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CRS-2

CATALYSIS FOR RENEWABLE SOURCES: FUEL, ENERGY, CHEMICALS

Lund, Sweden,
July 22-28, 2013

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Lund University, Sweden

Second International Conference

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ABSTRACTS

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Сборник включает тезисы пленарных лекций и устных докладов секций:

- **Section I.** *Catalytic processes for valuables production from biomass;*
- **Section II.** *Catalytic processes for biofuel production;*
- **Section III.** *Catalyst application for clean syn-gas and clean hydrogen production;*
- **Section IV.** *Catalytic Processes in Oleochemistry;*
- **Section V.** *Catalytic approaches for the processing of pyrolysis biomass products.*

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PLENARY LECTURES

USAGE OF BIOFUELS IN SWEDEN

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In Sweden, biofuels have come into substantial use, in an extent that are claimed to be bigger than use of fossil oil. One driving force for this have been the CO_2-tax that was introduced in 1991 (1). According to SVEBIO:s calculations (2) based on the Swedish Energy Agency´s prognosis, the total energy consumption in Sweden 2012 was 404 TWh. If the figure is broken down on the different energy sources (figure 1) one can see that the consumption roughly distribute in three different, equally sized, blocks, Biofuels, fossil fuels and water & nuclear power.

The major use of the fossil fuels is for transport and the water & nuclear power is used as electric power. The main use of the biofuels is for heating in the industrial sector and as district heating. In 2009 the consumption from those two segments was 85 TWh, and 10 TWh of bio power was co-produced giving an average biomass to electricity efficiency of 12%. This indicates a substantial conversion potential from hot water production to combined heat and power (CHP) production.

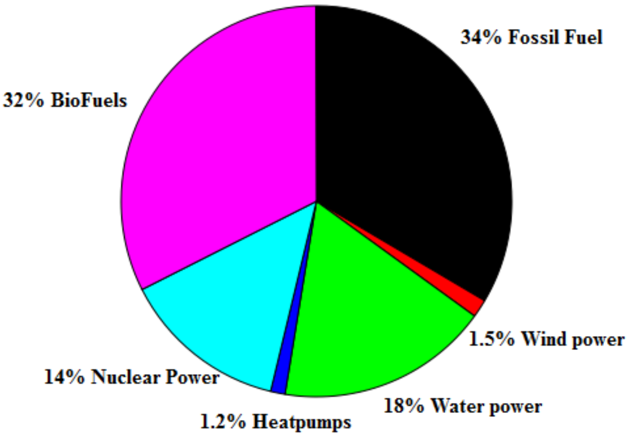

Figure 1. The total energy consumption, 404 TWh, in Sweden 2013 broken down on the different energy sources.

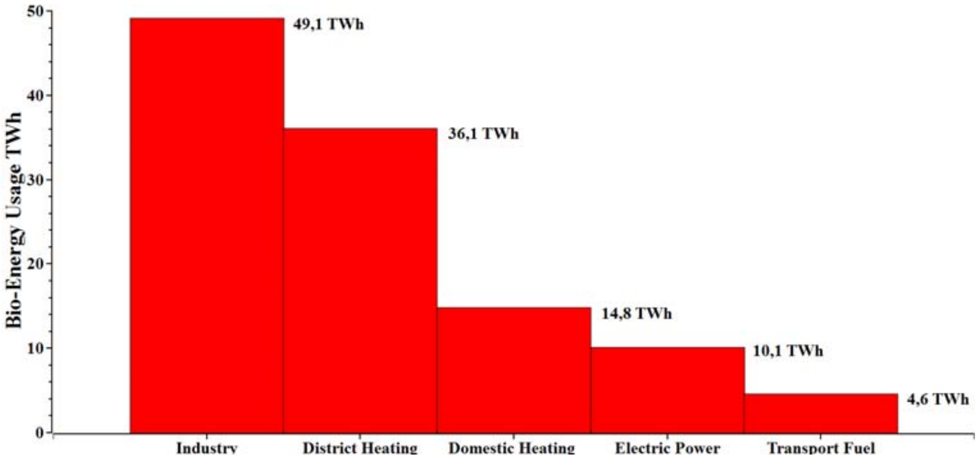

Figure 2. The bioenergy uses in Sweden 2009 (4).

In 2006 the pulp, paper and sawmill industry accounted for 95% of the bio energy consumption in the industrial sector, and the major biofuel consumed was black liquor (5). However, the pulp and paper industries also produced the black liquor in their own processes.

The major energy source (58%) for district heating during 2006 was woody biomass (chips, pellets etc.) followed by waste (24%), peat (6%) and others (12%) (5). The use of peat has probably decreased since 2006 since peat is no longer regarded as a renewable energy source.

While the use of biofuel for heating purpose is well developed and the bio-power is expected to grow, the use in the transport sector is small, 9 TWh or 7% in 2011. The main consumption there is due to the mandatory addition (5%) of ethanol to gasoline and FAME to diesel (6). The Swedish authorities have announced plans to increase the renewable content to 7.5 % in 2015 on the way to fulfill the EU's goal of 10 % renewable transportation fuels in 2020. However the new proposed fuel directive in EU says that a maximum of 5% renewable fuel may be produced from food sources like sugars and vegetable oils. Another bothersome fact is that, in principle, all rape seed oil produced in Sweden is consumed (95-97%) in the food sector, and consequently all FAME used (in principle) in Sweden is imported as FAME, rape seed oil or seed (6).

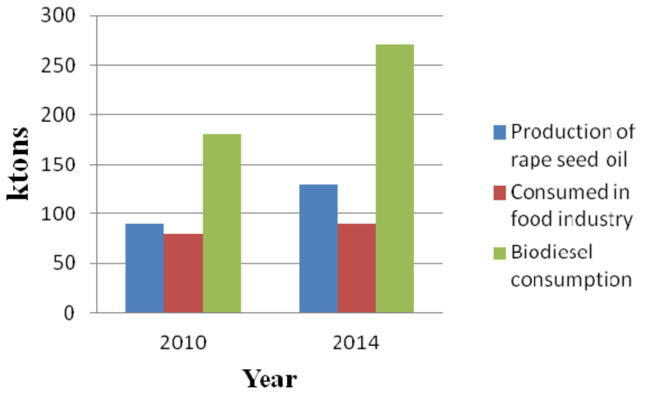

Figure 3. Production and consumption of rape seed oil in Sweden for 2010 and a prognosis for 2014. (6).

In Sweden a new source of biodiesel have emerged, tall oil diesel. Tall oil is extracted from black liquor and refined into a diesel fraction (not FAME) and can be mixed into fossil diesel, i.e. Preem Evolution diesel. The SUNPINE plant in Piteå have a capacity of 100 000 metric tons of tall oil diesel per annum, while the total potential in all of Sweden is claimed to be 200 000 tons (7). 100 000 tons of tall oil corresponds to 1% of the total diesel consumption in Sweden.

Accordingly, the profoundest task is to decrease the fossil fuel dependency in the transport sector, and clearly, the first generation biofuels can´t do this on its own. Biogas is a fuel gas with high methane content that can be used in a similar way to natural gas; for instance for cooking, heating and as transportation fuel. Today biogas is produced by fermentation of waste (municipal waste, sludge, manure), but can be produced by gasification of biomass, for instance from forest residues such as branches and rots (GROT in Swedish). To get high efficiency in the production, the lower hydrocarbons, mainly methane, in the producer gas, should not be converted into synthesis gas. Instead a synthesis gas with high methane content is sought. This limits the drainage of chemically bonded energy, due to the exothermic reaction in the synthesis step (so called methanisation). In 2011 0.7 TWh of biogas was produced in Sweden by fermentation of waste (6) and there were no production by gasification, at least not of economic importance. The potential seems to be large, though. In 2008 the total potential for biogas production, in Sweden, from waste by fermentation and gasification was estimated to 70 TWh (10 TWh fermentation and 60 TWh gasification) (8). This figure includes only different types of waste and no dedicated agricultural crops or dedicated forest harvest.

Activities in the biogas sector, by gasification, in Sweden are the Göteborgs energi´s Gobigas project in Gothenburg and Eon´s Bio2G-project, now pending, in south of Sweden.

If the producer gas is cleaned and upgraded into synthesis gas also other fuels could be produced. In Sweden methanol and DME productions are planned for in the Värmlands metanol-project and at Chemrecs DME production plant in Piteå.

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PL-2

RENEWABLE ENERGY, WTF TECHNOLOGIES, NEW PROCESSESES AND NEW CHALLENGES

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The analysis of the scalled industrial processes for fuels production from renewable raw materials is made. The limiting steps of fuel alcohols, biogas, syngas, biooils production technologies are identified and discussed.

Three main factors, economy – ecology and raw material resources are the basis of the general potential of fuel technology development. For Russia, having the competition inside the state with the well established traditional energetics, the only resource for biofuel development is the conversion of organic wastes. The annual volume of concentrated wastes for fuel production was estimated as 500 mln tonn.

The discussion of waste to fuel (WTF) technologies is the subject of presentation. WTF technologies solve the problems of energy production and ecology.

Modern approaches are based on combination of chemical and biotechnological methods. New solution for ethanol, butanol synthesis from biomass are demonstrated. Ketals and esters from the organic wastes were studied as car fuels. The basis of pyrolitic processes with conversion of polymers and biomass into biooil and synoil is analysed.

The new challenge for fuel industry is the rapid development of electricity production, accumulation and storage methods and the creation of the new types of electric cars on the basis of these methods.

The general tendencies of fuel/electricity competition are analyzed. The new methods for conversion of biomass and waste energy into electricity are described. The rocket engine is the new type of chemical reactor and the application of rocket technology (jetel-technology) for solution of this problem is demonstrated. The advantages and limitations of jetel-technology are discussed in details.

APPLICATION OF THE PRINCIPLES OF CHEMICAL REACTION ENGINEERING ON THE LOW-TEMPERATURE TRANSFORMATION OF BIOMASS

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Keywords: biomass, polyfunctional molecules, reaction, diffusion, reactor modelling

The global tendency towards the use of renewable sources is a big challenge not only for conceptual chemical technology, but to chemical engineering, too. We are shifting from relatively simple molecular structures appearing in crude oil and natural gas to the very complex ones in biomass. Molecules originating from biomass are, typically polyfunctional macromolecules. On the other hand, biomass is a well-organized entity, consisting mainly of cellulose, hemicelluloses and lignin.

Figure 1 shows the two-platform concept of a biorefinery system for the production of sugars and/or syngas and pyrolysis oils as platform chemicals for bio-based products and fuels. The sugar platform is based on bio-chemical conversion processes of biomass to sugar feedstocks, while the syngas, pyrolysis platform is based on thermo-chemical conversion processes of biomass to synthesis gas or pyrolysis oils for chemicals, materials and fuels.

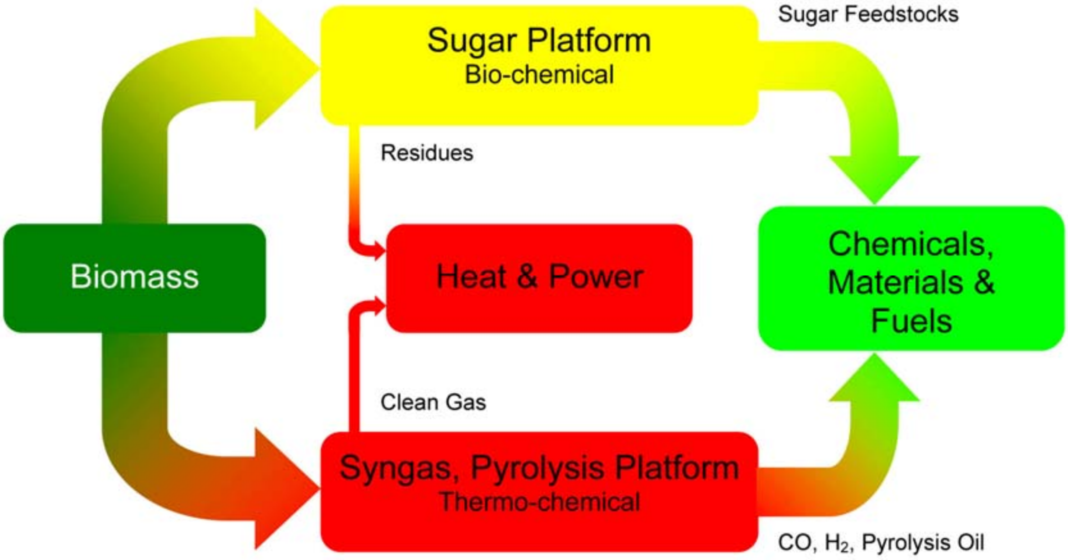

Figure 1. The two platform integrated biorefinery system for bio-based chemicals, materials and fuels

There are still several problems to be solved to make the mild-temperature sugar platform working in practise. One of the key issues is the catalyst development. In order to obtain platform chemicals from cellulose and hemicellulose, the glycosidic bonds should be broken by hydrolysis. Several catalysts have been proposed, such as homogeneous mineral and organic acids, heterogenized acid catalysts on carbon support, cation exchange resins as well as enzymes. The hydrolysis kinetics in the presence of several catalysts will be presented in the plenary lecture, along with kinetic modelling of autocatalytic phenomena appearing in the hydrolysis of polysaccharides.

From the mild-temperature hydrolysis process, valuable monomeric sugars are obtained: besides glucose, polyfunctional molecules, such as arabinose, galactose, mannose and xylose are obtained. These molecules can be used as such, or refined further, e.g. by hydrogenation, oxidation and isomerization. The process intensification approach starts with catalyst selection and optimization, kinetic studies, investigation of physical properties as well as mass and heat transfer phenomena. In general, it can be stated that the interaction of chemical reaction kinetics and internal mass transfer effects in the pores of solid catalysts plays a crucial role in the transformation of molecules from biomass. In many cases, catalyst deactivation interferes with kinetic and mass transfer phenomena.

In the transformation of molecules from biomass, conventional reactor technologies, such as semibatch slurry reactors and continuous fixed beds suffer from serious disadvantages. Continuous operation is difficult to apply to slurry reactors, and relatively large catalyst particles have to be used in fixed beds, which lead to a considerable internal mass transfer resistance, implying a low catalyst effectiveness factor. Structured solid catalyst elements, such as monoliths, fibres and solid foams provide a solution to this dilemma (Figure 2): a thin and effective catalyst layer is combined with a low pressure drop in the reactor. Several examples of the application of continuous structured reactors on the transformation of sugars to value-added molecules are shown in the plenary lecture. The approach covers all possible aspects: from the optimization of catalyst nanoparticles to the design of structured elements, kinetic and mass transfer studies, mathematical modelling of individual catalyst particles and continuous reactors. A general research strategy will be presented: from reaction kinetics to reactor design.

Figure 2. Carbon washcoated steel impregnated with ruthenium are used as structured catalyst materials for sugar hydrogenation

PL-4

FROM BIOMASS TO ADVANCED BIOFUELS: ALTERNATIVES TO BIODIESEL AND BIOETHANOL VIA CATALYTIC CONVERSION

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Concerns about diminishing fossil fuel reserves along with increasing levels of CO_2 in the atmosphere are driving society toward the search for new renewable sources of energy. Among them, biomass has the potential to significantly displace petroleum in the production of fuels. In this sense, bioethanol and biodiesel (e.g, conventional biofuels), produced by simple and well-known transesterification and fermentation technologies, are currently being utilized as diesel and gasoline replacements in the transportation sector. However, the different chemical composition of these oxygenated biofuels compared to those currently used in cars, trucks and jets (e.g. liquid hydrocarbon fuels) is creating serious compatibility issues limiting their penetration in the market. There are thus strong incentives for the development of new technologies able to transform biomass into high energy density, infrastructure-compatible fuels (e.g., advanced biofuels). In the past few years, these strong incentives have favored a dramatic change in funding directions from projects involving biodiesel and bioethanol to those aimed to the synthesis of advanced biofuels.

Heterogeneous catalysis, crucial for the petrochemical industry, is also expected to have a relevant role in biomass conversion, especially in the production of advanced biofuels. However, biomass composition obligates to design new and more challenging routes and impose new requirements to the catalytic materials. The present talk is aimed to provide an overview of the most relevant catalytic approaches leading to conversion of biomass into advanced biofuels such as higher alcohols and liquid hydrocarbons, with particular emphasis on aqueous-phase conversion of biomass platform molecules.

PL-5

STRUCTURED NANOCOMPOSITE CATALYSTS OF BIOFUELS TRANSFORMATION INTO SYNGAS AND HYDROGEN: DESIGN AND PERFORMANCE

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Design of efficient, inexpensive and stable to coking catalysts for transformation of natural gas/biogas/biofuels into syngas and hydrogen in the intermediate temperature range (600-800 °C) is a vital problem of sustainable and renewable energy field including hydrogen production, synfuels synthesis, internal reforming in solid oxide fuel cells etc. Promising approaches are based upon design of nanocomposite active components comprised of nanoparticles of metals (provide activation of C–H and C–C bonds in fuel molecules) fixed on the surface of complex perovskite-like or fluorite-like oxides with a high lattice oxygen mobility and reactivity. Monolithic substrates with a good thermal conductivity and corrosion stability are required for providing an efficient heat transfer within the reactor to prevent emergence of hot spots/cool zones deteriorating performance.

This work reviews results of extensive research aimed at design and characterization of such structured catalysts performance in transformation of a variety of biofuels (ethanol, acetone, ethyl acetate, anisole, glycerol, sunflower oil) [1-3]. Next basic problems are considered:

1. Effect of the metal/alloy nanoparticles (Ni, Co, Ni+Pt, Ni+Ru, etc) composition and genesis, composition of complex perovskite-like or fluorite-like oxides and metal-support interaction on the rates and routes of biofuel molecules transformation, oxygen mobility and coking stability;
2. Design of structured catalysts by supporting optimized active components on heat-conducting substrates (Ni-Al foams, Fe-Cr-alloy corrugated foils, gauzes and microchannel platelets, microchannel cermets);
3. Specificity of structured catalysts performance in pilot-scale reactors operating on real concentrated feeds.

Optimized nanocomposite active components of structured catalysts provide a high yield of hydrogen (H_2 content up to 50%) in the IT range both in steam and autothermal reforming of biofuels at short contact times, main by-product being CH_4

due to cracking. O_2 addition to the feed decreases C_2H_4 content, thus suppressing coking, stable performance was confirmed for more than 100 h time-on-stream. For glycerol and sunflower oil as fuels, stable performance was achieved only in the autothermal reforming mode with O_2 addition to the feed. Comparable performance was obtained using as substrates Ni–Al foam or Fe–Cr–alloy foil, gauze and microchannel platelets with protective corundum layers. At a proper fuel evaporation and mixing using unique electric current-heated monolithic unit along with optimized feed composition, no coking was observed even for sunflower oil as a fuel. No spallation or cracking of the active components on metallic substrates was revealed.

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PL-6

CATALYSIS IN BIOMASS VALORIZATION: EXAMPLES IN OLEOCHEMISTRY AND CELLULOSE CONVERSION

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The production of chemical supplies from renewable sources for industrial applications is one of major challenges of this century, and involves concepts of green chemistry and sustainability.[1,2] Many attempts have been then made to partially or totally replace non-renewable sources of feedstocks, and productos from oleochemistry and lignocellulosic biomasses may play an important role in this effort.

Sn(IV) complexes were initially tested as catalysts for esterification and transesterification reaction of fatty acids in the presence of methanol as alcoholysis agent. Parameters like reaction time, temperature, and catalyst amount were systematically evaluated in this work. All complexes were active at relative high reaction temperatures. These results prompted us to test BTA catalyst also in simultaneous esterification/transesterification reactions from a mixture of free fatty acids (FFAs) and TAGs in the presence of methanol. The results obtained and discussed in this work can help the development of new catalytic systems to biodiesel production from oils with very high acid content[3,4].

A systematic study of the dissolution and conversion of cellulose in the presence of Sn(IV) complexes under several reaction conditions was conducted to evaluate their potential as catalysts[5]. Results were compared with those obtained from non-catalyzed reactions, and from reactions using H_2SO_4 as catalyst. Sn(IV) catalysts are able to convert cellulose into valuable chemicals with interesting yield and selectivity, without the problems associated with the use of inorganic acids in these processes.

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BIOFUELS AND BIOBASED CHEMICALS: THE QUEST FOR EFFICIENT CATALYSTS

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

The first part of the presentation will deal with the conversion of hydroxymethylfurfural (HMF) to 1,6-hexanediol, and important bulk chemical for the plastics industry. A highly efficient two step route was developed using bimetallic Rh-Re catalyst giving 1,6-hexanediol in 85% yield. Catalytic performance and the effect of process conditions on product yields will be discussed.

Many sugar conversions to platformchemicals like HMF and levulinic acid, particularly in aqueous media, suffer from the formation of solid materials, known as humins. These negatively affect product yields and complicate product work-up, thus lowering the economic potential. An in-depth study on the characterization of humins from various sugar sources was performed to gain insights in molecular structure and formation pathways. A structural proposal will be provided and in addition, results on the valorization of the humins using fast pyrolysis technology will be given.

Finally, recent findings on the chemo-catalytic conversion of sugars and glycerol to lactic acid will be reported. Screening studies on the use of Lewis acids for the conversion C6 and C3 sugars to lactic acid will be provided, and it will be shown that 90% yields of lactic acid is attainable under optimized conditions using certain C3 sugars. Bimetallic Pt/Au catalysts on nanoceria were shown to be particularly good catalysts for the one pot oxidation of glycerol to lactic acid in high yields (> 80%).

KEY-NOTE LECTURES

SELECTIVE CATALYSTS FOR GLYCEROL DEHYDRATION

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There has been an increased interest over the last decade for replacing fossil based feedstocks with renewable ones. There are several such feedstocks that are currently being investigated such as cellulose, lignin, hemicellulose, triglycerides etc. However, when trying to perform selective reactions an as homogeneous feedstock as possible is preferable. One such feedstock example is glycerol, a side-product from biofuels production, which is a tri-alcohol and thus has much flexibility for reactions, e.g. dehydration, hydrogenation, addition reactions etc. Glycerol in itself is a good starting point for fine chemicals production being non-toxic and available in rather large quantities [1-2]. A key reaction for glycerol valorisation is the dehydration of glycerol to form acrolein, an unsaturated C_3 aldehyde, which may be used for producing acrylic acid, acrylonitrile and other important chemcial products.

It has recently been shown that pore-condensation of glycerol is an issue under industrial like conditions, leading to liquid-phase reactions and speeding up the catalyst activity and selectivity loss [3]. To address this issue, modified catalyst materials have been prepared where the relevant micro and meso pores have been removed by thermal sintering; calculations have shown that pores below 45 Å may be subject to pore condensation. The catalyst starting material was a 10% WO_3 by weight supported on ZrO_2 in the form of beads 1–2 mm and it was thermally treated at 400°C, 500°C, 600°C, 700°C, 700°C, 800°C, 850°C, 900°C and 1000°C for 2 hours. The catalysts were characterised using nitrogen adsorption, mercury intrusion porosimetry (MIP), Raman spectroscopy and ammonia temperature programmed desorption.

The thermal sintered catalysts show first of all a decreasing BET surface area with sintering commencing between 700°C and 800°C when it decreases from the initial 71 m^2/g to 62 m^2/g and at 1000°C there is a mere 5 m^2/g of surface area left. During sintering, the micro and meso porosity is reduced as evidenced by MIP and depicted in figure 1.

KN-1

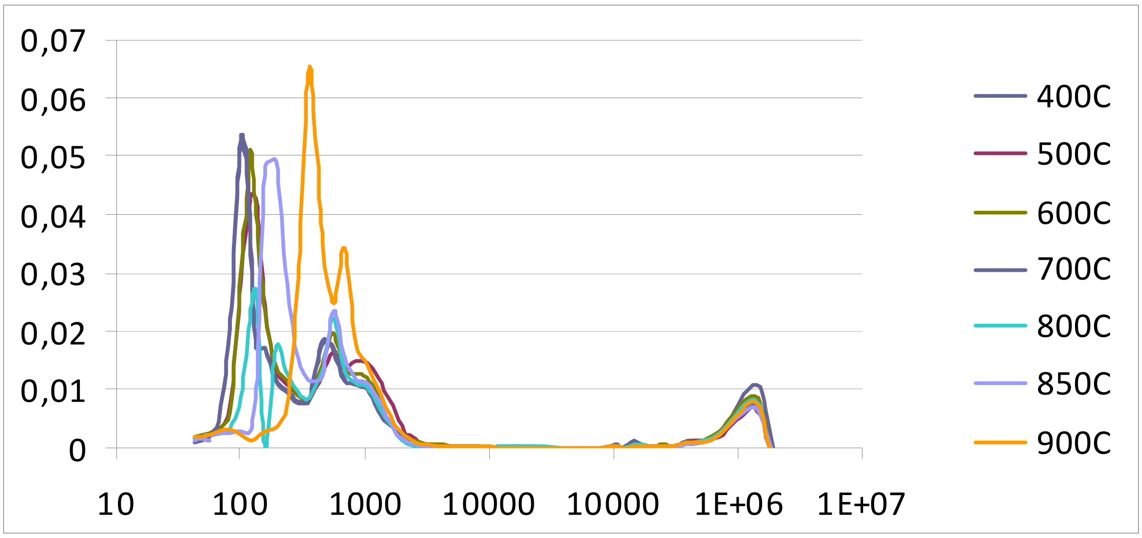

Figure 1 Incremental pore volume measured by MIP as a function of pore diameter (Å).

As may be seen in the figure, sintering decrease the amount of pores below and around 100 Å is reduced at a sintering temperature of 800°C and above. The most suitable catalyst based on the MIP appears to be the one sintered at 850°C which is further strengthened by the Raman analysis. There is a clear shift in the tungsten structure from monoclinic to triclinic between 850°C and 900°C and it is believed that the monoclinic phase is important for activity and selectivity. Further, the heat treatment shows that there is an increase in catalyst acidity measured as mmol $NH_3/(m^2/g)$ but a decrease in the acid strength as evidenced by a decrease in the desorption peak maximum temperature.

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SIMULTANEOUS CONVERSION OF TRIACYLGLYCERIDES AND FATTY ACIDS INTO FATTY ACID METHYL ESTERS USING ORGANOMETALLIC CATALYSTS

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The catalytic transesterification of TGAs in the presence of a short chain alcohol, such as methanol or ethanol, leads to biodiesel (a mixture of alkyl monoesters, FAMEs or FAEEs) and glycerol as the final products.[1] Several vegetable oils can be employed as source to obtain biodiesel. One of the main factors affecting their cost of production is the high price of this raw material.[2] Therefore, the use of low-cost feedstocks such as non-edible oil or waste cooking oil should improve the economic feasibility of biodiesel production.[3] However, these low-cost sources have high free fatty acid (FFA) content and in this case, at least, an esterification step must be employed.

Recent studies have shown that species based on complexes exhibiting Lewis acid sites present promising results in both esterification, transesterification and simultaneous processes.[4,5,6]

There are some examples of the use of tin(IV)-based homogeneous or heterogeneous catalytic systems in transesterification reactions.[7,8,9] However, as far as we are aware, no information is available about the performance of this class of catalysts face to esterification or simultaneous esterification and transesterification reactions. In this context, we carried out a systematic study on esterification, transesterification and simultaneous esterification/transesterification reactions in the presence of methanol, using tin(IV) compounds as catalysts (Fig. 1).

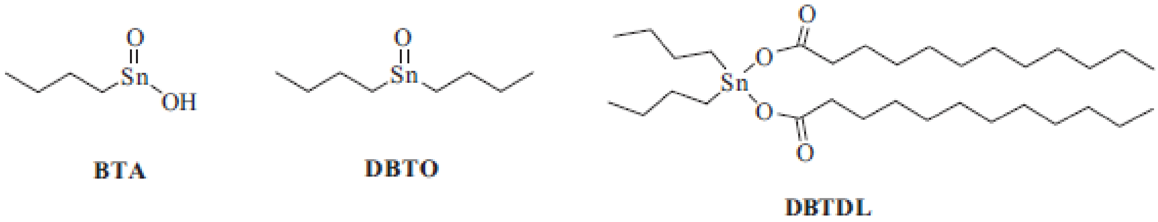

Fig. 1. Molecular structure of catalytic complexes.

KN-2

All complexes has been active on (trans)esterification highlighting **BTA**. Some of the results are presented on Table 1.

Table 1. Yields in terms of FAMEs after methanolysis of soybean FFAs, TAG and their mixtures, using BTA as catalyst, and temperature of 160 °C.

Reaction time (h)	Trasesterification	Mixture (FFA:TGA, wt%)			Esterification
	(0:100)	30:70	50:50	70:30	(100:0)
1	52	61	71	91	89
2	59	69	85	92	91
3	67	90	91	93	93
4	–	93	–	95	–

These results open new option of catalytic systems for biodiesel production that can be very suitable for esterification, transesterification, and simultaneous esterification/transesterification reactions. BTA is a surprisingly flexible catalyst to be used on oil sources (with low or high free fatty acid content), for example, palm oils, recycled oils, and animal fats can be a alternative to the development of new biodiesel production processes.

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Acknowledgements

CAPES, FINEP, CNPq, FINEP, FAPEAL, INCT-Catálise.

CATALYTIC PRODUCTION OF OXYGENATED ADDITIVES BY GLYCEROL ETHERIFICATION

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The growing production of biofuels by transesterification of vegetable oils imposes the development of efficient processes to convert glycerol to added-value products to validate the eco-sustainability of the global process [1]. Among different approaches proposed, the possibility to produce oxygenated additives to be used in blend with conventional diesel fuel has received a particular attention due to the benefits obtainable both in terms of global CO_2 emission containment and the abatement of particulate matter of diesel engine [2-3]. In particular, glycerol derived ethers has been recently considered as potential additives of diesel fuel since they are characterized by compatible physical-chemical properties in terms of flash point, viscosity, cetane number, etc. [4]. However, the mono-ethers of glycerol, due to their low solubility in diesel fuel, are not adequate, therefore the reaction must be shifted towards the formation of poly-substituted ethers [5].

Glycerol derived ethers can be obtained by etherification reaction over acid catalysts using isobutylene or tert-butyl alcohol as reactants. Recently, different solid catalysts [6-7] have been proposed to efficiently convert glycerol to poly-substituted ethers, but up to now the development of an efficient system is prevented by a number of catalytic and technological problems which need to be overcome.

Therefore, this paper aims at exploring the feasibility of an efficient process based on glycerol etherification reaction, using different reactants and catalysts, highlighting the catalytic limitations already encountered. A critical evaluation of the main factors affecting the catalytic reaction will be done with the aim to drive the research towards the design of both an appropriate catalyst and an efficient catalytic process.

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KN-4

HETEROGENEOUS CATALYSIS METHODS FOR LIGNIN VALORIZATION INTO CHEMICALS AND ACTIVE CARBONS

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Lignin is a main polymeric component of lignocellulosic biomass (15–30 % by weight). However, lignin has received a little attention then cellulose with regards to its valorization. Lignins of coniferous wood, deciduous wood and annual plant have the different composition. Besides, their composition and structure depend on method of lignin extraction from lignocellulosic biomass. These aspects should be taken into account in strategies of lignin catalytic conversions. This presentation focuses on reviewing the results obtained by authors in the field of lignin valorization into chemical and active carbons with the use of heterogeneous catalysis methods.

Wood lignin oxidative depolymerization over TiO_2 catalyst

TiO_2 catalysts can accelerate the decomposition of H_2O_2 resulting in the formation of $^{\bullet}OH$ radicals. They can diffuse into the liquid reaction medium to wood particles and to execute the oxidative destruction of lignin. The yield and composition of delignification products were controlled by variation of catalyst content, the wood nature, delignification conditions. The increase of temperature, concentration of H_2O_2 and CH_3COOH, liquor ratio and time results in the acceleration of a rate of delignification process and simultaneously reduces the cellulose yield. Based on kinetic studies the optimal conditions of lignin complete depolymerization were selected (100 °C and atmospheric pressure). They allow to obtain the pure cellulose with an yield near 45 % mas.

Lignin characterization

Lignins obtained by oxidative delignification of wood are amorphous fine powders which colour varies from light brown to dark brown. They have melting point 175–180 °C and low solubility in water and organic solvents. Their yields from the initial wood material are near 9.0–9.5 % wt. FTIR and NMR^{1}H data confirm the saving of a main part of phenylpropane structural units in studied lignins and the presence of high concentration of oxygen-containing groups (mainly carboxylic and cabonilic).

DTA-DSC studies of lignins extracted from aspen and birch wood showed that their thermal conversion includes two steps. First one corresponds a temperature range

160–480 °C and 160–360 °C, the second – 480–700 °C and 360–520 °C for aspen lignin and birch lignin, respectively. Thermal destruction of abies lignin includes only one step at 180–520 °C.

Lignin catalytic carbonization

Two ways of lignin thermal conversion to active carbons were used. One of them included oxidative carbonization of powdered lignin in a fluidized bed of Al-Cu-Cr oxide catalyst, the another – pyrolysis–activation of lignin impregnated by $Cu(Ac)_2$. The advantages of lignin carbonization in catalytic fluidized bed are the high productivity, the increased yield of char and the low level of harmful compounds in the gaseous products of lignin pyrolysis. The combination of the stages of catalytic carbonization and steam activation allows production of good-quality carbon sorbents (porosity up to 2.9 cm^3/g, surface area 750–800 m^2/g) with the yield of 15–19 % wt.

