learning algorithms.

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OP-III-17

INDUSTRIAL-SCALE GASIFICATION OF MUNICIPAL SOLID WASTE IN SUPERADIABATIC REGIME OF FILTRATION COMBUSTION

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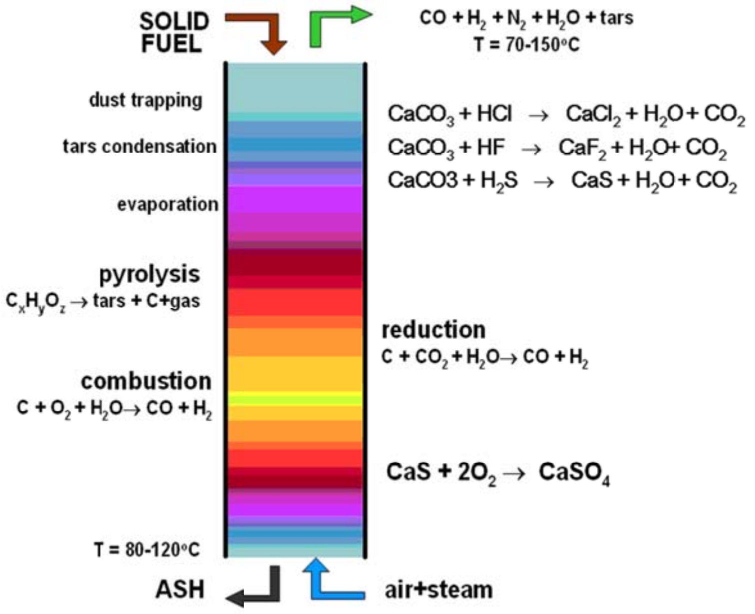
Idea of waste gasification using superadiabatic regimes of filtration combustion (FC) appeared naturally once the problem of massive MSW incineration became topical. It is just an application of well-known updraft gasification process to turn such a ‘fuel’ into combustible gas [1]. Succession of zones inherent in the updraft process is favorable for the waste incineration. From the top, the fuel passes through zones of drying, pyrolysis, char combustion, ash cooling. The process is naturally superadiabatic as both fuel (char) and oxidant (air) arrive to the reaction zone being preheated owing to heat exchange with products (producer gas and ash). This gasification process, additionally to common advantages of incineration via gasification, cleaner smoke gas and more energy efficient boiler [2] has its own merits. To mention a few: filtration of gas through the fresh fuel provides conditions to arrest dust particles and to neutralize acid gases, long stay of ash in hot air flow secures oxidation of organics.



The counterflow superadiabaic regime secures high energy efficiency. Optimal regimes for char gasification as dependent on carbon/ash ratio and steam in the oxidant gas assessed in [3] prompted use of additional solid inert heat carrier to the fuel. This circulating granulated solid enhances heat recuperation.

Additionally, it secures more uniform distribution of gas flow over the reactor cross-section. A very high chemical (cold gas) efficiency of gasification (90 % +) was confirmed in laboratory tests.

This allowed us to build an experimental industrial-scale (1500 mm ID) installation. The first tests performed confirmed high efficiency of gasification and relatively high environmental performance of the process. The limits for carbon monoxide, soot, hydrogen chloride, and hydrogen fluoride were satisfied without any gas cleansing, those for dust and heavy metals, sulfur oxides and dioxins exceeded insubstantially, so the smoke gas required only a minor cleansing.

However, the tests revealed substantial limitations related to mechanical instability of the process. While perfectly performing with piecewise or briquetted fuel, the process with actual MSW gradually developed instability of the combustion front that ultimately resulted in a burn-through at one side. This prompted development of a new type of gasifier reactor, tilted rotary reactor. Inclined at 45 degrees rotating reactor allowed us to combine fuel stirring and mixing as in conventional rotary kiln and a packed bed with efficient heat exchange with filtrating gas typical of a shaft kiln. Rotation at 2-3 rpm secured perfect stabilization of the FC front.

An industrial 1500 mm ID prototype reactor has been built and ignited in October 2019. The fuel gasified was tailings of MSW from the city of Moscow after aerobic composting; humidity of fuel was ~35 %, ash content ~35 % TS. The tests confirmed stability of the process. The generator gas had the following composition per dry gas (see Table, % vol.). Additionally, the gas contained steam and vapors (pyrolysis tars).

CO_2	Ar	O_2	N_2	CO	C_2H_4	CH_4	H_2
17.0	0.7	0.0	62.5	8.8	0.7	1.8	8.5

The gas perfectly burned in a swirl burner. Most important is that tests confirmed high environmental performance of the incineration process. Content of PCDD/PCDF in the smoke gas was 18.4 pg/m^3 TEQ (limiting value 100 pg/m^3); PCDD/PCDF concentration in the ash was TEQ 28.6 mg/kg (Russian national permissible limit for urban soil being 50 mg/kg).

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TEMPERATURE SWING ADSORPTION FOR CO_2 CAPTURE: PROCESS INTENSIFICATION WITH CONDUCTIVE PACKED FOAMS

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Temperature Swing Adsorption (TSA) processes are a promising alternative to the more established amine-wash technologies for post-combustion CO_2 capture. Differently from absorption-based separations, a TSA cycle is not operated as a steady state process, but rather as a sequence of steps undergone by the gas-solid contactors, which most standardly consist of fixed-bed reactors. A simple cycle is constituted by an adsorption step performed at low temperature to maximize CO_2 intake, a heating ramp up to 150 °C with the consequent release of the adsorbate during the desorption step, where a high-purity CO_2 stream is produced, and a final cooling to bring back the system to its initial state Some of the steps of the cycle are performed in static conditions (i.e., no inflow into the reactor), whereas others are typically performed at low velocities to contain the pressure decay.

When using commercial CO_2 sorbents, one way to increase the process cyclic capacity for CO_2 is accelerating the heat transfer kinetics. This requires overcoming the intrinsic heat transfer limitations associated with the operation of a packed bed, both in flow and in static conditions. Following an approach already suggested in the context of catalytic processes [2], heat transfer can be enhanced by the introduction of highly conductive open-cell foams within the reactor thus maximizing the heat transfer in static conditions through the adsorbent bed. In the proposed configuration the void cells are filled with the sorbent pellets, enabling to house solid inventories larger than those obtained with washcoated structured supports (per unit reactor volume). With this contribution, we propose the application of the packed metallic foams as an alternative to the standard fixed-bed configuration for adsorption-based separations in the case of a post-combustion CO_2 capture process.

In order to observe temperature gradients in both the axial and the radial direction within the reactor, a large cross-section (80 mm diameter and 200 mm length) jacketed cylindrical adsorption column has been adopted as experimental setup. It has been filled packing spherical zeolite 13X pellets (average diameter 1.8 mm) into a foam in aluminium with a void fraction of 0.95 and a cell size of 5 mm. For this arrangement a total sorbent volumetric fraction of 0.50 has been measured, which represents a 25 % reduction of the solid inventory compared to a standard packed column (at fixed reactor volume). A first series of steady-state and dynamic heat transfer tests has been completed by flowing inert gas (Argon) at different velocities through the column, and analyzing axial and radial temperature profiles across the packed foam. The profiles demonstrate that heat transfer rates are enhanced by up to a factor 2. A detailed mathematical model for the description of the heat effects within packed foams has been validated by means of the experimental results.

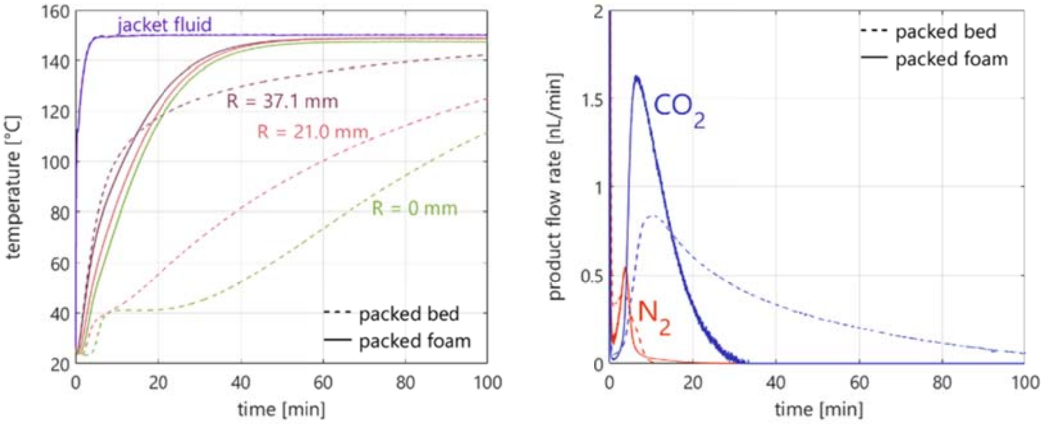

Figure 1. Experimental pro-files in time for temperatures (at different radial positions) and outlet flow rates. Results for packed bed (dashed) and packed foam (continue) configurations during the regeneration step of a TSA cycle are shown. The reactor is indirectly heated by a hot fluid flowing in the jacket.

A second series of experiments has reproduced the operation of a basic TSA cycle (adsorption, heated regeneration, closed cooling) for the separation of a binary 12/88 % v. CO_2/N_2 mixture. Both the temperature profiles within the adsorption column and the outlet composition of the gas have been monitored. The enhanced heat transfer results into a more homogeneous distribution of the temperature throughout the adsorbent, and enables a faster transition toward the final (steady) state during each step (Figure 1). This allows cutting off the duration of the regeneration and cooling steps by a factor of 3, thus considerably improving the overall process productivity.

Furthermore, the extension of the detailed model to account for adsorption is under development in view of its implementation in a process simulation tool. This will enable a systematic optimization of the process design, to explore the improvement margin available over the standard packed bed adsorber design in terms of process efficiency.

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Acknowledgements

The authors thank Casale SA for the financial and technical support granted to the project.

OP-III-19

CO_2 METHANATION WITH Ni AND Co CATALYSTS SUPPORTED ON γ-Al_2O_3 MODIFIED WITH La

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CO_2 valorization towards methane production through catalytic hydrogenation, known as the Sabatier reaction, can be carried out using various group VIIIB metal catalysts, supported on different solids having high surface areas, such as Ni-based catalysts supported on mesoporous Al_2O_3 [1][2].

The general objective of the present work is to develop suitable Ni and/or Co methanation catalysts for processes that combine capture and conversion of CO_2 derived from industrial effluents. The ultimate goal is to develop suitable structured catalytic reactors for the process. The study presented here focuses on evaluating the performance at atmospheric pressure of Ni and Co catalysts supported on γ-Al_2O_3, and the influence of modifying these catalysts with La and/or polyvinyl alcohol (PVA). The catalysts were characterized using different techniques, including N_2 physisorption, CO chemisorption, X-ray diffraction (XRD), Temperature Programmed Reduction under H_2 flow (H_2- TPR) and Transmission Electron Microscopy combined with X-ray Energy Dispersive Spectroscopy. The catalytic performance was evaluated in a laboratory-scale tubular fixed-bed setup using a 9 mm i.d. quartz reactor. The catalytic tests were typically run during 180 min. at a total pressure of 1.3 atm. Prior to the tests, the catalysts were subjected to *in situ* activation by reducing the catalyst at 500 °C under H_2 flow for 180 min. The gas feeding stream was composed of N_2, CO_2 and H_2 with a H_2/CO_2 molar ratio of 4:1.

In Figure 1, preliminary results showed that Ni and Co catalysts are quite stable as concerns CO_2 conversions over reaction time at a constant temperature of 400 °C. There is also a notable difference in the catalytic activity of the two systems evaluated using the same activation condition. In this case, Ni catalysts were significantly more active and selective towards methane than the Co ones.

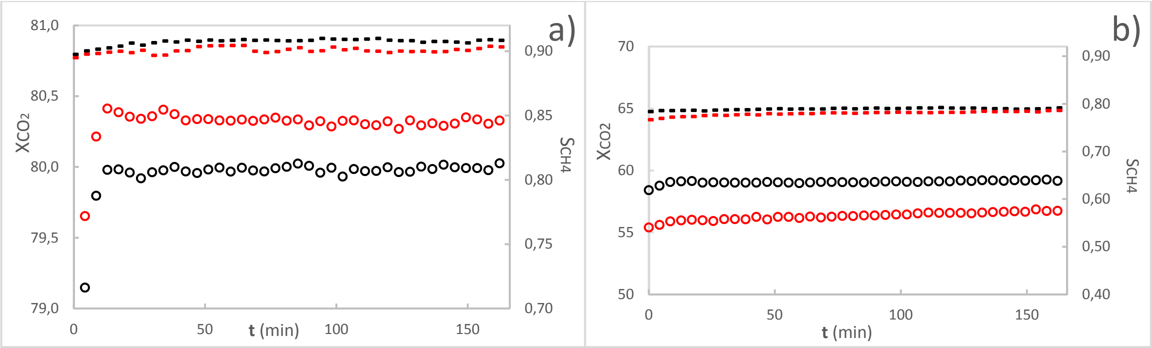

Figure 1. Hydrogenation of CO_2 at 400 °C and 12 LN (CO_2/g_{cat}*h): a) Ni catalysts; b) Co catalysts
○ XCO_2 M ○ XCO_2 M-PVA – SCH_4 M – SCH_4 M-PVA (M = Ni, Co)

Taking into account the H_2-TPR results and that the reduction conditions seem to have a direct impact on the observed catalytic performances, optimization of the activation conditions is underway by increasing the reduction temperature and time. The presence of PVA in the precalcined catalysts is investigated since this additive is used to prepare the slurries employed to prepare the structured monolithic catalysts. PVA does not have a significant effect on the selectivity but it has an influence on the CO_2 conversion, especially for the Co catalyst. Determination of the metallic dispersions are underway in order to suitably interpret these results.

Kinetic studies are also under progress. An apparent activation energy close to 97 kJ/mol has been preliminary obtained for the Ni catalyst, which is in line with values previously reported in the literature [3].

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Acknowledgements

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OP-III-20

PROCESS INTENSIFICATION (PI) OF TRANSFORMING CO_2 BY AUTO-METHANATION WITH STRUCTURED CATALYST SYSTEM

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The reduction and utilization of CO_2 emitted from the industrial process is currently a hot topic from the viewpoint of environmental conservation. The CO_2 methanation ($CO_2+4H_2 \rightarrow CH_4+2H_2O$, ΔH^0_{298} = -165 kJ/mol) has received attention as one of the effective methods for the conversion of CO_2 into useful resources, which can be used to store surplus electricity as a power-to-gas (PtG) technology1). In our previous study2), we found a novel route for CO_2 methanation with oxidation over a granular Ni/CeO_2 catalyst, which could be operated even in regions at room temperature. In brief, using a raw material gas containing 1-7 vol % oxygen, the methanation performance was greatly improved and realized even in a region at room temperature and atmospheric pressure. No one in the World has reported such transformation route yet. We named this novel route as auto-methanation. When using auto-methanation for reducing CO_2 emitted during an industrial process, the efficient treatment of large amounts of emitted gas and an efficient heat control are serious problems. A structured reaction system with a catalyst component directly loaded onto a metal substrate was shown to be suitable to address these issues3, 4).

In this study, using a structured Ni/CeO_2 catalyst, the auto-methanation was investigated by feeding a raw material gas containing 1-11 vol % oxygen. The obtained data suggested that the constructed catalyst system is extremely effective in reducing CO_2 and contributes to the PI technology for CO_2 methanation.

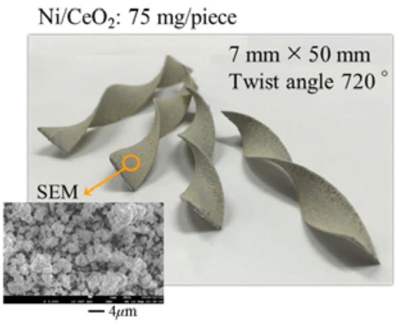

Fig. 1. Spiral Ni/CeO_2 catalyst

The structured catalyst was prepared by wash-coating a granular Ni/CeO_2 on an aluminum substrate. The substrate activated by NaOH and HCl solutions was dipped into a slurry of Ni/CeO_2 catalyst. Figure 1 shows the prepared spiral-type catalyst, demonstrating the uniform coating of the catalyst (75 mg) on the substrate. Prior to the methanation, the spiral catalyst (four pieces, catalyst: 300 mg) was placed in a conventional flow reactor (ID: 8 mm), reduced by H_2 at 500 °C. Methanation was carried out by introducing the feed gas into the reactor at 350 °C to room temperature. The raw material gas contained CO_2, H_2, O_2, and N_2 (balance). The CO_2 conc. was fixed at 10 vol % and the O_2 conc. was changed from 1 to 11 vol %. Total feed rate was 400 ml/min.

Figure 2 shows CO_2 conversion over the prepared catalyst. When oxygen was supplied at 1, 5, and 7 vol %, the drastic change in conversion at around 250 °C shifted toward a lower temperature, and the activity at a lower temperature range improved. Particularly, under 7 vol % oxygen co-feeding, high conversions of 25-50 % were achieved even at temperatures of 100 °C or less. When the oxygen concentration was 9 vol% or more, quite stable methanation activity was achieved from 200 °C to room temperature. Thus, methanation activities of 53-60 % were obtained even at room temperature, with external heating cut off. Utilization of the structured catalyst system will open a great deal of potential for converting CO_2.

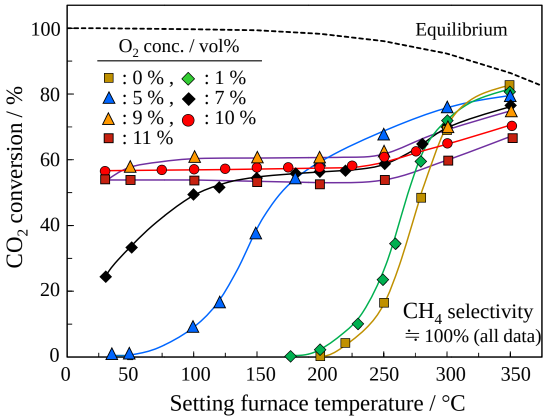

Fig. 2. Methanation profiles of spiral Ni/CeO_2 under O_2 co-feeding

Figure 3 shows a visual snapshot of auto-methanation over the spiral-type Ni/CeO_2 catalyst and an infrared thermographic image of the same region. The electric furnace was in an open state with heating cut off. The temperature profile of the catalyst part widely changed along with the distance. The maximum temperature region of ca. 300 °C was located around the entrance of the 1st catalyst, but a moderate temperature region of 150 °C or less appeared over the 2nd catalyst. Considering such a thermal profile, it was thought that the raw material gas rapidly reacted at the inlet part and was converted to methane with ca. 57 % during the 1st catalyst. An rapid material conversion was in progress, which suggests an advantage for the PI technology.

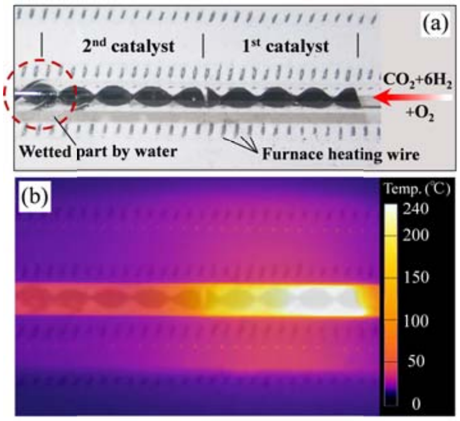

Fig. 3. Sanpshot of (a) auto-methanation over spiral Ni/CeO_2 and (b) infrared thermal image at same position

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OP-III-21

MEMBRANE INTEGRATED MICROCHANNEL REACTOR FOR CONVERSION OF CO_2 CONTAINING SYNGAS TO DME

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In recent years Dimethyl Ether (DME) has attracted considerable attention as an alternative fuel due to its favorable combustion characteristics, easy transportation, handling and relatively low CO and NO_x emissions. DME is traditionally produced by the so-called indirect (two-step) method. In the first step, methanol is produced from synthesis gas (syngas) typically on Cu-ZnO-Al_2O_3 catalyst. Methanol is then dehydrated to DME in the second step via acidic catalysts such as γ-Al_2O_3 or HZSM-5. As opposed to the indirect one, the direct (one-step) method involves co-existence of the synthesis and dehydration catalysts either as a physical mixture or in the form of hybrid catalysts [1] and aims to perform methanol synthesis and dehydration within the same reactor to reduce capital and operating expenditures. Exothermic nature of the reactions in the direct synthesis method imposes a strong need for effective heat removal from the catalyst bed. Wall-coated microchannel reactors offer heat transfer rates that are up to ~10^2 times higher than those of packed bed counterparts due to higher surface area/volume ratios enabled by the channel dimensions in the sub-millimeter range. Moreover, microchannel units with integrated cooling systems allow near isothermal conditions which allow optimization of the thermodynamic and kinetic effects to maximize reactor performance [2].

One-step conversion of CO_2-containing syngas to DME leads to reverse water-gas shift (RWGS) which generates water vapor as a by-product. Water vapor is undesired as it hampers DME production by shifting dehydration towards methanol formation and increases the risk of hydrothermal sintering of the catalysts [2]. Moreover, positive CO_2 consumption may not be realized as methanol produced by CO hydrogenation thermodynamically drives CO_2 hydrogenation in the reverse direction. These limitations can be overcome by *in-situ* removal of water vapor via selective membranes [1]. Owing to the high surface area/volume ratios (in the order of ~10^4 m^2/m^3) of the microchannel reactors, combining them with membranes can offers mass transfer rates that are significantly enhanced compared to those of packed-bed counterparts.

OP-III-21

In this study direct synthesis of DME from CO_2-containing syngas in a membrane microchannel reactor is simulated. The reactor consists of two neighboring channels, each having dimensions of 7.5×10^{-2} m (length), 3×10^{-4} m (width) and 6×10^{-4} m (depth). The channels are separated with a H_2O selective zeolite membrane. The reaction channel is washcoated with a 5×10^{-5} m thick, bi-functional Cu-ZnO-HZSM-5 catalyst, whereas the upper channel (i.e. permeate zone) used to sweep the H_2O coming from reaction zone through membrane. Gas inlet is the same for both reaction and permeate zones, and consists of syngas at 508 K, 30 bar with velocity of 0.01 m/s. Simultaneous, steady-state reaction and separation is modeled in 2D on ANSYS 19.2 platform. The resulting heat, mass and momentum transfer equations in both porous catalyst and fluid phases together with catalytic reactions and membrane separation are solved by the finite volume method. Membrane module, which uses Fick's Law to calculate permeation fluxes for H_2O and H_2, is implemented via a user defined function (UDF) as mass source terms at the boundaries of each channel. In order to see the effect of the membrane, reactor is simulated in the absence and presence of the membrane module. Preliminary results (Figures 1 and 2) indicate considerable H_2O removal with the zeolite membrane and lead to the improvement of CO_2 conversions. Studies are ongoing for deeper elucidation of the membrane integrated operation.

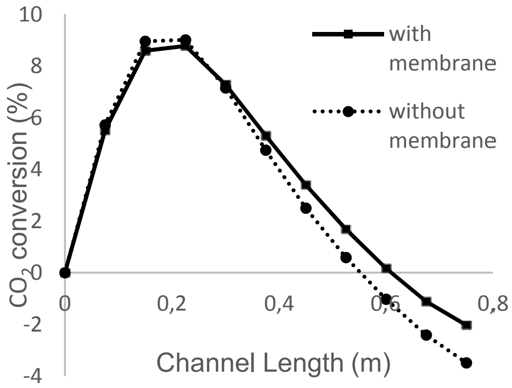

Figure 1. Comparison of CO_2 conversions in the absence and presence of membrane

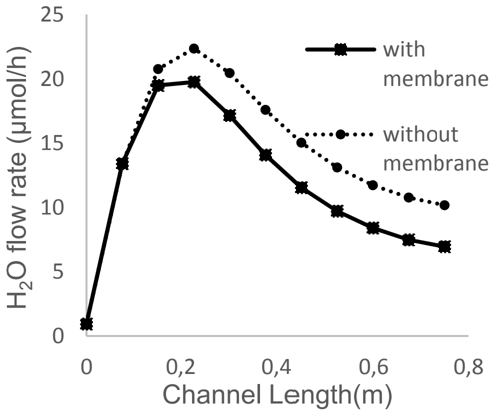

Figure 2. Comparison of H_2O molar flow rates in the absence and presence of membrane

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Acknowledgements

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OP-III-22

DEVELOPMENT OF A TWO STAGE REACTOR CONCEPT FOR THE METHANATION OF CARBON DIOXIDE FROM RENEWABLE SOURCES

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The methanation of carbon dioxide from biogas plants is a viable route to increase the economic attractiveness of the injection of biogas methane into the natural gas grid, which has a significant energy storage capacity. However, the hydrogen required for the reaction must originate from renewable sources such as water electrolysis applying excess electric power from wind energy or solar power plants (which is currently under certain conditions at negative cash flow when fed into the electric grid) to maintain overall sustainability and economic viability. The unsteady availability of the renewable electric power excess requires the dynamic operation of the electrolysis and the methanation reaction downstream.

Owing to the exothermic nature of methanation, reactors with integrated capabilities for heat removal are required to be able to follow the requirements of the dynamic operation and of the thermodynamic equilibrium of the reaction. To reduce the size of such a heat exchanger reactor a first reactor stage operated at high reaction temperature under adiabatic conditions is favourable, while a decreasing temperature profile along the length axis of the second reactor increases the conversion further towards the outlet.

Specific catalyst formulations were developed for the different operating temperatures of the reactors. The activity and sulphur tolerance of the catalysts were optimized.

The two stage reactor concept described above was verified experimentally in a small scale pilot plant. Adiabatic (monolithic) reactors and plate heat-exchanger microreactors coated with innovative catalyst formulations were built for the methanation reaction with a power equivalent of the corresponding water electrolyser of up to 50 kW. Full scale reactors were finally installed at a biogas plant along with a 50 kW electrolyser.

OP-III-23

INTENSIFICATION OF CO_2 METHANATION BY CATALIST AND PROCESS DESIGN

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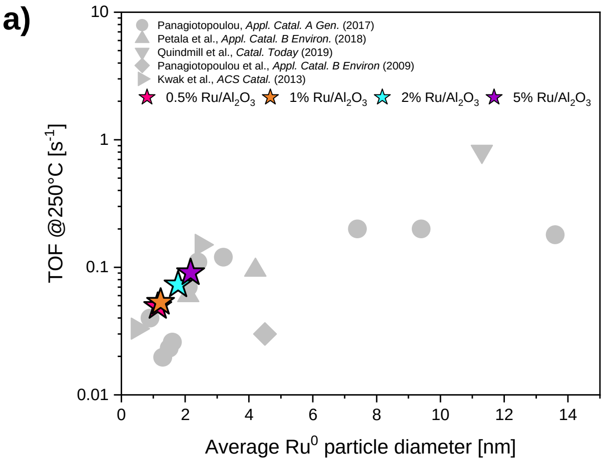
The utilization of low-cost CO_2 in combination with renewable H_2 is environmentally attractive and may help to stabilize the power grid. Among the proposed CO_2 (re)utilization technologies, its hydrogenation to methane to produce SNG through the Sabatier reaction is particularly appealing [1], especially where a highly integrated natural gas pipeline network is available. The exothermic CO_2 methanation is strongly limited by thermodynamics at high temperatures: the maximum reactants conversion is low and the CO selectivity quickly increases. Accordingly, in this work, we focus on the design of low-temperature Ru-based catalysts [2] appropriate for operations at the industrial scale. In particular, by experimental and modeling activities, we investigate the effects of: (i) the catalyst size; (ii) the active phase distribution; (iii) the catalyst activation conditions; (iv) the operating conditions; (v) the process configuration. The prepared samples are tested in a fully-automated lab-scale plant equipped with a fixed bed reactor, operating 24/7 in integral conditions and with concentrated H_2/CO_2 streams. The experimental set up allows operations with one reactor or with two reactors in series, with or without intermediate water condensation.

100 μm γ-Al_2O_3 powders, activated with 0.5, 1, 2 and 5 wt. % Ru, have been tested in kinetically controlled regime. No differences in activity, nor in selectivity, were observed when working at constant flowrate per gram of Ru. However, the metal dispersion of the active phase measured by CO chemisorption and HR-TEM indicated a relevant decrease in the average particle size. The turnover frequency (TOF) has been evaluated and compared with literature data. In this particle size range, an increase in the particle size is accompanied by an increase in the intrinsic activity of the exposed surface. The variation of metal surface area and TOF are effectively balanced, resulting in the same activity of the samples when working at constant flowrate per gram of Ru.

Since the 5 wt. % Ru/Al_2O_3 sample exhibited the highest activity per gram of catalyst, while still exploiting at best the amount of introduced Ruthenium, the recipe for its preparation has been scaled up using 800 and 2300 μm γ-Al_2O_3 microspheres to assess the role of pore diffusion under conditions of industrial interest. Both CO_2 conversion and CH_4 selectivity decrease when increasing pellet size due to the onset of diffusional limitations, indicating that the characteristic length of diffusion in these conditions is lower than 133 μm.

The process configuration was then investigated aiming at the production of a methane stream that meets the specifications required for its direct injection in the grid. In this context, the parameter of CH_4 purity (i.e. the dry molar fraction of methane at the reactor outlet) has been considered. In order to increase the CO_2/H_2 conversion, the possibility of working at low temperatures and space velocities was investigated. The adopted Ru-catalysts exhibited a stable behavior for 800 h on stream, even in presence of the large amounts of steam generated by the reaction, with CO_2 and H_2 conversion in excess of 95 %. Furthermore, using two catalytic beds in series at different temperatures, allowed to boost the methane yield. The best configuration is obtained by operating the first reactor at high temperatures to boost the process kinetics, while keeping the second reactor at milder conditions so to exploit the high CO_2 conversion and CH_4 selectivity at equilibrium. Condensing the water exiting from the first reactor further boosts the methane purity at the reactor outlet, allowing to reach a CH_4 purity compatible with grid injection (98.5 %), while working at atmospheric pressure (Fig.1b).



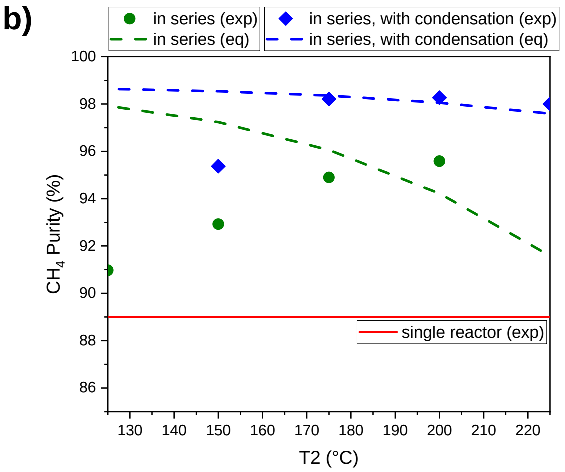


Figure 1a. TOF at 250 °C as a function of Ru particle size **Figure 1b.** Methane purity obtained: when operating a single reactor at 250 °C (red line), when operating the first reactor at 250 °C and varying the second reactor temperature in the range 125-230 °C in absence (green points-line) and in presence of intermediate water condensation (blue points-line). H_2/CO_2 = 3.9, 1 L(STP)/h/g_{cat}

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OP-III-24

CO_2 HYDROGENATION REACTOR: EXPERIMENTAL PROOF-OF-CONCEPT AND TECHNO-ECONOMIC FEASIBILITY ASSESEMENT

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Thermocatalytic conversion of CO_2-rich streams (e.g., landfill gas, biogas, industrial flue gases) into synthetic fuels is an attractive route for CO_2 utilization. This approach of Carbon Capture & Utilization (CCU) is an alternative to Carbon Capture & Storage (CCS) by storing CO_2 in geological formations and other similar routes. To make the process of thermocatalytic conversion sustainable, H_2 (required for CO_2 hydrogenation to fuels) should have negligible carbon footprint, which is achievable if H_2 is produced via water electrolysis using renewable (or nuclear) power. However, a number of technological issues remain to be resolved with respect to the design of the CO_2 hydrogenation process. These issues are mainly related to reactor design and system integration.

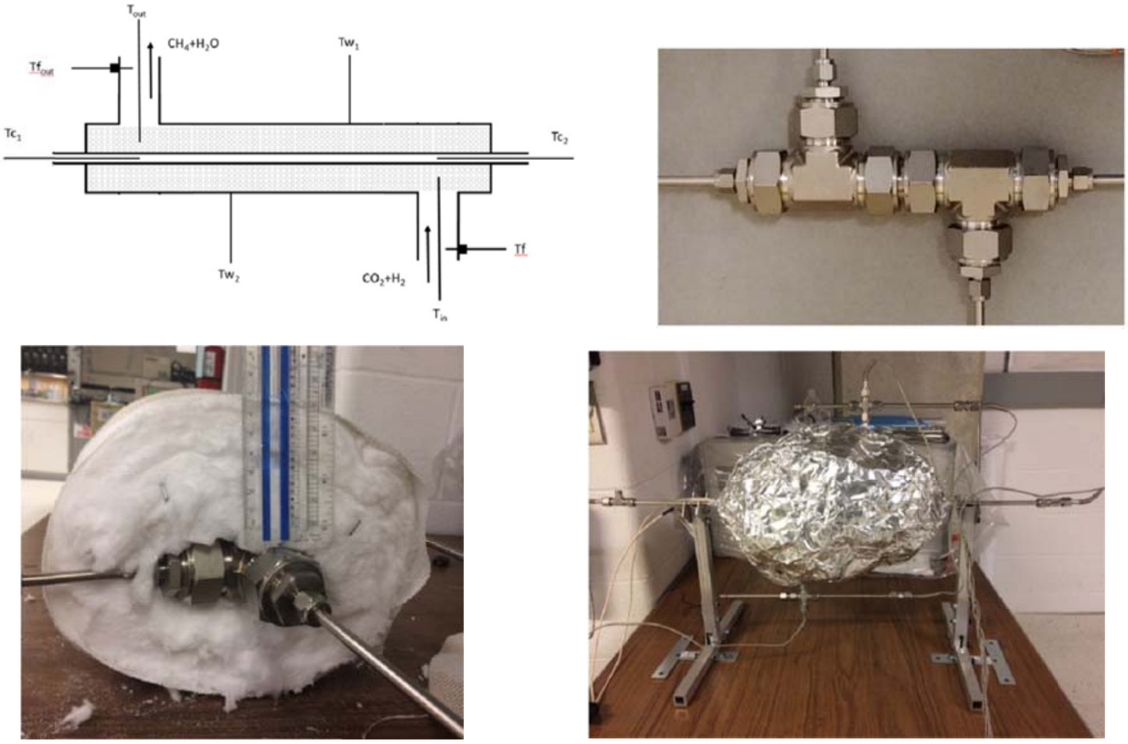

Figure 1. Lab-scale proof-of-concept Sabatier reactor. Upper panels show the reactor schematic and the actual unit without insulation (on the right). Lower panels show the reactor with thermal insulation (on the left) and the final configuration enclosed in the aluminum foil (to reduce radiative heat transfer)

This talk presents recent advances achieved in our group with respect to the thermocatalytic conversion of CO_2 into renewable natural gas (RNG) via the Sabatier reaction [1-6]. Our research focused on the thermal management and performance optimization of a stand-alone (thermally independent, compressed air cooled) Sabatier reactor. Results of the experimental proof-of-concept using a lab-scale unit (**Figure 1**), utilizing a low cost, Ni-based catalyst are presented. Effects of various operating parameters on the reactor performance in terms of CO_2 conversion and selectivity to CH_4 formation were carefully investigated in order to determine optimal operating conditions. We have demonstrated experimentally that it is possible to achieve 94 % CH_4 conversion with 100 % selectivity to CH_4 formation (**Figure 2**).

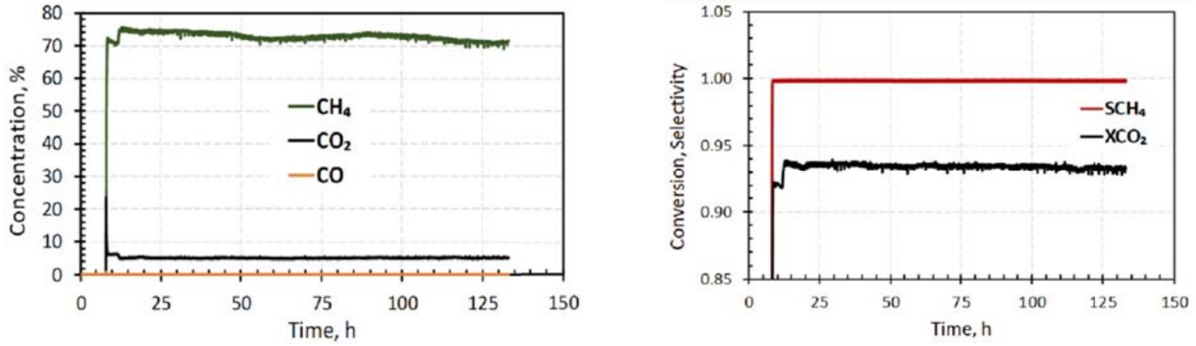

Figure 2. Stability test of the lab-scale reactor (80 g of Ni-based catalyst, H_2/CO_2 = 4; P = 13 bar, GHSV = 4,500 1/h)

Based on the experimental proof-of-concept, techno-economic assessment for a particular case of converting landfill gas to renewable natural gas (RNG) has been conducted. The scaled-up system was designed using Aspen HYSYS. The results of numerical simulations were used to assess the economic feasibility of a large scale process processing the landfill gas generated at a large, fully-enclosed landfill site with a landfill gas collection system. The production cost was estimated in the range of $15-25/GJ for electricity prices ranging from $0.04-0.10/kWh.

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OP-III-25

KINETIC MODELLING AND NMPC SIMULATION FOR THE EPOXIDATION REACTION OF THE SOYBEAN OIL

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One of the current trends in industrial processes is to consolidate the use of substances from renewable sources, replacing traditional nonrenewable substances. Inside this scope, the epoxidized soybean oil (ESO) has been a candidate to replace phthalate-based compounds as an element in plasticizers for polyvinyl chloride (PVC), due to the elevated toxicity of the phthalates [1]. The epoxidation reaction of the soybean oil usually occurs in a biphasic liquid system, with the addition of soybean oil, hydrogen peroxide and a carboxylic acid. Apart from the ESO, this reaction system also tends to produce undesired products due to ring opening reactions of the ESO. This can be minimized by adding selective catalysts and/or providing proper reaction conditions to the system. Aiming to increase the production of the ESO in this reaction system, the addition of catalysts might not be economically and environmentally advantageous. Within this, as a continuation of another project in our Department [2], the first objective of this study was to develop a kinetic model to represent this system in batch configuration, using values collected from studies in the literature. The second part of this project was the determination of an optimal temperature profile by dynamic optimization for the epoxidation reaction of the soybean oil, which tends to maximize the production of the ESO, based on the developed model. Lastly, this profile was used to simulate a nonlinear model predictive controller (NMPC) for the temperature of the system, manipulating the flow rate of water as a cooling fluid. Figure 1 presents the results for a simulation tested for a system reaction containing initially soybean oil, a hydrogen peroxide solution (60 % w/w) and a formic acid solution (85 % w/w), leading to an ESO with oxirane index above 6.6 % and iodine index below 5.5 g I_2/100 g oil, considering a batch time of 2 h. The optimal temperature profile (Figure 1a) shows an interesting behavior, in which high values of temperature should be implemented at the beginning of the reaction, in order to intensify the reaction rates. Then, the temperature should decrease linearly until the boundary stablished as 353.15 K, in order to avoid the degradation reaction of the hydrogen peroxide. The profile for the flow rate of the cooling fluid (Figure 1b) agrees with the proposed logic for the temperature profile: at first, this value should be high, in order to absorb the high energy generation rate associated to the exothermicity of this reaction [3]; then, the flow rate should gradually decrease as the reactions become slower. The authors believe these preliminary results may serve as alternatives to be implemented in industries in order to increase the productivity of the ESO. Additionally, the presented methodology may also be used to test different conditions for this reaction system.

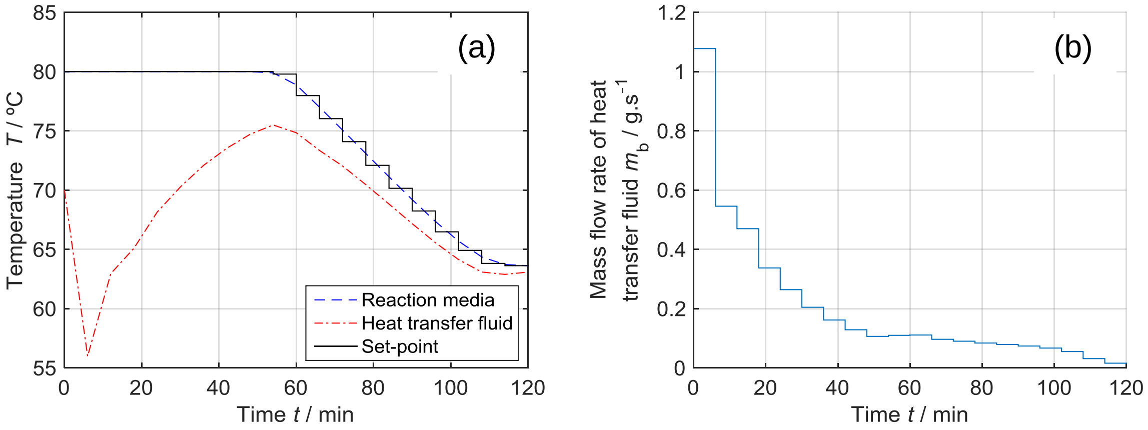

Figure 1. (a) Temperature profiles and (b) Flow rate profile of the cooling fluid for a NMPC simulation for the reaction system to produce ESO

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This work has been supported by Escola Politécnica da Universidade de São Paulo, São Paulo Research Foundation (FAPESP, grant #2019/00289-7) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, grant #140163/2019-0).

OP-III-26

STUDY OF AGITATION IN ANAEROBIC BIODIGESTERS

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The use of agitation in anaerobic biodigesters is known to affect biogas generation, but there is no consensus on the best type and the most appropriate intensity [1]. It has been observed that agitation systems in anaerobic digestion process have different configurations and operational variables, which make it difficult to identify, when and how agitation brings benefits. In addition, many studies do not provide necessary information to reproduce or scale up agitation since they use qualitative terms such as “manually”, “vigorously” and “minimally” to describe it. [2-6]. In this way, the goal of this work was to contribute with the study of agitation in anaerobic biodigesters.

Two biodigesters (8 L, nominal capacity), one with agitation system (B1) and the other without agitation(B2), were operated at 35 °C, using rice husk and swine effluent as substrates. Agitation was performed intermittently (every 6 hours) under laminar regime ($Re < 2000$), using effluent recirculation, provided by an external pump. In order to obtain the laminar regime, it was necessary to adjust the jet velocity and consider the biodigester dimensions. [7,8]. The duration of the agitation was considered to be the necessary time for mixing and homogenization. It was calculated as proposed by Fox and Gex [8] and it was called mixing time (MT). To obtain *Re* and MT, the specific mass and the substrate viscosity were also determined. The first step of this test consisted of the batch feeding of the biodigesters. It was performed for 21 days, that was the necessary time to stabilize biogas generation (BG). Then the biodigesters began to be fed semi continuously. The process performance was monitored by the quantification of the biogas generated throughout the process (using a gasometer), the amount of methane present in the biogas by chromatography [9] and physicochemical parameters. Considering the initial properties of the fluid, specific mass (1080.6 kg m^{-3}) and viscosity (0.0018 N s / m^{-2}); the dimensions of the biodigester and laminar mixing, the jet velocity should be set at 0.18 m/s and MT was set for 2 minutes duration (120 s).

Table 1 summarizes biogas production (L) at the batch step (21 days) and at the end of the complete process (55 days). From the results presented, it can be seen that intermittent agitation increased the amount of biogas produced. Biodigester B1 produced 17 % higher biogas compared to B2. The results are consistent with those obtained by Tian et al [10]. In semi continuous process, compared to the batch process, higher concentration of substrates and products coexist. This may be the reason why agitation becomes more significant in the process with semi continuous feeding, due to the greater need for mixing and homogenization of the medium. Methane concentration was similar for the two digesters investigated. From this study, it can be concluded that agitation was important to increase biogas production and also that it is possible to set criteria for its application, so that it can become reproducible in other studies, providing more reliable results about its benefits.

Table 1. Biogas production and methane concentration in the biogas sample

Parameter	Biodigester	
	B1	B2
Biogas on batch step	14,08	15,52
Biogas on complete process	86,30	71,48
CH_4 on biogas (% v/v)	33,6 ± 2,4	34,9 ± 5,0

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OP-III-27

EFFECT OF CATALYST AND REACTION CONDITIONS ON POLYMETHYL METHACRYLATE (PMMA) DEPOLYMERIZATION IN FLUIDIZED BED REACTOR

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Polymethyl methacrylate (PMMA) is a lightweight, transparent, thermoplastic polymer for which the world market exceeds 12.5 billion USD. Monomer recovery is the primary objective to depolymerize PMMA although processing it into hydrocarbons and syngas is also of interest albeit the economic incentive for the second option is several fold lower [1]. Depolymerizing PMMA in molten bath or heated screw feeder achieves above 80 % MMA yield; Kaminsky et al. claim that up to 97 % are possible in a fluidized bed (FB), although lower yields have been reported by Mitsubishi. FB decreases side products and carbon black due to excellent heat and mass transfer and low residence time of monomer in the reactor [1,2]. The monomer yield in a non-catalytic pyrolysis is highest at 550 °C, but increasing it to 590 °C produces light gases – methane, ethene, propene, carbon monoxide and dioxide [1]. In a FB, it begins to polymerize below 300 °C [2] and the high heat transfer coefficient in the bed promotes "thermal ablation" of polymer particles that degrades it, and reduces sticking and defluidization [3].

Catalytic FB pyrolysis decreases required operating temperatures while increasing product yield: Free radicals initiate the depolymerization of the PMMA in an inert atmosphere [4]. Heterogeneous catalysts (Bronsted acids) also initiate the PMMA depolymerization. Amorphous catalytic sites initiate cracking reactions [5] (high Si/Al ratio dictate the scission activity of the catalyst and its higher thermal stability [6]), while propagation and termination stages take place on the crystalline sites. In this regard, the surface area, acidic properties and the ratio of amorphous/crystalline part of catalysts are the most important parameters.

The reaction conditions – proportion between mass of catalyst and mass and particle size of PMMA, feeding gas flowrates, fluidization characteristics of the powder as well as the catalyst composition – will dictate yield and product quality.

Here we investigated depolymerization of PMMA in an 8 mm diameter fluidized bed reactor over Al_2O_3-SiO_2 aerogel and industrial FCC catalyst. We report screening tests conducted at 250, 300 and 350 °C in N_2 with PMMA powder (0.2 g) injected in the reaction zone by a pulse method. The reactor operated in the bubbling fluidization regime at variation gas flow rates of 180 $mL \cdot s^{-1}$ - 250 $mL \cdot s^{-1}$, water vapor fed in the reaction zone at 70 °C to transform ester into target products. GC-MS, GC and HPLC instrument analyzed reaction products. BET, XRD, LECO, SEM-EDS instruments characterized catalysts to express their activity.

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ORAL PRESENTATIONS
Section IV.
Advanced Reactors and Technologies for Energy-Related Applications

STRUCTURED CATALYSTS AND REFORMERS FOR GASEOUS AND LIQUID HYDROCARBON FUELS PROCESSING TO HYDROGEN-RICH GAS

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Over the past decades, the number of research projects aimed to the search and study of oxidative conversion catalysts (steam, autothermal conversion or partial oxidation) for gaseous fuel (natural gas, propane-butane mixtures, dimethyl ether) along with liquid fuel (kerosene, diesel, renewable natural raw materials – biodiesel and glycerin – a by-product of biomass processing), as well as engineering design of fuel processors for syngas or hydrogen-rich production has increased significantly. Considerable attention was paid to the development of structured catalysts.

To avoid hot spot formation during the autothermal conversion of hydrocarbons, alcohols and ethers, which arises due to the high exothermic effect of the oxidation reactions, mainly occurring in the frontal layer of the catalytic module, and the high endothermicity of the steam and carbon dioxide conversion reactions that occur in its outlet part, it was proposed to use metal foams and meshes with a higher thermal conductivity instead of cordierite ceramics [1,2]. The main problem that arises when using metal substrates is the difference in the thermal expansion coefficients of the metal and the deposited oxide layer. The use of standard suspension techniques leads to nonuniform deposition, poor adhesion and low mechanical strength of the catalytically active coating. In the conditions of thermal cycling, where the temperature difference can reach 1000 °C or more, its degradation, delamination and destruction occurs.

This problem was elegantly solved by developing a technique for growing aluminum hydroxide crystals on a metal surface, which, during calcination at a temperature above 600 °C, first goes into η-Al_2O_3, and then into θ-Al_2O_3 phase at a temperature above 900 °C [2]. This composite material was used as a primary support for preparation of catalysts for the all stages of hydrogen production: fuel conversion to syngas, CO water gas shift reaction and CO clean-up processes (CO preferential oxidation and CO selective methanation).

The peculiarity of the obtained coating is in the columnar (needle) structure of alumina crystals with a length of 30-60 μm, which are chemically bonded to the metal substrate. The structure is “breathing”, during the thermal expansion of the metallic material, the alumina crystals are spatially moved relative to each other without disrupting the interaction with the metal.

The study focuses on the experimental research of catalytic reformer operation in various reaction conditions and mathematical modeling of the catalytic processes for hydrogen production. As an example, Fig. 1 shows prepared catalytic modules for full scale reformer designed for syngas production and the results of diesel autothermal reforming simulation which was carried out by commercial software COMSOL Multiphysics in 2D axisymmetric geometry. The catalyst module was simulated as homogeneous porous medium. Reaction model included diesel oxidation, diesel steam reforming, water-gas shift reaction, CO methanation, CO oxidation and hydrogen oxidation. Simulating the experimental results including product distribution and temperature profile allowed defining the kinetic parameters corresponding to the best fit. The suggested simple quasi-homogeneous model describes experimental results (module temperature and outlet gas composition) with a good accuracy and could be used for process optimization and up-scaling.

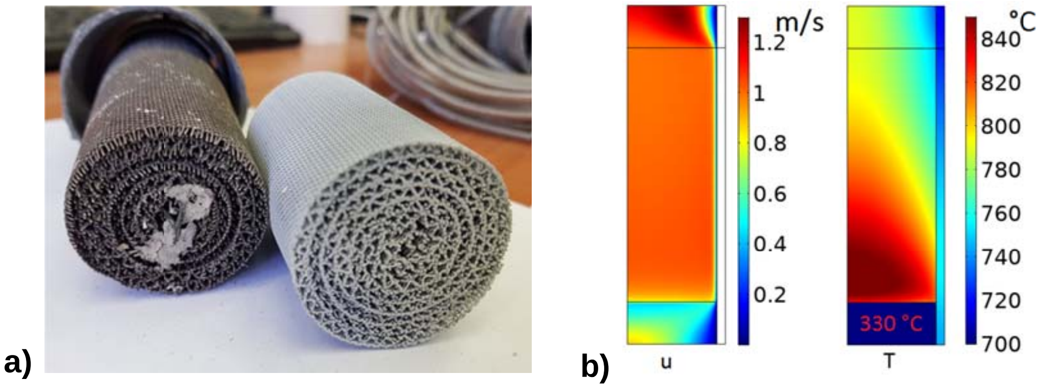

Figure 1. The experimental wire-mesh modules (a): freshly prepared (at the right) and after experiments (at the left) and computational fluid dynamics simulation of gas velocity with temperature distribution (b) of diesel autothermal reforming

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DIMETHOXYMETHANE FUEL PROCESSING FOR SOFC-APU: INSIGHTS FOR CATALYST AND REACTOR DESIGN

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In past decades, dimethoxymethane (DMM) has attracted a growing interest as an ecologically benign raw material with a wide scope of applications. DMM, as well as methanol and dimethyl ether is an easy to synthesize (from natural gas) oxygenated compound of C1 chemistry. It is worth noting that DMM synthesis on the basis of renewable feedstocks based on CO_2 produced from biogas and hydrogen supplied by water electrolysis are under development now. Since DMM is a non-corrosive, non toxic liquid compound, it can be easily stored and transported.

Recently, we demonstrated the feasibility of H_2/syngas production by DMM catalytic steam reforming [1] and partial oxidation [2] showing high promises for fuel cells. It is well known that steam reforming needs too much external heating to perform the highly endothermic process and evaporation of water, compared to catalytic partial oxidation. Syngas production by partial oxidation reactions is ideal for solid oxide fuel cells (SOFCs) due to their high tolerance to impurities in hydrogen. Besides the partial oxidation reactions usually shows several advantages over steam reforming such as short response time, compactness and easy start-up of SOFC-based power units. In addition the operation of such units (SOFC-APU) is made possible even at low temperatures by “water independence”.

The report focuses on outcomes lab-scale DMM catalytic oxidation experiments and our vision to create portable reformer. The experimental results indicate:

- the feasibility of syngas production by partial oxidation of DMM using supported Pt catalysts. In particular, granulated as well as structured Pt-catalyst provided complete conversion of DMM with high syngas concentration (up to 60 vol. %) at T = 400 °C and DMM:O_2:N_2 =28.6:14.3:57.1 (that corresponds to molar ratio DMM:air = 2:5) showing high promises for solid oxide fuel cells (SOFC) [3].
- as the O_2/DMM ratio increased from 0.5 to 4, the course of DMM oxidation changed from the partial oxidation (O_2/DMM = 0.5) to the deep oxidation of

DMM (O_2/DMM = 4). A successful self-ignition and sustainable operating of DMM combustion using supported Pt-catalyst was demonstrated. The heat was supplied to support partial oxidation reactor in the form of hot gases generated in deep oxidation reactor.

Thus, the results obtained allow as to propose the portable syngas reformer design included catalytic DMM burner (see Figure 1).

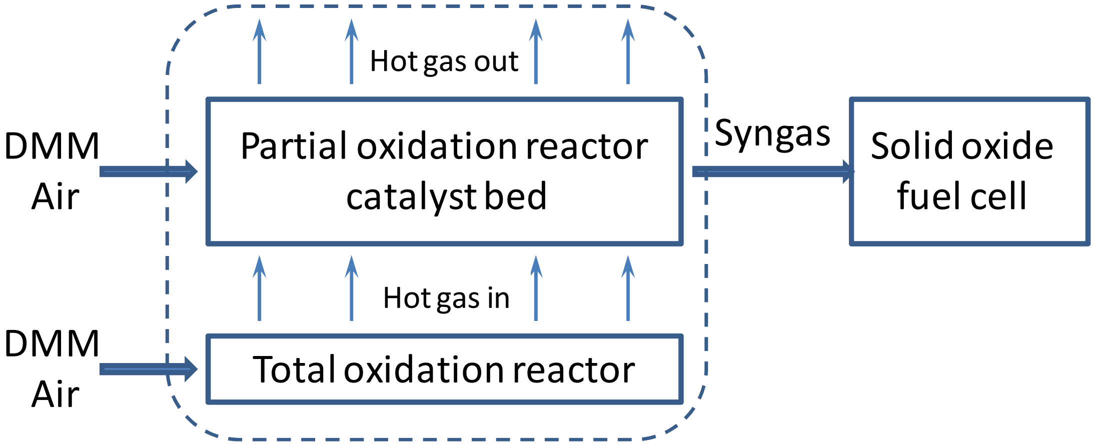

Figure 1. Schematic SOFC-based power unit on DMM reforming

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OP-IV-3

DEVELOPMENT OF HYBRID REACTION MODULE LINKED WITH LIQUID PLASMA AND ELECTROLYSIS FOR HYDROGEN PRODUCTION FROM WATER DECOMPOSITION

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Plasma in the liquid phase (PLP) is produced by discharging with a high voltage into the liquid directly. PLP has a high density by discharging, and releases strong UV light and more visible light accompanied with many active species. The discharge of pulse plasma at high voltage is an efficient technology for wastewater treatment [1,2]. PLP by high-voltage discharging for the removal of organic materials in wastewater has many advantages, such as no secondary pollution, faster degradation to pollutant materials, process at ambient temperature and pressure, and lower energy consumption. PLP can produce a higher plasma density and larger spatial distributions than ultraviolet lamp radiation [3]. The PLP process can induce the effective removal of pollutant materials and H_2 production, simultaneously.

In this study, a complex reaction system was developed in which the liquid plasma reaction and the electrolysis reaction were combined to further increase the decomposition efficiency and hydrogen generation rate of the hardly decomposable wastewater. The reaction system was used to decompose contaminants from the wastewater containing 1,4-dioxane and to investigate the hydrogen production rate.

Figure 1 shows a schematic diagram of a liquid phase plasma and an electrolytic hybrid reactor. The reactor may perform a continuous flow reaction and a batch circulating flow reaction. The reaction impact and efficiency of the two reaction systems were discussed. The decomposition efficiency and hydrogen production rate of the hardly decomposable wastewater through the development of the optimal photocatalyst system and the electrolyte for the application of the linkage system between the liquid plasma reaction and the electrolytic reaction were investigated.

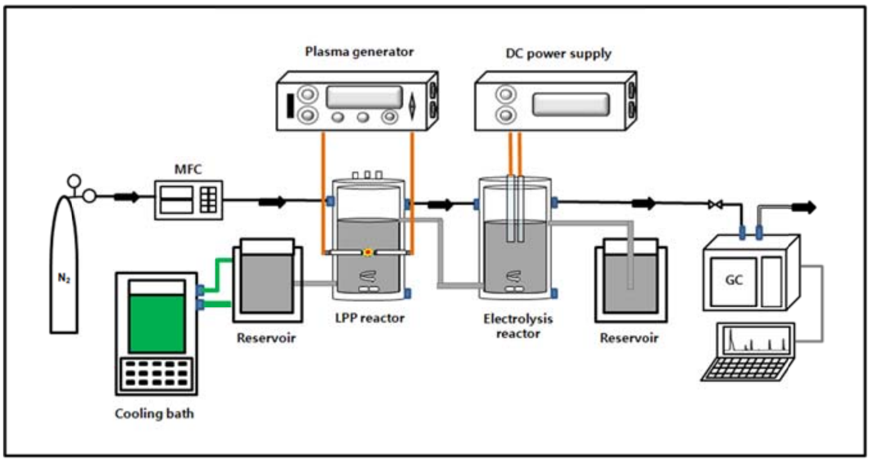

Fig. 1. Schematic diagram of LPP-electrolysis hybrid device and photograph

Figure 2 shows the removal rate and hydrogen generation efficiency of 1,4-dioxane in the liquid phase plasma reaction and the electrolytic reaction. The 1,4-Dioxane removal rate by both reaction systems was significantly faster than the results performed on each device. Hydrogen production rate also increased.

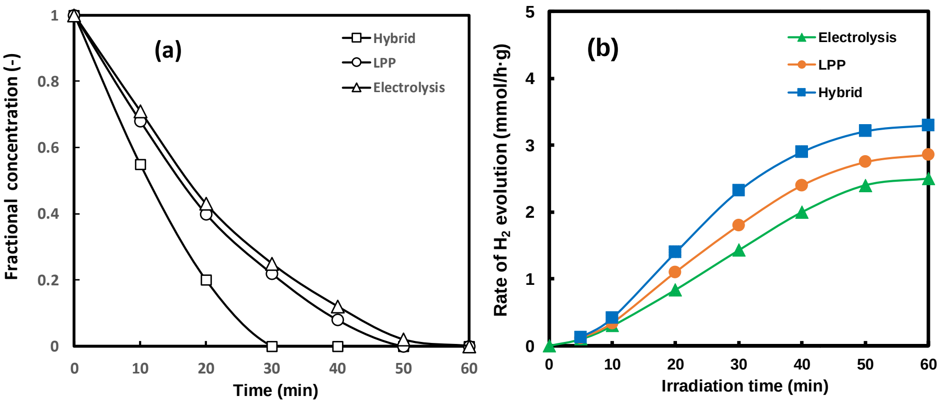

Fig. 2. Removal of pollutant and hydrogen production by the LPP-Electrolysis hybrid reaction system

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FLEXIBLE APPLICATION OF BIOGAS UPGRADING MEMBRANES IN POWER-TO-METHANE PROCESSES

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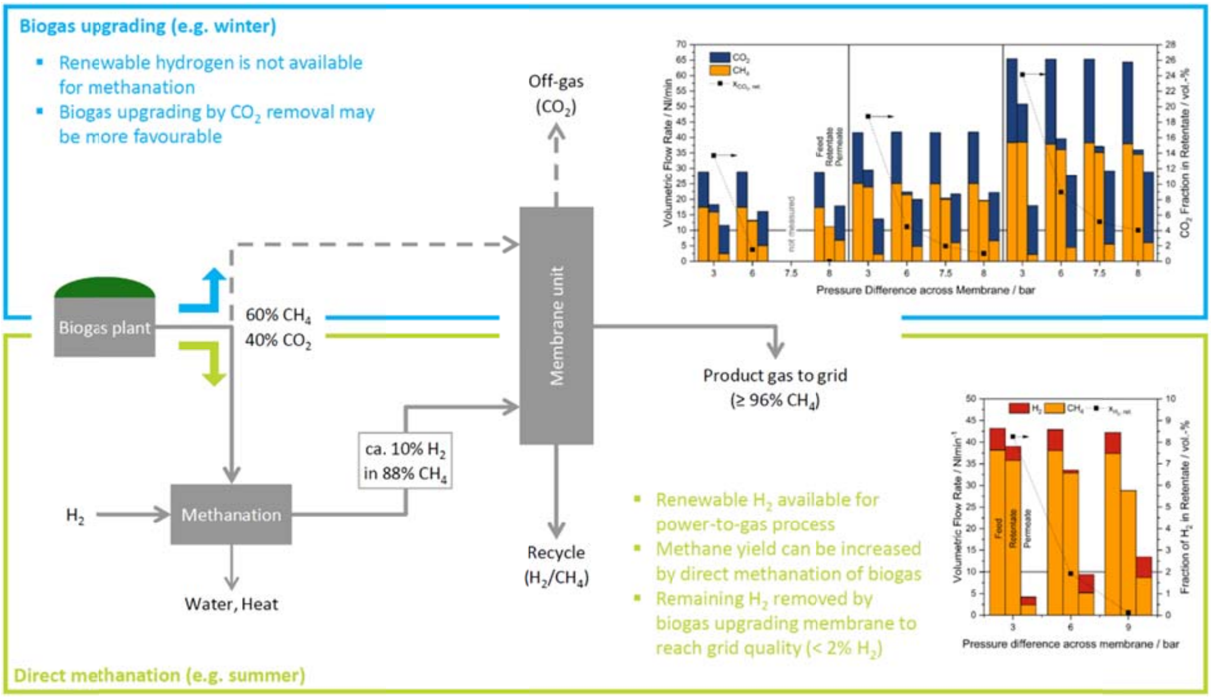
Biogas, a mixture of methane and CO_2, has to be upgraded before biomethane can be injected into the gas grid due to the quality specifications (>96 % CH_4, <4 % CO_2, <2 % H_2 in Switzerland and Germany). Upgrading can be achieved by separation of the CO_2 or its conversion to methane. This direct methanation of CO_2 in biogas enables the use of renewable CO_2 for power-to-gas operation, which allows the seasonal storage of electricity in the natural gas grid. The process was demonstrated using a 10 kW_{SNG} pilot plant, based in bubbling fluidized bed methanation [1]. In order to fully comply with gas grid requirements, separation and recycle of residual hydrogen and CO_2 is necessary. Witte *et al.* [2] showed that gas separation membranes could provide an economic solution to reach these requirements.