The promising way for carbon catalysts preparation includes the introduction of a metal compound into biomass with following carbonization. Some features of thermochemical transformation of lignin, modified by copper acetate and lignin mixture with oil slimes were studied by FTIR, DTA, XRD, BET and functional analysis. It was established that the interaction of copper acetate with the oxygen-containing lignin functional groups, leads to forming copper carboxylates and copper phenolates as well as to changing the lignin structure and reactivity.

As a result of the accomplished study, the optimal conditions of Cu-modified lignin and its mixtures with the oil slime providing the obtaining the active carbons with yield the 18–19 % wt. and the specific surface area near 600 m^2/g were selected.

Lignin liquefaction in spirits over oxide and zeolite catalysts

The high yield of liquids (up to 40-45 % wt.) was obtained by hydrolytic lignin liquefaction with methanol at 410 °C, 25 MPa in the presence of Fe-Zn-Cr catalyst supported on lignin. Catalyst increases the yield of liquid products up to 5-10 times. The obtained liquids have a low content of oxygen – 6–10 %.

The influence of sulfated ZrO_2 and ZrO_2–Al_2O_3 and zeolite catalysts with different silicate module on lignin conversion in ethanol and on the composition of obtained products was studied. Sulfated ZrO_2-containing catalysts incease by 1.4–1.5 times the degree of lignin conversion and the yield of ethanol-soluble fraction with b.p. higher 180 °C. All catalysts promote the formation of 1,1-diethoxyethane – promising additive for motor fuels. Its content in ethanol soluble fraction with b.p. > 180 reaches 67–90 %. Studied catalysts also decrease significantly the concentration of phenol and benzol derivatives in this fraction as compared to non-catalytic process.

KN-5

NEW GENETIC INSIGHTS TO CONSIDER COFFEE WASTE AS A FEEDSTOCK FOR FUEL, FEED AND CHEMICALS

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Research in my laboratory has focused on the microbial degradation of purine alkaloids (1-6). Prominent members of this class of natural products are caffeine and theobromine. Caffeine is biosynthesized by many plants as a defense chemical. Caffeine is also a popular component of many drinks ranging from coffee & tea to many soft and energy drinks. Thus, it is not surprising that caffeine reaches soil and other environments by various routes. Given caffeine's prominence presence in the environment, microorganisms have evolved mechanisms to “live” on caffeine.

Two different pathways of microbial degradation of caffeine and theophylline have been elucidated. Novel enzymes (and genes) are involved in the catabolism of caffeine. The entire genetic map of N-demethylation pathway of caffeine has been discovered in *Pseudomonas putida* CBB5 (1-4). The genetic map of an alternate pathway for caffeine degradation via C-8 oxidation has also been established (5,6). The genes and enzymes involved in caffeine degradation are of value in terms of:

(a). Decaffeinating spent coffee and tea extracts so that the left over solids can be used as feedstock for ethanol or as animal feed.

(b). Producing fine chemicals such as dimethyl xanthines and monomethyl xantines from cheap feedstock such as caffeine and theobromine.

(c). Converting coffee waste to garden soil.

(d). Biological decaffeination of coffee and tea, and

(e). Development of a diagnostic test for rapid caffeine detection in nursing mother's milk (a).

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ORAL PRESENTATIONS

SECTION I

Catalytic processes for valuables production from biomass

OP-I-1

ISOMERIZATION OF TERPENE OXIDES TO VALUABLE CHEMICALS OVER METAL MODIFIED ZEOLITES AND MESOPOROUS MATERIALS

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Terpenes are cheap renewable raw materials produced as by-products in kraft pulping. They can be transformed with percarboxylic acid to corresponding epoxides. Several unsaturated aldehydes and alcohols, which have applications in pharmaceuticals, flavors and parfumes, are produced via isomerization of terpene oxides over homogeneous, environmentally less benign catalysts [1]. Various heterogeneous catalysts, such as metal modified zeolites, heteropolyacids, binary oxides and molecular imprinted polymers have also been applied as catalysts. The aim of this work was to synthesize, characterize and test several metal modified zeolites, mesoporous materials and CeO_2-MCM-41 composite materials as catalysts for isomerization of α-pinene oxide (APO), β-pinene oxide (BPO) and verbenol oxide (VO) (Fig. 1a). The challenge was in achieving high selectivity to the desired product. The target compounds starting from APO, BPO and VO are campholenic aldehyde (CA) or trans-carveol, myrtanal and (*1R,2R,6S*)-3-methyl-6-(prop-1-en-2-yl)cyclohex-3-ene-1,2-diol, respectively. The latter product is a potent anti-Parkinson drug [2].

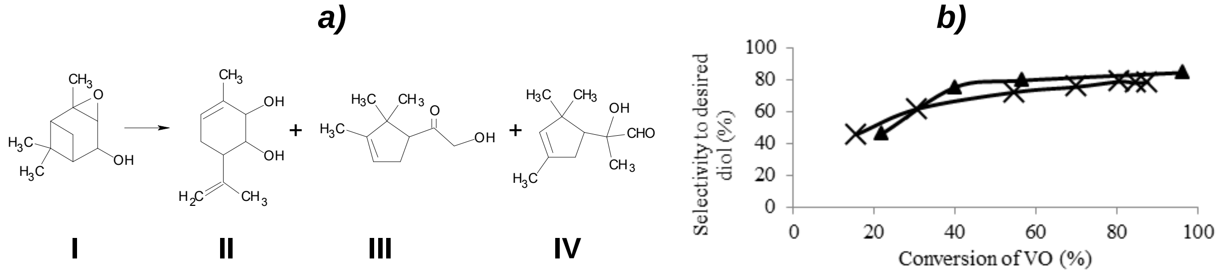

Fig. 1. a) Reaction scheme for isomerization of (I) verbenol oxide to (II) (*1R,2R,6S*)-3-methyl-6-(prop-1-en-2-yl)cyclohex-3-ene-1,2-diol, (III) 1-(2,2,3-trimethylcyclopent-3-enyl)-2-hydroxyethanone and (IV) 2-(2,2,4-trimethylcyclopent-3-enyl)-2-hydroxy-propanal and b) selectivity to diol (II) at 140°C in N,N-dimethylacetamide over Fe-Beta-300 (▲) and Ce-Si-MCM-41 (x).

Several microporous (Y, Beta, ZSM-5, ZSM-12, MOR) and mesoporous materials (SBA-15, H-MCM-41) and CeO_2-H-MCM-41 composite material were synthesized. Sn or Fe were introduced either by conventional or solid state ion exchange methods. The catalysts were characterized by the following physico-chemical methods: Nitrogen physisoprtion, XRD, pyridine adsorption, EXAFS-XANES, XPS. The isomerization experiments were typically carried out using the initial reactant concentration of 0.013-0.02 mol/l, 0.075 g of the predried catalyst in a batch reactor. A number of solvents, such as toluene, N,N-dimethylacetamide (DMA), N-methyl-2-pyrrolidone (NMP), 2-pentanol, acetonitrile were applied. Catalyst particle sizes below 90 μm and high stirring rates were used to perform the experiments in the kinetic regime. In addition to fresh catalysts, also reuse of a few selected catalysts was successfully demonstrated and the nitrogen adsorption measurements and thermogravimetric analyses of the spent catalysts were performed. The samples were analyzed with GC and confirmed with GC-MS.

After extensive catalyst screening experiments the best catalysts and reaction conditions were found for the synthesis of CA, trans-carveol, myrtanal and (*1R,2R,6S*)-3-methyl-6-(prop-1-en-2-yl)cyclohex-3-ene-1,2-diol. The most promising catalyst for formation of CA with the selectivity of 64% at 100% conversion was Fe-Y, which exhibited relatively large pores and contained both strong Brρnsted and Lewis acid sites. The main part of Fe was in the form of Fe^{2+}. For isomerization of BPO, the highest myrtanal selectivity (64%) at 72% conversion in toluene at 70°C was achieved with Sn-Beta-300 (the number denotes SiO_2 to Al_2O_3 ratio), which exhibited mild acidity and high amount of Sn^{2+} sites. The best selectivities, 45% at complete conversion for trans-carveol were obtained in NMP at 140°C over 20 wt% Ce-Si-MCM-41. In the isomerization of verbenol oxide the most selective catalyst was the mildly acidic Fe-Beta-300. The best results were achieved in basic DMA at relatively high temperature, 140°C with the selectivity of 84% at 96% conversion (Fig 1b). In the final work the catalyst performances are correlated with their properties.

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OP-I-2

SYNTHESIS AND CHARACTERIZATION OF METAL CATALYSTS FOR THE PRODUCTION OF SPECIAL FATTY ACIDS

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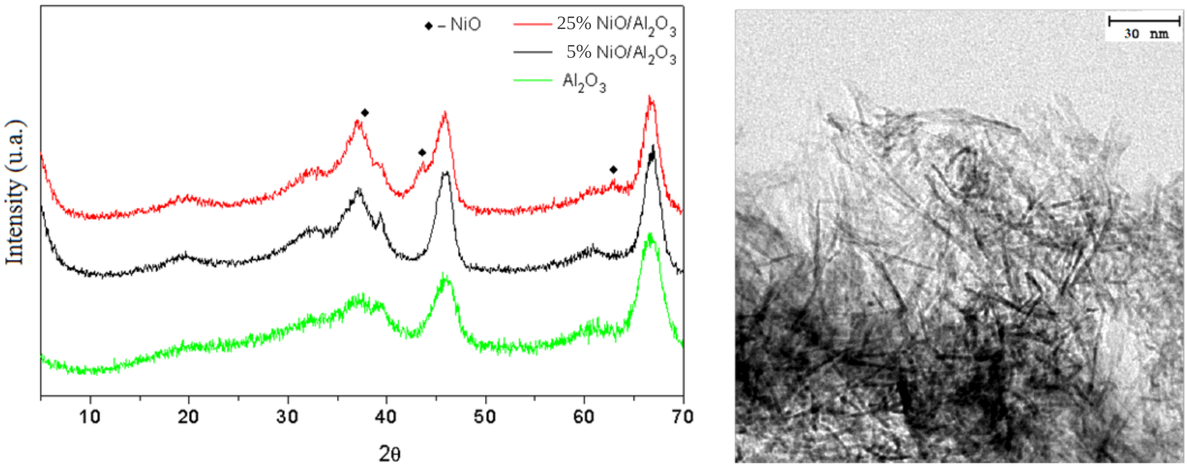
Hydrolysis reactions are of major importance to the oleochemical industry in the production of fatty acid and their derivates, especifically saturated fatty acids have high relevance. This paper presents studies and results on producing saturated fatty acid trough catalytic hydrolysis of soybean oil and tallow.

The catalysts used in the heterogeneous reactions were nickel supported on gamma alumina (5% NiO/Al_2O_3, 10% NiO/Al_2O_3 and 25% NiO/Al_2O_3). The synthesized catalysts were characterized by textural analysis techniques, X-ray diffraction (DRX), X-ray fluorescence spectrometry (XRF) and transmission electron microscopy (TEM) coupled with an Energy Dispersive X-Ray Spectrometer (EDS or EDX) (Figure 1). Reactions were performed in a stainless steel 300 mL batch reactor. Stirring velocity was kept constant (250 rpm). Reaction mixture consisted of 100 g of raw material and 100 g of water, providing a water/raw material molar ratio of 1. Reagents were introduced together with the appropriated catalyst mass (10% w/w, in relation raw material) and time of reaction (1 and 3 hours) was considered when required temperature (250 °C and 270 °C) was reached.



a) **b)**

Figure 1. Synthesized 25% NiO/Al_2O_3 catalysts a) XRD b) TEM.

OP-I-2

During the hydrolysis of soybean oil and tallow using nickel catalysts on alumina support was verified that the glycerol produced worked as hydrogen donor, allowing the hydrogenation of unsaturated fatty acids produced. Maximum conversion was achieved in 3 hours, catalysts 25% NiO/Al_2O_3, temperature of 250 °C and 270 °C and 250 rpm (Figure 2).

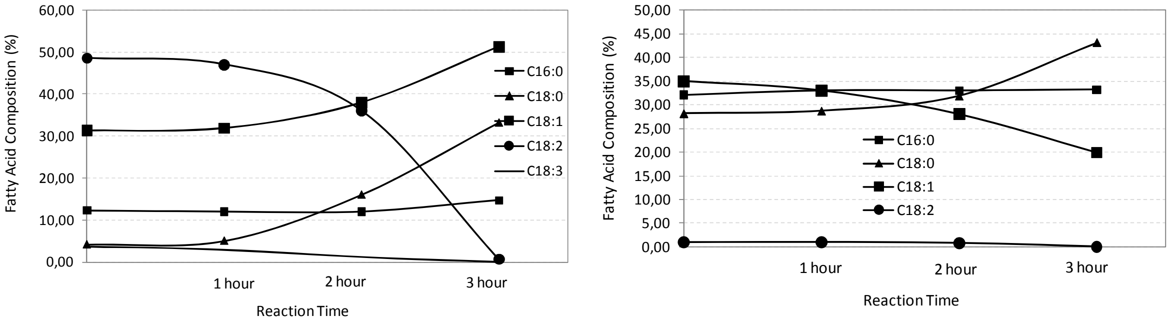


Figure 2. Fatty acid composition of hydrolysis – hydrogenation at 270 °C using 25% NiO/Al_2O_3, reaction time: 3 h. a) Soybean oil b) Tallow.

Geometry configuration, chemical and physical characteristics of catalyst will determine the hydrogenation selectivity. Linoleic and linolenic acids selectivity was estimated from the selectivity ratio (SR). SR was calculated using Allen's method [1] as original proposed by Albright [2].

$$\textbf{Linolenic} \xrightarrow{\mathbf{K_1}} \textbf{Linoleic} \xrightarrow{\mathbf{K_2}} \textbf{Oleic} \xrightarrow{\mathbf{K_3}} \textbf{Stearic}$$

K_1, K_2 and K_3 are kinetic constants.

It is observed that in the hydrolysis of soybean oil, linoleic acid was completely hydrogenated (more to 95%), this results demonstrates the high selectivity of hydrogenation. Similar result was shown in the reaction with tallow, transforming linoleic acid into oleic acid. To corroborate quantitatively these results, selectivities were calculated for hydrogenation of linoleic and linolenic acids for simultaneous hydrolysis/hydrogenation of soybean oil using 25%NiO/Al_2O_3.

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EFFECTS OF SYNTHESIS PARAMETERS AND CATALYST MORPHOLOGY ON THE PRODUCT DISTRIBUTION OF BIOETHANOL CONVERSION

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While most researchers have been of the view that combatting today's global energy problems is achievable using renewable and/or sustainable sources, the most suitable alternative to fossil fuels is still actively debated. Despite its wide application as a fuel blend in a number of countries, the need to modify engines makes it practically difficult for ethanol to fully substitute crude oil in the near future. However, there is growing interest in bioethanol due to its environmental friendliness and posibility of generation from wastes. To ensure optimum utilisation, there is need to consider the conversion of fermentation broth into products obtainable from fossil fuels.

This work studied the conversion of ethanol over catalytic systems into petrochemicals and hydrocarbons within the range of those obtainable from primary distillation of crude oil. The research investigated the product distribution from both operational and catalytic point of views. Reaction variables like temperature, space velocities, and purity were investigated. The catalysts used in the process were characterised using XRD, FTIR, SEM, EDS and BET analytical techniques.

The pre- and post-reaction analyses gives vital information into the catalyst deactivation. It was found that both reaction conditions and catalyst synthesis parameters affect the catalytic activities, product distribution and yield during ethanol conversion. Finally an economic analyses of the process from biomass production to fuels was also considered.

OP-I-4

KINETIC MODELING OF LEVULINIC ACID HYDROGENATION TO γ-VALEROLACTONE

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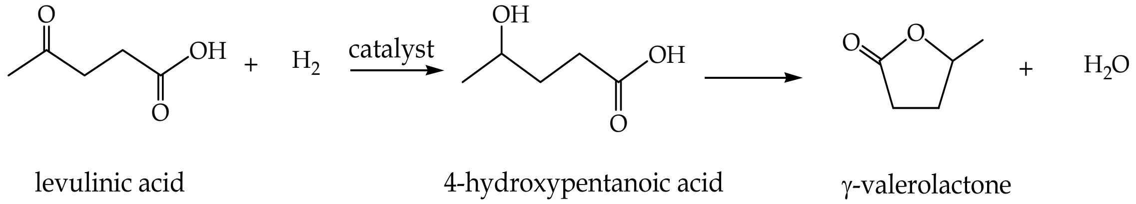
Levulinic acid (LA) is an attractive platform chemical and is available from the C6-sugars of lignocellulose biomass in good yields [1]. LA can be converted to a variety of useful compounds with high application potential, such as γ-valerolactone (GVL), 1,4-pentanediol, methyltetrahydrofuran (MTHF) and diphenolic acid [2]. GVL was described as an ideal, sustainable liquid which can be used for the production of both energy and carbon-based consumer products [4].

GVL is accessible by the (catalytic) hydrogenation of LA to the intermediate 4-hydroxypentanoic acid (4-HPA) and subsequent ring-closure [3], [5].



Various heterogeneous catalysts have been studied for the reaction and particularly Ru based (e.g. Ru/C) catalyst showed high conversion levels of LA and selectivity to GVL [3], [6], [7]. However, comprehensive kinetic models to be used as either input for reactor design or to gain insights in mechanistic pathways have not been reported to date.

In this contribution, we report a kinetic study on the hydrogenation of LA to 4-HPA and the subsequent ring closure to GVL for Ru/C (3 wt%, powder) in water in a batch set-up. Reaction conditions like temperature, hydrogen pressure and initial LA concentration were varied in a systematic manner. Both intra-particle and G-L mass transfer limitations were shown to be absent. To gain insight in product inhibition, hydrogenations in the presence of the product and intermediate were performed.

The hydrogenation of LA to 4-HPA was modelled using a Langmuir-Hinshelwood type expressions with competitive adsorption of LA and 4-HPA on the surface of catalyst. Both isothermal and non-isothermal models were developed.

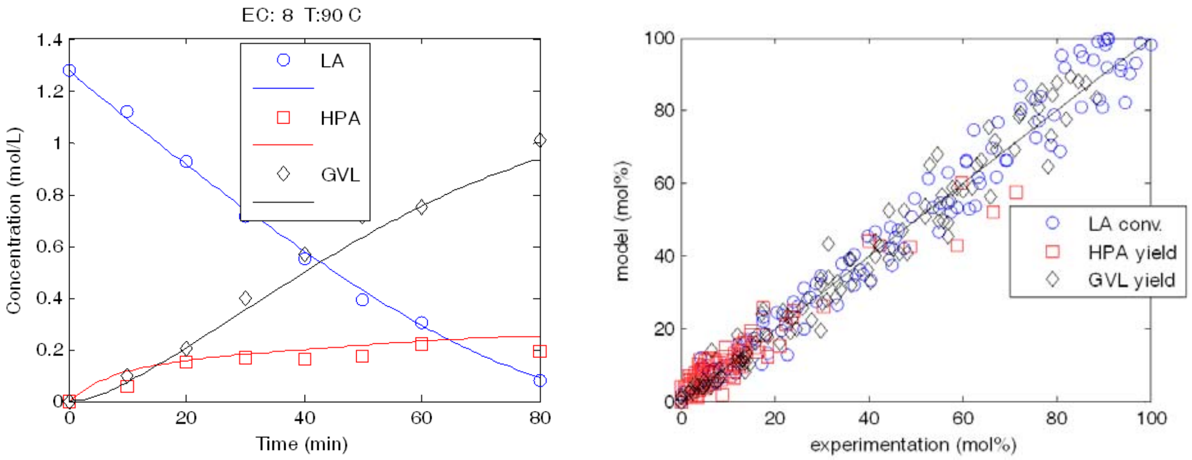


Fig. 1. Modeled and experimental profile for a representative experiment (left) and a parity plot (right).

The conversion of 4-HPA to GVL was modelled as an equilibrium reaction and assumed to occur in the bulk of the solution, catalysed by a Bronsted acid (H^+), in this case LA. Independent kinetic and equilibrium studies on the 4-HPA↔GVL equilibrium were performed using temperature depending NMR studies and were in good agreement with the model.

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Acknowledgements

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OP-I-5

ACETONATION OF GLUCOSE OVER SULFONIC ACID FUNCTIONALIZED ORDERED MESOPOROUS SILICA

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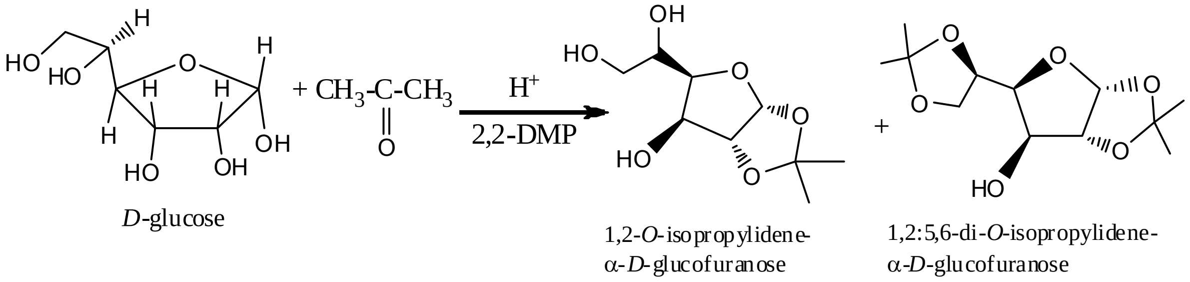
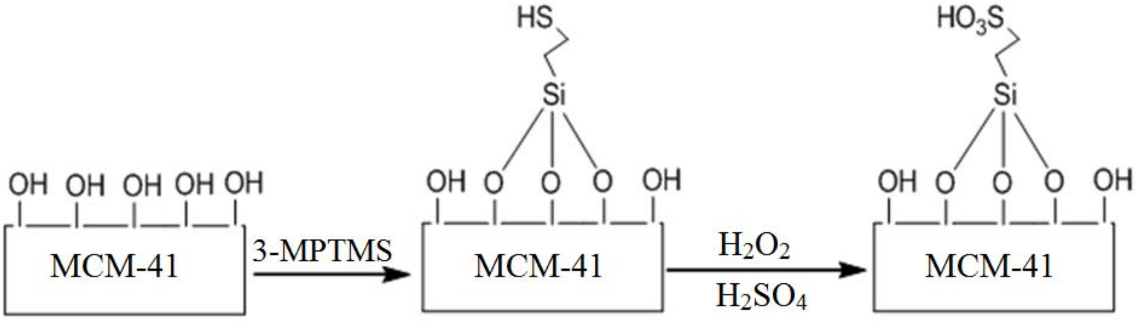
Biomass attracts much attention as a renewable feedstock as well as to its “CO_2 neutral” impact on the environment. In this context, acetonation of glucose is important reaction owing to its pharmacological properties and utility as reaction intermediates for the synthesis of bioactive molecules [1]. However, conventional catalysts used for this reaction (Scheme 1) are either moisture sensitive or sluggish in terms of reactivity at ambient conditions. Further, a tedious work-up involved in the isolation of the products limits the application. Therefore, development of environmentally benign and recyclable catalysts is of paramount importance. In this regard, solid acids are promising as heterogeneous catalysts for such purpose.



Scheme 1: Reaction scheme for Acetonation of *D*-glucose.

Sulfonic acid functionalized mesoporous silica (MCM-41-SO_3H) catalysts are a new class of inorganic solids which play a prominent role promising as the attached organic moiety imparts water tolerance, large uniform pore sizes activates bulky molecules, high surface areas enhances reaction sites, high thermal and hydrothermal stabilities offers greater flexibility in terms of reusability and relatively high acid strengths allows greater selectivity [2]. Hence, in this investigation, an attempt has been made to prepare a series of MCM-41-SO_3H *via* post-grafting method [3] of covalent attachment of thiol using (3-mercaptopropyl)trimethoxysilane (3-MPTMS) on the silica surface and subsequent oxidation of the composite with H_2O_2 followed by acidification with H_2SO_4 (Scheme 2).



Scheme 2: Sulfonic acid functionalized mesoporous silica *via* thiol grafting method.

The acetonation reaction of glucose was performed by liquid-phase condensation of *D*-glucose and dryacetone using 2,2-dimethoxypropane (2,2-DMP) in presence of MCM-41-SO_3H, and the results are presented in Table 1. It can be seen from this table that the acetonation reaction results in selective formation of the product, 1,2:5,6-di-*O*-isopropylidene-α-*D*-glucofuranose and that an optimum sulfonic acid loading is required to achieve a maximum yield [4].

Table 1: Acetonation of *D*-glucose over MCM-41-SO_3H catalysts.[a]

Catalyst		Conversion (%)	Selectivity (%)		
	CEC[b]		Di-[c]	Mono-[d]	Others[e]
MCM-41[f]	---	---	---	---	---
MCM-41-SO_3H (1:1)	0.35	100	85.7	0.6	13.7
MCM-41-SO_3H (2:1)	0.35	100	84.6	0.7	14.7
MCM-41-SO_3H (4:1)	0.30	91	71.1	8.9	11.0
MCM-41-SO_3H (8:1)	0.25	88	67.1	11.9	9.0

[a] Reaction conditions: Catalyst weight = 50 mg, Glucose = 500 mg, temperature = 333 K, N_2 atmosphere, dryacetone = 30 mL, 2,2-DMP = 2mL; [b] Cation (sodium ion) exchange capacity. [c] 1,2:5,6-di-*O*-isopropylidene-α-*D*-glucofuranose, [d] 1,2-*O*-isopropylidene-α-*D*-glucofuranose. [e] Others include acetone and some unidentified products. [f] No reaction.

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This work is supported by a grant-in-aid under India-Australia Fund for Scientific and Technological Cooperation Program (INT/AUS/P-18/08). The authors thank Prof. B. Viswanathan for encouragement; Department of Science and Technology, New Delhi for funding NCCR, IIT-Madras.

OP-I-6

SYNTHESIS OF GLYCEROL CARBONATE FROM GLYCEROL AND DIMETHYL CARBONATE USING CaO : IDENTIFICATION OF ACTIVE CATALYST FORM

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The synthesis of glycerol carbonate from glycerol and dimethyl carbonate was investigated in the presence of CaO under various reaction conditions. CaO was found to completely dissolve in the reaction mixture of glycerol and DMC in 5 min at 75 °C with molar ratio of glycerol/DMC/CaO of 1/2/0.01. The isolation and the characterization of the dissolved Ca species using TOF-SIMS, elemental analysis, and FT-IR revealed that an active species, $Ca(C_3H_7O_3)(OCO_2CH_3)$ is generated from the interaction of CaO with glycerol and DMC.

Introduction

Of the various types of renewable feedstocks, triglycerides are regarded as good prospective raw materials for biodiesel production, due to their easy availability from vegetable oils and animal fats. In the preparation of biodiesel from triglycerides, however, 10 wt% of glycerol is always co-produced, which inevitably reduces the economics of the process. In this context, transformation of glycerol into high value added chemicals is highly necessary. One of valuable glycerol derivative is glycerol carbonate, which have many useful applications such as a nonvolatile solvent, a component in coatings, detergents and membranes for gas separation, a source of polymeric materials such as polycarbonate and polyurethane.The transesterification between glycerol and DMC using CaO as the catalyst have been extensively investigated by Ochoa-Gomez et al. [1] who reported that the CaO is highly active heterogeneous catalyst for the transesterification. In this work, we found CaO is completely dissolved in reaction mixture at specific reaction condition. We conducted the characterization of the isolated Ca species dissolved in the reaction mixture by using elemental analysis, TOF-SIMS and FT-IR. The mechanistic pathways to the formation of active Ca species and glycerol carbonate are also discussed on the basis of experimental and spectroscopic results.

Results and Discussion

Result of TOF-SIMS analysis shows above the mass range of 100 m/z, the strongest peak was observed at 112.92 m/z, which could be explained as a dehydrated calcium monoglycerol species. Interestingly, except 112.92 m/z, major peaks detected at the positive detector were found to be composed of calcium compounds with both the glycerol and methyl carbonate moieties. Among these, $Ca(C_3H_7O_3)(OCO_2CH_3)$ seems to be the most probable structure on the basis of elemental analysis (calcd for $CaC_5H_{10}O_6$ (%): Ca, 19.4; C, 29.1: H, 4,9. Found: Ca, 18.8; C, 28.4; H, 4.6). The presence of a carboxylate group in the isolated calcium species is evident from the series of FT-IR spectra shown in Fig. 1. The strong peak observed at 1058 cm^{-1} corresponds to the C-O stretching frequency of glycerol group in the complex. Upon the interaction of CaO with glycerol and DMC, two strong peaks appeared at 1640 and 1324 cm^{-1}, which can be associated with the carbonyl (C=O) stretching frequency and C-O-C vibrational band of the CH_3-O-CO_2-Ca, respectively. A plausible mechanism for the CaO-catalyzed transesterification between glycerol and DMC is depicted in Scheme 1.

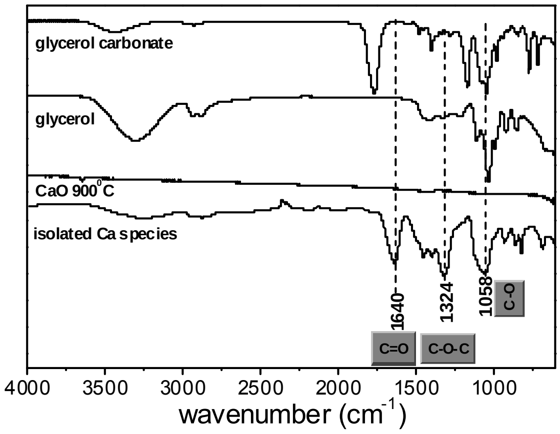
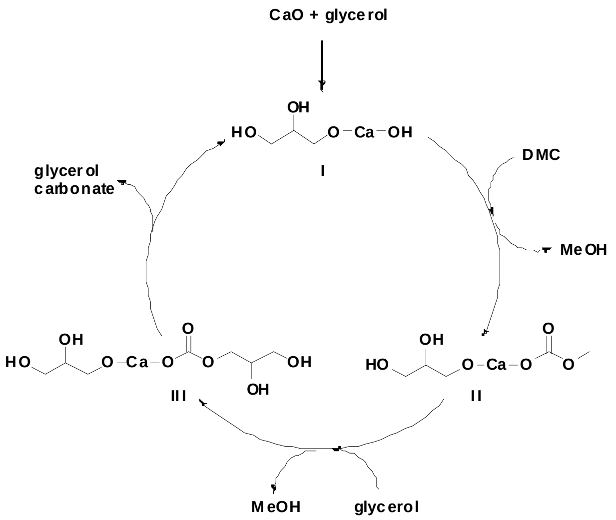


Fig. 1. IR spectra of (a) glycerol carbonate, (b) glycerol, (c) isolated Ca species



Scheme 1. A plausible reaction mechanism for the CaO-catalyzed transesterification of dimethyl carbonate with glycerol

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OP-I-7

IMPACT OF GLYCEROL ON *RHIZOMUCOR MIEHEI* LIPASE ACTIVITY DURING ENZYMATIC DEACIDIFICATION OF *JATROPHA CURCAS* CRUDE OIL

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Jatropha curcas L. is a tropical plant of the genus *Euphorbiaceae*. The plant is rather non-demanding – growing under various climatic conditions and able to survive in poor and stony soils. Since the seeds of Jatropha are rich in non-edible oil [1], research focus is set on its valorization for biodiesel production. One of the refining steps that the crude oil has to undergo prior to biodiesel production is the neutralization step. To overcome the disadvantages adherent to the conventional process, high oil losses and the consumption of chemicals and water, it is desirable to apply lipase-catalyzed neutralisation. Here the esterification of free fatty acids in the presence of glycerol is catalyzed by a carrier-bound lipase from *Rhizomucor miehei*. It is known that glycerol is inhibiting lipase activites [2,3]. However, the glycerol level is a key parameter for the reaction equilibrium between hydrolysis and esterification.

The work reported in this contribution is concerned with the optimization of the lipase-catalyzed neutralization reaction regarding the role of glycerol. Initial screening experiments confirmed that the glycerol content in the reaction medium is a crucial process parameter. In order to develop an improved process execution the type of inhibition mechanism was studied and an alternative for the direct addition of the glycerol was looked for. Reactions were performed at 60°C during 8 hours in heatable double-wall reactors utlilizing 100 g of Jatropha crude oil. Analytical evaluation of the process was done by wet chemical and gas chromatographic measurements. Kinetic parameters were determined graphically utilizing Lineweaver-Burk reciprocal analysis. It was found that the esterification reaction with *Rhizomucor miehei* lipase follows a Ping Pong Bi Bi mechanism with competitive inhibition by the substrate glycerol. Furthermore can the glycerol induced lipase inhibition be reduced through the stepwise addition of glycerol to the reaction mixture.

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OP-I-8

MAGNETICALLY NANOPARTICLES WITH ACID PROPERTIES FOR LEVULINIC ACID SYNTHESIS FROM CELLULOSE

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In the last decades catalysis became a strategic field of science representing the new way to meet the challenges of sustainability. In this context, one of the big challenges is the development of the cleaner catalytic processes to convert biomass to multiple platform molecules as strategic precursors for valuable products. In this context, levulinic acid (LA), as platform molecule, it is an important intermediate for the synthesis of numerous derivatives with multiple uses [1].

Creating nanocatalysts became the most important goals in the last years [2]. However, isolation and recovery of these tiny materials is not easy, this limitation hampering the economics and sustainability of these protocols. To overcome these limits, the use of magnetic nanoparticles has emerged as a viable solution; their insoluble and paramagnetic nature enables easy and efficient separation of the catalysts from the reaction mixture with an external magnet. Furthermore, magnetic separation is a “green” process since it avoids the complications of filtration, the waste and costs being greatly reduced [3].

Here, we report a highly selective transformation of cellulose to LA using magnetically nanoparticles (MNPs) catalysts with Lewis/Brönsted acid properties.

The preparation of the catalysts comprised three steps: (i) the synthesis of the silica-coated Fe_3O_4 nanoparticles [4]; (ii) the functionalization of the silica shell with aminopropyl groups; (iii) the impregnation of the MNPs carrier with triflic acid (HOTf), trifluoroacetic acid (TFA) and $La(OTf)_3$ as active species. The catalysts have been characterized using N_2 adsorption-desorption isotherms at 77 K, XRD, FTIR, UV-VIS, TG, AE and DLS. Activity tests in batch mode were carried out in the following procedure: to a slurry of 0.14 g α-cellulose in 8 mL of water, 0.06 g of catalyst were added and heated up to 423-453 K, under stirring, for 1-6 h. After reaction the catalyst was magnetically recovered by placing a permanent magnet on the reactor wall, the untransformed cellulose was filtered out from the slurry of products and the water soluble products were separated by distillation under vacuum.

The crystallite size was estimated by X-ray powder diffraction patterns [5], as being 7.9 nm for unmodified MNPs, 8.1 nm for MNPs modified with TfOH and 9.1 nm for MNPs-$La(OTf)_3$ (Figure 1). The broad peak from $2\theta = 20^0$ to 30^0 was due to the amorphous silica shell on the surface of the MNPs while the reflection planes at 2θ 30.1°, 35.4°, 43.1°, 53.4°, 57.1°, and 62.6° can be indexed as (220), (311), (400), (422), (511), and (440) lattice planes of cubic magnetite. For MNPs modified with TfOH and $La(OTf)_3$ a slightly decreasing of the relative intensity of diffraction lines was registered. DRIFT measurements confirmed the existence of these species on the NMPs surface. All techniques indicate that magnetic catalysts with Brønsted and Lewis acid sites were successfully obtained. The aqueous phase hydrolysis of cellulose to LA demonstrates the excellent activities (conversions > 70%) and particular characteristics of the novel family of NMPs based acids. Therefore, while NMPs materials modified with TFA convert cellulose to arabinose, D-xylose and arabino-pyranose, NMPs materials modified with HOTf and $La(OTf)_3$ provided selectivities higher than 50% to LA. The improved yields of LA on NMPs modified with Lewis acid species may be explained by the summarization of glucose into more reactive fructose and rehydration-induced ring cleavage to LA. Moreover, the catalyst/product(s) separation was easily achieved with a permanent magnet while the catalyst recovered after the reaction was reused without a significant loss of the catalytic performances.

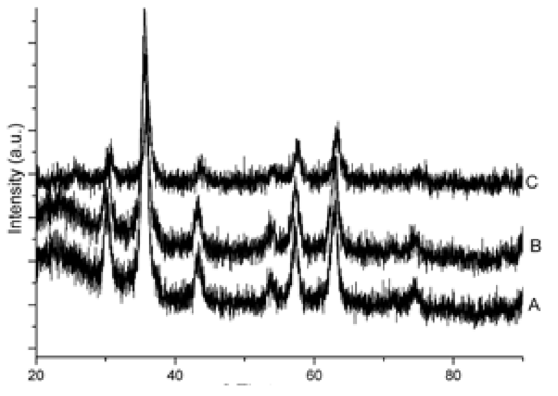

Figure 1 XRD diffractograms for MNPs (A); MNPs modified with HOTf (B) and MNPs with $La(OT)_3$ (C).

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OP-I-9

RENEWABLE GLYCEROL IN BIOREFINERY – BIOCATALYTIC SYNTHESIS OF GLYCEROL CARBONATE

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Glycerol is a key aspect of the biodiesel manufacture of biomass due to huge amount of glycerol produced during the biodiesel process (*e.g*. 2,4 kilo-tone glycerol for biodiesel production in EU only on 2012). Unfortunately, this glycerol posses low value for industry because its impurity content (*e.g.* methanol, water, soap, salts, *etc.*) and the purification alternative of the bio-glycerol is not feasible for small-scale production. The lack of proper management for glycerol entails soon to the decrease of the industry interest in biodiesel due to its high production costs. Another possible consequence is that glycerol will become a potential environmental pollutant due to the large glycerol amount stocked in the environment. Thus, glycerol as versatile biofeedstock has good multiple functionality and a number of immediately valuable or promising products can be envisaged based on the exploitation of Green Chemistry and green chemical technologies.

In this context, we lunched recently the concept of a biocatalytic conversion of glycerol (bio-glycerol) to glycerol carbonate (GlyC) [1-4] as a value-added product with numerous applications in cosmetics, pharmaceutics, detergents and adhesives industry. The biocatalytic process involved glycerol carbonylation with dimethyl carbonate (DMC) assisted by a lipase biocatalyst (*e.g.* enzyme-linked magnetic particles (ELMP), cross-linking enzyme aggregates (CLEA) and cross-linking enzyme aggregates onto magnetic particles (CLEMPA)) in solvent-free system (Figure 1).

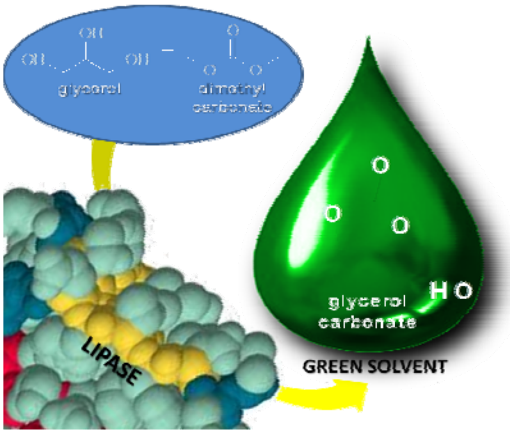

Figure 1. Biocatalytic synthesis of glycerol carbonate assisted by lipase enzyme.

Crude glycerol directly from biodiesel products was used as raw material for GlyC synthesis (Figure 2). Collected glycerol had different matrices according to the feedstock patterns (*e.g.* soybean, sunflower, rape, corn, olive, palm, and residual oil).

It indicates that under identical reaction conditions the nature of the fatty ester precursor is important. The higher yields were obtained from residual and soybean oils, where around 95% from the maximum GlyC yield were recovered. Glycerol from other sources led to smaller yields. Sunflower, olive and palm oils led to around 70 % from the maximum GlyC yield while the lowest conversion was obtained for samples derived from rape and corn.

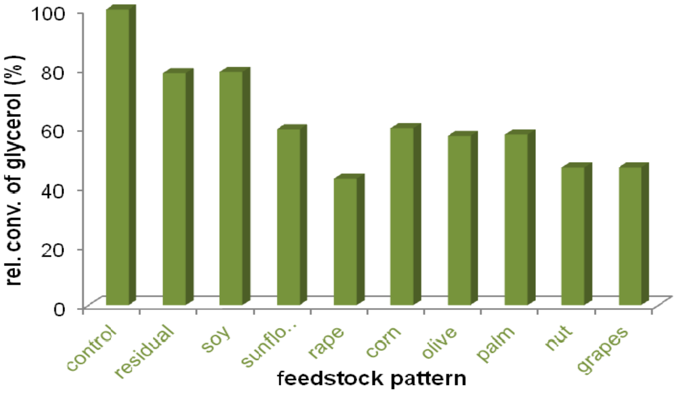

Figure 2. Crude glycerol on biocatalytic synthesis of glycerol carbonate.

The key aspect of the glycerol behaviour was the sample composition (*i.e.* bio-glycerol matrix). Chemical composition of renewable glycerol samples was determined taking into consideration the content in MeOH, water, soaps, metals (Na, K, Ca and Mg) and salts (P for phosphates and S for sulfates). The best performances correspond to a lower MeOH content (*e.g.* 6.5 and 6.2 % MeOH for residual and soybean oil, respectively). Calcium anions, as well as phosphates (phosphorus) and sulfates (sulfur) salts do not affect the biocatalyst activity. Surprisingly, manganese was identified in the glycerol from corn oil providing another reason for the low GlyC yield.

All of these aspects of our experiments will be details in the proposed presentation.

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OP-I-10

ONE – STEP CATALYTIC CONVERSION OF BIO – ETHANOL INTO 1, 3 – BUTADIENE IN THE PRESENCE OF AN INITIATOR

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Butadiene is important not only as a monomer for synthetic rubber, but also as feed stock in the production of synthetic fibers, particularly nylon.

The process of butadiene production was introduced in The USSR in the 1930's by S.V. Lebedeev and it was used then to meet the world's demand for synthetic rubber. It was however abandoned after the discovery of large oil reserves, from which butadiene is extracted, specifically from the butane – butylenes fraction of crude oil.

Currently, the trend for the production of butadiene has changed due to the forecast on the reduction of oil reserves. In view of this, we returned to S.V. Lebedev's process, thereby carrying out its modernization to increase the basic parameters of the process.

We have proposed an initiated catalytic process for obtaining butadiene from ethanol, which consists of the simultaneous action of an initiator and a catalyst. The initiator is introduced in an amount of 1 to 1.5 wt.% to the raw materials. To maximize the performance of the process, optimal conditions (temperature, space velocity) were selected, a new catalyst composition was developed, and technological solutions that support the operation of the initiator favourable to the formation of the desired product, thereby increasing the selectivity of the process, was adopted.

The catalyst was prepared based on ZnO / γ-Al_2O_3 system with different modifiers. In order to increase catalyst activity, its activation was of uttermost importance and was conducted using air, N_2, and H_2. The results of our experiments are promising and can be adopted for increasing the yield and selectivity to butadiene.

NOVEL CATALYSTS FOR REFINING OF UNSATURATED ACIDS OF VEGETABLE OILS TO HIGH INTERNAL OLEFINS

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The success of the chemical industry is in large part merit of the discovery and development of catalysts, and industrial catalysis is essential for most modern, cost and energy efficient means for the production of a broad range of petroleum refining, chemical products, pharmaceuticals and for environmental protection. The major sectors of catalysts sales are for the oil refining, chemical processing and emission control markets.

In petroleum refining catalytic processes provide almost entirely the high quality fuels required by the market facing successfully the more and more stringent, mandated fuel specifications and the deteriorating characteristics of crude oils in terms of sulfur and gravity. Industrial catalysis makes also real and economic the exploration of unconventional heavy crudes and the use of renewable raw materials with the production of biofuels.

Fossil resources, mainly oil and gas, additionally to represent the raw materials of choice for all synthetic materials surrounding us. Industrial application of catalytic processes concerns the large fields of the hydrocarbons transformation into intermediates and final products new catalytic technologies are under development for methane conversion and pose the basis for a new gas-based chemistry. Good hopes for the environment preservation rely firmly on catalytic processes in the production phase and in the emission control.

The studies finalized to develop and scale-up catalytic processes are by definition, application oriented – as a consequence the target of industrial catalysis is do make concrete innovation in better processes, better utilization of raw materials and energy as well in improving the environmental impact. In modern stage catalysts play a primary role in today technology. They are essential tool for chemicals and materials production, for fuel and other energy conversion systems, for combustion devices, for fuel cells and for pollution control systems. Often it is the key to making on entirely new technology. Therefore, the application of nano-sized catalysts in these processes is the main actual direction in petrochemistry at the modern period. So, the oxides of several metals, such as magnesium and titanium have been proposed as a nano-sized catalysts in our investigation. These catalysts were used in the process of decarboxylation of unsaturated acids, received from vegetable oils for the synthesis of highly internal olefins. These acids are oleic, linoleic and linolenic acids, and the products of their decarboxylation are internal olefins of C_{17} series, which have widely usage in the different field of the industry and agriculture.

Moreover, nano-sized oxide catalysts have been used in the process of decarboxylation of petroleum acids, received from crude oils. It is shown that, the application of nano-sized magnesium oxide or titanium oxide catalysts decreasing the total acid number of petroleum acid from 260 mg KOH/g to 1,5-3,1. At the same time, during the process of decarboxylation of petroleum acids the mixture of cyclic hydrocarbons (mono-, bi and polycyclic) have been received and it has high density and caloric ability, respectively 950-960 kg/m^3 and 41.500-42.000 MC/kg. Thus, receiving the mixture of cyclic hydrocarbons was proposed as a component for reactive fuels.

In the both cases, processes have been leaded in the flow reactor systems at the temperature 300-350 °C and volume rate 0,7-1,0 h^{-1} and the conversion of acids were reached 94-96 %.

Summarizing all, the application of nano-sized catalysts in the petrochemical synthesis can be solve many actual issues of petrochemistry, particularly receiving of petrochemical and organic products (such as components of fuels and chemicals) based on biologic raw materials.

STUDY OF LOCAL GAS HOLDUP, AND SPECIFIC INTERFACIAL AREA IN A SPLIT-COLUMN AIRLIFT BIOREACTOR USING SPHOSTICATED 4-POINT OPTICAL PROBE FOR CULTURING MICROALGAE/CYANOBACTERIA

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Local gas hold-up (ε), and local interfacial area (a) at different axial locations of the riser and downcomer of a split-column airlift bioreactor were investigated using sophisticated 4-point optical probe. Such type of a reactor has been found to outperform both bubble column and draft-tube airlift bioreactors for culturing microalgae. The effect of superficial gas velocity (0.3 – 2.8 cm/s) on both the gas hold-up and local interfacial area were studied using air-water system. It was found that both the gas hold-up and interfacial area significantly decrease from the top to the bottom of the downcomer for all superficial gas velocities while their variation from the bottom to the top for the riser was found to be much less than that of the downcomer at the same superficial gas velocities. It was found that the interfacial area of the riser tends to increase by 35% from the bottom to the upper middle point of the column (6.15 Z/D from the bottom), then declines by 10% at the top location (7.7 Z/D from the bottom). Having obtained variable interfacial area (a) at different locations of both the riser and the downcomer of the bioreactor, the local (K_La) consequently changes as a function of location of the bioreactor and hence, needs to be investigated locally as opposed to the current studies that have only measured and correlated the overall K_La.

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COLLOIDAL CATALYSTS ON THE BASE OF IRON(3+) OXIDES FOR OXIDATIVE TREATMENT OF BIOMASS

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Catalysts based on iron oxides are widely used in various chemical processes due to their low toxicity and relatively low cost. The analysis of chemical nature of processing and treatment of organic pollutants such as wood waste by fungus and bacteria was the starting point for innovative working up a new colloid catalytic system based on iron (3+) oxides combined with environmentally safe oxidants – hydrogen peroxide (H_2O_2) and/or atmospheric oxygen. According to [1-3], colloid catalyst can be synthesized by mild hydrolysis of Fe^{3+} salt ($FeCl_3{\cdot}6H_2O$) in the water solution containing a surfactant (~1%). The structure, composition, and size of colloidal particles were studied by the methods of Mössbauer spectroscopy, X-ray fluorescence, X-ray diffraction analysis, and TEM [2]. The aim of this study is to investigate the effect of catalyst concentration on the H_2O_2 decomposition and to test the new colloid catalyst for waste wood and biomass oxidative destruction with H_2O_2 in water solution at moderate temperature and atmospheric pressure.

Wood residues (conifers, deciduous, including eucalyptus), peat, straw (oat, rise, etc.), marc (olive, flax etc.), boon, technical lignin, etc. were treated by catalytic process. The oxidative catalytic cracking occurs in water media and results in water solution of organic acids, ethers and esters, sugars, and other low molecular products of cellulose and lignin destruction. IR spectrum of solid residues is often close to that of cotton cellulose. In dependence on the percentage of components biomass under treatment, catalyst, and oxidant, one can obtain various celluloses, tannins or mainly low molecular products of cellulose and lignin oxidative destruction. Treatment of technical lignin with this catalytic system results in water soluble acids and esters and solid hydroxylated residue which demonstrates an antioxidant effect on lipid oxidation.

The activity of the catalyst with respect to H_2O_2 decomposition undergoes nonlinear and nonmonotonic variations with increasing initial gross-concentration of catalyst ($[Fe^{3+}]$). In the absence of biomass, the catalyst obtained under optimal conditions exhibits high activity corresponding to the most efficient agents of H_2O_2 decomposition.

The comparison of catalytic H_2O_2 decomposition during oxidative treatment of various biomass (conifers saw dust, SD, peat, P, oat straw, OS, olive marc, OM, and technical lignin, L), taken at equal percentage conditions, shows that biomass retards the rate of H_2O_2 consumption, however, in different extent. The study of catalytic mechanism has shown that the initial nanosized catalyst, completely adsorbed on the biomass surface, is transformed depending from biomass nature and reaction conditions. The degree of oxidative cracking and depth of organic material conversion can be regulated by the reagent concentration ratio. We suppose, that the creation on the base of iron(3+) oxides self-assembly colloid (nano) catalytic system which occurs adjustment to the substrate oxidized can be considered as an attempt to follow the nature to utilize waste wood and lignin into valuable products.

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FABRICATION OF TITANIUM DIOXIDE NANOTUBE SUPPORTED ZEOLITE COMPOSITE CATALYST FOR ETHANOL DEHYDRATION TO ETHYLENE

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Ethylene is one of the most common building blocks in the petrochemical industry[1]. Bioethanol dehydration to ethylene is becoming a non-petroleum, environmentally friendly, potential and alternative route to meet the demand of ethylene with a complementary supply [2]. The catalyst plays a crucial role in the success of the reaction in terms of the rate and the yields [3].

Titanium dioxide (TiO_2) has been found to be an effective promoter to enhance the catalytic performance for ethanol dehydration to ethylene [4]. In this paper, a novel composite structure catalyst, TiO_2 nanotube (TiO_2NT) supported zeolite, was fabricated by decorating zeolite on the hydrothermally synthesized titanium dioxide via hydrothermal process and subsequent annealing. The catalyst was characterized by X-ray powder diffraction (XRD), Transmission electron microscopy (TEM) and Nitrogen adsorption-desorption (BET). The surface acidity of the catalyst was measured by means of Fourier transform infrared (FT-IR) spectrum of pyridine adsorption. And the catalytic activity for ethanol dehydration to ethylene was evaluated in a continuous flow fixed-bed reactor. The results show that TiO_2NT is decorated with zeolite as shown in Fig. 1, the anatase TiO_2NT is approximately uniform with the diameter size of around 15-20 nm and the length ranges from hundreds of nanometers to several micrometers. The concentration of Bronsted and Lewis acid sites on TiO_2NT supported zeolite composite catalyst are more than that on zeolite, which is attributed to the increase of the effective surface acid sites caused by titanium dioxide nanotube as electron acceptor. And TiO_2NT supported zeolite composite catalyst exhibits strongly enhanced activity for ethanol dehydration to ethylene (Fig. 2).

OP-I-14

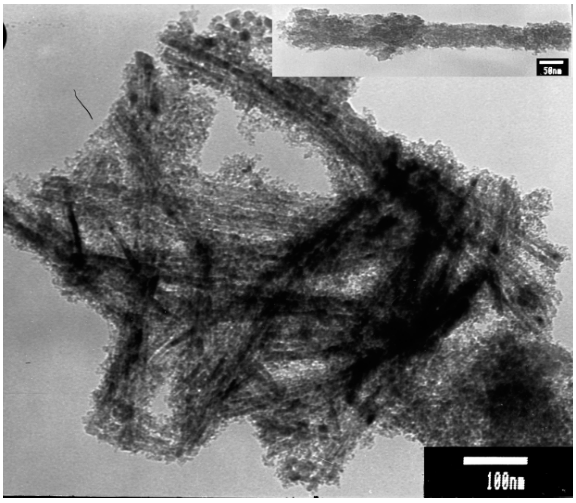

Fig. 1

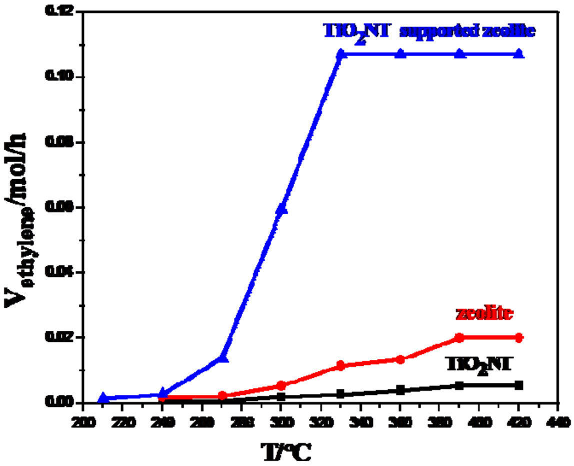

Fig. 2

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ORAL PRESENTATIONS

SECTION II

Catalytic processes for biofuel production

OP-II-1

ISOBUTANOL FROM GLYCEROL

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A new process has been developed in which glycerine and methanol are fed into a process which yields isobutanol, an excellent biobased substitutent for gasoline. A techno-economic evaluation has been performed which estimates the costs associated with the process, both capital expenditure and operation costs. Further, as the production process is similar to processes in traditional petrorefineries, the possibilities to integrate the process into an existing refinery have been investigated. Finally, the savings in greenhouse gas (GHG) emissions from using the glycerol-based isobutanol compared to fossil gasoline have been estimated.

The use of glycerol as feedstock in chemical process industry is increasing with the volumes available from conventional production and as a by-product from the production of first generation biofuels [1, 2]. As the quantities available on a global level are large, it will be difficult to use the abundant glycerine to produce high-value specialty chemicals which are traded only in minor volumes. Further, as the production of the glycerine already correlates with the demand for liquid biofuels, it seems feasible to utilize the available volumes to meet a share of the remaining demand for liquid biofuels. Isobutanol can be used as a drop-in additive to gasoline, but also as a major gasoline component, without requiring any modifications to ordinary internal combustion engines. Isobutanol is a better gasoline additive than bioethanol in several aspects [3,4].

In the proposed thermochemical production process glycerol is converted to propanal via acrolein. Propanal and methanal form methacrolein through a condensation reaction, which after a final hydrogenation process yields isobutanol. The three process modules are shown in Figure 1. The process was modeled using the software Aspen Plus. The energy demand was optimized with pinch analysis.

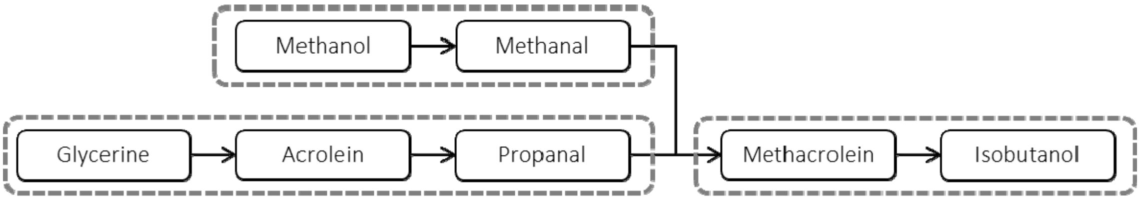

Figure 1. Simplified illustration of the three modules in the glycerol-based isobutanol production process.

The techno-economic assessment shows that the process benefits greatly from being integrated with an existing petro-refinery. The production cost for integrated production is 941 USD/m^3 whereas for a standalone production unit the cost is 1 090 USD/m^3. The production cost is thus rather similar to the cost for bioethanol produced from wheat when compared on an energy basis [5]. The glycerol-based isobutanol production process could thus be of great interest for refineries in areas with glycerol surplus. Threats to the feasibility are increasing glycerol prices, and policies restricting the possibility to use isobutanol as gasoline blendstock.

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NOVEL REACTOR AND CATALYTIC ENGINEERING FOR BIO AND GREEN FUEL PRODUCTION

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In order to ensure the competitiveness and sustainability of the processes to produce fuel and chemicals from biomass, critical technologies need to be developed. On the energy side new methods are currently being developed to convert biomass into so called second generation biofuels in which feedstock doesn't compete with food production and which will produce heat and electricity. The other approach is to crack the components of biomass in order to produce chemicals and materials.

Intensified catalytic microstructured reactors have been developed within a European Union funded project (www.suprabio.eu) to carry out conversion of syngas, derived from thermochemical conversion of biomass, to dimethyl ether (DME) via a direct process (without an intermediate methanol stage) and to middle distillate biofuels via Fischer-Tropsch synthesis (FTS). The aim is to provide efficient processes that are scalable to the distributed biomass treatment and conversion processes within an integrated biorefinery system. The approach is to achieve process and engineering integration and to utilise the enhanced heat and mass transfer properties of the reactor designs to overcome the cost penalties associated with downscaling plants.

The goal of SUPRABIO is to research, develop and demonstrate novel intensified unit operations that can be integrated into economic and sustainable biorefinery options for the production of second generation biofuels, intermediates and high value products, together with assessment of the outcomes to inform and enable sustainable implementation. Analysis has revealed that producing both chemicals and fuels in an integrated biorefinery concept meets the energy and economic goals simultaneously. Analysis has revealed that producing both chemicals and fuels in an integrated biorefinery concept meets the energy and economic goals simultaneously.

Together with the novel microreactor technology, a range of highly selective, novel nano-catalysts have been prepared and tested for these reactions. The development use and integration of improved catalysts and reactor design concepts to alleviate the mass transfer limitations in conventional fixed bed reactors, allows for very careful control of reaction temperature, and enhanced yields of desired products. The catalysts are prepared in a form that allows coating onto arrays of metal plates that are stacked and laser welded to form a mini-reactor. The challenges are to optimise catalyst properties, to achieve stable, adherent and uniform coatings and to design and optimise the reactor geometry to achieve fine control of reaction temperatures.

The experiments have been carried out over a wide range of reaction temperatures (210–300 °C), pressure (10–30 bar), H_2/CO = 1-2. The results indicate very promising levels of fuel and hydrocarbon yields.

Various loadings of transition metals on Al_2O_3 and/or HZSM-5 have been prepared by different methods and tested for their activity in (a) Fischer-Tropsch and (b) Dimethyl ether syntheses. For FTS, the best catalyst investigated is a 16% Co/Al_2O_3 formulation. 89% conversion to C_{5+} products was observed. The correct choice of operating parameters is of course critical for both optimum operation and for selective product production. For DME, typically, a mixed double function catalyst (Cu/Zn/Al, Cu/Zn/Cr, Cu/Zn/Zr) and a methanol dehydration catalyst based on zeolites were coated into microreactors. For DME, the best catalyst is one based on Cu/Zn/Al/ZSM-5 with the highest CO conversion being 80%. Prospects for scaled-up production shall also be addressed.

OP-II-3

LEWIS ACID CATALYSTS FOR BIODIESEL PRODUCTION: FROM BENCH TO A PILOT PLANT

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We prepared different mixed oxides of the type $(Al_2O_3)_{0.8}(SnO)_{0.2-x}(ZnO)_x$ $(0.2 \leq x \leq 0)$, from the co-precipitation of aluminum, tin and zinc hydroxides followed by calcinations and extruded them into pellets. The pellets were placed into the tubular reactor as a 30 cm long column (2.65 kg). The reactor was flowed with soybean oil (168 g h^{-1}) and methanol or ethanol (89 g h^{-1}) with the temperature fixed at 100 °C. It was possible to transesterify soybean oil in up to 80 % yield when using methanol and 40 % when using ethanol. Increasing the temperature to 180 °C, it was possible to ethanolise soybean oil with yields up to 90 %. It is important to note that after a steady state is achieved the conversions remained constant with time. It is also worth to mention that the fixed bed remained active for more than 200 h, showing no catalyst leaching or deactivation, and so far was not possible to determine its overall productivity.

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CATALYTIC CONVERSION OF BIOETHANOL INTO HYDROCARBON FUEL

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Due to the increase in global consumption of hydrocarbon based fuels and decline in crude oil reserves, there is active ongoing research in finding an alternative to the traditional source of hydrocarbons – crude oil. In the last decade, as a result of the problems raised by global warming and the agreement reached by many countries at the Kyoto convention which limits the volume of carbon dioxide given off to the atmosphere, there has been a significant interest in renewable energy sources.

Using crude oil, coal and natural gas cannot reduce CO_2 emission, since, the carbon in these materials on combustion gives off carbon dioxide. The only, known way of absorbing atmospheric CO_2 is by photosynthesis; where carbon dioxide is converted and to carbohydrate in plants, which if processed can give a vast number of important products, one of which is bio-ethanol. Bio-ethanol can be produced by fermentation of starch or sugar that is found in the sap and fruit of plants. Industrial wastes are also raw materials for bio-ethanol production.

In many countries, bio-ethanol is used as fuel for internal combustion engines in its pure form and also as a mixture with gasoline. However in Russia and other cold parts of the world, using ethanol as a fuel is hindered by many factors; high hygroscopic nature of ethanol, social factors and absence of legislative acts on ethanol.

A promising way of processing bio-ethanol into different hydrocarbons is converting it over zeolite catalysts. An example of such process is the production of butadiene and synthetic rubber from ethanol over natural zeolites using the Lebedeev's method. As a result of the discovery of large crude oil deposits, ethanol was forced out of this process by cheaper cracking products. However with increase in crude oil prices, the process of obtaining 1, 3-butadiene from bio-ethanol seems more promising.

We have developed a technology, which allows for obtaining a wide range of hydrocarbons from the conversion of ethanol over zeolite catalysts. Depending on the reaction conditions, nature of the doping oxides and metals, and also the presence of a binder, the reaction equilibrium could be shifted towards formation of ethylene, olefins, alkanes or aromatic compounds which are important petrochemical products. Another possible way of converting ethanol is its steam reforming to hydrogen containing gas which could later be used in fuel cells for producing eco-friendly electro energy.

ORDERED MESOPOROUS MATERIALS ON COBALT BASED CATALYSTS FOR FISCHER TROPSCH SYNTHESIS

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Introduction

Synthetic liquid hydrocarbons are produced from syngas in the Fischer Tropsch Synthesis (FTS). There are a vast number of variables in the catalyst preparation procedure that influences the catalyst activity in the FTS. Due to their high surface area, many studies are now focusing on mesoporous silica. Thus, MCM-41, pore expanded PE-MCM-41, SBA-15 and PE-SBA-15 materials could combine large pores, high pore volume and high surface area that makes it suitable support for FT catalysts [1]. Supported cobalt is active for carbon monoxide hydrogenation, selective hydrogenation, hydrodesulfurization, dehydrogenation of alcohols, and is capable of activating C-H bonds in methane [2]. If the entire catalyst preparation cycle is taken into account, the interactions between silica and metal ions, either in solution or solid, can have an important influence on the reducibility of the metal and on the behavior of the finished catalyst. The approach is to analyze and identify the stages of the cobalt in the final catalyst and study the effect of the mesoporous material on the cobalt-silicate formation.

Experimental/methodology

The synthesis of the MCM-41 was carried out by the atrane route (the use of an atrane complex between alkoxide and triethanolamine ligand, in presence of cetyl trimethyl ammonium bromide as surfactant) in order to form homogeneous and ordered hexagonal mesoporous supports [3]. In order to expand the pores of initial MCM-41, a co-surfactant such as dimethyldecylamine were added during the synthesis and kept in the same conditions and MCM-41 [4]. The SBA-15 and PE-SBA-15 was carried out by sol-gel method. SBA-15 silicas were synthesized using Pluronic P123 triblock copolymer EO20PO70EO20 as a template and TIPB as a

micelle expander for PE-SBA-15. In most cases, the molar composition of the synthesis mixture was:
TMOS:P123:TIPB:NH4F:HCl:H_2O=1:0.0165:0.196:0.0290:4.35:183 [2]. The materials are structurally and chemically characterized. Various techniques such as, N_2 Physisorption, H_2-TPR, TEM, IR, EDAX, ATG are used to determine structure/catalytic activity of the different catalysts.

Results and discussion

This approach of preparation mode makes possible the obtention of materials with high specific surface area with various pore sizes of uniform size distribution. That is confirmed by the obtained characterization results. SEM picture (Fig.1) shows the homogeneous morphology of the support, while the crystallinity of the cobalt oxide is shown from the X-rays diffraction spectra (Fig. 2) for Co/Pe-MCM-41. TPR and other characterization methods show the formation of cobalt silicate species that makes the cobalt oxide hard to reduce. Besides, preliminary FT catalytic tests were made to study the relationship between structure and activity of the catalysts.

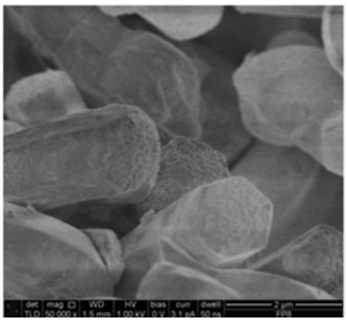

Fig.1. SEM images for MCM-41

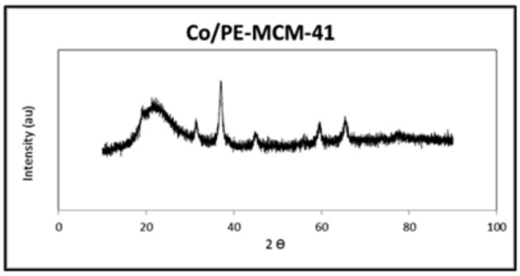

Fig.2. XRD spectra for of Co/PEMCM-41

Conclusions

An interaction of an oxidized form of cobalt with silica results in the inactivation of a portion of the cobalt. Based on TPR results in the literature, the proximate cause of the inactivation is probably irreducibility of the cobalt ions. On the other side, there is several ways to form cobaltsilicate species that affect the reducibility of the cobalt at relatevily low temperature. We explain the effect of pore diameter and surface area of the mesoporous silica on the cobaltsilicate formation in the final catalyst.