In this work, we show that a commercial polymeric membrane (Evonik Sepuran) can be used for both, biogas upgrading by CO_2 separation and for H_2 recycle in direct methanation of biogas. Experiments have shown that the biomethane produced in direct methanation still contains up to 11 % H_2 and 1-2 % CO_2 due to thermodynamic equilibrium. Therefore, the experiments were performed with the focus of decreasing the H_2 and CO_2 down to the required limits of 2 % (H_2) and 4 % (CO_2), on the one hand, and on upgrading a gas mixture representing fermentation-derived biogas (40 % CO_2 / 60 % CH_4), on the other hand.

The membrane unit was installed in the PtG demonstration unit and placed in a water bath, in order to maintain a stable temperature (20-40 °C). The inlet and outlet streams of the membrane were monitored regarding their composition (micro-GC) and flow rates (flow meters). The pressure of the system was controlled on the retentate side (product gas) of the module. The permeate (recycle) was kept at atmospheric pressure. The experimental data showed that it is possible to remove excess hydrogen from the SNG to fulfil the grid injection requirements. For this upgrading task, only a single step is required at a pressure level suitable to the methanation reactor. In addition, biogas upgrading could be demonstrated. Applying 6 bar pressure difference, a single membrane stage was also sufficient to reach grid quality. Nevertheless, in the recycle stream, a second separation step is required in order to limit the methane emissions from the plant in case of upgrading by CO_2 separation.



From the experimental data, an upgrading concept was derived which allows fast switching between biogas and biomethane upgrading. This dual-use concept of membranes allows the injection of renewable methane during the whole year, while using the direct methanation unit only during parts of the year when renewable hydrogen is available. The proposed concept includes only identical, commercially available CO_2 separation membranes, which limits the complexity of the overall system and has therefore a positive impact on the cost structure. This is especially favourable for small-scale biogas plants injecting their methane to the national grid.

Using the dataset obtained in these experiments, a counter current unit model of the membrane was developed, which is used for performance prediction and optimization in the techno-economic analysis of the process chain.

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OP-IV-5

LINKING HEAT AND ELECTRICITY SUPPLY FOR DOMESTIC USERS: AN EXAMPLE OF POWER-TO-GAS INTEGRATION IN A BUILDING

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A new system, coupling electricity and gas grid in a building, was designed. It consists in the retrofit of the existing photovoltaic system, consuming the electricity overproduction in the local synthesis of methane instead of injecting it in the electricity grid. Methane can be stored in the gas grid and used in winter in the existing gas burners, providing the required heat for house warming. Additionally the methanation system provides waste heat that is used to warm-up the sanitary water, eliminating the need for an electric boiler. The system was optimized according to the weather conditions and the dimensions of the main pieces of equipment were determined. With this system, the energetic independence of the house is maximized, thanks to the synchronous production of electricity, gas and heat, which is stored for use when needed. Therefore, the profitability of the photovoltaic system is ensured independently from the electricity feed-in tariffs.

The clean energy transition in residential buildings cannot leave out the supply of sustainable heat all over the year. However, while several incentives are currently available for the installation of renewable energy harvesting devices in buildings (e.g. solar panels on rooftops), the initiatives addressing the self-production of heat are rare and mainly exploited through the installation of solar collectors in regions with large solar irradiation. The solar energy availability, the electricity and heat demand are often subject to temporal phase shift, with the former being abundant in summer and during the day and the latter being required in winter and during the night. The combined action of all these phenomena causes an important mismatch between energy production and consumption, which, in perspective, may lead to problems in the technical and economic operation of the electricity grid. This may lead to two concurrent phenomena: the excess electricity in summer may cause a drop in the energy price and the deficit of energy in winter may generate an increase in the energy price. Additionally, the possible introduction of important carbon taxes may cause the important increase in the cost of standard gas-based heating systems.

For all these reasons, it is essential to design new energy systems that prepare residential building to cope both with the risk of not being able anymore to place the electricity on the market in summer and with the danger of having a substantial rise of the gas bill in winter. Hence, in this context, the concept of power-to-gas (PtG) becomes interesting for the energy supply of buildings. In fact, one may imagine using the excess electricity available in the summer (which has a low value for the above-mentioned reasons) for the local production of synthetic natural gas (SNG), via water electrolysis and CO_2 methanation. SNG can be stored in the natural gas grid as a carbon-neutral substitute of the standard fossil methane and bought back in winter for consumption in the standard gas-fired heating systems. In this way, the return on investment in the solar panels installation is guaranteed over time and the de-fossilization of the heating system can be achieved.

In this work, it is shown how such a small-scale PtG system can be optimally designed. The energy and heat supply is designed in all its part, from the available solar panels to the integration with the existing heating system and sanitary water structure. The system is based on a coupled electrolyzer/CO_2 methanation block with an electrical power input below 50 kW, whose operation was tested in previous works. The dimensions of the main apparatus are determined based on the measured conditions at the target location (solar irradiation and temperature). This work reports the possibility of connecting heat and energy supply at small-scale, by waste heat recovery of PtG in the heating of sanitary water. Furthermore, this work shows how the cross-disciplinary methodology can be applied in different economic and geographic boundary conditions.

OP-IV-6

THERMAL AND CATALYTIC PYROLYSIS OF POLYOLEFINS WITH VACUUM GAS OIL

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The world production of plastics has been increasing at a high rate, mainly due to the rapid urbanization, the development of China plastic market and the increase in world population [1]. Due to this increase, plastics have significantly contributed to development of countless countries [1]. However, most plastics use petroleum and natural gas as their raw materials [2]. Given this relationship, and other problems caused by the increase in plastic production, such as the increase in the accumulation of plastic waste and the worsening of global warming, it’s necessary not only to partially replace fossil fuels but also to efficiently manage plastic waste [1]. This work is focused on tertiary recycling of plastic waste, more specifically on the pyrolysis process of two of the most common types of plastic waste, polypropylene (PP) and low density polyethylene (LDPE) [1], in co-processing with vacuum gas oil (VGO). The objective is to evaluate the feasibility of co-processing plastic waste and a typical feed of a Fluid Catalytic Cracking (FCC) unit [3]. Preliminary experiments were carried-out in a TG-DSC at different heating rates (10 to 200 °C/min), with different types of plastic, with fresh and waste plastic, different types of catalyst (FCC, HZSM-5 and H-beta) and different VGO-plastic mass ratios.

Plastics have higher initial, maximum and final thermal degradation temperatures than VGO. Additionally, the thermal degradation processes of waste plastic begin and end later than the processes of pure plastic. It was also observed that the thermal degradation temperatures are higher in LDPE compared to PP and that the degradation process is influenced by the catalysts, particle shape/size, the origin of the plastic and the heating rate. When analyzing the VGO-plastic thermal and catalytic co-processing, it is observed that the degradation temperatures increase with the increase of plastic incorporation and that the final degradation temperature of the co-processing is higher than the one for single type plastics, meaning that

VGO may work as a retardant and the catalyst may be deactivated by the VGO and plastics. The thermal and catalytic degradation of these materials, as well as the co-processing, were also studied in a semi-batch reactor [4]. The liquid and gaseous products were analyzed by gas-chromatography and the solid products characterized by thermal analysis in the TG-DSC apparatus.

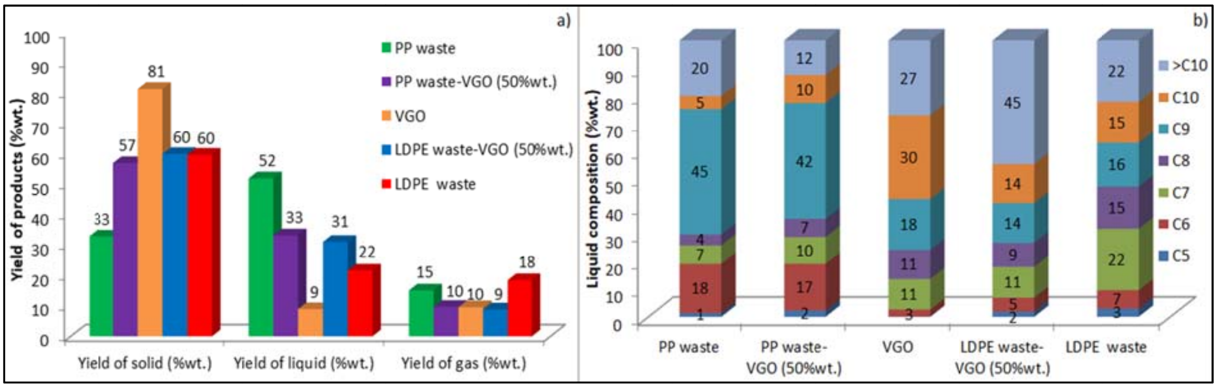

Figure 1. Thermal pyrolysis performed in the semi batch reactor with PP waste, LDPE waste and VGO. a) Yield of products (% wt.). b) Liquid composition (% wt.).

It was observed that PP degradation provides the lowest yield of solid and the highest yield of liquid and gasoline, LDPE degradation provides the highest yield of gas and VGO degradation provides the highest yield of solid and diesel fraction, and the lowest yield of liquid. It can be seen that the inclusion of plastic waste in the VGO significantly increases the liquid yield, which can be seen as a positive trend, and produces lower yield in solid products. The data obtained in this study also shows that the gas and liquid products are heavier when there's a low incorporation of PP or a high incorporation of LDPE. Also, in the catalytic degradation, a decrease in the yield of solids is observed, accompanied by an increase in the yield of gas and liquid, being the latter significantly lighter than the ones obtained in the non-catalytic processes. It can be concluded that the catalytic co-processing appears to be a viable way to co-process plastic wastes with the VGO, a typical feed for a FCC unit.

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OP-IV-7

MECHANISM OF C-FORMATION IN METHANE DRY REFORMING ON RH REVEALED BY SPATIALLY-RESOLVED OPERANDO-RAMAN AND MICROKINETIC ANALYSES

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In this study, the mechanism of carbon formation and its kinetic consequences in Methane Dry Reforming (MDR) over 4 % Rh/α-Al_2O_3 catalyst was investigated by means of an operando-Raman Annular reactor [1]. The spatially-resolved spectroscopic data and the kinetic analysis were interpreted with a detailed microkinetic scheme, thus making it possible to correlate experimental results to mechanistic insights [2,3]. This work takes place in the search for novel energy application for hydrogen and syngas production starting from CO_2-rich natural gas and biogas, for which MDR represents a promising route. However, poisoning of the metallic catalyst by carbon and sulfur is one of the major obstacles to the industrial upscaling of such application and it calls for the quantitative understanding of the catalytic consequences of C and S deposition for the catalytic activity. Our experimental campaign investigated the effect of the dilution of reactants on MDR at fixed space velocity and CO_2/CH_4 ratio (equals to 2), under different temperature conditions. A strong dependence of the catalyst performances on the concentration of reactants was evidenced and attributed to the combined effect of thermodynamic driving force and concentration of the most abundant reactive intermediates (MARI) of the process (H_2 and CO). The experiments were carried out in sequence, which allowed us to observe a progressive loss of activity. During the tests at constant temperature an increase of carbon signals in Raman spectra was observed with time on stream while only an initial decrease of CH_4 conversion occurred (Figure 1).

Spatially-resolved Raman analysis revealed C-deposits were not uniformly present at the catalyst, but they were stratified along the axis of the reactor, preferentially accumulated at the end of the catalytic bed. These findings were used in the formulation of a mechanism that describes how carbon aggregates form and grow at the catalyst surface causing its deactivation. Analyzing the system from a microkinetic point of view, we identified in the product CO and the reaction intermediate C the responsible for the formation of carbon deposits. As the reaction proceeds, in fact, CO concentration increases along the reactor, thus favoring the formation of C-aggregates precursor, since these two species are quasi-equilibrated. Moreover, the proposed C-growth mechanism explains the trend observed in catalyst deactivation. In accordance to experimental evidences, initially carbon deposition occurs at Rh nanoparticles, reducing the surface available for the reaction and thus the activity of the system. Then it continues to grow only on the support, without any further negative effect on the catalytic performance.

In addition, we tested the reactivity of C-deposits at the catalyst surface with a pure flow of CO_2 at high temperature, exploiting the reverse Boudouard reaction in the attempt of removing coke. As soon as carbon dioxide was fed to the reactor, a small amount of CO was detected by the micro-GC, confirming the removal of the carbonaceous species. With this “cleaning” treatment, the system recovered the initial methane conversion without compromising the Rh active sites. The new MDR tests, in fact, presented the same methane conversions of the “fresh” catalyst.

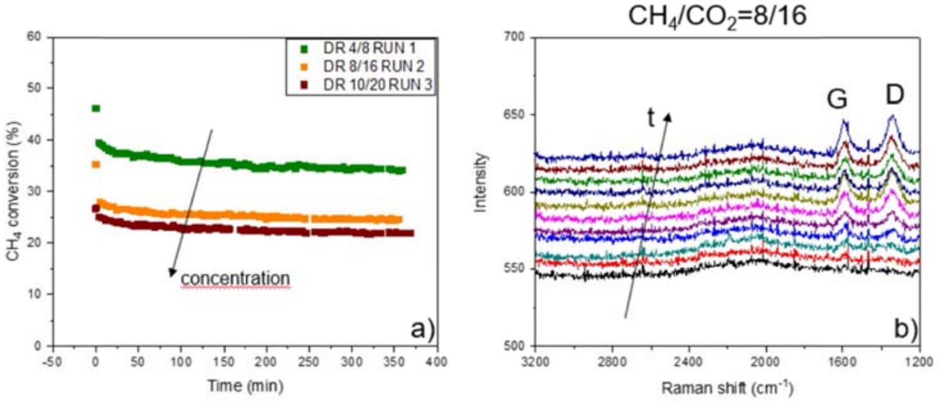

Figure 1. Effect of reactants’ dilution (a) and time-resolved Raman analysis of the catalyst surface with CH_4/CO_2 = 8/16 (b) recorded during MDR run performed at 600 °C

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AN INNOVATIVE KINETIC MODEL OF THE HYDROCRAKING OF A HDPE/VGO BLEND

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Introduction

The world plastic production has reached 359 million tons in 2018, with an increase of 11 million tons in comparison with the previous year [1]. Consequently, the amount of discarded waste plastic has also increased and, given the current mismanagement in the treatment of this waste, existing environmental issues are getting worst. This way, finding alternative routes to valorize plastics has become a crucial matter. The possibility of using refinery units to treat raw plastic blended with conventional streams has appeared as a promising alternative to conventional processes [2, 3]. Indeed, in a previous work we have assessed that hydrocracking unit can manage a blend of high-density polyethylene (HDPE) with vacuum gasoil, (VGO) leading to the formation of gasoline and diesel-like hydrocarbons [3]. In this work, we have gone a step further proposing a reaction scheme that describes this process and obtaining a kinetic model that reproduces quite accurately the experimental behavior of the blend.

Experimental

The feed has consisted of a blend of: (i) VGO with a boiling range of 314-519 °C and (ii) powdered virgin HDPE with an average molecular weight of 46,200 g mol^{-1}. Reactions have been carried out in a 100 cm^3 stirred tank reactor at 400-440 °C, at a pressure of 80 bar, for 15-120 min long under a continuous flow of H_2 (200 $ml\cdot min^{-1}$). Moreover, the following mass ratios have been used: VGO/HDPE, 4 and Catalyst/Feed, 0.05-0.1. The catalyst has been an in-house prepared Pt-Pd catalyst supported on Y zeolite, which has been characterized by several techniques [3]. At the end of runs, both gaseous and liquid products have been analyzed by chromatographic means.

Results and discussion

Figure 1 shows the kinetic scheme proposed for the hydrocracking of the HDPE/VGO blend, in which it can be seen how the polyolefin and the different fractions of the VGO are interlinked. It should be mentioned that given the lack of existence of these types of mechanisms in the literature, an extensive review has been performed in order to establish a proper mechanism that suits to the hydrocracking of the blend [4, 5].

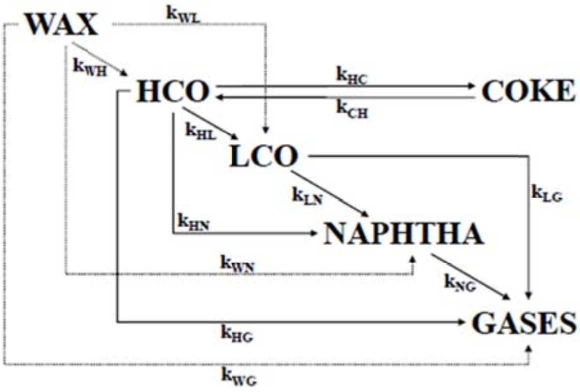

Figure 1. Proposed kinetic scheme

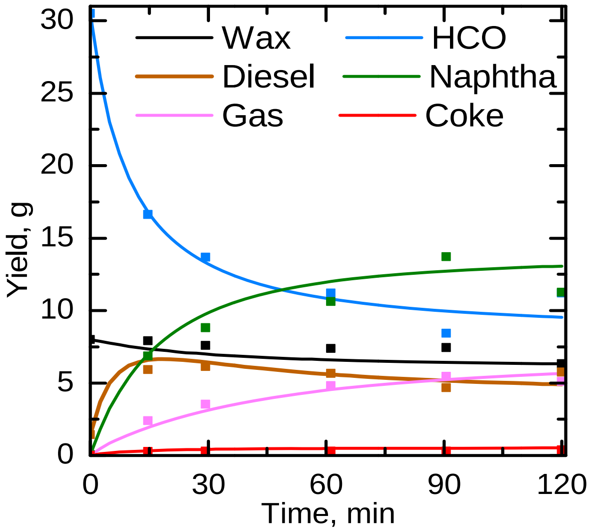

Figure 2. Fitting of the kinetic model

Six different lumps and twelve possible reaction pathways have been used to describe the process, in which it has been assumed that a heavy fraction can produce all the remaining lighter ones and coke is only formed from HCO fraction. On the other hand, Figure 2 shows the fitting of the model (lines) to the experimental data (dots) with respect to the time of contact at 420 °C and Catalyst/Feed ratio of 0.05. According to the model, the kinetic parameter of HCO production from Wax fraction, K_{WH}, is an order of magnitude greater than the kinetic parameter of LCO formation from HCO, K_{HL}, although the activation energy (E_{ij}) is lower for the second reaction. The model determines that the highest kinetic parameter was from the conversion of LCO to Naphtha, K_{LN}, furthermore has small E_{ij}. Although this model is in their early stage, laying the foundations as a first model and open the way to new research horizons such as research about the influence of other parameters in the model and test this model with other plastics.

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Acknowledgements

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OP-IV-9

DEVELOPMENT OF THE MATHEMATICAL MODEL OF DIESEL FUEL HYDRODEWAXING PROCESS TAKING INTO ACCOUNT N-PARAFFINS DISTRIBUTION IN THE FEEDSTOCK

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A significant problem in the oil refining industry is the inability to continuously determine the group composition of the heavy feedstock due to the lack of the necessary technical means. Laboratory and experimental methods are used for determining the group composition, for example, liquid chromatography, combined gas chromatography and mass spectrometry, fluorescence adsorption. However, the use of these methods for continuous determination of the feedstock composition is economically disadvantageous and unsuitable from a practical point of view for continuous monitoring due to their high cost and the duration of the analysis. At the same time, at the industrial unit of the hydrodewaxing process, the fractional composition and density of feedstock are continuously determined.

The aim of this work is to reveal the regularities of the distribution of the mass content of n-paraffins by the number of carbon atoms in the molecules in the hydrodewaxing feedstock as a stage of impoving the mathematical model [1].

As the initial data for the development of the methodology, hydrodewaxing feedstock compositions for different periods of operation of the industrial unit were used, which differ in the content of n-paraffins and the boiling point of 50 % of the fraction. The content of n-paraffins varies in a wide range from 14.81 % wt. up to 19.36 % wt. The boiling point of the 50 % fraction varies in a wide range from 288 °C to 313 °C. The experimental data on the determination of the mass distribution of n-paraffins in the hydrodewaxing feedstock show that there are two peaks on the curve reflecting that the mixed feedstock consists of two fractions (n-paraffins C_{12}-C_{18} and n-paraffins C_{19}-C_{27}), and distribution of n-paraffins in each of these fractions obeys the normal distribution. Then, it is possible to describe the distribution of the mass content of n-paraffins by the number of carbon atoms in the molecule in the mixed hydrodewaxing feedstock by describing the distribution of the mass content of n-paraffins by the number of carbon atoms in the molecule in each fraction making up the mixed feedstock using the normal distribution function.

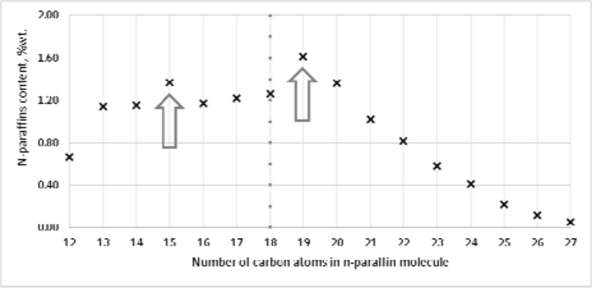

Figure 1. Peaks in the curve of n-paraffins mass distribution by the number of carbon atoms in the molecule (experimental data)

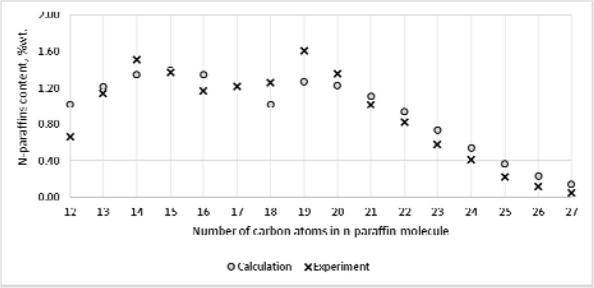

Figure 2. Comparison of calculated and experimental values of the mass content of n-paraffins by the number of carbon atoms in the molecule

Fig. 2 presents a comparison of calculated and experimental values of the mass content of n-paraffins in the hydrodewaxing feedstock. The calculation error is comparable with the error of the experimental determination of the mass content of n-paraffins by analytical methods.

Mathematical model, which takes into account n-paraffins distribution is written as:

$$\begin{cases} G\cdot\dfrac{\partial C_i(x)}{\partial Z}+G\cdot\dfrac{\partial C_i(x)}{\partial V}=\sum\limits_{j=1}^{n}k_j(x)\cdot C_i(x)+\sum\limits_{j=1}^{n}k_j(x)\cdot C_i(x)\cdot C_{H_2}+\sum\limits_{s}k_s(x')\cdot v(x,x')\cdot C_i(x') \\ G\cdot\dfrac{\partial T}{\partial Z}+G\cdot\dfrac{\partial T}{\partial V}=-\dfrac{1}{C_p^m}\cdot\sum\limits_{i=1}^{n}\sum\limits_{x=1}^{m}\pm\Delta H_i(x)\cdot w_i(x) \end{cases}$$

$Z = 0$, $V = 0$, $C_i = C_{i0}$, $T = T_0$

$C_i(x)$, $k_j(x)$, $k_s(x')$ – hydrocarbon content and reaction rate constants distribution functions; $v(x,x')$ – distribution function of probability of bond breaking in paraffin in hydrocracking; V – catalyst load volume, m^3; T – the process temperature gradient, K; C_p^m – the mixture heat capacity, J/mol·K; ΔH_i – the reaction enthalpy change, kJ/mol; x – the carbon atoms number in a hydrocarbon molecule; j – the hydrocarbon groups number. The first term in the material balance equation describes the reactions in which hydrogen is not involved, the second describes the reactions involving hydrogen, the third describes the paraffin hydrocracking reactions.

Thus, the regularities of n-paraffins distribution in the hydrodewaxing feedstock, as hydrocarbons that have the greatest influence on the low-temperature properties of diesel fuels, were revealed.

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Acknowledgements

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OP-IV-10

NUMERICAL SIMULATION OF THE WORK OF A SOAKER VISBREAKING UNIT

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An original mathematical model of the reacting flow of mixtures has been developed. The model consists of the Navier – Stokes equations for the mixture and a set of transport equations for the component concentrations. The model is multi-speed and has a single pressure. The separation of components is described by stationary sedimentation or rising due to buoyancy force. The mixing of components is described by a simple turbulence model based on the Boussinesq assumption. Other main features of the model include the assumption of weak compressibility of the phases, the considering of the average volumetric velocity of the mixture, and taking into account gaseous (bubbles) and solid (particles) components. The developed model is much simpler than it is usually used, but it describes all the necessary hydrodynamic processes in the soaker.

All equations are solved step by step. The numerical method for solving the Navier – Stokes equations is an improved SIMPLE-like method. It has a second order of approximation on time and space. The second order TVD and five order WENO schemes are used to solve the transports equations. The numerical model is implemented in the FORTRAN code for the 2D and 3D statement on a structured rectangular grid. The hydrodynamic part of the model has been verified against the solution of several benchmark problems. Good agreement with the results of other authors and experimental data is observed.

Three lumped kinetic models of the thermal cracking process have been developed. The entire numerical model, taking into account chemical reactions, has been tested on benchmark problems of cracking. Simulation of the vertical reaction chamber (soaker) of the visbreaking unit have been performed. Simulation results include flow patterns in the reaction chamber for various inflow conditions, places of the intensification of chemical reactions, the distribution of chemicals through the reaction chamber, and the chemical composition of the yields. Using obtained results, some optimizations of the shape of the reaction chamber and the internal structures (turbulent vortex generators) are proposed.

The reported study was funded by RFBR, project number 20-01-00440.

DEEP HYDRODESULFURIZATION OF GAS OILS WITH HIGH SULFUR CONTENT: KINETIC MODELING

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Hydrodesulfurization (HDS) that has been used in refineries for the production of ultra-low sulfur diesel (ULSD) for many years is facing new challenges now [1]. The depletion of oil resources along with the deterioration of oil quality is the reason for the involvement in the processing of straight-run gas oils with high, up to 2 mass. %, sulfur content (SRGO-S) and secondary diesel distillates, which contain the enhanced quantities of N-, S- containing compounds and aromatics.

The kinetics of oil fractions hydrodesulfurization is usually described in terms of lumps of sulfur-containing components which are converted according to first- or second-order kinetics [2]. Meanwhile middle distillates, like gas oils, includes a wide range of sulfur-containing compounds of different reactivity, the most refractory being benzothiophenes, dibenzothiophenes and benzonaphthothiophenes. So, modeling the deep HDS of a SRGO-S or its mixture with secondary gas oils requires more accurate kinetic modeling that considers more detailed components and rate equations of the Langmuir-Hinshelwood type.

The present work describes an approach to constructing of a kinetic model of the hydrodesulfurization process based on the combination (grouping) of the individual sulfur-containing compounds into four groups with various reactivities: three groups of dibenzothiophenes differing in structure and reactivity and one group for other sulfur-containing compounds. In developing the kinetic model, the experimental data were used, obtained during hydrotreating of SRGO-S and their mixtures with light coker gas oil (15 and 30 wt. %) over $CoMo/Al_2O_3$ catalyst at 0,8-3,5 h^{-1}, 3,5 MPa, 335, 350 and 365 °C. The sulfur content exceeds 2 wt. % in both SRGO-S (2,08 wt. %) and coker gas oil (2,286 wt. %).

The individual S-containing compounds were quantified with an Agilent 6890N chromatograph equipped with a JAS atomic-emission detector (Figure), the overall contents of S and N in the feed were determined using Antek 9000NS.

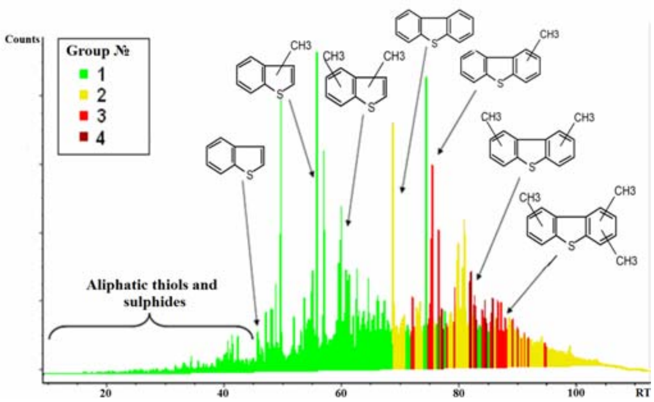

Figure. Typical ^{181}S chromatogram of sulfur-containing compounds in SRGO

The form of kinetic equations for each group of sulfur- and nitrogen-containing compounds was developed on the base the general form (see equation 1) by specifying the type that most accurately describes the experimental data. The parameters of kinetic equations are obtained by minimization of the sum of squares of residual of the sulfur- and nitrogen-containing compounds in experiments.

$$\frac{dC_i}{d\tau} = \frac{k_i C_i K_H P_{H2}^{\alpha}}{(1+\sum_j K_j C_j)(1+K_H P_{H2})^{\beta}}, \qquad k_i = k_{0i}\exp(-\frac{E_{Ai}}{RT}) \qquad (1)$$

were C_i – group of sulfur- or nitrogen-containing compounds concentration;
C_j – reaction inhibitors concentration; k_{0i}, E_{Ai}, K_H, K_j, α, β – model parameters.

The comparison of the experimental and calculated values of sulfur in the feed let us to conclude, that developed kinetic model describes the process of deep hydrodesulfurization of SRGO-S and theirs mixtures with light coking gas oil (up to 30 %) in a wide range of conditions (feedstock composition, temperature and pressure). The model takes into account the changing the composition of the feedstock with better accuracy compared to the models based on the traditional first- or second-order kinetics. As well, the developed kinetic model and the same set of parameters were successfully used for the prediction of sulfur content during HDS of the straight-run gas oil, differing in origin, sulfur and nitrogen content from SRGO-S (1,076 wt. % versus 2,082 wt. % of S; 113 versus 186 mg/kg of N). The obtained results demonstrated that proposed approach can be successfully used for the prediction of process condition needed for ULSD production from SRGO and their mixtures with coker gas oil.

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OP-IV-12

IMPACT OF CYCLOALKANES ADMIXTURE IN ALKANE HYDROCRACKING

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Introduction

One of the most widely employed routes to upgrade low-value oil refinery streams and alternative feedstocks is hydrocracking over bifunctional catalysts featuring both metal and acid sites [1]. A maximum isomer yield can be achieved by, so-called, *ideal* hydrocracking. As industrial hydrocracking feed is a complex mixture of, among others, alkanes, cycloalkanes and aromatics, the goal of the present work is to determine and to analyze impact of co-feeding cycloalkanes on alkane ideal hydrocracking.

Methodology and results

Ideal hydrocracking is experimentally indicated by a decreasing total conversion with increasing pressure. The transition between ideal and non-ideal hydrocracking is not only catalyst dependent [1], but can also be triggered by operating conditions and feedstock composition. Decrease of temperature and/or increase of total pressure favor ideal hydrocracking of pure fed alkane [2]. Furthermore, increase of H_2 to hydrocarbon ratio and carbon number of reacting molecule will favor non-ideal hydrocracking [2]. Differences in overall reactivity and/or types of elementary steps in hydrocracking of the components in real feedstock motivates us to investigate the impact of co-reacting cycloalkanes on ideal behavior of hydrocracking catalysts [3,4].

An experimental campaign covering the operating conditions as listed in Table 1, with n-octane and methyl-cyclohexane as model molecules has been performed to assess the impact of cycloalkane on transition from ideal to non-ideal hydrocracking of alkane.

Table 1. Experimental conditions

Feed, mol:mol	n-octane : methyl-cyclohexane 1:0 ; 0:1 ; 1:1
Catalyst	0.5 wt % Pt / USY(CBV712) zeolite
Temperature, °C	230 ; 250 ; 270
Pressure, bar	10 ; 20

Ideal n-octane hydrocracking was observed within the investigated range of operating conditions. The n-octane conversion decreased with increasing total pressure at all investigated temperatures, see Figure 1. Maximum yield of octane isomers, which has been observed for pure n-octane feed, was obtained in experiments with equimolar mixture of n-octane and methyl-cyclohexane as well, see Figure 2. This indicates that methyl-cyclohexane admixture did not impact ideal catalytic behavior in our experiments.

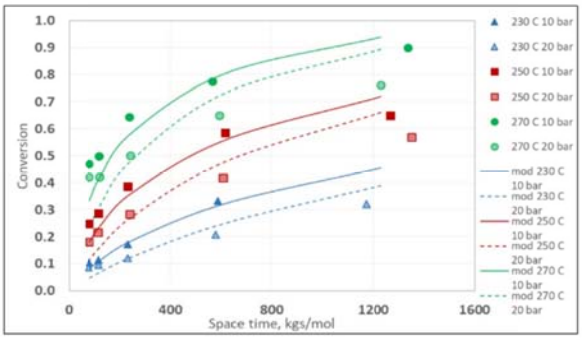

Figure 1. n-octane conversion (pure feed) on 230 °C, 250 °C, and 270 °C and 10 bar and 20 bar. Symbols : experimental data ; Lines : SEMK model

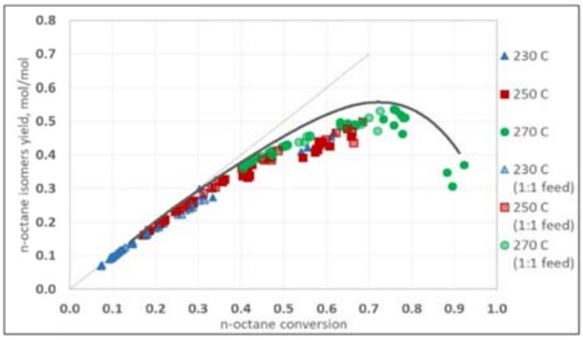

Figure 2. n-octane isomers yield dependence on n-octane conversion, process conditions and feed composition. Symbols : experimental data ; Line : SEMK model

Single-Event MicroKinetic (SEMK) modelling, due to its fundamental character, represents an adequate tool for assessing complex reactions such as hydrocracking [3]. For *ideal* hydrocracking of alkane and cycloalkane mixtures the existing model has been successfully employed to simulate experimental results without any adjustment of model parameters. Despite that, further development of this model to account for non-ideal hydrocracking will be necessary to quantify the transition between these regimes, when observed at more severe conditions or on another catalyst [5].

Conclusion and further steps

At the investigated operating conditions ideal hydrocracking behavior was observed for pure n-octane feed as well as in admixture with methyl-cyclohexane. To further probe the onset of non-ideal hydrocracking, additional experimentation with two catalysts with lower Pt loading (0.1 and 0.3 wt %) are being performed. In additional to this experimental work, the extension of the SEMK methodology to include non-ideality will be carried out.

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Acknowledgements

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OP-IV-13

HYDROTREATMENT OF CRUDE BIO OILS USING LOW COST SLURRY CATALYSTS

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Direct biomass liquefaction technologies have become mature in the last decade.

Fast and slow pyrolysis is operated at commercial scale, while several hydrothermal liquefaction processes are scaled up. Still, the produced crude bio oils have a low economic value. They contain significant amounts of water and ash as well as varying amounts of oxygen. The hydrotreatment research focusses strongly on trickle beds and commercial hydrotreatment catalysts. Challenges of this approach are the high reactivity of bio-based oxygenates, the poor bio crude miscibility with refinery streams resulting in mal-distribution and accelerated coking.

In this work we discuss an approach which is adopted from the original Bergius process and more recent developments of coal liquefaction. The process utilizes a slurry reactor and high boiling point solvents. The solvent functions as heat transfer agent, hydrogen donor and stabilizes catalyst and products against coking. Such reactors provide intense mixing of non-miscible phases and a complete wetting of the catalyst surface, combined with high mass and heat transfer rates. The use of non-toxic lowcost slurry catalysts for bio crude upgrading allows a simple replacement without the need of regeneration. The catalyst further acts as trap for ash and other inorganics providing a purified hydrogenated product that can be processed by downstream operations, such as hydrocracking or isomerization towards a premium fuel.

The catalyst was prepared based on the method of Li et al. [1]. This batch preparation method was translated into a continuous process applying flow chemistry principles and low-cost mixers. HTL crude oil from pine was produced at the pilot scale facility at Aarhus University. Details of the production conditions are given elsewhere [2]. The hydrogenation tests were performed using a stirred batch autoclave of 200 mL. Tetralin and a premixed paste of catalyst and HTL crude oil was transferred into the reactor and stirred overnight. Hydrogen was added at room temperature to provide a pressure at reaction temperature of 200 bar. The reactor was heated using 50 K/min under vigorous stirring to a reaction temperature between

300 and 450 degC. After 90 min at reaction conditions the reactor temperature was rapidly reduced using a cooling coil and the liquid and solid sample was taken for C13-NMR analysis. Additional oil analysis including TAN, viscosity, ash content etc. is in progress.

The optimization of the catalyst preparation method has resulted in a significant reduction of solvent consumption. In addition, the use of micromixers reduces the average catalyst particle size below 3 nm. This is crucial, as those materials show high hydrogenation activity only when the particle size is below 5 nm.

The catalytic tests produced a transparent low viscosity liquid phase and a glass-like solid phase. In Figure 1 the C13-NMR spectra of the liquid phase show a clear reduction in C bonded to O, both in form of carbonyl groups and alcohols & ethers in the hydrogenation product, still a few species are remaining. In addition, a significant reduction in amount double bonds indicate saturation of aromatic rings. The solid product contains the catalyst, inorganics and char-like structures with double bonds and aliphatic structures dominating, but also containing amounts of carbonyl groups.

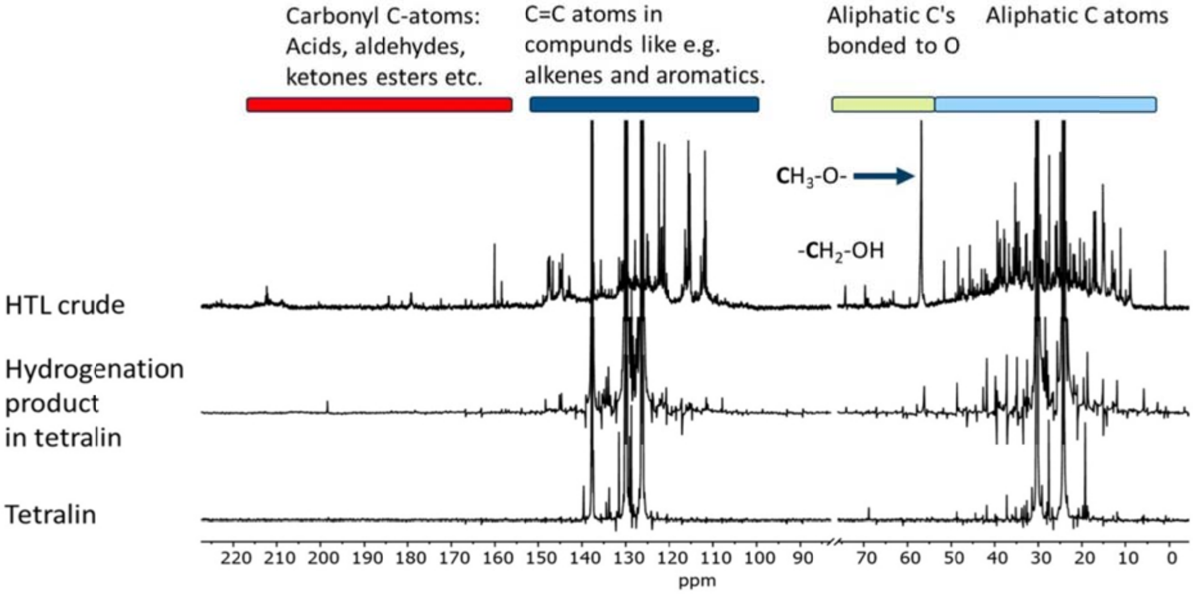

Figure 1. C-NMR spectra for crude and hydrogenated HTL oil

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OP-IV-14

MULTIFUNCTIONAL COBALT-BASED NANOREACTORS FOR THE COMBINED FISCHER-TROPSCH SYNTHESIS AND HYDROPROCESSING: MATERIAL SYNTHESIS AND CATALYSIS

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The broad product distribution obtained from Fischer-Tropsch (FT) synthesis requires additional workup by hydroprocessing, usually performed in a separate reactor at temperatures exceeding 350 °C. An alternative is the combination of both reaction steps within one single reactor, which requires a compromise between the non-compatible operation conditions. However, this concept was proven on different scales already with remarkable success [1-2]. We transfer this approach to the nanometer scale, by designing nanoreactors in a core-shell architecture. Those materials offer, besides the catalytic bifunctionality, also the stabilization of the active metal nanoparticle from deactivation by sintering. In addition it is possible to tailor the combination of physical and chemical functionalities [3]. While chemical functionality concerns the catalytic features, physical functionalities include the sieve effect among others. The sieve effect in particular is responsible for the nanoparticle stability and the exclusion of large molecule appearance at the same time. Kruse and co-workers demonstrated this novel concept already successfully, which is based on encapsulation of cobalt cores within a zeolitic matrix to link both FT and hydrocracking activity in one single nanoparticle [4].

The obtained results reveal a better resistance against catalyst deactivation for > 1000 h (time on stream), as well as a narrowed chain length distribution. In particular, Figure 1 exemplarily shows the product distribution of bifunctional catalysts, active in FT reaction and hydroprocessing (red) compared to those only active for FT synthesis (green). Obviously, the product distribution in presence of HZSM-5 is substantially different from those obtained with a non-acidic SiO_2 support material, exhibiting a larger fraction of long-chain hydrocarbons. The data thus shows a significant shift in product distribution, which is also underlined by the aggregation state of the wax samples at room temperature (Figure 1, right).

OP-IV-14

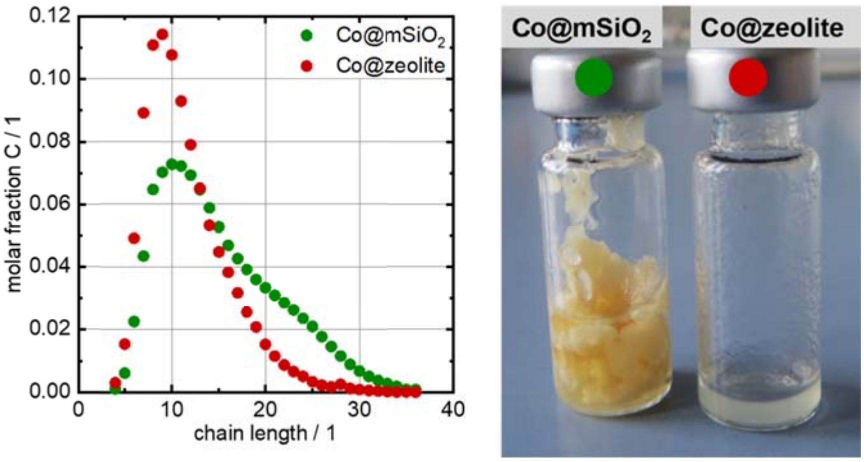

Figure 1. Product spectrum by carbon number at 250 °C (left) and comparison of appearance of waxy FT products at room temperature (right); catalysts with hydroprocessing activity are displayed in red

The present contribution primarily reports on the effect of pore structure and acidity on the obtained FT product spectrum. While the former affects the transport of long-chain FT products, the latter is responsible for cracking and isomerization of hydrocarbons both through the supporting matrix. Therefore, we synthesized the materials following a bottom-up approach introduced previously [4]. First, Co_3O_4 nanoparticles are synthesized and subsequently encapsulated by a mesoporous silica shell yielding Co_3O_4@mSiO_2. Afterwards, the SiO_2 shell is transformed into zeolite ZSM-5 through hydrothermal (HT) treatment, after the addition of an aluminium source. This strategy provides very similar size distributions of the cobalt cores in all material classes, which allows for unique comparability of the FT catalytic results. The materials are characterized by standard methods (e.g. XRD, N_2-physisorption, TEM), as well as electron tomography. The latter method provides information on the pore structure and the spatial distribution of the cobalt cores in the zeolite crystal. The catalyst stability was also studied by environmental TEM experiments up to 1000 °C under synthesis gas atmosphere. The FT product spectrum obtained from catalytic experiments was correlated with the characteristics of the catalyst material, setting the basis for designing the optimal FT catalyst.

The bifunctional nanoreactors reported will be used for designing the product distribution in FT synthesis after tailoring the transport trajectories in the catalytic composite material.

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OP-IV-15

MODELLING LAYERED FIXED-BED CATALYTIC REACTORS FOR THE OXIDATIVE COUPLING OF METHANE

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Introduction

Direct natural gas conversion to ethylene via Oxidative Coupling of Methane (OCM) has presented for decades an open challenge in catalytic reaction engineering [1]. However, the screening of numerous catalysts and reactor configurations has still not led to a real breakthrough in addressing the issues of low yields and high exothermicity. Among the possibilities for OCM performance enhancement, the layering of different catalytic materials in fixed-bed reactors has been proposed [2, 3]. Nevertheless, a dedicated study concerning the optimal catalyst layering is still missing and is, hence, addressed via modelling in the present work.

Methodology

The OCM kinetics are described via a previously developed microkinetic model [4], accounting for both gas-phase and surface reactions. The model catalysts considered are Sr/La_2O_3 (high activity and low selectivity) and $NaMnW/SiO_2$ (lower activity and higher selectivity). The layered reactor is simulated via an in-house heterogeneous fixed-bed reactor model which has been modified to explicitly take into account the transfer of reactive intermediates at the boundary between consecutive catalyst layers. This was indeed found to be crucial in modelling a layered fixed-bed reactor, as opposed to modelling reactors in series, see Figure 1.

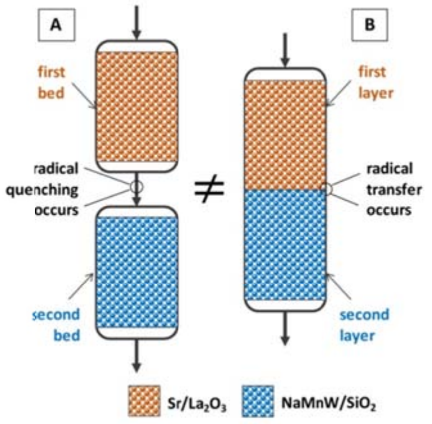
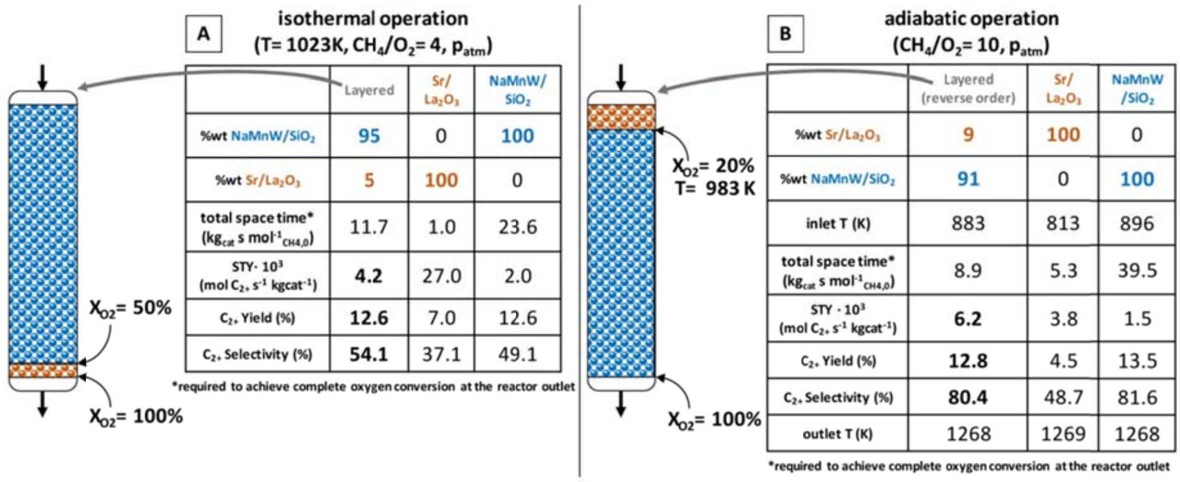


Figure 1. Catalytic reactors in series (A) and catalytic layers in series (B)

Results and discussion

In Figure 2, the performances of an optimized layered reactor are compared to the performances of the single catalysts, in both isothermal (A) and adiabatic (B) operation. The comparison is based on the C_{2+} yield, defined as CH_4 conversion × C_{2+} selectivity, and the C_{2+} space-time-yield (STY), defined as mol_{C2+} produced s^{-1} kg_{cat}^{-1}. Both performance indicators are evaluated at complete oxygen conversion. For the isothermal case, the optimal configuration, consisting of a long layer of selective NaMnW/SiO_2 catalyst followed by a thin layer of the active Sr/La_2O_3 catalyst, results in doubling the C_{2+} STY compared to the single NaMnW/SiO_2 and in a 80 % increase in the C_{2+} yield compared to the single Sr/La_2O_3. The Rate of Production Analysis pointed to the most selective catalyst NaMnW/SiO_2 being more beneficial in the upper part of the reactor, i.e., where methane concentration is higher. For the adiabatic case, the optimal layered configuration is reversed and, despite a slight decrease (5.2 %) in the C_{2+} yield compared to the single NaMnW/SiO_2, the resulting STY is four times higher, even at a lower inlet temperature. The higher activity of Sr/La_2O_3 was found to be key in developing a temperature profile along the reactor, which would then lead to the activation of the subsequent NaMnW/SiO_2 catalyst.



	Layered	Sr/ La_2O_3	NaMnW/ SiO_2
%wt NaMnW/SiO_2	**95**	0	**100**
%wt Sr/La_2O_3	**5**	**100**	0
total space time* (kg_{cat} s $mol^{-1}_{CH4,0}$)	11.7	1.0	23.6
STY· 10^3 (mol C_{2+} s^{-1} $kgcat^{-1}$)	**4.2**	27.0	2.0
C_{2+} Yield (%)	**12.6**	7.0	12.6
C_{2+} Selectivity (%)	**54.1**	37.1	49.1

*required to achieve complete oxygen conversion at the reactor outlet

	Layered (reverse order)	Sr/ La_2O_3	NaMnW /SiO_2
%wt Sr/La_2O_3	**9**	**100**	0
%wt NaMnW/SiO_2	**91**	0	**100**
inlet T (K)	883	813	896
total space time* (kg_{cat} s $mol^{-1}_{CH4,0}$)	8.9	5.3	39.5
STY · 10^3 (mol C_{2+} s^{-1} $kgcat^{-1}$)	**6.2**	3.8	1.5
C_{2+} Yield (%)	**12.8**	4.5	13.5
C_{2+} Selectivity (%)	**80.4**	48.7	81.6
outlet T (K)	1268	1269	1268

*required to achieve complete oxygen conversion at the reactor outlet

Figure 2. Comparison of an optimally layered configuration vs single-catalyst reactors, for isothermal (A) and adiabatic (B) operation of an OCM fixed-bed reactor. STY: space-time-yield; X_{O2}= oxygen conversion

Conclusions

Intensified ethylene production from natural gas can be achieved by exploiting synergies in sub-optimal OCM catalysts in layered fixed-bed reactors. For isothermal operation, adequate choice of the layering order can address selectivity limitations of individual catalysts. In adiabatic operation, lighting off the reaction with a 'pre-heating' catalyst layer [3] was confirmed to be crucial to maximize the space-time-yield without jeopardizing the C_{2+} selectivity.

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POSTER PRESENTATIONS

PP-1

MODELING OF SEPARATING REACTORS IN MINERAL PROCESSING TECHNOLOGIES

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In the processing of minerals and the beneficiation of various types of ores, flotation is one of the main methods. The physicochemical separation process is carried out in flotation machines, which can be attributed to separation reactors. According to the principle of organizing the flow of the flotation machine, it is possible to divide into reactors with a predominance of intensive turbulent mixing (mechanical and pneumomechanical types of machines) and reactors with a laminar mode of movement (column flotation machines). Depending on the type of rector, the basic model of the kinetics of the process is selected: plug flow or perfect mixing. To justify and select the type of flotation machines for the separation of mineral raw materials, the kinetics of the separation process and the modeling of the technological scheme using specialized software packages were studied. One of the most proven software systems for solving applied problems in the field of development of technological enrichment schemes is the program complex of JK Tech, Australia (JKSimFloat). The schematic diagram of the estimation of the separation process based on the first-order kinetic model is shown in Fig. 1

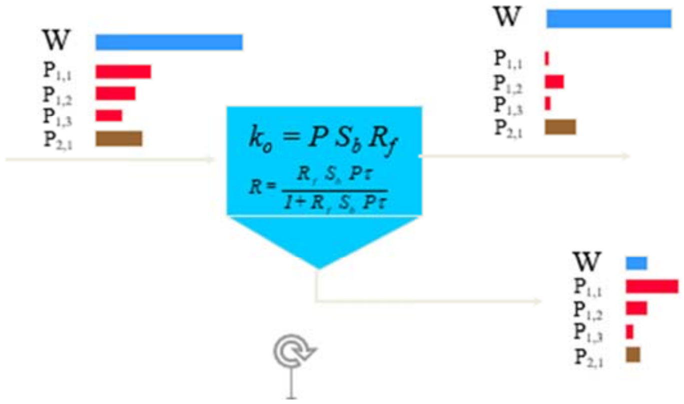

Figure 1. Schematic diagram of separation in a mechanical type flotation machine

Where: R – recovery by true flotation in the pulp, ko – flotation rate constant, t – flotation process time, Sb – bubble surface area flux P – ore floatability Rf – foam product yield.

In the JKSimFloat package, the kinetic approach is implemented through the industrial data distribution model of floatability classes (Floatability Component Scale-up model - FCTP), based on the assertion that extracting each floatability class into a concentrate is a function of several parameters [1].

The FCTP model is based on the assertion that the extraction of each class of floatability into a concentrate is a function of several parameters, and it is proposed to determine the kinetic constant by (1):

$$k = P \cdot R_f \cdot \frac{6 \cdot Q_A \cdot \sum_{i=1}^{n} d_i^2}{A \cdot \sum_{i=1}^{n} d_i^3} \cdot \qquad (1)$$

Rf is the foam product yield, fractions of a unit; QA – air flow, m^3 / s; di – diameter of a single bubble, cm; A – cross-sectional area of the working area of the flotation machine, m^2; P is an indicator of floatability, reflecting the probability of a particle fixing on a bubble and its further transfer to the foam product through the act of flotation or mechanical removal. In the course of the work, variants of the given technological scheme were simulated with the replacement of the type of flotation flotation equipment in cleaning operations. The methodological approach and modeling algorithm are described in [2].

The results of technological indicators are given in table 1.

Table 1. Comparison table of key technological indicators

	Conten FeS_2,%	Recovery FeS_2,%	Conten FeAsS,%	Recovery FeAsS, %
Initial design	19,536	65,561	4,010	60,523
Column flotation machines	19,361	94,562	3,978	88,618
Mechanical machines	18,760	95,817	3,869	90,126

Thus, the simulation of separating rectors (flotation machines) will allow us to justify the optimal technological scheme and equipment for its implementation from the point of view of extracting a valuable component.

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Acknowledgments

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PP-2

IMPROVED MICROKINETIC MODELS FOR OXIDATIVE COUPLING OF METHANE (OCM) USING DEEP REINFORCEMENT LEARNING AND HIGH THROUGHPUT EXPERIMENTS

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Increased production of natural gas has motivated interests to develop advanced chemical technologies that valorise methane. Oxidative coupling of methane (OCM) to produce C_2 paraffins and olefins is a promising route for producing value-added chemical feedstocks. However, to date, this chemical process has not been commercialized yet and it still relies on researcher's development. Improvements can be made through advancing micro-kinetic models describing the surface and gas-phase reactions. Past research in the development of OCM micro-kinetic models has been hindered by the lack of experimental measurements and incomplete understanding of how catalyst descriptors map onto kinetic model parameters. In this work, high throughput catalytic reactor experiments are combined with a deep reinforcement learning algorithm to study OCM catalysis micro-kinetics.

High throughput experiments are performed using the Avantium Flowrence equipment based on nanostructured LA_2O_3 catalysts. To reflect the effect of catalyst composition in the microkinetic models, different weight percent of metals, such as Sr, Ce, and Ir, are doped. Also, different process variables such as bed temperature, gas hour space velocity, methane to oxygen ratio, and operating pressure are investigated. Then, a novel informatics framework based on reinforcement learning (RL) acts as the connector between experiment results and simulation software. This provides a method of direct knowledge extraction from the experimental and numerical data. CHEMKIN PRO is used to simulate a packed bed reactor using Chen et al.'s [1] surface reactions and AramcoMech 3.0 gas-phase reactions. The parameters for each reaction are written in the form of Arrhenius' equation, as given in:

$$k = A * T^{\beta} * e^{-E_a/RT}$$

where the rate constant k is determined by the pre-exponential factor A, the temperature dependence factor β, and the activation energy E_a. The RL algorithm can figure out which kinetic parameters should modify to agree with the experimental results under the studied operating conditions. Also, the RL controller can search for the right combination of process variables to influence (increase or decrease) a specific product species. A general approach for the reinforcement learning (RL) reactor controller coupled with the high throughput reactor experiments is shown in Figure 1.

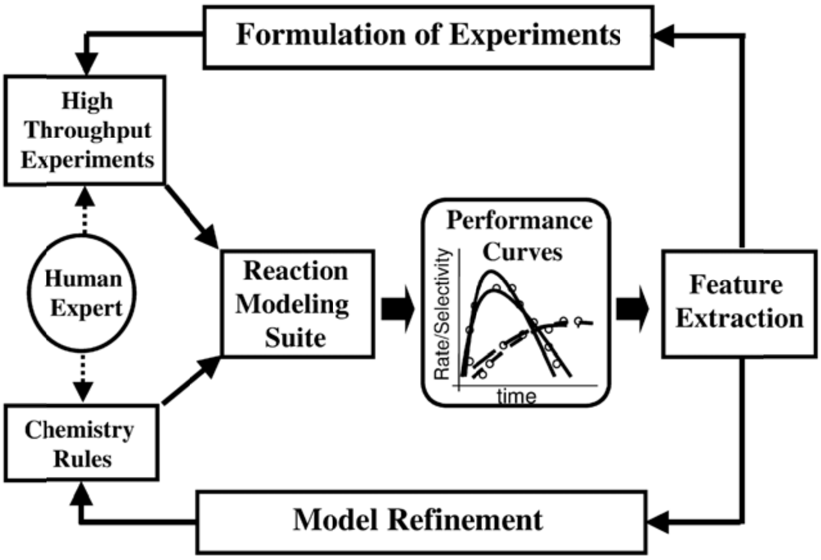

Figure 1. Schematic of coupling between high throughput experiments and micro-kinetic modeling for reactor simulations [2]

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MICROWAVE-ASSISTED SYNTHESIS OF ETHYL HEXANOATE FOLLOWING A Ping-Pong Bi-Bi KINETICS WITH INHIBITION BY BOTH SUBSTRATES

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Synthesis of ethyl hexanoate from hexanoic acid (A) and ethanol (B), in a solvent free system, has been modeled. Optimum conditions to carry out this reaction, whose rate equation can be described by the Ping Pong Bi Bi mechanism [1], are reached when temperature is around 50 °C, enzyme dose is about the 2 % w/w and molar ratio acid to alcohol is 1:3 [2]. Since the reaction is endothermic (ΔHr = 23000 J/mol), a microwave heating is provided to prevent its shutdown. Microwaves allow to maintain the temperature in an optimal range for enzymes and they can be successfully used in organic synthesis to reach high conversions [3]. Being the physical system a tube with length equal to L and radius equal to R, in which the reactant mixture moves as a plug flow with velocity v_z, the mathematical model, that takes into account the time-dependent heat and mass transfer equations and the frequency domain Maxwell equations, consists of the following partial derivatives equations and initial and boundary conditions, written for a cylindrical coordinate system (r, θ, z) [4]:

$$-2\mathrm{v}_z\frac{\partial \mathrm{C}_A}{\partial \mathrm{z}}+\mathfrak{D}\frac{\partial^2 \mathrm{C}_A}{\partial \mathrm{z}^2}+\mathfrak{D}\left(\frac{1}{\mathrm{r}}\frac{\partial \mathrm{C}_A}{\partial \mathrm{r}}+\frac{\partial^2 \mathrm{C}_A}{\partial \mathrm{r}^2}\right)-(-\mathrm{r}_A)=\frac{\partial \mathrm{C}_A}{\partial \mathrm{t}}$$

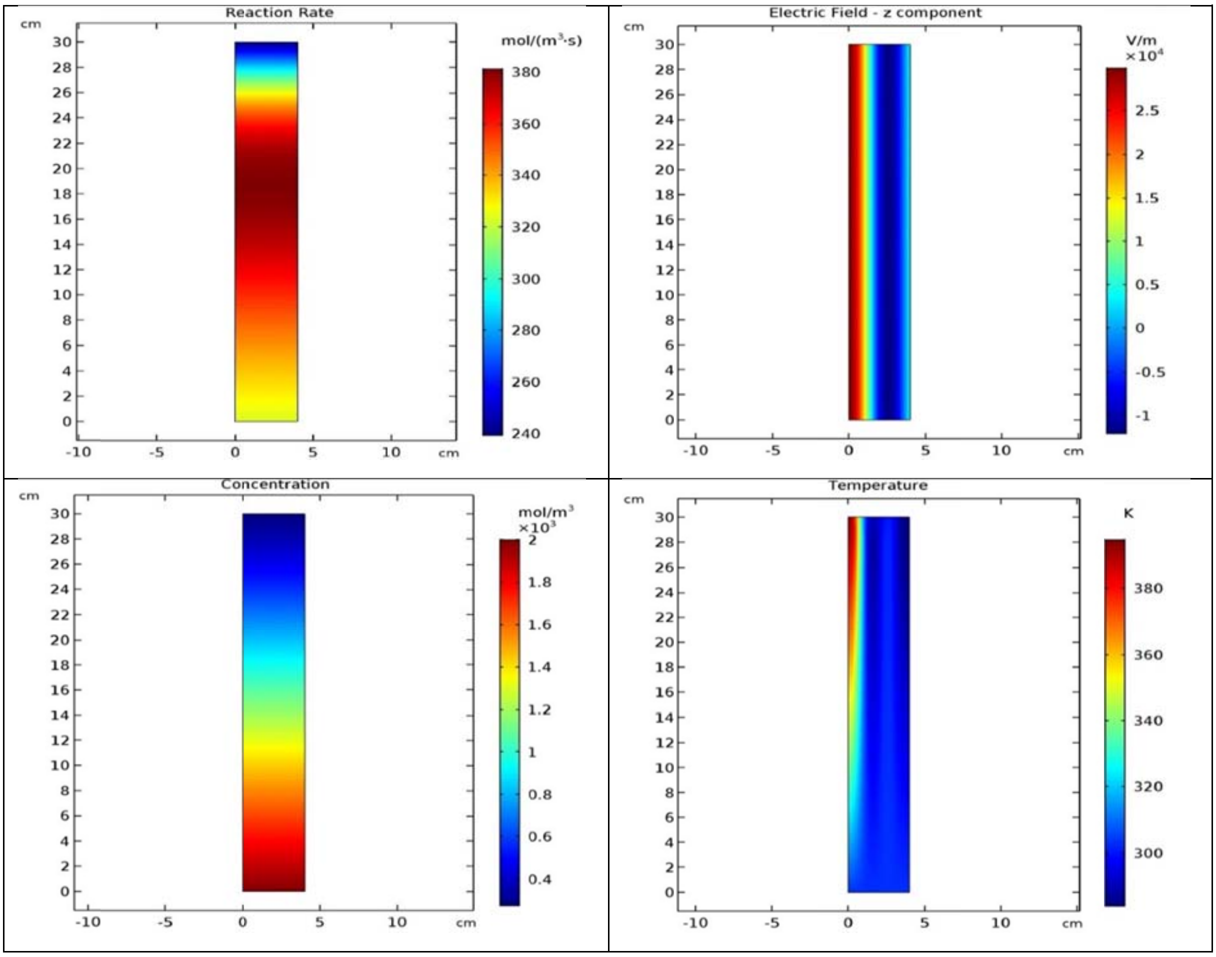
$$-2\rho c_p\mathrm{v}_z\frac{\partial \mathrm{T}}{\partial \mathrm{z}}+\mathrm{k}\frac{\partial^2 \mathrm{T}}{\partial \mathrm{z}^2}+\mathrm{k}\left(\frac{1}{\mathrm{r}}\frac{\partial \mathrm{T}}{\partial \mathrm{r}}+\frac{\partial^2 T}{\partial \mathrm{r}^2}\right)-(-\mathrm{r}_A)(-\Delta H_r)+\pi \mathrm{f}\varepsilon_0\varepsilon''|E_z|^2=\rho c_p\frac{\partial \mathrm{T}}{\partial \mathrm{t}}$$

$$(-\mathrm{r}_\mathrm{A})=\frac{(-\mathrm{r}_\mathrm{A})_{max}\mathrm{C}_A\mathrm{C}_B}{\mathrm{C}_A\mathrm{C}_B+\mathrm{k}_B\mathrm{C}_A\left(1+\frac{\mathrm{C}_A}{\mathrm{k}_{iA}}\right)+\mathrm{k}_A\mathrm{C}_B\left(1+\frac{\mathrm{C}_B}{\mathrm{k}_{iB}}\right)}$$

$$\frac{1}{\mathrm{r}}\frac{\partial E_z}{\partial \mathrm{r}}+\frac{\partial^2 E_z}{\partial \mathrm{r}^2}+k^2E_z=0$$

$t=0$	$\mathrm{C}_A=0$	$\mathrm{T}=\mathrm{T}_0$		$\forall \mathrm{r}, \forall \mathrm{z}$
$r=0$	$\frac{\partial \mathrm{C}_A}{\partial \mathrm{r}}=0$	$\frac{\partial \mathrm{T}}{\partial \mathrm{r}}=0$	$\frac{\partial E_z}{\partial \mathrm{r}}=0$	$\forall \mathrm{z}, \forall \mathrm{t}>0$
$r=R$	$\frac{\partial \mathrm{C}_A}{\partial \mathrm{r}}=0$	$\frac{\partial \mathrm{T}}{\partial \mathrm{r}}=0$	$E_z=E_{z0}$	$\forall \mathrm{z}, \forall \mathrm{t}>0$
$z=0$	$\mathrm{C}_A=\mathrm{C}_{A0}$	$\mathrm{T}=\mathrm{T}_0$	$E_z=0$	$\forall \mathrm{r}, \forall \mathrm{t}>0$
$z=L$	$\frac{\partial \mathrm{C}_A}{\partial \mathrm{z}}=0$	$\frac{\partial \mathrm{T}}{\partial \mathrm{z}}=0$	$E_z=0$	$\forall \mathrm{r}, \forall \mathrm{t}>0$

This differential equations system has been solved numerically by the finite element method. Results in terms of reaction rate, concentration, temperature and z component of the electric field are reported in the following steady-state maps.