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OP-II-6

NICKEL-SUBSTITUTED Ba-HEXAALUMINATES AS CATALYSTS IN STEAM-REFORMING OF TARS

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Gasification of woody biomass converts the solid organic material into a gaseous product with a higher energy value and by this mean provide a more carbon neutral gaseous fuel than the common fossil ones. The produced raw gas mainly contains H_2, CO, CO_2, CH_4, H_2O and N_2 together with organic (tars) and inorganic (alkali) components and fine particulates. The amount of impurities in the raw gas is dependent of the fuel properties and the gasification process technology and the quality of the resulting product gas determines its suitability for more advanced purposes. One of the major general concerns within the gasification processes is the formation of tars. Tars are a vast group of polyaromatic hydrocarbons and there are a number of definitions. On an EU/IEA/US-DOE discussion meeting in Brussels 1998, a number of experts agreed on a simplified classification of tars as “all organic contaminants with a molecular weight larger than benzene” [1].

The aim of this work is to investigate the steam reforming ability of a catalytic material not previously tested in this type of application in order to achieve an energy-efficient and high-quality gasification gas. The physical demands for an optimal tar-cracking and steam reforming catalyst is a high surface area, thermal stability, mechanical strength and a capacity to withstand high gas velocities, poisons such as H_2S or NH_3 and other impurities. Additionally it has to resist the process steam, as steam is well known to enhance sintering of porous materials. Nickel is a familiar catalyst for steam reforming. Hexaaluminate is a well-known catalyst support with properties that may answer to the requests of a non-abrasive, high-temperature stable and steam-resistant catalytic material. It is a structural oxide where the general formula for the doped unit cell is MIMII(x)Al12-xO19-δ where MI represents the mirror plane cation and MII is the aluminum site in the lattice where substitution may occur. MII is often a transition metal ion of the same size and charge as aluminum. MI is an ion located in the mirror plane of the structure and it is a large metal ion, often from the alkaline, alkaline earth or rare earth metal group. The stability and activity of these materials are often being related to the properties of MI and MII. The activity is highly dependent on the nature of the Al-substituted metal and partially by the nature of MII [2]. In our experiments we have tested the catalytic capacity of Ni-substituted Ba-hexaaluminates synthesised by the sol-gel method [3], both in a model set-up and in a gasification plant. In the lab-scale set-up different catalyst-formulae was tested under various temperatures for reforming of methyl-naphthalene. The results show a good catalytic activity for tar-breakdown. As expected the substitution level of Ni is clearly coupled to the reaction temperature. With the most highly substituted Ni-Ba-hexaaluminate at 900 °C all of the methyl-naphthalene has been broken down together with all of the resulting hydrocarbons.

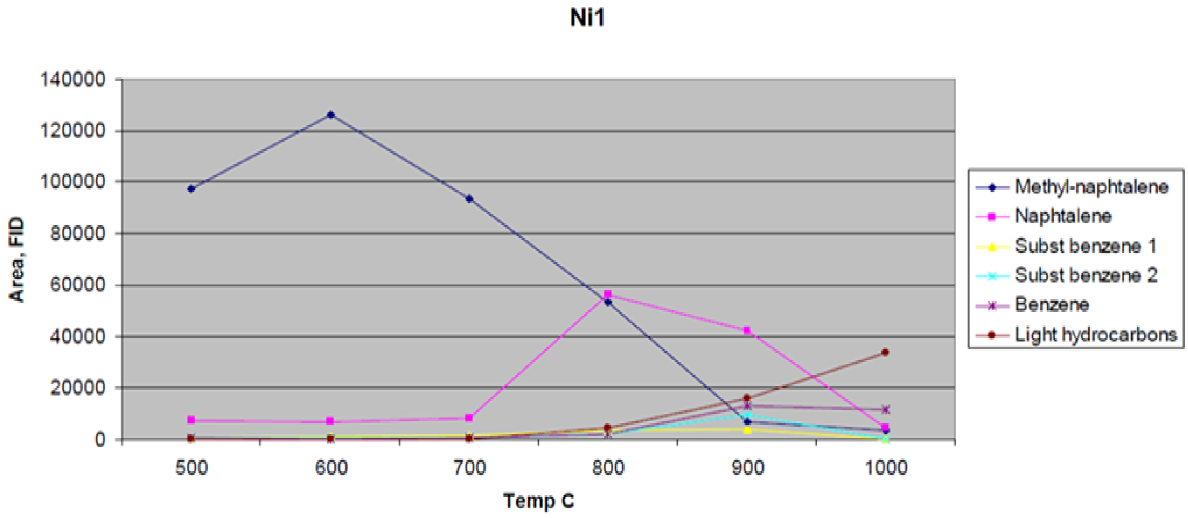

Fig. 1. Amount of Me-naphthalene and its decomposition products as a function of reactor temperature in one of the tested catalysts.

The Ni-Bahexaaluminate catalyst has recently also been tested in real process-gas. These results are still to be evaluated, but indicate a positive result.

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OP-II-7

CATALYTIC SYSTEMS FOR CLEAN HYDROGEN PRODUCTION ON THE BASE OF MOLYBDENUM CARBIDE

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Refractory metal carbides can be used in various branches of engineering due to their unique combination of chemical and physical properties. Nowadays, there are a lot of methods for refractory metals carbides synthesis. High-temperature electrochemical synthesis in molten salts is a very promising, because it can considerably reduce the technological scheme for production of powders and coatings of these compounds. The aim of this study is the development of refractory metals carbides coatings for the catalytic application.

The first goal of this study was the electrochemical synthesis of molybdenum carbide coatings on molybdenum and graphate substrates. Synthesis was carried out by galvanostatic electrolysis in an equimolar NaCl-KCl mixture containing 0.92 wt. % of Li_2CO_3 and 5 wt. % of Na_2MoO_4 at stoichiometric ratio of Mo/C = 2:1. Different types of molybdenum substrates were used: a) straight plates of 100 mm length, 10 mm width, with a thickness of 100 μm; b) crimped plates of 1.4 mm crimping height and with the same other dimensions; c) wire of 100 mm length and 250 μm diameter. The graphite granules with diameter 1-2 mm and a specific surface area 430-450 $m^2\ g^{-1}$ were used as a substrate too. Synthesis of Mo_2C on the molybdenum and graphite substrates was performed at 1123 K for 7 h with a cathodic current density of 5 $mA\ cm^{-2}$. The glassy carbon crucible served as anode.

The Mo_2C/Mo composition was tested as a catalyst in the water-gas shift reaction (WGS). The steady-state reaction rates for the Mo_2C/Mo coatings were higher than those for the bulk Mo_2C and commercial $Cu/ZnO/Al_2O_3$ catalysts over in the temperature range explored. The catalytic activity is enhanced by at least three orders of magnitude comparing to that of the pure Mo_2C phase. The methanation reaction was completely suppressed in the whole temperature range studied on the Mo_2C/Mo coatings. The catalytic activity remained constant during 5000 hours on-stream. The coatings were also stable during the thermal cycling, while the activity of commercial catalysts tends to decrease with time. The coatings were also tested under WGS conditions in presence of hydrogen sulphide. It was found that the H_2S does not affect on the activity, stability and selectivity of the catalyst.

The second goal of our investigation was to promote molybdenum carbide by nikel or cobalt. The synthesis of double molybdenum and Ni/Co carbides and Ni/Co promoter molybdenum carbides was carried out in two stages. First one was the preparing of molybdenum and nickel/cobalt alloys by two ways: electrolysis at a cathodic current density of 5 mA/cm^2 in the NaCl–KCl–Ni(Co)Cl_2–Ni(Co) melt (anode is metallic Ni(Co)), at a temperature of 1123 K, process time of 1 h; currentless transfer in the NaCl–KCl–Ni(Co)Cl_2–Ni(Co) melt at the same temperature and time. At the second stage the prepared molybdenum and nickel/cobalt alloys were carbonized. Carbonization was performed by electrolysis in an equimolar mixture of sodium and potassium chlorides containing carbonate ions (5 wt % Li_2CO_3) during cathodic polarization of a sample at a current density of 5 mA/cm^2. Carburizing in molten salts of these alloys led to the formation of double carbides, such as Ni_3Mo_3C, $Co_6Mo_6C_2$, Co_6Mo_6C, Co_3Mo_3C. It was found that in all cases of synthesis Mo_2C phase presents in the coatings.

OP-II-8

COMBUSTION OF SEWAGE SLUDGE INCLUDING MUNICIPAL WASTE IN FLUIDIZED BED OF CATALYST

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Solid wastes of chemical, petrochemical, pulp and paper industries and municipal economy represent a complicated mixture of various organic compounds, which often contain nitrogen, sulfur, halogens and metals. The amount of inorganic ash remains in the wastes can attain sometimes 30 wt.% and more. Large amount of wastes is formed as a raw biomass (active sludge) during biological purification of various sewages.

Nowadays, sewage sludge is utilized almost by burying or detoxication. The most universal way of their detoxication is the fire method involving oxidation, thermal decomposition and other chemical conversions taking place in the high-temperature products of fuel or wastes combustion. To provide the stable burning, the temperature of flue gas is to be maintained not below 1200-1300 °C. Thus, here the special construction materials of furnaces and the high consumption of additional fuel are required. The presence of easily melted mineral compounds hampers the produced ash removal. Also, there are such problem as the atmosphere pollution by nitrogen and sulfur oxides and by toxic compounds such as benzopyrenes and dioxins.

Combustion of such fuels in fluidized bed of catalyst holds great promise. In this case, the temperature of complete combustion can be lowered to 500-700 °C. Size and metal capacity can be reduced by more than 20 times. At moisture content less than 75% the process can be carried out in autothermal regime. As a result, the erosion of heat exchangers inserted in the bed decreases as well as requirements for the construction materials. Unlike the bed of inert material, here combustion is totally localized in the bed and is not extended to space over the bed. As a consequence, the apparatus sizes can be significantly reduced. The use of catalysts enables to increase the efficiency of combustion and processing of solid fuels and wastes. Also this technology allows us to eliminate or minimize the formation of toxic pollutants and to achieve a high degree of sewage purification from the dissolved and suspended matter.

CATALYTIC CONVERSION OF METHANOL TO LIGHT OLEFINS-GASOLINE-AROMATICS OVER H-ZSM-5 CATALYSTS AND DEVELOPMENT OF THE CATALYST ACTIVITY, SELECTIVITY AND CONVERSION USING ACTIVE METALS

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Methanol synthesised form biomass and other renewable resources is not only a valuable product as fuel, but a good feedstock for beneficial products. Recent years, many new catalytically developed precesses are proposed by scientists to to produce evaluated products as Gasoline or Light Olefins from methanol. One most polular process called MTO, was designed and operated using H-ZSM-5 catalysts to produce light olefins as main and Gasoline as by-product. During this research, best optional and beneficial opeartional condition consists of water dilution, WHSV and temperature was discovers by reactor tests first of all. Then synthesised catalyst was promoted by 7 main metals to achieve best production amount of desired hydrocarbones, using Wet-Dry Ultrasonically developed procedure. Main products of this process in gas phase can be limitted to C2 and C3, also toluene and xylenes in Liquid phase. By an effictive promotion, products can be qualified enough to conlcude a final promoted catalyst. Reaction test pilot was consists of 3 parallel reactors, one accurate dilution control system and 3 Gas Chromatographs. Therefore products are analyzed with the highest callibration lets us to detect and measue amount of 14 gas and 12 liquid fractions components. Also, it should be declared that all promoted catalysts were tested under specified operational condition, gained from previous step. Mainly 40-59 wt% dilution and 400-425 °C.

Acknowledgements

Petroleum University of Technology Gas Engineering Reasearch Center

Petroleum University of Technology Gas Engineering Faculty

Bandar Imam Petrochemical Company (B.I.P.C)

DEHYDRATION OF BIOETHANOL OVER BLOCK CATALYSTS WITH HONEYCOMB CHANNELS

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Plant biomass is a renewable raw material, its annual growth exceeds mined fossil raw materials. Now in the world an important and urgent problem is complex and deep processing of plant materials to produce valuable chemical raw materials and products for fuels. Last time the main process of plant raw materials is the production of ethanol, used as a motor fuel. However, the use of bioethanol as a fuel is complicated by the need to change the design of engines and the limited use in cold regions, particularly in Kazakhstan. This work is devoted to the catalytic dehydration of ethanol to biobutanol, which is also a motor fuel.

The advantage of biobutanol to bioethanol is no water absorption, so it can be used at any time of the year as an additive to gasoline and diesel fuels. Production of biobutanol by biological way meet certain technical difficulties. The most effective way of the synthesis of biobutanol is catalytic processing of bioethanol.

New block nickel-molybdenum catalysts with honeycomb channels based on heat-resistant steel, coated by secondary carrier – alumina with the addition of zeolites (NaY and NaX) has been developed.

The raised mechanical durability of the basis allows to eliminate isolating a lining between the case and a substrate and by that to reduce diameter of the case by 15 %. Thanks to a small thickness, the substrate design can be executed in such a manner that effective cross-section section considerably above, than at use of a ceramic material: appreciable decrease in hydraulic resistance is thus reached also.

Developed method of preparation of the honey comb carrier allowed to prepare continuous sheet block carriers of various type of the size.

The experiment was conducted in a flow set in the temperature range 300-600 °C at atmospheric pressure and the volume rate of 1-1.5 h^{-1}. The catalysts have been investigated by electronic microscopy, IR-spectroscopy. Uniform distribution of the active components of the surface of the corrugated carrier was shown. The particle size of the catalysts prepared from acetate solutions is 50-60 nm, while obtained from chloride solutions particle size is 200-300 nm. In the studied conditions the conversion of ethanol is upto 45%, and the yield of butanol – 38-40%.

OP-II-11

DEVELOPMENT AND TESTING OF NOVEL STRUCTURED CATALYSTS

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Structured metallic supports are currently found in catalytic converters for vehicles and similar, with a trend being towards the use of these in packed bed reactors to replace the pelleted catalyst structure [1]. Whilst the metal support offers exceptional heat transfer, the use of the system is currently limited due to surface adhesion issues. However, optimization of the wash-coat approach presents a possible solution to the issue, ensuring greater surface adhesion through the use of a platelet substructure formed by thermally oxidising FeCralloy rods [2 - 4].

In this work, 0.5mm diameter FeCralloy® rods were calcined at 950 °C for 10 hours, forming a γ-Al_2O_3 surface with high porosity and surface area. This structured layer acted as an anchor to bind additional coatings of alumina via dipcoating the rods in an alumina slurry, thereby improving the layer thickness and increasing adhesion of the catalytic surface. The alumina slurry used was a dispersion of γ-Al_2O_3 (d=5 μm, PURALOX®, *supplied by Sasol*) in HNO_3. Coated samples were calcined in a furnace at 650 °C for 2 h, following which SEM and EDX were utilized to determine the surface morphology and composition. Further characterization of the alumina phase by XRD was conducted, and finally Platinum was loaded onto the prepared support by wet impregnation, with the catalyst tested under a range of operating conditions in a dehydrogenation rig – as shown in table 1.

Table 1: Range of Operating Conditions

Operating Variable	Unit	Value Range
Temperature	°C	300-400
Pressure	bar	1-9
MCH flowrate	$cm^{-3}hr^{-1}$	3-6
H_2 flowrate	$cm^{-3}min^{-1}$	70-200
H_2/MCH ratio		0-9
WHSV	hr^{-1}	0.2-0.5

SEM analysis revealed platelet-like morphology on the surface of the FeCralloy® rods indicating the formation of the desired γ-Al_2O_3 subsurface following thermal oxidation, with the alumina coated samples (post calcination) possessing a uniform adherent coating with a thickness of ~6 μm, which remained intact following catalytic testing. This was clarified by SEM analysis post catalytic testing.

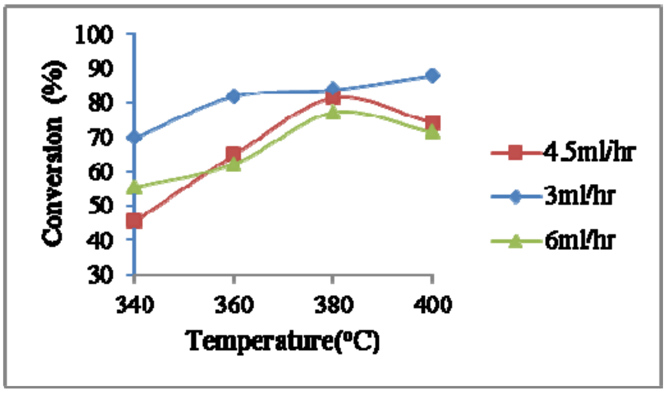

Figure 1. Conversion of 1% Pt/γ-Al_2O_3/FeCralloy® Versus Temperature at V(MCH)=3-6 cm^{-3}hr^{-1} P=1 bar WHSV=0.24-0.49 hr^{-1}

High conversion (fig. 1) of MCH during dehydrogenation testing was achieved using the FeCralloy® rods, with the reaction showing increased selectivity (>99%) towards the formation of toluene and significantly improved conversions at higher temperatures and reduced temperature drop across the reaction bed. The developed supported catalyst proves to be highly beneficial where improved heat transfer across the catalytic bed is required, to avoiding the formation of hot or cold spots and thus improving the conversion and kinetic interpretation.

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ORAL PRESENTATIONS

SECTION III

Catalyst application for clean syn-gas and clean hydrogen production

BIOMASS DERIVED FORMIC ACID FOR CLEAN HYDROGEN PRODUCTION VIA DECOMPOSITION OVER K-DOPED Pd CATALYSTS

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The Carbolea research group of the University of Limerick is involved in creation of technologies for biomass conversion to valuable products via gasification, pyrolysis and hydrolysis. Acid catalyzed hydrolysis of biomass gives levulinic acid, furfural, char and formic acid. Development of this technology may lead to the necessity of new ways for utilization of the hydrolysis products. Formic acid being an important chemical can be used in hydrogen production via decomposition and in hydrogenation of biomass derived products. Noble metals are known as good catalysts for these reactions. The present research was aimed to the development of catalysts for hydrogen production from formic acid and to the understanding of promoting effect of alkali metal ions which give a very significant improvement in the rates of this reaction.

Alkali carbonates were deposited on a Pd powder and 1 wt.% Pd catalysts supported on C, Al_2O_3 and SiO_2 by incipient wetness impregnation using ultrasonic agitation. The materials were heated in a 1% H_2/Ar mixture at 573 K for 1 h and then cooled in He to reaction temperature. The reaction products were analyzed by gas chromatography. The catalysts were characterized by EDS/TEM, XRD, DRIFTS, XPS and CO chemisorption as well as by BET surface area measurements. Full experimental details are given elsewhere [1,2].

Fig. 1 shows the conversions of formic acid as a function of temperature for the undoped and doped catalysts. It is seen that the K doping leads to a strong shift of the conversion curves to lower temperatures and to a considerable enhancement of the rates at a constant temperature. The best results were obtained for the Pd/C catalyst with optimized K content – 10 wt.%. The improvement reached 10-100 times depending on the temperature. The value of activation energy changed from 65 kJ mol^{-1} for the undoped catalyst to 97 kJ mol^{-1} for the doped samples with 2 and 10 wt.% of K indicating a change of the reaction mechanism with K doping.

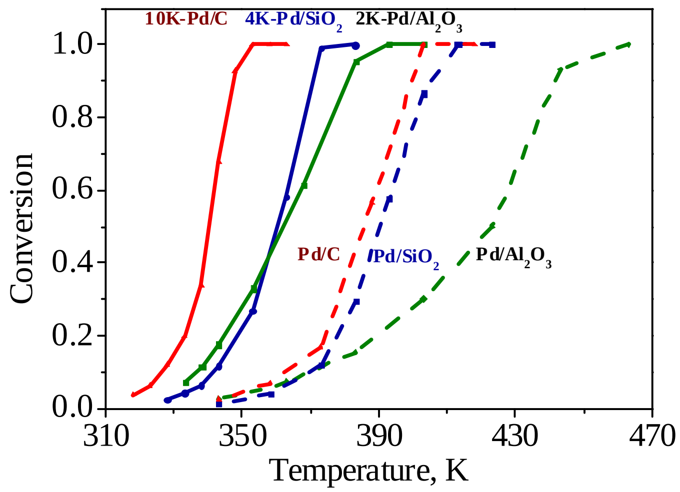

Fig. 1. Conversion of formic acid over undoped and K-doped Pd catalysts containing 0.68 mg Pd (2 vol.% HCOOH/He, 51 ml min^{-1})

A stability test of the Pd/C catalyst with 10 wt.% K for 22 h of operation at 343 K indicated that the catalyst gave a steady conversion of 63-66% with an excellent selectivity (>99.8%,<30 ppm of CO); the reaction system thus approached the demands for CO-free hydrogen production for fuel cell applications.

Under the same conditions a K-doped C support showed no activity. Doping of a Pd powder by K ions also led to an increase of the catalytic activity, but the change (<10 times) was lower than that for the Pd/C sample. Potassium was the best promoter for the Pd/C sample as compared to other alkali metals; the sequence of conversions was: K≥Cs>Na>Li>undoped. EDS/TEM and XRD data indicated that K ions at concentrations lower than 10 wt.% were uniformly distributed over the Pd/C catalyst surface. At higher concentrations, inactive crystallites of K salts were also formed. Although TEM showed that the mean Pd particle size did not change, the CO chemisorption values decreased by a factor of 1.5, indicating that the K ions are located not only on the surface of the carbon but also on the Pd particles. We conclude that K formate species dissolved in a formic acid/water liquid formed in the catalyst's pores are the intermediate species on the K-promoted samples. These species provide improved hydrogen generation by decomposition on Pd sites via the reaction:

$$KHCOO + H_2O_{ads} \rightarrow H_2 + KHCO_3$$

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SYNGAS PRODUCTION BY BIOGAS REFORMING OVER THE Co-BASED MULTICOMPONENT CATALYSTS

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Biogas containing mainly methane and carbon dioxide in amount 50-87 and 13–50 % respectively represents itself a ready feedstock for dry reforming of methane. Dry reforming of methane is an elegant way for utilizing both greenhouse gases – carbon dioxide as well as methane, with producing syngas according to the reaction: $CH_4 + CO_2 \rightarrow 2CO + 2H_2$. The main efforts in this direction are directed to creation of the effective and coke resistant catalysts.

In the work, the model biogas with varying content of CH_4 and CO_2 from 50-75 and 25-50 % respectively have been used for dry reforming. In bireforming, biogas composition has been corrected by adding water steam in amount of 10-40 vol. % to get the reactive source with necessary atomic ratio of C/O~1/1. The bimetallic and multicomponent Co-based catalysts supported on alumina have been used in both dry reforming and bireforming of methane. The processes were carried out at a flow quartz reactor under conditions: atmospheric pressure, space velocity – 1000 hr^{-1} and varying temperature from 300 to 800°C. The gaseous initial and final reaction products have been on-line analysed by the gaseous chromatographs. The catalysts were studied by electron microscopy, BET, X-Ray analysis.

The complete methane conversion has been observed over all the catalysts at P=0.1MPa, T<800°C and space velocity – 1000 hr^{-1}. Complete carbon dioxide conversion occurs at using biogas with content of CO_2 is less than 50 %. Synthesis gas with a ratio of $H_2/CO>1.0$ is a main product of dry and bireforming of biogas. Higher content of CO_2 in a feed facilitates methane conversion. Adding water steam in a feed leads to higher yield of hydrogen in syngas produced.

The catalysts show the stable activity during all period of their exploitation (100 hours).

Acknowledgements

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ENHANCED ACTIVITY OF PLATINUM-BASED BIMETALLIC CATALYSTS IN AQUEOUS PHASE REFORMING OF GLYCEROL

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Aqueous phase reforming (APR) of biomass-derived compounds such as sugars and polyols (e.g. glycerol) is an attractive process to generate hydrogen (for fuel cells and biorefineries) and useful chemicals at low temperatures and mild pressures [1]. APR involves the dehydrogenation of the feed molecule followed by C-C cleavage and subsequent water-gas shift (WGS) reaction to yield H_2 and CO_2. Another reaction path involved in the APR mechanism is the cleavage of C-O bonds and formation of alcohols/alkanes through subsequent hydrogenation [2]. Recently, PtRe catalysts have been found to give enhanced activity and stability in APR when compared to the conventional Pt/C catalyst [3]. However, the role of the alloy and the nature of the active sites are not fully understood yet. This work aims at providing a thorough understanding of the Pt-Re synergy by a combined experimental and theoretical approach.

A series of Pt-Re catalysts supported on carbon with varying Re:Pt ratios (0.5-5) were synthesized by pore volume impregnation. In addition, a second series of PtRe catalysts supported on reducible oxide supports (ceria, zirconia, ceria-zirconia and titania) were also prepared. The samples were extensively characterized. HRTEM and EXAFS data show that the particle size of the PtRe alloy becomes smaller with increasing Re content. Overall activity in APR of glycerol was significantly increased in the presence of PtRe catalysts when compared to monometallic Pt catalysts (Fig.1a). For the carbon supported samples, activity increased with Re content. The higher ratio of C-O/C-C bond cleavage products is thought to be due to an increased rate of dehydration which is consistent with indications of acidity generation from NH_3-TPD measurements of steamed samples. In addition, our results in acetaldehyde decomposition showed that C-C bond cleavage is also enhanced on PtRe catalysts.

The WGS reaction is an important step in H_2 production in the APR reaction mechanism, as it removes strongly adsorbed CO from Pt sites. PtRe catalysts show increased activity in WGS when compared to the Pt-loaded samples (Fig.1b). Since the reducible oxide supports promote water activation, the Pt-loaded samples in those cases are already much more active than Pt/C. Another interesting finding of our studies is that Re/C is more active in the WGS reaction than Pt/C.

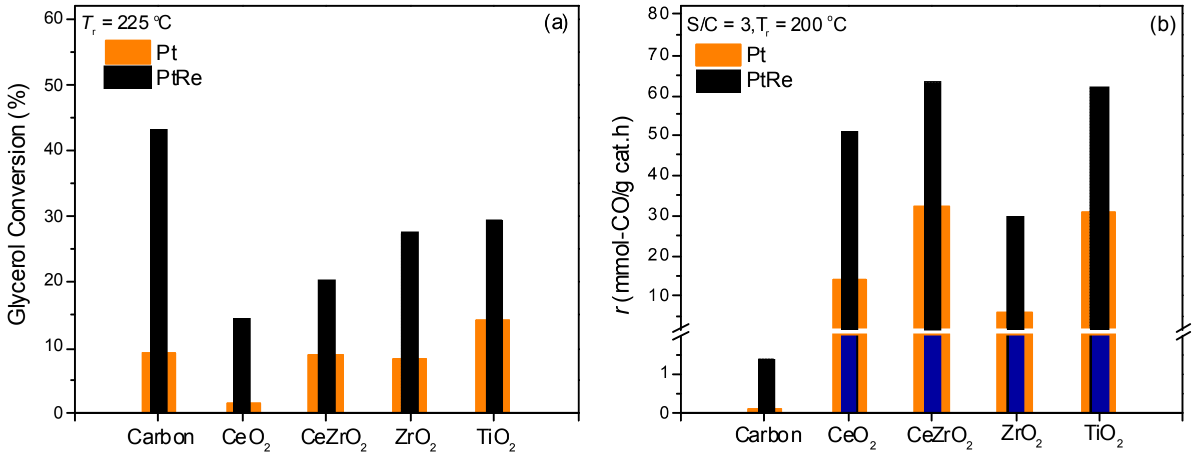

Figure 1. Activity of Pt and PtRe catalysts supported on carbon and reducible oxide supports in (a) APR of glycerol and (b) WGS.

As water dissociation to OH and O intermediates needed for the WGS reaction is endothermic for Pt, we hypothesized that the role of Re is to facilitate the dissociation of water. Our computational studies for water dissociation on close-packed Pt and Re surfaces show that the formation of OH and O intermediates is endothermic on Pt. Although the activation barriers for the water dissociation steps are not very different between Pt and Re, O and OH formation on Re is exothermic, implying that their steady-state coverages are higher. Based on a microkinetic model of PtRe alloys we find that their higher WGS activities derive from high steady-state coverages of OH and O on Re surface sites and of CO on Pt sites.

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STEAM REFORMING OF BIO-OIL MODEL COMPOUNDS

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Introduction

Steam reforming (SR) of water-soluble bio-oil fractions can be used to produce sustainable hydrogen or synthesis gas, either as stand-alone unit or as part of bio-refinery, where bio-oil is catalytically upgraded to transportation fuels through hydrodeoxygenation [1, 2]. One of the main problems in SR of bio-oil is carbon deposition and subsequent short lifetimes of the catalysts [2]. One option could be to phase separate the bio-oil by adding water, which yields an aqueous phase with a S/C-ratio of 6-8 [2] suitable for upgrading through SR, and an organic phase, which can be used for production of fuels or chemicals. In this work the SR of model compounds of the aqueous phase of bio-oil will be investigated to elucidate reaction mechanisms, differences in reactivity, and deactivation.

Materials and Methods

SR of ethanol, acetic acid, acetone, acetol (hydroxyacetone), 1-propanol, and propanal was carried out in a laboratory scale quartz reactor. A mixture of water and oxygenate was pumped to an evaporator operated at 300 °C and fed to reactor. The feed composed of approx. 2-3 vol % oxygenate 37 vol % H_2O, and N_2 as balance. Analysis of the effluent gas was conducted with a Variant GC 3800 and a Karle GC. The catalyst, 8 wt% Ni on $MgAl_2O_4$, was prepared by incipient wetness impregnation using $Ni(NO_3)_2$ followed by drying at 110 °C and calcination at 800 °C for 2 *h*. The catalyst was reduced in-situ at 600 °C for 1 *h* in 50 % H_2 in N_2.

Results and Discussion

Steam reforming of ethanol, acetic acid, acetone, acetol, 1-propanol, and propanal was investigated over Ni/$MgAl_2O_4$ at temperatures between 400-700 °C and at 600 °C with varying W/F. Dehydration and dehydrogenation was found as major side reac-tions for alcohols, while for acetol selfcondensation yielding cyclic compounds was observed, and for acetic acid ketonization forming acetone was observed. The side reactions mainly occurred at temperatures below 600 °C and were most pronounced for acetol, where a yield of by-products of 75 % and 50 % was observed at 400 °C and 500 °C, respectively. The product distribution as function of temperature in SR of propanol at S/C of 6 can be seen in fig. 1. Products included propene, ethene, and propanal at low degrees of conversions. The yield of C_2 and C_3 hydrocarbons decreased as the conversion increased while the yield of CH_4 increased and had a maximum at 600 °C. At this temperature the yield of larger compounds was negligible. The yield of H_2 increased with temperature for all of the model compounds. Decreasing W/F had the same effect as decreasing the temperature e.g. increasing the yield of byproducts, decreasing conversion and yield of H_2.

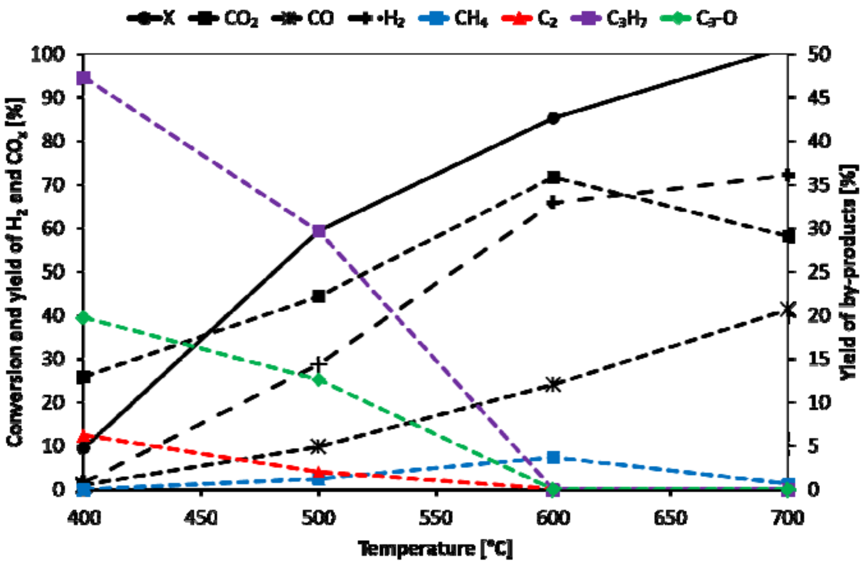

Figure 1: Conversion and yield of H_2, CO, CO_2, CH_4, and C_2H_4, C_3H_7, and propanal as function of temperature in SR of propanol. 8.0 wt% Ni/$MgAl_2O_4$, S/C=6.0, m_{Cat}=50 mg, Flow=230 NmL/min, x_{PO}= 2 %, x_{H2O}= 37 %, N_2 as balance.

In the SR of acetone only C_1-species were observed as products, while C_2 and C_3-species were formed in SR of compounds with terminal oxygen groups, e.g. 1-propanol and propanal. Based on these results, it appears that the mechanism for SR of oxygenates was adsorption of the oxygenate through the oxygen followed by sequential cleaving of C-C-bonds. Carbon deposition was especially pronounced during SR of alcohols, which was due to a large production of ethene and propene as these are coke precursors.

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PILOT SCALE DEMONSTRATION OF BIOMASS SYNGAS CLEANING VIA CATALYTIC REFORMING

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Catalytic conditioning of biomass-derived syngas by tar and hydrocarbon steam reforming has been studied on catalysts developed at NREL [1-3]. Supported nickel-based catalysts with various promoters have been the most widely studied class of materials and generally show good initial activity, but are susceptible to deactivation from contaminants in raw syngas, such as hydrogen sulfide, ammonia, hydrogen chloride, tars, and other trace contaminants. These impurities require removal, usually through catalytic conditioning, in order to produce a quality syngas for end-use synthesis of liquid fuels such as ethanol and hydrocarbon fuels. Reforming the hydrocarbon contaminants in raw syngas to additional syngas results in higher carbon utilization of the biomass feedstock and requires that the catalyst be able to reform recalcitrant olefins and methane, which can make up to 20 vol% (dry basis) of biomass-derived syngas. To complete the U.S. Department of Energy Biomass Program's 2012 demonstration of cellulosic ethanol production via indirect gasification, a 1000 kg batch of tar reforming catalyst was synthesized and used for conditioning biomass-derived syngas in the integrated ethanol synthesis demonstration run. The work reported here describes the pre- and post-use physical and chemical properties of the NREL reforming catalyst during 200 h of use for conditioning oak derived syngas.

Fluidized catalyst preparation is described in previous work [2, 4] and the circulating fluid bed reformer used to clean raw syngas is described in [1]. Pre and post use catalyst characterization was conducted with sulfur K-edge XANES (performed at the Stanford Synchrotron Radiation Lightsource); XRD, TPR and TRP, SEM/EDS, ICP and C and S analysis were conducted with NREL instrumentation as was particle size and surface area. Catalyst samples were taken as a function of time on stream and assessed for regenerability in laboratory scale microactivity tests systems described in [2]. A typical oak syngas composition contains on average and in mol%: 36% H_2, 13% CH_4, 19% CO, 26% CO_2, 3% ethylene, with the remaining 3%

comprised of 2% helium as trace, ethane propylene, propane, ethane and acetylene. H_2S content ranged from 18-39 ppmv.

The reforming catalyst was used continuously for 200 h of syngas conditioning. Activity for tar reforming remained at > 99% conversion though methane dropped to a steady state conversion of 20% during the run. Previous work showed that gas phase sulfur species reaction with the nickel catalyst surface causes the reduction in methane reforming activity. To identify surface sulfur nickel compounds and assess regeneration extent, post-reaction and regenerated catalysts were analyzed using sulfur X-ray absorption near edge spectroscopy (XANES) to determine i) if or how much sulfur remained on the catalyst following regeneration and ii) if so, what chemical state(s) of sulfur was present on the catalyst. Post-reaction catalysts showed the presence of sulfides on H_2S-poisoned sites. Although H_2S was observed to leave the catalyst bed during regeneration, sulfur remained on the catalyst and a transformation from sulfides to sulfates was observed. XANES spectra showed these transformations on the fresh, post-reaction, regeneration, and regenerated-then-reduced catalysts. These results are significant as they show that residual surface sulfur cycles between nickel sulfide and sulfate forms in a recirculating bubbling bed reformer with continuous contact of catalyst and syngas. We found that reducing contact time of catalyst with these species by using a recirculating regenerating reformer with short contact time improved regenerability by reducing sulfate formation.

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Ni(Co)-CONTAINING CATALYSTS BASED ON PEROVSKITE-LIKE FERRITES FOR STEAM REFORMING OF ETHANOL

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Catalytic steam reforming (SR) as the main pathway to produce hydrogen from alcohols and other oxygenates derived from fast pyrolysis of biomass is a perspective trend nowadays. The main problem in SR of all oxygenates is heavy coking of Ni-containing catalysts which are the most suitable for the practical application due to their low cost [1-2]. The use of perovskites as catalysts precursors or supports is a promising approach to develop highly active and stable to coking catalysts. In this work, the effect of the preparation method and composition of catalysts based on perovskite-type ferrites on their structural, morphological, redox features and performance in ethanol steam reforming (ESR) has been studied.

Two series of the catalysts based on praseodymium ferrite were prepared and tested in (ESR). The first series was Ni(Co)-containing $PrFe_{1-x}Ni(Co)_xO_3$ (x=0.3-0.4) perovskites prepared by modified Pechini route followed by calcination at 900°C and the second one was 5%wt.Ni(Co)/$PrFeO_3$ prepared by impregnation of $PrFeO_3$ calcined 700 and 900°C) and with nickel acetate or cobalt nitrate followed by drying and calcination at 500°C. In the second series the catalysts were modified by supporting of 5%wt. Mo on the oxidized or reduced samples.

Catalysts were characterized by XRD, BET, TEM with EDX and H_2 temperature-programmed reduction (TPR). ESR was carried out over 0.25-0.5 mm catalysts fraction in a plug-flow reactor in the temperature range of 500-800°C, 0.02-0.07 s contact time in the feed of 10% C_2H_5OH+40% H_2O, N_2 – balance and in the real feed of 30% C_2H_5OH+60%H_2O+10%N_2 at 700°C, contact time 0.1s.

The BET surface area of all catalysts is 7-15 m^2/g being typical for such systems. According to XRD data, initial samples of the first series mainly contain the perovskite phase of orthorhombic structure with minor admixtures of NiO in some cases. Reduction of perovskites in the H_2 flow or reaction mixture leads to segregation of Ni(Co)-Fe alloy with the perovskite phase being remained at 600°C and partially decomposed at 800°C. The starting catalysts of the second series are comprised of Ni(Co) oxides and unchanged $PrFeO_3$. For Mo-doped catalysts, there are no reflections of Mo or mixed Ni(Co)Mo oxides in XRD patterns. However, the formation of mixed NiMo oxides has been evidenced by TEM with EDX and H_2-TPR data: the shift of the low-temperature peak assigned to reduction of NiO to high temperature is observed.

The testing of the catalysts in ESR shows that Ni-containing catalysts are more active than Co-based samples. At temperatures above 700°C, for all catalysts, the main products are hydrogen and CO. At temperatures below 700°C, the ethanol conversion and the hydrogen yield are higher for supported catalysts as compared with ones derived from Ni(Co)-containing perovskites. Selectivity of products depends on the composition and preparation method of the catalysts influencing Ni(Co) state and dispersion. Thus, for catalysts formed from $PrFe_{1-x}Ni(Co)_xO_3$, the presence of acetaldehyde at 600-650°C and the only trace concentration of ethylene evidence that the main route of ESR reaction over these catalysts is the dehydrogenation of ethanol. For 5%wt.Ni(Co)/$PrFeO_3$ catalysts prepared by impregnation, selectivity and ethanol conversion are defined by Ni dispersion and Mo addition. The catalyst 5%wt.Ni/$PrFeO_3$(900°C) of low Ni dispersion providing the high ethanol conversion below 600°C simultaniously shows high H_2, CH_4 and CO_2 selectivity whereas C_2H_4 is not detected in all temperature range indicating dehydrogenation route of ESR. In the case of the catalysts 5%wt.Ni/$PrFeO_3$(700°C), higher dispersion and addition of Mo leads to appearance of C_2H_4 showing some share of ethanol dehydration route in ESR. Mo addition only slightly influences on activity and stability of Ni/$PrFeO_3$(700°C): according to TEM with EDX, formation of NiMo carbides or alloy are not formed under ESR conditions. The long-time tests and TEM study of used catalysts show that perovskite derived catalysts due to formation of Ni(Co)-Fe alloy particles strongly interacting with parent perovskite matrix have higher coking stability than perovskite supported ones.

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ORAL PRESENTATIONS

SECTION IV

Catalytic Processes in Oleochemistry

SIMULTANEOUS ESTERIFICATION AND TRANSESTERIFICATION FOR BIODIESEL SYNTHESIS WITH MOLYBDENUM OXIDE CATALYSTS

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INTRODUCTION

Biodiesel yet cannot compete with petro-diesel from an economic point of view because of its high production costs. This cost can be significantly reduced by using cheaper feedstock, *e.g.* used cooking oil or animal fats. However, these raw materials content high levels of free fatty acids (FFAs) that deactivate forming soaps the basic homogeneous catalysts used in industry. Heterogeneous acid catalysts can simultaneously convert FFAs and triglycerides into methyl esters, *i.e.* biodiesel. However, acid-catalysed transesterification needs higher temperatures than the basic-catalysed one. In this work, three samples of molybdenum oxide have been evaluated as acid catalyst into the simultaneous esterification and transesterification process using methanol.

EXPERIMENTAL

The molybdenum oxides studied consisted in a commercial material (Sigma-Aldrich) and two synthesised samples. Ammonium heptamolybdate (AHM) was employed as the molybdenum source in both synthesis methods. AHM was dissolved (0.1 M) in deionised water and, in the first method, HNO_3 (3.0 M) was used as precipitation agent. After drying and calcination, molybdenum oxides were obtained and named as Mo-1 (T), where T is the calcination temperature (300-700 °C). As for the second synthesis method, an amorphous molybdenum citrate precursor was prepared by mixing 0.139 moles of citric acid in 0.1 M HPA solution. After drying and calcination Mo-2 (T) samples were obtained. X-ray diffraction (XRD) patterns were obtained using a 'D-Max Rigaku' diffractometer. Specific surface areas were measured in a Micromeritics® Gemini V apparatus. Surface acidity was characterised by temperature programmed desorption of ammonia (NH_3-TPD) in a Micromeritics® Autochem 2920 apparatus. Catalytic performance tests were conducted in a Parr 4843 reactor with mechanical stirring and controlled temperature and pressure. Reaction conditions were: 5 wt. % of FFAs (Acid value, AV = 14.0 mg KOH/g), 2 wt. % of catalyst referred to the mixture of oil and FFAs, (oil + FFAs)/MeOH molar ratio 1:12, pressure of 10-30 atm, and temperature between 100 and150 °C. Reactions evolution was monitored through size exclusion chromatography (SEC), and AV was determined as per AOCS method Te 1a-64.

RESULTS

XRD patterns demonstrated that calcination at 500 °C was necessary to obtain pure MoO_3. Table 1 includes some characterization results. Commercial MoO_3, Mo-1 (300) and Mo-1 (500) showed the highest specific surface areas. Mo-1 (500) exhibited the highest acidity. Solids calcined at 300 °C were not completely decomposed and compounds released above 300 °C made impossible to perform quantitative NH_3-TPD analyses.

Table 1. BET and NH_3-TPD results

	S_{BET} [m^2/g]	NH_3 desorbed [mmol/g]
MoO_3 (Commercial)	4.4	0.01 (164 °C) 0.01 (673 °C)
Mo-1 (300)	3.6	-
Mo-1 (500)	3.3	0.10 (430 °C)
Mo-1 (700)	1.2	0.02 (449 °C)
Mo-2 (300)	0.9	-
Mo-2 (500)	1.0	0.01 (547 °C)
Mo-2 (700)	1.1	0.01 (450 °C)

Fig. 1 shows a selection of the results corresponding to the evolution of the triglycerides conversion (X_{TG}) with reaction time at 100 °C and 10 bar. Experiments at different pressures (10-30 bar) demonstrated that this variable had negligible influence. AVs were reduced to less than 1.5 mg KOH/g with all the catalyst within the first 60 min, meaning that the conversion of the FFAs is relatively fast. Catalysts with higher surface areas and acidities showed best activities. Mo-1 (500) was recuperated, calcined, and used in a second reaction cycle. The reused solid kept its original activity. Reaction temperature had a strong influence on the activity: after 1 h, X_{TG} was 0.88 at 125 °C and 0.99 at 150 °C. These results evidence the potential of MoO_3 as catalyst for biodiesel synthesis from low-value feedstocks. Further work is under progress regarding MoO_3 synthesis and the influence of the operating variables.

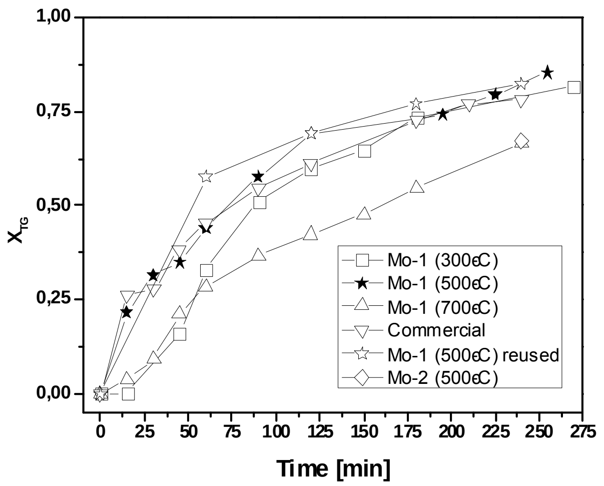

Fig. 1. Evolution of the triglycerides conversion with reaction time.

Acknowledgements

Financial support by the Spanish Ministry of Science and Innovation (TRACE: TRA2009-0265, ENE2009-14522) and of Economy and Competitiveness (ENE2012-37431-C03) is gratefully acknowledged.

OP-IV-2

BIODIESEL FROM PALM OLEIN OIL BY HETEROGENEOUS CATALYSTS

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Biodiesel is an environmentally benign fuel and normally produced by transesterification of triglycerides in vegetable oils or animal fats with a short chain alcohol in the presence of a homogeneous (base or acid) or heterogeneous (base, acid or enzyme etc.) catalyst. Formation of soap and large amount of waste water are some of the drawbacks of using homogeneous catalysts in the transesterification reaction. Use of heterogeneous catalysts would not create such problems. Disadvantages of using heterogeneous catalysts are that the reaction is normally slow, and possibility of leaching of metal ions from the catalyst into biodiesel. CaO has been used as a heterogeneous low-cost base catalyst for transesterification of soybeen oil and during this process, leaching of Ca^{2+} ions from the catalyst to biodiesel is reported [1]. Objective of the present study was to develop an efficient low-cost method to produce biodiesel which has not been contaminated by metal ions leached from the catalyst.

In the present study a catalyst consists of calcium methoxide and calcium glyceroxide was synthesied using a literature method [2]. Direct transesterification by refluxing (15h.) palm olein oil and methanol (1:6, oil: methanol molar ratio) with the catalyst (1.5 wt. % of palm olein oil), separating the biodiesel layer, washing with hot distilled water and then drying was not successful due to the formation of white fakes in biodiesel within 3-4 days. Formation of white fakes is due to leaching of Ca^{2+} ions from the catalyst to biodiesel [1]. Ion exchange chromatography (Amberlite-IR 120 H) to remove Ca^{2+} ions from the above biodiesel was also not successful. This method solve the problem of formation of white flakes, but increased the acid number of biodiesel from 0.29 to 1.3 mg KOH g^{-1} which exceeds the recommended level by ASTM D664 (0.50 mg KOH g^{-1}). Increase in acid number is due to the exchange of the Ca^{2+} ions with H^+ ions of the sulphonic acid sites of the resin. In the next method developed, during the period of above transesterification process Na_2CO_3 was used to precipitate Ca^{2+} ions [2]. Na_2CO_3 itself also can act as a catalyst for the transestrification process. The acid number of biodiesel obtained in this manner was 0.23 mg KOH g^{-1} and it is in the recommended range in ASTM D664. Optimum conditions required were studied by repeating the above process at different oil: methanol molar ratios, different reaction temperatures and different amounts of the catalyst. According to the GC analysis, Palmitic acid (38.23 %), Stearic acid (3.40 %), Oleic acid (36.86 %) and Linoleic acid (15.78 %) respectively are the major fatty acid methyl esters present in the biodiesel.

Optimum conditions for the transestrification process are the temperature of 65 °C, reaction period of 3h., catalyst: oil 0.5% (by weight) and MeOH: oil molar ratio of 12:1. Ca^{2+} ions in biodiesel could be removed by carrying out the transesterification reaction when Na_2CO_3 is present in the reaction medium.

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CATALYTIC HYDROTHERMAL PROCESSING OF VEGETABLE OILS USING METAL EXCHANGED ZEOLITE

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In order to tackle the increase of greenhouse gases and the depletion of crude oil an alternative fuel with an low environmental impact should be found. Hydrothermal liquefaction is a promising route to process biomass into fuels; it has been used to upgrade carbohydrates [1] microalgae [2] and lipids [3]. Compressed water or subcritical water is able to hydrolyse biomass components such as triglycerides and cellulose and, unlike pyrolysis, no prior drying is necessary. Water behaves as an non-polar solvent at elevated temperature and pressure which allows the lipids to be soluble under subcritical conditions [4] and creates the possibility for further reaction of dissolved fragments. Lipids from different sources such as plant based oil seed crops (sunflower oil, rapeseed etc) or even microalgae, can potentially be upgraded into diesel-like fuels using HZSM5 zeolites. It has been demonstrated that fatty acids are relatively stable under subcritical condition in water alone with a low conversion into aliphatic hydrocarbons [5]. The addition of a catalyst is likely to increase the selectivity towards production of n-alkanes.

During this work, sunflower oil and other vegetable oils have been processed at 350°C in subcritical water alone and with HZSM5 doped with ion-exchanged transition metals (molybdenum, cobalt and chromium). The resulting product has been analysed using a variety of methods, including size exclusion chromatography, boiling point distribution (using thermogravimetric analysis), FTIR spectroscopy, ^{1}H NMR spectroscopy, and GC-MS. The starting plant oils and hydrothermal oils are also analysed by GC-MS following conversion of existing fatty acids to FAME. The purpose of this work was to identify catalysts suitable for producing hydrocarbons from lipids suitable for use as fuels and to investigate the main mechanisms occuring during the hydrothermal liquefaction of lipids and fatty acids.

It was determined that during hydrothermal liquefaction of sunflower oil with a high content of linoleic acid, (absence of catalyst) the majority of the triglyceride was hydrolysed into fatty acids. Furthermore, FAME analysis indicated that the the C18:2 linoleic acid has been reduced into C18:1 or C18:0 or smaller fractions. Using

HZSM5 or MoZSM5, triglycerides were upgraded into smaller molecules including alkenes and aromatics. Most of the linoleic acid was converted into smaller molecules and the main fatty acid remaining is C16:0.

In this work, the impact of different degrees of unsaturation has been investigated using different vegetable oils (soya oil and linseed oil) and at different temperatures (250-300-325°C), in order to understand the mechanism with and without the zeolite catalysts.

Overall, It has been shown that the Mo/ZSM5 favours the formation of aromatics during the hydrothermal liquefaction of sunflower oil.

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OP-IV-4

CATALYTIC HYDROPROCESSING OF RAPESEED OIL – REACTION MECHANISMS AND RATE DETERMINATION

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Recently, traditional oil refineries have started to hydroprocessing vegetable oil and fatty acids. Nowadays, NiMo/Al_2O_3 catalyst in refineries to process tall oil, vegetable oil with diesel blending have been concentrated to meet EU standard with reduction of sulphur and increase of cetane value. Indeed it needs sulphur as supportive for S-binding active sites. Recent publications show good emphasis on Pd/C catalyst for high selectivity and activity to higher cetane value of the product. In attempt to see the comparison of both catalysts, we worked on triglycerides from rapeseed origin without free fatty acids to identify the reaction mechanism [1-3].The stainless steel batch reactor of the Parr instrument, 300 ml capacity consists of a gas inlet attached to two separate valves through which nitrogen and hydrogen gases were passed to the bottom of the reactor. The sample outlet was connected to the gas inlet pipe with a separate valve to control the flow of the gases. The thermocouple, heating system and magnetic stirrer were integrated in a process controller to maintain the steady state of the operating condition. The reactor was loaded with 150 ml of solution that includes a defined amount of catalyst and carried out with identical speed of stirrer. The catalyst bought under the trade name of Trilobe HDN-60 (NiMo/γ-Al_2O_3) from Cirterion Catalyst and 205680 (5 wt% Pd/C) from Sigma-Aldrich. The reaction conditions had been tested between 250 to 350 °C at constant H_2 pressure in batch reactor with reactant as 20 wt% rapeseed oil with decane.

The product distribution was comparatively different on both catalysts test. The selectivity of C_{17}, which was formed due to thermal decomposition, plays crucial role in the reaction mechanism, as shown in Figure 1, related to the reaction mechanism of catalytic hydroprocess. Partial hydrogenation was observed with Pd/C catalyst, but better selectivity identified with NiMoS/γ-Al_2O_3. NiMo-S has weak surface acidity in which C_{18} was higher composition than C_{17} [4, 5]. Weak S-binding intended to deactivate by H_2 to produce H_2S, the vacant sites could be replaced with coke, and so fresh S was in need to regenerate the active sites. Pd/C had high advantage on active sites reproductive which doesn't affect by coke on sites. C_{17} was main product it. However, esterifies compounds determine the rate of deoxygenation.

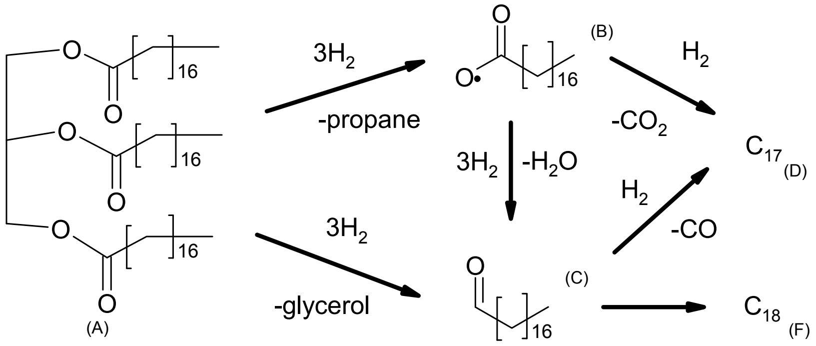

Figure 1: Catalytic hydro-processes of rapeseed oil through NiMo-S/γ-Al_2O_3

The investigation on NiMo/γ-Al_2O_3 shows the free fatty acids formation appears initially and soon been diversified with deoxygenation and decomposition. The results can be observed in Figure 2, this catalyst doesn't produce effective yield, loss active sites by coke.

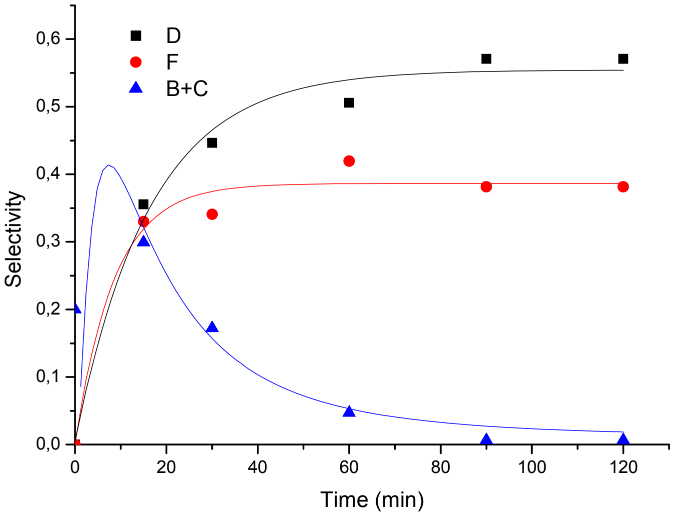

Figure 2: Rate determination for rapeseed oil hydroprocess at 350°C with catalyst and partial pressure of hydrogen (4 MPa) in batch reactor

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CATALYTIC CONVERSION OF THE PLANT LIPIDS TO BIOFUELS

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Keywords: biodiesel, transetherification, hydrodeoxygenation, hydrotreatment, catalyst

Introduction

Today, fossil fuels such as coal, oil, and natural gas provide more than three quarters of the world's energy. However at present renewable feedstock attracts attention due to increasing of fossil fuels cost and its graceful irretrievable consumption. At that, now the technologies level of biomass processing into engine fuels is lower than oil-refinery industry. This is a main reason of higher prime cost of bio-fuels production. But, for bio-fuels production increasing scientific society has to not only improve present biotechnologies, but develop new biomass processing technologies with widening of renewable feedstock list, including wood and agricultural waste. The new catalytic technologies of biomass processing should play a key role in the bioenergetics evolution.

In Boreskov Institute of Catalysis the intensive investigations are carried out in the field of biodiesel production in the presence of heterogeneous catalysts, high-cetane fuels production from biodiesel and plant oils directly.

Development of heterogeneous catalysts for plant oils transetherification

The specificity of the work is development of new effective catalysts, adjusted to renewable feedstock. The one of developed technology is based on conjugated catalytic processes of transetherification and mild hydrocracking sequentially [1,2].

Main features of developed technology are:

- biofuel production of two types: biodiesel and green diesel;
- varying of biodiesel and green diesel yields depending needs;
- optimization of hydrogen consumption;
- energy-supply of both stages via burning of gaseous products, produced on 2nd step.

Catalytic characteristics of the technology include application of heterogeneous basic trasetherification catalysts under 200-220 °C and 2.0 MPa and possibility of multiple catalyst regeneration for the first stage. For the second stage these ones comprise using of non-sulfided and non-noble metal catalysts, mild reaction conditions (300-340 °C and 2.0 MPa H_2) and possibility of green diesel production with different cetane number via hydroisomerization catalysts application [3].

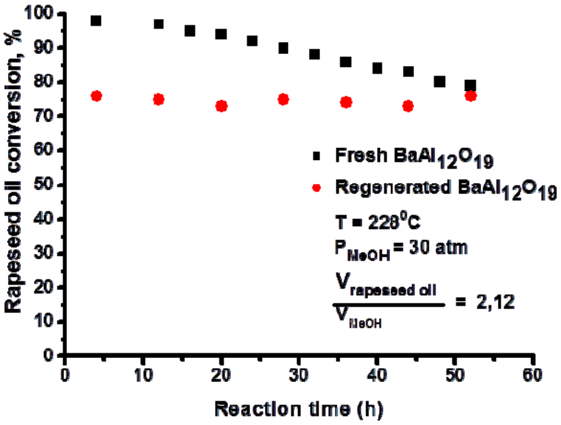

Fig. 1. Fresh and regenerated $BaAl_{12}O_{19}$ catalysts performance for transetherification of plant oils (biodiesel production). Catalyst was regenerated in the air atmosphere at 700 °C for 3 h.

It was found (via XPS data) fresh $BaAl_{12}O_{19}$ catalyst has two forms of active components – strong-bond centers and weak-bond centers which were removed from catalyst surface during first cycle. After regeneration catalyst was showed constant activity in target process (Fig. 1).

Conclusions

The new type of transetherification and hydrocracking catalysts were proposed which possess high thermal and mechanical stability in biodiesel and green diesel production process.

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ORAL PRESENTATIONS

SECTION V

Catalytic approaches for the processing of pyrolysis biomass products

OP-V-1

PRODUCTION OF HIGH VALUE CHEMICALS AND BIOFUELS BY CATALYTIC PYROLYSIS OF BIOMASS/LIGNIN MIXTURES

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This work focused on the concept of producing high added value platform chemicals and fuels from Biomass and Lignin with the process of catalytic pyrolysis. The lab and pilot plant scale units used in this work have been described elsewhere [1, 2]. Biomass (Beechwood) and Softwood Lignin mixtures were produced according to a proprietary method developed in CPERI. The method developed was focused on producing intimate mixtures of the components in a simple way that uses existing infrastructure and practices of today's biomass and paper industry.

Mixtures of up to 20 wt.% lignin in wood sawdust were produced and successfully catalytially pyrolyzed with a commercial ZSM-5. Figure 1 presents the pilot plant yields of the main products.

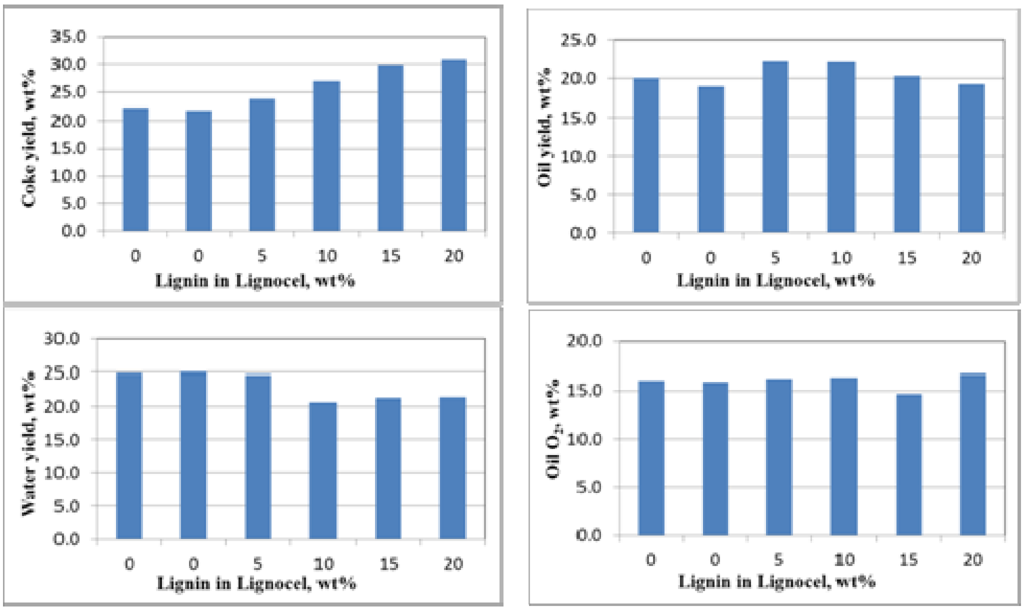

Figure 1. Pilot plant yields of coke, oil, water and oil O_2 vs lignin percentage

Oil O_2 remained fairly stable while it was noted that as the lignin content increased the coke yield was also increased, while oil yield slightly decreased. Lignin has been reported to produce coke due to its complex network of cross-linked aromatic molecules that are difficult to decompose and therefore has high thermal stability, which resulted in high coke yield [3]. Moreover, lignin coke also formed from the secondary thermal degradation of the volatiles released during pyrolysis [4]. Figure 2 presents the concentrations of the most abundant compounds in the oils produced from the various mixtures. The internal standard method was employed with a 2DGC-TOFMS technique for accurate characterization of the oils.

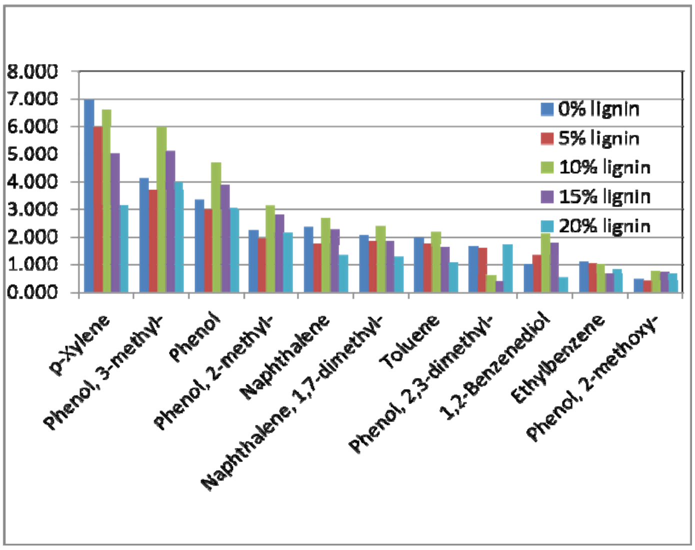

Figure 2. Most abundant compounds of lignin/wood sawdust mixtures derived biooil

As lignin concentration increased, the aromatic compounds, especially phenols, seemed to increase. Studies on the decomposition of lignin with model compounds [5] have shown that the thermal decomposition of lignin begins by cleavage of the weak α-ether and β-ether bonds of the lignin structure, which releases guaiacyl- and syringyl-type aromatics, depending on the lignin source. Softwood lignins have only guaiacyl-type nuclei, while hardwood lignins have both [6]. As expected guaiacyl-type compounds were detected in the produced biooil.

Since the C-O bond in the phenol molecule is refractory to ZSM-5, the presence of the catalyst was not expected to have any significant impact on the composition of the catalytic bio-oil. Methoxy- and methyl- substituted phenols, benzendiols and polysubstituted phenols were still the prevalent compounds.

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IN SITU UPGRADING OF BIOMASS FAST PYROLYSIS OIL WITH ACIDIC AND BASIC CATALYSTS

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Biomass is a renewable energy source expected to play a substantial role in the future global energy balance. More specifically, lignocellulosic biomass is capable of providing a wide range of liquid, solid and gaseous raw materials utilized for the production of thermal and electrical energy, transportation fuels and chemicals. The *biomass fast pyrolysis (BFP)* is an important thermochemical process that aims at the production of high amounts of pyrolysis oil (bio-oil) [1]. Bio-oil is considered as a low quality fuel (low heating value) since it contains water and oxygenated compounds in its organic (oil) fraction and is relatively acidic, corrosive and unstable upon prolonged storage because of the nature of its main components (i.e. carboxylic acids, carbonyls, etc.). Catalytic hydrotreatment and/or cracking of bio-oil, in mixtures with petroleum fractions (i.e. gas-oil), using conventional refinery processes can lead to the production of the so-called “green gasoline” and “green diesel”. On the other hand, depending on its composition, bio-oil can serve as a source of platform chemicals, such as phenols, furans, and others. The *catalytic fast pyrolysis of biomass* or often named as the *in situ catalytic upgrading of bio-oil*, can be utilized in order to fine-tune the composition of bio-oil and thus improve its physical and chemical properties for further use [1-5].