The concentration follows the decay typically observed in a PFR reactor; the reaction rate increases from the inlet until a maximum (due to the substrate inhibition at high concentration) and then it decreases until the outlet section. Both the endothermicity of the reaction and the microwave heating, that play in an opposite way, affect the temperature, keeping it in an acceptable range to let the enzyme work. However, temperature profile is strongly uneven, mainly due to the electric field distribution.

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PP-4

DEEP OXIDATION OF TOLUENE ON GLASS-FIBER CATALYSTS IN THE STRUCTURED CARTRIDGES OF VARIOUS SHAPES

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Catalytic abatement of organic solvent vapors for the reduction of environmental pollution is an important problem in the modern world. One of the directions for its solution is application of deep oxidation reactions on glass-fiber catalysts (GFCs). Such catalysts are of interest because they exhibit a high efficiency of mass transfer, low hydraulic resistance, and a very low content of precious metals in comparison with other catalytic systems [1]. The aim of this work is to study the dependence of apparent activity of the structured GFC cartridge upon the different GFC layers arrangement in relation to the reaction mixture flow, as well as the influence of structuring elements of different shapes and glass-fiber of various weaving types.

Platinum was used as an active component. The precursor solution was applied to the glass-fiber support by incipient wetness impregnation. After preparation, the catalyst was structured in cartridges in various ways. The studies were carried out in a laboratory flow reactor. The flow rate of the reaction mixture of toluene and air was 2.5 l/min per gram of catalyst. The sample was exposed to temperature range from 100 °C to 450 °C (forward passage) and vice versa (reverse passage). Two types of glass fiber supports were used for manufacturing of catalysts: sateen (SF) and openwork (OF). GFC layers in the cartridges were located longitudinally and transversely to the flow. A 3D mesh or flat and corrugated mesh layers were used as structuring elements between the catalyst layers. Multilayer packing with transverse propagating flow was made with the use of structuring elements and without them. Fig. 1 shows the examples of catalytic cartridges and glass fiber types.

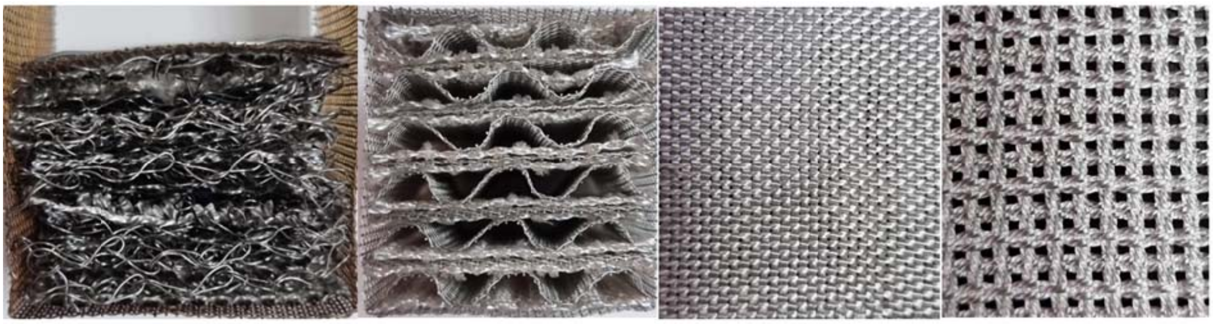

Fig. 1. From left to right: multilayer packing (MLP) with propagating flow, packing with longitudinal arrangement of layers, sateen GFC, openwork GFC

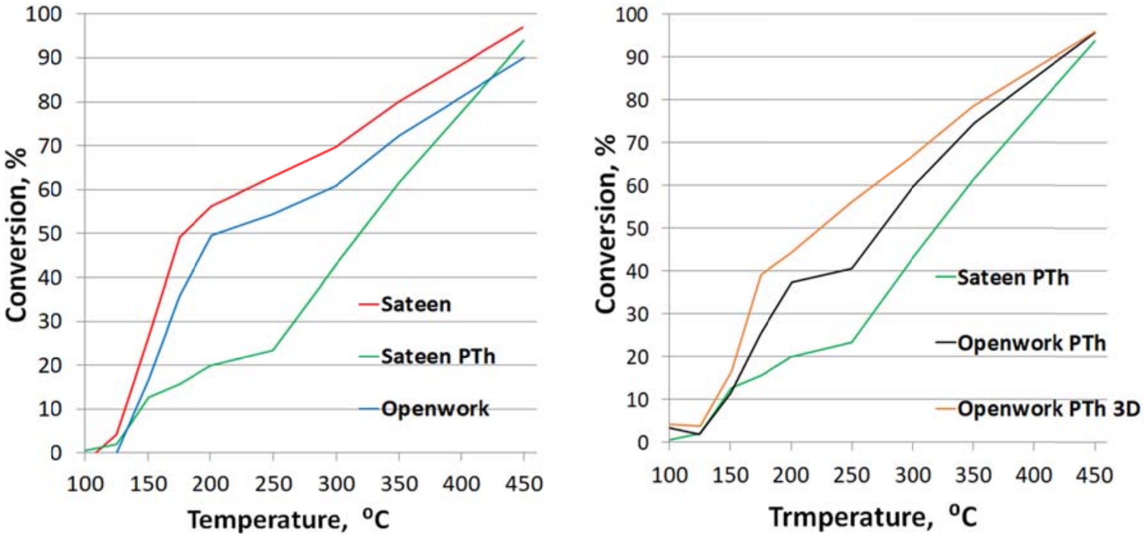

Fig. 2. Comparison of toluene conversions in different packaging and glass fiber weaving types

Fig. 2 shows the dependence of toluene conversions upon types of used GFCs and GFC packings. The left plot shows that with the longitudinal catalyst packing, the openwork weaving is inferior in activity to sateen weaving. However, MLP packing exhibited a significantly reduced activity of sateen weaving, since the catalyst layers overlapping each other has high pressure drop, thus forcing the reaction flow to find local passages with increased permeability, deteriorating the excess of the reactants to the part of the catalyst surface. The right plot compares layered packing types. Again, sateen MLP is seen to be the least active. The openwork MLP sample showed higher activity due to the higher flow permeability and better uniformity of flow distribution in the GFC packing. It should be noted that when the 3D mesh is located between the catalyst layers (openwork MLP 3D sample), the activity grows due to an additional increase in access to the active component and redistribution of the flow between the layers.

Thus, analyzing both graphs, we can conclude that the longitudinal packing shows a higher activity than the transverse one. However, the use of structuring elements has a positive effect on the catalytic activity during deep oxidation of toluene. Openwork MLP 3D showed catalytic activity comparable to the longitudinally packed cartridges and this method is of interest for further research.

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REGULARITIES OF CHEMICAL TRANSFORMATIONS IN HYDROTREATING OF VACUUM GAS OIL DERIVED FROM KAZAKHSTAN OIL

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The efficiency of vacuum gas oil catalytic cracking depends on the activity, selectivity and stability of microspherical zeolite catalysts to the greatest extent. The irreversible loss of activity and selectivity of the cracking catalyst occurs due to poisoning by heavy metals such as Ni and V. In this case, pore blocking and destruction of the zeolite structure occur [1]. Therefore, thorough preparation of the raw materials before processing in the catalytic cracking process is required.

The main purpose of the vacuum gas oil hydrotreating is hydrodesulfurization with the aim of preparing raw materials for further processing at a catalytic cracking unit. Preliminary upgraiding of raw materials is achieved by removing heteroatomic, unsaturated compounds and partially polycyclic aromatic compounds from petroleum fractions in a hydrogen atmosphere on catalysts.

Mathematical models of hydrocarbon feed conversion processes are reliable tools for predicting the yield, composition and properties of the products, evaluating the degree of catalyst deactivation, increasing the resource efficiency of processes by optimizing process parameters and extending catalyst service life [2].

The aim of this work is to develop a mathematical model of vacuum gasoil hydrotreating.

The initial stage in the development of a mathematical model is to establish the regularities of chemical transformations during the process.

To identify the key components involved in chemical transformations during the vacuum gas oil hydrotreating, analysis of the compositions and properties of raw materials and products was carried out. The following methods were used: the cryoscopy method at the KRION-1 apparatus for determining the molecular weight of substances; Stabinger viscometer SVM3000 (Anton Paar) for measuring density, dynamic and kinematic viscosity of samples; SPECTROSCAN S X-ray energy dispersive analyzer for measuring the mass fraction of sulfur in petroleum fractions.

The sulfur content in the raw materials varies from 0.006 % wt. to 0.010 % wt., in the product – from 0.000 % wt. to 0.002 % wt. The density of raw materials varies from 901 kg/ m^3 to 907 kg/m^3, the density of the product – from 890 kg/m^3 to 893 kg/m^3. The content of aromatic hydrocarbons in the raw materials varies from 43.0 % wt. to 45.5 % wt., the content of paraffins and resins varies from 57.0 % wt. to 54.5 % wt. The aromatic hydrocarbon content in the product varies from 36.0 % wt. to 41.0 % wt., the content of paraffins and resins varies from 64.0 % wt. to 59.0 % wt.

Fig. 1 presents the developed formalized scheme of chemical conversions in vacuum gas oil hydrotreating process.

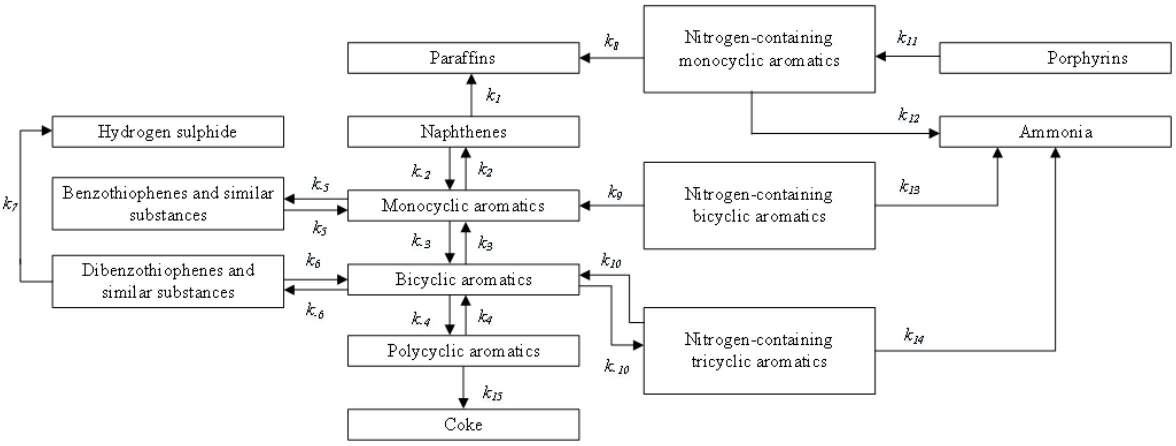

Figure 1. Formalized scheme of chemical conversions in vacuum gas oil hydrotreating process

The developed formalized chemical conversions scheme includes the conversion of hydrocarbons, sulfur, nitrogen, and metal compounds.

This degree of formalization allows takinge into account key chemical transformations that affect the quality of vacuum gas oil preparation for further processing.

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WASHCOATING AND MICROSTRUCTURE CHARACTERIZATION OF CATALYTIC FILTERS FOR EXHAUST GAS AFTERTREATMENT

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Emissions produced during the operation of automotive combustion engines contain traces of harmful substances such as CO, NO_x, unburned hydrocarbons and particulate matter (soot). Catalytic converters are used to clean up gaseous emissions while the soot is trapped in a filter. The fundamental part of both catalyst and filter is a ceramic monolith with honeycomb structure formed by a number of parallel channels. The particulate filter has channels plugged alternately at the inlet and outlet so that the gas is forced to flow through the porous wall into the adjacent channel and the soot is trapped. The current development aims on particulate filters with an integrated active catalyst that can simultaneously convert the harmful gas components and trap the soot.

This contribution focuses on lab-scale deposition of a model catalytic layer ($Pt/\gamma\text{-}Al_2O_3$) into the channels of cordierite monolith substrates by washcoating, and characterization of the resulting microstructure by X-ray tomography (XRT), scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP) [1]. By changing the deposition conditions of the catalyst layer, it was possible to control the amount of catalyst inside the substrate wall or on top of the wall.

X-ray tomography provided 3D image of the porous channel wall with the resolution 1 micron and it was possible to segment the two solid phases (substrate and coating). In addition to the conventional XRT, a time-resolved XRT imaging of the sample during the drying process was performed in a special rotating cell. The SEM and MIP provided further insight into smaller internal pores in the coated zones. Porosity, thickness and uniformity of the layer along the channel were evaluated from the electron microscopy images. The obtained data provide detailed information on the 3D morphology of the samples, which can be then employed in pore-scale simulations of flow, diffusion, reaction and filtration in the microstructure of the catalytic filter wall [2].

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CHEMCONNECT: AN INTELLIGENT REPOSITORY OF EXPERIMENTAL AND MODELING INFORMATION

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CHEMCONNECT distinguishes itself from other repositories by having an extensive knowledge base [1] of experimental devices, protocols and data, created in collaboration with experimentalists and modelers in the field. This knowledge base is represented in an extensive interconnected network of concepts and data. These concepts allow for convenient uploading of data, its subsequent interpretation and efficient search of chemical information.

The knowledge base gives context and meaning to the data that is uploaded to the database. It also allows the experimentalist and modeler to upload data in their format convenient to them. The goal of CHEMCONNECT is not to restrict input to any particular format.

The interlinking of data and concepts within CHEMCONNECT facilitates efficient and thorough search for data within the repository. The interface promotes linking data to the devices (even sensors and subsystems of the device), protocols (methodologies and procedures used to generate the final results), researchers (the institution, the lab and even who performed the experiment) and external sources and references (websites and publications).

Ontology knowledge base of devices, protocols and datasets

The primary tool representing combustion knowledge is the ontology from the semantic web [2]. The ontology also drives the user interface. Common combustion instrumentation, such as shock tubes, rapid compression machines, heat flux burners, molecular beam experiments, perfectly stirred reactors, to name a few, and data have been characterized and represented within a comprehensive ontology. This was done in collaboration with researchers using and developing these devices. Included within these ontology descriptions is a hierarchy of concepts and purposes giving extended context for more generality.

The ontology knowledge base [3] provides a template description of the devices, the protocols and the data. These general templates are filled in with characterizing details (particularly differences) of the devices and protocols. For example, the device template views an experimental device as a set of subsystems, modules and sensors. Associated with each component is a set of parameter descriptions (established through literature search and collaboration with experimentalists), references (both web and publications), images, and text describing these parts and the data produced. These descriptions characterize a particular component and differentiates them from other similar components. The data is also characterized through protocols from 'raw' data coming from the instrument sensor, to intermediate results and interpretations of the data to the final published results. Protocol templates link data sets with methodologies, devices and further protocols that manage data to the final published result. A dataset template is a set of groups measurements. Only the type, such as 'temperature' is specified, not the specific unit (that choice Is left to the specific application of the template).

CHEMCONNECT is implemented and available (requires signing up for a freely available account) on a cloud-based server [4]. An extensive interface facilitates data entry visualization and search. Data uploaded by a user can be private, available to a consortium or made public.

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EXPERIMENTAL AND MODEL-BASED STUDY OF INTEGRATED REACTOR CONCEPTS FOR THE DEHYDROGENATION OF PROPANE

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Introduction

Accompanied by experimental investigations, process simulation and numerical methods are a widely used tool to evaluate new concepts in various fields of engineering [1]. In this work dynamic reactor models were developed to simulate different reactor setups incorporating reaction kinetics, catalyst deactivation and regeneration as well as mass and heat transfer. Using a conventional fixed bed reactor (FBR) as benchmark, more complex integrated reactor setups like a fixed bed membrane reactor (FBMR) and an integrated fixed bed membrane reactor (FBMRint) were studied theoretically. Selected concepts were validated experimentally (Fig.1) [2].

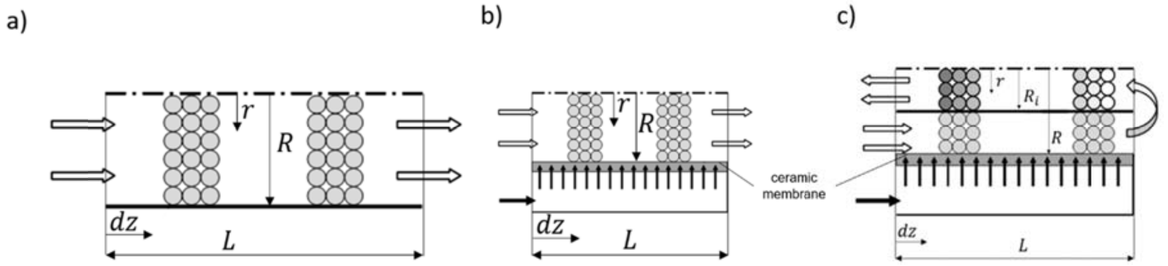

Figure 1. Reactor setups studied: a) fixed bed reactor (FBR), b) fixed bed membrane reactor (FBMR), c) integrated fixed bed membrane reactor (FBMRint)

As an industrial relevant model reaction, the dehydrogenation of propane was chosen. The growing demand of propene draws attention to on purpose propane dehydrogenation processes. Due to the properties of the reaction network, including oxidative dehydrogenation (ODH) and the thermal dehydrogenation reaction (TDH), an autothermal operation of an integrated reactor seems to be possible, which makes an integrated reactor setup attractive. A well-known problem for the TDH is temporal catalyst coking requiring periodically and regeneration, which has been also considered.

Experimental

For all experiments a VO_x catalyst (Al_2O_3 support) has been used [3]. For the parametrization of a kinetic model for the main and side reactions, experiments have been conducted in a laboratory FBR. Temperature, residence time and composition of the feed gases have been varied systematically. The product gas streams were monitored by GC (Agilent 7890B GC System). To get an understanding of the deactivation of the catalyst/reaction system, long-term FBR experiments have been performed. The feed gas was varied between propane and propene diluted in nitrogen and air at different concentrations. Propene was identified as the main coke precursor in this reaction network [4]. For an online monitoring of coke growth, a thermo gravimetric setup (Netzsch STA 449 F5) was used to observe deactivation of the catalyst under defined conditions. As well as in the FBR coking experiments inlet feed composition and temperature were varied systematically. The outlet gas flow was analyzed dynamically by Fast/Micro GC (Agilent 490 Micro GC System) during the experiments. The coked catalyst was afterwards regenerated by gasifying the coke deposits in a TGA. To describe the deactivation and regeneration phase, different kinetic approaches have been formulated and were parametrized and validated.

Simulation

To find suitable reaction conditions for pilot plant experiments, numerous simulations with different levels of detail were carried out. For 1-D simulations MATLAB® was used. In more complex 2-D models the simulations were performed with Comsol Multiphysics® 5.4. Special interest was paid to different transport phenomena inside of the catalyst bed ($\lambda(r)$- model or α_W- model). Furthermore, the different reactor configurations and resulting temperature trend caused by scale-up from lab to pilot scale were evaluated.

Results

It was possible to model the dehydrogenation dynamics of propane considering different levels of complexity (1-D vs 2-D, $\lambda(r)$- model vs α_W- model) and evaluating multiple experiments in a broad range of operation conditions. More recently, experiments on pilot scale have been performed to evaluate the results.

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SIMULATION OF HYDROCARBON PYROLYSIS NON-STATIONARY PROCESS

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For various industries in the petrochemical industry, such a process as pyrolysis of hydrocarbons is one of the main large-capacity supplier of raw materials.

Improvements in the field of pyrolysis are carried out via two main approaches. One of them is modernization of the pyrolysis technology itself, e.g., the development of more efficient burner devices or search for the new catalysts. Another one is creation of stochastic or deterministic mathematical models to determine the most optimal working conditions. From this point of view, creation of a deterministic model is of greatest interest, since such models allow us to analyze the process from all sides [1].

The analysis of hydrocarbon pyrolysis was performed using the model of the kinetics of the process proposed by Y. Zhorov et al. This model is based on a simplified reaction network, which, however, makes it possible to calculate the concentrations of the of the mixture in a wide temperature range.

The model of kinetics includes 8 reactions listed below, where 12 components are present [2]:

$$C_2H_6 \rightarrow 0.47C_2H_4 + 0.53CH_4 \quad (1)$$

$$C_3H_8 \rightarrow 0.32C_2H_4 + 0.34C_2H_6 + 0.16C_3H_6 + 0.18CH_4 \quad (2)$$

$$C_4H_{10} \rightarrow 0.10C_4H_6 + 0.32C_2H_4 + 0.27C_3H_6 + 0.15C_2H_6 + 0.16CH_4 \quad (3)$$

$$C_5H_{12} \rightarrow 0.16C_3H_6 + 0.37C_2H_6 + 0.35C_2H_4 + 0.12CH_4 \quad (4)$$

$$C_2H_4 \rightarrow 0.15C_2H_2 + 0.85H_2 \quad (5)$$

$$C_2H_4 \rightarrow \text{polymers} \quad (6)$$

$$C_3H_6 \rightarrow \text{polymers} \quad (7)$$

$$\text{polymers} \rightarrow \text{coke} \quad (8)$$

Thus, mathematical model of kinetics of pyrolysis process consists of 18 equations. 7 of them are exponential equations designed to calculate rates of reactions.

$$K_j = K_{0j} P_0 \exp\left(\frac{-E_j}{RT}\right), j \in \{1..7\} \quad (9)$$

The remaining 11 are differential ones. These equations govern changes of concentrations for each of the components included in the model during the pyrolysis process.

Therefore, the obtained system of differential and linear equations was solved using Runge-Kutta method. Since the main objective of this paper was to estimate usage of the model under conditions of sporadically changing composition of feedstock, isothermal mode was considered in order to accelerate calculations [3]. Figure 1 shows dynamics of coke layer thickness in the reactor during the process of pyrolysis along the length of the reactor`s tube.

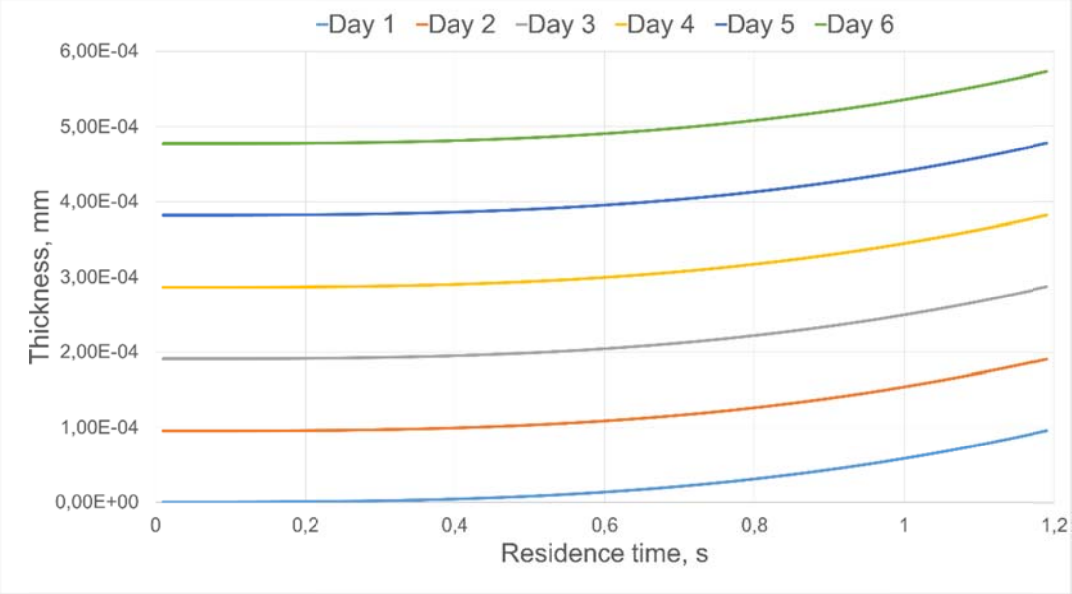

Figure 1. Accumulation of coke in the tubes within certain period of time

Thus, although, the obtained model needs further development, it will help to make recommendations for reactor operating mode.

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PP-10

STUDY OF THE PROCESS OF THERMAL DEGRADATION OF WASTE CROSS-LINKED POLYETHYLENE

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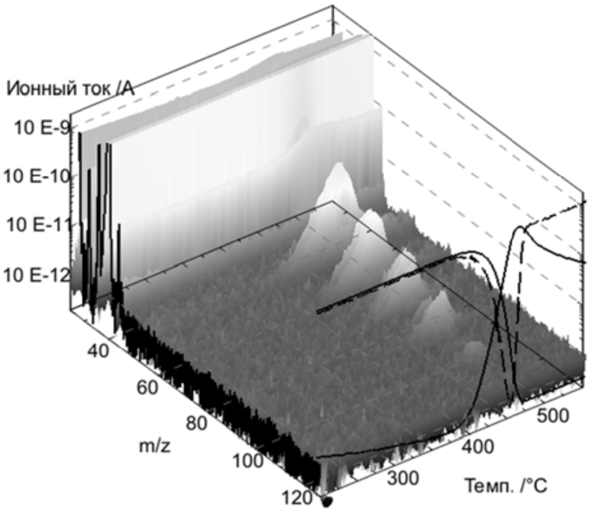
The need to dispose of environmentally resistant waste plastics is primarily associated with their negative impact on the environment. Crosslinked polyethylene is used in the production of insulation of cables, sanitary pipes and fittings for hot water supply [1, 2]. The problem of cross-linked polyethylene waste recycling is becoming more and more urgent every year, because the complexity of cross-linked polyethylene processing is the presence of a mesh structure that does not allow waste recycling by extrusion. Therefore, the majority of cross-linked polyethylene waste is burned as fuel or subjected to burial [3, 4].

Recently, methods of thermal processing of cross-linked polyethylene waste attract the attention of research teams [5, 6]. Thus, according to the article [5], liquid pyrolysis products of cross-linked polyethylene can be used as a replacement for liquid fuels or as a raw material for the production of chemicals.

During the initial stage of the work, thermogravimetric study of cross-linked polyethylene samples in the temperature range from 35 to 600 °C was performed using the Aeolos QMS 403D NETZSCN mass spectroscopic prefix.

On the basis of the obtained data of thermal analysis, a method of conducting experiments to study the pyrolysis process at a laboratory installation in the temperature range of 450-550 °C in an inert gas – nitrogen environment was developed.

Fig. 1. Molecular weight distribution of cross-linked polyethylene thermal degradation volatile products



PP-10

With the help of a laboratory set-up, the dependence of the conversion of cross-linked polyethylene into gaseous and liquid products depending on the pyrolysis temperature was established.

The nonlinear regression method was used to determine the kinetic parameters of each stage separately and the model of the cross-linked polyethylene pyrolysis process.

Comparison of estimates of the applied kinetic models allowed to determine that the most accurate process of thermal destruction of crosslinked polymer is described by a model containing 2 successive stages.

The process of destruction of cross-linked ethylene occurs most intensively in the temperature range 433.3-465.3 °C. The optimum temperature of the pyrolysis process is 500 °C, which allows to obtain the highest yields of liquid products and to achieve the maximum calorific value of the resulting pyrolysis gas. The process of thermal destruction most likely proceeds in two consecutive poorly separable stages with activation energies of 224 and 310 kJ/ mol.

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STUDY OF CATALYTIC PYROLYSIS OF OIL RESIDUES

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Oil refining, as well as the synthesis of oil-related products, involves the formation of oil residues. Oily waste can be a valuable source of energy and chemicals.

Among the various methods of thermal processing of oil residues, pyrolysis [1], gasification [2], combustion [3], and joint pyrolysis [4] are the most studied.

During thermal destruction, valuable gaseous and liquid products, mainly hydrocarbons, are obtained [5]. The composition of the product depends on the nature of the oil residue, process conditions and the presence of a catalyst [6].

The process of catalytic pyrolysis of oil residues with the use of natural (kaolin and bentonite clay) and synthetic (H-beta-25 and H-ZSM-5) aluminosilicates as a catalyst is investigated.

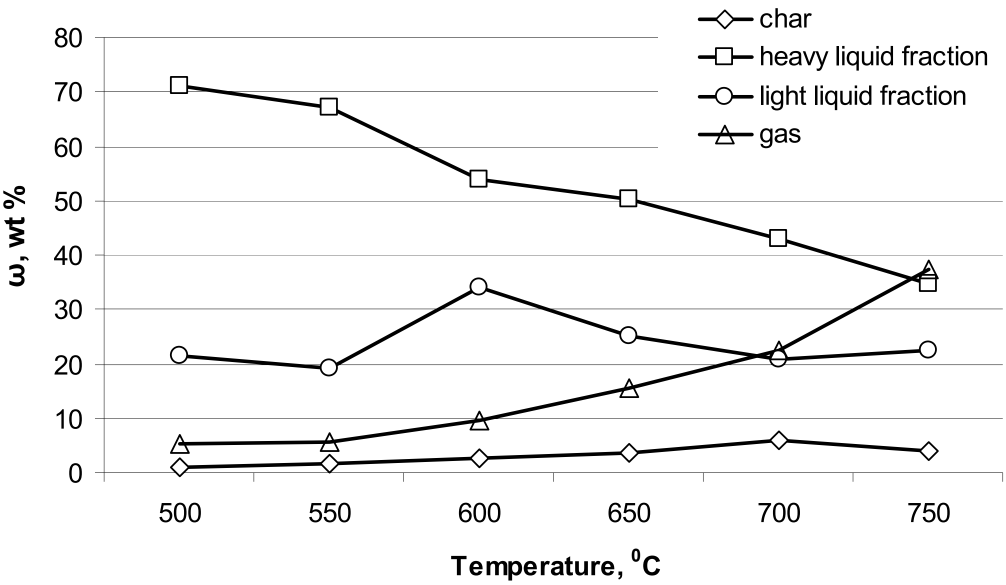
A catalyst was also synthesized by mixing of bentonite clay and zeolite (H-ZSM-5).

The study of the pyrolysis process was carried out on a laboratory set-up consisting of a continuous metal reactor. The residence time of raw materials in the heating zone of the reactor was less than 20 seconds. The heating of the reactor was carried out by an electric furnace with a thermoregulator, providing temperature maintenance in the range of ±5 °C. The temperature of the process varied in the range of 500-750 °C. During the experiment, the rate of release of gaseous products was recorded. Pyrolysis gases were analyzed by gas chromatography. The specific heat of combustion of gases was determined on a specially designed analyzer based on a flame temperature detector.

The effect of the pyrolysis process temperature on the yield of solid, liquid and gaseous products was investigated. As the process temperature increases, the yield of the heavy oil fraction gradually decreases over the entire study range, and the yield of gaseous products increases.

The study of the influence of aluminosilicates on the process of destruction of oil residues was carried out at a temperature of 600 °C. All the studied catalysts increased the yield of solid carbon residue, which indicates an acceleration of the reaction of coke formation on the surface of aluminosilicates. The highest yield of gaseous and liquid products was observed in the presence of zeolite H-ZSM-5. The mass of gas increased by 37 %, the light oil fraction by 18 % compared to the non-catalytic process. In the presence of this catalyst, the yield of heavy oil fraction is significantly reduced from 54 to 37 % (wt.)

The optimum temperature of the pyrolysis process of oil residues was determined – 600 °C. Synthetic aluminosilicates showed the greatest activity in the process of thermal degradation of oil residues. They increased the yield of gaseous products and light petroleum fraction. Synthesized catalyst bentonite/H-ZSM-5 has lower activity than zeolite H-ZSM-5. But its application increases the yield of gaseous products and light oil fractions compared to the non-catalytic process. The introduction of bentonite clay into the catalyst reduces its cost, which makes catalytic pyrolysis using a synthesized catalyst more promising.



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EFFECT OF CATALYSTS ON TAR CARBONIZATION

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One of the most economically feasible routes for processing heavy oil residues is delayed coking, which yields additional valuable petroleum products and more advanced oil processing at a minimum cost [1]. The main goal of carbonization processes is to produce various types of oil cokes depending on the quality of the used precursors. The generally accepted mechanism of the oil residue carbonization is the so-called “consecutive scheme” of hydrocarbon consolidation [2]. The carbide cycle mechanism opens new opportunities for enhancement of the delayed coking technology [3,4]. Nickel metal has the highest activity in the formation of carbon nanostructures. One can expect that the addition of nickel catalysts to the carbonization feedstock will result in the interaction of the active catalyst particles with the hydrocarbons present in the heavy oil residues yielding oil coke reinforced with carbon materials. Furthermore, nickel catalysts are widely used in oil desulfurization. The present study was devoted to catalytic tar carbonization in the presence of Ni/Sibunit, Cu/Sibunit and Ni-Mo/Sibunit catalysts. Particular attention was paid to the contents of sulfur compounds in the reaction products.

The tar carbonization was studied in the temperature range of 350-500 °C. The gaseous products formed during the tar carbonization at 450 °C were analyzed for the concentration of sulfur-containing compounds. The original tar contained 1.5 mass. % S. H_2S and COS were observed in the reaction products. So, sulfur was partially removed from the tar with the gas phase during its thermal carbonization. An increase of the carbonization temperature from 450 to 550 °C led to the decrease of the coke yield due to deeper cracking of the tar components and simultaneous decrease of the sulfur concentration in the coke.

The addition of the Ni/Sibunit catalyst to the tar improved the properties of the obtained oil coke. The coke yield increased from 28 to 33 % whereas the sulfur concentration in the coke decreased.

The efficiency of the carbonization process and the properties of the obtained coke were further improved by placing three different catalysts Ni-Mo/Sibunit, Cu/Sibunit and Ni/Sibunit in different zones of the autoclave where the tar carbonization was performed. In zone 1 the tar was subjected to cracking and desulfurization over the 8%Ni-2,5%Mo/Sibunit catalyst. In zone 2 sulfur was trapped by the Cu/Sibunit catalyst in the form of copper sulfide. In zone 3 coke was formed over the Ni/Sibunit catalyst predominantly from the gases formed by the tar cracking. Due to such catalyst arrangement, the coke yield in zone 1 was 27 % of the initial tar weight, whereas its yield in zone 3 was as high as 18 %. So, the total coke yield was equal to 45 % (Table).

Table. Coke and sulfur distribution in different zones of the autoclave after the tar carbonization at 450 °C

Number of zones	1	2	3
Catalyst	Tar +Ni-Mo/Sibunit	Cu/Sibunit	Ni/Sibunit
Coke yield, wt. % of the initial tar	27	4.5	18
S concentration, wt. %.	1.28	1.1	0.56

Meanwhile, its yield during the thermal carbonization was only 28 wt. %. The three-zone arrangement of the catalyst also led to a substantial decrease of sulfur concentration in the solid reaction products. Thus, the coke in zone 3 of the autoclave contained only 0.56 % S. This is due to the capture of sulfur in the form of copper sulfide in the second zone of the reactor.

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PP-13

GOLD AND PLATINUM-CATALYZED HYDROGENATION OF MONOTERPENOID OXIMES TO VALUABLE AMINES AND CARBONYL COMPOUNDS

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Terpenoids form the largest group of natural compounds and are extensively applied as platform molecules in food, pharmaceutical and perfumery industries. Terpenoids often contain asymmetric centers and several functional groups, including reducible ones. Development of stereo-, regio- and chemoselective catalysts for reduction of different functional groups in terpenoids aiming at production of valuable intermediates for fine chemicals and pharmaceuticals is a challenging task. Hydrogenation of monoterpenoid oximes is one of the key steps in the synthesis of valuable compounds, including those with carbonyl and amino groups. In the present work, the focus was on the catalyst design for direct transformation of monoterpenoid oximes into valuable amines or carbonyl compounds.

Liquid-phase hydrogenation of monoterpenoid oximes was carried out in a batch reactor at 353-373 K under H_2 atmosphere. Gold, gold-platinum and platinum catalysts on metal oxides, including TiO_2, ZrO_2, Al_2O_3, MgO, were prepared by the deposition-precipitation and impregnation methods, respectively. The catalysts were characterized by N_2 physisorption, TEM, XPS, XRF. The reaction mixture was analyzed by GC (HP-5), GC-MS (HP-5ms) and NMR. Monoterpenoid oximes with different structures, including menthone, carvone, fenchone, camphor oxime, were selected taking into account their practical interest. A detailed study of menthone oxime hydrogenation was performed. The active metal, the metal nanoparticles size and the support nature affected noticeably the catalytic behavior. An increase of the gold nanoparticles size and application of metal oxides with a strong basic character such as magnesia favored deoximation to menthone. Au/Al_2O_3 and Pt/Al_2O_3 catalysts with metal nanoparticles sizes of 2.0 and 0.9 nm, respectively, were shown to provide higher catalytic activity and selectivity to menthylamine. The solvent nature on the reaction regularities was explored using apolar and aromatic, polar aprotic and protic solvents. The reaction kinetics including the recyclability and the impact of the deactivation was studied using Au/Al_2O_3 catalyst allowing to propose a detailed reaction scheme. Selected catalysts were successfully used for camphor and fenchone oximes hydrogenation to the corresponding amines. The reaction conditions were tuned depending on the substrate structure to provide the highest yield of the target amine and to avoid the catalysts deactivation. A one-pot synthesis of dihydrocarvone comprising sequential transformations of carvone oxime to dihydrocarvone over Au/TiO_2 catalyst (Fig. 1) [1], which is a novel approach to obtain a valuable additive in food industry, was developed.

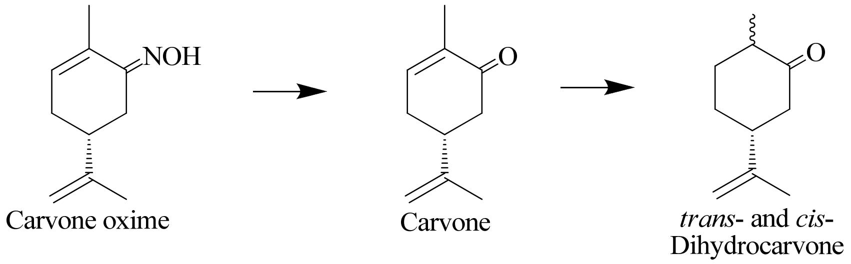

Fig. 1. Carvone oxime transformation to *trans-/cis*-dihydrocarvone over gold catalysts

Compared to Au/TiO_2 catalyst there was both hydrogenation of all reducible functional groups as well as deoximation in the presence of Pt catalysts, with activation of isopropyl fragment being preferred. Gold catalysts were less active but provided selective carvone oxime deoximation to carvone followed by conjugated C=C bond hydrogenation leading to dihydrocarvone.

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Acknowledgements

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PP-14

FORMATION OF TETRALINES AND SULFONES DEPENDING ON THE CONSTRUCTION OF THE LINEAR ALKYLBENZENES FILM SULFONATION REACTOR

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Linear alkylbenzene sulfonates are the main biodegradable component of the production of synthetic detergents obtained by sulfonation of linear alkylbenzene (LAB). The process of producing alkylbenzenesulfonic acid (ASA) consists of the following stages: dehydrogenation of linear alkanes C9 - C14; hydrogenation of di- and triolefins to monoolefins; alkylation of benzene with olefinic hydrocarbons; sulfonation of linear alkylbenzenes with sulfuric anhydride in a film reactor to obtain ASA.

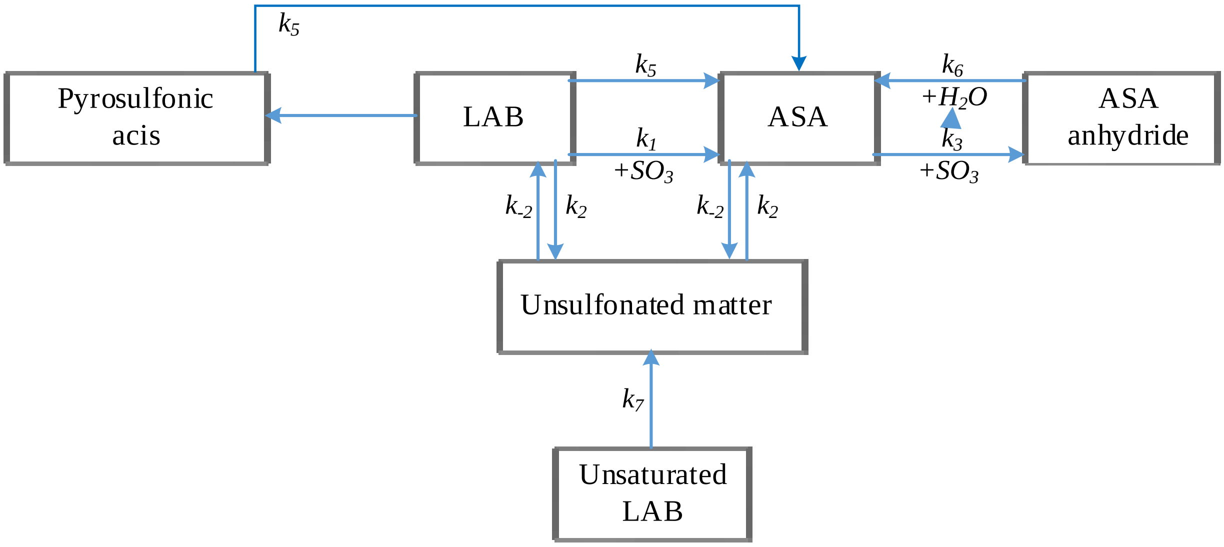
In gas-liquid processes of chemical technology, reactors of various designs are used, which do not always provide the required product quality. The low speed of gas transport in the liquid phase, as well as the high gas flow rates in bubble reactors complicate the technology.

In this regard, the urgent task is to develop the effective reactors that provide a high speed of gas transport to the liquid. The most promising are film-type reactors, since the film-like flow of a liquid makes it possible to increase (several times) the mass transfer coefficients in the liquid phase in comparison with the bubbling regime. Artificially created turbulence can increase the intensity of heat and mass transfer of the liquid and gas phases in the film reactor. However, the industrial implementation of film-type reactors is largely constrained by the lack of experimental data to develop a scientifically based methodology for their calculation and design.

In the process of LAB sulfonation with sulfuric anhydride in a film reactor, the process is complicated by occurrence of side reactions, the products of which are viscous substances - tetralins and sulfones. The accumulation of viscous components leads to clogging of the reactor tubes, so that the hydrodynamic regime of the film flow is violated and the yield of the target product is reduced. Upon reaching a critical concentration of highly viscous components in the reactor, it is flushed with water, which allows the removal of viscous compounds.

The purpose of the work is to determine the optimal design and technological mode and mathematical modeling method.

The main disadvantage of a single-tube film reactor is a short period between the reactor washings, which leads to the need to replace it with a multi-tube film apparatus. Ensuring a satisfactory yield at the maximum possible duration of the cycles can be achieved by optimizing the design parameters of the reactor using the method of mathematical modeling:



As a result of the calculations using a mathematical model that adequately describes the process, the dependence of the concentration of ABSK and the viscous component in the output stream is obtained.

An analysis via mathematical modeling was performed of the influence of the design of a film reactor for LAB sulfonation on the rate of tetralins and sulfones formation of. The optimal design of the sulfonation reactor with the number of tubes n = 40 and diameter d = 43 mm was determined. It was shown that with a change in the LAB flow rate in the reactor tube, the mass transfer coefficient increases. So, at a LAB volume flow rate per tube V = 0.95 · 10^{-5} m^3/s, the mass transfer coefficient is 1.73 · 10^{-2}, and at V = 2.86 · 10^{-5} the coefficient is 2.08 · 10^{-2}.

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PP-15

METHANOL TO HYDROCARBONS TRANSFORMATION OVER MODIFIED ZEOLITES

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Nowadays the supply of main chemical synthesis and the transport sector of the economy is based on hydrocarbons extracted from oil. The forecast of the international energy agency [1] for the next 25 years includes an increase in hydrocarbon consumption by 25-30 %, with a decrease in extraction by 10-15 %. Consequently, significant changes and revisions of the raw materials base for hydrocarbon production processes are necessary for the possible replacement of traditional methods for producing hydrocarbons from raw oil. Biomass and waste is the only renewable alternative to fossil sources of hydrocarbons and energy in chemical synthesis and the transport sector of the economy. The production of liquid hydrocarbons from biomass and waste through synthesis gas is considered as a promising process in the short and medium term, either by Fischer-Tropsch synthesis, or by means of the catalytic transformation of methanol into hydrocarbons [2, 3].

Samples of an iron-modified commercial zeolite H-ZSM-5 were synthesized by modification of H-ZSM-5 in a solution of Iron chloride(III), the samples were designated ZSM-5-$FeCl_3$-0.001M, ZSM-5-$FeCl_3$-0.005M, ZSM-5-$FeCl_3$-0.01M, ZSM-5-$FeCl_3$-0.05M, ZSM-5-$FeCl_3$-0.1M, ZSM-5-$FeCl_3$-0.5M. Catalysts testing were provided in tube reactor filled with investigated catalysts, the reactor was heated to 350 °C the DME low rate was maintained as 0.16 kg(DME)/(kg(Cat)*h). The reaction samples were analyzed by online chromatography.

The introduction of iron into the zeolite H-ZSM-5 matrix reduces the number of micropores from 303 to 190 m^2/g, while the surface area of mesopores increases slightly from 55 to 106 m^2/g with increasing of iron concentration from 0.004 % to 0.032 % and with further increase of concentration to 0.24 % decreases to 45 m^2/g.

Modification of zeolite H-ZSM-5 with iron chloride, results in increase of dimethyl ether for 25-30 %. The increase in the conversion of dimethyl ether and the rate of its transformation with iron modification can be associated with modification of active sites.

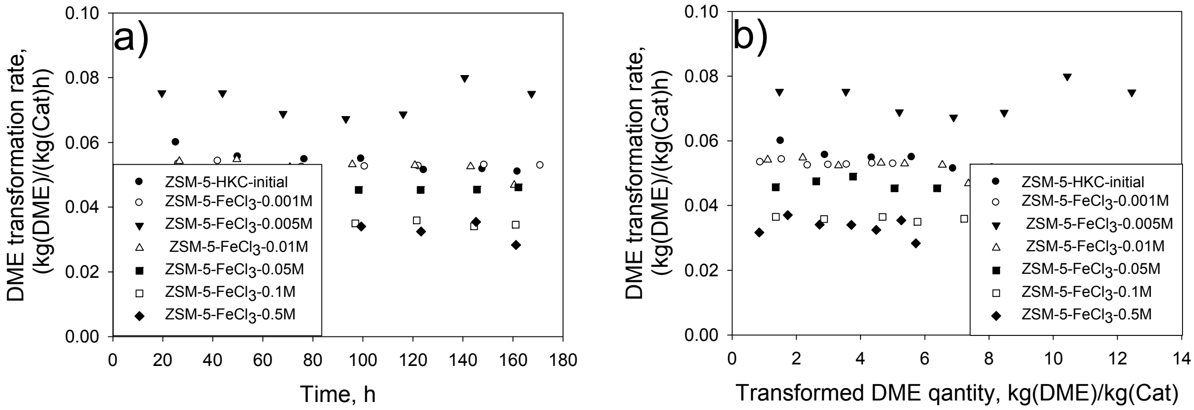

Figure 1. Dimethyl ether transformation rate versus a) time, b) specific transformed dimethyl ether quantity for H-ZSM-5 samples modified with iron chloride, (W(CH_3OCH_3) = 0.16 kg(Me)/(kg(Cat)*h), t = 350 °C, p = 1.1 atm)

A series of iron modified H-ZSM-5 zeolites were synthesized by ion exchange methods. The sample containing 0.007 wt. % of iron showed higher activity compare to initial sample

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PP-16

ENHANCING EFFICIENCY OF HYDROCARBONS TO SYNGAS CONVERSION VIA PARTIAL OXIDATION

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Ideal partial oxidation conversion of hydrocarbons to syngas provides maximum yield of carbon monoxide and hydrogen with zero net heat effect of gross reaction $\Delta H = 0$. Thus, it must involve an endothermic oxidant, e.g. water, to compensate the heat release of oxygen reaction. For methane ($x^* = 0.426$):

$$CH_4(-74.8\ \text{kJ/mol}) + xO_2 + (1-2x)H_2O(-241.8\ \text{kJ/mol}) \rightarrow CO(-110.5\ \text{kJ/mol}) + (3-2x)H_2$$

The conversion should be performed at a high temperature, otherwise the chemical equilibria will bring the reaction to methane, water, and carbon dioxide. The high-temperature reaction products carry away the reaction heat, which unavoidably is positive. A higher heat efficiency process recovers the sensible heat of hot products to be transferred to raw reactants. That is superadiabatic combustion (SAC).

The filtration combustion (FC) in a porous medium provides an opportunity to realize SAC, as the porous medium provides both heat exchange surface and a heat carrier. The traveling wave SAC of ultra rich gas mixtures was proposed [1]. However, the FC of premixed gases involves a fundamental limitation. A gas mixture 'chooses' itself a combustion temperature controlled by its own kinetics of ignition [2].

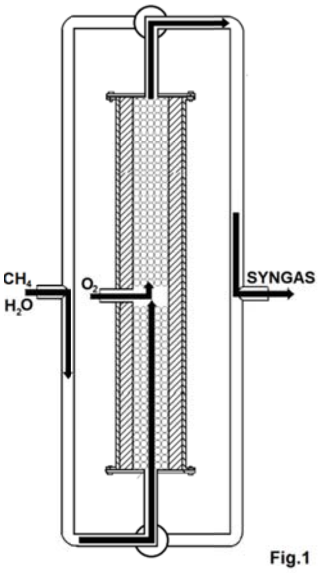

Fig.1

An improvement proposed by authors was to arrange non-premixed FC to provide preheating of one gaseous reactant from the porous medium prior to mixing and it can be arranged in reversed-flow reactor [3] or a continuous flow reactor [4]. With steam-oxygen conversion this process with steam- methane preheating and pure oxygen supply (Fig. 1) promised as low *x* as 0.48 (Fig. 2).

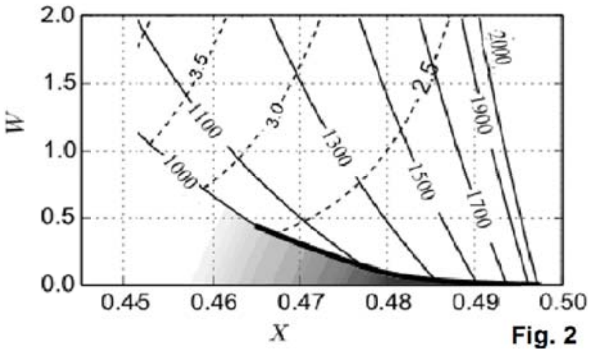

Fig. 2

Further improvement in the efficiency

of conversion even with air used as an oxidant can be attained with preheating of both reactants [4, 5] (Figs. 3-4) in a moving bed reactor.

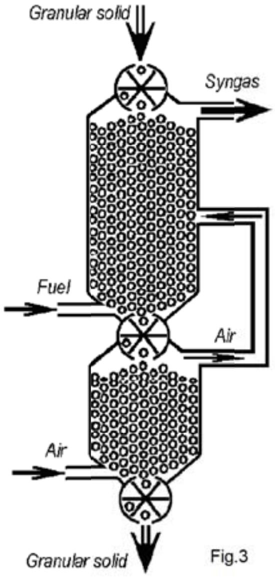

Fig.3

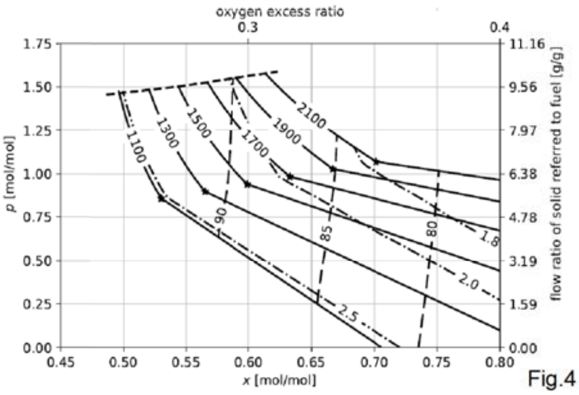

Fig.4

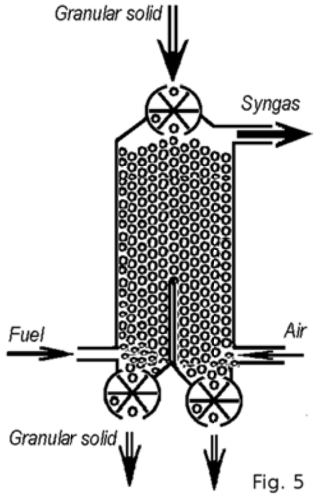

Fig. 5

Preheating of methane and partial preheating of air-steam mixture with residual heat of the solid heat carrier provide conversion with > 90 % chemical efficiency for x < 0.55. The process in Fig. 3 provides very high efficiency even for low caloric pyrolysis gas [5].

This consideration prompts a way for further improvement in the POX conversion. One should achieve a **complete preheating of both reactants**. Such reactor of a dream is schematically shown in Fig. 5. Looks not excessively feasible in its design, yet very promising in energy efficiency.

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PP-17

METAL ORGANIC FRAMEWORKS SUPPORTED OF CERAMIC FOAMS FOR CYCLOHEXENE AND BENZYL ALCOHOL OXIDATION

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Despite numerous literature reports regarding the synthesis and application of metal organic frameworks (MOF) in catalytic processes, there are many problems regarding their chemical and mechanical stability as well as their post-modification to conform high industrial standards such as activity and selectivity. Starting from early 90's, more than 70 000 MOF structures have been reported, showing the unique chemical and catalytical properties. Despite the potential use of these materials in catalytic processes, e.g. oxidation or hydrogenation, the lack of thermal or chemical stability might be problematic to their industrial use. Another problem relates to their shaping into desired structures to allow sufficient heat and mass transport properties [1].

In this study we present detailed study on preparation and characterisation of Cu-HKUST, CuCo-HKUST, CuPd-HKUST metal organic frameworks deposited on ceramic foams. The catalysts were characterized by various methods including, *in situ* DRIFT, XRD and BET. The synthesized catalysts have proven good mechanical and chemical resistance and the ability to uniform deposition on structured supports. The catalytic results on cyclohexene and benzyl alcohol oxidation showed that prepared structured catalysts may be successfully used in organic synthesis.

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ANALYSIS OF THE LEACHING OF PHOSPHATE ORE IN PHOSPHORIC ACID MANUFACTURING PROCESSES

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In the phosphate industry, phosphate ore is often mined from open-pit mines and then beneficiated in a series of flotation units. The ore thus upgraded is then sent to a (wet) phosphoric acid process to produce phosphoric acid which is the key component of the phosphate industry where it is used in the production of fertilizers, in the food industry and even in the pharmaceutical industry [1]. The manufacturing process which is widely used in the phosphate industry consists mainly of a digestion tank, a filtration unit, and a concentration unit. However, despite its wide use, its functioning still poses several problems due the lack of knowledge on many complex phenomena involved in the process. The understanding of these phenomena as well as accurate experimental measurements of the relevant variables are some of the key issues that should be addressed to optimally design and operate the phosphoric acid processes.

The leaching process takes place in the digestion tank and consists in reacting the phosphate ore particles of different sizes with a mixture of concentrated sulfuric acid and recycled phosphoric acid to produce phosphoric acid and gypsum. The digestion tank which is the heart of the process is therefore critical to the performance of the downstream units, i.e., filtration and concentration units. The control of its operation is therefore of utmost importance for the entire phosphoric acid process.

The objective of this contribution is to analyze the effect of the particle size distribution (PSD) on the leaching process by developing a first-principle model for mono-sized particles first, and then incorporating a PSD to take into account the actual operating conditions in the digestion tank.

The leaching is considered as a set of non-catalytic fluid/solid chemical reactions with consumption of the solid. Its modelling is therefore based on the approach of shrinking core model with elimination of the products. Furthermore, the model involves several phenomena including mass transfer and transport of reagents (products) to (from) the particle surface, and reactions at the surface of the solid. The model equations describe the mass balances within the liquid bulk, the liquid film surrounding the particles, and the particles, and involve several unknown parameters. A global estimability analysis is then carried out to determine the parameters which are estimable from the available measurements. The most estimable parameters are then identified from the measurements of the phosphate ore conversion rate for uniform particles, and then for particles with a size distribution in order to match reality [2]. The effect of the type of PSD is evaluated by using different distributions (Rosin–Rammler, Gamma, Gaudin–Schuhmann and Log-normal distributions) and a variation coefficient is used to quantify the influence of its shape on the leaching model predictions [3].

For different operating conditions of the leaching process, the predicted results using the identified parameters of the model with incorporated PSD are more consistent with the experimental data and consequently allowed us to significantly improve the understanding of the phenomena involved in the digestion.

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SYNTHESIS OF CARBON NANOMATERIALS IN A CYCLIC COMPRESSION REACTOR USING BUFFER GASES

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Carbon nanoparticles (CNs) have recently become the subject of research but due to the uniqueness of the already studied properties of CNs they are widely used. They are used in the production of universal adsorbents and filters [1] and as carriers for catalysts [2] and as fillers for polymer and inorganic matrices [3]. CNs are the main components of biocompatible materials. CNs are also considered for use in enhanced oil recovery technologies [4]. The variety of physicochemical properties of carbon materials of the new generation – fullerenes, nanotubes, bulbous structures and ultradispersed diamonds – opens up the prospects for using CNs in different allotropic forms in existing technologies and in the development of new ones.

The disadvantages of the existing technologies for the synthesis of CNs are their high cost and non-ecological compatibility. Already obtained products, as a rule, require further technological processing using "wet" chemistry consisting of various acids and organic solvents or the use of heat treatment for purification from accompanying impurities. High price and low yield of CNs complicate their widespread use. The industrial methods of producing soot particles using combustion reactors result in significant greenhouse gas emissions. The redox methods generate large amounts of liquid waste [2].

We present an effective method for the synthesis of CNs by pyrolysis in a cyclic chemical compression reactor [5]. The technique allows the use of various carbon-containing precursors in the gaseous and liquid phases. The reactions take place in adiabatic compression-rarefaction cycles with a controlled frequency in an atmosphere of various buffer gases with a controlled concentration. It is possible to influence the course of reactions by changing the pressure and using catalysts. All these factors make it possible to produce CNs with a varied composition and morphology. In this paper we present the results of experiments on the production of CNs with argon and helium as buffer gases. In a number of experiments dopants were used. In the case of using argon as a buffer gas CNs were obtained close to bulbous with a highly developed specific surface which were globular carbon particles and structures with and without an inner cavity. The use of helium in a mixture for the pyrolysis of hydrocarbons leads to the formation of onion structures at high pressures and scaly structures at low pressures. A further decrease in pressure leads to the formation of finely dispersed amorphous carbon with a gradual increase in its fraction in the product.

Various light hydrocarbons were used as precursors – acetylene, ethylene, pentane, a mixture of pentane and butane, etc. The progress of the hydrocarbon pyrolysis reaction was monitored on-line using a UGA-200 universal gas analyzer. The CNs are characterized by high-resolution transmission electron (TEM) and scanning electron (SEM) microscopy and X-ray diffraction analysis and Raman spectroscopy and EDS-spectrometry.

The buffer gas used in the synthesis process and the pressure inside the reactor volume affects the morphological characteristics of the products. Changing the conditions of gas-phase synthesis allows customizing the process to obtain a specific product. The resulting product in the process of synthesis is chemically pure. Its impurity is determined only by the degree of purification of the initial reagents. The technological process do not introduce additional impurities into the product. The resulting product does not require further processing, unlike most of the proposed methods, and it is ready for use in technologies and problems of materials science.

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MODELING OF CATALYTIC SEWAGE SLUDGE COMBUSTION IN FLUIDIZED BED USING ASPEN PLUS

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Sewage sludge from urban wastewater treatment plants is a diluted suspension of microorganisms and their metabolic products, harmful organic substances and mineral components in water (up to 99 % of water). The composition of sewage sludge includes substances with toxic, cancerogenic and other negative properties. Due to the high humidity, the initial sludge requires mechanical drying up to 73-84 % of humidity to facilitate transportation, logistics and storage. An increase in the volume of sewage sludge from treatment plants is becoming a serious worldwide environmental problem [1].

Due to the presence of organic substances in the composition, sludge is a valuable energy raw material that can be used to produce heat or fuel (synthesis gas, bio-fuel). Such methods of sludge processing include hydrothermal oxidation, combustion, pyrolysis and gasification. The combustion is an industrial method of sludge utilization and carried out in a fluidized bed of an inert material at more than 850 °C. Under such conditions, mechanically dried sludge cannot be combusted in autothermal mode, which requires either an additional drying step or the supply of additional fuel [2].

One of the effective ways to obtain energy from fossil raw materials is the technology of its catalytic combustion in a fluidized bed. Catalytic combustion is fundamentally different from the traditional combustion processes, since organic substances and CO are oxidized on the surface of a heterogeneous catalyst without the formation of a flame. Using the technology of fuel combustion in a fluidized bed of catalyst allows one to achieve the following advantages: significantly reduce the temperature of the process to 700-750 °C due to an increase in the rate of oxidation reactions; reduce the requirements for thermochemical properties of structural materials; to achieve high values of calorific intensity inside the combustion zone, which can significantly reduce the dimensions, weight and metal consumption of structures; significantly reduce the concentration of harmful substances in flue gases [3].

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This work presents the results of simulation of a sewage sludge combustion plant with a productivity of 6 tones per hour using an ASPEN Plus®. It is shown that catalytic combustion technology can be used for the efficient utilization of mechanically dehydrated sludge with a humidity of ~ 75 % in autothermal mode (without the use of additional fuel). At the same time, the plant for utilization of 6.0 tons of sludge per hour allows one to obtain 3.07 MW of heat energy. It is shown that the sludge humidity and its calorific value significantly affect the combustion process. Thus, at a humidity of less than 72 %, an additional water supply is necessary to avoid overheating of the catalyst bed. In the case of an increase in sludge humidity of more than 76 %, an additional supply of fuel (for example, brown coal) is required. In addition, the article discusses the emissions of harmful substances generated during sewage sludge combustion and methods for their utilization.

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PP-21

THE OXYGEN INTERACTION WITH THE SURFACE OF STRONTIUM FERRITES AND COBALTITES, DOPED BY MOLYBDENUM

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The transport of oxygen through oxygen-permeable membranes or electrochemical devices, such as solid oxide fuel cells (SOFC), is controlled by inner volume properties, such as the energy of diffusion activation barriers, and surface processes – adsorption, desorption of oxygen molecules and their dissociation into oxygen ions. At typical SOFC operating temperatures (700-900 °C), surface processes play a limiting role in oxygen exchange, and understanding this stage is critical for determining the performance of such devices, and is also important for a fundamental understanding of the process as a whole. Advances in quantum chemical calculation methods using DFT approaches allow us to investigate the quantitative characteristics of these processes by computer modeling.

An effective approach for creating new functional materials for SOFC and membranes is modification by doping with highly charged cations, for example, replacing Co or Fe with Mo. This modification allows to solve a number of important problems-to increase the stability of the material in the atmosphere of CO_2, suppresses unwanted phase transitions. But these materials are new and their properties are unknown in details and are in focus of scientific interest now - in particular one need to understand details of surface oxygen exchange processes too.

We perform calculations of the oxygen O_2 molecule properties on (100) surface of $SrFe_{1-y}Mo_yO_{3-x}$ and $SrCo_{1-y}Mo_yFe_{3-x}$ using VASP DFT code. The role of oxygen vacancies on the surface of oxide in O_2 molecule neighbor was analyzed. Energy and electronic processes for cobalt and iron-containing oxides are compared.

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DESIGN OF ACTIVE STRUCTURED REACTOR FOR BIOGAS EXHAUST ABATEMENT

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Biogas is a valuable alternative fuel that can be used to produce heat and electricity in biogas engines or cogeneration units. However, turbines powered by this fuel are specific type of the combustors which places them somewhere between conventional industrial boilers and natural gas combustors. Depending on the initial biogas substrates used, the biogas composition varies in main components: CH_4 (50-75 %), CO_2 (25-45 %), H_2O (2-7 %), N_2 (< 2 vol %), O_2 (< 2 vol %), H_2 (< 1 vol %) and H_2S (20 – 20,000 ppm) [1,2]. The complex gas composition, relatively high NOx concentrations, high oxygen content and elevated temperatures requires unique catalysts that will conform high activity and selectivity requirements. Therefore, there is an urgent need to develop the highly efficient catalytic system to control the emission from biogas fueled engines. Because the concentration of unburned methane in the exhaust gases is too high from an environmental point of view, therefore we present the results of our work on $CoPd/Al_2O_3$ catalyst for methane oxidation processes. The catalyst was prepared by sonication method and supported on metallic gauzes, that revels high activity in a wide temperature and flow ranges. Two different exhaust composition mixture were tested: composition I – simulates dry exhaust gas composition without ammonia and unburned methane in 0.40 vol % to simulate biogas engine start-up or shut-down, and composition II – simulates the dry reacting mixture containing both unreacted methane and real gas mixture at the end of biogas engine. The obtained results for methane catalytic conversion (composition I) represent classical light of curves. The $T_{50\%}$ for the 1 dm^3/min is achieved for ca. 250°C and moves to the higher temperatures with the increasing of the gas exhaust flowrates. The almost complete conversion is achieved for all considered flowrates at 500 °C. As the reaction mixture becomes more complex (composition II), the $T_{50\%}$ moves towards the higher temperatures ca. 300 °C for flowrates 2-6 dm^3/min. The conversion at 500 °C varies between 90 % and 100 %, with the lowest catalytic activity for the shortest resident time.

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PP-23

Fe-FER FOR DeNO$_x$ AND DeN$_2$O APPLICATION: THE IMPORTANCE OF STABILITY FOR INDUSTRY

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Nitric acid is one of the most produced commodities worldwide. It is mainly used as a strategical chemical for the synthesis of fertilizers and in 2013 the production reached 78 million tons [1,2]. In recent years, the higher awareness in the greenhouse effect and in the environmental pollution, have highlighted the importance of a new development in the nitric acid tail gas treatment, especially concerning the N_2O and NO_x species [1]. Many metal oxide and zeolite catalysts have been developed for N_2O and NO_x abatement, each one with benefits and drawbacks. The state-of-the-art materials are based on Fe-zeolites which both show NO_x and N_2O abatement with the same catalyst. Many Fe-zeolites have been explored, such as Ferrierite (FER), ZSM5 and BEA [3]. In this paper, the comparison of fresh and laboratory aged Fe-FER and Fe-ZSM5 industrial catalysts, both supplied by ALSYS, was carried out. Fe-FER catalyst is a proprietary catalyst of CASALE and ALSYS and it is used in nitric acid plants [4]. The results from field and laboratory showed that Fe-FER will allow customers to benefit from a higher catalytic activity and greater stability compare to the current commercial solution with Fe-ZSM5.

Fe-FER and Fe-ZSM5 extruded catalysts were subjected to a simulated aging procedure to investigate the catalytic behavior under stressed condition. The catalysts showed a uniform cylindrical shape with a diameter close to 2 mm (with typical composition and shape of industrial catalyst). The catalytic tests were performed under relevant industrial deN_2O and deNO_x reaction conditions. The aging treatment lasted for 150 h at two temperatures (600 and 700 °C) with 12 % of O_2 and 6 % of H_2O.

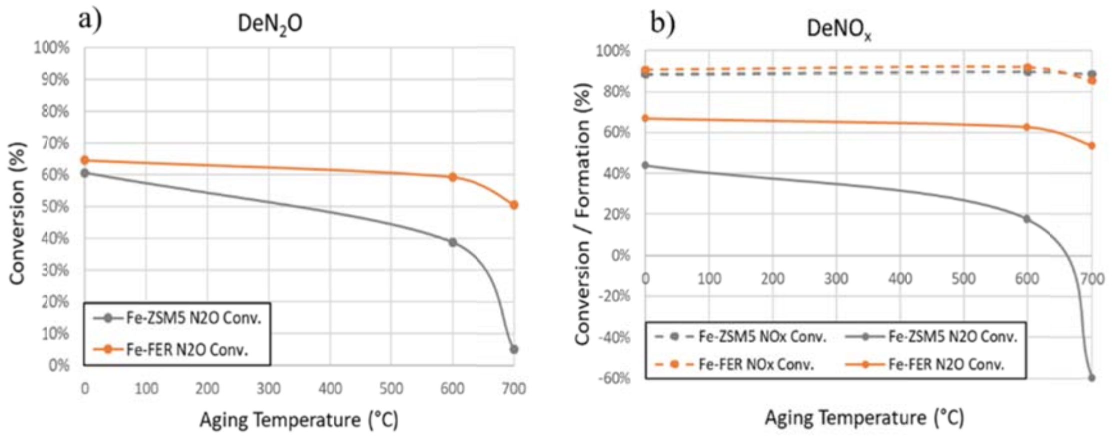

Figure 1. N_2O conversion in section a) and NO_x and N_2O conversion/formation in section b). deN_2O condition: NO 70 ppm, NO_2 30 ppm, N_2O 900 ppm, O_2 3.0 %, H_2O 0.3 % and N_2 balance; deNO_x condition: NO 325 ppm, NO_2 325 ppm N_2O 40 ppm NH_3 650 ppm, O_2 3.0 %, H_2O 0.3 % and N_2 balance. The point reported at 0 °C represents the fresh catalyst

The results, figures 1 a) and b), display the higher catalytic activity of Fe-FER compared to Fe-ZSM5. The superior Fe-FER catalytic activity becomes particularly significant after the aging procedure where a different catalytic behavior is observed. Fe-FER slightly decreased its activity, after the aging treatment, while the Fe-ZSM5 dramatically dropped its performances. In addition, N_2O formation is detected under deNO_x condition for Fe-ZSM5, while the Fe-FER does not exhibit any N_2O formation.

The characterizations performed revealed that the reduced activity of Fe-ZSM5 compared to the Fe-FER is due to the Fe species present in the catalyst.

In this work, representative industrial catalysts were investigated in industrial conditions before and after severe aging treatments. Results showed that Fe-FER is the most stable catalyst and exhibits high performance that can be used for tail gas treatment in nitric acid plants. Moreover Fe-FER is extremely selective in N_2 even after severe aging while the Fe-ZSM5 exhibited a larger undesired N_2O formation. The Fe-FER catalyst for deN_2O and deNO_x applications has superior performances compared to the Fe-ZSM5.

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GAS MIXING DYNAMICS IN VORTEX MIXER

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With the spread of mini/micro reactors in industrial applications, operational and geometrical parameters that govern the mixing mechanism in fast mixers have attracted many researches both by CFD modelling and experimental techniques. While the effect of the operational parameters on the flow field and the mixing mechanism in Confined Impinging Jets and T-Jets mixers have been studied extensively, hydrodynamics and mixing mechanism in mixers, made of a chamber connected by two or more tangential opposed jets, a.k.a. Vortex mixers, have not been assesed fully. These mixers, by design, offer a swirling vortex pattern near the jets [1] and because there is no impingement zone, establisment of equal momentum of jets is not necassary [2]. The effect of the operational parameters in terms of Reynolds numbers of the jets, on the hydrodynamics have been assesed for the mixing of methane/methane and methane/nitrogen gases using a vortex mixer of 10 mm diameter with two of 5mm feeding jets. The Reynolds numbers of the jets are covered for laminar and turbulent flows to identify the critical Reynolds number at which the flow regime changes. Flow dynamics were assessed by Smoke tracer using PIV system as well as 3D CFD.

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SERIES SOLUTIONS TO REACTION-DIFFUSION PROBLEMS IN CATALYTIC PELLETS WITH EXTERNAL MASS AND HEAT TRANSFER RESISTANCES

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The overall rate of many industrially important catalytic reactions depends not only on reaction kinetics but also on the rate of mass and heat transfer from the bulk phase to the outer surface of the catalyst pellet and the rate of mass and heat diffusion in the pellet. Depending on the pellet morphology and kinetic, process and transport parameters, the reaction behavior in the pellet can be complex, including the formation of a so-called dead zone where no reaction takes place [1-3]. The numerical solution of the corresponding two-point boundary-value problems is a time-consuming and sometimes even challenging task. Thus, approximate solutions are desirable as they can be easily implemented in the overall reactor model.

The primary aim of the present study is to derive the approximate solutions to the non-isothermal reaction-diffusion problems in the catalytic pellets for the case of arbitrary reaction kinetics, taking into account the presence of external mass and heat transfer resistances. The Taylor series expansion was successfully applied to solve reaction-diffusion problems with power-law kinetics [3]. In the present paper, we extend our approach to problems with arbitrary kinetics. Our analysis is justified by comparing approximate results with analytical and numerical ones for problems with and without dead-core solutions. The results confirmed that Taylor series expansion at x=1 is more precise than the one at x=0 for large values of Thiele modulus, as illustrated in Fig. 1. Moreover, even the six-term Taylor series expansion at x=1 is precise enough for engineering calculations as confirmed by comparison with exact analytical results.

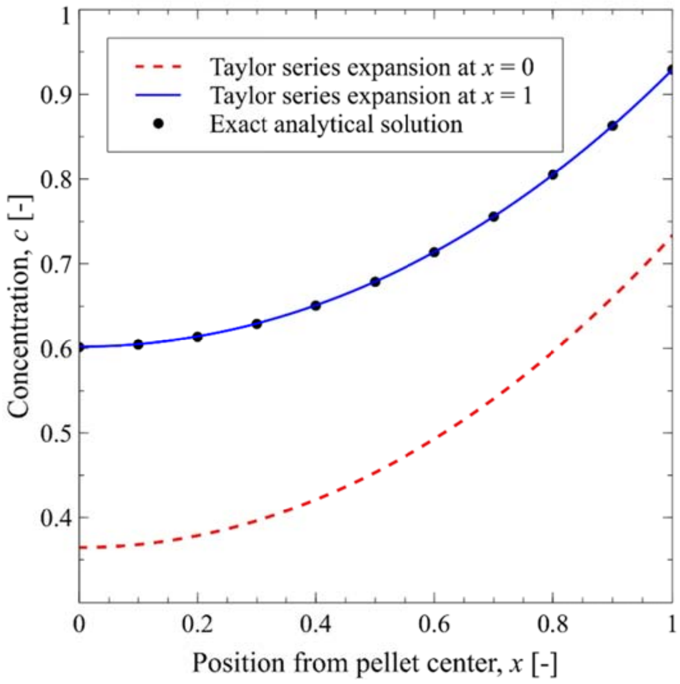

Figure 1. Comparison of approximate solution using Taylor series expansion at x=0 and x=1 with the exact analytical solution for the first-order reaction in a slab catalyst: Biot number Bi_m=10, Thiele modulus f=1.

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PP-26

CATALYTIC PERFORMANCE OF NICKEL SUPPORTED ON La-HEXAALUMINATE HIBONITE TYPE SYNTHESIZED FROM ALUMINUM SALINE SLAGS IN THE DRY REFORMING OF METHANE

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In recent years, there has been a disproportionate increase in the concentrations of greenhouse gases (GHG) present in the atmosphere. CH_4 and CO_2 are the gases that have the most contribution to the greenhouse effect. Dry methane reforming (DRM), offers an alternative to reduce the impact of these gases, since it uses them as a raw material for the production of synthesis gas (H_2 and CO).

The catalysts based on hexaaluminates are of great interest in catalytic reactions at high temperature due to their prominent thermal stability and resistance to sintering. In this work the synthesis of NiLa-hexaaluminates from the aluminum extracted from a saline slag waste [1-3] is presented and the materials used as catalysts for the dry methane reforming. Briefly, a refluxing 2 mol/dm^3 solution of HCl is used to extract the aluminum, giving 8.9 g_{Al}/dm^3 along with other metals as Fe, Ca and Mg, in lower concentrations. The aluminum solution is used to synthesize hexaaluminates by mixing with a stoichiometric amount of lanthanum nitrate and four methods of preparation are considered to obtain materials with differences in the textural properties. The nickel catalysts (10 wt.%) are prepared by wet impregnation of the supports previously calcined at 1273 K.

The solids were characterized by chemical analysis, adsorption of N_2 at –196 °C, TPR, SEM/EDX, and XRD.

The dry methane reforming reaction was carried out on an automated bench-scale catalytic unit, model Microactivity Reference from PID Eng&Tech, at 700 °C. The reactor was a tubular, fixed-bed, downflow one with an internal diameter of 0.9 cm. Catalyst samples (25 mg) were mixed with inert material in order to dilute the catalyst bed and avoid hot spot formation. The reactant mixture consisted of CH_4 and CO_2 with a molar ratio of 1:1, with helium as the balance gas up to a total feed flow of 50 cm^3/min., thus achieving a gas space velocity of $1.2 \cdot 10^4$ cm^3/g·h. Before reaction, the catalyst was reduced at 700 °C for 2 h. The reactant and the product streams were analyzed using an Agilent 6890 gas chromatograph system.

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The XRD characterization results for the catalysts are presented in Figure 1 (left), where the hexaaluminate phases can be observed indicating that it is possible to obtain this oxide from an industrial waste. The catalytic performance and stability of the synthesized catalysts are also summarized in Figure 1 (right). The catalyst with a higher specific surface also shows greater stability with the reaction time.

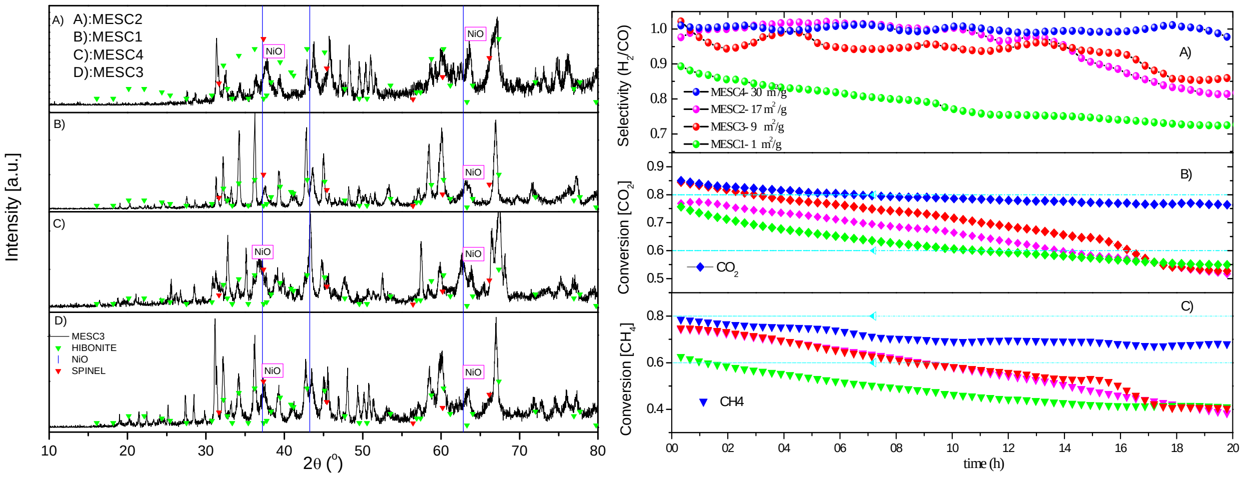

Figure 1. (Left) XRD patterns of the NiLa-hexaaluminate catalysts synthesized from aluminum extracted saline slags. Symbols: ▼ Spinel pattern 00-021-1152, ▼ Hibonite pattern 00-007-0785. (Right) Catalytic performance and stability of the synthesized catalysts, A) H_2/CO selectivity, B) CO_2 conversion, C) CH_4 conversion

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PP-27

INFLUENCE OF PARAMETRS OF GLASS-FIBER CATALYST PACKING ON ITS APPARENT ACTIVITY IN NO, CO, C_3H_8 MIXTURE

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At present time there is necessity to remove nitrogen oxides in gas mixtures where carbon monoxide and hydrocarbons are present, e.g. diesel fuel. Glass-fiber catalysts are known to possess unique properties such as low pressure drop, high transfer efficiency, high activity in NO reduction, CO and C_3H_8 oxidation [1]. The structure of cartridge and the preparation method is suggested to make contribution to catalytic activity. The aim of this study is to investigate the effect of preparation method and structured elements.

The precursor of active component was supported by both the conventional impregnation method (Pt/GFC-i) and by spraying the precursor solution (Pt/GFC-i) on the surface of glass-fiber fabric. Testing the activity of the samples was carried out on the lab-scale experimental setup. The total flow was 1.85 l/min per cartridge of catalyst. The catalyst cartridge is a system of alternating layers of fiberglass, corrugated and flat metal mesh or fiberglass and volume metal mesh. The catalyst design is shown in Fig. 1.

Fig. 1. Catalyst design with volume metal mesh (left) and corrugated and flat metal mesh (right)

The dependence of CO, NO, C_3H_8 conversion upon temperature at all GFC samples is demonstrated in Fig. 2. Conversion of CO starts at the low temperature and reaches 70 % at 150 °C. However, with a further rising temperature the CO conversion increases slowly without reaching 100 % due to external diffusion inhibition of reaction. At temperatures above 400 °C further CO conversion decreases and conversion of C_3H_8 begins, indicating that propane is oxidized to form both CO_2 and CO. The maximum conversion of C_3H_8 reaches 80 % and 68 %

depending on catalyst. The NO conversion begins at 200 °C, goes through a maximum at 300 – 350 °C and then decreases with increasing temperature due to more active involvement of oxygen as an oxidant instead of NO.

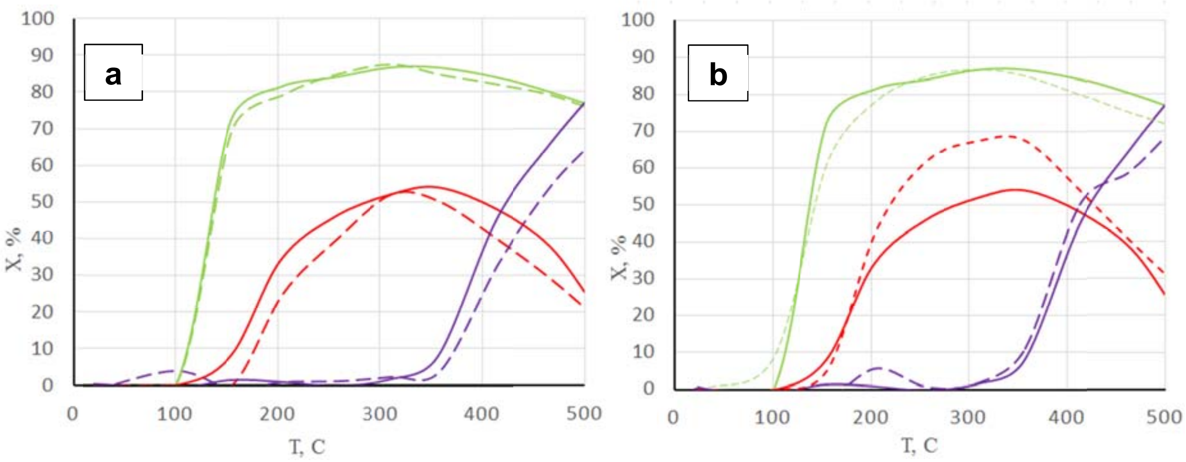

Fig. 2. CO (green), NO (red), C_3H_8 (blue) conversion vs temperature at a) Pt/GFC-i (solid) and Pt/GFC-s (dash) b) volume metal mesh (dash) and corrugated and flat metal mesh (solid)

It is seen that the activity of sample synthesized by impregnation is slightly more active. However, it should be noted that content of platinum in the sample obtained by impregnation is 4 times higher than that in the sample obtained by spraying, 0.085 wt % and 0.022 wt %, respectively. The geometry of structured elements doesn't appear to significantly affect the catalytic activity of CO and propane oxidation but produces definite difference in NOx reduction rate, with higher reduction activity for cartridges with volume metal mesh.

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PP-28

OPTIMUM CONTROL OF GASOLINE CATALYTIC REFORMING BASED ON OF KINETIC MODEL

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To start new catalytic processes in industry and intensification of existing production, it is necessary a detailed study of the laws of chemical reactions, which is fully reflected in the kinetic model of the reaction. The development of a kinetic model is the basis for the subsequent decision of problems of optimum control study catalytic processes.

When considering the catalytic processes taking place in multistage reactors, the optimal control methodology is used. Catalytic processes in multistage reactors or a cascade of reactors, with a series connection of the inputs and outputs of devices located one after another, are called multi-stage. In such reactor units y_0 – reactant concentration at the input to reactor stage; y_N – concentration at the exit from it. The reaction mixture at the exit of one apparatus is the input to the next apparatus. Real catalytic processes are described by phase variables y_i and control action vectors u_j. In fig. 1. presents the management of a multi-stage catalytic process.

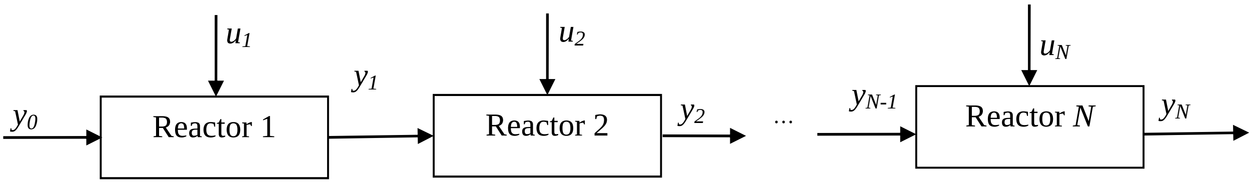

Fig. 1. Control of a multi-stage catalytic process

The paper considers the optimal control of catalytic reforming of gasoline based on the kinetic model [1-3]. The reactor block of the catalytic reforming process consists of three adiabatic reactors, each of which receives a mixture heated to the required temperature. Therefore, the conditions for the control: the temperature at the input to the reactor T^0_j, $j = 1,…3$.

For a complex industrial process of catalytic reforming of gasoline, the following optimality criteria are characteristic: 1) increase in the octane number of the reformate (the octane number by the research method – ONRM); 2) the indicator of the yield of the target product (the share of the product minus cracking gases); 3) restriction of volume fractions of benzene and the amount of aromatic hydrocarbons in the composition of marketable gasolines, in accordance with environmental requirements for Euro-5 grade brands.

A decrease in the content of aromatic hydrocarbons and benzene will lead to a decrease in the octane number of the reformate. Therefore, criteria 1) and 3) are contradictory. Then the optimal control problem is a multi-criteria optimization problem. The solution of the multicriteria optimization problem was carried out by the NSGA-II Pareto approximation algorithm [4].

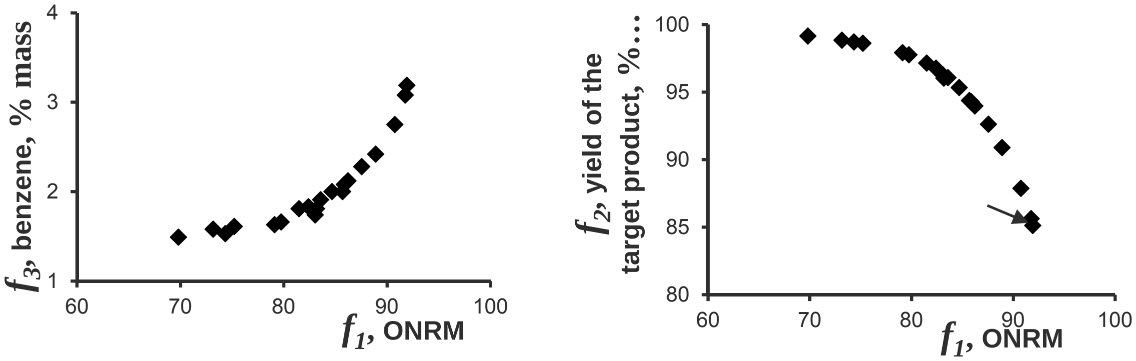

Fig. 2. Approximation of the Pareto front MCO-problems of catalytic reforming of gasoline

The non-improved combinations of the benzene content, ONRM, and reformate yield presented in the graphs of Fig. 2 – the boundary of the range of possible combinations of objective functions (Pareto front). The physical meaning of each point is as follows: at the current ONRM, the minimum possible benzene content (Fig. 2a) and the maximum reformate yield (Fig. 2b); at the current benzene content, the maximum possible ONRM and reformate yield; and at the current value of the reformate yield, the minimum benzene content with a possible maximum of ONRM. For each value Fig. 2 the optimal control is calculated – the temperature at the input to three rectors.

As a result, a regime was determined under which a reduction in the content of the amount of benzene from 4 to 3 % of the mass with a loss of ONRM by 1 point and an increase in the yield of reformate by 1.5 % of the mass is achieved.

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BATCH-TO-CONTI CONVERSION OF THE HOMOGENOUS MANGANESE CATALYZED GUERBET REACTION OF ETHANOL TO BUTANOL

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The sustainable conversion of (bio)ethanol, which is a widely available bioderived substrate into (bio)butanol, is a key step for upgrading the fuel properties of renewable produced ethanol as a fuel additive. The conversion of ethanol to butanol leads to fuel properties which are much closer to regular gasoline (90 % energy density compared to 70 % for ethanol).[1] A catalytic upgrade via the Guerbet reaction is an attractive route for this conversion. In the first step of this reaction a redox catalyst reduces primary alcohols and in presence of a basic catalyst the formed aldehyde undergoes an aldol condensation reaction to the resulting α,β-unsaturated aldehyde. This aldehyde is hydrogenated afterwards with the hydrogen (which is gained in the first step) to a longer alcohol. Although this reaction is known as a Guerbet reaction for more than hundred years and is well applicable for longer primary alcohols than ethanol, the conversion of ethanol to butanol has major issues in terms of yield and selectivity. Recent investigations of the reaction kinetics of the Guerbet reaction in our group had shown, that the complex reaction network is like a Ball-in-a-Maze-Game with a few different stepping stones with undesired reaction pathways (see figure 1).[2]

Figure 1. Representation of the Guerbet reaction network as a ball-in-a-maze game

Manganese pincer transition metal complexes have shown great potential for enabling this conversion, with 34 % yield for ethanol to *n*-butanol and with good selectivity.[3] Manganese as metal atom could be an ideal candidate for catalyzing this conversion because of its economic and environmental friendliness. With further optimization of this manganese-based catalyzed reaction, a batch-to-conti transition is to be carried out in a continuous plug flow reactor for an economic feasibility study. Furthermore, an investigation of a suitable reactor design calculated with reactor design programs should find an applicable reactor for this complex one-pot multi-step-reaction to reduce the mentioned issues the Guerbet reaction has with ethanol (low conversion rates and bad selectivities).

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REVIEW OF KINETIC MODELS OF OXIDATIVE COUPLING OF METHANE AND METHANE DEHYDROAROMATIZATION

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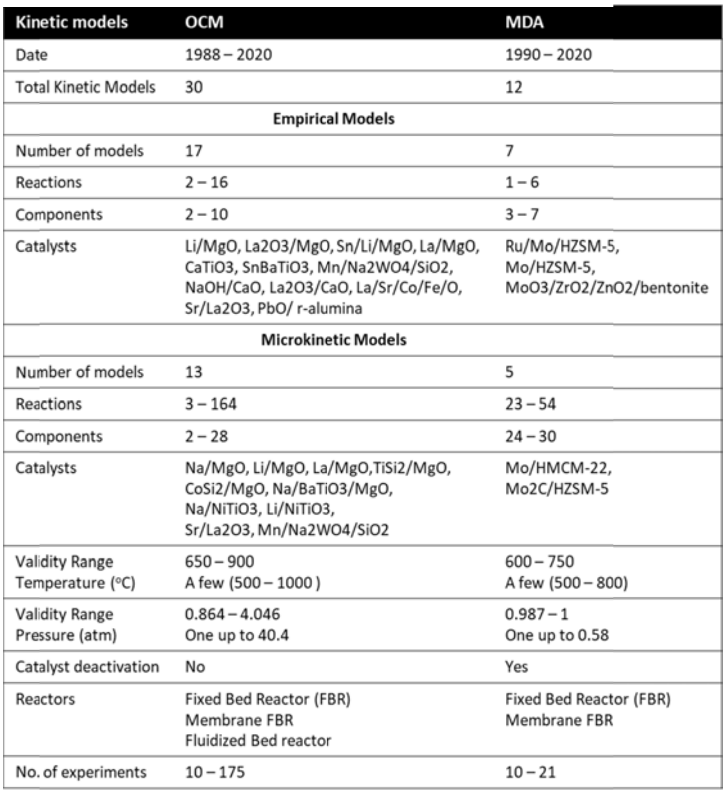
This work compiles, reviews and highlights the pitfalls of reported kinetics models in the open literature related to two promising direct methane conversion to chemicals processes – oxidative coupling of methane (OCM) and methane dehydroaromatization (MDA) reactions. Both are highly attractive and promising reactions to produce C2+ and C6+ compounds, respectively, in a direct step that simplifies the production process, makes it more energy-efficient, and reduces its CO_2 emissions. However, both reaction routes are not yet commercial due to various technical challenges related to strict heat management as in OCM, very fast catalyst deactivation as in MDA, and high energy requirements overall [1]. Mathematical modeling across the scales from micro to macro is essential to overcome these technical challenges. Both reactions are catalytic, have complex reaction schemes with many intermediate components in the gas phase and at the catalytic surface, and require special considerations to obtain reliable kinetic experimental data [2]. Several studies have been reported in the literature to develop kinetic models for these reactions [3]. This work aims to review all of these studies and highlight pitfalls in the formulation and reporting of these kinetic models. The selection to study these specific reactions is part of an ongoing project that aims to find the potential for synergetic effects by combining both chemistries to overcome the earlier mentioned technical challenges.

First, a list was compiled for all kinetic models of these two reactions. They were then classified based on the catalyst used, validity ranges of the operating conditions, components and reactions, formulation basis, type of experimental validation, number of kinetic experimental data, type of experimental setup and number of citations of the kinetic model. Further, a tree diagram was built for a few kinetic models to present how the kinetic model is improved and utilized in various other studies.

Table 1 shows an overview summary of all the kinetic models for both reactions as collected in this work. All kinds of kinetic models have been reported, from simple power law models to more detailed mechanistic models. The total number of found kinetic models for OCM and MDA are 30 and 12, respectively. For OCM, most kinetic models are reported for Li/MgO and Mn/Na_2WO_4/SiO_2 with reactions involving CH_4, O_2, C_2H_6, C_2H_4, C_3H_8, C_3H_6, CO, CO_2, H_2 and H_2O. Whereas, for MDA, most kinetic models are reported for Mo/HZSM-5 with reactions involving CH_4, C_2H_4, C_2H_6, C_6H_6, C_7H_8, $C_{10}H_8$, H_2 and inert.

literature



Kinetic models	OCM	MDA
Date	1988 – 2020	1990 – 2020
Total Kinetic Models	30	12
	Empirical Models	
Number of models	17	7
Reactions	2 – 16	1 – 6
Components	2 – 10	3 – 7
Catalysts	Li/MgO, La2O3/MgO, Sn/Li/MgO, La/MgO, CaTiO3, SnBaTiO3, Mn/Na2WO4/SiO2, NaOH/CaO, La2O3/CaO, La/Sr/Co/Fe/O, Sr/La2O3, PbO/ r-alumina	Ru/Mo/HZSM-5, Mo/HZSM-5, MoO3/ZrO2/ZnO2/bentonite
	Microkinetic Models	
Number of models	13	5
Reactions	3 – 164	23 – 54
Components	2 – 28	24 – 30
Catalysts	Na/MgO, Li/MgO, La/MgO,TiSi2/MgO, CoSi2/MgO, Na/BaTiO3/MgO, Na/NiTiO3, Li/NiTiO3, Sr/La2O3, Mn/Na2WO4/SiO2	Mo/HMCM-22, Mo2C/HZSM-5
Validity Range Temperature (°C)	650 – 900 A few (500 – 1000)	600 – 750 A few (500 – 800)
Validity Range Pressure (atm)	0.864 – 4.046 One up to 40.4	0.987 – 1 One up to 0.58
Catalyst deactivation	No	Yes
Reactors	Fixed Bed Reactor (FBR) Membrane FBR Fluidized Bed reactor	Fixed Bed Reactor (FBR) Membrane FBR
No. of experiments	10 – 175	10 – 21

An effort was made to replicate some of the empirical kinetics models which lead to identifying major pitfalls in the reporting and formulation of these kinetic models that were related to typing errors, incomplete or wrong kinetic expressions formulations, missing design parameters, misrepresentation of results, unavailability of readily usable experimental data and statistical results for model's accuracy. Besides the challenges of having reliable intrinsic experimental data due to steep temperature profiles, important information is missing which includes like accounting for key components and lumping of many components.

Full details of this review and its finding will be presented in this work. Sharing these findings will have a high scientific value, highlight common pitfalls, and create a discussion on ways to avoid technical challenges for kinetic modelling and obtaining experimental kinetic data. Further, this work will draw attention towards reconsidering how kinetic models and experimental data are exchanged in the scientific community with the rapid advancements of the digital era we live in.

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PP-31

HYDROAMINOMETHYLATION OF A LONG CHAIN OLEFIN: INFLUENCE OF OPERATING PARAMETERS

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Introduction

Amines are important basic chemicals, which are widely used in many research areas as chemistry, medicine, biology and material science and industrial productions [1]. The reaction of the hydroaminomethylation (HAM) offers a direct and atom-efficient way specially to provide aliphatic amines, which are a versatile feedstock and key intermediate for advanced chemicals [2]. In the frame of «Green Chemistry» renewable raw materials getting more and more important. Therefore, the Collaborative Research Center Transregio 63 (SFB) financed by the German Research Foundation (DFG) develops methods and strategies to adapt established reactions to process renewable feedstocks. Focus of our work is the evaluation of the potential of complex homogeneously catalyzed tandem reactions using the rhodium-catalyzed HAM (hydroformylation (Hyfo) + reductive amination (RA)) of 1-decene as example. To recover the expensive Rh-catalysts, innovative thermomorphic solvent systems (TMS) are applied [3]. In TMS the separation between products and catalysts is realized through exploitation of temperature dependent miscibility gaps in mixture of solvents of different polarity [3]. In this contribution the observed reaction network (figure 1) and the reaction kinetics of the HAM will be investigated for process development and optimization. The influence of the operating parameters: temperature, pressure and synthesis gas composition are experimentally and model-based studied.

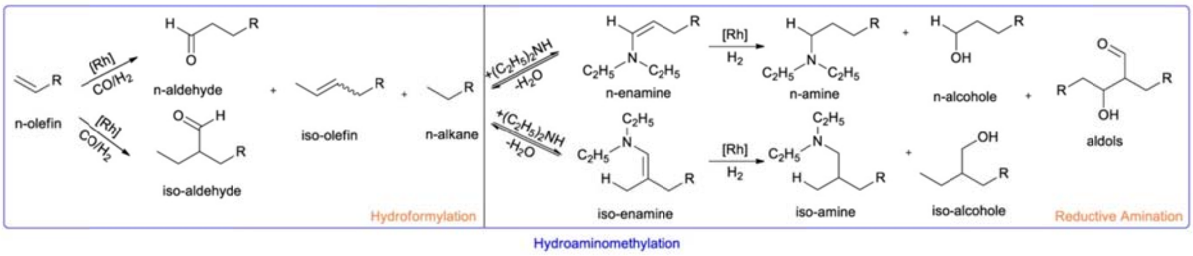

Figure 1. Main and side products of the rhodium-catalysed HAM of a linear olefin

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Experimental

Kinetic experiments were conducted in a high-pressure reactor system (Parr) equipped with pressure and temperature controller as well as a gas supply system [4]. The solvent system was constituted of 1-decene (Dec), methanol (MeOH) and dodecane (Dod) (w_{MeOH} : w_{Dod} = 50:50, w_{Dec} = 10 w-%). The second substrate diethylamine (DEA) was added in the ratio $\alpha_{DEA:Dec}$ = 8:7. The catalyst was formed from the pre-catalyst Rh(1)(acac)(COD) and the ligand SulfoXantphos. For the parameter study and estimation, experiments in the temperature range of 100 °C – 140 °C, the pressure range of p_{total} = 15 bar - 50 bar and with a hydrogen fraction of 0.33 – 0.66, were performed.

Results and discussion

Based on the experimental observations a reaction network for the HAM of a long chain olefin (1-decene) was developed considering 16 species (figure 1): the Hyfo interme-diates *n/iso-aldehydes*, the Hyfo side products *iso-olefin* and *n-alkan*, the RA interme-diates *n/iso-enamine*, the desired product *n-amine*, the RA side products *iso-amine*, *iso/n-alcohol* and *aldols*, the RA co-product water and the educts 1-decene, diethyla-mine, hydrogen and carbon monoxide.

In contrast to the RA [5], initial HAM experiments re-vealed a reduced reaction rate concerning the for-mation of the desired amine. Temperature and pressure have been increased to achieve almost total conversion of the substrate 1-decene and a yield of n-amine of about 86 %. Based on the experiments varying temperature, pressure and gas composition as well as the postulated catalytic reaction mechanisms for the first time a mechanistic kinetic model was derived and the parameters have been esti-mated [4]. Looking at the temperature influence model and experiments are in good agreement (figure 2).

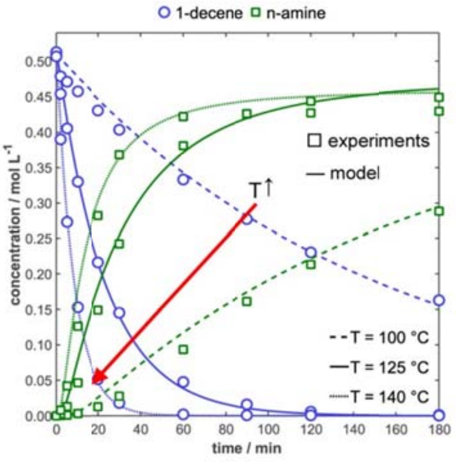

Figure 2. Temperature influence of the Hydroaminomethylation reaction, con-ditions: MeOH:Dod = 50:50, $\alpha_{DEA:Dec}$ = 8:7, w_{Dec} = 10 w-%, x_{Cat} = 0.08 mol-%, $\alpha_{Rh:P}$ = 1:7, T = 125°C, p_{tot} = 40 bar, CO:H_2 = 1:2

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POTENTIAL OF MONOLITHIC MEMBRANE PORE-THROUGH-FLOW BIOREACTORS FOR THE PRODUCTION OF GALACTO-OLIGOSACCHARIDES

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Introduction

Immobilized enzymes are widely used in biocatalysis and bioprocess technology. The advantages of immobilized enzymes instead of enzyme solutions are the increasing stability, the opportunity to operate in a continuous system and the sustainability with respect to consumption of cost intensive enzymes. In any case the type of support is crucial for immobilization efficiency and substrate mass transfer [1]. Methacrylate based monolithic macro porous carriers with suitable hydrodynamic properties can be used as Convective Interaction Media (CIM®). These monoliths are characterized by high mechanical and chemical stability as well as efficient mass transfer by convective pore flow through the pores. The convective transport of the molecules in the monolithic pore structure to the active centers dominates and there are no diffusion limitations [2]. To reduce protein surface interactions and maintain a stable linkage with the support, the immobilization technique must be well selected. To prevent an activity loss of the immobilized enzyme it is crucial that the functional groups involved in the linkage with the support are not situated on active sites of the protein [3].

The main goal of this study is to demonstrate the potential of carboxydiimidazol (CDI) activated pore-through-flow monolith as support for a covalent immobilized β-galactosidase to catalyze the synthesis of galacto-oligosacchachides (GOS) from lactose (Fig. 1A). To evaluate the potential in a broad parameter range, the conventional batch reactor experiments serve as a reference to compare with the membrane bioreactor. Furthermore, different reactor configurations were studied by simulations based on a pore-through-flow membrane reactor model and suitable reaction kinetics [4-5].

GOS synthesis in a CIM® CDI monolithic enzyme reactor

GOS are classified as prebiotics, defined as non-digestible food ingredients which stimulate beneficial colon bacteria. There is a great interest in the application of GOS as health-promoting food supplements [5-6]. In screening experiments the monolithic reactor was studied initially for 3 different chemical linkers (ALD, EDA, CDI) and activation procedures.

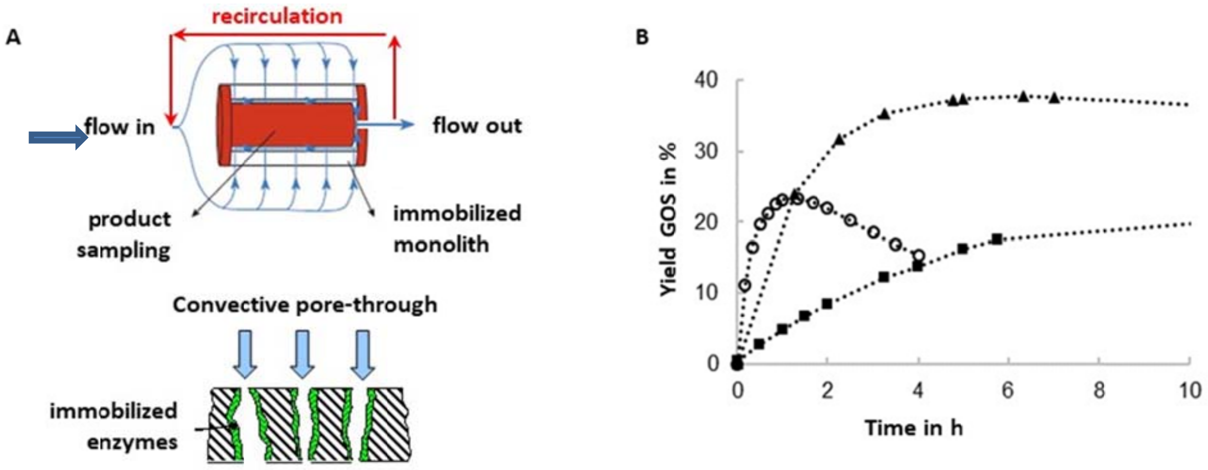

Fig. 1. (A) Principle of monolithic enzyme reactor and (B) GOS yield produced in Batch (O) and with the immobilized enzyme in a monolithic reactor on CDI (▲) and ALD (■)

Experimental and model-based characterization of the monolithic reactor

In terms of protein binding, performance and long-term stability of the enzyme regarding GOS synthesis, the CDI activated support was selected as illustrated in Fig. 1B. It can be recognized that the highest yield of GOS was obtained in the monolithic reactor with internal recirculation, which outperformed the batch reactor with free enzyme at comparable times. In particular, the GOS degradation as an undesired series reaction can be sufficiently suppressed if the reaction is not controlled by diffusion. The recirculation stream in the monolithic reactor offers a new degree of freedom for reaction and process control of the biocatalytic reaction. Therefore, further model-based simulations studies based on mechanistic reaction kinetics [5] were performed for the immobilized monolithic pore-through-flow membrane reactor [4] to optimize the operating parameters and to support an upscaling.

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BIOGAS CONVERSION TO SYNGAS IN AN ENLARGED LABORATORY PILOT TUBULAR REACTOR

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The increasing energy demand and need to reduce greenhouse gas (GHG) emissions over the last decades have become the two most serious challenges of the modern era. Biogas is one of the renewable sources that could be used for the production of syngas and hydrogen via syngas. Hydrogen is the most promising energy carrier, while syngas is a building block for producing a wide number of petrochemicals. Among the existing biogas utilization technologies, dry reforming can convert two major greenhouse gases in biogas – methane and carbon dioxide into syngas (mix of hydrogen and carbon monoxide).

In our previous work [1] the high-effective multicomponent Co-based catalysts for hydrogen-enriched syngas production dry and steam conversion of model biogas were developed and tested at laboratory scale using a quartz flow reactor with a volume of 20-100 ml. In application works, the completion of a laboratory stage of studying is followed by a scale-up of the process, which implies a gradual enlargement of a set accompanied with increasing the target product production [2]. To provide the enlarged scale of the catalyst testing and optimization of the process parameters, a laboratory reactor was designed to meet the following requirements:

- resistance to the corrosive environment under high temperatures (steam and carbon dioxide, which are the main components of feedstock);
- operation in a broad range of temperatures varied within 50-1000 °C;
- operation under pressures varied within 1-30 atm (despite the fact that the optimal pressure for methane reforming is an atmospheric one, higher pressures are necessary for the following synthesis gas conversion);
- reactor type with a fixed bed of catalyst is a tubular one, which is characterized by simplicity of construction and operation;
- low cost of the reactor and its repair. Drawings of the reactor and its parts were made using AutoCAD-2016 software corresponding to CAD systems (computer-aided design).

To make a flow tubular reactor the Inconel 600 alloy, which is the nickel-chrome alloy developed purposely for systems requiring high resistance to corrosion under high temperatures, was chosen. The tube of Inconel with an inner diameter of 20 mm, the wall thickness of 10 mm, and a tube length of 900 mm that corresponded to the inner reactor volume is 300 ml was used. The impossibility of welding of Inconel items caused the need to use two types of 4-bolt flanges – captive flange and split flange made of stainless steel. The thermocouple was placed in a special thermo- and corrosion stable cover and inserted from the top of the reactor through the fitting.

The reactor was connected with other standard parts of a set including gas flow meters, temperature and pressure regulation and control units, water pump, cooler, and separator.

The test of the catalyst in the designed reactor showed acceptable convergence and confirmed high stability of the Co-based catalyst in the production of syngas from model biogas in the temperature range of 700-800 °C, P = 1-2 atm. Under these conditions, the extent of conversion of methane was higher than 80% and stable for 100 hours. The H_2/CO ratio in the formed syngas was varied depending on the feed composition.

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PP-34

WAX ESTER PRODUCTION FROM WASTE FISH OIL

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Wax esters are long-chain esters derived from fatty acids and alcohols, both with chain lengths of twelve carbons or more [1]. They are non-toxic and biodegradable and can be extracted from animal and plant materials such as beeswax, spermaceti oil and jojoba oil. They are widely used in lubricant, pharmaceutical, cosmetic and plasticizer industries [2]. However, costs and availability of this resources hinder the large-scale application of wax ester synthesis. Thus, attempts to synthesize wax esters with cheaper raw materials in a shorter time are issues of great significance. In this context, the valorization of wastes and biomasses, long treated and minimized to reduce environmental impact, is a valid and promising alternative.

Nowadays the fishing is one of our most important industries which always try hard to increase the production. This wealth has led to increased production, transformation and preservation of fish industries which generate large amounts of waste. During fish processing operations, indeed, a significant amount of fish by-products is generated in the form of viscera, frame, head, skin scales, etc… [2]. Although, some parts of these processes wastes are utilized as low-cost ingredients in animal feed production or as fertilizer, the main bulk is looked at as worthless garbage and dumped into the river or landfill, creating both disposal and pollution problems [2,3]. It has been noticed that most of these wastes, especially the visceral mass, contain a high amount of oil in the range 2-35 wt. %, depending on species. In fact, many recent studies have been interested in the valorization of fish-waste. The one that has received the greatest attention is the synthesis of biofuels. Moreover, considering that fish oil possesses several fatty acids with health benefits it can be considered wax ester production for cosmetic and pharmaceutical productions. In particular, the wax ester synthesis can be carried out by esterification reaction of alcohol and fatty acid, or transesterification of vegetable oils or fats with alcohols in the presence of a chemical catalyst. On the other hand, chemical catalyst presents several limitations, while a good alternative can be the use of enzymatic catalysis. The application of enzymes, in particular lipases, in a large scale process is often limited due to their high cost, and sensitivity to high temperature and organic solvents. Moreover, it is difficult to separate enzymes from the reaction system, which limits its recovery and may lead to contamination of the final product. In order to overcome these problems, lipases have been immobilized by several methods. Indeed, immobilization of an enzyme can: (i) reduce the operational process cost and (ii) enhance the reusability. Immobilized enzymes are often more stable with pH than free enzymes [4].

The aim of this work was to synthesize wax ester from fish oil for use in cosmetic and pharmaceutical applications. Particular attention has been devoted to the optimization of the preparation of the enzymatic catalyst, which consists of hydrophilic hyper-cross-linked resin (NH_2-HCL) anchoring the enzyme through physical bonds. The immobilization process and catalytic tests were monitored using Magnetic Resonance Imaging (MRI). The synthesized wax ester was compared with a natural wax and analyzed according to the Standards.

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PP-35

OPTIMIZATION OF MULTISTAGE GASOLINE PRODUCTION IN HYDROCRACKING, CATALYTIC CRACKING, REFORMING AND COMPOUNDING PROCESSES

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The study of motor fuels production processes mechanisms and kinetic regularities is an important issue. The existing gasoline and diesel fuels production technologies do not consider the chemical interaction between the mixture components, necessitating the need for quality margin of the important properties (octane and cetane numbers, pour points, etc.). This translates to the economic indicators drop due to the overspending of expensive components used during production. The diseconomies reaches a significant value at large scale plant.

The aim of the work is to solve a multiobjective problem using mathematical modeling, taking into account the hydrocarbon conversion thermodynamics and kinetics, the processes unsteadiness and the mixed gasoline components chemical interaction both at the catalytic conversion and the intermolecular interactions intensity at the compounding stages. The main gasoline production processes are naphtha reforming and vacuum gasoil catalytic cracking. The vacuum gasoil catalytic cracking kinetic description basis [1] is the reactions scheme of high molecular weight alkanes (C_{13}–C_{40}), cycloalkanes and arenas of feedstock, light and heavy gas oil, arenas, cycloalkanes, alkenes and alkanes (C_5–C_{12}) of gasoline.

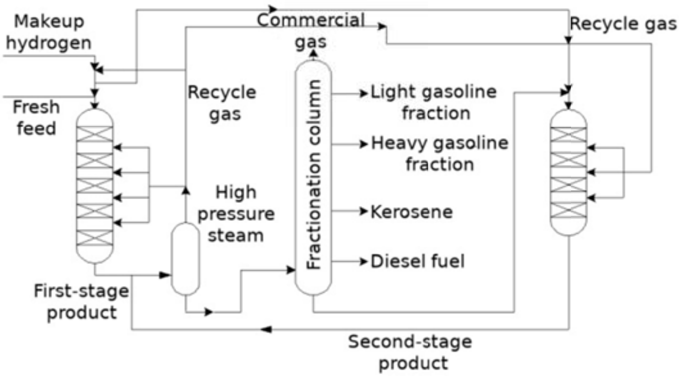

Figure 1. Brief description of hydrocracking

Unlike catalytic cracking, hydrocracking and reforming occur in a hydrogen atmosphere that inhibits the coke formation and have the common mathematical description. The hydrocracking feedstock and product composition studies and the quantum-chemical calculations showed that the most probable reactions are hydrocracking: $C_nH_{2n+2} + H_2 = 2C_nH_{n+1}$, isomerization $H\text{-}C_nH_{2n+2} = H\text{-}C_nH_{2n+2}$, polyalkyl aromatics hydrogenization $C_nH_{2n-6} + 3H_2 = C_nH_{2n}$ and coke formation.

The new gasoline production optimization method was proposed, implemented and introduced into industrial plant as the research result. The method essence is to optimize the manufacturing processes of mixture components, such as the hydrocracking and catalytic cracking gasoline, reformate, isomerizate, alkylate.

$$\begin{cases} G\cdot\dfrac{\partial C_i(x)}{\partial Z} + G\cdot\dfrac{\partial C_i(x)}{\partial V} = \sum\limits_{j=1}^{n} k_j(x)\cdot C_i(x) + \sum\limits_{j=1}^{n} k_j(x)\cdot C_i(x)\cdot C_{H_2} + \sum\limits_{S} k_s(x^{/})\cdot \nu(x,x^{/})\cdot C_i(x^{/}) \\ G\cdot\dfrac{\partial T}{\partial Z} + G\cdot\dfrac{\partial T}{\partial V} = -\dfrac{1}{C_p^m}\cdot\sum\limits_{i=1}^{n}\sum\limits_{x=1}^{m} \pm\Delta H_i(x)\cdot w_i(x) \end{cases}$$

$$Z = 0, V = 0,\ C_i = C_{i0}, T = T_0;$$

$C_i(x)$, $k_j(x)$, $k_s(x^{/})$ – hydrocarbon content and reaction rate constants distribution functions; $\nu(x,x^{/})$ – probability distribution functions of the alkanes bond breaking in hydrocracking; V – catalyst load volume, m^3; T – the process temperature gradient, K; C_p^m – the mixture heat capacity, J/mol·K; ΔH_i – the reaction enthalpy change, kJ/mol; x – the carbon atoms number in a hydrocarbon molecule; j – the hydrocarbon groups number (alkanes, isoalkanes, cycloalkanes, arenas, resins, coke). The first term in the material balance equation describes the reactions in which hydrogen is not involved, the second describes the reactions involving hydrogen, the third describes the alkanes hydrocracking reactions.

The fuel compositions optimization, based on data on the hydrocarbons composition in mixed flows, physico-chemical properties and the mixture components volume, must be carried out taking into account changes in the catalyst activity and processed feed hydrocarbon composition. The new method allows to reduce commercial gasolines quality margin by regulating the mixed gasoline formulation in accordance with the requirements and the feedstock and end product work-order quantity. The principle of the proposed method is to perform successive stages of calculation and optimization of the mixed components manufacturing processes.

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PP-36

CFD MODELLING OF REACTORS FOR REDUCING THE ENVIRONMENTAL IMPACT OF SO_2 EMISSIONS

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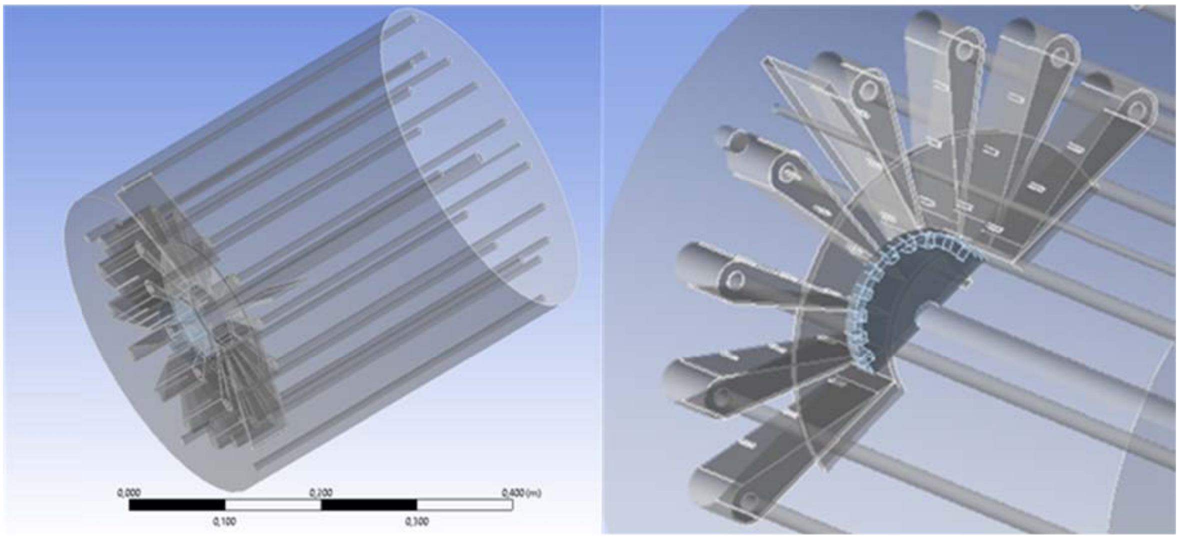
According to current regulations, the concentration of SO_2 in flue gas should not exceed 200 mg/m^3 (STP). In the case of SO_2-rich gases in metallurgical processes (>4 vol. % of SO_2), an alternative to the production of sulphuric acid may be absorption in limestone suspension combined with the production of quality gypsum. In the Institute of Non-Ferrous Metals (IMN) in Gliwice a method has been developed and verified based on large-scale laboratory experiments. The method focuses on deep desulphurisation of the process gas containing up to 10 vol. % of SO_2, with the process carried out in a bubble reactor equipped with a slot gas disperser. To study the large-scale implementation of the process a CFD model of the reactor was developed. The present study shows the geometrical representation of the bubble reactor in ANSYS Fluent numerical environment, alongside simulation results concerning the hydrodynamics of process gas desulphurisation in bubble reactors at a laboratory (40 dm^3) and large-scale laboratory (1.5 m^3) scales. In the simulations the following operating parameters were varied: gas load on the paddles of the slot disperser, rotation velocity and direction, the flow rate of the oxidizing gas and gypsum concentration in the suspension, and the effect of these parameters upon suspension velocity and the velocity and compression of the gas phase was assessed. Also, a detailed analysis was performed of the hydrodynamic phenomena occurring in the various areas of the two reactors. This analysis confirmed the principal qualitative and quantitative conclusions resulting from the relevant experimental desulphurisation studies in both laboratory and large-scale laboratory bubble reactors.



Geometry of bubble reactor of 40 dm^3 volume designed in CFD programme

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PP-37

SIMULATION THE HYDRODYNAMIC CHARACTERISTICS OF AN EBULLATED BED

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Ebullated-bed reactors are used for hydroprocessing technologies and for the deep conversion of oil residues. The packed catalyst bed is fluidized by a bottom-up flow of liquid feedstock mixed with a hydrogen-containing gas. Moreover, only part of the solid particles occurs in the suspended state. Slight fluidization of the bed makes it possible to push apart the catalyst particles in the bed and significantly reduce pressure drop on the bed. This makes it possible to more efficiently use hydrogenation catalyst by reducing its size [1, 2].

The study of the hydrodynamic characteristics of the ebullated bed was carried out using CFD simulation. The Euler multiphase approximation was used to study the behavior of catalyst particles in a two-phase gas-liquid flow.

The parameters of the two-phase flow and catalyst particles used in the simulation are shown in Table 1.

Table 1.

No	Parameter	Units	Range
1	Liquid density	kg/m^3	703
2	Liquid viscosity	kg/(m*s)	0,00012
3	Superficial liquid velocity	m/s	0,005--0,13
4	Superficial gas velocity	m/s	0,003
5	Particle density	kg/m^3	1814
6	Volume equivalent diameter	mm	0.25--3.0
7	Pressure	Pa	1.038*10^7
8	Temperature	K	698

The influence of the velocity of the liquid phase and the particle size of the catalyst on the porosity and pressure drop in the ebullated bed is investigated.

Figure 1 shows the effect of the superficial liquid velocity on the value of the Euler number divided by the height H of the ebullated bed. $Eu = \Delta P/\rho_{gasoil}W^2_{0,gasoil}$. W^0_{gasoil} is the superficial input velocity of the liquid phase. It is shown that an increase in the velocity of the liquid phase leads to a decrease in the Euler number in inverse proportion to the square of the velocity of the liquid phase, $Eu/H \sim W^{-2}_{0,gasoil}$.

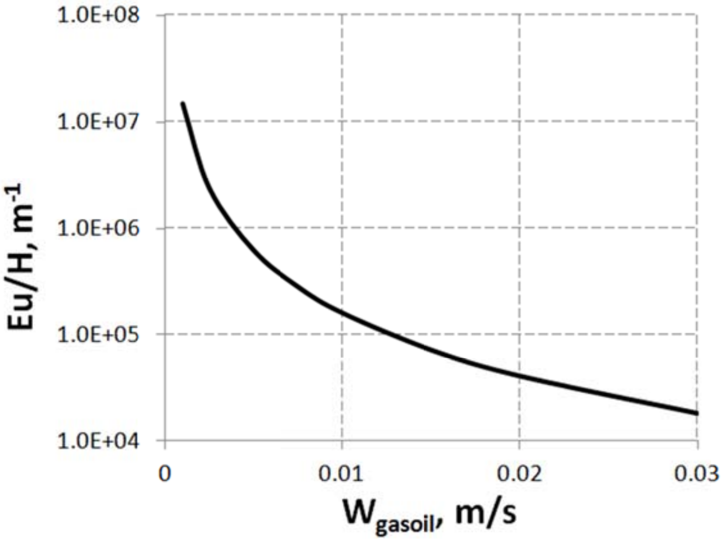

Fig. 1. Dependence of the value of the Euler number on the velocity of the liquid phase

Figure 2 shows the effect of the particle size of the catalyst on the volume fraction of the catalyst VFp averaged over the volume of the ebullated bed. VFp = 1-ε, where ε is the porosity of the bed.

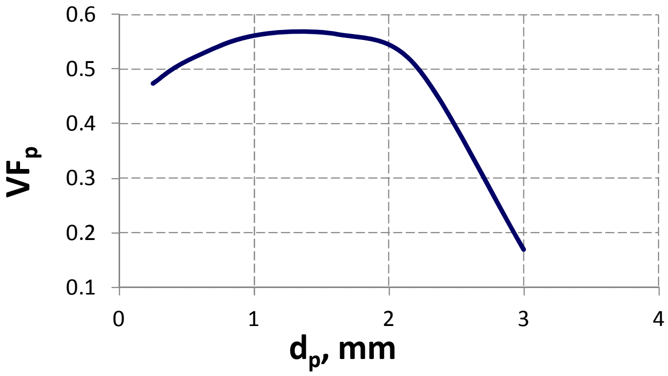

Fig. 2. The effect of the particle size of the catalyst on the volume fraction of the catalyst VFp, averaged over the volume of the ebullated bed

The dependence $VF_p = F(d_p)$ has a maximum for particles with an equivalent diameter in the range $1.0 < d_p < 2.0$ mm.