In this paper we present an overview of our results on the catalytic fast pyrolysis of biomass and the upgrading of bio-oil by the use of various acidic microporous zeolites (USY, Beta, ZSM-5, Silicalite), mesoporous aluminosilicates (MCM-41, SBA-15, MSU-S) and hybrid ZSM-5 zeolites with meso/macroporosity, as well as basic catalysts (MgO and mixed oxides derived from Layered Double Hydroxides). Acidic catalysts usually lead to increased production of water and coke and decreased yield of the organic fraction of bio-oil. On the other hand, they promote de-oxygenation and aromatization reactions, thus leading to less oxygenated compounds in the bio-oil and more aromatic hydrocarbons.

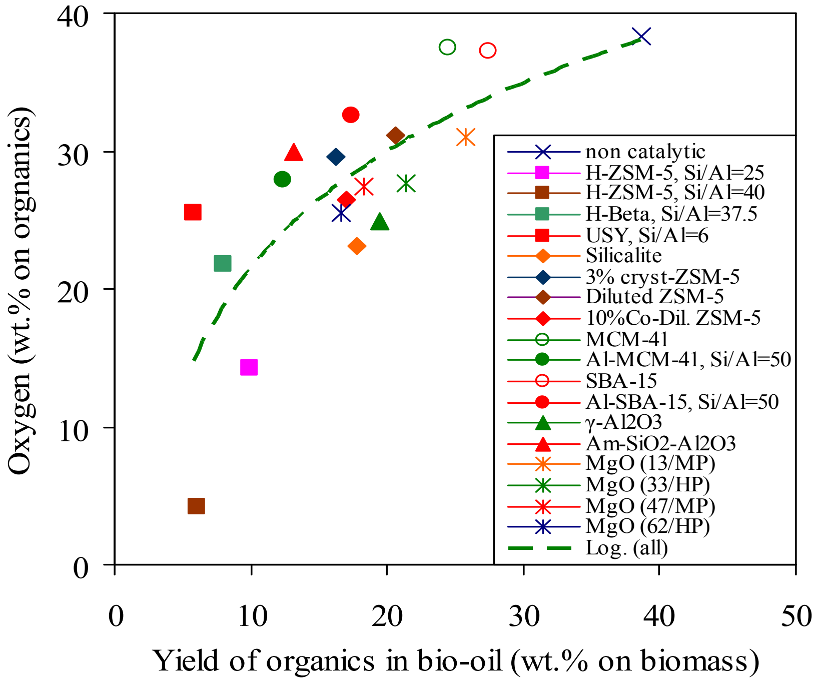

Fig. 1. Correlation between the yield and oxygen content of organic phase of bio-oil

The basic materials induce different effects on product yields and selectivity of bio-oil components mainly via ketonization and condensation reactions. Due to the presence of lignin in significant portion in the biomass, some acidic and basic catalysts favor the formation of high added value phenols. Despite the different nature of the active sites in acidic and basic catalysts, the data in Figure 1 shows that there is a fairly good correlation between the oxygen content of bio-oil's organic fraction with its concentration/amount. Deviations from this average curve are attributed to the differences in the acidic-basic properties, as well as the textural characteristics (porosity, morphology) of the catalysts.

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Ni-BASED CATALYSTS WITH IMPROVED STABILITY FOR BIO-OIL HYDROTREATMENT

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The limitation of petroleum resources and constant growth of human energy demands become more evident with the lapse of time. This results in the increased attention towards the application of lignocellulosic biomass for the motor fuels production. One of the prospective approaches for the biomass conversion into biofuels is thermochemical treatment by fast pyrolysis which yields a liquid product − bio-oil. Co-processing of bio-oil and conventional oil refinery products on the FCC units using traditional oil refinery equipment is of particular interest [1]. But before co-processing an upgrading of crude bio-oil is required to reduce its polarity and increase its miscibility with non-polar petrochemicals. An effective way to improve bio-oil quality is catalytic hydrotreatment (hydrodeoxygenation, HDO), which allows a selective removal of oxygen from the biomass pyrolysis products. The main chemical reactions of this process are hydrocracking, decarbonylation, decarboxylation, hydrodeoxygenation, cracking and hydrogenation. However, the catalytic hydrotreatment of pyrolysis oils is far from the commercial scale in contrast to the conventional refining, and intensive research is required. Much attention is currently paid to the development of catalysts suitable for the bio-oil hydrotreatment. Numerous studies have shown that the catalysts for HDO process should meet the following requirements: the low cost, non-sulfided nature, high activity and stability to coking, stability in corrosive media (against leaching) at high temperatures and pressures, high thermal stability (e.g. against agglomeration) and ability for multiple regeneration by coke combustion.

Recent works have shown that NiCu bimetallic catalytic systems are very attractive for use in hydrotreatment process due to their low cost and high activity in hydrogenation, hydrodeoxygenation and hydrocracking reactions [2, 3]. However, despite high activity of NiCu bimetallic catalysts, they had a number of disadvantages: low stability in acidic medium (active component leaching), low thermal stability (active component particles agglomeration) and tendency to coking [2]. A possible way to improve catalysts is the use of modifying additives.

In the present study the Ni-based sol-gel NiCu/SiO_2-ZrO_2 catalytic system was modified by P-/Mo-containing agents to improve its mechanical strength and stability in acidic medium [4, 5]. This catalyst was similar to NiCu/SiO_2 and NiCu/SiO_2-ZrO_2-La_2O_3 systems previously studied in HDO of guaiacol, and their high activity was reported about [6]. The modified catalysts were tested in hydrotreatment of guaiacol. HDO process has been carried out in an autoclave at 320 °C, 17 MPa initial hydrogen pressure, reaction time 1 hour. It was shown that phosphorus and molybdenum addition to the catalysts composition results in the decrease of guaiacol conversion and deoxygenation degree. On the other hand, the yield of undesirable gaseous reaction products (mainly CH_4) and coking of the catalyst were lower for the modified catalysts in contrast to the initial NiCu/SiO_2-ZrO_2 system. The catalysts treatment by glacial acetic acid at 118 °C showed that modification by P and Mo gives a significant improvement of catalysts stability in acidic medium (mass loss decreases from 53 wt. % to 1 wt. %). Moreover, a significant improvement of bulk crushing strength has been observed for PMo-modified samples (from 0.5 MPa to 1.2 MPa). The results obtained show that PMo-modified Ni-based catalysts are promising systems for hydrotreatment of pyrolysis oils.

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STABILITY AND RESISTANCE OF NICKEL-BASED CATALYSTS FOR HYDRODEOXYGENATION

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Introduction

Conversion of biomass through flash pyrolysis followed by hydrodeoxygenation (HDO) has been identified as a prospective path to engine-fuels usable in the current infrastructure [1]. A challenge in HDO, and the scope of the present work, is to obtain sufficient lifetime of the catalyst for this reaction. Aspects of carbon deposition and deactivation from impurities have to be considered. Carbon arises because many of the oxy-compounds of the bio-oil are potential carbon precursors due to their high reactivity. Impurities in the bio-oil can be sulphur, alkali, and chlorine, among others, which all constitute a potential risk to the catalyst [1].

Nickel based catalysts have in recent work been identified as prospective catalysts for HDO with high activity [2]. In the current work the stability and resistance of this type of catalyst is investigated.

Experimental

5 wt% Ni/ZrO_2 was prepared through the incipient wetness method from $Ni(NO_3)_2$ on a high surface area ZrO_2. Reduction and calcination were done in the setup prior to the experiments at 500 °C with 250 Nml/min H_2 and N_2 for 2 hours. 2.5 g of catalyst diluted in 250 μm glass beads was used in the experiments. All experiments were performed in a new high pressure continuous flow reactor setup with on-line GC-TCD analysis at 250 °C, 100 bar, a gas flow of 400 Nml/min H_2 and 100 Nml/min N_2 and a liquid flow of 0.2 ml/min 10 vol% Guaiacol in 1-octanol; giving a WHSV of 4.1 h^{-1}. Liquid samples were collected at intervals of two hours and analyzed with GC-MS/FID.

Results and discussion

A series of experiments were made where the catalyst was: 1) exposed to sulphur (added as octanethiol corresponding to 0.05 wt% S in the feed); 2) exposed to KCl (predoped to the catalyst); 3) exposed to chlorine (added as chlorooctane corresponding to 0.05 wt% Cl in the feed); 4) exposed to no poison as a reference case. In all experiments, Ni/ZrO_2 was found to convert the 1-octanol to heptane and initially hydrogenate the guaiacol to 2-methoxy-cyclohexanol followed by deoxygenation to cyclohexane.

The 4 experiments are summarized as degree of deoxygenation (DOD, moles of oxygen removed relative to feed) in Figure 1. The non-poisoned case maintained a constant degree of DOD throughout a period of more than 100 h. Contrary; all three types of poisons severely decreased the activity for deoxygenation. Sulfur was the most severe poison, as the activity dropped to zero in a short time frame after this was introduced in the feed. Chlorine caused a reversible deactivation as the activity could be regained by removing chlorine from the feed. KCl was found as a persistent poisoning, giving a constant low DOD through 24 h of operation.

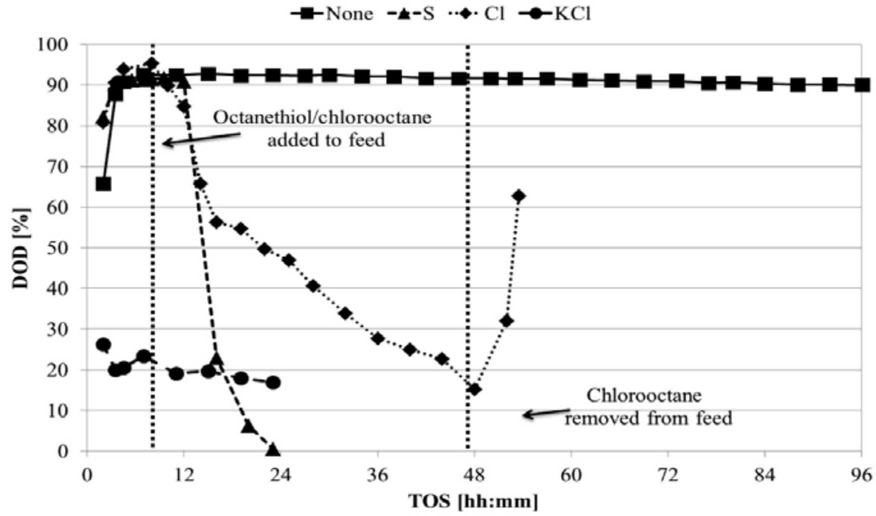

Figure 1. DOD in the three cases with different poisons relative to the case with no poison. Catalyst: 5 wt% Ni/ZrO_2, oil: 10 vol% Guaiacol in 1-octanol, T = 250 °C, P = 100 bar, F_{H2} = 400 Nml/min, F_{N2} = 100 Nml/min, F_{oil} = 0.2 ml/min, WHSV = 4.1 h^{-1}

Overall it can be concluded that sulphur, KCl, and chlorine, all will deactivate the catalyst, with the severity of the different phenomena aligning qualitatively as:

Sulphur >> KCl « Chlorine >> Coke

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CHARACTERIZATION AND CATALYTIC PROPERTIES OF HIGH-LOADED Ni-Cu CATALYSTS: THE EFFECT OF Ni/Cu RATIO ON ACTIVITY AND SELECTIVITY IN ANISOLE HDO

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Nowadays when a great attention is paid to the reduction of fossil fuels consumption, the use of renewable energy resources is essential. One of the most promising renewable feedstock is pyrolysis oil. The processing of the bio-oil with the oil fractions in standard refinery equipment can be interesting. However, it requires a preliminary hydrotreatment of the bio-oil to reduce the high oxygen content (about 20-40%) and to increase the hydrogen content. The hydrodeoxygenation (HDO) and hydrogenation (HYD) processes are the key reactions for stabilization, bio-oil upgrading during HDO allows one to reduce the oxygen content and to produce the products with the desired properties. It was shown previously [1] that the Ni-Cu catalysts are active in hydrodeoxygenation of bio-oil and its model compounds. Catalysts containing nickel have been used in various industries for a long time. It is known that the introduction of copper into the nickel catalyst not only prevents the carbon formation but also inhibits the sintering of the active phase in methane steam reforming and hydrocarbons decomposition reactions [2]. In addition, the introduction of copper in Ni-based catalysts enhances the activity and selectivity, for example, in the reaction of methane steam reforming in the presence of CO_2 [3], hydrogenation of ethylene [4, 5], the selectivity of 1,3-butadiene hydrogenation [6]. These changes in the catalytic properties are associated with changes in the electronic properties of the active component in the alloy, with the influence of the geometrical effect, or with a combination of these effects [7].

The objective of the present study was to investigate the effect of Ni content in the active component of NiCu-SiO_2 bimetallic catalyst on the selectivity of anisole conversion products formation. Anisole was chosen as a model compound of phenolics in pyrolysis oil because it contains an isolated methoxyl, one of the major functional groups of the lignin phenolics. The effect of the Ni-Cu alloy surface composition on the specific catalytic activity was also examined. To obtain the alloys with the homogeneous phase composition the catalysts were prepared by simultaneous decomposition of metals salts with subsequent stabilization with 10% wt. SiO_2. The prepared catalysts were characterized using temperature-programmed reduction, X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy combined with energy dispersive microanalysis. Bulk and surface composition of the active component was determined from data obtained by XPS and X-ray analysis. It is shown that in all the catalysts with Ni content ranging from 15 to 85% wt., there are two types of solid solutions, one of which has a constant composition $Cu_{0.95}Ni_{0.05}$ and does not depend on the ratio of Ni/Cu, and in the second solid solution Ni content increases with increasing Ni concentration in the active component. Anisole hydrotreatment was carried out at 280 °C and a hydrogen pressure of 6 MPa in a batch reactor. On the basis of obtained kinetic data, a reaction scheme of anisole conversion was proposed. The scheme includes two parallel routes, one of which leads to C_{ar}-O bond cleavage with the formation of benzene, which is then converted to cyclohexane (HDO route), while the second route leads to hydrogenation of the aromatic ring of anisole with the formation of methoxycyclohexane and cyclohexanol (HYD route).

The selectivities of both reaction routes of anisole conversion (HDO and HYD) were found to be independent of the Ni content except for the nickel-rich and copper-rich sides. The specific catalytic activity in the HDO route rises with an increase in the nickel content in the whole range of Ni concentrations in alloy.

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POSTER SESSION

PP-1

SOLID BASE CATALYST: SYNTHESIS OF GLYCERYL CARBONATE BY TRANSESTERIFICATION

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Catalysis promotes chemical reaction without it being consumed or produced during a reaction. Conventionally, homogeneous catalyst either acidic or basic, are commonly used in oleochemical processes. On the other hand, heterogeneous catalysts (solid catalyst) in oleochemical reactions are becoming important because it poses a define catalytic site, thus increased catalytic activity and process efficiency by enhancing selectivity. A number of solid catalysts with different molar ratio of divalent cations solution to trivalent cations solutions (M^{2+}/M^{3+}) were prepared via co-precipitation method. The evolution from fresh hydrotalcite (solid base catalyst) to their mixed oxides form were assessed upon calcination of the fresh hyrotalcites at temperatures of 400 °C, 500 °C, 600 °C, 700 °C and 800 °C for 5 h based on their hydrotalcite pattern structure, specific surface area, morphological properties and elemental composition analysis. It was confirmed by XRD that the materials had hydrotalcite structure. The measured surface area was in the range of 209 to 305 m^2g^{-1}. The hydrotalcite catalyst, HT3.0c calcined at 500 °C for 5h with Mg^{2+}/ Al^{3+} molar ratio of 3.0 exhibited the highest catalytic activity in the transesterification. The optimum operating condition chosen was 1:1 molar ratio of ethylene carbonate to glycerol at temperature of 80 °C for 5 h reaction time. The highest percentage of glycerol converted was 88.43% using HT3.0c catalyst. Moreover, the solid base catalyst could be easily separated and possibly be recycled.

Keywords: *co-precipitation, solid base catalyst, glyceryl carbonate*

PP-2

JATROPHA PERFECT FEEDSTOCK FOR RURAL ELECTRIFICATION

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A decentralized power generation plant fuelled by straight jatropha oil is implementing in various villages in Ghana. The project aims to improve socio-economic conditions of small rural populations in Africa through small-scale electrification ,demonstrate the potential of CHP generators as a means of bringing electrification to small, off-grid villages in Africa,demonstrate the potential of jatropha oil and other Straight Vegetable Oils (SVOs) from oil-bearing energy crops as a means of running a small CHP generator (40 kW),identify and demonstrate potential communal or small-holder ownership models for the successful sustainable management of the generator/extractor and jatropha seed production and disseminate the model for replication in other areas.In summary, the jatropha-based electrification in Ghana will reduces greenhouse gas emissions. However, environmental benefits can only be achieved if jatropha is cultivated not to compete with food. Under this condition, jatropha-based electricity generation might be a useful alternative to other renewable electrification options, as the technology is very sturdy and can be maintained even in remote and highly under-developed regions.

PP-3

PRESSURIZED PYROLYSIS OF BIOMASS USING MCM-41 CATALYST

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SUMMARY

In this study, poplar sawdust was chosen as a biomass sample and the pressurized fast pyrolysis of this sample was carried out with or without catalyst in a fixed-bed reactor. Experiments were carried out a pyrolysis temperature of 500 °C, with a heating rate of 450 °C/min, under pressures of 1 or 20 bar in the nitrogen atmosphere. In the catalytic experiments, MCM-41 and Al-MCM-41materials were used. The bio-oil yield was reduced, whereas the char yield increased in the pressurized experiments. This decreasing in bio-oil kept on with using catalyst. Increasing pressure from 1 to 20 bar reduced bio-oil yield by roughly 10.6 wt% in non-catalytic procedure. This reduce is 11.6 and 12.4 wt% using MCM-41 and Al-MCM-41 in the experimental procedure. Pyrolysis oils were examined by using GC/MS and char product was evaluated by SEM.

Keywords: Poplar sawdust, pressure, pyrolysis, bio-oil, GC/MS.

The effect of pressure on biomass pyrolysis has been studied [1-3] but still remains to be further explored. Biomass samples exposed to the higher pressure than atmospheric are more cracked. The aim of using a catalyst on pyrolysis is more removing of the oxygen from the oil products. Although oxygenated oils are used in many heat and power generation applications, they cause a decrease in efficiency when used in turbine and motors.

Table 1. Experimental data with or without catalyst

		without catalyst		with catalyst (bio-oil %)	
Pressure (bar)	bio-oil (%)	char (%)	gas (%)	MCM-41	Al-MCM-41
1	31.1	22.4	38.5	30.2	29.4
20	27.8	24.8	42.4	26.7	25.8

Pyrolysis experiments were conducted in a pressurized fixed-bed reactor equipped with temperature and pressure controller and a power supplier.

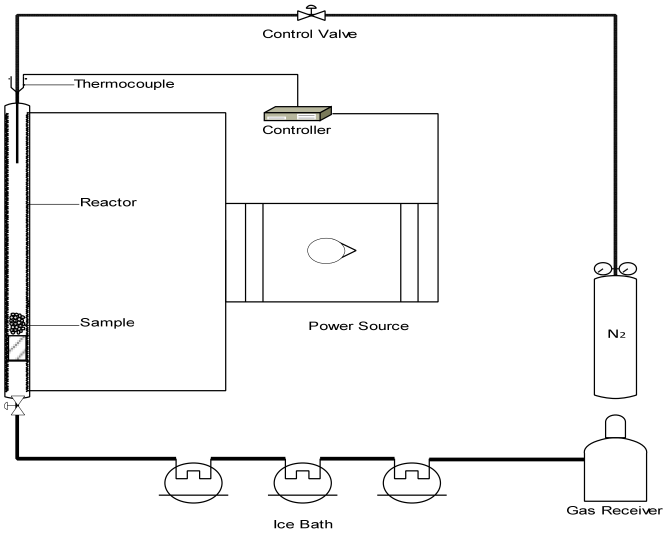

Fig.1. Schematic diagram of the experimental apparatus

The sample (3 g) and catalyst, which supported steel wool, have been placed in the different distances but into the same thin tubular reactor. The reactor was then closed by placing the flanges in the bottom and top of the reactor. Nitrogen was introduced into the reactor and adjusted with control valve. The valve going to the condensers was closed until the reaction completed. After completing the pyrolysis reaction, the valve was slightly opened to leave of the volatiles from the reactor. The liquid products were collected in a cold trap maintained at 0 °C. Char yield was determined from the overall weight losses of the reactor tube.

Pyrolysis oils were examined by using GC/MS. High pressure has influenced most of the components of bio-oil. PAHs like Phenanthrene, Anthracene, Fluoranthene, Pyrene, Naphthalene and their derivatives formed at higher pressures. They have not been identified in atmospheric studies. In the catalytic experiments at higher pressure, same compounds were detected with close yields. But naphthalene and derivatives was increased as twice as using catalyst.

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PP-4

A COMPARISON OF COBALT- AND IRON-BASED FISCHER-TROPSCH CATALYSTS FOR BIOMASS-DERIVED DIESEL AND SNG COPRODUCTION

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Shortage of fossil fuels and awareness of environmental issues caused by the utilization of these fuels are two driving forces for actions towards a more sustainable energy system. At the moment, no other renewable source but biomass can diminish the oil share in the transportation sector. Therefore, the conversion of biomass into liquid and gas fuels are becoming interesting technologies [1].

The “Biomass-to-Liquids” (BTL) process consists mainly in two steps: the conversion of biomass into synthesis gas (a mixture of hydrogen and CO) and the Fischer-Tropsch (FT) synthesis where the synthesis gas is converted into a wide range of hydrocarbons via hydrogenation of CO over a heterogeneous catalyst [2].

The FT reaction can be classified in two modes: the High-temperature FT (HTFT) in which linear low molecular mass olefins, gasoline and oxygenates are mainly produced, and the Low-temperature FT (LTFT) in which the main products are high molecular mass paraffins (FT waxes). The FT waxes produced in the LTFT are subsequently hydrocracked to maximize the production of diesel [3].

Lately, the “Biomass-to-Gas” (BTG) process to produce synthetic natural gas (SNG) from biomass via methanation has also attracted much attention [4]. Moreover, the idea of co-producing diesel and SNG by methanating the off-gas resulting from the Fischer-Tropsch reactor has been technically and economically assessed, and has resulted in an increase in biomass to fuel efficiency [5].

Among all the metals known to catalyze the FT reaction, only iron- and cobalt-based catalysts have been used for FT industrial applications [6]. Conventionally, cobalt is the preferred for Gas-To-Liquid (GTL) applications [7, 8] whereas iron is for Coal-To-Liquid (CTL) processes [9, 10].

At the moment, there is no conventional knowledge regarding the most suitable Fischer-Tropsch catalyst for BTL applications.

This work will focus on the differences between cobalt- and iron-based catalysts for application in a biomass-derived diesel and SNG co-production system.

Two conventional iron- and cobalt-based catalysts were prepared in order to compare their catalytic properties. The molar composition of the iron catalyst is 100 Fe/ 1.2 K/ 1 Cu/ 1 SiO_2 and was prepared by co-precipitation of Fe, Cu and SiO_2 and subsequent incipient wetness impregnation of K. On the other hand, the cobalt catalyst was prepared by incipient wetness impregnation of cobalt and platinum over a γ-Al_2O_3 support and consists of 12% wt. Co and 0.5% wt. Pt.

The catalysts were tested under FT industrial relevant conditions and their catalytic properties (activity, selectivity and stability) were determined. Further work is necessary to evaluate the suitability of iron- and cobalt-based catalysts for this specific application.

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PP-5

COMPARATIVE LCA STUDY FOR BIODIESEL PRODUCTION IN ROMANIA AND SPAIN

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This paper analyzes and compares from an environmental point of vue the production of biodiesel derived from winter rape (RME) cultivated in romanian and spanish agroclimate conditions. Athough vegetable oils as fuels are considered to be CO_2 neutral, there are important emissions during the cultivation and conversion processes. To evaluate the environmental effects of all these processes and to compare biofuels produced in Romania and Spain, life cycle assessment methodology is used. The study performed shows that the biodiesel produced in Romania determines an important reduction in 5 of the 10 impact categories considered, specifically of 77,80% in Acidification Potential (ADP), 4,88% in Global Warming Potential (GWP), 115,83% in Ozone layer Depletion Potential (ODP), 60,83% in Human Toxicity Potential (HTP) and 158,30% in Photochemical oxidation Potential (POP). However, the biodiesel produced in Spain shows better results in Abiotic Depletion Potential (ADP) reducing it by 30,75%, also Eutrophication Potential (EP) is reduced by 198,43%, Fresh Water Aquatic Ecotoxicity Potential (FWAEP) is reduced by 74,50%, Marine Aquatic Ecotoxicity Potential (MAEP) is reduced by 248,83% and also Terrestrial Ecotoxicity Potential is reduced by 275,79%. Important emissions could be avoided if the romanian cropping system wouldn't require irrigation. Also the fertilizers used in both cropping systems have significant impact on the environment, impact that can be reduced by using alternative fertilizers from agriculture.

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PP-6

ONE-POT MICROWAVE ASSISTED CATALYTIC TRANSFORMATION OF VEGETABLE OIL INTO GLYCEROL-FREE BIODIESEL

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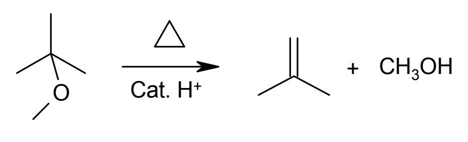
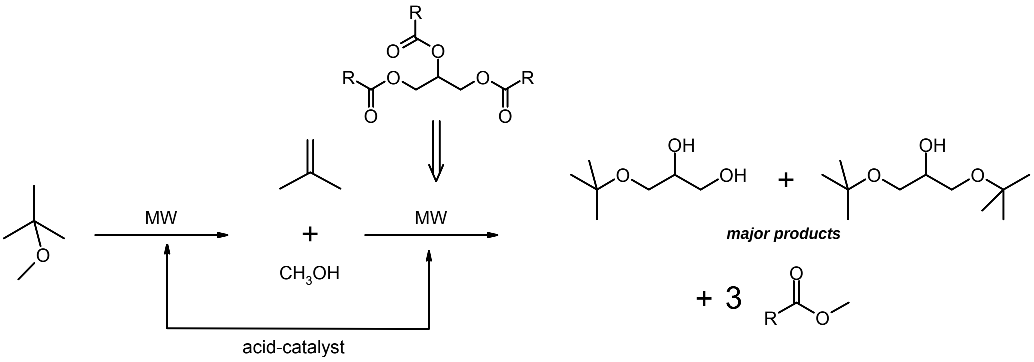
Biodiesel is a non-toxic and biodegradable alternative fuel obtained from renewable sources and it is a potentially important component to mitigate greenhouse gas emissions and substitute fossil fuels. Biodiesel is a mixture of methyl esters of fatty acids (FAMEs) obtained by the transesterification reaction of vegetable oils with methanol in presence of an acid or basic catalyst or by using an enzymatic catalyst. However, the foremost problem is the inevitable production of glycerol as the co-product which must be removed and whose formation impacts on the expense of the entire process. Among the different alternatives, the use of glycerol-derivatives that may be exploited as biodiesel additives is being explored. Etherification of glycerol appears to be the better solution for production of "clean" additives both for diesel and internal combustion engines. The etherification of glycerol by isobutene gives a mixture of mono-, di- and tri-t-butyl ether, GBTEs [1]. It is known that acidity of catalyst is a key factor for the etherification of glycerol by isobutene or using tert-butanol, hence catalysts such as sulfuric acid or sulfuric acid-functionalized mesoporous silicas have been considered [2-4]. Recently, Gowda *et. al.*, have reported an efficient synthesis of tert-butyl ethers using TBME (tert-butyl metyl ether) under mild reaction conditions using sulfuric acid as catalyst [5]. In this context, it has been observed that methyl tert-butyl ether alone decomposes to give isobutene and methanol (Scheme 1).



Scheme 1

We have focused our attention on developing a robust protocol for one-pot microwave assisted transformation of vegetable oils to a mixture of FAMEs and glycerol ether derivatives catalyzed by amorphous silica oxide functionalized with 10wt% of sulfonic groups [6] and using the commercially available TBME as single source both as transesterification and transetherification reagent. The final mixture could be exploited to make biofuels (Scheme 2).

PP-6



Scheme 2

When glyceryltripalmitate as substrate and TBME (1:20), in presence of 1% catalyst (w/w), was submitted to the microwave radiation, in 3 hours we observed a complete conversion into the corresponding methyl palmitate and a mixture of glycerol derivatives, composed mainly of 1,3-di-tert-butyl glycerol ether and 1-tert-butyl glycerol ether in a ratio 30:70. As desired, negligible traces of glycerol were detected (Fig. 1).

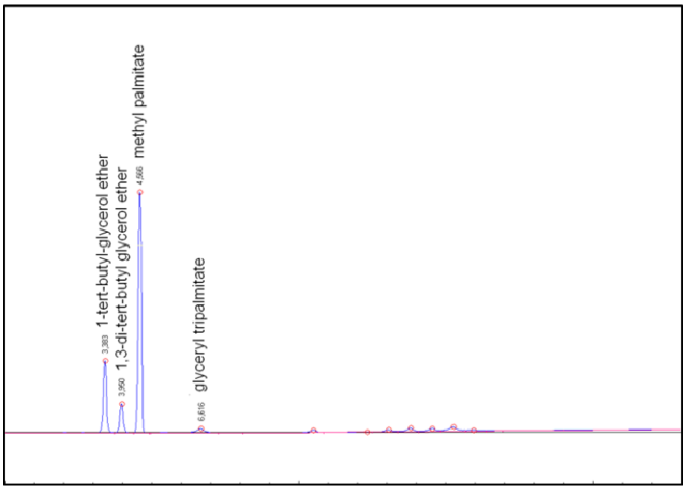


Figure 1

There are several practical and cost-saving advantages making this process very attractive, among which the obtained mixture, which is without glycerol, only needs to be separated from the catalyst, achieved by a very simple filtration, and it may be used directly in the energy chain [7-8].

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GETTING IONIZABLE PRODUCTS ON THE BASIS OF BIOPOLYMERS BY THE INFLUENCE OF CATALYTIC REAGENTS

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Search of new technologies of reception of demanded products on the basis of renewable natural raw is a topical problem of modern chemistry of biopolymers. The biomass of plants is a source of valuable chemical raw for the production of promising materials of various purposes. Obtaining of new products is based on the chemical transformation of the components of the biomass. Biopolymers, such as cellulose and lignin are major components of the biomass of plants.

The difficulty of the study of natural systems is associated with a variety of species of cellulose and lignin, their phase heterogeneity and multicomponent composition of lignin-carbohydrate complex.

As a rule, obtaining of lignincellulose powder materials is based on traditional methods of the destruction of lignin-carbohydrate complex. These are associated with a long duration processing of the biomass of plants, with formation of related products and with the use of significant quantities of natural water.

Lewis acids are the highly efficient catalytic reagents for chemical transformation of lignin-carbohydrate complex. They are capable not only to destroy, but also to modify the macromolecules of biopolymers. A distinctive feature of application catalysis of lignin-carbohydrate complex by Lewis acid in organic solvents is the possibility of obtaining products for a special purpose with predetermined consumer properties for a short period of time. The possibility of regeneration organic solvents of used in catalysis creates preconditions for the development of the technologies of the closed cycle.

The using of those or other treatment steps of lignin-carbohydrate complex we can get products with small or large content ionizable groups.

The products of the catalytic destruction lignin-carbohydrate complex received by the influence Lewis acids in arid environments have multifunctional composition and are characterized by high chemical reactivity. This is confirmed by modern physico-chemical methods of research of biopolymers.

Work is executed at financial support of the Project 12-P-3-1024 (the program of the Presidium of the Russian Academy of Sciences).

PP-8

SUPPORTED Co AND Ni CATALYSTS FOR HYDROGEN GENERATION IN PARTIAL OXIDATION OF ETHANOL

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Hydrogen can be directly obtained from ethanol by steam reforming and partial oxidation. For these processes to be economically feasible, it is necessary to identify effective, long-time stable and low-priced catalysts. Among transition metals, Ni- and Co-based catalysts have been observed to be highly active during C-C bond scission, and particularly, toward dehydrogenation reactions [1-5].

In this study, we examined Co and Ni catalysts supported on AlZn mixed oxide for the generation of a H_2 and CO rich fuel gas by ethanol partial oxidation. The ternary Ni(Co)AlZn oxide catalysts were prepared by the sol-gel method using aqueous nitrate solutions as precursors and citric acid as a chelating agent. The resultant powders have been characterized by various techniques to examine the effect of phase composition on reducibility, structural and morphological properties, catalytic activity and stability.