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OXYGEN PERMEABILITY OF THE MIEC OXIDES MICROTUBULAR MEMBRANES PRODUCED WITH ADDITIVE METHODS

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Complex oxides with mixed ionic-electronic conductivity (MIEC oxides) attract attention by the possibility of their application in the chemical, gas and energy industries. They can be used in different technologies, for example, producing pure oxygen, methane conversion, electrochemistry processes. Membranes based on MIEC oxides allow separating oxygen from the air with 100 % selectivity. The integration of such membranes into catalytic reactors will allow combining the stages of oxygen separation and partial oxidation of hydrocarbons.

It is necessary to develop technologies of obtaining gas-tight membranes based on MIEC oxides for successful application in catalytic reactors. The most promising way is the production of membranes in the form of microtubes, that can significantly increase the oxygen permeability.

Vision of the oxygen transport processes and their dependence on the geometric parameters of the membrane are needed to control the functional characteristics of the membrane. The lack of standard techniques for the synthesis of microtubular membranes leads to an irreproducible microstructure of the final product [1-3].

The aim of this work is studying of oxygen permeability of a porous MIEC oxides microtubular membrane with a controlled microstructure using 3D printing, phase inversion and dip-coating methods for their production.

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PP-39

MODELING OF CELLULOSE ASSISTED COMBUSTION SYNTHESIS TECHNIQUE FOR CATALYST PREPARATION FOR HYDROGEN PRODUCTION FROM ETHANOL REFORMING

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1. Introduction

Cellulose assisted combustion synthesis (CACS) has emerged as a novel variation of traditional solution combustion synthesis (SCS) over the past decade for the synthesis of catalytically active nanomaterials [1–3]. Fig. 1 shows a schematic representation of the CACS process, where the active solution is impregnated in a thin cellulose paper, which is dried and locally combusted to initial the exothermic combustion reaction. Due to exothermic nature of the reaction, a self-sustained combustion front propagates leaving behind the nanoparticles with high porosity and large surface area suitable for catalytic applications. Presence of cellulose acts as an extra fuel to enhance combustion, while being restricted to a thin layer helps in post combustion quenching of the products resulting in smaller nanoparticles with high surface area. Presence of fine cellulose fibrils affects the thermo-physical properties and energy density of the system that in turn alters the nature of combustion reaction and thermal wave propagation in CACS. In addition, the void spaces and pores may generate a complex network of micro and nano-reactors as opposed to a continuous volume of reacting species in SCS. The goal of this presentation is to understand the reaction kinetics and develop a theoretical model to describe the effect of various parameters that influence the CACS process, such as combustion temperature, heat transfer, combustion wave propagation velocity etc.

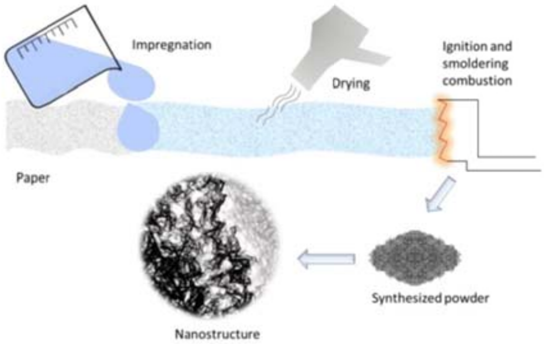

Fig. 1. A schematic representation of cellulose assisted combustion synthesis [1]

Specifically the objective is to model the movement of the temperature profile and identify the key parameters that control the heat transfer processes taking place in the combustion front. These factors are critical to determine the temperature of the reaction front, which in turn determines the textural and chemical characteristics of the catalysts.

2. Method

To develop the model, experimentally combustion front was monitored to evaluate combustion temperature, wave propagation velocity etc. using an IR Camera, along with a digital camcorder. For simplicity, we assumed one dimensional geometry and finite length with an exothermic reaction between two reacting solids (nitrate/cellulose and glycine) generating another solid (catalyst) and gases being evolved during reaction. Differences between the properties of products and reactants and their effect on the combustion front are also included in the model. The reaction media containing a mixture of two solids is ignited at one end with a specify amount of heat flux to start the exothermic reaction. The reaction is represented approximately as a non-catalytic reaction with the following stoichiometry:

$$A(s) + B(s) \quad C(s) + n_gD(g) \qquad (1)$$

In addition, the following major assumptions are made to simplify the model:

- Each individual phase is uniform and homogeneous
- Conduction in each solid media takes place along with cooling due to heat transfer to the environment and evolution of gases. Heat generation occurs due to reaction.
- Thermal and physical properties of each individual phase do not change with temperature.
- Reaction is assumed to be of first order in A and zero order in B.
- The reaction media is ignited at one end by using a heat flux for a specified period of time
- No mass transfer by diffusion takes place
- Based on these assumptions, a corresponding energy and mass balance equations were developed, and solved by implementing following initial and boundary conditions:
- Initial condition: temperature is uniform everywhere and equal to room temperature; concentration of the entire system is equal to the reactant concentration.
- Boundary condition: at the ignition end – heat transfer equals to the applied flux; whereas at the other end – heat transfer equals to the convective losses to the environment.

Results and Discussion

The effect of various parameters such as exothermicity of the reaction system, thermal diffusivity differences in reactants and products, amount of gaseous products etc. were investigated on the combustion temperature profile, and wave propagation velocity. These outcomes were further correlated with the estimated particle size and surface area of the solid product synthesized. For example, Fig. 2 shows the impact of thermal diffusivity differences in reactants and products on the combustion wave movement. A large difference in thermal diffusivity (with product having a higher value of thermal diffusivity) would decrease the combustion temperature and slow down the combustion velocity as heat dissipation will be more (Fig. 2a)[4]. In most cases, a faster combustion wave would allow only short time for the synthesized solid materials to stay under high temperature, thus reducing the impact of sintering that helps in maintaining a smaller particle size (Fig. 2b). This effect will be even more pronounced in presence of gases as the decrease in combustion velocity is accompanied by a decrease in combustion front temperature, on account of evolving gaseous products removing some of the heat from the system.

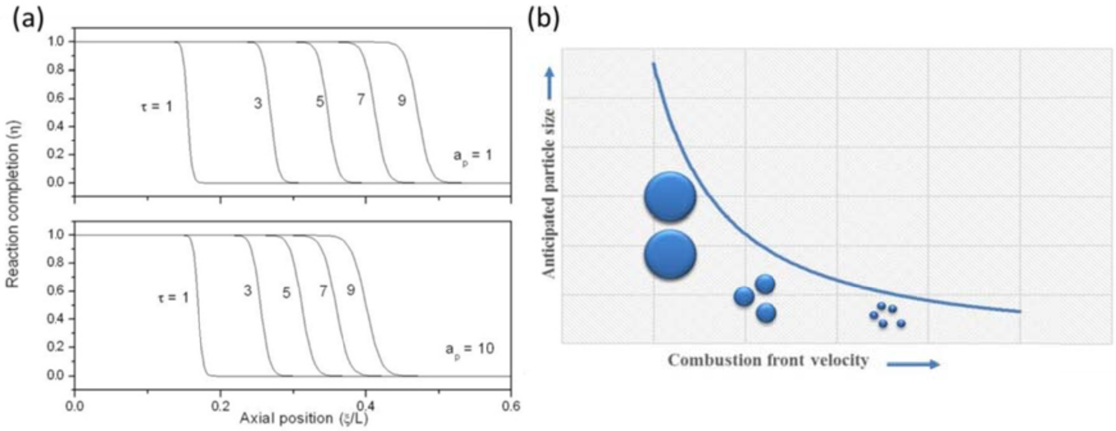

Fig. 2. (a) – effect of thermal diffusivity on combustion front velocity [4], (b) – a representation of combustion front velocity on particle size of the solid product in CACS [1]

Various catalysts were synthesized using this technique including the transition metals such as Ni, Cu and Co, which were evaluated for hydrogen production from ethanol dehydrogenation reaction. The results indicate that the synthesis environment do affect the activity of the catalysts, as they tend to impact the oxidation states of the synthesized metals along with their porosity. A detailed mechanistic study on these catalysts (Ni, Cu and Co) were also investigated using in-situ DIRFTS studies that are planned to be presented during the conference.

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PP-40

EFFECT OF PARTICLE SIZE ON ADSORPTION OF WATER VAPOR ON POROUS ALUMINIUM OXIDE MATERIALS: EXPERIMENT AND KINETIC MODELING

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The study of adsorbents on the basis of low-temperature forms of aluminum oxide (η-, γ- and χ-) obtained by calcination of products of alkaline or acid hydration of thermally activated aluminum hydroxide is actual [1]. Aluminium oxide is distinguished by its thermodynamic stability, easiest way of obtaining, and availability of raw materials, which ensures its wide application along with such adsorbents as zeolites and silica gels.

It is known that the most important factors determining the results of the adsorption process are the maximum adsorption capacity of the adsorbent and the process speed [2]. The evaluation of the maximum adsorption capacity is necessary for determining the volume of the adsorbent that can be fed into the industrial adsorber. Usually, adsorption of water from air and various gases is carried out in fixed granular layers of adsorbent. However, the saturation with adsorbate of each particle of adsorbent in the adsorber depends on the diffusion rate of adsorbate molecules inside the granule, which at a certain thermodynamic mode determines the intensity of mass transfer [3]. Due to the fact that industrial adsorbate granules usually take the form of cylinders and spheres of different sizes, the study of the influence of grain size on the adsorption kinetics is of great practical importance. Few works reported experimental results on the adsorption kinetics of water vapor on activated alumina [4, 5].

In this paper, an experimental study on adsorption kinetics of water vapors on a active aluminium oxide, which was a product of centrifugal thermal activation of hydrargillite, was performed. Mathematical modeling of the data obtained for adsorbent grains of various sizes was carried out; kinetic parameters were determined. To conduct the experiment, the following fractions of this sample were taken: 0.25-0.5 mm and 0.5-1.0 mm and a 3.7 x 6 mm granule. The experiments on the study of kinetics on the aluminium oxide sample of the mentioned fractions were carried out on an laboratory installation using McBain-Bakr quartz balance by the procedure described in [6]. According to the XRD results, the porous material under study was a mixture of low-temperature modifications of aluminium oxide - $(\gamma+\chi)$-Al_2O_3. The influence of the adsorbent granule size on the adsorption dynamics of water vapors on fractions of 0.25-0.5 mm and 0.5-1.0 mm and a 3.7 x 6 mm granule was investigated. It was shown that when the fraction size is greater than 0.5-1.0 mm, the water vapor adsorption rate on this adsorbent decreases, which is connected with the influence of internal diffusion. This happens due to the presence of fine mesopores (3÷7 nm), which is evidenced by the data obtained by the BET method.

Mathematical treatment of the obtained data was carried out. The basis was the kinetic equation of adsorption, proceeding by the first order relatively the water vapor concentration. The model fits well with the experimental data on the adsorption kinetics of water vapors on the aluminium oxide adsorbent. The kinetic parameters included in the equation were determined. According to the data of the kinetic experiment the optimal grain size (diameter) of the adsorbent was obtained, which was 2÷6 mm for balls and 2÷6 mm for cylinders with the ratio of grain length to its diameter ~1÷2.

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PP-41

THE FORMATION FEATURES OF A SOLID OXIDE FUEL CELL AND ITS INFLUENCE ON THE PERFORMANCE

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Solid oxide fuel cell (SOFC) is a promising electrochemical source of electricity presenting high efficiency, tolerance to various types of fuel, and low pollution. At the moment, the most commercialized electrochemical cells are based on zirconium dioxide stabilized by yttrium (YSZ) or other rear metal [1]. The demand for new materials to apply as SOFC electrolytes or electrodes is increasing as well. However, the impact of the microstructure is often left out of the SOFC related research. Currently, the majority of studies involving SOFCs are carried out on cells with a thin-film electrolyte instead of a bulk supporting electrolyte. This approach is meant to reduce the internal resistance of the cell and to enhance performance [2,3]. There are several different ways to produce thin oxide films and among them, dip-coating and tape casting are ones of the most prominent. These techniques require relatively simple equipment and could produce films of a thickness of around 10 μm [4]. Although dip-coating and tape casting are used frequently in oxide electrochemical cell manufacturing, the results are often controversial. This happens because small adjustments in those methods could lead to drastic differences in microstructure and performance.

This work focuses on the influence of formation factors of SOFCs. The supporting Ni cermet anodes produced by the tape-casting technique and the anode functional layer, electrolyte, and two cathode layers are obtained using dip-coating. The most advantageous composition of a dispersive medium is developed for each level of a cell. One of the most challenging parts of obtaining a ceramic multilayer cell is co-sintering of the layers. To adjust all of the parameters of the process heating microscopy was used, as it is shown in Fig. 1.

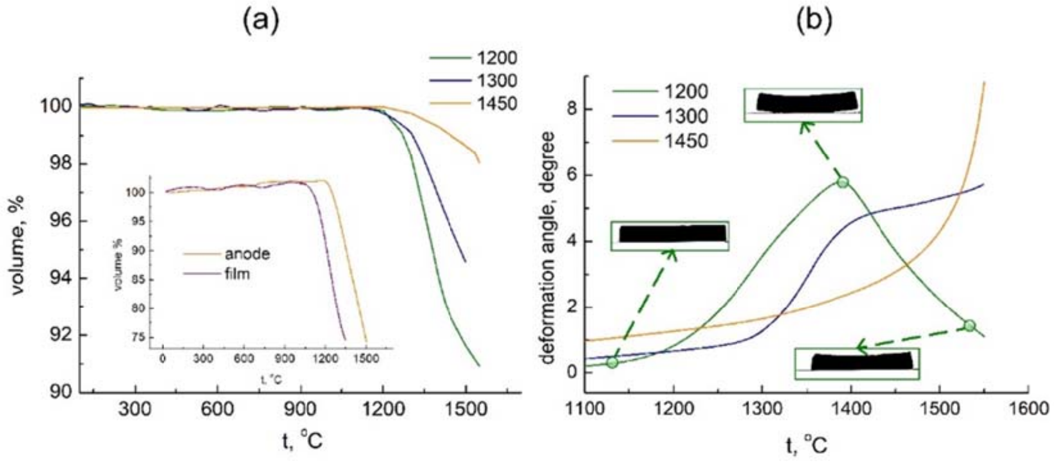

Fig. 1. (a) – densification curves of the cells on substrates sintered at 1200, 1300, and 1400 °C. Inset: separately studied densification of SSZ film and supporting anode sintered at 1200 °C. (b) – change of the deformation angle during the heating of the same cells. Insets: heating microscope images of the cell sintered at 1200 °C

The electrochemical performance and long-term durability were studied on three types of SOFC: NiO-YSZ|SSZ|SDC|SDC-LNO (cathode and anode are impregnated with $Pr(NO_3)_3$ and $Ce(NO_3)_3$ respectively); NiO-YSZ|SSZ|SDC|SDC-LNO without impregnation and NiO-YSZ|SSZ|SDC-LNO – without the barrier SDC layer. Peak power densities at 850 °C were found to be 515.3, 435.5, and 337.3 $mW \times cm^{-2}$ respectively (H_2 + 3 % H_2O used as fuel). The impregnation of the cathode and anode with $Pr(NO_3)_3$ and $Ce(NO_3)_3$ proved to be useful in terms of decreasing polarization resistance.

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PP-42

STUDY OF THE ELECTROCHEMICAL REACTION OF D-GLUCOSE CONVERSION IN THE PRESENCE OF AN ENZYME ELECTRODE

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Enzymatic biofuel cells are a type of fuel cell that uses enzymes as electrocatalysts to catalyze the oxidation of fuel and / or the reduction of oxygen or peroxide to convert chemical energy into electricity [1,2]. Most conventional fuel cell electrocatalysts are catalysts made of conductive metal nanoparticles that operate at temperatures between 45 and 150 °C. These catalysts have the advantage of high stability and high activity in a strongly acidic and / or basic environment. However, they suffer from passivation problems that require simple and high-purity fuels (i.e. hydrogen and methanol). Enzymatic biofuel elements are a successful alternative [3]. One common example of a bioelectronic device is an enzyme biofuel element, as shown in figure 1 (a).

The classical potentiometric enzyme electrode is a combination of ISE with an immobilized (insoluble) enzyme, which provides high selectivity and sensitivity for the determination of a particular substrate.

In this work, the potentiometric response of a glass ion-selective electrode modified by an enzyme-polymer complex based on glucooxidase included in the matrices of polyvinylpyrrolidone (PVP), acetylcellulose (CA) and polyacrylamide (PAN) was studied. The reaction to determine the activity was the oxidation reaction of D-glucose, with an external supply of oxygen. The activity of the immobilized enzyme was determined by the reaction product of gluconic acid, the formation of which was determined potentiometrically.

It was assumed that the potential of these electrodes depends on the concentration of glucose, oxygen and hydrogen peroxide in solution, as well as the presence of functional groups on the surface of the glass electrode. Potentials were calculated as the difference between measured and background values (without glucose). The reference electrode is Ag/AgCl (in 1M KCl).

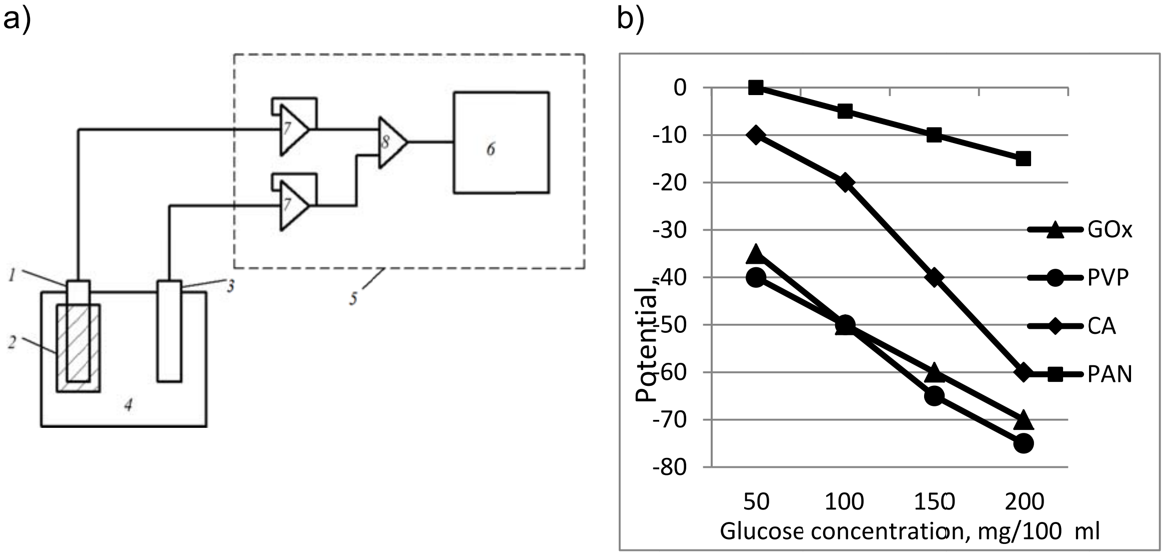

Figure 1. a) General electrical circuit for measuring the biosensor potential at an indicator electrode other than the ISE. 1 - indicator electrode; 2 - enzyme-polymer complex on the indicator electrode; 3 - comparison electrode; 4 - electrolyte containing the substance to be determined; 5 - high impedance potentiometer; 6 - display; 7 - operational amplifier current repeater; 8 - comparator; b) potentiometric response glucose oxidase ionselective glass electrode in an oxygen-saturated solution of D-glucose at pH = 7.4 (0.1 M sodium phosphate buffer solution)

As seen in Fig. 1 (b), the dependence is nerstovsky at concentrations of glucose of 50-200 mg/100 ml. the slope of the curves in Fig. 1 (b) is about – 40 mV/pC glucose. The method of adsorption immobilization used in this work has proved to be the simplest and provides a strong adsorption of the enzyme on the electrode surface while maintaining high activity.

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PP-43

USE OF CFD IN THE EVALUATION OF TEMPERATURE EVOLUTION IN THE LIQUEFACTION OF LEMON BAGASSE

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The liquefaction yield and time reaction are directly influenced by the temperature process [1][2][3]. Despite of it, there it is still necessary to set a methodology to help researchers choose these operational parameters. The aim of this work was to use the Computer Fluid Dynamics (CFD) to evaluate the thermal profile in a jacketed vessel used to liquefy the lemon bagasse. A numerical 3-D model with two computational domains was built. The first domain considered the fluid flow of superheated steam inside the heated jacket at steady state flow rate. The second domain represented natural convection of glycerol and lemon bagasse mixture (polyol) considering transient fluid motion. The simulation time was 90 minutes with time-step of 0.1 seconds, 40 iterations for each time-step. The fluids' physical properties were obtained considering the ideal conditions (glycerin and lemon bagasse properties).

The Figure 1 indicated the predominance of natural convection (enhanced by convection of momentum and energy) during the first 20 minutes of heating. The high temperatures appear first in the superior part and there was a slow heating from above to below. However, there was a centerline at the vessel axis where the temperatures remain significantly lower than in rest of the domain, due to the downward stream produced by the natural convection cell. Temperatures stability was achieved below 60 minutes, although satisfactory biomass conversion required more time, according to previous study performed by this group [2]. Therefore, CFD model appear to be a helpful tool to guide researchers choose temperatures and minimal time which heat process will start steady state in liquefaction process.

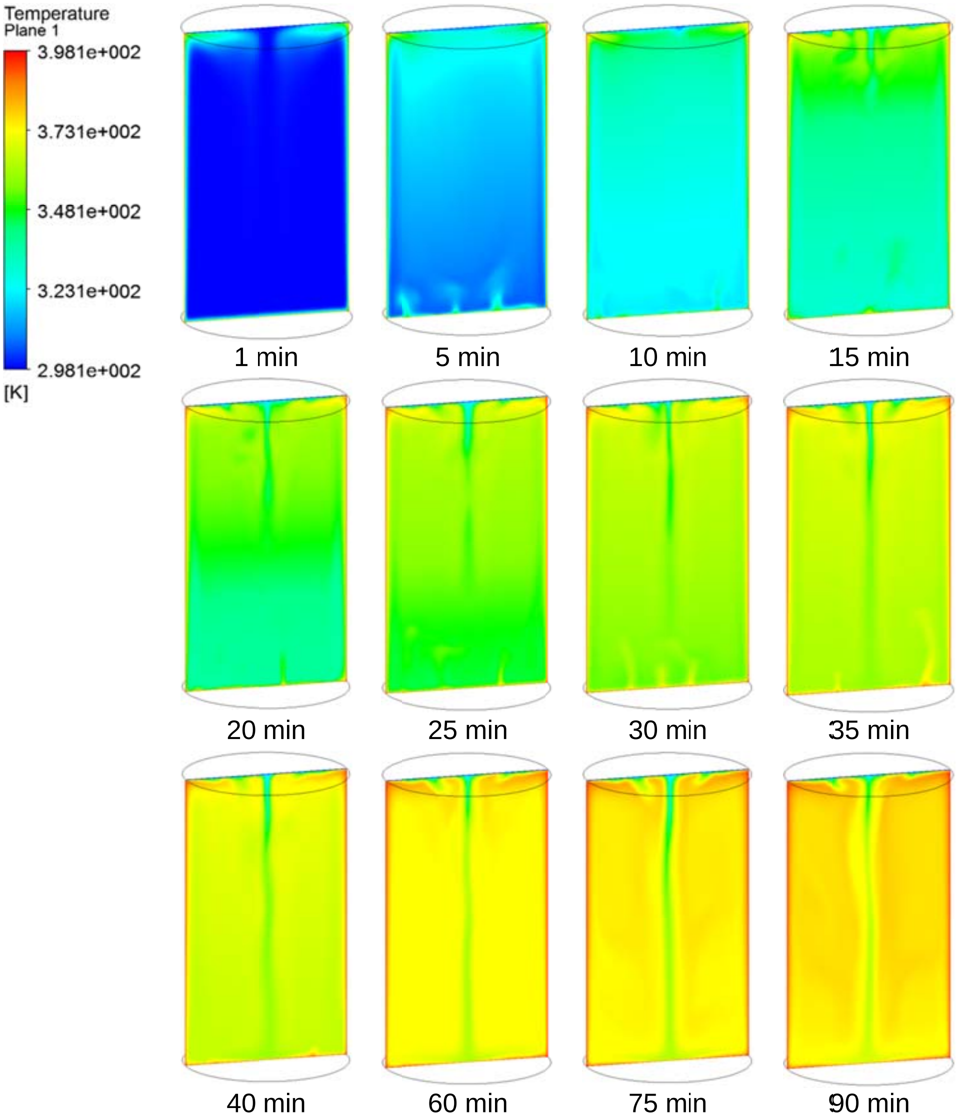

Figure 1. Time evolution of thermal profile in vertical plane for the glycerin mixture inside the liquefaction vessel

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PP-44

HYDROTHERMAL LIQUEFACTION OF LIGNOCELLULOSIC INTO BIOFUELS AND ITS UTILISATION IN ENERGY

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Fossil fuels which are found in nature are formed through a process of thermochemical conversion from organic matter buried beneath the ground and subjected to millions of years of high temperature and pressure [1]. Combustion of fossil fuels results in a net increase in greenhouse gases which could be controlled if alternatives to petroleum are used to produce fuels and chemicals. Increase in world's population has resulted in an increase in energy consumption, the global dependence on non-renewable fossil fuels to meet energy's need cannot be sustained for a long time [2,3].

Lignocellulosic biomass such as wood, straws and stack has received great interest because they are abundant, renewable, and environmentally friendly and are obtainable from different sectors including agriculture and food processing. The wide variety of their origin also reflects on the nature of this biomass. Most biomass is obtained with a certain amount of moisture [4].

Hydrothermal liquefaction is a chemical reforming process through which organic matters are depolymerized and reformed in a heated, pressurized, oxygen-free enclosure. Operating temperatures, retention time and biomass content are amongst factors that control the yield and quality of biofuels. The primary product is an oily organic liquid while other products include solid residue, aqueous products and gases. The oils produced from this process has a lot of potentials as a biofuel. Biofuel can be used as fuel for burners, boilers, stationary diesel engine or turbines, it can also serve as a starting material for valuable petroleum-based fuels [1,3,5].

In this work, the potentials of agricultural and food wastes as feedstock in hydrothermal liquefaction will be investigated. The choice of materials stems from the need to focus on second generation biofuel production. The process will be conducted in a hydrothermal reactor while varying the ratios of the various biomass to be investigated. A high temperature, high pressure reactor will be used for all experiments. Alongside the feed composition, the effect of process parameters such temperature and time on the yield and distribution of products will be investigated. After an experimental run, gaseous products will be vented while solid and liquid products will be collected from the reactor. The liquid hydrocarbons produced will be separated form solids using the appropriate washing solvents. The reaction products will be characterised using gas chromatography. The calorific values of the products obtained will be investigated with a view to harnessing their energy potentials. Structural properties related with functional groups of biofuels will be identified using FTIR Spectrometry. Thermal gravimetric analysis will be used to gain insight into the thermal stability of the feedstock.

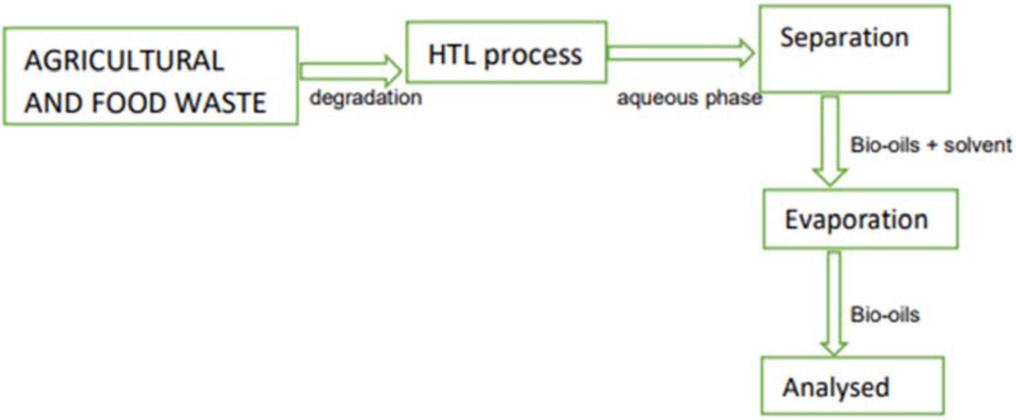

Fig. 1. The schematic representation of HTL process

The project is focused on combating the challenges of Energy while adding values to wastes from Agricultural activities and the food processing.

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PP-45

ANFIS MODELLING APPLIED IN BIODIGESTERS

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Biogas production is an important response of the performance of anaerobic biodigestion process. Apart from its economic relevance, biogas production is important from environmental and operational point of view, since it represents a reduction in the organic matter of the effluent. Other operating parameters, such as pH, medium alkalinity, temperature and organic content (in and out), are also important for performance evaluation and control of the anaerobic biodigestion process, in order to increase biogas production [1].

Research developed by this group shown that biodigestion process was satisfactory modelled using artificial neural networks. ANFIS model was capable of predicting the biogas volume, with a determination coefficient of 0.81209, using reactor type, temperature, pH and FOS/TAC as inputs [2]. From these results, the goal of this work was to improve the use of neural network models in order to predict biogas generation, as a function of monitored parameters. The idea is to produce a tool capable to control the process and optimize biogas generation.

In this sense, a model adaptive neuro fuzzy inference system (ANFIS) was proposed in order to predict biogas production 12 h ahead, according to the operational conditions used in the previous work [2]. Determination coefficient (R^2) and root mean square error (RMSE) were used to ensure the quality of the results. Three biodigestion sets were operated in order to gain data to feed the neural networks model. All of them were operated at the same conditions. The biodigesters had different design: 1st) jacketed inox reactor, without recirculation of the effluent, 5 L nominal capacity; 2nd) reactor made of PVC, with internal heating coil, without recirculation of the effluent, 7 L nominal capacity and 3rd) reactor made of PVC, with internal heating coil, with recirculation of effluent to provide mixing, 7 L nominal capacity. They were fed with a mixture of swine sewage and rice husk, in order to provide organic load between 1.0 and 1.5 g of volatile solids (VS) L^{-1} d^{-1}. Biogas production was monitored and measured at a regular interval through water displacement method and converted to the volume in Normal Temperature and

Pressure Conditions (NTP). Organic load, alkalinity (FOS/TAC) and pH measurements were performed according to Rego et al [2].

The ANFIS modeling concerned the prediction of biogas volume produced 12 h in advance. The network architecture consisted of 6 input variables (temperature, reactor type, pH, FOS/TAC, biogas volume 12 h before and biogas volume at the present time). The total data consisted of 84 values for each input, which were split into training (67 %) and test (33 %). A Sugeno inference method was used to model the biodigestion system following a similar methodology used by Rego et a. [2]. This method creates rules based on the input variables values and the output is given by a Membership Function (MF) in the defuzzification. In the present study, neuro fuzzy system based on the Subtractive Clustering (SC) was used, with a linear output and hybrid training algorithm. The MF used in the SC was the Gaussian curve function (gaussmf) and the four parameters present in SC (range of influence, squash factor, accepted ratio and rejected ratio) were varied to achieve the best configuration. The R^2 and RMSE values were used to evaluate the performance in Matlab 2018b.

All the tested architectures alongside its determination coefficients and errors values are depicted in Table 1. Overall, the model presented good results and the best performance was achieved using the configuration number 2, which presented the highest R^2 value (0.988) as well the lowest RMSE value (2.51E-1). The change in the ANFIS parameters caused the set of rules to change as well. However, the number of rules do not dictate that the network will have a better performance, which can be observed by configurations 2 and 4, that had different performances despite having the same amount of rules.

Table 1. ANFIS configurations used for biogas volume prediction 12 h in advance

Configuration	Range of influence	Squash factor	Accepted ratio	Rejected ratio	Number or rules	RMSE	R^2
1	0.5	2.5	0.5	0.15	8	1.28E-1	0.713
2	0.75	1.25	0.5	0.15	11	2.51E-2	0.988
3	0.65	1.25	0.5	0.3	10	7.00E-2	0.915
4	0.5	2	0.5	0.25	11	4.82E-2	0.959
5	0.6	2.5	0.5	0.15	5	1.21E-1	0.745

Figure 1 depicts the comparison between experimental data and the output of the ANFIS model for the best configuration. Both graphs show that the model had an excellent performance in predicting the biogas volume.

PP-45

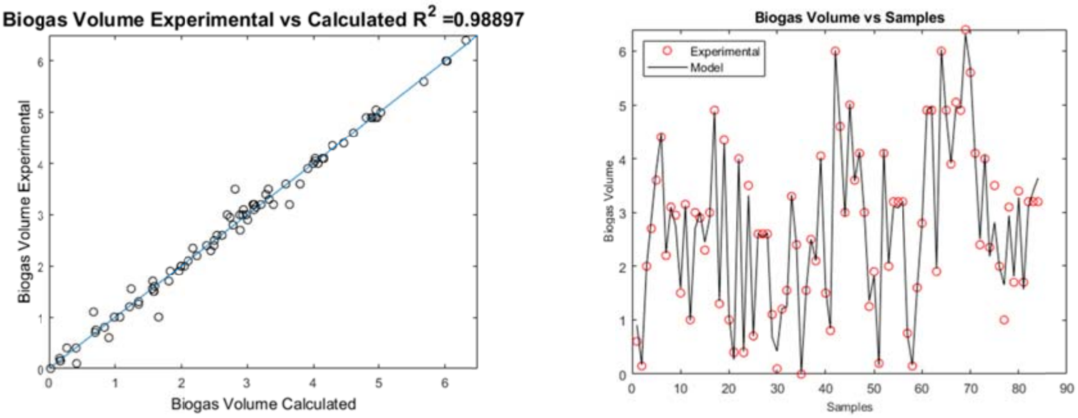

Figure 1. Comparison graphs of the experimental and model values. Regression plot of the biogas volume (left) and biogas volume for each sample in the test (right)

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PP-46

CATALYTIC DEVICES ON THE BASE OF GLASS-FIBER CATALYST FOR AIR PURIFICATION AND ENVIRONMENTALLY SAFE HEATING SYSTEMS

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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 [1,2]. The flow-sheet of the catalytic combustor [3,4] is presented in Fig. 1.

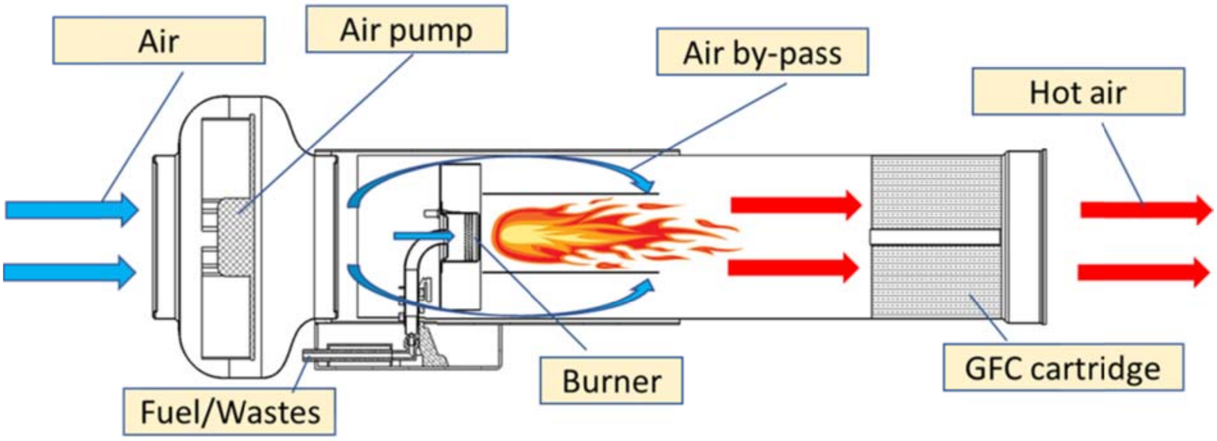

Fig. 1. The flow-sheet of the catalytic combustor

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 device uses the thermostable Pt-containing GFC IC-12-S111 [5] within the spiral cartridge structured with metal meshes (Fig. 2). Such cartridges are characterized with high efficiency of mass transfer and low pressure drop [1,2].

Fig. 2. The GFC-based structured catalytic cartridge

Fig. 3. shows the external view of the catalytic devices for combustion of gaseous (LPG) and liquid (diesel) fuels

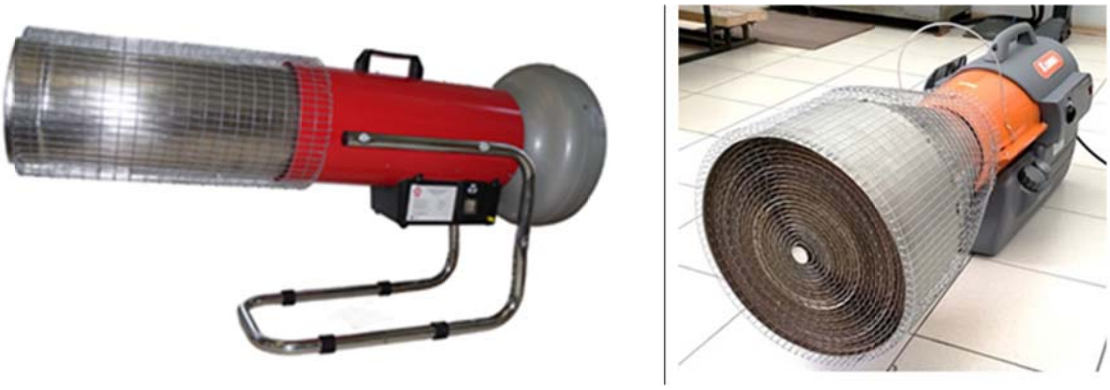

Fig. 3. Catalytic devices for combustion of gaseous (left) and liquid (right) fuels

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. Potential application also include air disinfection from various viruses and bacteria.

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PP-47

MAGNETICALLY RECOVERABLE POLYMERIC CATALYST FOR CELLULOSE HYDROGENOLYSIS

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Glycols are an important feedstock; they are commonly used in different branches of modern industry [1, 2]. It is obvious that the demand for these polyols is extremely high. New possibilities in catalysis are offered by the use of magnetically recoverable catalysts [3]. In this research, a novel catalysts on the base of hypercrosslinked polystyrene (HPS) with magnetic properties are proposed for the one-pot processes of the cellulose conversion into ethylene glycol (EG) and propylene glycol (PG). Synthesized magnetically recoverable supports and catalysts were characterized by different physical-chemical methods. The magnetic properties of the supports Fe_3O_4/HPS MN270 and the corresponding catalysts were studied. The use of this catalyst in the process of microcrystalline cellulose hydrogenolysis in subcritical water allows PG and EG selectivities of 20.0 and 22.6 %, respectively, at 100% of cellulose conversion.

HPS-based magnetically recoverable Ru-containing catalysts were synthesized according to the following procedure. 0.3 g of HPS was placed to the 10 mL of EtOH with preliminarily dissolved calculated amounts of $FeCl_3$ and CH_3COONa. Then, the sample was heated up to 200 °C in argon medium and maintained at this temperature for 5 h. Resulting Fe_3O_4/HPS was washed with distilled water and then with EtOH. Washed sample of magnetically separable Fe_3O_4/HPS containing *ca.* 20 wt. % of Fe.

For the synthesis of Ru-Fe_3O_4/HPS catalyst, Fe_3O_4/HPS MN270 was impregnated according to moisture absorption capacity with the solution of the calculated amount of ruthenium (IV) hydroxochloride in a complex solvent consisting of tetrahydrofuran, methanol. Then the catalyst was reduced in hydrogen flow (flow rate 100 mL/min) at 300 °C for 2 hours, cooled in nitrogen and kept under air. In this way, Ru-containing system with calculated ruthenium content of 3 wt. % was synthesized.

The experimental samples were shown to have a high saturation magnetization (4.0 ± 0.5 emu/g, Figure 1). The magnetization curves no remanence or coercivity is observed, demonstrating superparamagnetic behavior which is characterized for magnetite. A high value of saturation magnetization allows for fast magnetic separation of the Fe_3O_4/HPS MN270 particles (Figure 2).

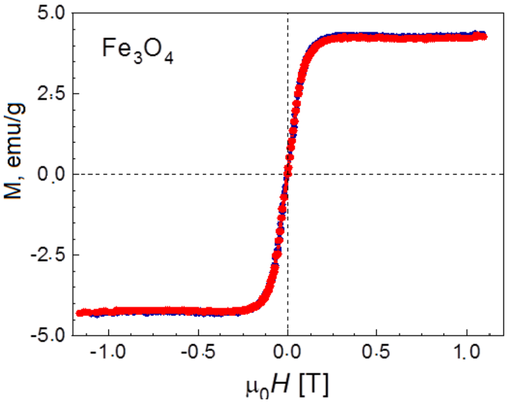

Figure 1. Magnetic properties of Fe_3O_4/HPS MN270

Figure 2. Fe_3O_4/HPS MN270 before and after magnetic separation

The synthesis method of catalyst (3 % Ru-Fe_3O_4/HPS MN270) was developed. Synthesized magnetically recoverable supports and catalysts were characterized by different physical-chemical methods. The use of this catalyst in the process of microcrystalline cellulose hydrogenolysis in subcritical water at 255 °C, 60 bar hydrogen pressure in 50 minutes allows PG and EG selectivities of 20.0 and 22.6 %, respectively, at 100 % of cellulose conversion. The catalyst is stable under hydrothermal conditions of the process; it is easily separated from the liquid phase with the external magnetic field and can be reused. Therefore, the results of the research prove the advantages of the use of magnetically retrievable catalysts in biomass processing into chemicals.

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PP-48

PHOTOCATALYTIC REDUCTION OF CARBON DIOXIDE IN CONTINUOUS FLOW PHOTOREACTOR USING TiO_2-BASED COMPOSITES

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Solar-driven photocatalytic reduction of carbon dioxide is recognized as a promising approach to address both energy and environmental issues. The process is usually performed on different kinds of materials, including inorganic semiconductors, carbon-based semiconductors, metal complexes, supermolecules, and their derivatives. Among them, titanium dioxide is one of the most well-known and widely studied materials due to its abundance, high thermal stability, and non-toxicity.

Despite the progress made during the last three decades, the photocatalytic application of this material is still challenging due to a few reasons. One of these limitations is poor solar energy utilization due to a wide bandgap (3-3.2 eV) of TiO_2 which significantly limits adsorption of solar radiation to the UV light range accounting for only about 5% of the solar spectrum. Also, the following problem is a slow reaction rate due to the rapid recombination of the photogenerated electron-hole pairs.

Therefore, lots of efforts have been put into the development of new effective catalysts with enhanced photocatalytic properties, such as nano – and microstructured TiO_2, metal-decorated TiO_2, and TiO_2 – based composites [1].

The current research work deals with the investigation of physicochemical and photocatalytic properties of WO_3/TiO_2, CNT/TiO_2, and Me/TiO_2 photocatalysts. These catalysts were prepared by co-precipitation and chemical vapor deposition methods. Then, the samples were characterized and the photocatalytic activity was evaluated in a continuous-flow photo-microreactor under solar or UV irradiations. The effects of type and content of promoter on the physicochemical and photocatalytic properties of TiO_2 were investigated.

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PP-49

DEVELPOMENT OF MEMBRANE REACTOR FOR HYDROGEN AND SYNTHESIS GAS CO-PRODUCTION

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The importance of hydrogen as an energy carrier and a raw material for the chemical industry is growing rapidly, initiating the development of new methods for its production. Recently, different ways of hydrogen generation based on water splitting have drawn increased attention [1,2]. These methods are attractive because water is an inexhaustible resource, and hydrogen obtained from water is originally clean, in contrast to that traditionally produced by steam conversion of methane. The most promising is the combination in a membrane reactor of water splitting (WS) and partial oxidation of methane (POM) for simultaneous production of hydrogen and synthesis gas, respectively.

This work presents the test results of a ceramic tubular membrane of $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ under the condition of simultaneous POM and WS processes, as well as an assessment of the fundamental possibility of industrial use of this approach for the production of ultrapure hydrogen and synthesis gas based on the results of testing a reactor with 10 membranes.

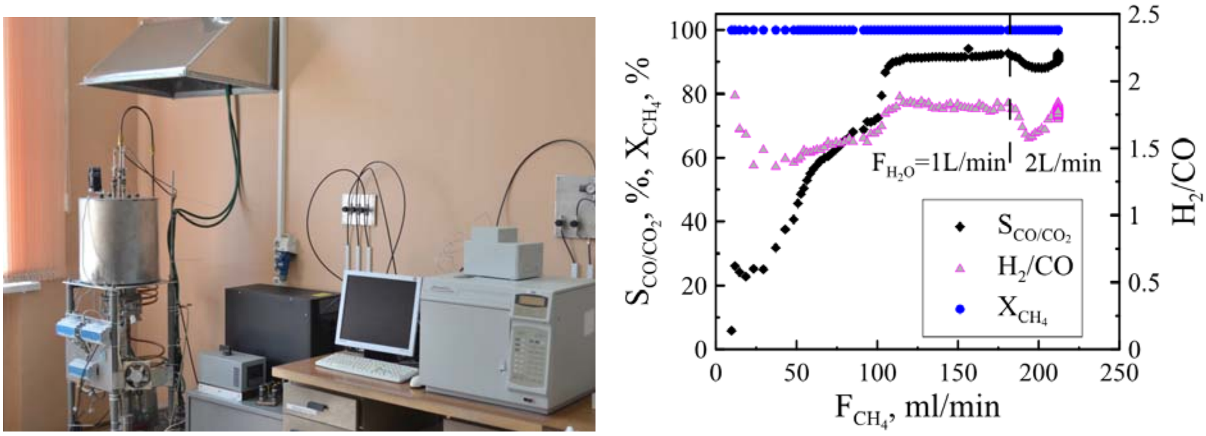
Powder of $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ prepared by the glycine-nitrate method and characterized by X-ray diffraction as a single phase oxide. The membranes were made by hydrostatic pressing method. Reactor was equipped with 10 membrane elements of the same sizes and with the total effective area of about 140 cm^2, Glass rings glued to the end surfaces were used to seal the tubular membranes in the reactor provided a separation of the POM and WS compartments. A nickel catalyst for the partial oxidation of methane was placed on the outer side of the membrane in the POM compartment. The computerized experimental setup was equipped with temperature controllers and gas flow controllers. The analysis of outlet gases was carried out with the help of a gas chromatograph. The experimental setup is shown in Fig. 1a.

Based on volume concentrations of outlet sweep gas components, x_i, the POM process was characterized by conversion, X_{CH4}, CO selectivity, S_{CO}, hydrogen to carbon monoxide ratio, H_2/CO, flux of the dry synthesis gas, F_{SG}, and oxygen separation flux:

$$X_{\mathrm{CH_4}} = \left(1 - \frac{x_{\mathrm{CH_4}}}{x_{\mathrm{CO}} + x_{\mathrm{CO_2}} + x_{\mathrm{CH_4}}}\right) \cdot 100\% , \quad S_{\mathrm{CO}} = \left(\frac{x_{\mathrm{CO}}}{x_{\mathrm{CO}} + x_{\mathrm{CO_2}}}\right) \cdot 100\% ,$$

$$F_{\mathrm{O_2}} = F_{\mathrm{SG}} \cdot \left(1.5x_{\mathrm{CO}} + 2x_{\mathrm{CO_2}} + x_{\mathrm{O_2}} - 0.5x_{\mathrm{H_2}}\right).$$

Results of testing a membrane reactor at 900 °C showed that the methane conversion in the process of partial oxidation was not less than 99.0 %, at CO selectivity of 92 %, Fig. 1b. The oxygen flow density reached 1 $ml \cdot min^{-1} \cdot cm^{-2}$. The specific hydrogen flux in accordance with the material balance conditions was ~ 2 $ml \cdot min^{-1} \cdot cm^{-2}$. A long-term stability test during more than 200 h showed the ceramic membrane of $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ provides an appreciable stability of the process characteristics in a stationary state at 900 °C and in a reversible temperature change between 950 °C and 900 °C.



(a) (b)

Figure 1. (a) – the experimental setup of membrane reactor and (b) – parameters POM processes as functions of methane flow at 900 °C

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PP-50

PYROLYSIS OF CONIFEROUS AND DECIDUOUS WOOD WASTES

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The problem of processing raw materials of plant origin in order to obtain energy every year becomes more and more urgent due to the limited supply of traditional energy carriers.

According to experts, the annual increase in biomass is about 170 billion tons, which makes it possible to include it in the production of energy resources and use it as an alternative to fossil resources [1]. The use of plant biomass will maintain the balance of CO_2 in the atmosphere, as well as reduce the negative impact on the environment by reducing the amount of unused waste.

Currently, effective methods of processing solid lignin-containing waste to produce products valuable for industry are thermal processing methods [2]. As experience gained in the field of thermal processing of biomass waste shows, the most effective and easily industrially feasible method is the pyrolysis method [3], which allows one to obtain gaseous, liquid, and solid carbon-containing products [4].

An experimental study of the process of pyrolysis of wood waste was carried out for 50 minutes in a nitrogen environment using a batch laboratory setup. As samples of wood waste, sawdust of pine and birch was used with a moisture content of 3.20 % and 3.18 %, and an ash content of 0.36 % and 0.17 %, respectively. Sawdust with an average particle size of 0.25-1 mm was used in this study; 1-2 mm; 2-3 mm. The process of pyrolysis of wood waste was carried out in the temperature range from 400 to 500 °C. The choice of the temperature range was based on previously obtained data from thermogravimetric analysis.

Thermogravimetric study of wood waste showed a difference in the processes of destruction of pine and birch samples, which is most likely due to the different component composition and structure of these samples. The heat of combustion of gaseous products of hardwood pyrolysis is 1.1-1.2 times higher than that of conifers, which is associated with higher concentrations of ethane and lower concentrations of hydrogen, which has a low volumetric heat of combustion.

Table. Kinetic parameters of the wood waste pyrolysis process calculated by thermogrammetric analysis

Wood type	Model independent methods		Linear kinetics methods
	ASTM E698	ASTM E1641	
Birch			
E_A, kJ / mol	141.1±7.3	123.6±9.0	128.2
A_{exp}	$9.\ 90 \cdot 10^{-1}$	$9.03 \cdot 10^{-1}$	$9.3 \cdot 10^{-1}$
n reactions	-	-	2.53
R (coefficient)	-	-	0.9978
Pine			
E_A, kJ / mol	126.0±5,7	76.3±17.4	119.3
A_{exp}	$9.89 \cdot 10^{-1}$	$4.37 \cdot 10^{-1}$	$8.4 \cdot 10^{-1}$
n reactions	-	-	2.31
R (coefficient)	-	-	0.9975

Samples of birch wood had greater thermal stability compared to samples of pine wood, which confirms higher values of activation energy (see table).

Analysis of the data presented in table allows us to judge that the activation energy of pyrolysis of birch sawdust is greater than pine sawdust, according to various estimates, from 8.9 to 15.1 kJ / mol. This confirms the lower thermal stability of pine wood in the studied temperature range of the process.

The optimal temperature for the pyrolysis process of the selected wood waste samples is 450 °C with a fraction size of 1-2 mm. Coal residues of pyrolysis of wood waste by the values of the specific surface area correspond to the characteristics of cheap carbon sorbents used in industry, which indicates the possibility of their practical application.

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TORREFACTION OF FOREST RESIDUES USING A LAB-SCALE REACTOR

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Lignocellulosic biomass is one of the sources that are under investigation in the effort to obtain renewable fuels. It is characterized by a low bulk density, poor grindability, low calorific value and high moisture content [1]. Pre-treatment of solid biomass by torrefaction can improve its properties and generates a solid product (charcoal) with lower moisture content, higher bulk density, higher heating value, higher hydrophobicity and higher grind ability than the original raw biomass [2]. In addition, collecting and using this forest waste can also result in increased safety, in relation to forest fires. In this work we studied, as a possible energy source, shrubs that occur widely in the Portuguese forest, e.g *Cistus ladanifer* (Esteva), and which have an invasive character. A laboratory scale reactor was built for the torrefaction process, with a Schlenk-type glass vessel placed in an oven for which the temperature was controlled at predefined levels. The gases exiting through the top of the reactor were cooled by a condenser and collected in a liquid collection system. A pump fed the coolant fluid to the condenser, from an external thermostat kept at 20 °C, to ensure an efficient collection of the liquid fraction and control the composition of the gaseous phase products in the outlet. The slow pyrolysis experiments were carried out by initially flushing the lab-scale reactor with N_2, and then feeding the reactor with varying biomass quantities and heating it to a specified temperature. The torrefaction temperatures were varied from 250 to 350 °C maintaining a reaction time of 30 min with a heating rate of 10 °C min^{-1}. The solid obtained at the end of the torrefaction (charcoal) was collected from the schlenk. After the torrefaction process, the heating value of the torrified samples were determined by combustion using thermal analysis coupled with differential scanning calorimetry (TG/DSC apparatus). The morphological characteristics of the biomass samples were assessed, before and after thermal analysis, by microscopy techniques. To evaluate the torrefaction performance for the experimental conditions tested, mass and energy yields (Figure 1 and Figure 2) of the torrified materials were determined. From the results, it can be seen that the torrification process, in particular at the higher temperature, significantly decreases the mass of the material with a more limited reduction of the heat content. For example, torryfying 6g of biomass at 350 °C for 30 min leads to the production of 48 % of char that contains ca. 90 % of the initial energy content, with a lower heating value (LHV) of 10 kJ/g compared with 6 kJ/g of original biomass. This process can allow for more economical biomass transport and enable the future use of this forest waste to be more efficient.

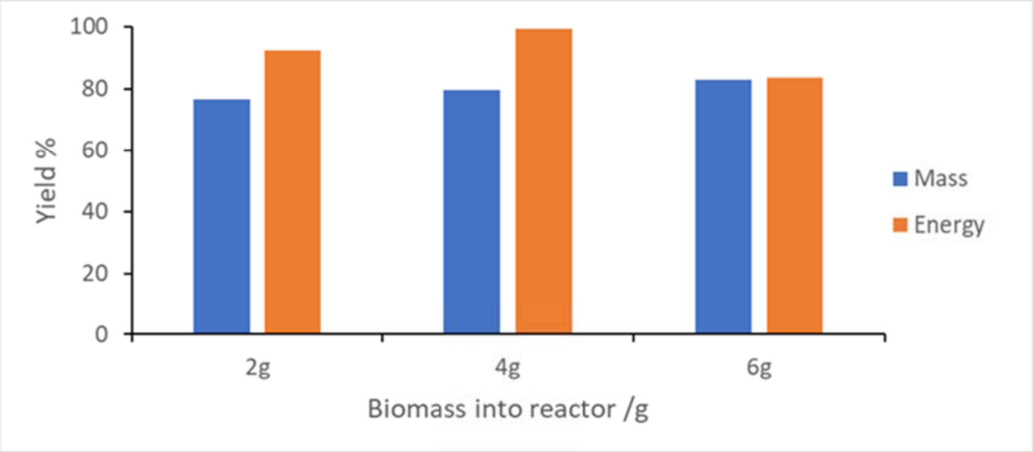

Figure 1. Effect of biomass quantity on energy and mass yields for torrefaction at 250 °C during 30 min

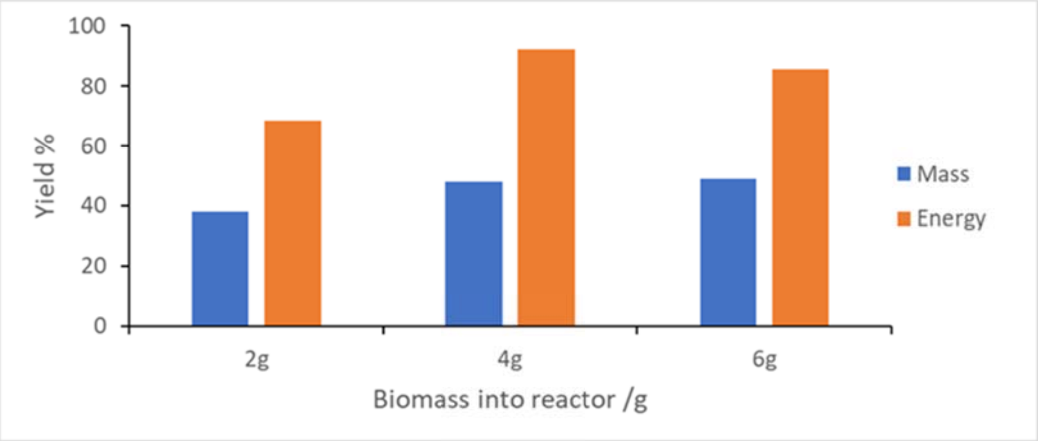

Figure 2. Effect of biomass quantity on energy and mass yields for torrefaction at 350 °C during 30 min

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PP-54

MATHEMATICAL MODELING OF VACUUM GAS OIL CATALYTIC CRACKING FROM WEST SIBERIAN AND KAZAKHSTAN OIL BLEND

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This paper presents the adapting results of the catalytic cracking mathematical model [1] to an industrial conversion unit of vacuum distillate from West Siberian and Kazakhstan oil blend. The mathematical model takes into account the physical-chemical patterns of catalytic cracking hydrocarbon transformation. A set of laboratory studies using liquid chromatography, structural group analysis, optical, cryoscopic methods, etc., performed on TPU basis of, allow us to establish the main characteristics and a wide range of the feedstock composition changing (table 1).

Table 1. Feedstock composition to model calculation

Characteristics	Content, wt % .				
	№1	№2	№3	№4	№5
Saturated hydrocarbons	59.79	58.95	63.89	66.83	73.13
Aromatics	35.46	36.61	33.47	30.24	23.31
Resins	4.75	4.44	2.64	2.93	3.56
Saturated hydrocarbons, aromatics and resins ratio (CSH/CA/CR), unit	0.35	0.36	0.72	0.75	0.88

To verify the model, we compared the calculated and experimental data on the products yields, the content of the PPF and BBF in the rich gas, the coke content on the catalyst, the gasoline hydrocarbons group concentration and the cracking temperature. As a result, the calculation error does not exceed 7.0 %. The mathematical model application allows us to investigate how the feedstock composition influences the catalytic cracking product distribution, the yield and coke content on the catalyst.

It is shown that, the yield of gasoline fraction changes by 1.37 wt % with increasing the saturated hydrocarbons, aromatics and resins ratio from 0.35 to 0.88 units. Application of the catalytic cracking mathematical model makes it possible to evaluate comprehensively how the feedstock composition and technological parameters influence the yield and composition of the process products (Figure 1).

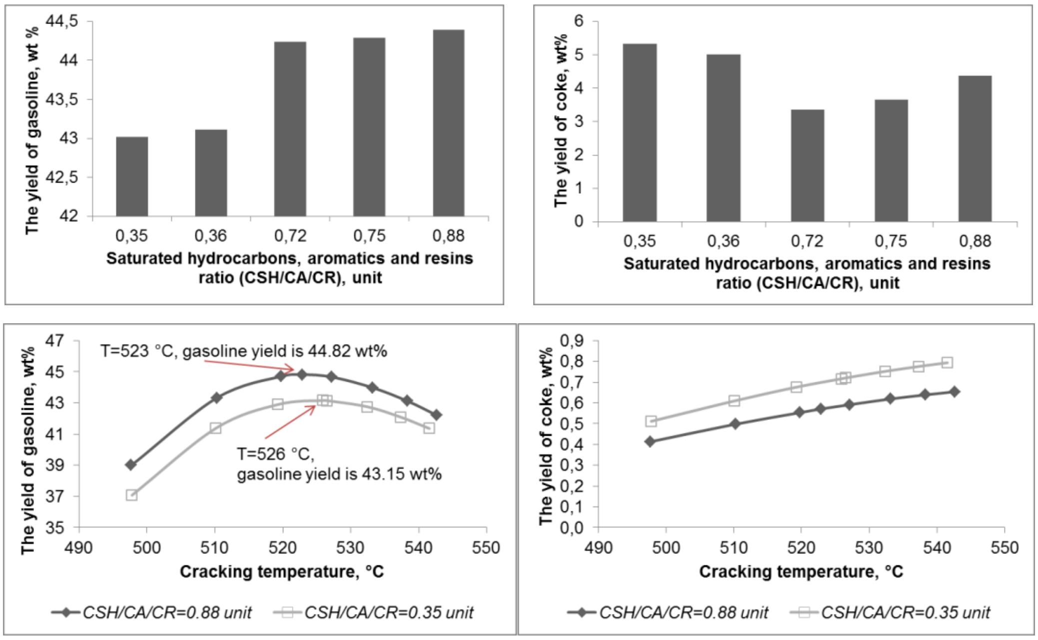

Figure 1. a) The catalytic cracking gasoline and coke yields depending on the feedstock composition b) The catalytic cracking gasoline yield and coke content on the catalyst depending on the feedstock composition and cracking temperature

According to figure 1 the gasoline yield are characterized by extremum with increasing the cracking temperature (44.82 and 43.15 wt %, if saturated hydrocarbons, aromatics and resins ratio (CSH/CA/CR) are 0.88 and 0.35 unit respectively). Importantly, that when optimizing the process, it is required to consider that the maximum gasoline yield is shifted to low temperatures from 526 to 523 °C, when the feedstock saturated hydrocarbons amount increases.

Predictive calculations provide us to adjust the riser process conditions in order to increase the target product yields and to reduce the excess coke formation, depending on these factors. In the future, we are going to account the reversible and irreversible catalyst deactivation and to develop the methodology for the feedstock group composition calculation on the basis of plant laboratory regular data about the fractional composition, the density, the molecular weight, the refractive index and other quality indicators to expand the model application.

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PP-53

DESIGN OF BIOCATALYSTS FOR EFFICIENT ONE-POT PROCESS FOR CASCADE REACTIONS

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Biocatalysts based on immobilized enzymes received considerable attention due to important applications in syntheses of value-added chemicals, pharmaceuticals and drug intermediates with great catalytic efficiency and high yields of target molecules. The important advantages of such biocatalysts are enhanced stability in tolerant pH and temperature range, separation from reaction solutions, stability in repeated use, etc. In this report, we discuss recent findings in biocatalyst design, in particular, types of promising supports, the biocatalyst surface modification, and incorporation of magnetic nanoparticles for facilitated magnetic recovery. Furthermore, we highlight the development of multienzyme and enzyme/nanoparticle catalysts for cascade reactions, which are carried out in a one-pot process and allow elimination of isolation and purification of intermediates. We will focus on most promising supports, methods of enzyme attachment as well as on multienzyme biocatalysts and biohybrid catalysts for cascade reactions. The cascade reaction catalysts represent an emerging technology inspired by Nature where the spatial localization allows for the high chemo-, regio- and stereoselectivity

Among supports for biocatalysts, functionalized porous materials with a hierarchical pore structure containing large mesopores or macropores appear promising as they possess high surface areas and can accommodate large amounts of enzymes in a controlled manner. However, for better performance, often an additional modification is needed for protecting enzymes or making a biocatalyst more hydrophilic or hydrophobic. Magnetically recoverable biocatalysts are clearly a hot topic as they allow easy magnetic separation without loss of catalytic performance and in some instances, show the catalytic property enhancement.

The most prominent trend in the biocatalyst design is the development of catalysts for cascade reactions using multiple enzymes or combining enzymes with catalytic NPs. Both areas of research are still very new but they already showed promise for the development of biocatalytic processes, where several reactions occur in a one-pot reactor. The best biocatalysts display exceptional catalytic efficiency and a minimal loss of activity compared to native enzymes and require low energy consumption. For the cascade reaction catalysts, there is no need for isolation of intermediates, no hazardous chemicals are formed, and the waste is minimized compared to conventional consecutive reactions, resulting in the same target products. We believe this is the most promising direction for the development of biocatalysis.

As an example, the results of the synthesis of biocatalytic systems based on immobilized enzymes of the oxidoreductase class are presented. The main aspect of the report is the using of magnetic silica and alumina and magnetite nanoparticles based on mesoporous zirconia and titania as a supports. We control acidity, porosity, and crystal structure of these supports, which puts us in a unique position of acquiring a new knowledge for further biocatalyst development.

The obtained fundamental and applied data about the biocatalytic oxidation processes of aromatic compounds and monosaccharides including one-pot cascade process will allow creating the innovation technologies for the production of biologically active compounds which are high-demand by pharmaceutical.