TEM analysis reveals that non-promoted $ZnAl_2O_4$ and Co- and Ni-promoted oxides have similar morphology with spherical polycrystalline particles which, however, differ in size. ED pattern and XRD analyses of CoAlZn and NiAlZn show the presence of Co_3O_4 and NiO, respectively, together with spinel phase of $ZnAl_2O_4$, see Fig. 1. These phase compositions were confirmed by XRD and TPR analyses of the catalysts. It was shown by IR spectra of adsorbed pyridine that the original acid/base properties of the individual oxide were modified by formation of the mixed oxides. Although strong metal-support interactions decrease the reducibility of metallic particles, these strong interactions produce higher values of exposed surface metallic active sites, and thus increase the catalytic performance.

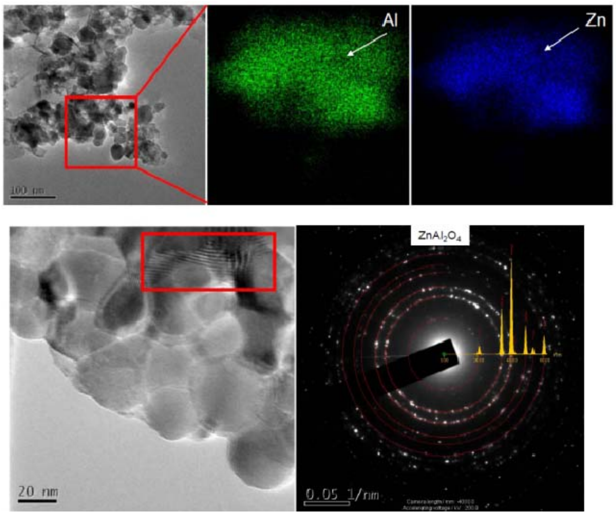

Figure 1: TEM photographs and EDS results for the AlZn sample.

The CoAlZn and NiAlZn catalysts were tested in ethanol partial oxidation (molar ratio O_2/ethanol = 0.75) using a fixed-bed reactor at atmospheric pressure in a temperature range between 300 °C and 750 °C. The ethanol conversion started at 400 °C and nearly complete conversion was obtained at 500 °C. As a first step of the reaction network thermal decomposition to acetaldehyde was observed. With increasing temperature the formation of H_2 and CO increases dramatically at the expense of acetaldehyde. The NiAlZn catalyst showed the highest hydrogen productivity with 96 % H_2 selectivity after 120 min time-on-stream at 750 °C and 88 % selectivity to CO, whereas CO_2 was formed as the only by-product with 12 % selectivity. The more subtle difference between CoAlZn and NiAlZn was attributed to different reducibility and lattice oxygen mobility of these materials. NiAlZn showed lower Lewis acidity, but provided much higher mobility of lattice oxygen at ≥200 °C than CoAlZn. Higher concentration of reduced Ni/NiO_x species on NiAlZn than of Co/CoO_x on CoAlZn makes the former more active in C–H bond cleavage resulting in higher hydrogen selectivity at ≥600 °C. At higher temperatures, concentration of mobile O species and vacancies on NiAlZn is higher than on CoAlZn, hence better catalytic performance was achieved in the 600-750 °C temperature range.

The 10 wt.% NiAlZn catalyst showed high stability over 100 h time-on-stream at 700 °C. Hydrogen selectivity was around 90 %, and CO, CO_2 and minor amounts of CH_4 were the only carbon containing products. This highly effective catalyst was deposited onto a ceramic monolith makes them suitable for application in solid oxide fuel cells. In situ co-precipitation with sol-gel method provides a higher thermal and mechanical stability compared to conventional wash-coating method as well as higher homogeneity.

Figure 2: Ceramic monolith co-precipitated with NiAlZn catalyst.

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TRANSFORMATION OF GLUCOSE ON Pt/C UNDER CONTINUOUS-FLOW CONDITIONS

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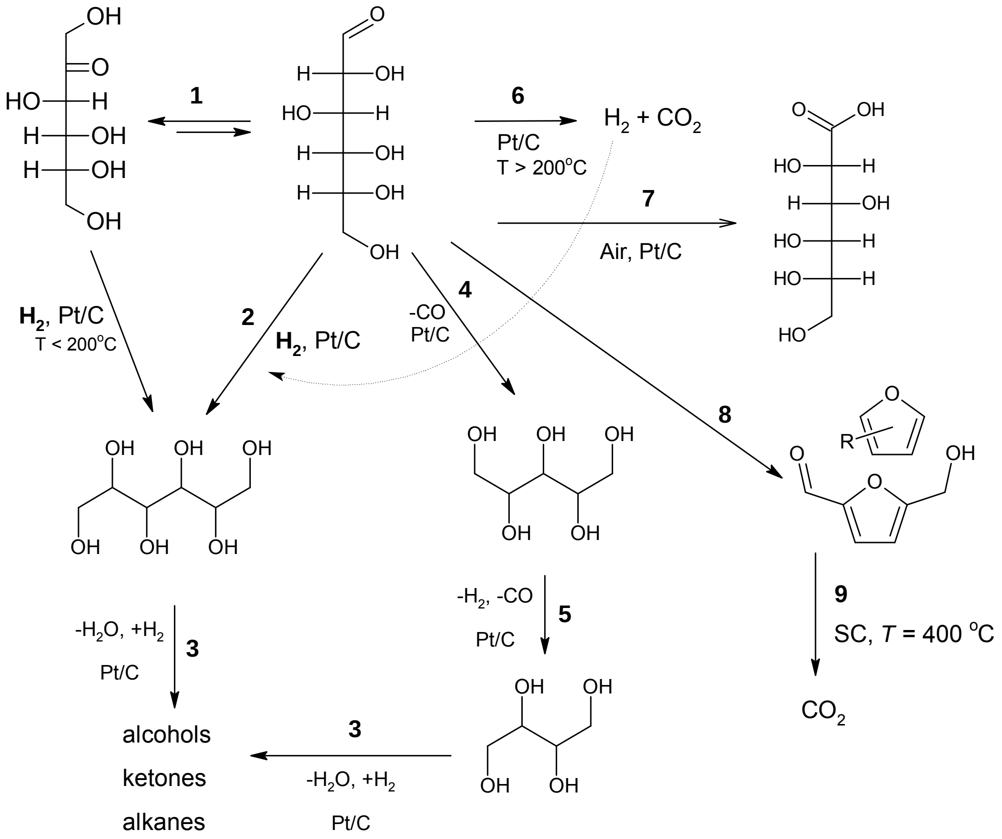
In connection with the intensive development of the environmental trends in the chemical industry there is of considerable interest to obtain valuable chemical compounds from renewable sources. Biomass can be considered as a promising feedstock. Biomass is readily available and renewable natural raw material that can be used in the production of chemical substances or energy into the future of environmentally friendly technologies. The main component of biomass is cellulose. The initial task of processing cellulose is hydrolysis up to low molecular weight products as glucose and oligosaccharides, that are subjected to a deeper conversion to obtain valuable chemicals or products of gasification (hydrogen and gaseous hydrocarbons C_2-C_4). So the study of conversion of mono- and oligosaccharides is one of the most important problem in the development of technologies for processing biomass.

The aim of this study was an investigation of possible routes of glucose transformation under different conditions in reactor with fixed-bed catalyst. The selection of glucose is determined by its high availability, low cost and, most importantly, the prevalence in nature as the monomer of cellulose.

The investigation of the thermodynamic and kinetic characteristics of the hydrogenation of glucose on Pt/C at temperatures 120–200°C and a pressure of 60 atm was performed. The kinetic parameters of glucose reforming was obtained. The rate constants of the conversion of glucose and the activation energy of this reaction were found to be 55 kJ/mol.

The catalytic conversion of glucose in the presence of hydrogen, oxygen and helium on supported Pt/C catalyst was investigated at 120–400°C and pressures up to 250 atm. The hydrothermal conversion of glucose under sub- and supercritical conditions without catalyst was also studied. The scheme of products formation depending on reaction parameters was proposed.



Isomerization (1) of glucose to fructose is the simplest transformation of the initial substrate. In the presence of hydrogen glucose is hydrogenated to sorbitol (2). The lower temperature requires for high selectivity of this reaction. Further various alcohols, ketones, and alkanes are produced in reactions of dehydration and hydrogenation (3) or hydrogenolysis of C-O bond. The formation of products with carbon number less than in the original substrate is possible as a result of decarbonylation (4, 5) of aldehydes formed as intermediates. At elevated temperature aqueous-phase reforming of glucose to H_2 and CO_2 occures on the catalyst Pt/C (6). In a flow of helium, hydrogen produced by the reaction (6) participates in the hydrogenation of glucose (2) and subsequent reactions (3-5). In the presence of air glucose undergoes oxidation (7) to form gluconic acid. Under subcritical conditions furan derivatives are formed during sequential dehydration of the initial substrate (8). The conversion of an aqueous solution of glucose under supercritical conditions is characterized by a process of complete oxidation.

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THEORETICAL RESEARCH OF PROMOTION SOME COMBUSTION REACTIONS

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In 2007, more than $100 billion was invested in new renewable energy capacity, manufacturing plants, and research and development – a true global milestone. Yet perceptions lag behind the reality of renewable energy because change has been so rapid in recent years. In many developing countries wood has been used as a fuel. The situation is growing so desperate that wood is poached from forest reserves. As a result the ecosystem is degrading deplorably. So, in order to protect the natural environment, there is every necessity of producing alternative source of energy for the needs of the people from one hand, from other hand economy of fuels can be reached by more full combustion of current fuels.

It was shown before [1], that CF_3H could be inhibitor for hydrogen combustion. Hydrofluorocarbons (HFC) have been generally viewed as environmentally acceptable alternatives fire extinguishing agents to halons, as HFC do not contain Cl or Br atoms, which were prohibited by Montreal Protocol [2] and hence have ozone depletion potential of zero. But there are some papers [3, 4] where the more full combustion of methane flame have been observed in the presence of CF_3H and used α-alumina tube surface. It was difference between conversion CH_4 and CF_3H and rates of formation of major products as a function of time on stream during the reaction of CF_3H with CH_4 in fresh and used α-alumina reactors under determined conditions [3]. The formation of CO_2 during reaction was unexpected effect for experimental researchers [4]. For detail research of the mechanisms of methane activation by fluoromethane CF_3H the quantum-chemical calculations by ab initio methods (6-31G* basis set) have been provided. First of all the reaction energies were calculated for CF_3H destruction ways:

$$CF_3H \rightarrow CF_3^{\bullet} + H^{\bullet} \qquad (E= 95,56\ kcal/mol) \qquad (1)$$

$$CF_3H \rightarrow CF_2^{\bullet\bullet} + HF \qquad (E= 66,82\ kcal/mol) \qquad (2)$$

As you can see from the calcultion results the more preferable reaction way is (2). As a rule this elementary reaction leads to deactivation of CF_3H, because the neutral molecule HF and stable biradical $CF_2^{\bullet\bullet}$ have formed. But, as we can assume in the presence of used α-alumina tube surface, as catalyst the reaction way of activation methane fuel is becoming following:

$$CF_3^{\bullet} + CH_4 \rightarrow CHF_3 + CH_3^{\bullet} \qquad (E= 48.69\ kcal/mol) \qquad (3)$$

The more full combustion of fuel facilitates also oxygen on the unfreshed α-alumina tube surface. So at the elementary reactions during conversion CF_3H level the more full combustion of CH_4 was explained by catalytic effect of used α-alumina tube surface. It was shown, that CH_4 activation in the presence of CF_3H occurs due to the lowering of activation barrier of reaction (1) and one of the reaction products $CF_3^{\bullet}$ simultaneously leads to activation of fuel molecule and regeneration new molecule CHF_3 by reaction (3).

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BIOLOGICALLY DECOMPOSING LUBRICANTS ON THE BASE OF OXYETHYLATED GLYCERIDES

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Development and implementation of biodegradable lubricants is a promising direction for the world petrochemical industry. A leading role in addressing this problem is due to biological resources – vegetable oils, especially rapeseed oil and products of its transesterification. These biological resources is an acceptable alternative feedstock for the production of oil and lubricants. We offer the most simple way to get biodegradable ethoxylated oligomers by reacting vegetable glycerides with glycols. As vegetable glycerides to produce high-quality lubricants we suggest the use of rapeseed oil which has exceptional lubricating properties. Rapeseed oil was in the presence of polyethylene glycols ethoxylation titanosilicates as catalyst. Found that the greatest catalytic activity titanosilicate has the following composition: $2Na_2O \cdot SiO_2 \cdot TiO_2$. The catalyst allows the synthesis at 73-75 °C with a product yield of 93%. This yields an oily viscous liquid – oxyethylated ethers hydroxyethyl groups to the number of 2 to 13 (the ether subsequently designated E2-E13 respectively). Varying the degree of ethoxylation and certain content in a mixture of ether can get a variety of products: from unique mineral conservation materials and grease emulsifiers to food and cosmetics. Thus the most suitable to create a water-miscible lubricant material is a product based on ether E9 containing the last 65-70% (tentatively called product P9). P9 product has an extremely high tribological properties. 2% aqueous emulsion P9 superior on all counts more concentrated emulsions of cutting domestic funds (Ukrinol-1M) and imported (Shell S-8265) production. Another important scope of the ether is to use them as a protective agent against the buildup welding spatter. The most effective use for these purposes were 8-17% aqueous emulsion mixture of products based on esters of E2, E6 and E13 (conditionally designated P-2-13). P2-13 emulsion significantly improves the quality of welded joints. Number of adhering emulsion spray the treated surface of the plate was 10-15% of the spray to adhere raw emulsion plate. The treated emulsion plate weld not interrupt their length. P2-13 emulsion effectively degrease machined surfaces due to good detergency. It creates a temporary corrosion protection. This ultimately minimizes time and money in the final processing of metal surfaces. Currently the Company "Instrumental and mechanical plant" Eurostar" Ltd (Novocheboksarsk) product P2-13 is produced under the brand name "Technological mean KSA-202M" (TU 9141-002-71033606-2010). This mean has successfully established itself as an alternative replacement of famous foreign means: Binzel-spray, Dusofix-paste, Metallotion Protec CE 15L. The obtained products, such as P2 and P9-13, belongs to the class of rapidly degraded surfactants (GOST R 50595-93).

Thus on the basis of vegetable triglycerides we have developed biodegradable ethoxylated oligoesters. These oligoesters are effective lubricants, means from sticking welding spatter and provides the necessary performance characteristics.

PP-12

CATALYSIS PROCESSES IN BIOMASS GASIFICATION FOR FUTURE GENERATION DEMANDABLE BIOFUELS IN EGYPT

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Catalysis process is one of the appropriate popular petro-chemical processes in the contemporary world. Catalysis is a broad technical field rather than a product. Setting targets for the development of catalytic designs or production is, therefore, different from setting targets for particular products. Catalysis has been defined as the process by which chemical reaction rates are altered by the addition of a substance that is not itself changed during the chemical reaction. Catalysts are usually used so that chemical reactions can occur at temperatures and pressures low enough for producers to use economically priced equipment or to ensure that the rate of production of a desired product is greater than the rates of production of undesirable by-products. Catalysis-based chemical synthesis accounts for 60 % of today's chemical products and is a factor in 90 % of current chemical processes.

Based on the availability of Agro-biomassand high increasing demand of energy in the Arabian region especially in Egypt has been motivated to implement this existing catalysis process in fuel energy generation through using biomass as raw materials. As a case analyses it will be implemented to realise and understand the petro chemical engineering development for recover fuel energy in Egypt. For Catalysis process introduce in Egypt it will be designed for two steps such as Catalyst develop where 3 issues will be considered like Productivity, Attribution resistance, Stability; in the 2nd step is Process development where two issues will be considered such as reaction kinetics and integration strategy. These two sections will create the Technology Development Approach (TDA). Under this TDA process the central process would be Catalytic Pyrolysis Process which process will slurp biomass and reject O_2 and generate Bio-crude, as a whole TDA will scale up and be commercialized in field level.

It is expecting that through this TDA the biomass pyrolysis will generate Gas (15 %), Char (15 %) within 550 °C temperature and 70 % would be pyrolysis vapours and will entered as Liquide-plase and upgrade H_2, H_2O, O_2 others. Through this process the Syngas will be cleaned and finally will produce Methanol Synthesis which will produce Dimethyl Ether Synthesis: $2CH_3OH = CH_3OCH_3 + H_2O$ it is LPG and Diesel fuel, the final production will be LPG and bio gasoline. The objective of this study is to understand the scenarios of the biofuel demand in the Arabian region. To introduce Catalytic process as low cost and local raw materials oriented instrument for bio fuel energy generation and fulfil the future demand in the region. Make some recommendations for future collaboration and implementation of Catalytic process in petro-chemical engineering sector to improve the biofuel demand in the Arabian region.

Keywords: Catalysis Process, TDA, Biomass, Gasification, Biofuels, Demand, Collaboration and implementation.

HETEROGENEOUSLY CATALYZED CONVERSION OF BIOFEED COMPONENTS: A STEP TOWARDS CARBON-NEUTRAL FUELS

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The possibility of biofeed components conversion to fuel components offers a route to carbon-neutral fuels. Intensive growth of biofuel production poses a new challenge to face: new green fuels need new green additives. Today this issue overlaps another important one, namely valorization of biofeed components.

In our investigations we have focused the attention on the valorization routes of such promising bio-derivatives as bioglycerol, biobutanol and acetone. The first of them is known as a by-product of biodiesel production, and the main difficulty about it's usage in pharmacy and cosmetics is that biodiesel-derived bioglycerol contains impurities of methanol and water. Together with increasing volumes of bioglycerol production these facts are the basis of bioglycerol valorization processes actuality. Other biocomponents – acetone and biobutanol – are also known to be produced from biotic resources.

Some of glycerol, acetone and butanol derivatives are potential new green chemicals that can be used as biofuel components and eco-friendly solvents. For example, glycerol ketalization with acetone followed by the subsequent etherification of ketal by isobutene is known as the route for production of STBE (solketal tert-butyl ether). STBE is a promising octane-increasing agent for gasolines. The process of STBE synthesis in the multi-section flow reactor includes sulfuric acid usage [1]. In our studies we have attempted to develop the process of STBE synthesis according to the main postulates of green chemistry.

The synthesis of STBE from glycerol, acetone and tert-butanol catalyzed by zeolite-BEA can be held in one stage in the flow reactor under very mild conditions (35-55 °C, atmospheric pressure, LHSV from 0.5 up to 1.5 h^{-1}). Glycerol conversion yields a mixture of solketal and STBE. The catalyst shows high selectivity (yields of tert-butyl glycerols and acetone condensation products are negligible) and great stability.

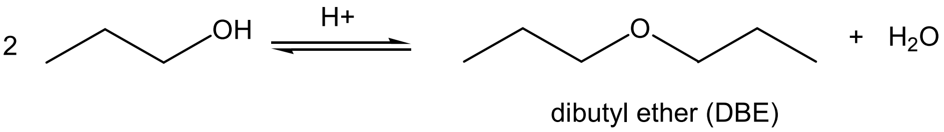

Fig.1. Butanol-1 intermolecular dehydration.

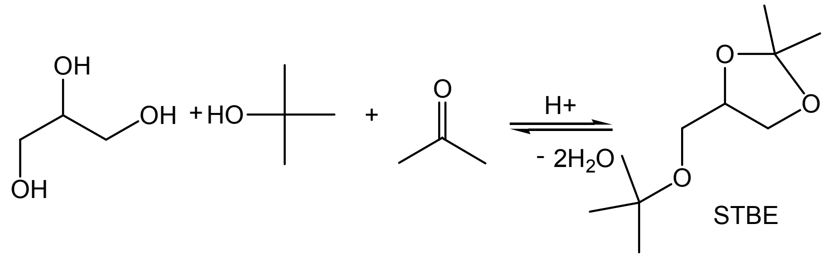

Fig.2. Formation of STBE from glycerol, acetone and TBA.

Another good example of promising oxygenate fuel additive is di-n-butyl ether (DBE). DBE has cetane number about 100-105 [2], melts at -90 °C, improves lubricity of diesel fuels [3] and has quiet high combustion heat for a fuel oxygenate (approximately 41 MDj/kg). DBE could be new green additive for diesel fuels.

DBE synthesis using perfluorinated sulfonic resins is described [4] as a way of deep selective 1-butanol conversion. Unfortunately, these catalysts are quiet expensive today. We have studied DBE synthesis from 1-butanol on our flow plant using such catalysts as zeolites, γ-Al_2O_3, Ambelyst 70. The latter yields about 55% mol. of DBE with high selectivity under mild conditions: 100-140 °C, atmospheric pressure, LHSV=0.5-1.0 h^{-1}. Reaction proceeds with a visible exothermic effect. Zeolite catalysts yield up to 63% mol. DBE under 130-200 °C, atmospheric pressure, LHSV=0.2-2.0 h^{-1}. These results make it possible for us to consider DBE synthesis as a potential industrial way for green cetane-enhancing diesel additives production.

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PP-14

ENVIRONMENTALLY BENIGN CATALYTIC PRODUCTION OF FINE CHEMICALS

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Integrated processing of natural renewable raw materials, including wood using industry waste, makes it possible to produce industrially claimed materials, such as epoxides, mono and dicarboxylic acids. These materials have found a wide application in different fields. The carboxylic acids, involving along with carboxylic groups some other functional groups, can be used as matrixes and building blocks for synthesis of medical preparations or their precursors.

The method of phase-transfer catalysis with bifunctional homogeneous catalysts based on the peroxopolyoxotungstates is a very promising way to perform oxidation transformations of natural raw materials into novel biologically active materials. The peroxo compounds formed in systems $H_2O_2 – H_3PO_4 – Na_2WO_4$ and $H_3PW_{12}O_{40}$ – H_2O_2 are sufficiently stable and anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$ exhibits high activity in the oxidation reactions [1]. A simultaneous application of phase-transfer catalysts as quaternary ammonium cations (Q^+) and oxidation catalysts as peroxopolyoxotungstates permits one to perform oxidation processes during one technological step.

In the present work we have screened different substrates such as cycloolefins, unsaturated fatty acids and their ethers, lupane-type triterpenoids and coumarins. The oxidation reaction was performed in a two-phase system in the presence of $Q_3\{PO_4[WO(O_2)_2]_4\}$. Most of the resulting products – derivatives of betuline, peucedanine and unsaturated fatty acids – exhibit antiviral, antiinflammatory and anticancer action [2].

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BIODIESEL FROM HETEROGENEOUSLY ACID-CATALYZED ETHANOLYSIS OF SUNFLOWER OIL

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INTRODUCTION

At present, the homogeneous base-catalyzed methanolysis reaction of vegetable oils is the most often used process for the industrial biodiesel production. The toxicity of methanol, its non-renewable character and the possibility of ethanol production from renewable resources (bioethanol) have contributed to the development of a vegetable oil ethanolysis process for biodiesel production that is gaining importance. Compared with homogeneous catalysis, heterogeneous catalysis offers advantages such as reduced amounts of wastewater produced, simpler purification processes, besides facilitating the recovery of the solid catalysts by simple filtration and the possibility of reuse [1]. Heterogeneous catalysis requires however more severe reaction conditions, notably in terms of temperature and pressure. Acid heterogeneous catalysts have several advantages over solid base catalyst mainly the fact that they are less affected by the presence of free fatty acid and water which is interesting for processing low-value and inedible feedstocks [2]. This communication describes the ethanolysis of sunflower oil with acid metal oxide catalysts.

EXPERIMENTAL

Commercial (Sigma-Aldrich) oxides (Zr (IV), Nb (V), Mo (VI), W (VI) and Ta (V)) and Phosphotungstic acid hydrate (HPA) have been studied. Catalytic performance was assessed in a 250 ml glass reactor with magnetic stirring by reactions at 75°C with refined sunflower oil and ethanol, using different ethanol/oil molar ratios (12-24) and catalyst concentrations (2-5 wt. % referred to the oil loaded into the reactor). A Parr autoclave reactor with mechanical stirring was used for experiments at higher temperatures. Powders catalysts were characterized by N_2 adsorption (Gemini V Micromertics®) and NH_3 temperature programmed desorption (NH_3-TPD, Micromeritics® Autochem 2920). Ethyl esters (biodiesel) contents were analyzed by size exclusion chromatography (SEC).

RESULTS AND DISCUSSION

A preliminary screening was performed to identify the most promising solid acid catalysts. Some of the characterization and reaction results are included in Table 1.

Table1. Characterization results and triglycerides conversion after 24 h of reaction (ethanol/oil molar ratio 12:1, catalyst concentration 5 wt. %, 75 ºC, 1 atm)

Catalysts	**Conversion (%)**	**S_{BET} [m^2/g]**	**NH_3 desorbed [mmol/g]**
Zr_2O	2.7	5.0	0.01 (153ºC)
Nb_2O_5	6.1	5.2	0.00 (167ºC)
MoO_3	39.2	4.4	0.01 (164ºC) 0.01 (673ºC)
WO_3	4.4	4.4	0.00 (135ºC)
Ta_2O_5	2.7	5.3	0.01 (151ºC)
HPA	28.5	2.0	0.52 (169ºC) 0.46 (549ºC)

As indicated in Table 1, there were significant differences in the activities among the different catalysts. Except for MoO_3, the single oxides WO_3, ZrO_2, Nb_2O_5 and Ta_2O_5 exhibited in general very low catalytic activities. The HPA solid, despite being highly acidic, showed moderate activity. Moreover, the solubility tests showed that it was found to be completely soluble in ethanol. According to these results molybdenum (VI) oxide was selected as the catalyst for the rest of the study. Results are shown in Figure 1.

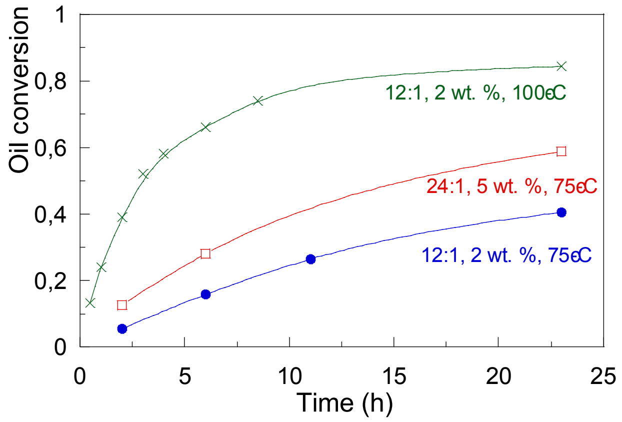

Fig. 1. Evolution of the ethanolysis conversion with reaction time using commercial MoO_3 as catalyst.

It can be seen that the oil conversion increases with the ethanol/oil molar ratio and MoO_3 concentration. Reaction temperature is seen also as a variable that greatly affects the activity resulting in significantly higher conversions at 100 °C. In view of the results obtained, we are investigating even higher reaction temperatures. In the same way, the stability of the catalyst and its reuse are under study, as well as the influence of the presence of free fatty acids and water on the MoO_3 performance for the ethanolysis reaction.

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LIQUID PHASE OXIDATION OF BENZYL ALCOHOL CATALYZED BY MANGANESE OXIDE: KINETIC ANALYSIS

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Manganese oxide was prepared by mechano-chemical process in solid state and was characterized by chemical and physical techniques. The catalytic activity of manganese oxide was studied by carrying out the oxidation of benzyl alcohol in liquid phase using n-octane as solvent over the temperature range of 323-373 K and oxygen pressure of up to one atmosphere. Benzaldehyde and benzoic acid were identified as the reaction products. However, benzoic acid appeared in reaction mixture after complete conversion of benzyl alcohol to benzaldehyde. Typical batch reactor kinetic data were obtained and fitted to the Langmuir-Hinshelwood, Eley-Rideal and Mars-van Krevelene models of heterogeneously catalyzed reactions. The Langmuir-Hinshelwood model was found to give a better fit. However, the adsorption sites for benzyl alcohol were found to be homogeneous in nature and therefore, the adsorption of benzyl alcohol was taking place according to the Langmuir Adsorption Isotherm. The heat of adsorption for benzyl alcohol was determined as -18.14 kJ/mol. The adsorption of oxygen followed the Temkin Adsorptin Isotherm, and therefore, the heat of adsorption of oxygen shows a linear decrease with increase in the surface coverage. The maximum heat of adsorption for oxygen at surface of catalyst was –31.12 kJ/mol. The value of activation energy was found to be 71.18 kJ/mol, which was apparently free from the influence of the heat of adsorption of both benzyl alcohol and oxygen.

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PP-17

CATALYTIC BIOMASS GASIFICATION USING THE METHOD OF FILTRATION COMBUSTION WITH SUPERADIABATIC HEATING

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Use of catalysts for an intensification of process, increase in the yield of useful products, and a decrease in the processing temperature is an important trend in the development of thermal processing of biomass. Implementation of catalysis in biomass processing faces several competing factors. Those are: complexity of the mechanism of reagents interaction, diffusion limitations on the transport of initial substances, the catalyst, and reaction products, heterogeneity of raw materials, and impurities deactivating the catalyst.

In biomass gasification in a regime of filtration combustion with superadiabatic heating, up to 70 % from its dry mass can be converted into liquid products. The liquid hydrocarbons can be used as raw materials for producing motor fuels or valuable chemical products. The objective of this study was to investigate effect of catalysis in biomass gasification on the yield of valuable products to be used as fuel or in the chemical industry. We addressed the possibility to use catalysts during gasification of wood as means for preliminary processing of liquid hydrocarbons within the gasifier reactor, so as to improve their quality.

We report experimental results on gasification of wood with the natural catalyst, zeolite of the general formula $(Na, K, Ca, Mg)\cdot Ca[Al_6Si_{30}O_{72}]\cdot 20H_2O$ added to the processing mixture. Two series of experiments on gasification of a wood mixed with lumpy solid material were performed. In the first series, the solid material (heat-carrier) was inert chamotte brick (it is not a catalyst). In the second, the zeolite catalyst was used. Experiments on wood gasification were carried out in a 46-mm-diameter quartz reactor. In order to reduce the heat loss, the lateral surface of the reactor, it was shielded with a heat-insulating screen made of aluminum foil. During experiments, temperature profiles at particular reactor points were registered and gaseous and liquid products were sampled. The temperature was measured using chromel-alumel thermocouples. The collected samples of wood tar and water with the organic substances dissolved in it were weighed and further, after drying and repeated weighing, analyzed using the method of burning in oxygen.

The average element composition of tar (by mass)

	C, %	H, %	O, (as difference) %
With zeolite	66.0	7.0	27.0
With chamotte	73.0	7.5	19.5

The temperature measurements showed that, with the zeolite, the combustion temperature was100-200 °C lower, than in case of chamotte used. With an increase in the wood content in the processing mixture the difference between the maximum values of temperature decreases. This can be explained by a lower surface of contact between the catalyst and wood or pyrolysis products, thus the catalyst plays the role of a heat carrier. Owing to lower combustion temperature, with the zeolite used in gasification mixture, the gaseous products showed incompleteness of reaction of oxygen and carbon presence on zeolite particles was observed. The solid products do not contain carbon in the case of chamotte used. The composition of gaseous products changes but slightly for two solid materials used as heat carriers. The yield of liquid products of wood pyrolysis was lower in the case of the zeolite/wood mixtures, compared to the chamotte/wood. A decrease in the content of heat carriers results in decreasing difference between the tar yields for the heat carriers used. The combustion rate behaves similarly. The element composition of tar (see the table) virtually does not change in the wood content in the processing mixture from 10 to 70%. Zeolite used in gasification results in a decreased carbon content and respective increase in the oxygen content in the liquid products; this indicates that their quality changes.

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PP-18

SYNTHETIC JET FUEL FROM MICROALGAL BIOMASS

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The use of biomass as energy source will provide an excellent opportunity for mitigtion of greenhouse gas emission and reducing global warming through the sustitution of conventional fossil-based energy sources. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009, on the promotion of the use of energy from renewable sources, aims at achieving by 2020 a 20% share of energy from renewable sources in the EU's final consumption of energy and a 10% share of energy from renewable source in each member state's transport energy consumption.

In this favorable context, our research was focused on an integrated system for obtaining synthetic jet fuel, based on production and complete valorisation of microalgal biomass. The first stage refers to mixotrophic microalgae culture on nutrient media supplemented with crude glycerin as carbon source, and protein hydrolysate as nitrogen source, both of them resulting as by-products in the later stages of the process. Harvested microalgal biomass was extracted, to produce algal oil, and deoiled fraction comprising carbohydrates was further processed to furan derivatives, as precursors for synthetic aviation fuel. Algal oil and furan derivatives was transformed by catalytic hydrogenation in hydroxyl compounds. Finally, by catalytic dehydration, hydrocracking and isomerization processes will result a mixture comprising iso/n alkanes.

A few catalysts was evaluated concerning their efficiency in obtaining hydroxyl compounds and finally branched hydrocarbons. These are suitable for, or as a blending component for, uses such as an aviation biofuel. Biofuel obtained in this way, satisfied all the requirements of the ASTM D7566 - 12a Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons.

The reaction intermediates and final product were characterized analytically by FT-IR and GC-MS methods.

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K-Ni-MoS_2 CATALYST PREPARED BY MICROEMULSION FOR MIXED ALCOHOL SYNTHESIS

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Environmental concerns and the shortage of fossil fuels have recently increased the search for new energy sources. Second-generation biofuels, including ethanol, become a promising alternative to conventional fuels while avoiding problems related to food and feed production. Second-generation ethanol can be produced by means of either a biochemical or a thermochemical route.