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MATHEMATICAL MODELING OF VACUUM GAS OIL CATALYTIC CRACKING FROM WEST SIBERIAN AND KAZAKHSTAN OIL BLEND

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It is shown that, the yield of gasoline fraction changes by 1.37 wt % with increasing the saturated hydrocarbons, aromatics and resins ratio from 0.35 to 0.88 units. Application of the catalytic cracking mathematical model makes it possible to evaluate comprehensively how the feedstock composition and technological parameters influence the yield and composition of the process products (Figure 1).

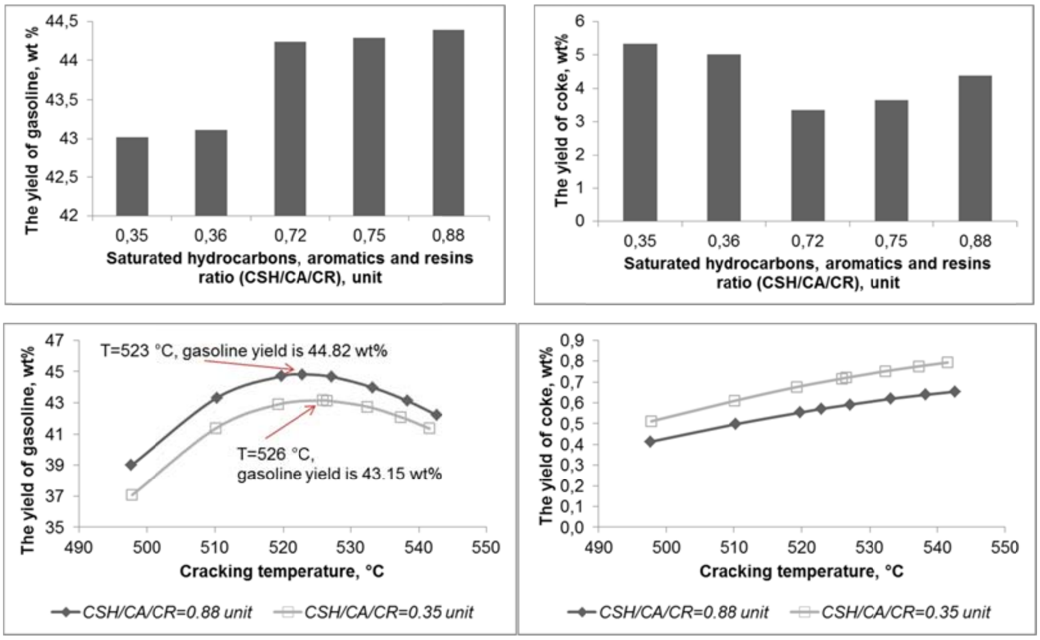

Figure 1. a) The catalytic cracking gasoline and coke yields depending on the feedstock composition b) The catalytic cracking gasoline yield and coke content on the catalyst depending on the feedstock composition and cracking temperature

According to figure 1 the gasoline yield are characterized by extremum with increasing the cracking temperature (44.82 and 43.15 wt %, if saturated hydrocarbons, aromatics and resins ratio (CSH/CA/CR) are 0.88 and 0.35 unit respectively). Importantly, that when optimizing the process, it is required to consider that the maximum gasoline yield is shifted to low temperatures from 526 to 523 °C, when the feedstock saturated hydrocarbons amount increases.

Predictive calculations provide us to adjust the riser process conditions in order to increase the target product yields and to reduce the excess coke formation, depending on these factors. In the future, we are going to account the reversible and irreversible catalyst deactivation and to develop the methodology for the feedstock group composition calculation on the basis of plant laboratory regular data about the fractional composition, the density, the molecular weight, the refractive index and other quality indicators to expand the model application.

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MATRIX CONVERSION OF PROPANE-BUTANE MIXTURE TO SYNGAS

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Currently, technologies that will enable the use of unconventional sources of gaseous hydrocarbon raw materials to produce petrochemical products with high added value are extremely relevant. One of these types of unconventional hydrocarbon raw materials is associated petroleum gas (APG), rich in propane and butane, most of which is flared [1].

One of the effective methods of processing of APG can be a matrix conversion of hydrocarbons to syngas, flowing in the super-diabatic combustion conditions in which the conversion of fuel-rich mixtures [2, 3]. The resulting synthesis gas (a mixture of CO and H_2) can be directed to the subsequent catalytic stages of the synthesis of methanol, dimethyl ether, and synthetic liquid hydrocarbons [4].

Experimental tests of the matrix conversion of propane-butane mixture were carried out using air as an oxidizer. The studies were carried out when the values of the main process parameters changed: the initial ratio of fuel and oxidizer, the pressure inside the Converter, and the flow rate of the initial mixture. As a result, for further optimization of the process was determined as the region of parameters in which there is a stable combustion of propane-butane mixture.

To date, a synthesis gas has been obtained with a hydrogen content of 11.5 % vol, CO - 13.5 % vol, and CO_2 - 4.7 % vol with a specific fuel mixture consumption of 10 l / h per 1 cm^2 of the matrix surface and an excess oxidizer coefficient $\alpha = 0.4$.

During the matrix conversion, in addition to the main components of the synthesis gas, a small amount of acetylene is obtained, at the level of 0.5 – 1 % vol., which is a catalytic poison in the further processes of obtaining petrochemical products. In this work, it is experimentally shown that adding water vapor to the initial mixture allows reducing the acetylene content in the synthesis gas by 2-3 times.

Thus, for the first time, studies were conducted on the matrix conversion of propane-butane mixture into synthesis gas at various process parameters. Atmospheric air was used as an oxidizer. It is worth noting that under the studied conditions, a complete conversion of all reagents was observed. The total content of CO and H_2 in the nitrogen-ballasted syngas was more than 25 % vol.

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PP-56

ACTIVE AND STABLE Ru AND Ni-BASED CATALYSTS FOR CO_2 REFORMING OF GLYCEROL TO SYNGAS

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Glycerol emerges as a continuously and undesirably accumulating side product of biodiesel, a trending renewable counterpart of the conventional diesel. Catalytic reforming of glycerol with CO_2 offers simultaneous valorization of a greenhouse gas with a renewable and commercially available hydrocarbon to synthesis gas, a value–added feedstock for the production of methanol, synthetic fuels and dimethyl ether. While co–utilization of the two wastes to syngas attracts increasing interest [1], the literature is still open for the catalysts that are both active and stable under the conditions of glycerol dry reforming (GDR). In this respect, La_2O_3 (L), ZrO_2 (Z) and La_2O_3–ZrO_2 (LZ) supported Ru and Ni–based catalysts are studied at GDR conditions to elucidate the roles of active species and support material on catalytic activity and stability. The active species, Ru and Ni, are selected on the basis of their superior performance in transforming hydrocarbons and CO_2 to syngas [2].

The catalysts containing 1 wt. % Ru and 5 % Ni are synthesized by incipient-to-wetness impregnation technique explained elsewhere [3]. Upon calcining them at 800 °C for 4 h, the catalysts are reduced under 99.99 % pure H_2 flow (Linde) at 800 °C for 2 h prior to the GDR tests. Experiments are conducted in a quartz reactor at the residence time range of 0.5–3.75 mg·min/Nml. Dosing of high purity (>99.5 %) glycerol (Sigma-Aldrich) and gaseous species (CO_2 and N_2, purities: 99.99 %, Linde) are made by an HPLC pump (Shimadzu LC-20AD) and mass flow controllers (Brooks 5850E), respectively. In all experiments, glycerol and total flow rates at inlet are fixed to 4 and 40 Nml/min, respectively. Molar inlet ratio of CO_2–to–glycerol (CO_2/G) and temperature are studied in the ranges of 1–4 and 650–750 °C, respectively. Glycerol conversion is calculated by elemental balance of H existing in gaseous species detected by the gas chromatographs [3]. Activity and stability are quantified in terms of CO_2 conversion which is obtained directly from the measured inlet and exit CO_2 molar flow rates, making it a more reliable metric for catalyst performance. Equilibrium conversions of CO_2 and glycerol are calculated by GFE minimization in CHEMCAD (v7.1.4) suite.

The initial tests involved testing of the Ru/LZ and Ni/LZ catalysts at 750 °C, 0.5 mg·min/Nml and $CO_2/G = 1–4$. Upon increasing CO_2/G, thermodynamic CO_2 conversions decreased monotonically, whereas experimental CO_2 conversions remained almost unchanged until $CO_2/G=2-3$ and then decreased. Ni/LZ and Ru/LZ performed closest to (>90 % of) the theoretical limits at CO_2/G of 2 and 3, respectively. At these conditions, Ru/LZ gave 31.2 % CO_2 and 73 % glycerol conversions, whereas Ni/LZ was capable of converting 38.9% and 71 % of the inlet CO_2 and glycerol, respectively. Syngas was produced at $H_2/CO = 0.7–0.9$. Performance of Ni/LZ is noted as the highest among those of the other Ni–based catalysts reported in the GDR literature [1]. Based on these findings, monometallic Ru/L, Ru/Z, Ni/L and Ni/Z catalysts are tested for their activity and 72h time on stream (TOS) stability (Figure 1). The results show increased activity and stability upon supporting metals on LZ. The extent of increase is more obvious in Ni. Even though Ni/Z and Ru/Z are initially more active than their La_2O_3-supported counterparts, they deactivate more rapidly. In this respect, addition of La_2O_3 to ZrO_2 is believed to improve the dispersion of the active species, which enhanced activity and suppressed deactivation due to coking and sintering. These findings are subject to validation by the currently ongoing structural and functional characterization studies.

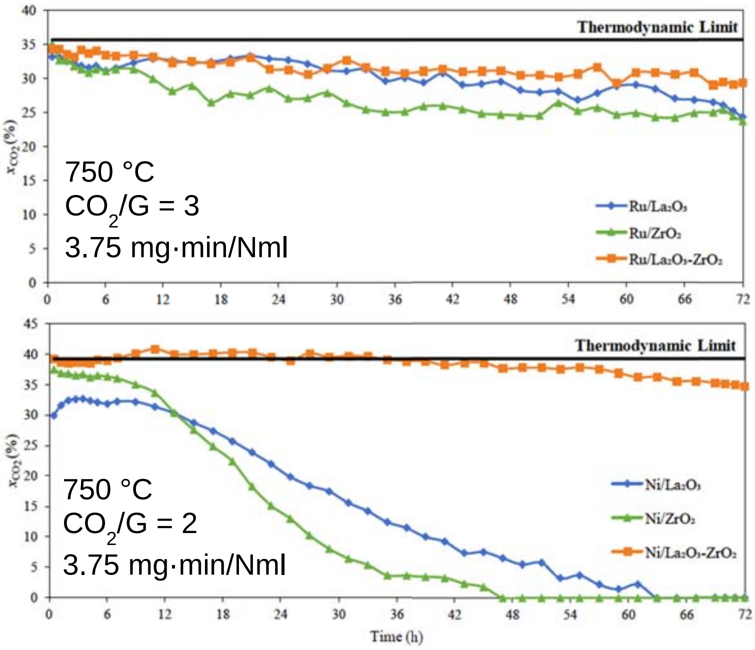

Figure 1. 72h TOS tests for Ru- and Ni-based catalysts

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PP-57

ISOMERIZATION OF *n*-BUTANE AND C4 REFINERY FRACTIONS ON Pd PROMOTED SULFATED ZIRCONIA. KINETIC ASPECTS AND PROCESS MODELING

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Catalyzed by sulfated zirconium, isomerization of n-butane is an alternative method to the conventional one. Highly active and stable Pd-modified sulfated zirconia catalysts (*Pd-SZ*) can significantly improve the *n*-C4 isomerization process and are promising for industrial implementation [1]. Further in-depth studies of the kinetic aspects and the process when using real feedstocks, such as C4 refinery fractions, were the goal of the present work.

Kinetic experiments on *Pd-SZ* catalysts were performed in the isothermal flow reactor in the *n*-C_4 conversion range of 5…25 %. Reaction conditions were as follows: temperature 125…160 °C; WHSV 1…11 h^{-1}; H_2/C_4 0.1…1.0 mol/mol, and pressure 6…25 bar. A simplified kinetic model of *n*-C_4 isomerization was proposed.

Effect of the real feedstocks (Table) on the isomerization process was studied at 20 bar, with variating temperature (120…160 °C), feedstock WHSV (1.0…2.5 h^{-1}), and H_2/*n*-C_4 (0.1…0.5) [2]. Conditions were determined that prevent excessive formation of C1-C3 alkanes and provide a high isobutane yield. Based on the experimental data, mathematical modeling of the process in an adiabatic reactor was performed. Key indicators of the catalytic process for the C4 refinery fractions isomerization have been evaluated.

Table. Composition (%wt.) of *n*-butane and C4 refinery fractions

Composition	*n*-C_4	C4 refinery fractions	
		A	B
Ethane	–	–	0.002
Propane	0.017	0.008	0.294
Isobutane	0.125	1.192	9.470
n-Butane	99.724	98.063	89.623
Neopentane	0.134	0.713	0.604
Isopentane	–	0.020	0.004
n-Pentane	–	0.004	0.003

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PP-58

EFFECT OF C3-ALCOHOLS IMPURITIES ON ALUMINA CATALYZED DEHYDRATION OF BIOETHANOL TO ETHYLENE. EXPERIMENTAL STUDY AND PROCESS MODELING

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The transition of the energy and traditional petrochemical industries to renewable sources of plant origin is consistent with the Principles of Green Chemistry. Bioethanol produced from non-food phytogenic feedstock can be used to produce ethylene as a platform product for a large number of downstream derivatives [1]. After distillation, bioethanol contains impurities of C3-alcohols, which can have an adverse impact on its further processing [1-3]. In the present work, we focused on the studies of the organic impurities influence on the dehydration of contaminated ethanol to ethylene and the catalytic activity of the proprietary alumina catalyst [4].

We examined two samples of real 2G bioethanol and found that C3-alcohols (1- and 2-propanol) were the predominant impurities. A series of model 92 % wt. bioethanol samples with 1-propanol or 2-propanol loading from 0.1 to 5 g/L were prepared and used for dehydration. The catalytic activity was studied in an isothermal flow reactor at 370-400 °C using the acid-modified alumina catalyst [4] under kinetically controlled conditions. The maximum allowable content of C3-alcohols in ethanol was found to be 1 g/L, which is equivalent to 0.05 % mol in gaseous feedstock. With such a loading, ethanol conversion and ethylene yield are not suppressed by impurities, but the yield of by-products (acetaldehyde, hydrogen, butenes) is greatly reduced, which significantly improves the quality of ethylene produced.

Based on the experimental results, mathematical modeling of dehydration process in the multitubular fixed bed reactor was performed. We applied a pseudohomogeneous 2D reactor model [5] with an extended basic kinetic model. Key indicators of catalytic process have been evaluated for using bioethanol with C3-alcohols impurities.

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PP-59

METHOD FOR PREPARATION OF THE DEFECTIVE SURFACE OF PRODUCTS MADE OF HEAT-RESISTANT NICKEL ALLOYS FOR BRAZING

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There are large number of ways for cleaning the surfaces of various components made from metals or their alloys. These methods are based on the use of organic liquids, aqueous solutions of detergents and etchants in combination with mechanical cleaning technique like, for example, pneumatic and hydroabrasive jets. Most of these procedures are applicable to easily accessible surfaces of metal components. A special case is the high-quality cleaning of the hard-to-reach surface of the cracks from metal oxides and fuel combustion products, formed on the turbine blades during the operation of aircraft engines and power plants.

It is known that DAYTON technology is widely used to repair cracked metal components, that increases the service life of these components, saves materials and reduces labor costs compared to the manufacture of the new ones.

Repair of the components using this technology is carried out in two stages: cleaning the surface of cracks from metal oxides; high-temperature brazing of cracks with special high-heat-resistant solders. The key stage in the DAYTON technology (developed and patented by the UDRI-University of Dayton, Research Institute in 1980) is the process of high-quality removal of metal oxides from the surface of the cracks mouth (FCP-Fluorocarbon Cleaning Process) [1].

Thus, preparation of cracks surface, i.e., removal of metal oxides and hydrocarbon combustion products, is a requirement for repairing cracked components by high-temperature vacuum brazing. In the Boreskov Institute of Catalysis SB RAS, together with the Lavrentyev Institute of Hydrodynamics SB RAS, interdisciplinary research was carried out to develop the new method for cleaning microcracks in metallic materials, taking into account the aspects of chemical, thermophysical and hydrodynamic processes in capillary structures of micron and submicron sizes [2,3]. Concept and the new approach based on the use of a contact solution in the liquid phase have been developed. Compositions of contact solutions have been developed and setup-stand for experimental justification of the new method was created. The experiments were carried out on simulator samples made of nickel-base alloy (see Table) and pre-treated under operating conditions. In the experiments, the state of the cracks surface of the samples-simulators was controlled by an INCA Energy (X-ray energy dispersion) spectrometer, installed on the LEO-420 focused beam electron microscope. The process of cleaning the dirty surface of alloys from metal oxides is carried out without the use of high temperatures (about 100 °C versus 500-1100 °C for DAYTON FCP technology) and pressures (≤ 1 atm).

Table. Composition of alloys

Alloy	**C**	**Cr**	**Al**	**Ti**	**Mo**	**W**	**Co**	**Nb**	**B**	**Ni**
C-1023	0.15	15	4.2	3.6	8.25	-	10	-	-	Basis
ЖС6У	0.1-0.2	8-9.5	5.1-6	2-2.9	1.2-2.4	9.5-11	9-10.5	0.8-1.2	< 0.05	Basis

It is shown that the selected gas and hydrodynamic parameters of the process with variation of the temperature and composition of the contact solutions provide multi-cycle flushing of narrow gaps in times not exceeding 30 min, achieving complete removal of the metal oxides and of the hydrocarbon fuel combustion products.

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PP-60

ENHANCEMENT OF BTEX IN EX-SITU CATALYTIC UPGRADING OF BIOMASS PYROLYSIS VAPORS ON METAL LOADED HZSM-5 CATALYST UNDER METHANE ENVIRONMENT

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Abstract

To address the environmental issues caused by fossil fuels utilization, and achieve energy sustainability, the production of BTEX (benzene toluene ethylbenzene xylenes) which are important feedstock's in petrochemical industry should be produced from biomass [1]. Catalytic fast pyrolysis is an intensive technology by which solid biomass can be converted into bio-oil. However, the it not suitable to use as drop in fuel, hence it has to be upgraded on catalysts before the pyrolysis vapors condensed. Ex-situ catalytic upgrading is best method to produce the aromatics. The vast reserves of the methane around the world, motivated the researcher to employ co-feeding gas in the catalytic upgrading process of pyrolysis oil [2]. Methane, with highest H/C eff ratio = 2, could provide the methyl radical in the pyrolysis process and increase the bio-oil yield, the hydrogen radicals can maintain the bronzed acidic sites on zeolite by exchanging the proton with zeolite and thus suppress the deactivation of zeolite. In this context, we employed the methane as the co-feeding gas to create different hydrogen rich environment in the ex-situ upgrading of yellow poplar pyrolysis to increase BTEX content in the upgrading bio-oil.

Experimental

Ex-situ catalytic experiments performed in down flow fixed bed reactors connected in Series. The following parameters were used applied, biomass: Yellow poplar (15g), Catalysts: Z: HZSM-5 (5g), 1Ga-Z: 1Ga/HZSM-5 (5g), C/B = 0.33, Reaction environment: N_2, CH_4 (with and without decomposition), the effluent as from the methane decomposition was fed into ex-situ upgrading reaction.

Results

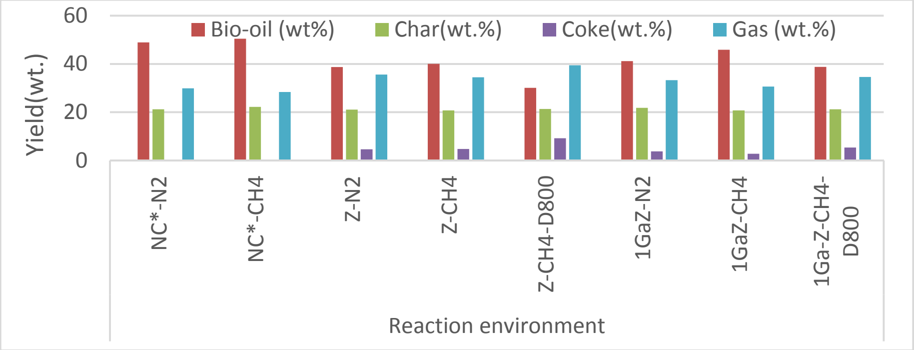

Figure 1. Distribution of ex-situ upgrading products

NC* represents, Z: HZSM-5, 1GaZ:1%Ga/HZSM-5, CH4D800 represent environment of the methane decomposition at 800 °C

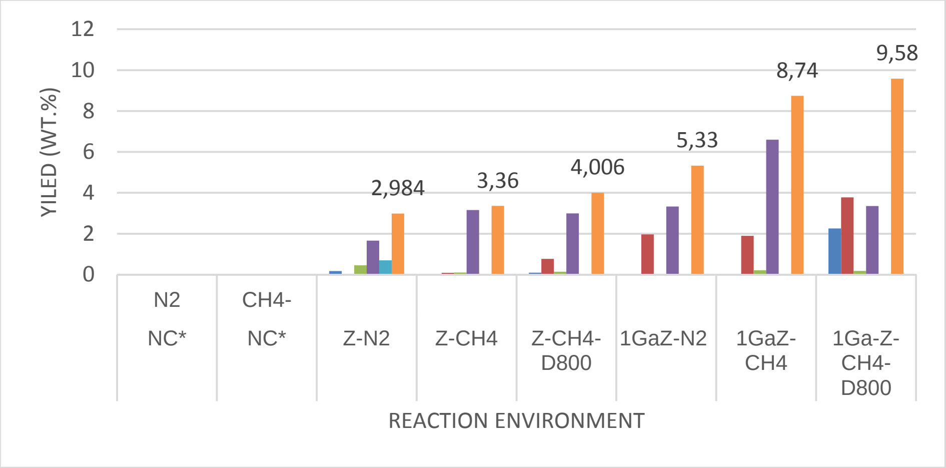

Figure 2. Comparison of BTEX yield under N_2, methane environments

Conclusions

The yield of BTEX in the catalytic ex-situ upgrading of yellow poplar pyrolysis was reached to maximum of 9.58 wt. %, when reaction environment switched from N_2 to methane decomposition. Methyl and hydrogen radicals generated from methane, reduced the oxygenated products in the upgraded oil.

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PP-61

INFLUENCE OF OXYGEN EXCHANGE IN PEROVSKITE-LIKE OXIDES ON MICROTUBULAR MEMBRANE REACTOR

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Oxygen-transport membranes (OTM) composed of oxides with mixed ionic-electronic conductivity (MIEC) are widely used in various innovative technologies. They have 100 % oxygen selectivity can be easily incorporated into high-temperature processes, for example, partial oxidation of hydrocarbons (methane conversion to syngas, etc.).

In our previous work [1], we show the opportunities given by the heating of OTMs by passing AC through the membranes. This way not only allows us to enhance the energy efficiency, productivity of the membranes, and gives fast-response control of the reactor temperature but also opens the access to the surface of the operating membrane and therefore makes it possible to study the mechanism of oxygen permeability *in situ* with the help of physicochemical techniques.

Moreover, we have developed new oxygen release techniques (QEOR and OPPR) to obtain kinetic and equilibrium parameters in grossly nonstoichimetric oxides [2, 3].

The aim of this work was to carry out a comprehensive analysis of the effect of oxygen nonstoichiometry on the kinetic parameters in the processes of oxygen transport and relaxation measurements. A theoretical model has been developed for comparing the results of three independent methods. The influence of oxygen nonstoichiometry to the process of oxygen transport through gas-tight microtubular membranes was carried out. Obtained data were used to optimize the developed microtubular membrane reactor.

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PP-62

EXPERIMENTAL INVESTIGATIONS OF THERMAL COMBUSTION OF LEAN METHANE AIR MIXTURES IN CERAMIC FOAM BED

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The work refers to the issue concerning thermal combustion of lean methane air mixtures in ceramic bed. Such mixtures are known as Ventilation Air Methane (VAM) and are released into the atmosphere by the coal mine industry. The methane concertation in VAM is usually below 1 vol. %. The process of VAM utilization by thermal combustion can be successfully accomplished in thermal flow reversal reactors (TFRR) [1, 2]. The combustion process in TFRR is initialized in a monolith ceramic bed where temperature is higher than the ignition temperature. The ceramic bed in the form of honeycomb monoliths with many parallel channels is commonly used in many industrial apparatus due to the low flow resistance as well as excellent heat transfer and mechanical properties for a large thermal gradient. However, their structure do not allow mixing of the reactants in the reactor cross-section, what can be relevant in high temperature processes. It seems that such a cross-mixing can be achieved by the application of a ceramic foam. The idea was born during the work on aerodynamic simulations of the pilot scale of TFRR (35,000 m^3_{STP}/h) with monolith bed [3]. The simulations revealed that the uniformity of gas flow in the outlet section of the reactor was not satisfactory. This is caused by too high gas velocity in the channel at the top of the TFRR what causes turbulence at the entrance to the monoliths of the outlet section. One solution is the modification of the geometry of the top part of the TFRR reactor. Good idea could also be modification depends on a partial replacement of monolith by foam. The structure of the foams enables the flow of gas through the bed in all directions what in the case of high temperature processes is reflected in better temperature distribution in the cross-section of the reactor and better use of the bed to storing the heat released during the reaction. The new comparative experiments of thermal combustion of VAM were carried out in a tubular reactor with foam bed with similar surface area to that of monolith called as B in [4]. The set of experimental parameters were identical to those carried out in the monolithic system. It was found that the ignition temperature of the VAM mixture in the tested foam bed is almost identical to that determined in the comparable monolith. In the experiments, the combustion zone was assumed as the volume of the reactor in which the temperature is higher than the ignition temperature. The determination of such a zone was possible by the measurements of the temperature along the bed by a moveable thermocouple. The achievement of the temperature profile in foam bed similar to that measured in the monolith, was possible for the lower furnace temperature, i.e. by about 70 °C. A comparison of the reactants content for similar temperature profiles along the combustion zone in foam and monolith, showed that the methane conversion is higher in case of the foam bed. It was found out that the increase of a furnace temperature by 10 °C has a significant influence on methane conversion value. It was also observed that the differences in methane conversions between experiments carried out in the foam and monolithic bed for the similar temperature profiles, are growing up with the temperature increase from 1.5 times for lower temperatures to 5.8 times for higher temperatures. Lean methane-air mixtures burn to the same products: CO and CO_2 in both variants of the bed. Comparison of the products for the similar methane conversion and for similar inlet methane concertation, revealed that the combustion process in foam generates mainly CO_2 with smaller amount of CO what is opposite to results obtained in monolith bed. The poster presentation will include the results of experiments, listed above, their comparison with monolith bed of the similar surface area and the basic properties of the foam used in the experiment.

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PP-63

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF Al-SBA-15 CATALYST

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The growing demand for safe industrial processes has led to the development and use of environmentally friendly solid catalysts intended for use in acid-catalyzed value-added reactions. Acid catalysis is one of the most common processes in the chemical industry. Industrially important organic transformations include esterification and transesterification, etherification, dehydration, oxidation, acetylation, silylation and biodiesel synthesis [1,2]. Solid acid catalysts, known as «green catalysts», are used as a substitute for homogeneous acid catalysts. They contain more environmentally friendly components, while providing greater activity and selectivity compared to existing homogeneous catalysts [3]. An example of a heterogeneous catalyst is mesoporous silica – modified SBA-15, which is used in many organic reactions.

The focus of this study was to synthesize a solid acid catalyst based on mesoporous silica SBA-15 with incorporated metal Al. By trapping the metal in a silicate matrix, the activity and selectivity of the catalyst is improved, it becomes more temperature-resistant and has a greater potential for reuse. The synthesized catalyst was characterized by nitrogen adsorption-desorption (BET), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), dynamic light scattering (DLS), thermogravimetric analysis (TGA), temperature programmed desorption (TPD), and temperature programmed reduction (TPR). Furthermore, using this catalyst, a series of oleic acid esterification reactions in methanol were carried out with the production of oleic acid methyl ester. All experiments were performed in a laboratory batch reactor. The influence of reaction temperature (50, 55, 60, and 64.5) °C and catalyst mass (0.025, 0.05, 0.1, 0.2 and 0.3 g) on the reaction conversion were studied. The reaction efficiency was monitored by determining the concentration of oleic acid and methyl oleate using GC-FID. We also checked the loss of catalyst activity after repeated use. The results show that the conversion increases with increasing temperature and mass of the catalyst up to 0.2 g. Further mass increase didn't result in increased conversion. The study was upgraded by determining the kinetic parameters; thus, the Langmuir-Hinshelwood-Hougen-Watson model was:

$$\frac{dX_A}{dt} = k\, c_{A0}\, (1 - X_A)(M - X_A)$$

Table 1. Activation energies at different loadings of the catalyst

m_{cat}/g	0.025	0.05	0.1	0.2	0.3
E_{a}/kJ mol^{-1}	80.3	59.9	52.2	34.9	42.1

Activation energy decreases with increasing mass of the catalyst up to 0.2 g. After further increase of the catalyst mass it slightly increases. This is due to mass transfer limitations and possible formation of catalyst aggregates.

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Acknowledgement

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PP-64

CONVERSION AND PRESSURE DROP IN CATALYTIC PARTICULATE FILTERS

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Catalytic converters and particulate filters are required to meet strict emission limits for vehicles with internal combustion engines. The exhaust aftertreatment systems can be spacious and expensive. To address these issues, catalytic particulate filters have been developed with an active catalytic layer deposited directly onto or into the walls of the porous filter substrate. In this way, harmful gaseous emissions are eliminated and particulate matter trapped in one device. However, the catalytic material has to be properly distributed to achieve a high conversion and filtration efficiency while keeping a low pressure drop [1].

In this work we present results of lab measurements of several catalytic particulate filters with $Pt/\gamma\text{-}Al_2O_3$ catalyst washcoated on a cordierite filter. The samples differ in particle size distribution of the coated slurry, which leads to different properties and location of the catalytic washcoat in the filter. The samples were tested in a lab reactor with the inlet mixture of synthetic gases (CO, O_2, H_2, C_3H_6, NO, CO_2, H_2O, and N_2) simulating the real exhaust gas. The outlet gas composition was analyzed by FT-IR MKS HS 2030 and MS Hiden QGA. Conversion and pressure drop of the filters were measured at several different flow rates.

The obtained results indicate that compact on-wall coating leads to an unacceptably high pressure drop. A balanced distribution of the coating onto and into the filter wall seems to provide a promising structure for optimum performance of the catalytic filter.

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PP-65

STRUCTURE, STABILITY, AND TRANSPORT PROPERTIES OF NEW COMPOSITE MATERIALS FOR HYDROGEN ENERGY

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The concept of hydrogen energy over the past decades has been considered as one of the main vectors of development of the energy industry in the future. Hydrogen obtained by chemical, physical, and electrochemical transformations can become a universal energy carrier, which makes it possible to construct the global and local energy supply systems most efficiently, and combine the production, transportation, storage, and use of energy by various consumers into a single complex. The use of hydrogen in mobile (transport) and stationary power plants will largely solve the problem of environmental pollution by fuel combustion products. The development of effective and cost-efficient technologies for the production of pure hydrogen is one of the fundamental tasks of hydrogen energy. Another important aspect, in addition to producing pure hydrogen, is the efficient production of electricity. For this goal, proton-ceramic fuel cells (PCFCs) are promising candidates. The use of PCFCs makes it possible to obtain electricity with very high efficiency, minimal emission, and use hydrogen or hydrocarbons as fuel.

This work is aimed at studying the features of the formation processes and the physical properties of new composite materials for electrochemical devices for producing hydrogen and generating electricity. Composites are very difficult objects to study since many factors influence their formation and characteristics. The development of fundamental ideas about the principles of the formation of composite systems and the processes that occur during this process is of great scientific importance. The creation of a technology based on the materials under study will significantly increase the efficiency of production of pure hydrogen, as well as use not only natural gas in hydrogen production, but also exhaust gases from power plants and chemical by-products. In electricity generation, composite materials can be used in PCTE as electrodes to expand the electrochemically active region and reduce polarization losses.

PP-65

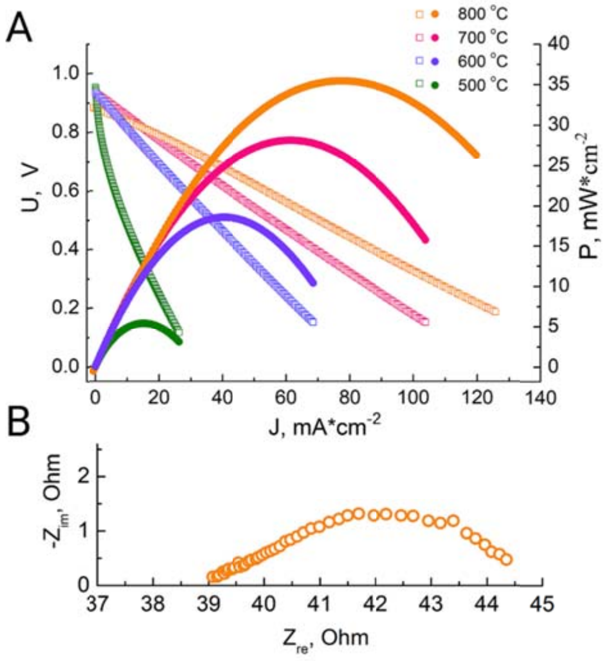

Fig. 1. A – I–V and power density curves. B – impedance spectrum of the protonic-ceramic fuell cell with composite electrodes based on $La_{0.9}Sr_{0.1}Sc_{0.9}Co_{0.1}O_{3-d}$

In our previous work, we have extensively studied proton-conducting oxides based on $LaScO_3$ and determined the advantages of those materials in terms of chemical stability, conductivity, and electrochemical activity [1-5]. In this work, we develop a foundation composite electrodes, that contain a ceramic matrix of a triple conducting material $La_{0.9}Sr_{0.1}Sc_{1-x}Co_xO_{3-d}$ and an electronic conductor $La_{0.9}Sr_{0.1}CoO_{3-d}$. The tailoring of performance is base on particular attention to the microstructure f the composite as well as to the method of its formation.

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PP-66

STEAM-OXYGEN CONVERSION OF METHANE IN A POROUS BED REVERSED FLOW REACTOR: KINETIC MODELING

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The idea of reversed flow non-premixed reactor [1] (Fig.1) promises the a substantial enhancement of both the energy efficiency and safety for partial oxidation conversion of hydrocarbon gases to synthesis gas. On the example of methane

$$CH_4 + X{\cdot}O_2 + W{\cdot}H_2O \rightarrow m{\cdot}CO + h{\cdot}H_2 + m{\cdot}CO + w{\cdot}H_2O$$

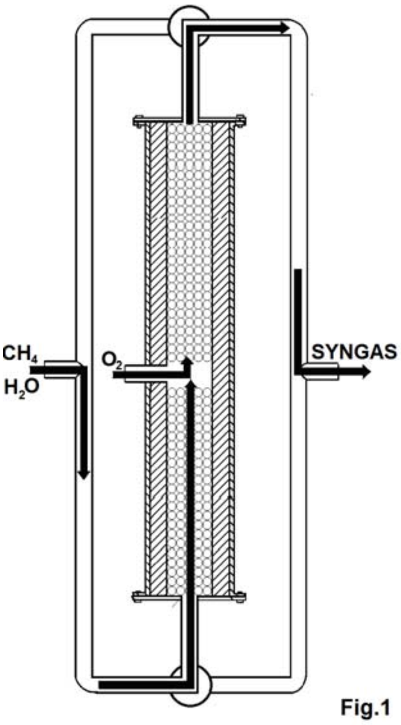

Fig.1

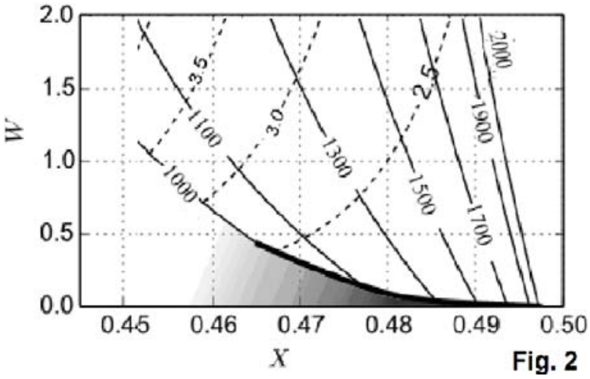

Fig. 2

The thermodynamic model given in [1] predicts for established regime of conversion a very high efficiency. The preferable embodiment for steam-oxygen conversion in this case is supply of steam-methane mixture via the heat exchanger reactor filled with a porous heat carrier and injection of oxygen in the middle part of the reactor.

Before this promising approach can become a practical technology, the predictions of the thermodynamic model need to be checked both numerically and experimentally addressing the following problems, what are the kinetic rate limitations on the reactor throughput, what effect has the interphase heat- and mass-transfer, how the transients associated with the flow reverse affect the overall performance. We used a numerical model previously developed for modeling of premixed air-steam-methane conversion in a chemically inert porous medium. The one-dimensional two-temperature (gas/solid) non-stationary model considers 90 reactions of 28 reactive species including soot (carbon) formation on the inert solid surface and soot reactions with oxygen, steam, and carbon dioxide. Figs. 3-4 show several calculated distributions during first cycles of flow reverse for *X* = 0.47 and *W* = 0.49 These flowrates are close to the limits predicted by the model [1] (See Fig. 2).

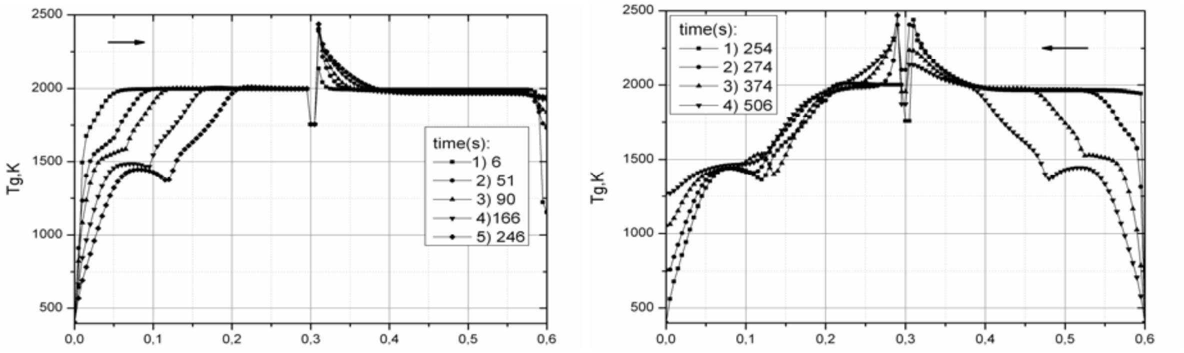

Fig. 3. Distribution of gas temperature during first two cycles of flow reverse

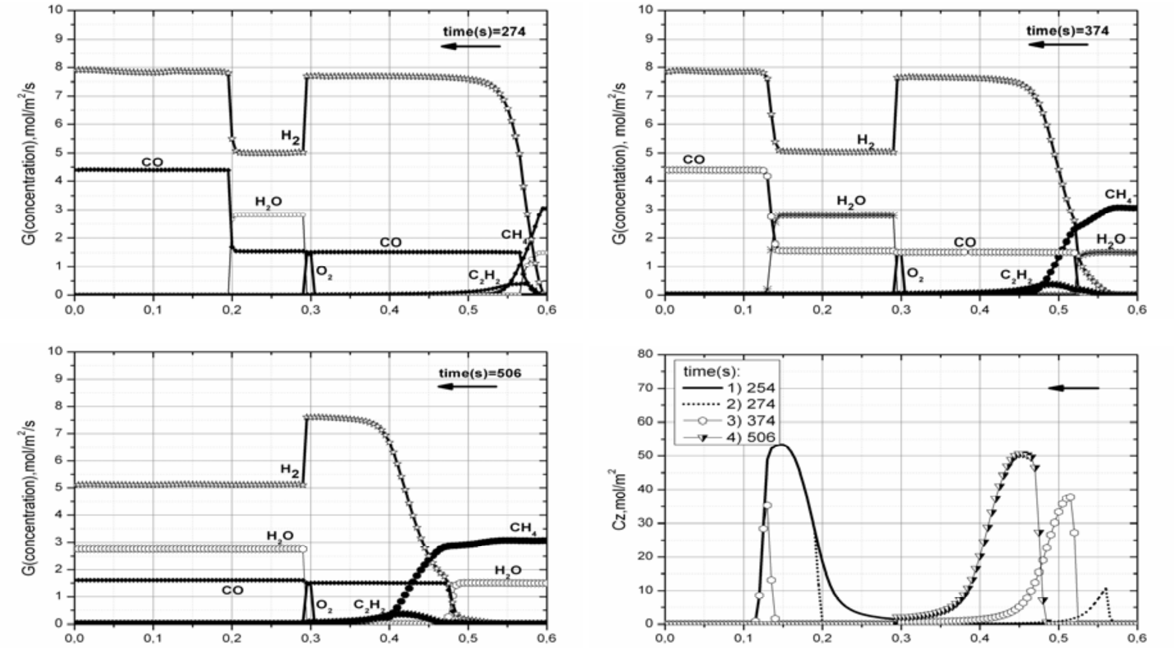

Fig. 4. Snapshots of gas flowrates and soot concentration during the second cycle

The process is substantially non-stationary. Initially soot accumulates at the side where methane is supplied. This accumulated soot is further consumed with the excess steam formed as the hydrogen reacts with the oxygen supplied to the center of reactor. In several reverses of the flow the process comes to an established cycle.

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PP-67

CONVERSION OF 2-PROPANOL TO SYNGAS VIA PARTIAL OXIDATION IN FILTRATION COMBUSTION

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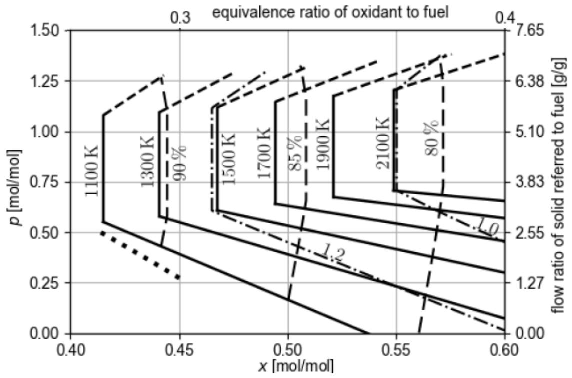
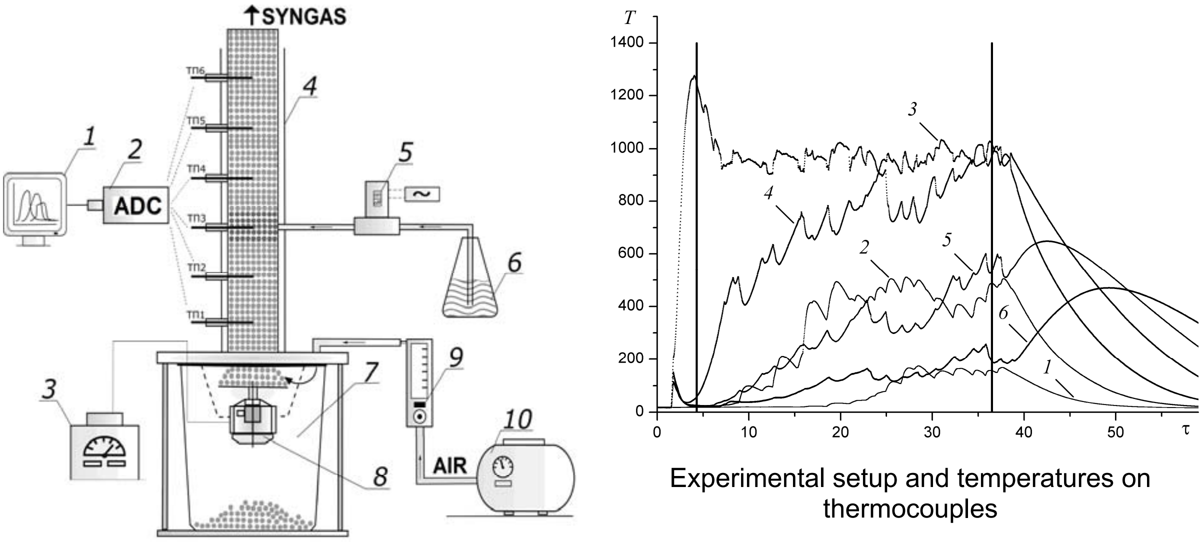
Conversion of various hydrocarbon feedstocks into syngas via partial oxidation (POX) in regime of filtration combustion (FC) in inert porous matrix promises substantial improvements over conventional methods. To mention a few, heat recuperation on the solid matrix providing high energy efficiency, a possibility to avoid cocking of a catalyst, omnivorous in feed, a possibility to use air for oxidant.

A version of such process, conversion of hydrocarbons in a non-premixed moving bed FC reactor with fuel supplied to the middle part of the reactor to react with preheated air flow was proposed in [1]. Predictions of [1] (conversion regimes and combustion) made with strongly simplified model need an experimental test.



Predictions of thermodynamic model [1] for 2-propanol air conversion



Experimental setup and temperatures on thermocouples

We used quasi-continuous heat-insulated 65-mm id vertical quartz reactor with a rotary grate to controllably discharge granular solid (porcelain Raschig rings) to the discharge bin. The air was supplied from below. Combustion was ignited in the reactor on the level of TC3 and 2-propanol was supplied there with a constant supply rate ~6 ml/min. The discharge of granular solid was controlled to maintain the temperature on TC1 for the established regime at a constant value. Fresh solid was charged atop to maintain constant charge level. Syngas was withdrawn from the upper part of the reactor and analyzed using a gas chromatograph.

The experimental procedure was similar to that previously used to gasify pulverized coal [2, 3]. The established regimes were studied for varied air flowrates. The control of discharge secured solid flowrate equal in heat capacity to that of air (transition to intermediate regime in terms of [1]).

Major characteristics of isopropanol conversion depending on oxygen excess ratio α

α	Concentration of gases, % vol.							Q_g, MJ/m^3	T_c, °C
	CO_2	CO	O_2	C_3H_6	C_2H_4	CH_4	H_2		
0.34	7.47	15.4		4.5	1.8	4.61	3.73	8.64	923
0.52	8.17	14.2		1.43	1.25	2.19	1.7	4.55	990
0.61	11.8	13.6		1.21	1.05	1.74	1.11	3.96	1005
0.80	6.84	9.48	8.29	1.21	0.68	1.1	1.11	2.03	1050
1.69	2.76	7.53	16.2	0.02	0.15	0.25	0.21	1.10	1070
1.95	1.8	7.29	17.8	0.02	0.08	0.12	0.11	0.97	1060

The gas analyses show general qualitative agreement of the trends of combustion temperature and gas composition with the predictions of [1]. However, the temperature was much lower than that predicted for adiabatic reactor. The gas is far from equilibrium and contains light hydrocarbons. Another complication revealed was poor gas mixing within porous bed indicated by the quenched combustible species in gaseous products for fuel-lean supply ratios.

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PP-68

SELECTIVE ACETIC ACID ELECTROCHEMICAL SYNTHESIS ON ACID SUPPORTING SINGLE ATOMS CATALYSTS

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Methane is present in large amounts on the earth, being the main constituent of natural gas and coming from many other sources [1]. Moreover, CH_4 is a greenhouse gas whose negative effects on the environment are over 30 times more potent than CO_2. More and more attention for fruitful methane oxidation and conversion versus an effective utilization and emission reduction is thus desirable. The methane combustion produces a smaller amount of CO_2 compared to emissions from the other fossil fuels, making the use of methane a promising intermediate step before a total replacement with renewable sources. On the other hand, methane availability encourages for upgrading methane into value-added products, too. However, the use of methane as chemical raw materials is still insufficient. Indeed, methane is inherently difficult to activate, this is due to its lack of polarity and chemical inertness. Moreover, for CH_4 conversion to syngas or other products, large scale production facilities and/or high temperatures and energy still constitute significant drawbacks.

Despite its direct transformation, via conventional heterogeneous and homogeneous catalysis, has been the object of a lot of studies, it still remains a challenge. Electrocatalytic approaches represent promising alternatives [1], overcoming the methane chemical inertness thanks to the rapid generation of highly reactive species, and supplying partially oxidized stable products at relatively low temperatures.

An efficient catalyst for this process must be able to fulfil different functions: activate oxygen; adsorb and activate methane; and, allow the formation of specific molecules, avoiding subsequent oxidation. In this scenario, the use of multi-components, with different functionality to optimize activities, selectivity and costs, is the way forward. Supported single-atom metals [2], maximizing atom efficiency (activity >1,000 times higher than that of free cations), have been demonstrated promising materials for C–H bonds activation.

Herein, to develop an enhanced catalyst for direct and selective oxidation of methane at low temperature, single atoms (Rh, Ir and Ru) dispersed on Al_2O_3, were prepared. Magnetic resonance imaging was employed to map the solid phase distribution of the active component precursors within the support bodies. Brønsted acid sites, important for carbonylation reaction and acetic acid yield, were generated by NH_4BF_4 modification. We found that the prepared nanocatalyst can catalyse efficiently the selective oxidation of CH_4 to acetic acid.

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HIGHLY DISPERSED Ni/$Ce_{0.75}Zr_{0.25}O_2$ CATALYSTS FOR LOW-TEMPERATURE STEAM REFORMING OF FLARE GASES

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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:

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

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \qquad (2)$$

It was shown that catalyst activity is proportional to metallic Ni available surface area. Conventional Ni-based natural gas steam reforming catalysts with Ni loading of 10-15 wt. % have got too low Ni surface area and are not appropriate for the reaction. Industrial Ni-based methanation catalysts with Ni loading of 30-50 wt. % demonstrate sufficient activity in the process. But they however suffer from complicated activation procedure, pyrophoricity and insufficient thermal stability. Thus, there is a need for development of highly active Ni catalysts with moderate Ni loading, which will simplify activation/passivation procedure, i.e. high Ni dispersion is required.

In the present work we proposed Ni/$Ce_{0.75}Zr_{0.25}O_2$ (further X % Ni/CeZr) prepared via incipient wetness impregnation by water-glycol solution of Ni(II) nitrate. Catalysts demonstrated high Ni dispersion (Table 1) which kept unchanged after catalytic tests. Catalysts were studied in LTSR of model propane-methane mixture and compared with industrial Ni-Ref and Ni-Meth catalysts (Fig. 1). It is seen, that all Ni/CeZr are more active than industrial catalysts despite much lower Ni content.

High activity of Ni/CeZr catalysts was attributed to high Ni dispersion (Ni particle size is 5-10 nm according to TEM data not presented here) which was provided by preparation technique and strong metal-support interaction between Ni and ceria-zirconia.

Table 1. Physical chemical properties of the catalysts

Catalyst	Ni, wt.%	S_{BET}, m^2/g	S_{Ni}***, m^2/g_{cat}
5% Ni/CeZr	4.7	80	4.0
9% Ni/CeZr	9.1	78	7.3
12% Ni/CeZr	12.2	70	5.8
15% Ni/CeZr	15.9	71	7.4
Ni-meth*	40	137	3.3
Ni-Ref**	15	15	0.6

*Industrial NIAP-07-05 methanation catalyst.
**Industrial AlfaAesar R110 natural gas reforming catalyst.
***According to CO chemisorption for the used catalyst.

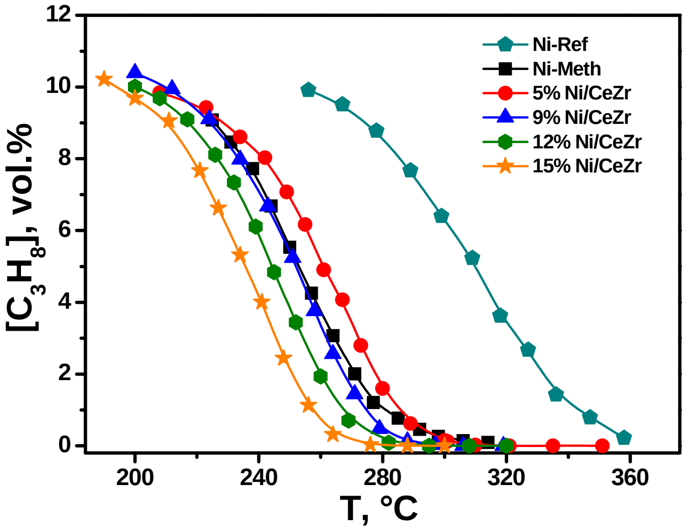

Fig. 1. Temperature dependencies of propane outlet concentration (on dry basis) for steam reforming. Inlet gas mixture (vol. %): 54 CH_4, 6 C_3H_8, 40 H_2O. P = 1 bar, GHSV = 3000 h^{-1}

Acknowledgements

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PP-70

LPG PARTIAL OXIDATION OVER Rh/Ce$_{0.25}$Zr$_{0.75}$O$_2$-Al$_2$O$_3$/FeCrAlloy FOR MICROTUBULAR SOLID OXIDE FUEL CELL FEEDING

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Solid oxide fuel cells (SOFC) are considered as the most efficient systems for the electric power generation from conventional hydrocarbon resources (natural gas, liquefied petroleum gas, jet fuel or diesel). Microtubular (MC) SOFCs are of great interest for portable applications due to availability of small power units and fast start up. To provide stable SOFC operation, initial fuel, before feeding to the SOFC anode, should be converted in a fuel reformer to synthesis gas with high content of hydrogen. Catalytic partial oxidation (CPOX), steam (SR), or autothermal reforming (ATR) are the most appropriate reactions for this purpose. The optimum temperature for these reactions ranges 550-900 °C; it falls within the SOFC working temperature interval.

Liquified petroleum gas (LPG) is a primary choice for portable applications as it is widely available and easily transportable fuel with high energy density. LPG CPOX is an attractive route of syngas production for MC SOFCs feeding due to high performance, application of air as a reagent and exothermicity of the reaction. CPOX process couples highly exothermic reactions of hydrocarbons total oxidation and endothermic reactions of hydrocarbons steam reforming. To provide high performance in CPOX the catalyst has to combine high activity, stability and heat conductivity.

Composite 0.24 wt. % Rh/(12 wt. % Zr$_{0.25}$Ce$_{0.75}$O$_{2-\delta}$-η-Al$_2$O$_3$)/FeCrAlloy catalyst was suggested for LPG CPOX. It was tested in LPG CPOX at 850 °C (measured at the surface of catalyst module outlet) at GHSV 40000-80000 h^{-1}. During the experiments the temperature at the surface of the catalyst module inlet ranged 950-960 °C. The main products were H$_2$, CO, CO$_2$, and N$_2$, which concentrations were close to equilibrium values at GHSV up to 80,000 h^{-1}. C$_4$H$_{10}$ was not observed in the outlet gas mixture, while the concentrations of C$_3$H$_8$ and CH$_4$ increased from trace amount to 0.02 and from 0.05 to 0.08 vol. % with increasing space velocity, respectively. The TPO experiment with the used composite catalysts showed no carbon formation during LPG CPOX. The resulted gas mixture contains high concentrations of H_2 (27 vol. %) and CO (20 vol. %). The maximum syngas (CO + H_2) productivity per catalyst volume was 53 $m^3L_{cat}^{-1}h^{-1}$ (STP) at GHSV of 80,000 h^{-1}.

Summarizing, the Rh/ZCB/FWM catalyst is active and stable both under natural gas and liquid petroleum gas catalytic partial oxidation conditions during repeated start/stop cycles carried out in experimental runs. The composite catalyst exhibits high Rh dispersion, sufficient thermal stability and good adhesion of catalyst coating to the metal support.

To ensure the compatibility of LPG CPOX with MC SOFC, the performance of Ni-YSZ|YSZ|GDC|LSCF-GDC MC SOFC was tested with the use of pure H_2, diluted H_2 and syngas as a fuel (Fig. 1). All experiments were carried at low fuel consumption below 10 %. It is seen that the presence of CO does not affect MC SOFC performance and syngas after LPG CPOX could be successfully used for MC SOFC feeding.

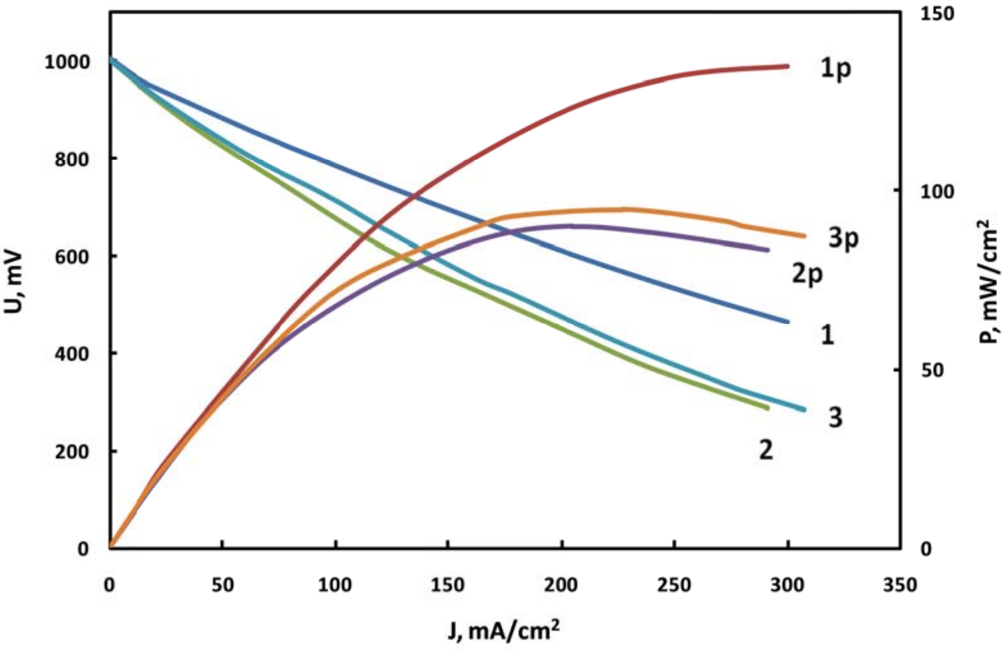

Fig. 1. Voltage (1-3) and power density (1p-3p) as a function of current density for MC SOFC fed by H_2 (1, 1p), 30 vol.% H_2 in N_2 (2, 2p) and syngas (H_2:CO:N_2 = 30:20:50) (3, 3p)

Acknowledgements

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PP-71

MODIFICATION OF $Rh/Ce_{0.75}Zr_{0.25}O_2/Al_2O_3/FeCrAl$ CATALYTIC MODULE: TOWARD ENHANCED EFFECTIVITY OF AROMATIC COMPOUND CONVERSION

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Nowadays fuel cells are one of the perspective ways towards green energy. Hydrogen is often used as a fuel for fuel cells. This choice of fuel is due to the purity and uniformity of hydrogen fuel and leads to a stable working process of the system. On the other hand, liquid products of the oil industry – gasoline and diesel – are more convenient in the case of transportation and storage. Based on the above cases optimal decision will be reforming of liquid fuels immediately before the start of working cycle of fuel cells [1]. Currently, only 16 % of global hydrogen production is produced from liquid fuels. According to these facts' development of highly-efficient catalysts for reforming of diesel and gasoline to syngas is an actual and important task.

In the previous work [1] it was shown that the catalytic module $Rh/Ce_{0.75}Zr_{0.25}O_2/Al_2O_3/FeCrAl$ was very effective in the case of ATR conversion of hexadecane and isooctane, but unconverted liquid oily residues were observed in the cases of commercial diesel fuel and gasoline. Compositions of the oily residues were studied by GC MS and was shown that the unreacted mixtures mainly consist of mono- and diaromatic compounds. To understanding processes inside the catalytic module, the calculations of reforming parameters of the model mixture were conducted by COMSOL Multiphysics software. According to the calculation data, the most part of hexadecane together with the whole oxygen in the mixture were converted in the front zone (up to 1/3 of length) of the catalytic module. In the middle and end zones of the catalytic module, the steam reforming processes of less-active components (aromatic compounds) prevailed.

Modifications of the catalytic module in the goal of enhancing of activity in the steam reforming processes of aromatic compounds were conducted. There are two ways for modification: active metal and composition of support. In the literature the positive influence of presence lanthanoid oxides in support composition to resistance for coke formation and stability of catalysts in autothermal reforming of hydrocarbons was reported [2], [3]. On the other hand, the high efficiency of Ni-based catalysts in

ATR of aromatic compounds was reported too [4]. Firstly, the composition of supported oxides was changed. The GdO_2 was added to the composition of the first layer of support to obtain $Ce_{0.75}Zr_{0.2}Gd_{0.05}O_2$ mixed oxide. According to the second way Ni particles stabilized by MgO were added in the composition of active metal layer (4 wt. % of each component). The modified catalysts were tested in the autothermal conversion of hexadecane and model blends of hexadecane with aromatic compounds. Both modifications were very promising in the case of hexadecane (75 %) – o-xylene (20 %) – naphthalene (5 %) blends: product distribution was close to equilibrium, C2+ hydrocarbons concentration were smaller than 1 % and full conversion of fuel was observed. Modified catalysts were more active than initial catalyst in ATR of the same blends in the same conditions: more than 2 % of C2+ hydrocarbons in outlet gas products and ~90 % of fuel conversion was observed in the case of $Rh/Ce_{0.75}Zr_{0.25}O_2/Al_2O_3/FeCrAl$ (Table 1).

Table 1. Products concentration in ATR of model blend hexadecane (75 %) – o-xylene (20 %) – naphthalene (5 %) in presence of different catalysts

Catalyst composition	Product concentrations, vol.%					X_{fuel}
	H_2	N_2	CO	CH_4	CO_2	
Equilibrium	41.8	33.3	11.8	0	12.5	100
$Rh/Ce_{0.75}Zr_{0.25}O_2/Al_2O_3/$ FeCrAl	30.1	40.1	12.1	1	8	80
$Rh/Ce_{0.75}Zr_{0.2}Gd_{0,05}O_2/Al_2O_3$ /FeCrAl	37.5	38.8	9,6	0	13.2	99.5
Rh/Ni-MgO/ $Ce_{0.75}Zr_{0.25}O_2/Al_2O_3/FeCrAl$	34.6	37.9	12.4	0.5	11.4	100

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PP-72

SENSITIVITY ANALYSIS OF THE KINETIC MODEL OF GASEOUS AUTOCATALYTIC PROPANE PYROLYSIS

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A kinetic scheme of radical chain reactions in autocatalytic pyrolysis of propane was studied using a sensitivity analysis method, bringing in the experimental data.

In the gas-phase kinetic experiments, propane pyrolysis was carried out in laboratory reactors with the reaction mixture heated by CO_2 laser irradiation [1,2]. Due to a large number of parameters affecting the yield of products, investigation of this process is based not only on experiments but also on numerical modeling of the dynamics of chemically active gas in a laboratory reactor by means of the Ansys Fluent software. The reduced (compact) kinetic schemes describing the most essential aspects of the mechanism of a chemical process are needed for such simulations. Note that the inclusion of chemical reactions in non-stationary numerical model even as gross schemes significantly increases the computational costs. However, in the majority of studies, gross schemes cannot satisfactorily describe spatial distribution of chemical reactions with the radical chain mechanisms over the reactor. On the other hand, the detailed mechanisms, which include hundreds of elementary steps, lead to unacceptable calculation time of 3D problems even on advanced supercomputers. Thus, creation of reduced schemes for pyrolysis of hydrocarbons is an important problem [3]. The reduction of detailed schemes implies a replacement of the initial system by a system with a lower dimensionality, which is equivalent in some respect to the initial system, or specifically, describes the changes in concentrations of the target substances for the modeled process in a similar way. The dimension of the compact scheme (the one resulting from the reduction) is defined by a range of conditions (temperature, pressure, response time) within which it is required to adequately describe the yield of the target monitored substances.

We have developed a procedure for constructing reduced schemes of chemical reactions predicting the concentrations and the major yields of reactions with the desired accuracy and requiring moderate computing resources [4]. The efficiency of using this procedure was demonstrated for modelling propane pyrolysis using detailed and reduced schemes. The reduction of the 157 reactions in the detailed propane pyrolysis scheme to the 30 reaction scheme was carried out using this procedure. The stages which may be excluded from the scheme are identified on the basis of the Sobol's variance based strategy applied for the sensitivity analysis evaluation. The reduced kinetic model of low-temperature pyrolysis of propane is proposed. This model adequately describes the yield of the reaction products in the temperature range 820-980 K at atmospheric pressure. The dynamics of the propane pyrolysis gas flow was calculated for the laboratory reactor and taking into account the diffusion processes, thermal effects of the reaction and other thermal processes in the reactor using ANSYS Fluent software package including the newly developed kinetic model.

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PP-73

KINETICS AND MECHANISM OF GLYCEROL HYDROCHLORINATION IN A SEMIBATCH REACTOR

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Large amounts of glycerol are formed as a stoichiometric co-product in the production of bio-diesel from triglycerides. What to do with this glycerol? Several industrially very important molecules can be obtained from glycerol, provided that active and selective catalysts are at disposal and the reaction conditions can be optimized. Typical potential products from glycerol are acrolein, propylene glycol, diols, ethers, carbonates, glycidol and epichlorohydrin. Hydrochlorination of glycerol with HCl in the presence of a homogeneous acid leads to 3-chloro-1,2-propanediol (α-MCP), 2-chloro-1,3-propanediol (β-MCP), 1,3-dichloro-2-propanol ($\alpha\gamma$-DCP) and 1,2-dichloro-3-propanol ($\alpha\beta$-DCP) as displayed in Figure 1. The final product $\alpha\gamma$-DCP is particularly useful, because it is able to react with alkali (NaOH and KOH) giving 1-chloro-2,3-epoxypropane (epichlorohydrin) as the end product. Epi-chlorohydrin is used extensively by chemical industry to produce epoxy resins and plastisizers. Compared to the traditional pathway for epichlorohydrin manufacture, halogenation of propene, the hydrochlorination process is a greener alternative, because a high selectivity of $\alpha\gamma$-DCP is achieved and the appearance of stoichiometric co-products is completely avoided [1].

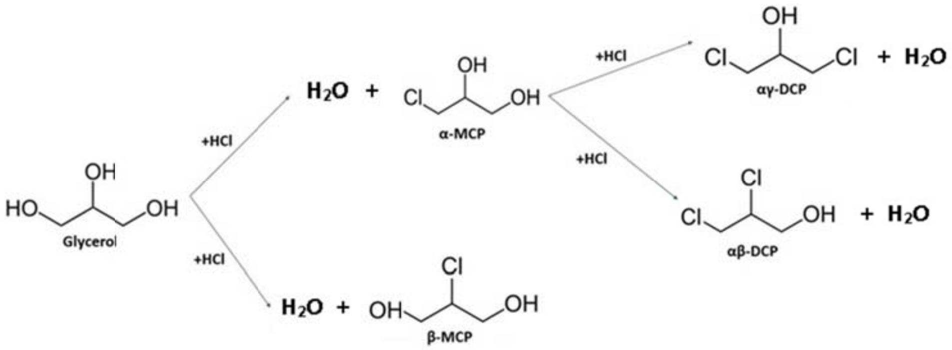

Figure 1. Reaction scheme for glycerol hydrochlorination in the presence of a homogeneous acid catalyst

Hydrochlorination of liquid-phase glycerol with gaseous hydrogen chloride was carried out in a laboratory-scale semibatch reactor, where glycerol, catalyst and hydrochlorinated products were in batch, while gaseous hydrogen chloride was continuously bubbled through the liquid phase. High stirring rates and gas flows were used to ensure the operation within the regime of kinetic control. Acetic acid was used as the homogeneous catalyst and the reaction temperature was varied between 70-100 °C. All the experiments were conducted under atmospheric pressure. A hypothesis on the reaction mechanism was presented, based on the existence of esters and epoxides as reaction intermediates. An improved gas-chromatographic method was developed to analyze the esters quantitatively. The kinetic experiments revealed that a considerable fraction of the acid catalyst is bond to glycerol and the α-hydrochlorinated reaction product, particularly at high catalyst concentrations. Inspired by this observation and a previously proposed mechanism for glycerol hydrochlorination, new kinetic equations were derived. Examples of the rate equations leading to the formation of the α- and αγ-chlorinated products are shown below,

$$r_3 = \frac{k\prime_3 c_A\, c_{HCl}^2 \left(\frac{c_{0cat}}{c_W + K' c_A + K'' c_\alpha} + \kappa'\right)}{\frac{c_{0cat}\, c_W}{c_W + K' c_A + K'' c_\alpha} + \alpha_{3HCl} c_{HCl} + \alpha_W c_W} \tag{1}$$

$$r_7 = \frac{k\prime_7 c_\alpha\, c_{HCl}^2 \left(\frac{c_{0cat}}{c_W + K' c_A + K'' c_\alpha}\right)}{\frac{c_{0cat}\, c_W}{c_W + K' c_A + K'' c_\alpha} + \alpha_{7HCl} c_{HCl}} \tag{2}$$

The reactor vessel was described as a completely backmixed stirred tank, which resulted in a set of ordinary differential equations which were solved numerically. The new kinetic model was tested with the experimental data and it was confirmed that the rate equations are able to describe the experimental observations even at high catalyst concentrations. The new model reduces to the previously proposed kinetic model at low catalyst concentrations.

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PP-74

DFT STUDIES ON THE MECHANISM OF THE Ru-MACHO-CATALYZED GUERBET REACTION OF ETHANOL TO BUTANOL

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The use of bioethanol is of high interest for the chemical industry and research due to its sustainability [1]. It is already used as a fuel additive (E10 fuels), but there are some issues. It has a lower energy density than regular fuel (around 70 %), is water miscible, and corrosive towards modern combustion engines [2]. The catalytic conversion of (bio)ethanol to (bio)butanol, e.g., via the Guerbet reaction leads to better additive properties (90 % energy density of regular fuel, immiscibility with water, non-corrosive against combustion engines) [2]. In the first step of the Guerbet mechanism a redox catalyst reduces a primary alcohol. The formed aldehyde reacts to an α,β-unsaturated aldehyde via an aldol condensation under basic conditions. The aldehyde gets hydrogenated to a longer primary alcohol in a last step. The Guerbet-reaction is an example of hydrogen-borrowing chemistry, as the hydrogen formed in the first reaction step is used for the hydrogenation of the aldehyde in the last step. The conversion of ethanol to butanol following the Guerbet mechanism still has major issues in terms of yields and selectivity. Previous internal studies with the Ru-MACHO catalyst (Carbonylhydrido(tetrahydroborato)-[bis(2-diphenylphosphinoethyl)amino] ruthenium (II)), including experimental data and microkinetic simulation, showed, that the named catalyst only performs the conversion from ethanol to 1-butanol poorly and found, that acetate and acetaldehyde oligomers are formed as side products. The reaction network can metaphorically be described as a 2D-ball-in-a-maze (see figure 1) with two axes of rotation, where a variation of the reaction parameters leads to tilting the maze. The product is determined by the point where the ball stops. “Playing” the game for multiple times leads to a product distribution [3]. After exploring the formation of 2-butanol in addition to 1-butanol in recent studies, the reaction system was optimized in batch experiments leading to an overall yield of 62 % butanol (55 % of 1-butanol and 7 % of 2-butanol). In search for sustainable fuel additives the selective synthesis of 2-butanol would be an improvement to 1-butanol due to its higher anti-knock characteristics.

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Figure 1. Representation of the Guerbet reaction as a ball-in-a-maze [3]

DFT calculation methods may lead to further understanding of the reaction. The calculations using the BP86/def2SVP-functional and including empirical dispersion will give a closer look into the mechanism of the formation of 2-butanol. Furthermore, they will help to detect the issues causing low selectivities and yields by pointing out high activation barriers, very stable ground states and unstable transition states. In addition, the mechanism using a Mn-MACHO catalyst will be considered in the calculations, because manganese pincer transition metal complexes have shown the potential for enabling the said reaction with 34 % yield and good selectivity [4]. Due to its economic and environmental advantages manganese could be a good alternative to ruthenium. The calculations on the manganese catalytic species shall also point out mechanistic differences leading to the formation of 2-butanol while using the Ru-MACHO catalyst.

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PP-75

INVESTIGATION OF Pd-Bi/Al_2O_3 CATALYSTS IN THE REACTION OF LIQUID-PHASE GLUCOSE OXIDATION

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The use of renewable sources as feedstock is associated with the economic efficiency of the chemical industry [1]. In particular, carbohydrates are indicated as raw material, given their wide availability and high degree of complexity. The great commercial interest for gluconic acids and its relative salts, is due to their wide use as chelating agents of water-soluble cleaners or additives for food and beverages, the component of tablet dosage forms and the acidity regulator of cosmetics [2]. Gluconic acid and its derivatives are obtained by the enzymatic treatment of carbohydrates at present. However, this method has a lot of disadvantages such as separation of product, waste removal, low yield of the desired product, inability to reuse enzymes and, finally, dangerous consequences for the environment [3]. An alternative method of producting gluconic acid, which eliminates these disadvantages, is the oxidation of carbohydrates by molecular oxygen in the presence of bimetallic catalysts supported on a carrier stable in an aqueous medium. Palladium-based catalysts promoted by various metals proved to be effective. The performance of bimetallic palladium catalysts is associated with the occurrence of electronic interactions between palladium and the promoter and disappearance of β–PdH. However, the question of the influence of the catalyst preparation method is still debatable [4].

The present work deals with the preparation and characterization of alumina-supported bimetallic catalysts obtained according to two experimental procedures, and tested for their catalytic performances towards the reaction of glucose oxidation to form gluconic acid.

A catalyst PdBi/Al_2O_3 was prepared from organic solution of $Pd(acac)_2$ and $Bi(ac)_3$ by co-impregnation of alumina. A $Pd \rightarrow Bi/Al_2O_3$ catalyst was prepared from an organic solution of $Pd(acac)_2$ and aqueous solution of $Bi(NO_3)_3 \cdot 5H_2O$ by successive impregnation of the support. The total metal content on the surface of the catalysts was 2.6 %. The atomic ratio Pd / Bi = 2. The particle size distribution and the local chemical composition of the nanoparticles were determined by transmission electron microscopy (TEM) and energy-dispersive X-ray spectrometry (EDX). The bimetallic nanoparticles for sample Pd→Bi/Al_2O_3 have a narrow size distribution (1–9 nm) with average particle size of 4 nm. In the case of nanoparticles in PdBi/Al_2O_3 the size distribution is broader (1–16 nm). Actually, together with smaller particles distribution, a few larger particles (> 35 nm) also exist.

Electronic properties of Pd and Bi on the Al_2O_3 support were investigated by XPS. It was shown that the fraction of metals on the surface of the Pd→Bi/Al_2O_3 catalyst is in the form of PdO. At the same time, palladium is less oxidized than bismuth. It was observed that palladium and bismuth in the composition of the PdBi/Al_2O_3 catalyst are oxidized in approximately equal proportions.

The prepared catalysts PdBi/Al_2O_3 and Pd→Bi/Al_2O_3 were tested in the reaction of liquid-phase oxidation of glucose to gluconic acid. Oxidation of glucose solution (0.6 mol/l) carried out in a thermostatic glass reactor with a volume of 25 ml, equipped with a stirrer, an oxygen supply system, a peristaltic pump, supplying NaOH (3.00 mol/l) and a pH electrode. Acids from the oxidation of glucose were neutralized by the addition of an aqueous solution sodium hydroxide to maintain a constant pH = 9 in reaction medium. The reaction was carried out for 110 min. The highest yield and selectivity of gluconic acid (approximately 95 %) were achieved in the presence of a PdBi/Al_2O_3 catalyst. This observation is due to the fact that, in the case of preparation of the catalyst by co-impregnation, bimetallic structures with less oxidized bismuth are formed compared to the catalyst sample Pd→Bi/Al_2O_3. Bismuth in the composition of the bimetallic particle PdBi improves the electronic properties of the catalyst, preventing oxidation of active component Pd and providing high values of the yield product and selectivity of the desired product, according to the oxidative dehydrogenation mechanism proposed by the authors [5].

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SIMULATION OF THE PHENOMENON OF THE BIRTH OF WEAK SHOCK WAVES IN THE OXIDATION OF HYDROGEN AND HYDROCARBONS AT THE PRESENCE OF SURFACE ACTIVE CENTERS (WATER + NEGATIVE ION OF CHLORINE)

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The phenomena of self-organization (synergetic), in particular, periodic changes in characteristics (concentration, temperature pressure, pulsating intensification of light emission, etc.) during chain reactions are of interest both for understanding the mechanism of these reactions and for the safety of carrying out chemical processes [1].

As is known, external factors are playing an important role in such processes – the so-called slow subsystems, which can be as energy exchange through the walls of reaction vessels, and relaxation of internal energy, and other characteristic.

In this work, we consider the effect of surface active centers (by the example of adsorbed on the surface complexes of water molecules with a negative halogen ion) as a source of formation of weak shock waves.

Light radiation of shock front products excited to metastable levels presented itself in the form of pulsations of light emission in particularly in the infrared region of the spectrum, which we observed in our study of the oxidation of propane.

The basis of the model is the processes that lead to the transformation of the intermediate product of the above reactions of H_2O_2 into ozone O_3 molecules, the self-decomposition or reaction of which leads to the release of a large amount of heat in the local place of the reactor (places of concentration of water + negative halogen ion complexes) due to the chain of processes [1]:

$H_2O_2 + H_2O{\cdot}Cl^- \rightarrow H_2O{\cdot}O^- + H_2O{\cdot}Cl$, $H_2O{\cdot}O^- + O_2 \rightarrow H_2O + O_3^-$, $O_3^- + H_2O{\cdot}Cl \rightarrow O_3 + H_2O{\cdot}Cl^-$. In the first elementary act there exist the possibility of resonance.

Due to the release of a large amount of energy in a local place of the near-surface layer of the reactor, as a result of which brings to formation a fast flow to the center of reactor.

It is better to consider this problem in terms of Hugionio theory, as was first done by R. Becker [2].

Based on the equation of state of an ideal gas, in dimensionless variables, the adiabates of Hugionio are written as [3]:

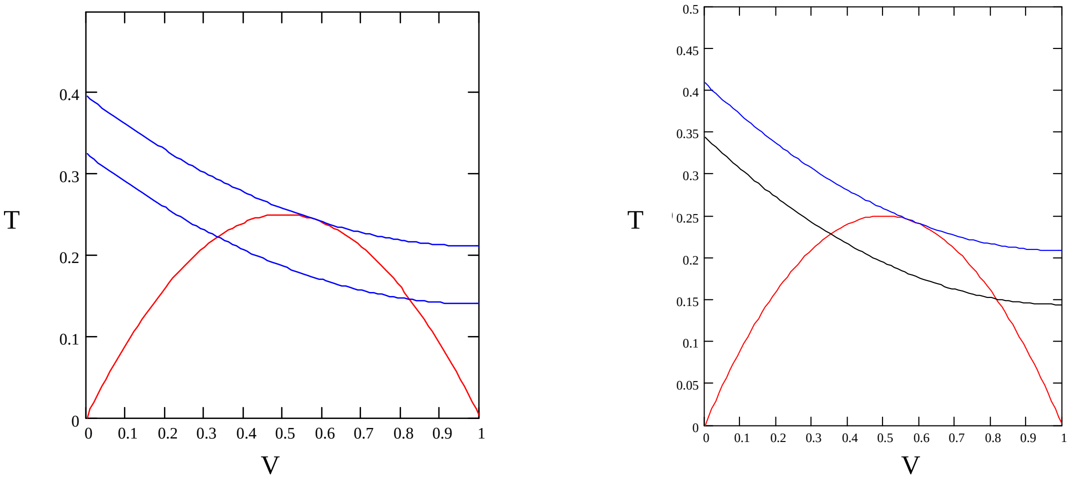
$$M(V,T) = T/V + V - 1 \qquad (2)$$

$$L(V,T) = T/\gamma - 1 - 1/2(V-1)^2 - \beta$$

where, V – flow volume; T – temperature; $\gamma = c_p/c_V$ – heat capacity ratio; β – flow constant.

If the parabolas M (V, T) = 0 and L (V, T) = 0 in the phase space (V, T) intersect at two points, then a shock wave can be generated in the system.

As the calculation results show within the limits of the Gugionio theory (see Fig. 1), there is an intersection of the adiabates of Hugionio fo the cases of propane oxidation and hydrogen oxidation.



a ***b***

Figure 1. Mutually location of the adiabates of Hugionio on the phase plane (V, T) calculated by the formula (2) is presented. ***a*** – propane oxidation; ***b*** – H_2 oxidation

The intersection of the adiabates of Hugionio at the values of the parameters obtained above proves the possibility of the creation of a weak shock wave.

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PP-77

MODELLING METHANOL TO FORMALDEHYDE OXIDATION PROCESS IN THE ENVIRONMENTALLY SAFE MICROSTRUCTURED SLIT-TYPE REACTOR

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Unlike tubular reactors, microchannel reactors (MCR) are distinguished by more intense heat and mass transfer, which provides better heat removal from the reaction zone; in addition, the effective mixing of reagents reduces the risk of flames. Oxidation of methanol to formaldehyde is a strongly exothermic process that can be carried out in MCR at higher methanol loads than in conventional tubular reactors [1]. This will increase the formaldehyde productivity of the catalyst, while ensuring the operational safety.

In our previous work [2], we studied the process of methanol to formaldehyde oxidation in a slit-type MCR, assuming that all the channels operate under the same thermal conditions; the model described a single channel surrounded by catalytic plates. However, when modelling the process in the MCR formed as a disk with the parallel catalyst-filled channels, we found [3] that the channels operate under different conditions. The mutual influence of the processes occurring in the channels with the catalyst and in the metal disk was shown.

The present paper focuses on the simulation of methanol to formaldehyde oxidation in the slit-type MCR, consisting of 5 porous plates 40 mm long, each plate containing 4 channels 0.4 mm high and 5 mm wide, see Fig. 1. Finely dispersed particles of industrial Fe-Mo catalyst are evenly distributed within the porous matrix.

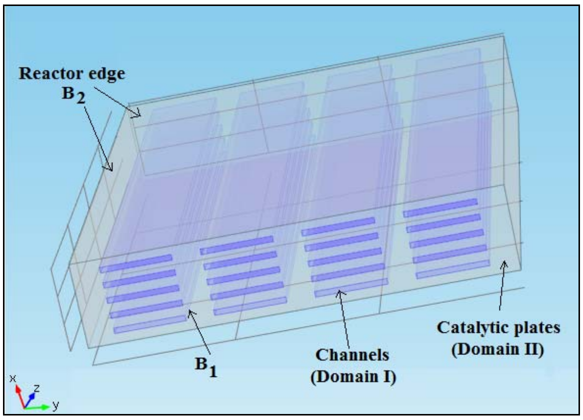

Fig. 1. The layout of the computational domains

The stationary three-dimensional mathematical model describes the processes in two computational domains and at the boundaries (Fig. 1). In the Domain I (the reaction mixture in the channels), axial heat and mass convection and axial thermal conductivity and diffusivity are taken into account.

In the Domain II, catalytic conversion of methanol to formaldehyde and by-products, reaction heat release, and thermal conductivity in transverse and axial directions are taken into account. Heat and mass exchange between the Domains I and II are taken into account at the boundary $\mathbf{B_1}$. A constant temperature equal to the temperature of the cooling agent is set at the boundary $\mathbf{B_2}$.

The modelling was done using the COMSOL Multiphysics software package. To check the adequacy of the mathematical description of the methanol to formaldehyde oxidation in a slit-type MCR, the simulation results were compared with experimental data. The simulated and observed results agreed sufficiently, this validates the modeling approach and demonstrates the model's ability to predict the values of temperature, conversion and yield in each specific channel.

In the modeling, we fixed the inlet methanol concentration of 6.5 or 12 vol. %, the O_2/CH_3OH ratio was 1.5. The temperature of cooling agent varied from 240 to 340 °C, the linear gas velocity from 0.1 to 0.35 m/s, and the thermal conductivity of the plates from 2 to 10 W/(m K). The influence of the parameters on the methanol conversion and formaldehyde yield at the reactor outlet, and on the maximum temperatures in the central and peripheral channels was studied.

At the cooling agent temperature of 340 °C, the linear velocities of 0.1-0.15 m/s and methanol concentrations of 6.5 and 12 %, the methanol conversion and the formaldehyde yield are higher than 88 and 80 %, respectively. In this case, the formaldehyde productivity per unit volume of Fe-Mo oxide catalyst shall be 1.5−3.0 times higher than in a conventional tubular reactor on the Fe-Mo oxide catalyst, with no catalyst overheating.

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PP-78

NEW STREAMLINED CATALYTIC CARRIERS OF ENHANCED TRANSPORT PROPERTIES: EXPERIMENTS VS. CFD

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Dangerous atmospheric pollutants cause serious problems concerning environment and public health [1]. So far, the most effective remedies for majority of air pollutants are catalytic processes like catalytic combustion [2]. Great achievements have been made in the field of catalyst microstructure and composition, but the design of the catalytic converter has not changed significantly. Up to now, reactor fillings of intense heat/mass transfer display large flow resistance, and vice versa (e.g. packed bed vs. monolith).

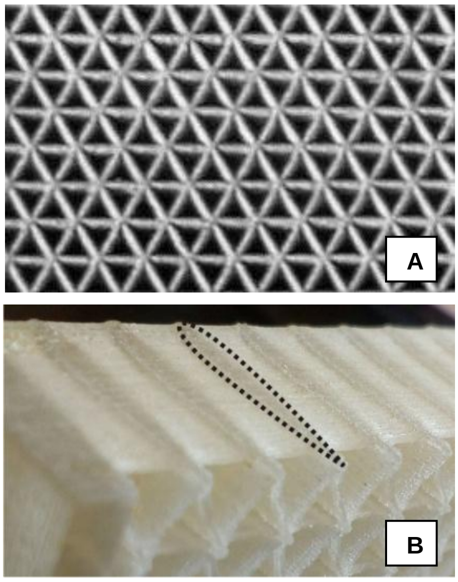

Fig. 1. Wing catalytic carrier:
A – metal carrier side view,
B – Polymeric carrier top and back view, aerofoil shape marked with dashed line

The main task of this study is a new generation of structured reactor internals (catalyst carriers) called “streamlined" or "wing" structures (Fig. 1). They are similar to short-channel structures (short monoliths of diverse cross-sectional channel shape, for more details see [3, 4]). The main innovation is channel wall shaped as an aircraft wing.

The streamlined structures of triangular shape and 3, 6 and 12 mm long were created and analyzed with Ansys CFD (Computational Fluid Dynamics) software. Then, they were 3D printed. Finally, experimental investigation of their heat transport and flow resistance was performed. The novel structures display improved heat/mass transfer properties in comparison to monolith and beneficial pressure drop (see Fig. 2). The channel length *L* (within single structure) can be regulated to attain appropriate heat/mass transfer coefficients, similarly to the short monoliths studied before [3, 4]. The experimental results are in good agreement with CFD ones (maximum relative error does not exceed 26 %).

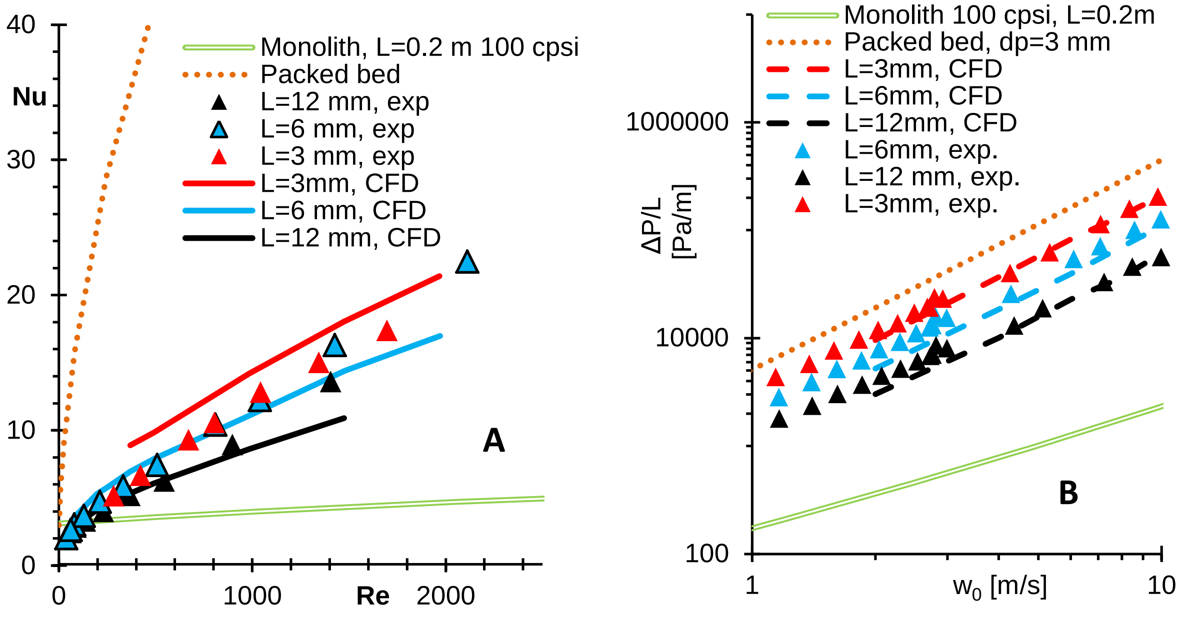

Fig. 2. Transport – flow properties of strealmined catalytic carrier in comparison to packed bed and monolith [5, 6]: A – Nusselt number *Nu* vs. Reynolds number *Re,* B – ΔP/L presure drop per unit of structure length vs. superficial fluid velocity $w_{0;}$ *dp* – grain diameter

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PP-79

DEAD-CORE SOLUTIONS TO FAST DIFFUSION EQUATION FOR CATALYTIC PELLETS WITH EXTERNAL MASS TRANSFER RESISTANCE

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We present semi-analytic approaches for solving two-point boundary value diffusion-reaction problems for catalytic pellets in the case of power-law reaction kinetics with fractional exponent and fast diffusion by considering the presence of external mass resistance. In this work we extend our analytic approach [1,2,3] to the model problems with non-linear diffusion. The dimensionless steady-state mass balance for a single *n*-th order chemical reaction and diffusion in the catalytic pellets of planar geometry is given by

$$\frac{d^2}{dx^2}\left(c^m\right) - \phi^2 r\left(c\right) = 0 \text{ with } r(c) = \begin{cases} c^n, & c > 0, \\ 0, & c = 0, \end{cases} \tag{1}$$

where the reaction term, $r(c)$, corresponds to the power-law kinetics, m stands for the diffusion exponent, and $\phi > 0$ denotes the Thiele modulus. We consider the physical solutions that satisfy $0 \le c(x) \le 1$ for all $0 \le x \le 1$ and fulfill the boundary conditions

$$\frac{dc^m}{dx}\left(1\right) = Bi_m\left(1 - c\left(1\right)\right) \quad \text{and} \quad \frac{dc^m}{dx}\left(0\right) = 0. \tag{2}$$

For certain combinations of the pellet size, effective diffusivity, mass transfer coefficient, bulk reactant concentration, reaction order and reaction rate constant, the exponent $m > 0$, the dead zone of length x_{dz} can be formed close to the pellet center. In this case the rate of the reactant supply by nonlinear diffusion flux through the pellet porous structure is much lower than the rate of the reactant consumption by reaction. In the dead zone, the reactant vanishes and the reaction ceases, i.e., $c(x) = 0$ in the pellet region $0 \le x \le x_{\mathrm{dz}}$, where the location of x_{dz} is a-priori not known.

We study two families of solutions to the boundary value problem (1)-(2). One class of solutions exhibits dead cores which appear if the Thiele modulus exceeds its critical value ϕ^* depending on the reaction order n, Biot number Bi_m and $1 > m > n > 0$, whereas the other class of solutions does not possess dead-cores if the Thiele modulus does not exceeds its critical value ϕ^*. The class of dead-core solutions is separated from the class of non-dead-core solutions by the solution for $\phi = \phi^*$ which will be derived analytically. In the case of $m = 1$ we show that we recover results from [3]. The effects of process parameters on the concentration profiles and formation of dead-cores are illustrated numerically.

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PP-80

BIOMASS AND OILS CO-HYDROPROCESSING IN SUPERCRITICAL CONDITIONS

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The steadily increasing demand for motor fuel, the depletion of crude oil reserves, the decline in the quality of produced oil, and the environmental problems associated with the emission of greenhouse gases into the atmosphere lead to the need to replace fossil fuels with alternative, environmentally friendly energy resources, which include biomass. The existing liquid fuels from biomass (including bio-oil and biodiesel) do not always have good miscibility with petroleum fuels and require additional modification to meet fuel standards. This modification consists in the removal of oxygen and isomerization of the resulting hydrocarbons in the presence of hydrogen (the so-called hydrotreatment). Typically, the same conditions and catalysts are used in the hydrotreatment of fuel from biomass as in the hydrotreatment of oil fractions (hydrodesulfurization, hydrocracking, hydroisomerization). Therefore, the integration of biofuel hydrotreatment processes in the existing technology of hydrotreatment of oil fractions is one of the promising directions for the production of liquid motor fuel.

Co-processing of biogenic raw materials and oil fractions has recently become increasingly important. This process includes cracking, hydrogenation, hydrotreating of renewable and mineral feedstock for the production of gasoline, kerosene and diesel hydrocarbons. To date, the co-processing of oil fractions and biofuels is carried out in three main directions: 1) hydrotreatment of diesel fuel and vegetable oils; 2) hydrotreatment of gas oil and bio-oil (pyrolysis liquid or liquid products of hydrothermal wood processing); 3) hydrocracking of vacuum gas oil and bio-oil. The use of large amounts of hydrogen gas and high temperatures, as well as the rapid deactivation of catalysts, which affects the cost of the final product, are the main problems of the existing approaches. Solving these problems is one of the most urgent tasks of the researchers. In order to decrease the cost of hydrotreatment processes, it is proposed to use supercritical solvents, which, in addition to reducing the temperature of the process, are donors of atomic hydrogen and, thus, are able to decrease the consumption of hydrogen.

Currently, there are several works on deoxygenation of components of vegetable oils and bio-oil using supercritical solvent, such as water, hexane, propane, carbon dioxide [1-3]. The most optimal solvent, according to the literature [1, 3], is hexane, as it allows the process to be carried out under relatively mild conditions and mixes well with the substrate under normal conditions.

Catalysts used in hydrotreatment are divided into two types: 1) transition metal compounds (sulfides, nitrides, phosphides) deposited on aluminum oxides, silicon or zeolites, and 2) noble and rare earth metals (Pt, Pd, Re, Rh) deposited on carbon or oxide supports. The main disadvantage of existing catalysts is the restriction of adsorption of large molecules of the feedstock, which leads to a decrease in the activity of catalysts, as well as the behaviour of secondary processes such as cracking, which leads to a loss of selectivity and low yields of products. Also, such catalysts are easily carbonized, thereby losing their activity during prolonged use. Hydrothermal synthesis is one of the ways to solve such problems. This approach allows ultrafine crystalline metal oxides to be obtained from their inorganic salts, and does not require additional calcination [4-6].

In this work, we study the joint conversion of model compounds of biomass (bio-oil and fatty acids) and petroleum fractions in the medium of complex supercritical solvent (hexane-propanol-2). The influence of solvent composition as well as the presence of hydrogen was investigated. The process was carried out in the presence of transition metal catalysts deposited on the polymeric matrix of hypercrosslinked polystyrene in the medium of subcritical water.

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PP-81

DESIGN OF MULTISTAGE REACTOR SYSTEMS FOR THE PRODCUTION OF HIGH CARBON NUMBER HYDROCARBON FUELS FROM FURANS BY DISTRIBUTING MULTIFUNCTIONAL CATALYSTS

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Xylose and other pentoses have been prepared as wastes of lignocellulose-biorefinery for producing glucose-based bioalcohols. While the biological conversion of xylose has been less preferred compared to that of glucose, the chemical conversion of xylose to furans, then further converted to high carbon number hydrocarbons has been suggested [1]. For the production of high carbon number hydrocarbons from furans, the condensation of furans to higher carbon number oxygenates and the hydrodeoxygenation of condensates are required (Figure 1) [2]. While homogeneous and heterogeneous catalysts have been suggested for the condensation of furans [3,4], the hydrodeoxygenation step requires supported hydrogenation catalysts or metal-based hydrodefunctionalization catalysts [5]. Because the different catalysis systems are sequentially connected by transferring products of early steps to reactants of latter steps, the multiple reactors must be independently operated.

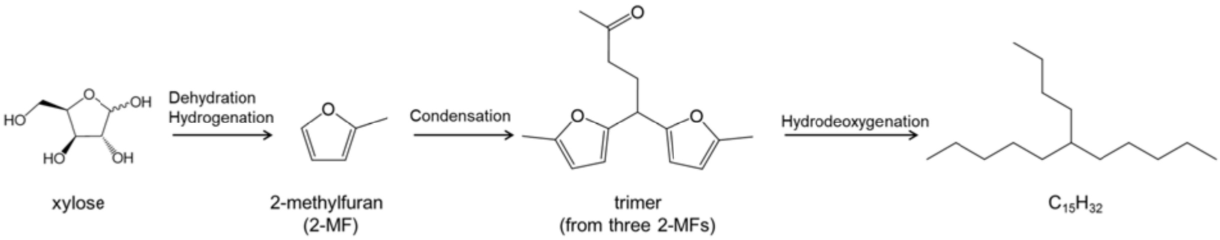
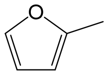
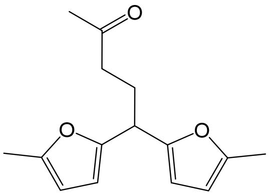
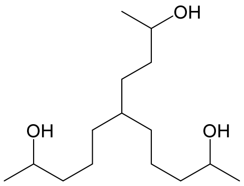
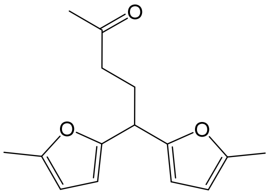
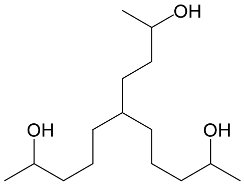
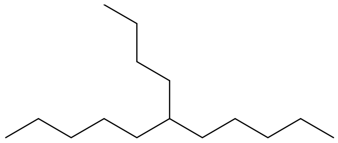


Figure 1. Production of high carbon number hydrocarbons from furans

In this presentation, single reactor containing three-stage reaction systems performed using single multifunctional catalyst is suggested. The multifunctional catalyst exhibiting acidic, hydrogenating, and hydrodeoxygenating activities depending on the pretreatment method was used at three different stages of this study. The successful production of deoxygenated C15 hydrocarbons from furan reactant was observed. The local reaction conditions were manipulated for the purpose of each stage.

Table 1. Reaction conditions for three stages using multifunctional catalyst A

Stage	Condensation	Hydrogenation	Hydrodeoxygenation
Reactant			
Product			
Reaction temperature (°C)	80–100	150–200	250–300
Reaction pressure (bar)	100	100	100

Using single catalyst for three different stages, we observed the successful production of hydrodeoxygenated hydrocarbons. Acidic and hydrogenating properties of multifunctional catalyst were observed using acid titration, NH_3-TPD, H_2-TPR, and other characterization methods, which confirmed the presence of catalytic activity depending on the reaction conditions of each stage.

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PP-82

HIGH EFFECTIVE BIOCATALYTIC SYSTEMS ON THE BASE OF HORSERADISH PEROXIDASE IMMOBILIZED ON MAGNETIC NANOPARTICLES

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In recent years, the use of enzymes in industrial processes has increased dramatically, due to their effective catalytic properties. However, when using biocatalytic systems based on enzymes, there is a problem of their regeneration and reuse. To solve this problem, scientists use the immobilization of enzymes on various supports [1].

In this work, horseradish root peroxidase (HRP) was immobilized on magnetite (Fe_3O_4) nanoparticles. The synthesized biocatalyst was tested in the oxidation reaction of 2,3,6-trimethylphenol with hydrogen peroxide.

The synthesis of magnetic nanoparticles was carried out by the polyol method and the co-precipitation method. Nanoparticles synthesized by the co- precipitation method had granular heterogeneity and large size distribution. Nanoparticles synthesized by the polyol method formed large clusters with an average diameter of 111 nm, consisting of small nanoparticles. In this regard, nanoparticles synthesized by polyol method were chosen as a support for peroxidase, since their morphology is more regular, representing a properly formed sphere.

For strong binding of magnetic nanoparticles to the enzyme, Fe_3O_4 was treated with 3-aminopropyltriethoxysilane (APTS) of different concentrations (1, 2, 3 mg/mL). Experiments have shown that the concentration of APTS 2 mg/mL was optimal, since at this concentration the maximum yield of the product is achieved. Further, the nanoparticles coated with APTS were treated with HRP solution with an optimal concentration of 0.15 mg/mL. To characterize the synthesized biocatalyst, the following physical and chemical analysis was performed: transmission electron microscopy, IR-Fourier spectroscopy, magnetic characteristics study using a vibration magnetometer, x-ray photoelectron spectroscopy and low-temperature nitrogen adsorption.

The optimal oxidation conditions of 2,3,6-trimethylphenol, namely the initial concentration of the substrate (1.5 mmol/l), pH (6.5) and temperature (40 °C) were also selected.

To assess the stability of the synthesized biocatalysts, several consecutive oxidation experiments were performed using heterogeneous biocatalysts in the recycle (Fig.1).

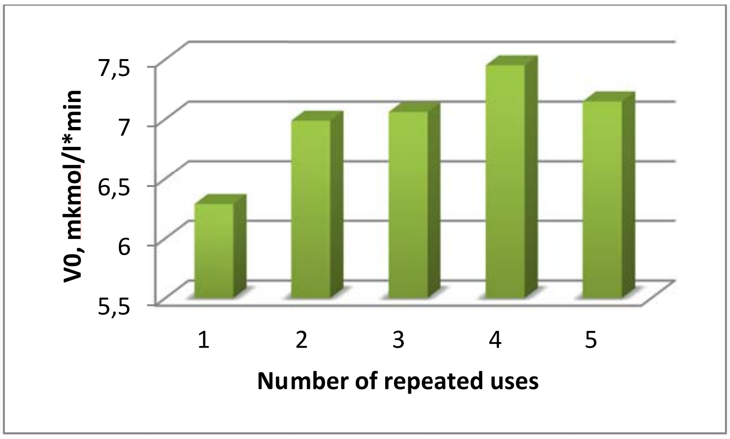

Fig. 1. Initial 2,3,6-trimethylphenol oxidation rate at a multiple biocatalyst reuses (c_0^{TMP}= 1.5 mmol/L, c_0 (H_2O_2)= 1.5 mol/L, pH 6.5, T = 40 °C, c_{kat}= 0.2 g/L)

From Fig. 1 it is seen that as a result of fixing the active centers of the enzyme immobilized HRP becomes stable. The increase in biocatalyst activity may be caused by an increase in the number of active enzyme centers. The stability of the biocatalyst based on HRP immobilized on magnetic nanoparticles is confirmed by RFES studies, since the profiles of high-resolution spectra, sublevel binding energies and composition after the catalytic cycle are preserved.

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KINETICS OF PELARGONIC ACID ESTERIFICATION WITH 2-ETHYLHEXANOL IN BATCH AND CONTINUOUS REACTORS

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Esterification of carboxylic acids with alcohols is commonly catalyzed using soluble acids, such as sulfuric acid and *p*-toluenesulfonic acid. These catalysts are characterized by high activity, but they show several negative aspects, i.e. their corrosive nature and they cannot be easily separated from the reaction mixture. Heterogeneous catalysts represent an important alternative, as they can be easily removed from the liquid mixture after the reaction, they are not corrosive to the equipment and the side reactions can be almost completely suppressed [1].

Esters are generally used as plasticizers, solvents, flavor chemicals and as precursors for pharmaceuticals, agrochemicals and other fine chemicals. Among carboxylic acids, pelargonic acid has a great importance as it can be obtained from vegetable oils. Pelargonic acid esters can be used in chemical industries as a chemical intermediate for synthetic flavors, cosmetics, pharmaceuticals and corrosion inhibitors [2] and as solvents for bio–based varnishes in combination with a commercial resin as reported by Benessere *et al*. [3]. The obtained solvents showed an excellent ability to disperse resins derived from rosin in unprecedented mass percentage, in shorter time and at lower temperature with respect to commonly used solvents [3]. Sharma *et al*. [4] investigated the esterification of pelargonic acid with methanol with homogeneous catalyst (H_2SO_4) and heterogeneous ones (Amberlyst 15, Amberlyst 35, Dowex 50WX2).

Earlier studies [5] established that the cation exchange resin Amberlite IR120 as an affordable, green esterification catalyst capable of being used repeatedly without a significant decrease in its capacity.

In the present work, the kinetics of pelargonic acid esterification with 2-ethylhexanol was conducted using Amberlite IR120 as heterogeneous catalyst both in a batch and in a continuous reactor.

Tests were conducted varying different operating conditions (i.e. stirring rate, temperature, catalyst load, reactants molar ratio) in order to evaluate the effect on the reaction rate. It is shown as example the effect of the temperature in Figure 1.

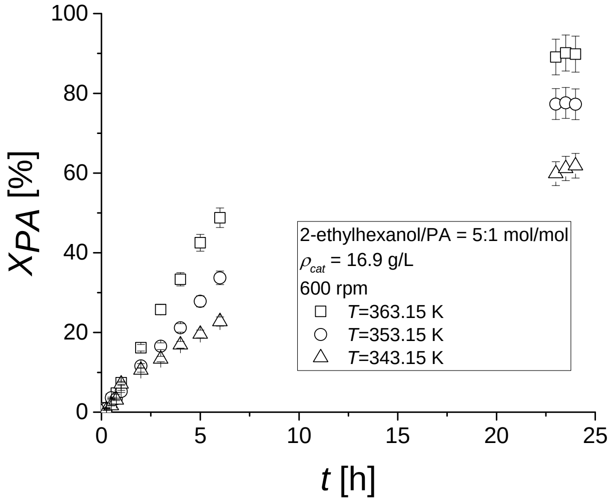

Figure 1. Temperature effect on the pelargonic acid conversion. Experiments performed at 600 rpm, 2-ethylhexanol/pelargonic acid 5:1 mol/mol, 5 bar N_2, 16.9 g/L Amberlite IR120

From tests performed in batch reactor it was possible to observe the absence of external mass transfer limitation while intraparticle mass transfer limitation occurred.

Tests conducted in a continuous reactor confirm the kinetics investigated in batch experiments and a kinetic model was developed to interpret in detail the experimental data and to evaluate chemical and mass transfer phenomena involved in the reaction network.

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PP-84

HIGHLY-DISPERSED ZINC SPECIES ON ZEOLITES FOR THE CONTINUOUS AND SELECTIVE DEHYDROGENATION OF ETHANE WITH CO_2 AS A SOFT OXIDANT

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The CO_2-assisted ethane dehydrogenation is a novel promising approach to generate ethene, while exploiting abundant C_2H_6 from shale-gas and anthropogenic greenhouse gas CO_2 in a circular manner [1]. We report herein the preparation, characterization, and catalytic performance of a series of heterogeneous catalysts featuring highly dispersed zinc sites on zeolitic SSZ-13 and ZSM-5 frameworks [2]. The materials are evaluated in the CO_2-assisted oxidative ethane dehydrogenation, a very important reaction for the synthesis of platform chemicals. In particular, we find that $Zn_{2.92}$/SSZ-13 exhibits high reactivity in the conversion of C_2H_6 and CO_2 and high ethene selectivity. In line with the experimental results, we show that the selective character of the catalyst is due to the characteristic compositional structure of the support and its topology that can effectively confine CO_2 molecules. An in-depth molecular analysis via operando studies and DFT calculations shows that the rate-limiting step of the reaction with CO_2 is the second C-H bond dissociation to give C_2H_4. The addition of CO_2 effectively reduces the energy barrier of this step, favoring desorption of C_2H_4 while limiting byproduct formation. Overall, this work demonstrates the breakthrough potential of catalysts made of highly dispersed zinc species on zeolites in relevant transformations.

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PP-85

CONVERSION OF VEGETABLE FEEDSTOCK, PEAT AND COAL TO POROUS CARBON-MINERAL COMPOSITES AND CARBONS VIA OXIDATIVE CARBONIZATION IN FLUIDIZED CATALYST BED

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Currently, seeking new energy efficient and environmentally friendly approaches to carbon dioxide utilization is one of the hottest topics in chemical engineering science [1]. As an effective approach to CO_2 capture can be its consumption by vegetable biomass followed by carbonization to produce biochar and porous carbon materials, thus, converting the major part of CO_2 to solid amorphous carbon based products. Compared to pyrolysis-based approaches, oxidative carbonization of biomass at low temperatures in fluidized catalyst bed (FCB) and air, as the gaseous medium, can allow one to hold the process in autothermal mode with avoiding the necessity of creation of inert atmosphere. Furthermore, the use of a deep oxidation catalyst turns the process to clean one, as it was demonstrated in combustion of such hazardous and difficult to utilize feedstocks as high sulfuric heavy oil and sewage sludge [2,3].

In this work, three types of renewable raw materials (wheat bran, rice husk, and highly mineralized peat Sukhovskoy), as well as brown coal were investigated to produce porous carbon-mineral composites (chars) and porous carbons. Wheat bran (WB) and rice husk (RH) were used as vegetable feedstocks, while peat and coal – as sedimentary ones having different composition and properties of mineral and carbon-containing phases. The mineral component of peat is represented mainly by $CaCO_3$, coal – by a mixture of SiO_2, Al_2O_3 and Fe_2O_3, WB – by oxides of alkali and alkali-earth metals, and RH – by SiO_2.

At the first step, the feedstocks were subjected by oxidative carbonization in a reactor with fluidized bed of a deep oxidation catalyst at 465, 550 and 600 °C, and the contact time of ca. 1.0 s, to produce the composites. It was found that content of mineral phase increase with the carbonization temperature in all cases. The lowest ash content was in the case of coal (16-20 wt. %) and the highest – for peat and rice husk (both ca. 56-79 wt. %). Investigation of their properties showed that BET specific surface area of the materials (A_{BET}) can achieve 170 $m^2 \cdot g^{-1}$, and total pore volume (V_Σ) – 0.2 $cm^3 \cdot g^{-1}$. The further removal of their mineral phase, playing a role of a template, through acid leaching allowed for obtaining porous carbons (Figure). It was found that the use of such approach allowed for synthesis of porous carbon materials with A_{BET} up to 369 $m^2 \cdot g^{-1}$ and V_{Σ} – 0.28 $cm^3 \cdot g^{-1}$. It was also discovered that in the case of biomass feedstocks, porosity development via mineral phase removal is more effective, that can be explained by its higher dispersion, in contrast to those of peat and coal, probably because of different accumulation mechanisms.

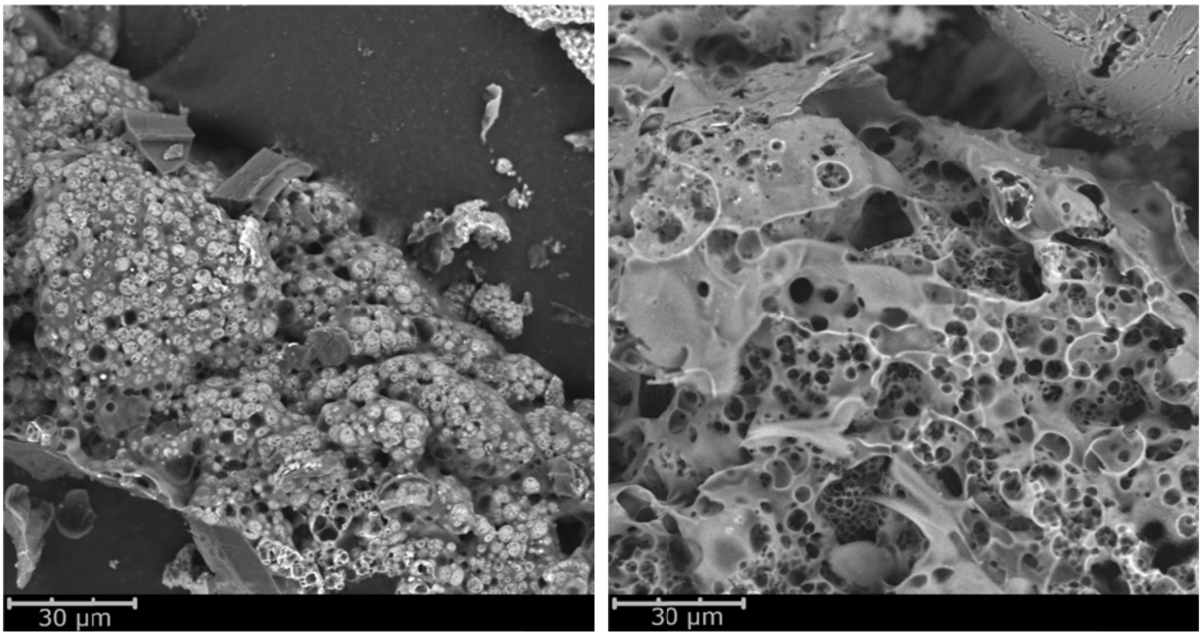

Figure. SEM images of porous carbon-mineral composite (left) and porous carbon (right) obtained via its acid leaching, synthesized from WB through carbonization in FCB reactor at 550 °C

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PP-86

STABILITY OF PLATINUM-RUTHENIUM CATALYSTS IN THE SELECTIVE SYNTHESIS OF H_2 AND CO

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The results of the stability of study of the developed optimal composition Pt : Ru = 1 : 1 (Pt : Ru = 0.7 : 0.3, at.%) of the catalyst in the reaction of SCO (selective catalytic oxidation) and the steam oxygen conversion (SOC) of methane to synthesis gas at millisecond contact times. Methods of catalyst regeneration were determined.

Synthesis gas is an important raw material for the production of numerous chemical products. Depending on the ratio of hydrogen and carbon monoxide in the synthesis gas, it is used to produce liquid hydrocarbons or oxygen-containing compounds, including methanol, acetic acid, formaldehyde, and dimethyl ether. The methane co-reaction, which gives a molar ratio of $H_2/CO = 2.0$ in the products, could be an alternative reaction to the steam reforming of methane for the production of synthesis gas.

One of the most important characteristics of catalysts is their stability. We conducted a stability test on the developed fine-dispersed optimal composition of Pt-Ru = 1 : 1 of the catalyst in the reaction of COX and PAC of methane to synthesis gas at millisecond contact times. Figure 1 shows that the catalyst did not lose its activity until 225 hours. Then the methane conversion rate gradually decreased from 100 to 40 %. The catalyst was regenerated by treatment with a reducing mixture with a high CH_4 content, and then reduced to a mixture of H_2+Ar. But the most optimal solution was to add water vapor to the reaction mixture. Only then did the activity return to its original value. Next, the process of methane PAC was carried out with the water vapor concentration found experimentally, which was optimal. It should be noted that these processes use only 10 milligrams of catalyst diluted four hundred times with quartz.

Thus, the synthesized 1.0 % Pt-Ru (at. %)/2 % Ce/($\theta+\alpha$) – Al_2O_3 the catalyst selectively worked without losing its activity for 410 hours in the reaction of COX and PAC of methane.

Process conditions of SCO of methane: $CH_4 : O_2 : Ar = 2{,}0 : 1{,}0 : 97{,}0$, %, $T = 1173$ К, $V = 9 \cdot 10^5\ h^{-1}$, $\tau = 0{,}004$ s

SOC of methane: $CH_4 : O_2 : H_2O : Ar = 2{,}0 : 1{,}0 : 2{,}0 : 95{,}0$, %, $T = 1073$ К, $V = 1 \cdot 10^5\ h^{-1}$, $\tau = 0{,}036$ s.

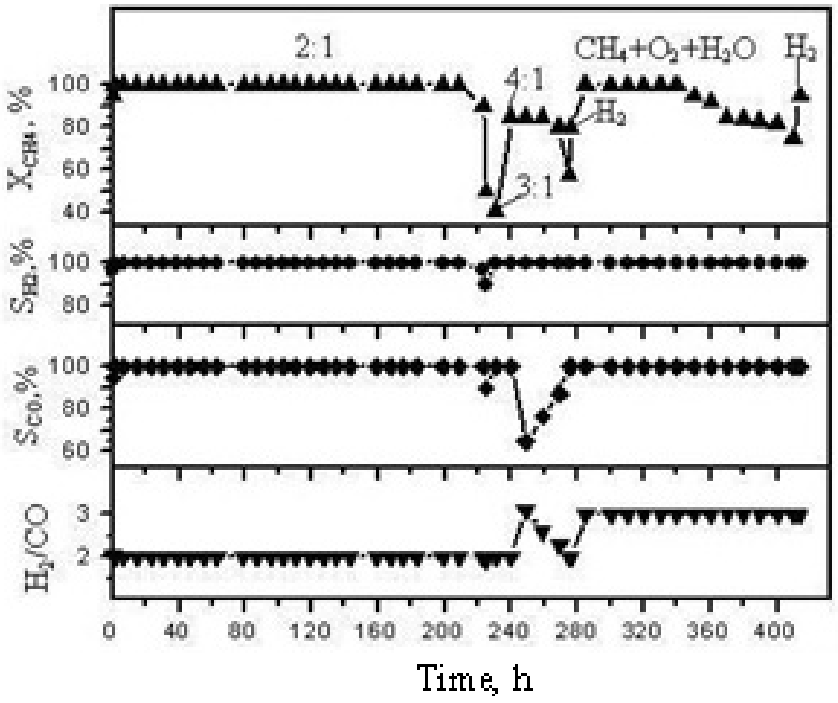

Fig. 1. Investigation of stability 1,0 % Pt-Ru (1:1)/2 % Ce/$(\theta+\alpha)Al_2O_3$ catalyst.

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PP-87

BIOGAS REFORMING ON SOLUTION COMBUSTION SYNTHESIS

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In recent years, an intensive study of processes involving biogas as an alternative source of not only energy, but also raw materials for petrochemical production began in the world due to the inevitable exhaustion of non-renewable energy sources and raw materials for petrochemical production. Biogas resulting from the anaerobic fermentation of biomass and from any organic waste is a practically inexhaustible renewable resource for obtaining of valuable products such as synthesis gas, hydrogen, and hydrocarbons. Even biogas of "low" quality are suitable for its processing into valuable raw materials for power engineering and petrochemistry, which makes it possible to avoid expensive methods of its production.

The results of carbon dioxide reforming of CH_4 (model biogas) on the catalysts prepared by solution combustion synthesis (SCS) and impregnation of moisture capacity methods are presented. Investigation of the activity of catalysts produced from initial mixture of Ni-Co-Mg-Ce-glycine of different composition was carried out for the production of synthesis-gas and comparison of SCS and traditional impregnation methods preparation of catalysts.

The studies were carried out at various space velocities, temperatures and the composition of the reaction mixture. A gas mixture containing methane and carbon dioxide (or oxygen) diluted with an inert gas (Ar) in the presence and absence of water vapor was used for reforming. Dry reforming of methane was studied on a catalyst obtained by solution combustion synthesis at $W = 860\ h^{-1}$ and the ratio of the components of the reaction mixture $CH_4 : CO_2 : Ar = 33.3 : 33.3 : 33.3$, and also at $W = 2500\ h^{-1}$ when the ratio of the components of the mixture of $CH_4 : CO_2 : Ar = 46.7 : 23.3 : 30.0$. Figure 1 shows the effect of space velocity and the addition of water vapor on the conversion of raw materials and the yield of reaction products. It can be seen from the figure that when the space velocity decreases from $2500\ h^{-1}$ to

860 h^{-1}, the CH_4 conversion, the yields of H_2 and CO increase, and the addition of water vapor further increases the conversion of the feed and the yield of H_2.

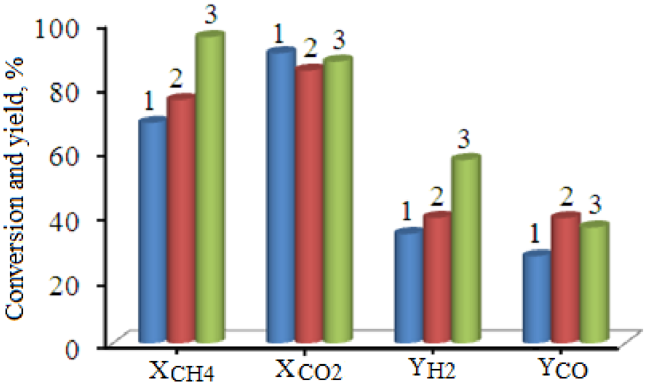

Fig. 1. The effect of space velocity and the addition of water vapor on the conversion of raw materials and the yield of reaction products. 1 – 2500 h^{-1} in the absence of water vapor, 2 – 860 h^{-1} in the absence of water vapor, 3 – 860 h^{-1} in the presence of water vapor

Similar experiments were carried out on the same composition of the catalyst, prepared by the method of impregnation by moisture capacity at space velocities of 860 and 2500 h^{-1} at 850 and 900 °C in the presence and absence of water vapor. Comparative results show that the preparation of catalyst by impregnation is inferior to the SCS method, in which higher values of feed conversion and H_2 yield are obtained. As a result of the temperature change, it was found that carrying out the process at 900 °C allows one to achieve high values of both yield and selectivity for H_2 and CO, but the H_2/CO ratio decreases from 6.1 (T = 700 °C) to 3.9 (T = 900 °C) at W = 2500 h^{-1}.

Acknowledgments

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PP-88

ENANTIOSELECTIVE ALKYNYLATION OF ALDEHYDES AND KETONES BY CATALYST KOH-Et_3N-Et_2O OR THF

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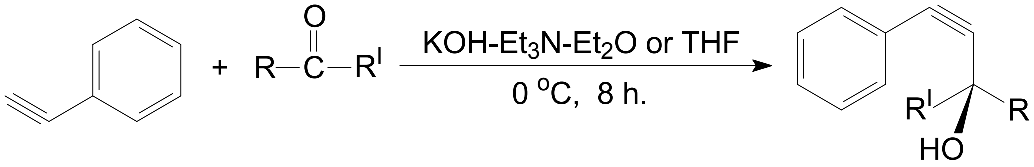
Currently, the global diversification of oil and gas industry, including the introduction of innovative technologies in the petrochemical or heavy organic synthesis in modern conditions is 62-67 % [1]. To date, the introduction of the world chemical industry in modern technology synthesis of new aromatic acetylene alcohols, based on their creation of polymeric and plastic materials with unusual properties, solvents, fungicides, stimulants, antibiotics, hormones, adhesives and paints is perspective task [2-5].

This work was the first time to study reactions based on phenylacetylene and some aldehydes and ketones in the presence of KOH-Et_3N-Et_2O or THF catalysts. Reaction scheme is proposed below, that is based on literature sources [9].



Where: RR^{I}= −Me (**I**); R= −Me, R^{I}= −Et (**II**); R= −Me, R^{I}= −Pr (**III**); RR^{I}= −Et (**IV**); R= −Me, R^{I}= −^{i}Pr (**V**);
R= -Me, R^{I}= ^{tr}Bu (**VI**); R= -Ph, R^{I}= -Me (**VII**); R= -MeCHCH, R^{I}= -H (**VIII**); R= -Me, R^{I}= -H (**IX**);
R=- *c*He, R^{I}= -H (**X**); R= -Ph, R^{I}= -H (**XI**); RR^{I}= -*c*He (**XII**); RR^{I}= -Me*c*He (**XIII**);
RR^{I}= -Me^{i}Pr*c*He (**XIV**); RR^{I}= -Me_3*bic*He (**XV**)

For achievement of high yields of aromatic acetylene alcohols it was systematically investigated influence of different factors – temperature, duration of reaction, nature of solvents and catalysts, mole ratio of initial compounds. The results are shown in the table.

At THF in comparison with Et_2O of medium increased and it using active complexes were formed; constant of reaction rate has increased and the result of transmition of KOH in solutions favorable homogeneous catalytical conditions for formation of active centers and compatibly to increasing of yields of products. Owing to that electronic pairs of oxygenation of Et_2O are placed in one plane, and at THF the negative charge in delocalization state in cycle catalytical activity of KOH has increased owing to which hydrolysis of acetylenides and alcoholates forming during of reaction was increased.

At carring out of difficulty of formation of KOH suspension formation of catalytical active centers and interaction of molecules of reagent were decreased what carried out to decreasing of reaction rate and yields of products. At temperature 0°C velocity of moving of molecules of initial compounds and solvent was increased and their influence with alkalies have formed active particles with high energy. With increasing of number of such particles have nucleophilic interactions; instability of acetylenids and alcoholates increased and proper yields of aromatic acetylene alcohols have increased. Also conducting of process at 0 °C, ionic bonds in molecules of alcoholates and acetylenides are destructed with formation of cations what is promoted to increasing of reaction of phenylacetylene with ketones. At increasing of temperature 20 °C yields of products were decreased owing to partial polymerization of aromatic acetylene alcohols, by-products- acetates, polyacetates and vinyl alcohols.

Influence of nature of solvents on yields of aromatic acetylene alcohols

Synthesized acetylene alcohols	Yields of product, % KOH-Et_3N-Et_2O	Activation energy, kcal/mole	Yields of product, % KOH-Et_3N-THF	Activation energy, kcal/mole
I	79	8,65	84	9,80
II	72	7,52	76	8,11
III	71	7,12	73	7,94
IV	69	6,52	71	7,52
V	66	8,48	68	9,32
VI	61	8,82	67	9,54
VII	80	7,56	87	7,67
VIII	67	8,08	68	8,46
IX	73	6,54	79	7,32
X	62	6,31	66	7,01
XI	83	8,80	86	9,97
XII	57	7,44	60	8,04
XIII	54	8,36	55	8,54
XIV	48	8,07	51	8,28
XV	42	9,52	48	9,73

According to the obtained results of our experiments the optimal conditions for synthesis of aromatic acetylene alcohols have been determined, which reaction was conducted in presence of KOH in solution of THF, temperature 0 °C and duration 8 h.

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ONE-POT PROCESSES OF *PARA*-QUINONES SYNTHESIS IN THE PRESENCE OF Mo–V–P HETEROPOLY ACIDS SOLUTIONS

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Quinones are a class of organic compounds with a number of important properties. Therefore, at present new methods for the quinone synthesis are of great demand. One of methods of quinones production is diene synthesis from benzoquinone (BQ) or 1,4-naphthoquinone (NQ) and 1,3-dienes in the presence of oxidizers [1-2].

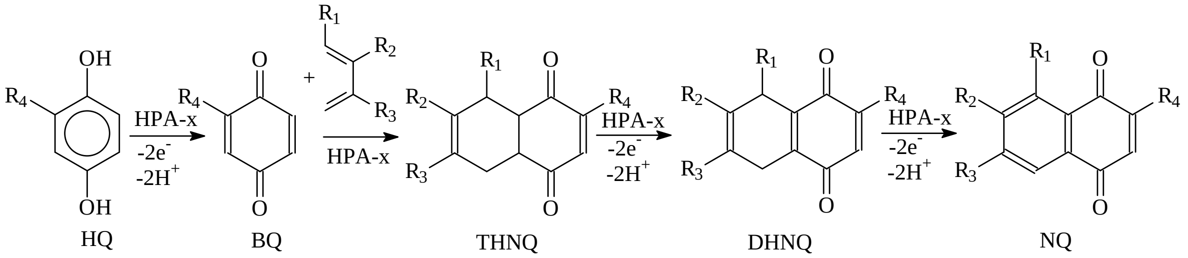
As oxidizers Mo-V-P heteropoly acids $H_{3+x}PV^{V}_{x}Mo_{12-x}O_{40}$ (HPA-x) can be used. Unlike many other oxidizing agents, the vanadium-containing HPA solutions are able to be regenerated by O_2.Thus they can catalyze the two-stages oxidation of various substrates by O_2. It is known also that vanadium-containing HPA-x solutions can be used as acid catalysts of cycloaddition reaction (diene synthesis) for getting *para*-quinones from quinones and 1,3-dienes [3]. Therefore, HPA-x solutions can be bifunctional (i.e. oxidative and acidic) catalysts in this *one-pot* process.