The biochemical route is responsible for most of the ethanol produced today [1]. The biomass is first pretreated to break the cellulose-hemicellulose-lignin interactions and make it more accessible to enzymes; the pretreated biomass is then hydrolyzed to obtain fermentable sugars; finally, the hydrolyzate is fermented to ethanol [2]. The main drawback of this alternative is the low conversion achieved, since lignin cannot be used and it represents around 25-30 %wt of biomass. Hydrolysis of cellulose and hemicellulose is also difficult [3] and there are some recalcitrant materials that must be necessarily handled with the thermochemical approach. The complex pretreatment steps and the enzyme cost make this alternative not appropriate [2].

On the other hand, the thermochemical route begins with the production of synthetic gas, or syngas, primarily via gasification. Syngas can then be converted to ethanol by a chemical or a biological conversion. Currently, syngas is mainly produced from fossil fuels such as coal, natural gas and naphtha [4], but it can also be obtained from biomass and a wide variety of waste products (MSW, sewage sludge, industrial waste gases, black liquor, glycerol), given this alternative a high flexibility when compared with the biochemical approach.

Catalytic conversion of syngas to ethanol and higher alcohols has been widely studied. Sulfided molybdenum-based catalysts are one of the most promising alternatives because they are sulfur resistant and deactivate slowly by coke deposition [1]. The addition of alkali metals has proven to shift selectivity from hydrocarbons to alcohols. Further addition of transition metals such as Co or Ni increases the selectivity to higher alcohols [5].

Previous studies within our research group describe the behaviour of an unsupported K-Ni-MoS_2 catalyst for mixed alcohol synthesis from syngas [6, 7]. The aim of this work is to develop and study the performance of a K-Ni-MoS_2 catalyst prepared by the microemulsion technique and compare it with a conventional catalyst prepared by coprecipitation. Catalysts prepared by the microemulsion method, which was first presented in 1982 [8], have shown enhanced properties in many applications when compared with conventional catalysts [9].

Preliminary results show that the new preparation method enhances syngas conversion. Further work is necessary in order to evaluate the performance of the novel catalyst.

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COPPER BASED CATALYSTS FOR RECEIPT OF ETHYLENE FROM BIOETHANOL

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Increase in oil prices in the last few years leads to an increase in prices of basic petrochemicals. Now there is an active search for a new basic raw materials that can replace oil in the production of products for the chemical industry. Bioethanol is the most alternative renewable raw materials with an unlimited supply. Plants containing starch (potatoes, wheat, corn, etc.), as well as waste of wood, pulp and paper industry, field crops and livestock can be the raw material for the production of bioethanol.

Huge range of intermediate and target products of petrochemical and organic synthesis, such as aromatic hydrocarbons, hydrocarbons of gasoline range, hydrogen-containing gases, and olefins (ethylene, propylene, etc.) can be obtained from bioethanol.

It is known that olefins are widely used in industry. Due to the presence of double bond the olefins are reactive which makes them important products in the various processes of organic chemistry. For example, ethylene, the most needed intermediate product of organic synthesis which is a basic chemical raw materials for the production of polyethylene, polypropylene, plastics, styrene and other products.

Currently, pyrolysis of gasoline and liquefied petroleum gas (propane-butane fraction) is the primary method for producing of ethylene. This process is carried out at high temperatures – 780-1200 °C. Assessment of industrial emissions shows that 180 million tons of carbon dioxide released into the atmosphere during the production of ethylene by such technology. Therefore it is possible the use of C_1-C_4 alcohols to produce of olefins as a cheap and environmentally friendly materials.

In this paper, the results of the conversion of ethanol and water-ethanol mixtures on copper-containing catalysts are presented.

Figure 1 shows the results of the dependence of yield of ethylene in the products of ethanol conversion from space velocity on various catalysts at reaction temperature of 400°C and the concentration of mixture = 43.4 g/m^3. Effect of space velocity was studied in the range from 1500 to 6000 h^{-1}. As can be seen from Figure 1 the catalyst

$3\%Cu/20\%Al_2O_3+80\%H\text{-}ZSM\text{-}5$ was the most active at lower space velocities. Catalytic activity varies with the introduction of 1% Ni in the $3\%Cu/20\%Al_2O_3+80\%H\text{-}ZSM\text{-}5$, the yield of ethylene increases with increasing the flow rate of reaction. Addition of 1% Ce in the $3\%Cu/20\%Al_2O_3+80\%H\text{-}ZSM\text{-}5$ catalyst has promoting effect for all space velocities. At 1500 h^{-1} on $3\%Cu+1\%Ce/20\%Al_2O_3+80\%H\text{-}ZSM\text{-}5$ catalyst, the yield of ethylene is increased from 85 to 88.9% compared to the copper catalyst without additives. The highest yield of 93% was obtained at space velocity 3000 h^{-1}. Effect of water concentration on the yield of ethylene on catalyst $3\%Cu+1\%Ce/20\%Al_2O_3+80\%H\text{-}ZSM\text{-}5$ at T = 400 °C, W = 3000 h^{-1} was studied (Figure 2).

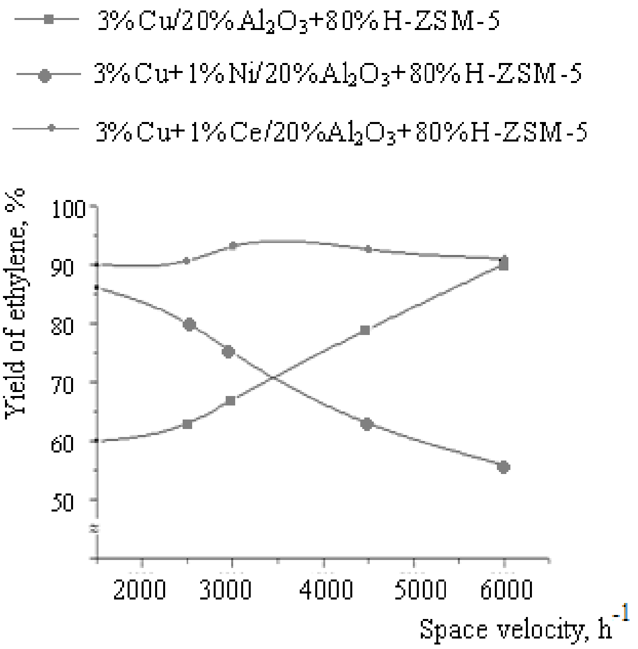

Fig. 1. Effect of space velocity on the activity of catalysts.

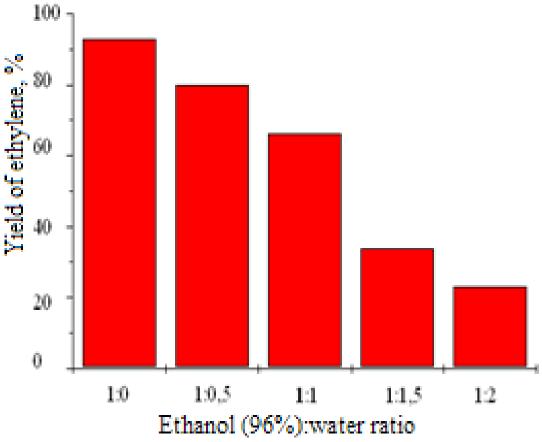

Fig. 2. Effect of water concentration on the yield of ethylene.

It can be seen that with increasing the concentration of water in ethanol (96%) – water mixture the ethylene yield decreases. Formation of methane, hydrogen, and trace amounts of acetaldehyde were observed in the reaction products except of ethylene when water is added.

PREPARATION OF THE CATALYST FOR DELIGNIFICATION OF WOOD

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At present, anthraquinone (AQ) and its derivatives are used as the catalysts in the processes of delignification of wood. A growing demand for AQ and its derivatives cannot be provided with archaic technologies of their manufacture. Acylation of benzene by phthalic anhydride according the Friedel-Krafts reaction followed by cyclization of *ortho*-benzoylbenzoic acid is the main industrial method of AQ preparation. However, in this process there is a problem of utilization of excessive acid catalyst. In another industrial process based on 1,3-butadiene reaction with 1,4–naphthoquinone (NQ), high boiling organic solvents, concentrated alkalies, and strong inorganic oxidants are used [1]. The two industrial processes produce a lot of wastes. Thus there is a problem of creating a new environmentally friendly process of AQ production.

For this purpose heteropoly acids can be used. Now processes using aqueous solutions of Mo-V-P heteropoly acids $H_{3+x}PV^{V}_{x}Mo_{12-x}O_{40}$ (HPA) are widespread [2]. Unlike many other oxidizing agents, the vanadium(V) containing HPA solutions are able to be regenerated by O_2. Thus they can catalyze the oxidation of various substrates by O_2. In the presence of the HPA solutions these processes consist of two stages carried out in separate reactors **1** and **2**. In the 1st stage a substrate is oxidized by HPA. In the 2nd stage HPA is regenerated by O_2. Thus the HPA solutions may be considered as *reversible oxidants*. Furthermore, the aqueous HPA solutions are strong Brønsted acids and can be used as acid catalysts. Therefore, the HPA solutions can be *bifunctional* (i.e. oxidative and acidic) catalysts.

We have developed a new process of AQ production in the presence of the HPA solutions [3]. At that, we have combined *in a single technological stage* two types of reactions: 1) the acidic-catalyzed Diels-Alder reaction of 1,3-butadiene with NQ giving 1,4,4a,9a-tetrahydro-9,10-anthraquinone (THA); 2) oxidation of THA by HPA with the formation of 1,4-dihydro-9,10-anthtaquinone (DHA) and then AQ. Thus, our *one-pot* process is described by scheme 1.

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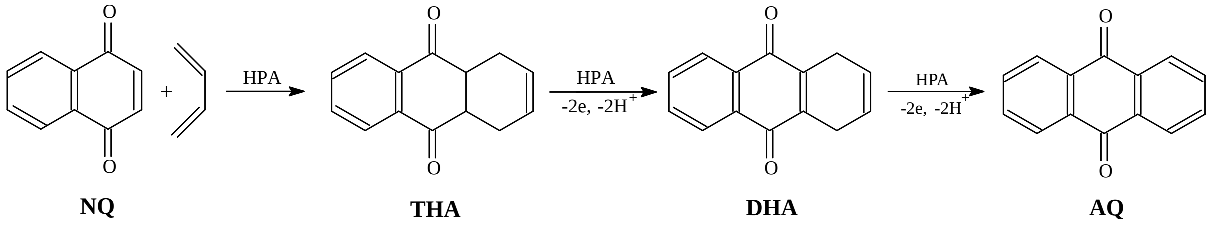

Scheme 1. Preparation of AQ in the HPA solutions.

In this process the HPA solution is used as the *bifunctional* catalyst. The process proceeds at 70-80°C in the reactor **1**. A slightly soluble (AQ + THA + DHA) mixture formed is practically quantitatively (96%) separated by filtration from the reduced HPA catalyst. The content of AQ in the mixture obtained under these conditions reaches 60%. It is important that our one-pot process proceeds *without organic solvent*.

Further the reduced HPA solution is oxidized by air O_2 in the reactor **2** at $t > 100$°C and $P_{O_2} = 2$-4 atm. In so doing, a direct contact between 1,4–butadiene and O_2 is excluded.

Our total process *is waste-free* owing to ability of the aqueous HPA solutions to be regenerated with O_2. Studies in Siberian Scientific-Research Institute of Wood and Pull-and-Paper Industry (Bratsk, Russia) have shown that the (AQ + THA + DHA) mixture may be used as the *effective catalyst for delignification of wood*. On criteria such as acceleration of delignification and stabilization of cellulose, this mixture is fully comparable with usual commercial anthraquinone obtained via the many-stage technology.

Our technology of production of the delignification catalyst has become more effective after we had developed a new method of synthesis of the modified HPA' solutions ($H_aP_zMo_yV_{x'}O_b$) that are stable at elevated temperatures (160-170°C) and can be fast regenerated by air O_2. This feature of the modified HPA' solutions has ensured high productivity of the process depicted in the Scheme 1.

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ELECTROMAGNETIC REACTOR OF WATER TREATING FROM OILS AND HYDROCARBONS

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The problem of clearing of water resources from oil pollution is rather actual now. Annual total emission of mineral oil in the seas and oceans as a result of consequences of extraction and emergencies is estimated on different sources, including the National academy of sciences the USA on the average from 6 up to 8 million tons. Nevertheless, the problem of operative and effective liquidation of consequences of similar emissions is far from the decision in view of low efficiency of existing technological decisions, and including, absence high-efficiency the reactor equipment. The majority of known processes of clearing of water environments from oil pollution is based on use the methods of oxidation [1], flotation [2], absorbtion [3], and also methods of biological clearing [4]. Under the total characteristics, including productivity, a degree of clearing, simplicity of technological decisions, the economic and power efficiency, the mentioned ways are conditionally suitable for the decision of similar problems.

The clearing process of water environments from oil pollution and dangerous hydrocarbons aromatic and olefinic the lines, based on use is developed and tested in industrial scale as basic reactionary unit of the device of electromagnetic processing water environments. The principle of work is based on the phenomenon of acceleration microparticles association of mineral oil in conditions of interaction of an external variable magnetic field with ferromagnetic sorbent which particles have own constant magnetic field. As a result of such interaction there are intensive association processes the hydrocarbonic components being consequence of concentration in places of impacts of ferromagnetic particles of electromagnetic, thermal and mechanical energies. Further, passing through the polysorbtional layers, the integrated particles of hydrocarbons are absorbed much faster, than similar particles of smaller diameter.

Working parameters of a reactor electromagnetic association:

Initial concentration of mineral oil – 100 ÷ 1 mg/L

Final concentration of mineral oil – 0,5 ÷ 0,05 mg/L
Working volume of a reactor – 30 L
Productivity on initial water – Up to 100 m^3/h
Operating mode – Continuous
Working temperature – 0 ÷ 50 °C
Working pressure – 0 ÷ 1,0 MPa

Besides direct use of the specified installation during water treating, there are variants of her modification, allowing her use in a number of adjacent tasks of oil extracting and processing. In particular, her use is planned during preliminary processing, tars, bitumen sand, in manufacture of dyes, etc. spheres.

The general distinctive characteristics of installation:

1) High efficiency;
2) Stability to a high level of pollution of communications (a rust, sand, fine stones);
3) Standardization of a design with an opportunity of fast replacement of elements (a grid, a pipe, nozzles and so forth);
4) Absence of a problem of deterioration in case of use the plastic case of a reactor.

Installation has passed industrial tests in a zone of the Caspian pool: Russia, Republic Dagestan. On a method of clearing of water environments from mineral oil with participation of the described device the patent of the Russian Federation – №2371232 «THE METHOD OF CLEARING OF THE WATER ENVIRONMENT FROM MINERAL OIL», a priority – from 27.06.2008 is received.

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THE STUDY OF THE EFFECT OF INORGANIC CATALYSTS ON THE KINETICS OF THE LIGNIN PYROLYSIS

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Pyrolysis is one of the promising ways to convert lignin into fuels. Among various aspects of the pyrolysis very interesting is a study of the effect of catalysts on this process. The main criterion for determining the catalytic activity of substances on pyrolysis is their effect on kinetic parameters, such as the relationship between reaction progress and temperature, reducing activation energy, etc.

In this study, we investigated the pyrolysis process of hydrolysis lignin in argon atmosphere in the presence of inorganic salts (5% by mass) by TG-DSC on STA 409 PC (NETZSCH, Germany). These investigations were carried out in the temperature range 25-600 °C, with a heating rate 10 °C/min. Kinetic studies using Coats-Redfern method allows us to determine the activation energy and the order of the reaction of the initial stages of the hydrolytic lignin pyrolysis in the presence or absence of salts.

Table - Kinetic parameters of catalytic pyrolysis of lignin

catalyst	T_{pyr}., °C	charcoal yield, %	n	E, kJ / mol
without cat.	230,7	44,1	3	63,13
NaCl	231,1	41,2	3	64,41
KCl	231,1	38,0	3	66,40
$AlCl_3 \cdot 6H_2O$	232,1	42,0	3	62,79
$BaCl_2 \cdot 2H_2O$	231,9	38,8	3	65,56
$FeCl_3 \cdot 6H_2O$	226,6	43,2	0	50,53
$CaCl_2$	232,6	41,9	3	69,14
$CuBr_2$	231,7	46,2	3	55,31
$ZnCl_2 \cdot 1,5H_2O$	219,5	41,5	3	45,20
$NiCl_3 \cdot 6H_2O$	234,4	41,4	3	74,75
$SnCl_2 \cdot 2H_2O$	215,7	40,4	3	71,33
KBr	231,1	40,1	3	64,72

Using $FeCl_3$, $ZnCl_2$ and $SnCl_2$ as catalysts of pyrolysis leads to reduce the temperature of the beginning of the pyrolysis (T_{pyr}). Using $CuBr_2$, $FeCl_3$ and $ZnCl_2$ reduces the activation energy for pyrolysis of lignin. The initial part of the curve of thermal decomposition of the original sample and almost all samples which contain catalysts was described by the equation of third order reaction. This indicates the presence of a complex mechanism consisting of parallel and sequential stages. Perhaps, zero order of the thermal decomposition reaction in presence of $FeCl_3$ is the result of successive interdependent stages. Almost all additives of the salts (except $CuBr_2$) are leading to lower yield of charcoal. Perhaps the using of these catalysts leads to the fact that depolymerization reactions with forming volatile products (liquids and gases) begins to dominate over the condensation reactions.

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METAL NANOPARTICLES SUPPORTED BY NANODIAMONDS AS NOVEL CATALYSTS FOR STEAM ETHANOL REFORMING REACTION

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The method for the formation of metal-carbon catalysts with VIII group metals nanoparticles, fixed on detonation nanodiamonds (DND), for steam reforming of ethanol was developed. DND as the support for ethanol steam reforming catalysts are observed for the first time. Formation of metal-carbon catalyst occurs via IR pyrolysis of precursor. The compositions based on compounds of Pd, Ni, Ru (dissolved in DMFA) and DND were employed as the precursors. The sources of metals were Pd $(CH_3COO)_2$, $NiCl_2$, $RuCl_3$. IR pyrolysis of precursor was carried out in a pulse photon annealing laboratory device at 700 °C. The formation of chelate between metal ions and ether bonds presented on the surface of DND was shown with IR Fourier spectroscopy for nanocomposite DND/$NiCl_2$ which was taken as example. The distribution of metal particles was studied by transmission electron microscopy. It was shown that metal particle size depended on metal concentration in the precursor. Thus there were only very small metal particles (about 0.5–1.5 nm) in DND/Pd-Ru(1%). And there were both types of nanoparticles in DND/Pd-Ru(20%): 1 nm and 15-20 nm. The X-ray diffraction showed that there are reduced metals in the prepared nanocomposite for nanocomposites (for example DND/Pd and DND/Pd-Ru were taken). There were an alloy nanoparticles in the nanocomposite in case of the presence of two metals in the precursor. The calculations of the structural characteristics of the metallic phase in nanocomposites were performed. And the Pd-Ru alloy is very similar to the intermetallic compound Pd_9Ru.

Applying metal-carbon nanocomposite DND/Pd as heterogeneous catalyst in the reaction of steam reforming of ethanol caused considerable increase of ethanol conversion from 60 up to 90% in the temperature range 400–600 °C. The highest yield of hydrogen was achieved at 600 °C and it was 1.83 mol H_2/ mol EtOH. The catalyst DND/Pd-Ru was proved to be more effective than DND/Pd. The catalyst DND/Pd-Ru showed almost total conversion of the ethanol at temperature above 500 °C.

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LOW-TEMPERATURE CONVERSION OF ETHANOL OVER BINARY NICKEL-COPPER CATALYST

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Hydrogen is promising fuel for various power plants, low-power devices (1-50 W) included. However, accumulation and storage of molecular hydrogen nowadays present a problem. One of possible pathways to overcome the difficulties can be hydrogen production from hydrocarbons, e.g. alcohols (methanol or ethanol), by water-vapor catalytic conversion. In this work we studied low-temperature steam reforming of ethanol over a bimetal nickel-copper catalyst deposited onto a quartz fiber of small specific surface.

Ethanol reforming was performed in a cylindrical flow microreactor 70 mm long and 6mm inner diameter. The main products of conversion are hydrogen, methane, carbon monoxide and carbon dioxide. The conversion of ethanol starts at 200 °C and completes almost by 90% at 350 °C. As the conversion proceeds, the concentration of all products increases. The concentration ratio of hydrogen, methane and carbon monoxide remains constant, with the hydrogen concentration being twice as high as those of methane and carbon monoxide. At 300 °C carbon dioxide appears in the gas phase, its content increases abruptly at 350 °C and makes 20 mol% at 400 °C. At this temperature, the carbon monoxide concentration reaches the maximum and then drops to 10 mol%, evidently due to the shift-reaction and carbon monoxide disproportionation. The selectivity of hydrogen and methane slightly decreases (by 10-15%) as the temperature rises because of an increase of CO_2 content in the gas phase; the selectivity of carbon monoxide reaches the maximum at 350 °C. At temperature below 300 °C, the selectivity of carbon dioxide is low but increases abruptly with temperature. Also the conversion of the ethanol-water mixture should produce 2 moles of hydrogen per 1 mole of ethanol. The experiments showed that the bimetal nickel-copper catalyst on quartz fibers is highly efficient for ethanol reforming at relatively low temperatures, in spite of its rather small specific surface.

THERMOCHEMICAL CONVERSION OF COTTONSEED OIL WITH USE OF NATURAL NANOTUBES

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Pyrolysis and cracking of vegetable oils is a simple and effective method of the involvement renewable raw materials of the structure of modern refineries to produce fuels, components and petrochemicals.

It was investigated the process of obtaining a C_2-C_4 olefins by thermocatalytic conversion of cottonseed oil with using of halloysite as a catalyst. Halloysite belongs to the kaolinite family of the clay minerals with high Al/Si ratio compared to other alumosilicates. It is due to acidic sites provided by aluminum oxide that cracking of the hydrocarbons occur. Halloysite consisting of layers of aluminum and silicon oxides. These layers in the mineral halloysite twisted into tubes, in which a layer of silica is on the outside of the tube, while the aluminum oxide layer refers to the inner surface of the lumen. Outer diameters of the tubes range from 40 to 100 nm. Internal lumen diameters range from 10 to 50 nm and an average length equal of tubes are in the range of 0.5 to 2.0 microns.

The different chemical structure of the outer layer and the inner sides of halloysite nanotubes attached of halloysites unique properties that do not exist in other nanotubes.

Thermochemical conversion of cottonseed oil with use as a catalyst halloysite investigated in the temperature range 500-800 °C and the mass velocity of the feed 22 hours^{-1}.

It was investigated when temperature of the process increase from 500 up to 800° yield gas fraction increases from 13.9 up to 91.9 wt%.

The content of ethylene in the hydrocarbon gases increases from 32.9 up to 43.1 wt.%, propylene content varies between 24.5-15.9% by weight.

In the temperature range 600-800 °C the yield of ethylene increased to 38.7-43.1% by weight, propylene yield decreased to 18.6-15.9% by weight, but remains much higher than the yield of propylene in the thermal conversion of cottonseed oil (4.8%).

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A NOVEL ROUTE APPROACH TO INVESTIGATION OF ELECTROCATALYTIC BEHAVIOR OF $Ni(OH)_2$/NiOOH MODIFIED GLASSY CARBON ELECTRODE WITH ANIONIC SURFACTANT IN ALKALINE SOLUTION

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In this work, NiO nano particles with SDS (Sodium dodesyl sulfate) such as anionic surfactant modified glassy carbon electrode (GC/Ni/SDS) prepared with consecutive cycling in nickel solution for their redox process and electrocatalytic activities, towards the oxidation of Saccharose in alkaline solutions. The methods of cyclic voltammetry (CV), chronoamperometry (CA) are applied. The cyclic voltammogram of GC/Ni/SDS demonstrates the formation of stable redox behavior of the Ni (III)/Ni (II) couple of the nickel oxyhydroxide under prolonged repetitive potential cycling in alkaline solution. In CV studies, in the presence of Saccharose GC/Ni/SDS modified electrode shows a significantly higher response for Saccharose oxidation. The peak current of the oxidation of nickel hydroxide increase is followed by a decrease in the corresponding cathodic current in presence of Saccharose. The anodic peak currents show linear dependency with the square root of scan rate. This behavior is the characteristic of a diffusion-controlled process. Under the CA regime, the reaction followed a Cottrellian behavior in agreement with the values obtained from CV measurements. The ionic nature of the surfactant used in the preparation of nickel oxyhydroxide layers shows a considerable effect on their electrocatalytic behavior. The GC/Ni/SDS sample exhibits the highest surface redox reactivity and shows the specific electrocatalytic behavior related to modified electrode without SDS.

POSSIBLE DEVELOPMENT OF METHODS OF POSITRON ANNIHILATION SPECTROSCOPY FOR RESEARCH OF NANOPHENOMENA TO OIL AND GAS INDUSTRY

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It is known that the structure of pore spaces of oil and gas breeds is defined first of all by its geometrical characteristics, such as the nanopore sizes and nanocapillaries and distributions of the areas and volumes of pores on them on radiuses. As one of methods of definition of parameters of pore spaces of rocks, especially for the sizes in nanometer a range can to serve the method of positron annihilation spectroscopy (PAS). Positronics including also in the structure and PAS (see, for example, [4-7]), allows to define both electronic structure of the perfect crystals, and various imperfections of especially small sizes in solid state and porous systems, such as vacancies, vacancion clasters and free volumes up to one cubic nanometer (nanoobject emptiness). It includes in the basic three methods: studying of time distribution of annihilation photons (TDAP), angular distribution of annihilation photons (ADAP) and Doppler broadening of annihilation lines with energy 0,511 MeV (DBAL) [4]. Below methods of definition of the nanoobject sizes, their concentration and a chemical compound of the environment surrounding of nanoobjects on experimentally measured parameters of TDAP and ADAP spectra for annihilation positrons in porous systems and defective solid state on an example of porous silicon and the plates of silicon irradiated by protons on the basis of the theoretical representations developed in [1-7] are considered.

Thus the structure of pore spaces of oil and gas breeds is defined first of all by its geometrical characteristics, such as the nanopore and nanocapillars sizes and distributions of the areas and volumes of pores on them on radiuses. As one of methods of definition of parameters of pore spaces of rocks, especially for the sizes in nanometer range can to serve method of positron annihilation spectroscopy (PAS). It is shown, that to one of effective methods of definition of the nanoobject sizes (vacancies, vacancion clasters), free volumes of pores, cavities, emptiness, cylindrical channels and capillaries, their concentration and a chemical compound in a annihilation place in rocks (porous systems, some defective breeds and especially in breeds with nanopores) is the method of positron annihilation spectroscopy (PAS). As an example the brief review of experimental researches of nanodefects in quartz, powders of quartz, porous silicon, the silicon irradiated by protons [5-8] is given.

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STUDY OF CATALYTIC SYSTEMS FOR METHYL LACTATE DEHYDRATION

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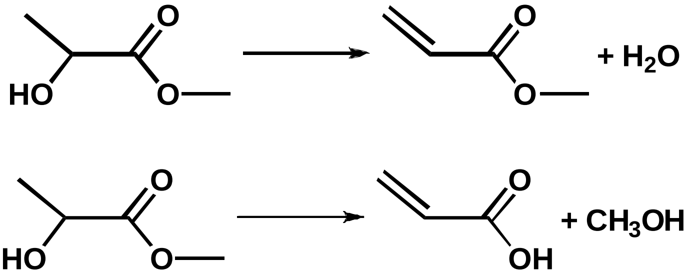
Development of new highly productive and selective methods of lactic-acid fermentation of biomass provides now to consider the lactic acid as a basic «building block» for the production of a wide variety of large-capacity organic chemicals, such as alkyl lactates, lactide and polymers on its basis, propylene glycol, etc.

One of the most attractive areas is the lactic acid and its esters dehydration into acrylate monomers. Bottleneck in the realization of these reactions is the selection of effective catalyst. The object of this research is the development of catalytic systems for the gas-phase methyl lactate dehydration:



The investigation was carried out in a fixed-bed reactor. Initial lactate diluted with water steam to suppress polymerization and polycondensation side reactions. Catalysts of different types have been tested: zeolites and their modifications; oxides of different metals; alkaline and alkaline-earth phosphates, sulfates, and other salts; as well as combined systems. For each of the catalyst the optimal process parameters, such as temperature, residence time and the initial mixture composition were found.

The most promising results were obtained with the salt systems. So, when methyl lactate dehydrated over the $Ca_3(PO_4)_2/SiO_2$ (80/20 wt.%) at 370 °C, residence time 1 s and the initial “methyl lactate : water” ratio 20:80 (wt.%) the selectivity of acrylate products was 68.6% and conversion was 24.2%. Over $CaHPO_4/SiO_2$ (80/20 wt.%) at the same contact time and feed composition, but at 390 °C, the selectivity at conversion 24.0% reached 75.5%.

PP-30

CHEMICAL, MECHANOCHEMICAL AND ENZYMATIC DESTRUCTIONS OF LIGNOCELLULOSE TO OBTAIN VALUABLE PRODUCTS

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Development of effective technologies for conversion of plant raw material for the process of obtaining second generation biofuel is becoming a priority issue for society. It causes by increasing need for the fuel, created environmental problems and reduction energetically minerals. Creating biofuels through cellulosic promising, due to availability of lignocellulosic bio, such as perennial plants, agricultural residues and wastes of wood processing.

This work aims at finding new approaches to processing transformation of grassy lignocelluloses for further converting it into valuable products – raw material for biochemical processing.

The emphasis is on the use of renewable raw materials-waste of agriculture – oat husks and straw stalks of rye, flax waste and *Miscanthus sinensis Anders* biomass (Institute of Cytology and Genetics SB RAS). Effective methods of lignocellulosic selection of the raw material are offered. Identifies the chemical compositions of lignocellulosic materials, evaluate their quality.

The directed catalytic destruction lignocellulose, isolated from straw stalks of rye and flax, in the powder forms, characterized by low average degree of polymerization and the change of degree of crystallinity of cellulose, is carried out. The most effective for this purpose is application of acids of Lewis, heteropolyacids and mechanoacoustic influences activating these processes. It supposes that such approaches lead to increase of reactionary ability of a material to further biotransformation.

Some samples of lignocellulosic materials are testing as substrates for degradation complex enzymes. Regularities of the enzymatic degradation of material type and way of receiving are determined.

The studied lignocellulosics were shown to be promising substrates to produce glucose-xylose hydrolyzates. At this point of the study, it found that the lignocellulosic samples – the products from dilute nitric acid treatment of oat husks and Russian *Miscanthus* – exhibited higher reactivity towards fermentation under the given conditions. In both cases, the yield of the reducing agents reaches 73-87% calculated as substrate weight [1].

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PP-31

PERFORMANCE OF SPOUTED BED GASIFICATOR OF BIOMASS WASTES FROM PAPER INDUSTRY

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Spouted beds technology of conical geometry has a good behaviour for treatment of solids sticky, of irregular texture [1], of a wide particle size distribution or density with low segregation [2], due to the vigorous cyclic movement of particles [3]. This technology has also been used in thermal processes, for combustion [4-6], for drying [7-8], for gasification [9] and for pyrolysis [10]. Spouted bed is a promising technology for biomass gasification.

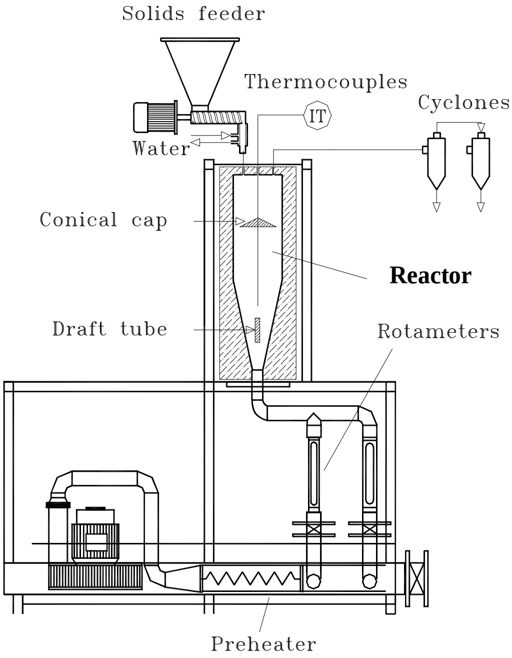

Fig 1. Experimental equipment

The experimental unit designed at pilot scale, is provided with a blower, two mass-flow meters for flow rate measurement, valves to regulate the gas flow, thermocouples to measure temperature at different positions in the reactor and probes for the measurement of the static and dynamic pressure and it allows to work with conical reactors of different geometry, Figure 1 and with and without internal draft tubes [15]. Operation has been carried out in a conical spouted bed gasificator at gas velocities over 1.3 times minimum spouting velocity with a great bed voidage (dilute spouted bed). The solids studied (fine particles) are Ca based catalysts limestone and dolomite; olivine and alumina.

In previous papers, the hydrodynamics and the stable operations conditions of beds consisting of uniformed coarse particles [2-3, 11], as well as, of fine particles catalysts [12] for catalytic polymerizations [13] and for catalytic combustion [14] have been studied in conical spouted beds without any internal devices. In order to study the performance of production of chemical synthesis (biofuels, methanol, or chemicals) or of power generation (hydrogen fuel cell, gas turbine, or engine) from biomass wastes from paper industry, in this paper, the stable operating conditions of beds consisting of catalyst particles have been determined, based on preliminary studies of hydrodynamics and on cycle times of the particles of catalyst of the reactor and the effect of the geometric parameters of the geometric on gasification process has been studied.

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