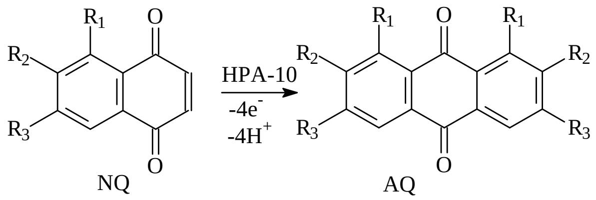
We have developed new processes of quinones production from hydroquinone (HQ) or NQ in the presence of HPA-x solutions [3-5]. At that, we have combined *in a single technological stage* three types of reactions:

1) oxidation of HQ by HPA-x to BQ;

2) the acidic-catalyzed Diels-Alder reaction of different 1,3-dienes (1 or 2 mol) with BQ or NQ giving substituted 1a,4a-tetrahydro-NQ (THNQ) or 1,4,4a,9a-tetrahydroanthraquinone (THAQ) respectively;

3) the sequential oxidation of THNQ or THAQ by HPA-x with the formation substituted NQ or AQ. Thus, our *one-pot* processes are described by the following scheme:





Results are presented in the Table.

№	Substituents	Yield of product, %	Content main product in precipitate, %
	a) Naphthoqinones		
1	$R_1 = H, R_2 = CH_3, R_3 = R_4 = H$	63	98
2	$R_2 = R_3 = R_4 = H, R_1 = CH_3$	62	97
3	$R_2 = R_3 = CH_3, R_1 = R_4 = H$	72	90
4	$R_1 = R_2 = R_3 = R_4 = H$	51	99
5	$R_1 = R_2 = R_3 = H, R_4 = CH_3$	32	96
	b) Anthraquinones		
6	$R_1 = H, R_2 = R_3 = CH_3$	78	98
7	$R_1 = R_2 = R_3 = H$	70	97
8	$R_1 = R_3 = R_4 = H, R_2 = CH_3$	72	96
9	$R_1 = R_3 = R_4 = H, R_1 = CH_3$	91	99
Conditions: a) 2×10^{-3} mol HQ, 10 mL 0.25 M $H_7PMo_8V_4O_{40}$ (HPA-4) water solution, volume ratio HPA-4 : 1,4-dioxane = 1 : 1, reaction time 30 h, temperature 20 °C. HQ conversion ≥ 99 %; b) 1.3×10^{-3} mol NQ, 3,9 mL 0.20 M $H_{17}P_3Mo_{16}V_{10}O_{89}$ (HPA-10) water solution, volume ratio HPA-10 : 1,4-dioxane = 1 : 2; reaction time 7 h, temperature 80 °C. NQ conversion ≥ 99 %.			

In the industrial version, these processes can be realized in separate reactors **1** and **2**. In the 1st stage a substrate is oxidizing by HPA-x. In the 2nd stage HPA-x is regenerated by O_2.

At the 1st stage, solutions of catalyst and substrate react in a jacketed glass reactor equipped with agitator and reflux condenser in the absence of oxygen. After reaction completion, the obtained mixture is transferred to a filter where solid product are filtered away. After that catalyst solution is submitted to an unique plug-flow air reactor and regenerated for 20-25 min at 160-170 °C and $Po_2 = 0.4$ mPa. The regenerated HPA-x catalyst is fed again for the next catalytic cycle.

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VIRTUAL PRESENTATIONS
(PUBLICATION OF THE ABSTRACT IN THE ELECTRONIC BOOK)

VP-1

MIXING EFFECTS IN $GdFeO_3$ PARTICLE PRECIPITATION PROCESS BY USE OF IMPINGING JETS MICROREACTOR

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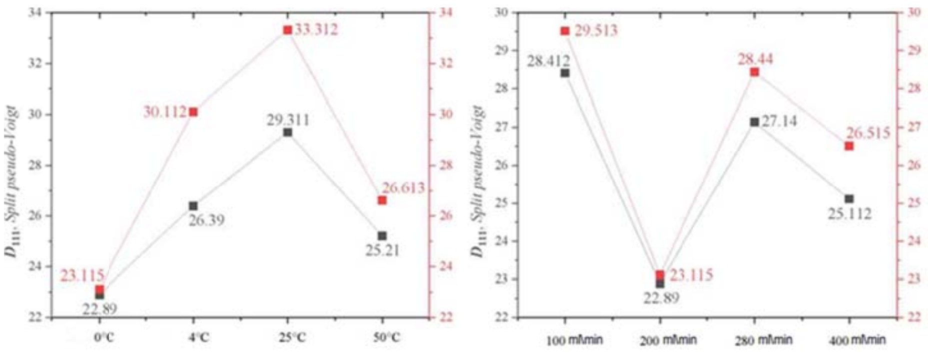
Impinging jets microreactors are one of the new and perspective ways for processes intensification of chemical precipitation due to better micromixing. The very high mass transfer rates resulting from very low reaction-volume/surface-area ratios make microreactors potentially attractive for the synthesis of inorganic materials [1]. This method promises long-term solutions to the modern challenges in synthesis of nanosized particles, the rapidly growing research interest is confirmed by recently published papers, books [2] and book chapter [3].

Free impinging jets reactors are relevant to nanoscale particle synthesis by using liquid precipitation. It refers to the rapid formation of moderately soluble crystalline or amorphous solid particles in a liquid solution, whereas particle formation occurs under high supersaturation conditions. Precipitation involves the simultaneous and fast occurrence of primary nucleation and growth together with the secondary processes such as Ostwald ripening, aggregation and breakage. Usually the solid product has a wide crystal size distribution which determined by the intensity of mixing and other process conditions, such as the viscosity and temperature of solutions. This method can strongly minimize crystal size distribution by the ability to generate fast micromixing, the timescale of which is on the order of milliseconds [3].

Chemical reactions applied in so-called reactive crystallization processes are usually very fast, which means that their course depends on mixing as well. Due to the high sensitivity of primary nucleation to supersaturation, the number of primary particles is controlled by nucleation and affected by mixing, whereas crystal growth is less important, because after complete unloading of supersaturation, it is more the number of crystals than the rate of their growth that determines their final size. The growth rate can, however, affect their shape [4].



In the course of this study the influence of temperature of the solutions, Reynolds number, and the angle between impinging jets on products microreactor synthesis of the coprecipitated hydroxides of gadolinium and iron (III) and their subsequent heat treatment in air were carried out, as a result of which nanocrystals of gadolinium orthoferrite were produced. The hydroxides were investigated by x-ray spectral microanalysis, synchronous thermal analysis and powder x-ray diffraction. The heat treated products were investigated by powder x-ray diffraction.

According to the results of calculations of the average crystalline size of $GdFeO_3$, it can be concluded that during microreactor synthesis of the coprecipitated hydroxides of gadolinium and iron (III), that temperature and Reynolds number have a greater impact than the impingement angle between jets (see Figure).

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VP-2

CALCIUM PHOSPHATES CATALYTIC PROPERTIES AND THERMAL STABILITY IN METHYL LACTATE DEHYDRATION

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Introduction. The stable growth, around 3-4 % per year, of the world's acrylic acid (AA) production capacity over the past decade suggests that final products using AA remain in demand even during times of economic crisis. At the same time, with the growth of the technology segment for the production basic monomers from renewable raw materials, it shows the promise of this direction. The main problem in the implementation this technology now is lack of lactic acid and ethers understanding of the dehydration mechanism and parameters affecting on stability of the proposed catalyst systems.

In this work, we evaluated the catalytic activity and thermal stability of various calcium phosphate [1] salts and proposed the most promising phosphate forms for the LA and ethers dehydration to AA.

Results. On figure #1 shows all types of calcium phosphate salts, as well as the conditions for their synthesis and decomposition/transition between different types.

The most low stable from phosphate is dihydrogen calcium phosphate (CaDHP - $Ca(H_2PO_4)_2$), according to [3] and our TGA, with increase temperature on first stage the salt witch lose water with the following decomposition and formation of metaphosphate with structure: $Ca_3(P_3O_9)_2$ or $-[Ca(PO_3)_2]-$, dependence from final calcination temperature. The calcium hydrogen phosphate (CaHP - $CaHPO_4$), according to [3] and our TGA, decomposition with removal water and turns into pyrophosphate form, at temperatures around 430-440 °C. The ortho- and pyrophosphate (CaOP - $Ca_3(PO_4)_2$ / CaPP - $Ca_2P_2O_7$) are stable up to temperatures 700 °C, which is significantly higher that the temperature range of the dehydration ML.

Also we can synthesis an intermediate between CaHP and CaHAp are formed octophospahte calcium [4] with the following composition: $Ca_8(HPO_4)_2(PO_4)_4$ (CaOctP), that phosphate form stable till 350 °C and decomposition at first stage to CaDHAp in temperature range 350-600 °C and than with temperature over 600 °C in CaPP and CaOP. The calcium deficient hydroxyapatite (CaDHAp - $Ca_9(HPO_4)(PO_4)_5(OH)$) can synthesis over "wet" way, according [5] and our TGA, and keep stable till 600 °C. At the temperature above 600 °C the CaDHAp are decomposition on ortho- and pyrophosphate. The calcium HAp, with the structure $Ca_{10}(PO_4)_6(OH)_2$ can synthesis by hydrothermal or solid-phase methods.

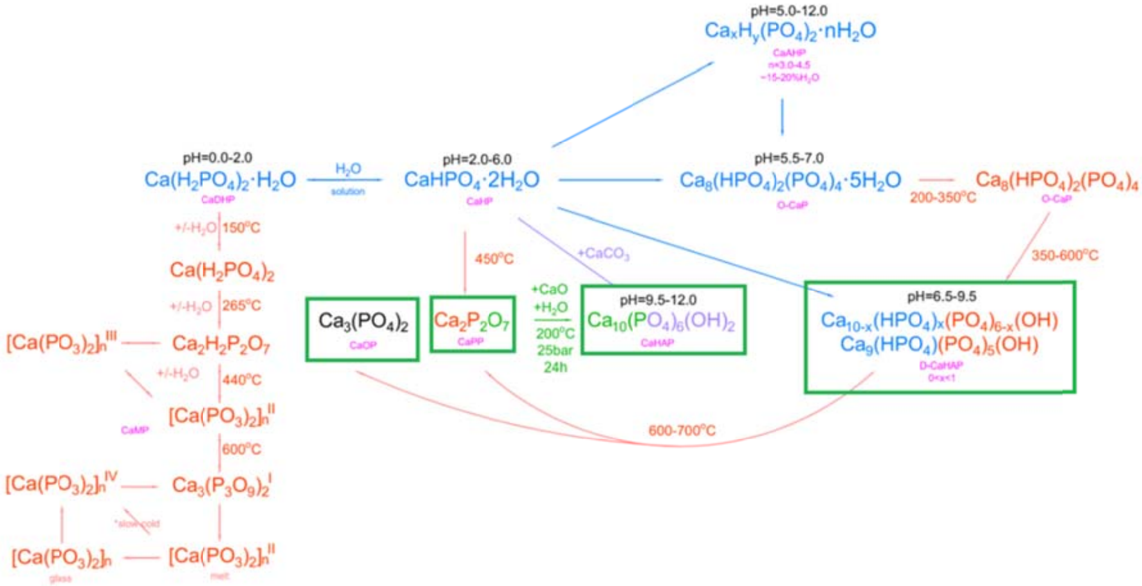

Fig. 1. Overall scheme calcium phosphate salts synthesis and transformation

The catalytic activity of different phosphates salts are presented in Table #1 in comparison with Ca/P ration in each type phosphate.

Sample	CaDHP	CaPP	CaHP	CaOP	CaOctP	CaDHA
X_{ML}, % m	31.6	38	48	53.3	99.5	93.2
S_{AA}, % m	4.5	15	14	18.5	25.3	21.4
Ca/P ratio	0.64	1.29	1.29	1.93	1.72	1.94

Conclusions. Based on experimental data of thermal stability different phosphate salts we can proposal that for reaction ML dehydration more prefer to develop catalytic system based on ortho-, pyro- or hydroxyapatite phosphates type. Also with growing Ca/P molar ration leads to increase ML conversion and AA selectivity, these results allow to assume with increase vacant calcium atoms on the surface catalyst has positive effect on main reaction of AA formation.

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VP-3

CATALYTIC CONVERSION OF ETHANOL TO ETHYL ACETATE

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The reason for specifically studying the dehydrogenation of ethanol is that ethanol could be one of the future feedstock of the chemical industry. Ethyl acetate produced from ethanol has a low toxicity and it is broadly employed as a solvent in many industrial products such as paints, adhesives and coatings, as a green alternative, eliminating the use of aromatic compounds. Different catalytic systems have been applied for dehydrogenation of ethanol using Cu and Pd-based catalysts supported on different carriers [1].

In present work, direct transformation of ethanol to ethyl acetate was studied over supported cooper catalysts: $Cu/ZnO/Cr_2O_3$ and Cu/ZrO_2. Catalysts were prepared by incipient wetness impregnation of support with a solution of $Cu(NO_3)_2*3H_2O$ in methanolThe solids were dried at 423 K and calcined at 773 K for 12 and 5 h, respectively. Activity and selectivity of the catalysts were carried out in a continuous-flow, tubular reactor. Samples were reduced in situ by heating in pure H_2 flow.

Catalyst	Contact time, s	Temperature, °C	Conversion, %	Selectivity, %				Carrier gas
				AA	EtOAc	AcH	Buthanol-1	
$Cu/ZnO/Cr_2O_3$	3	270	55,7	8,8	1,4	29,3	0	N_2
	6,2	250	47,8	8,2	2,1	32,3	0	N_2
	5,9	270	55,8	9,9	2,2	26,4	0	N_2
	5,6	300	63,8	13,5	2,2	22,3	0	N_2
Cu/ZrO_2	3,3	225	80,7	0,3	4,2	7,6	7,2	N_2
	3,3	225	67,6	0,1	2	3,2	7,9	H_2
	3	270	79,9	0,3	3,3	5,2	12,2	H_2
	3	270	59,4	0,1	1,5	11,3	6,6	N_2

AA – acetic acid, EtOAc – ethyl acetate, AcH – acetaldehyde

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VP-4

BLACK BOX OPTIMIZATION-ASSISTED DESIGN OF AN ETBE REACTIVE DISTILLATION PROCESS

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Ethyl tert-butyl ether (ETBE) is produced by the reaction between isobutene and ethanol $(CH_3)_2C = CH_2 + C_2H_5OH \leftrightarrow (CH_3)_3C - OCH_2CH_3$, in a general flowsheet as presented in fig. 1. C4 cut is used as source of isobutene; an isothermal reactor converts about 80 % of the isobutene, while the remaining conversion and ETBE separation from the unreacted hydrocarbon mixture takes place simultaneously in a reactive distillation (RD) column. Reaction kinetics and homotopy analysis of the RD column are presented in [1], [2].

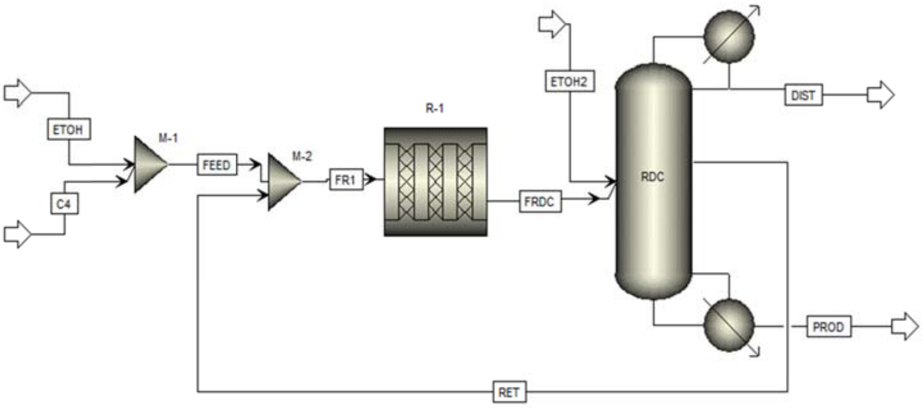

Figure 1. Reactive distillation process superstructure for ETBE synthesis

The integration of reaction and separation introduces dramatic improvements in plant size reduction, reactant conversion and selectivity [3]. Mathematical optimization allows to systematically select the design that maximizes reactant conversion and product purity, as the design problem can be modeled as a mixed integer nonlinear optimization problem (MINLP) [4].

$\min_{X} \Psi = \sum C_{\text{кап}} + \sum C_{\text{оп}} = f(X)$	Target function as total capital and operative costs. A function of integer and continuous variables
Subject to the constraints:	
$F(X) = 0$	Material and energy balances
$G_1(X) \leq 0$	Column hydraulics relationships
$G_2(X) \leq 0$	Conversion and purity arbitrary requirements
$lb \leq X \leq ub$	Search bounds for independent variables

Deterministic methods for the solution of this problem consist in finding the roots of the extended Lagrange function gradient, i.e. $\nabla\Psi(x^*) + \sum \lambda_i \nabla f_i(x^*) + \sum \mu_j \nabla g_j(x^*) = 0$ [5].

In this work the reactive distillation process was modeled in Aspen Plus. While this allows to avoid the time-consuming step of writing and coding the mathematical model of the process, it difficults the calculation of the F and G constraints derivatives, as there is no algebraic formulation and its numerical estimation can make the solution time prohibitively large.

In order to circumvent this obstacle, a stochastic derivative-free method is implemented. The mesh adaptive direct search algorithm MADS in its software implementation NOMAD [6] was coupled with Aspen Plus via an ActiveX visual basic interface written in Microsoft Excel. The optimized variables and solution scheme are presented in figure 2. The cost functions are written following the correlations presented in [7], column hydraulic relationships are taken from [8].

Constructive and operative optimization variables X	
Catalyst load by reactive plate, kg	1
Number of plates	2
Feed plate	3
Start – end of reactive part	4 – 5
Reboiler heat load, kW	6
Reflux ratio	7
Isothermal reactor temperature, °C	8
Secondary ethanol flowrate, kg/h – feed plate	9 – 10
Recycle flowrate, kg/h – extraction plate	11 – 12
Column diameter, m	13
Distance between plates, m	14
Performance requirements and target function	
ETBE product purity (mass fr.)	$g_1 \geq 0.95$
Isobutylene conversion degree (mole fr.)	$g_2 \geq 0.98$
Total capital and operative costs (1000$/year)	Ψ

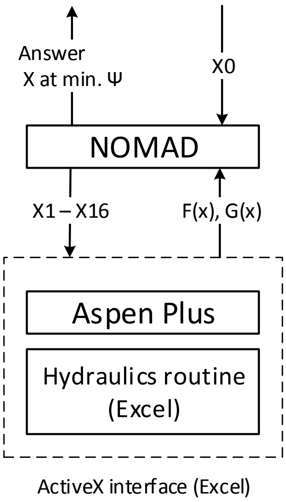

Figure 2. Optimization variables and solution diagram

This approach proved to be an effective solution strategy to the optimal design problem that, that makes use of the time-saving modeling advantage offered by commercial process simulation tools. Total capital and operative costs are reduced in more than 20 % compared to an unoptimized flowsheet with the same performance requirements.

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VP-5

WACKER-TYPE OXIDATION OF FATTY ACIDS AND DERIVATIVES

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Nowadays the use of renewable sources of raw materials is widespread and popularized in relation to the environmental dimension. It is replacement for raw materials of petrochemical origin. Due to the presence of double bonds in vegetable oils and their derivatives, they can be functionalized into value-added products. An interesting and little-studied direction of the modification of the double bonds of the vegetable oils derivatives is the “Wacker type” reaction to produce ketocarboxylates, as well as the further conversion of these groups to carboxylic. The oxidants are may be, for example, hydrogen peroxide and organically peracids [1].

The Wacker process or the Hoechst–Wacker process originally referred to the oxidation of ethylene to acetaldehyde by oxygen in water in the presence of a palladium tetrachloride catalyst. This chemical reaction was the first organometallic and organopalladium reaction applied in industrial scale (*e.g.* [2]). However, the catalyst system and reaction conditions are also applied to oxidations and oxidative cleavage of renewables [3, 4, 5]. The purpose of the work is to select the conditions for the oxidation of unsaturated fatty acid derivatives and vegetable oils and the identification of oxidation products.

Oleic acid was chosen for beginning the research. The conditions of the process are the pH = 0-2, the temperature 60-70 °C, $PdCl_2$ = 0.3-0.5 weight %, $CuCl_2$ = 10-25 weight % (water solution of the salt are used), the oxidant is the air's oxygen. The synthesis is carried out in a cylindrical three-necked reactor with magnetic stirring. Air was bubbled through the reaction mass (feed rate – 0,5 liter/min). The reaction time is 16 hours, the temperature is 70-80 °C.

The presence of ketones groups in the resulting product was confirmed by qualitatively assesing the anisidine value test (GOST 31756-2012, SO 6885:2006). If the sample weight is 0,164 g, the anisidine value is 122.6. Besides, the peroxide number was determined. The presence of peroxide groups is 0,28 mmol/g.

Because of the result shows we can conclude that the conditions of the industrial “Waker type” process apply to the production of fatty ketones without creating excessive pressure in the system when the oxidant is the air's oxygen. Selective obtain of fatty ketones by this method is allow to obtain valuable organic synthesis products (dicarboxylic acids, fatty alcohols, plasticizers, polyesters, biodegradable fibers).

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VP-6

KINETICS OF HEAVY REFORMATE TRANSALKYLATION OVER ZSM-5- AND MORDENITE-BASED CATALYSTS

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Reformate is the major source of bulk aromatic compounds such as benzene, toluene, and xylenes. In transalkylation units, heavy reformate is valorized by converting the C9+ alkyl aromatics to benzene and mixed xylenes. A ZSM-5- and mordenite-based catalyst was screened in a high-throughput reactor system to study the kinetics of heavy reformate transalkylation in the presence of toluene and excess H_2 at 598-648 K and 2 MPa. A mechanism was developed based on dealkylation, transalkylation, and disproportionation reactions. Mass balances describing these reactions were solved numerically together with least squares fitting of experimental data to estimate the kinetic parameters. The dealkylation of alkyl aromatics, namely propylbenzene, methylethylbenzene, and methylpropylbenzene, exhibits the highest rates among the reactions considered and results in the formation of benzene and toluene. Toluene further reacts and undergoes transalkylation and disproportionation at the same activation energy (~57 kJ mol^{-1}) to give benzene and xylenes. Measured rates signify trimethylbenzene and toluene transalkylation as a prevalent pathway to mixed xylenes.

VP-6

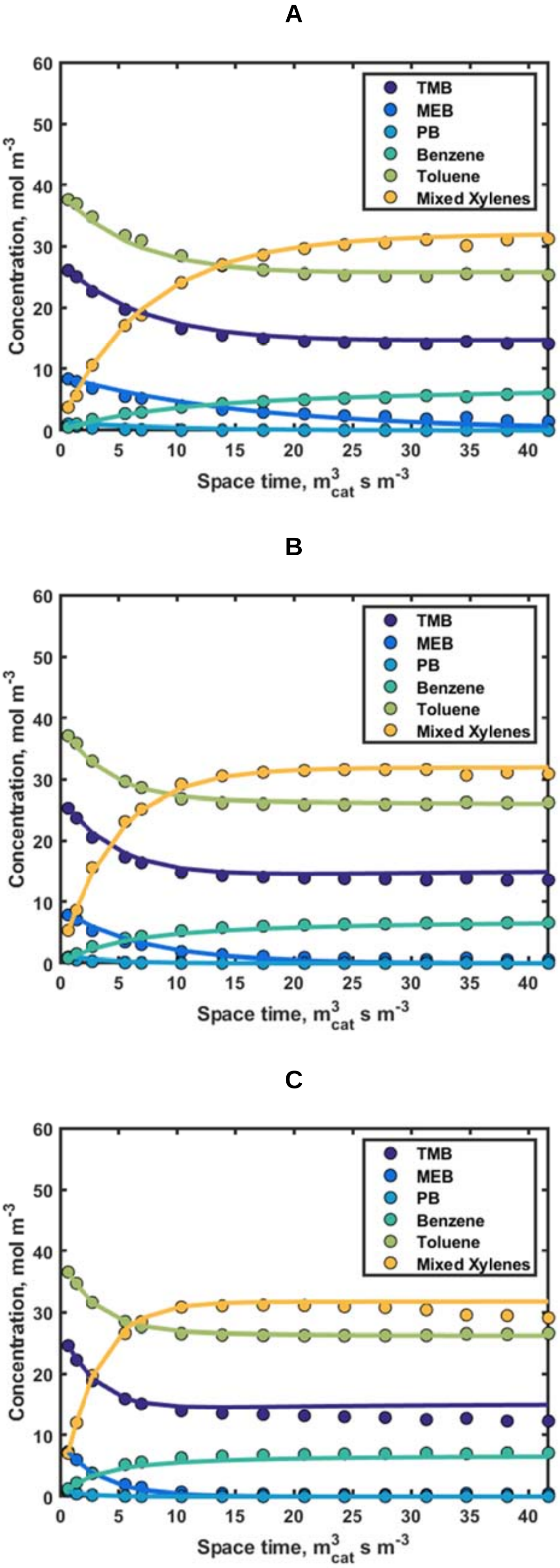

Figure 1. Concentration profiles of species at 598 K (A), 623 K (B), and 648 K (C). TMB: Trimethylbenzene; MEB: Methylethylbenzene; PB: Propylbenzene

STUDIES OF WASTEWATER TREATMENT PROCESS OUT ASPHALT-RESIN OIL PRODUCTS BY LIQUID PHASE EXTRACTION

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The features of the liquid-phase extraction process for the development of technology for wastewater treatment from asphalt-resinous petroleum products using organic solvents are studied. The physicochemical problems associated with the processes of liquid-phase extraction are analyzed.

In the processes of liquid-phase extraction, the main factor is the mass transfer between two immiscible liquids. The liquid extraction of organic compounds from wastewater is a mass transfer process occurring in an interfacial film and is carried out by dispersing the solvent extract in an aqueous medium and extraction in an interfacial film, characterized by diffusion transfers of the corresponding components to the interfacial surface.

The efficiency of mass transfer in extractors is determined by the size of the droplets of solvent obtained by crushing it under stirring conditions. The process of liquid-phase extraction of organic impurities in wastewater with a solvent proceeds under conditions of intensive mixing and dispersion, due to which the isotropy of the turbulent flow in the extractor is achieved. An equation is written that describes the distribution of the concentration of a substance in the approximation of a boundary layer on the surface of a single extractant droplet, with the participation of boundary conditions. The mass transfer coefficient was determined between the turbulent flow and a drop in the form.

$$\begin{aligned} &\lambda > \lambda_0, \qquad \beta_L = C_{11}\left(\varepsilon_R R\right)^{1/6} U^{1/2}\left(\frac{\alpha}{1+\gamma}\right)^{1/2} \\ &\lambda < \lambda_0, \qquad \beta_L = C_{12}\left(\frac{\varepsilon_R}{\nu_c}\right)^{1/4}\left(UR\right)^{1/2}\left(\frac{\alpha}{1+\gamma}\right)^{1/2} \end{aligned} \tag{1}$$

Здесь $\beta_L -$ mass transfer coefficient; $\lambda -$ scale of turbulence; $\lambda_0 -$ scale of Kolmogorov's turbulence; $\varepsilon_R -$ dissipation energy per unit mass; $R -$ radius of the drop; $U -$ flow rate away from the droplet; $\alpha -$ coefficient; $\gamma -$ the ratio of the viscosity of a drop of isopropyl ether to the viscosity of water; $\nu_d, \nu_c -$ kinematic viscosity of a drop and medium; $C_{11}, C_{12}, C_{13} -$ coefficients.

The Sherwood number was determined by the formula

for $(\lambda < \lambda_0)$,
$$\mathrm{Sh} = \frac{\beta_L R}{D_T} = C_{12}\mathrm{Sc}^{1/2}\left(\frac{\nu_c^3}{\varepsilon_R R^4}\right)^{1/4}\left(\frac{\mathrm{Re}_d}{1+\gamma}\right)^{1/2} \tag{2}$$

for $\lambda > \lambda_0$
$$\mathrm{Sh} = C_{11}\mathrm{Sc}^{1/2}\left(\frac{\nu_c^3}{\varepsilon_R R^4}\right)^{1/6}\left(\frac{\mathrm{Re}_d}{1+\gamma}\right)^{1/2} \tag{3}$$

where D_T – is the coefficient of turbulent diffusion; Sc – Schmidt number.

In mixing devices under conditions of isotropic turbulence for a liquid – liquid system, the turbulent diffusion coefficient, according to [1], is determined as $D_T \approx \left(\varepsilon_R / \nu_c\right)^{1/2} \lambda^2$. Under conditions of intensive mixing, it can be assumed that the length of the path of movement of the liquid particles is equal to the radius of the mixer, i.e. $\lambda \approx d/2$. Then, considering that $\varepsilon_R = f\left(\mathrm{Re}_d\right)\frac{n^3 d^5}{\upsilon_0}$, the turbulent diffusion coefficient can be determined as follows

$$D_T \approx \frac{1}{4}\sqrt{f\left(\mathrm{Re}_d\right)}\left(\frac{n^3 d^7}{\nu_C \upsilon_0}\right)^{1/2} \tag{4}$$

where $f\left(\mathrm{Re}_d\right)$ – is the coefficient of resistance of the medium, depending on the number Re_d, υ_0 – the volume of liquid in the mixer. As follows from equation (4), the turbulent diffusion coefficient is directly proportional to the rotational speed and diameter of the mixer $n^{3/2}$ and inversely proportional to the viscosity of the medium $\nu_C^{1/2}$, i.e. with increasing viscosity of the medium (at low temperatures), the coefficient of turbulent diffusion decreases. In principle, the effective diffusion coefficient is defined as $D_E = D + D_T$, moreover, under conditions of intensive mixing, we have $D_T >> D$, that is, the turbulent diffusion coefficient is much larger than the molecular diffusion coefficient.

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VP-8

HYDROGEN-FREE CONVERSION OF FATTY ACID METHYL ESTERS TO ALCOHOLS

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Fatty alcohols are important intermediates for the production of detergents, surfactants, food additives, pharmaceuticals, cosmetics, and for polyesters used for textiles, lubricants, and industrial solvents [1]. Currently, fatty alcohols are produced by hydrogenating fatty acids and their esters in the presence of hydrogen. The reaction takes place on copper catalysts with the addition of metals (Cr, Ni, Zn, Fe) under harsh reaction conditions (Figure 1 (a)).

In turn, the process of simultaneous dehydrogenation of methanol and hydrogenation of methyl ester of fatty acid is known [2]. The process of producing fatty alcohols from methyl esters of fatty acids without additional introduction of hydrogen on a copper catalyst, which performs two functions: obtaining hydrogen by splitting methanol and hydrogenation of fatty acid esters with this hydrogen (Figure 1 (b)).

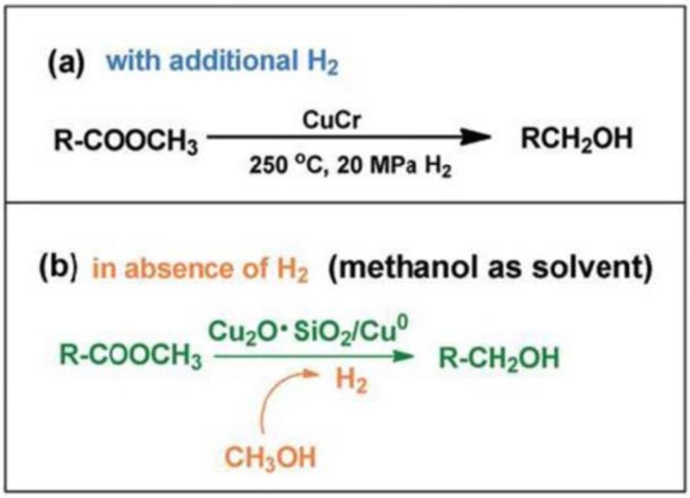

Figure 1. The reaction sequences for conversion of fatty acid methyl esters to alcohols in methanol via (a) with additional H_2 and (b) in the absence of H_2

We conducted research in an autoclave at a pressure of 7-9 MPa and a temperature of 240 °C. A mixture of methyl esters of fatty acids (C_8-C_{18}) and methanol in 1 to 14 moles was loaded into the autoclave. The table 1 shows that the process takes place at a lower pressure. The pressure is created by the collapse of methanol (H_2 and CO), which begins at a temperature of 150 °C. Also, the process does not require additional hydrogen in the reaction. The reaction was carried out for 5 hours.

During the study, it was found that the process-using methanol as a solvent greatly softens the process conditions in contrast to the main hydrogenation, but the process indicator is lower. The values of the two methods are shown in table 1.

Table 1.

	With additional H_2	**In absence of H_2**
Temperature, °C	250	240
Pressure, MPa	20	8
Conversion, %	100	65
Selectivity, %	90	90

In conclusion, we investigated a simple and efficient one-pot process for the selective conversion of acid methyl esters to fatty alcohols with nearly 90 % selectivity using a highly active and inexpensive Cu/SiO_2 catalyst in methanol without extraneous H_2.

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VP-9

NON-CATALYTIC PROCESS FOR THE PRODUCTION OF TRIMETILOLPROPANE-BASED SYNTHETIC OILS

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Currently, there is a steady tendency to replace petroleum products with environmentally friendly analogues. First of all, this is due to the non-renewability of sources of raw materials and the long biochemical decomposition of products. From this point of view, biomaterials are free from flaws. Derivatives of vegetable oils find many different applications – the production of plastics, resins, cosmetics. A significant proportion also falls on lubricants and biodiesel. Global castor oil and derivatives market was valued at US$ 709 Mn in 2017 and is expected to reach US$ 1195.17 Mn by 2026 [1].

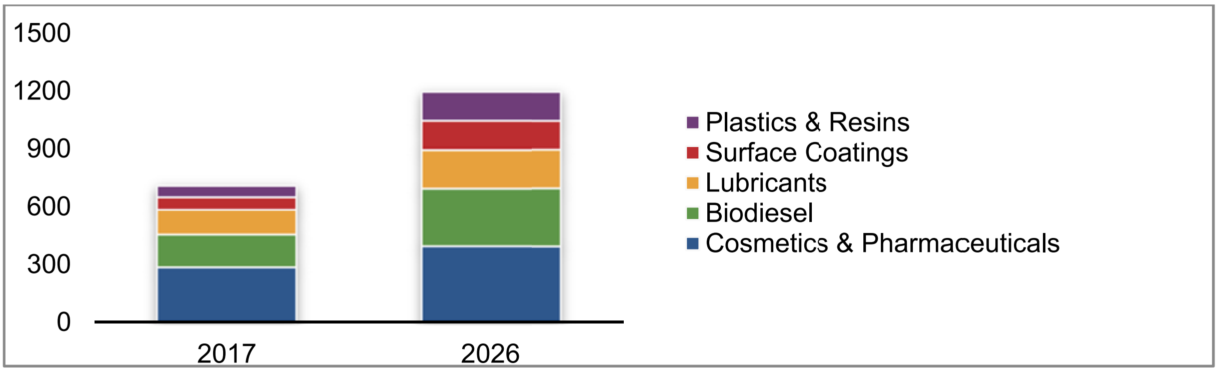

Figure 1. Global castor oil and derivatives market by application [1]

The rapidly growing automotive and aviation industries have a positive effect on the demand for lubricants. For example, McKinsey predicts an increase in the lubricants market by 14.5 % by 2035 [2].

Today biolubricants are produced by acid-catalytic esterification. There is also a tendency to switch to esters as a raw material for the transesterification process. Basically, sodium and calcium methoxides are used for basic catalytic alcoholysis of fatty acid methyl esters [3], but KOH can also be used for these purposes [4]. In addition, researchers also developed a method for transesterification of acids and alcohols in the presence of lipase enzymes [5]. The main disadvantages of the proposed methods is the presence of side reactions, for example, saponification reactions in the process with KOH, as well as the need to neutralize and purify catalyst residues. Therefore, the aim of this work was to assess the fundamental possibility of carrying out the transesterification process non-catalytically.

In this work, experiments were carried out on the transesterification of esters and polyol without the use of a catalyst. The raw materials used are methyl esters of fatty acid (FAME) obtained from sunflower oil and trimethylolpropane (TMP). The experiments were carried out in the mixing reactor at 170-210 °C and observed [FAME] : [TMP] = 3:1. It was conducted with distillation of methanol. By this method, a conversion of 24-26 % was achieved. It was found that the output product depends on temperature and reach maximum at 170 °C. The presence of TMP and FAME was confirmed by TLC.

Thereby, the principal possibility of non-catalytic synthesis of trimethylolpropane and fatty acid esters is obtained. The described method can be modified in order to increase the conversion of FAME and bring the process parameters to similar cases of catalytic synthesis.

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VP-10

KINETICS OF NON-CATALYTIC N-BUTYL LACTATE PRODUCTION FROM AMMONIUM LACTATE

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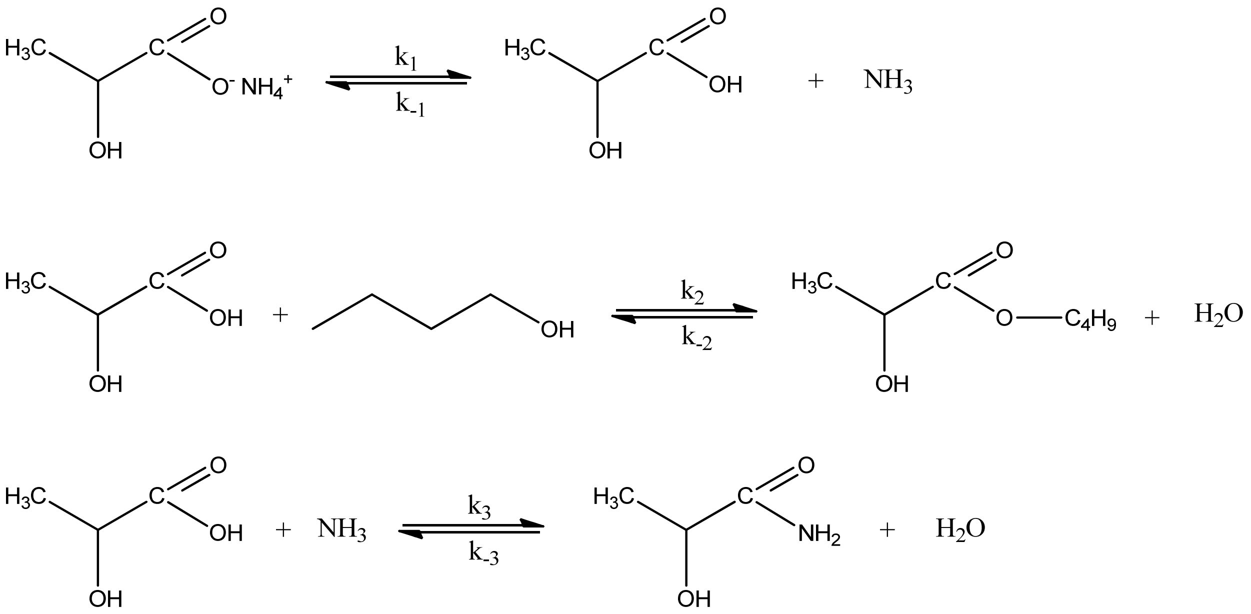
Currently, the world is facing an acute problem of polymer waste. For this reason, there is an increasing need for biodegradable polymer materials. One of the most demanding biopolymers today is polylactic acid. The raw material for polylactide production can be the lactic acid obtained from vegetable renewable sources by carbohydrates fermentation.

There are different methods to extract the lactic acid from fermentation broth. An effective way of these is a conversion of lactic acid to butyl lactate ester with following purification by vacuum rectification. However, the conversion of lactic acid to butyl ester is complicated by the presence of lactic acid in the ammonium lactate form. Thus, it is not possible to use an acid catalyst due to its deactivation with an ammonium ion. At first, it is necessary to carry out a non-catalytic stage until the almost complete conversion of ammonium lactate. In addition, this stage is complicated by the formation of a by-product, which reduces the selectivity of the process. The next catalytic stage proceeds quickly and without difficulties. Therefore, non-catalytic esterification step of ammonium lactate with butanol is more interesting for research.

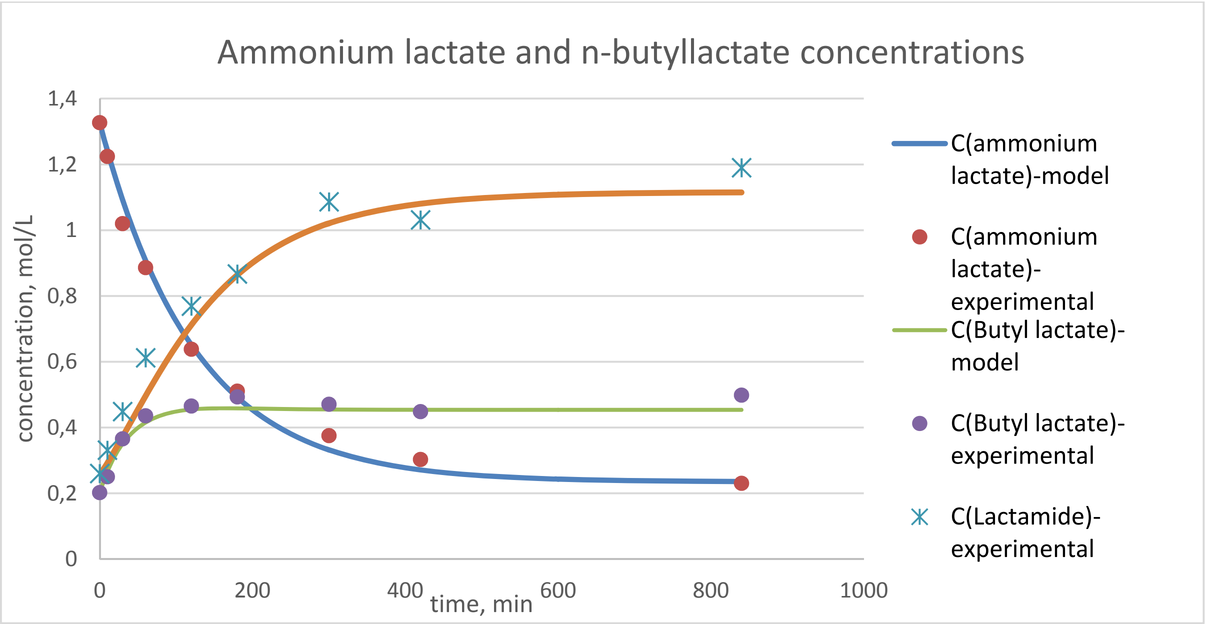
Currently, in the literature, we can notice a lack of research on the kinetics of ammonium salts non-catalytic esterification. Therefore, this process requires additional study. In order to study this process, a series of experiments at different temperatures was carried out in closed system. The experiments were carried out in a jacketed autoclave, equipped with a stirrer. There were accomplished a series of experiments at 130 °C, 150 °C and 170 °C.

Experimental results have been analyzed and the following reaction scheme was offered.

VP-10



Thus, based on this scheme there were suggested a kinetic model that adequately describe the experimental data. The graphs below shows a comparison of the proposed model and experimental points.



VP-11

REGULARITIES OF CATALYTIC CONVERSION OF HYDROCARBONS IN CATALYTIC REFORMING OF NAPHTHA WITH PRESSURE REDUCTION

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The improvement of catalytic naphtha reforming process mainly focused on three important issues: developing catalysts with higher activity and selectivity, modernization of industrial equipment and optimization of the technological mode of operations.

In this studies, the influence of total pressure on catalytic naphtha reforming process was investigated and the technological mode of the process, in which the optimal ratio between the yield, quality and coke formation rate considering composition of the feedstock was determined.

Mathematical model of a fixed bed reforming reactors performed as system of material and heat balances:

$$\begin{cases} G_c \dfrac{\partial C_i}{\partial Z} + G_c \dfrac{\partial C_i}{\partial V} = \sum\limits_{j=1}^{m} a_j \cdot r_j \\ G_c \dfrac{\partial T}{\partial V} + G_c \dfrac{\partial T}{\partial Z} = \dfrac{1}{\rho \cdot C_p^{mix}} \sum\limits_{j=1}^{m} a_j \cdot r_j \cdot \left(\dfrac{RT}{P}\right) \cdot \Delta H_j \end{cases}$$

The initial conditions:

at $z = 0$, $C_i = 0$, $T = 0$;

at $V = 0$, $T = T_0$, $C_i = C_{i0}$;

where G_c is a raw material flow rate, m^3/s; C_i is a concentration of ith component, mol/m^3; Z is a volume of raw material processed from the moment when the fresh catalyst (new catalyst, no regenerations were done) was loaded, m^3; V is a catalyst volume in the reactors, m^3; a_j is a catalyst's activity; r_j is a reaction's rate, mol/m^3·s; i is a component's number in a mixture; j is a reaction's number due to formalized scheme accepted; T is a temperature, K; ρ is a density, mol/m^3; C_p^{mix} is a heat capacity of mixture, kJ/mol·K; ΔH is jth reaction heat, kJ/mol; R is the gas constant, 8,314 MPa·l/mol·K; P is a pressure, MPa.

The adequacy of the model was verified by comparing the experimental data from reforming units and the data calculated with the mathematical model.

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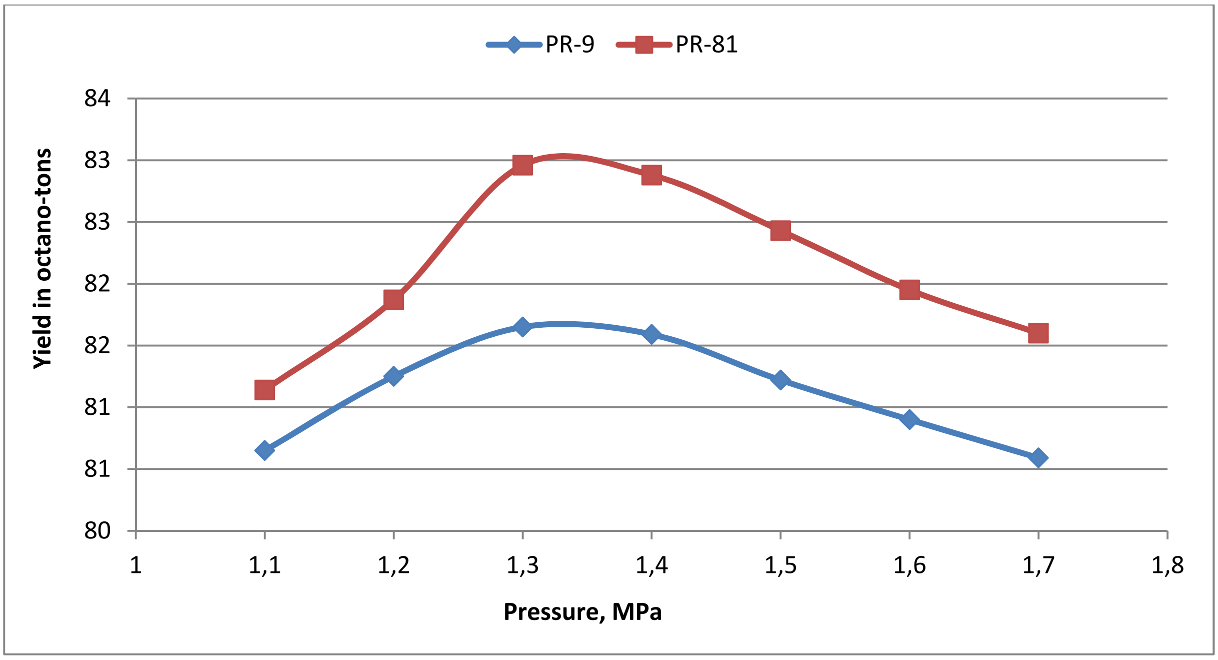

Figure 1. The dependence of yield from pressure

It was found, that decrease in the pressure range from 1,5 to 1,2 MPa at the temperature 478-481 °C and feedstock space velocity is 1,4 hour^{-1} induces an increase in yield or 1-2 % mass. due to increase in the aromatization reactions rate and deacrease in the hydrocracking reactions rate depending on feedstock composition and catalyst's type, but at the same time do not induces in the isomerization reactions rate.

It is shown that the decrease in pressure is limited by the requirements for the catalyst stability due to the increase in the coke formation rate. It was found, that with the temperature at the reactor entrance is 478 °C, the raw material flow rate is 64,3 m^3/h and the naphthenic feedstock the total amount of coke is evenly increased by 0,5-1,0 % mass. depending on pressure and catalyst's type.

It is proposed that the criterion of optimality is the yield, expressed in octano-tons. It was calculated with the mathematical model, that with the naphthenic feedstock using the pressure should vary in the range from 1,3 to 1,5 MPa.

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VP-12

BASIC REGULARITIES OF GLYCOLYSIS PET WITH KOH CATALYSIS

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Nowadays utilization of plastic wastes is one of the most important ecological directions in global chemical industry. Due to its properties polyethylene terephthalate (PET) is widely used as beverage bottles and at textile industry. For this reason it represents 6 % wt. from total global polymer waste amount [1]. Chemical recycling is more difficult than mechanical recycling, but it provides an opportunity to produce clean monomers (terephthalic acid, dimethyl terephthalate or bis(2-hydroxyethyl) terephthalate (BHET)) as well as their functional derivatives. Glycolysis is the most promising among them and great number of scientific works concerned with it. There are a lot of different catalysts of the process from very simple (as zinc chloride [2] or sodium carbonate [3]) to very effective but complicated ones (such as manganese or cobalt nanocatalysts [4,5] or ionic liquds [6]).

In this work PET glycolysis by ethylene glycol (EG) in the presence of KOH was studied. As a feedstock were used only ethylene glycol, potassium hydroxide and waste PET, obtained from bottles of soft drinks, with particles size of 2.5x0.5 cm, without any pretreatment. It was noticed that in first term KOH quickly reacts with plastic with formation of dipotassium terephthalate (DPT) and further DPT acts as a catalyst (figure 1). It has been discovered that kinetics of the process strongly correlates with microstucture of PET. Activation energy and frequency factor was determined and they were 129,3 kJ/mole and $3{,}37 \cdot 10^{14}$ respectively.

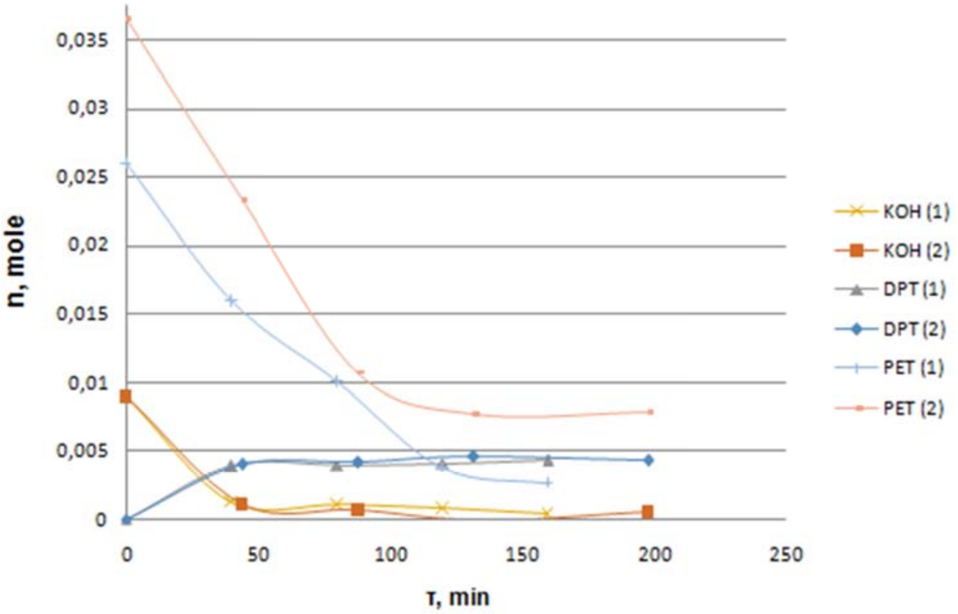

Figure 1. Dependence of KOH, DPT and PET amount during time. Reaction conditions: Temperature 185 °C; pressure 1 atm; ω(KOH) = 0,5 % wt.; EG:PET mass ratio: 1 – 20,0; 2 – 14,3

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Acknowledgments

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VP-13

THE DETERMINATION OF THE KINETIC CONSTANTS OF THE PROCESS OF THE AROMATIZATION OF THE NATURAL-GAS CONDENSATE ON THE CATALYST MFI40

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Aromatic hydrocarbons are the most important starting products in the industry of basic organic and petrochemical synthesis. They produce plastics, synthetic fibers, resins, rubbers for various purposes, dyes, surfactants and pharmaceuticals, as well as plant protection products. The most widely used light arenas are benzene, toluene and xylenes. Currently, aromatic hydrocarbons are mainly obtained by aromatization [1].

Improving energy and resource-saving indicators of petrochemical industries is not possible without a thorough study and analysis of reactor processes, as a rule, occurring in heterogeneous catalytic reactors. The solution of these problems requires simulation of chemical reactors where it is possible to take into account the influence of the main physicochemical and technological parameters of production and, above all, the influence of a specific type of catalyst [2].

Determination of the kinetic constants of chemical reaction equations is currently an urgent task, due to the variety of possibilities of experimental studies to determine them, and the new more advanced and modern instrumentation design of laboratory equipment [3].

The experience of the using model components for modeling reactor processes with a large number of chemical reactions is described in the article [4]. On the base of the experimental data and their analysis the system of reactions describing these transformations was proposed [5-6]:

1. $2C_{10}H_{22} \rightarrow 2C_9H_{18} + C_2H_6 + H_2$;
2. $C_9H_{18} \rightarrow C_6H_5CH_3 + C_2H_6 + 2H_2$;
3. $C_9H_{18} + H_2 \rightarrow C_4H_8 + C_3H_6 + C_2H_6$;
4. $2C_4H_8 \rightarrow C_6H_4(CH_3)_2 + 3H_2$;
5. $3C_3H_6 \rightarrow C_6H_3(CH_3)_3 + 3H_2$;
6. $C_7H_{14} \rightarrow C_7H_{12} + H_2$;
7. $2C_7H_{12} \rightarrow C_{10}H_{12} + 2\,C_2H_6$;
8. $2C_6H_4(CH_3)_2 + 8H_2 \rightarrow 2C_{10}H_{22} + C_3H_6 + C_3H_8$;

Values of the rate reactions are based on the analysis of experimental data and calculated as follows: $r_1 = k_1 c^2_{C_{10}H_{22}}; r_2 = k_2 c_{C_9H_{18}}; r_3 = k_3 c_{C_9H_{18}} c_{H_2}; r_4 = k_4 c^2_{C_4H_8};$

$$r_5 = k_5 c^2_{C_3H_6}; r_6 = k_6 c_{C_7H_{14}}; r_7 = k_7 c^2_{C_7H_{12}}; r_7 = k_7 c^2_{C_6H_4(CH_3)_2} c^8_{H_2};$$

c_i – concentration of i-component [mol/g. Kat];

k_j – is the conversion factor for the rate of the reaction to [mol/(g(cat) h)];

The dependence of the conversion factor of the temperature for the rate of the reaction the equation describes: $k_j = \exp(\mathrm{A}_j - \frac{\mathrm{B}_j}{\mathrm{T}})\ (\mathrm{j} = 1,2,.....8)$

A_j, B_j – kinetic constants (*j=1,2…..8*);

The task of parametric identification of the model was solved simultaneously for all the sets of experimental data in the starting material with the general criteria for minimization of the target function: $S = \sum_{u=1}^{f} \sum_{k=1}^{n_{\mathrm{fr.}}} [Y^{calc.}_{\mathrm{fr.}} - Y^{\mathrm{exp.}}_{\mathrm{fr.}}]^2;$

n_{fr} – number of the fractions; *Y*- yield of the fraction [%]

Initial values if the kinetic constants:

A_{10}=10;A_{20}=10;A_{30}=10;A_{40}=0;A_{50}=10;A_{60}=10;A_{70}=10;A_{80}=10;B_{10}=5000;B_{20}=5000; B_{30}=5000;B_{40}=5000;B_{50}=5000;B_{60}=5000;B_{70}=5000;B_{80}=5000; S=7976

The determined constants

A_1=11.72;A_2=8.07;A_3=1.27;A_4=4.47;A_5=11.37;A_6=10.43;A_7=10.91;A_8=2

B_1=4965; B_2=5039;B_3=5010;B_4=5001;B_5=5004;B_6=4983;B_7=5014;B_8=5001; S=639

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VP-14

MASS TRANSFER IN THE PROCESS OF CATALYTIC OXIDATION OF LIGNOCELLULOSES INTO VANILLIN AND PULP

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Agricultural wastes, in particular, flax shives (FS) are useful renewable lignocellulosic resources. Oxidation of lignocelluloses produces vanillin (V), syringaldehyde and cellulose. The influence of mass transfer on the yields of the listed aldehydes is almost not studied [1]. The purpose of this work is to study the influence of the mass transfer rate on the process of catalytic oxidation of flax shives into vanillin and cellulose.

Air-dred FS containing 29.5 wt. % lignin and 41.4 % cellulose was used. Prehydrolysis of the FS was carried out with hydrochloric acid at room temperature down to the mass loss of 10 %. The catalytic (CuO slurry) oxidation was carried out in a stainless steel autoclave (volume 1 l, diameter of the reactor and magnetic stirrer 94 and 60 mm respectively) at 160 °C and a partial oxygen pressure of 0.2 MPa.

The obtained dependences of oxygen consumption on time during the oxidation of the initial non-hydrolyzed FS have a stepwise and unreproducible character. These problems are more pronounced under the lower mass transfer rates in the system.

The results obtained indicate three types of diffusion limitation of the process of oxygen consumption by the components of the liquid phase. The first barrier locates at the gas-liquid interface in the form of gastight films of flax mucilage and determines the stepwise nature of the oxygen consumption curves. This type of braking is mainly overcome by the FS and flax mucilage prehydrolysis. The second type of diffusion limitation is caused by the viscosity of the liquid phase volume. The third type of diffusion limitation appears at large loads of the reaction mass and is associated with the non-Newtonian nature of suspended reaction mass at low mass transfer rate of volumes located far from the stirrer.

Oxygen consumption became more reproducible after FS prehydrolyses, and the rate and amount of consumed oxygen increases. Prehydrolysis of flax shives also led to an increase in the yield of vanillin during the oxidation (by 20-40 %). The rate of oxygen consumption increases with increasing the stirrer speed (Fig. 1A) and does not depend on the volume of the reaction mass in the range of 200-350 ml. All the obtained results show that the studied oxidation process carries out at the diffusion limitation.

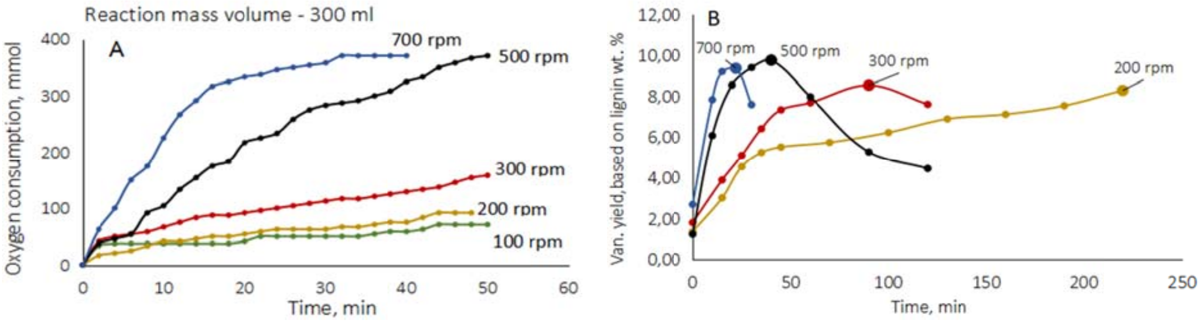

Figure 1. Influence of the stirrer speed on the kinetics of oxygen consumption (A) and vanillin accumulation (B) during the oxidation of prehydrolyzed flax shives

The relationship between the stirrer speed and the initial rate of oxygen consumption in logarithmic scales is satisfactorily fitted by a linear equation with the tangent of the line slope angle tg φ_{exp} = 1.79 ± 0.24. The similar correlation is observed between the time of attaining the maximum vanillin concentration and the stirrer speed, and it has close modulus of tangent of the slope angle tg $\varphi = -1.86 \pm 0.08$ (found from the data of Fig. 1B). The simplest model of the effect of the stirring intensity on the mass transfer rate in a gas-liquid system states that the latter is proportional to the stirring energy density in the volume of the liquid phase [2]. This model leads to a linear logarithmic dependence of the rate of oxygen consumption on the stirrer speed in a three-phase system with tg φ_{theor} = 1.85, which coincides with the experimental values of tg φ_{exp} = 1.79-1.86.

Comparison of the vanillin yield in the processes of oxidation of flax shives with nitrobenzene (NBO, 15.0 %) and molecular oxygen (12.5 %) permits the next conclusion to be made. Despite the distinctly diffusion limitation of the catalytic oxidation of the shives with oxygen, the vanillin yield in it is only 17 % lower compared to the results of NBO, and, hence, compared to the theoretical maximum selectivity of this process in the kinetically controlled process.

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VP-15

OBTAINING BIO-AVIATION KEROSENE BY HYDRODEOXYGENATION OF COCONUT OIL

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Currently, hydrodeoxygenation of vegetable oils and animal fats is one of the most popular areas for processing renewable raw materials to produce fuel fractions, such as bio-aviation kerosene and "green" diesel. This process allows you to get environmentally friendly fuels that are identical in characteristics to oil. The resulting hydrodeoxygenation products can be used both in pure form and in a mixture with petroleum products [1,2].

Production of biofuels in the industry takes place in several stages. The first of them is hydrolysis of vegetable oil or animal fat. This reaction is the hydrolysis of triglycerides to produce glycerol and fatty acids. The second stage is hydrodeoxygenation of the obtained fatty acids to form a mixture of C_8-C_{18} hydrocarbons [3,4].

The purpose of this work is to study the process of hydrodeoxygenation of coconut oil using a Pd/Cact catalyst in the presence of hydrogen. The result is a hydrocarbon fraction that corresponds to the hydrocarbon composition of the kerosene fraction. The process consisted of two stages: hydrolysis of vegetable oils with the release of a fraction of fatty acids; hydrodeoxygenation of the resulting fatty acids to produce hydrocarbons corresponding in composition to bio-aviation kerosene.

The hydrolysis reaction was carried out in a mixing reactor at a pressure of 20-30 atm and a temperature of 200-250 °C in the presence of fatty acids for 2-4 hours at a mass ratio of coconut oil : water = 1 : 1 - 20. As a result, the conversion rate of triglycerides is complete, and the yield of fatty acids is 55-80%.

Next, the process of hydrodeoxygenation of the obtained fatty acids is investigated. The reaction of deoxygenation derived fatty acids is carried out in a mixing reactor at a pressure of 12 ATM and a temperature of 300-350 °C in the presence of a catalyst Pd/Cact in the amount of 2-4 % by weight of the total weight of the reactants, the mass ratio of fatty acid : tsetan = 3 : 7, for 3-6 h. the catalyst is activated in flowing hydrogen for 1 hour at 300 °C. As a result, the degree of conversion of fatty acid 30-33 %, while the output fraction biokerosene is 42 %.

Further research is aimed at finding catalytic systems of the hydrodeoxygenation stage that allow increasing the yield of the kerosene fraction, as well as eliminating expensive catalysts based on precious metals.

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