

Borshkov Institute of Catalysis SB RAS, Novosibirsk, Russia
Missouri University of Science and Technology, USA
Petrobras, Brazil

St. Petersburg Scientific Center RAS, Russia
Scientific Council on Catalysis RAS, Russia

INTERNATIONAL CONFERENCE CATALYSIS FOR RENEWABLE SOURCES: FUEL, ENERGY, CHEMICALS

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ABSTRACTS

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PLENARY LECTURES

DESIGN OF CATALYSTS AND CATALYTIC PROCESSES FOR BIOFUELS PRODUCTION

Parmon V.N.

Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia
E-mail: parmon@catalysis.ru

The consumption of petroleum has surged during the 20th century, at least partially because of the rise of the automobile industry. 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. Bioethanol and biodiesel are produced from food raw materials. Bio-fuels competition with food sector plays negative role for bioenergetics progress. So, 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 Boriskov 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, upgrading of bio-oil – product of wood flash pyrolysis, production of bio-syn-gas and carbonaceous materials.

**ENVIRONMENTALLY SUSTAINABLE BIOFUELS:
ADVANCES IN BIODIESEL RESEARCH**

Palligarnai T. Vasudevan, Robert C. Davison

University of New Hampshire, Durham, NH 03824, USA. E-mail: vasu@unh.edu

Due to diminishing petroleum reserves and the deleterious environmental consequences of exhaust gases from fossil-based fuels, research on renewable fuels has received a lot of impetus in recent years. With oil at high prices, alternate renewable energy has become very attractive. Besides ethanol, other unconventional choices are: biodiesel made from non-edible sources or waste cooking oil; biobutanol; and gas-to-liquids from the abundance of natural gas, coal, or biomass. Current research on the synthesis of biodiesel can be classified into five areas: i) the source of substrates, namely triglyceride and acyl-acceptors, ii) reaction mechanism, iii) catalysts for transesterification, including the application of inorganic base and acid catalysts as well as biocatalysts, iv) solvent effects on biodiesel synthesis, especially in enzyme-catalyzed processes, and v) operations and reactors involving traditional batch reactors, continuous reactors, novel membrane reactors and micro-channel reactors. In this presentation, we examine advances made in environmentally friendly fuels such as biodiesel in recent years and also the challenges we face in the production of biodiesel.

CATALYTIC TRANSFORMATIONS FOR PRODUCTION OF BIOFUELS, SPECIALTY CHEMICALS AND PHARMACEUTICALS FROM WOODY BIOMASS

Dmitry Yu. Murzin

Åbo Akademi University, Turku, Finland

Biomass as a source of renewable energy and chemicals is attracting more and more attention. Woody biomass utilization in particular can lead, besides a range of such biobased products as lumber, paper and pulp, furniture, housing components and ethanol, also to chemicals and fuels.

Chemical treatment of wood can have several targets. One option is delignification of the biomass leading to cellulose and some residual hemicelluloses, which are further applied in production of paper or board, or the derivatives of cellulose. Thermal (or catalytic) treatment of biomass, e.g. thermal or catalytic pyrolysis, is a route to bio-based synthesis gas and biofuels. Depolymerization of wood components (cellulose, hemicelluloses and lignin), which can be done with an aid of heterogeneous catalysts, results in the formation of low-molecular-mass components (sugars or sugar alcohols, phenols, furfural, various aromatic and aliphatic hydrocarbons, etc.), e.g. unique building blocks for further chemical synthesis.

In addition wood biomass contains many valuable raw materials for producing fine and specialty chemicals, such as fatty acids, terpenoids and polyphenols, i.e. stilbenes, lignans and tannins. The catalytic derivatization methods for these chemical compounds will be reviewed in the lecture.

PROGRESS IN THE DEVELOPMENT OF BIOMASS FAST PYROLYSIS TECHNOLOGY AND ITS APPLICATIONS

Wolter Prins

University of Ghent, Faculty of Bioscience Engineering, Coupure Links 653,
B-9000 Gent, Belgium, Wolter.Prins@UGent.be

Thermochemical conversion of biomass is referring to processes in which the biomass is decomposed at high temperatures to produce char and vapors that can either be:

- burnt completely and simultaneously, to produce heat: *combustion*
T > 800 °C;
- burnt partially, to produce a combustible or synthesis gas: *gasification*
T < 900 or T > 1250 °C;
- or separated as bio-char and/or bio-oil (condensed vapors): *pyrolysis*
T > 300 °C.

Fast pyrolysis of biomass is the process of thermal decomposition in absence of oxygen, at about 500 °C and at atmospheric conditions, with the aim to produce a high quantity of liquid product (bio-oil) that can be easily stored, transported and further processed. The technology has developed to a level of large scale demonstration and could be commercialized within the next five years. Potential applications of bio oil are manifold but, apart from direct combustion or co-combustion, up to now insufficiently developed. There are however a number of drivers that create an increasing interest in the technology.

One of the reasons that food/ feed industries, refinery companies and catalyst companies show a distinct interest these days, is the need for second generation biofuels. Fast pyrolysis is, to a large extent, a non-selective biomass conversion technique that accepts a wide variety of lignocellulosic feedstock materials such as forestry, agricultural or plantation residues, and industrial waste streams from e.g. food/feed, bio-ethanol or bio-diesel production. Moreover, this fairly simple liquefaction technique offers significant logistic advantages, allowing shipping to central sites (refineries, chemical plants, power stations) for large scale conversion to final products. In fact, fast pyrolysis has the potential to become a key process in various biorefinery concepts.

In this contribution the principles of fast pyrolysis will be discussed, and the main technologies reviewed. Possible product applications are discussed in relation to the bio-oil properties. General mass and energy balance are provided as well, together with some remarks on the economics. Challenges for the coming years are i) improvement of the reliability of pyrolysis reactors and processes, ii) the demonstration of the oil's utilization in boilers, engines and turbines, and iii) the development of technologies for the production of chemicals and biofuels from pyrolysis oils.

PRODUCTION OF BIODIESEL BY A TWO-STEP NIOBIUM OXIDE CATALYZED HYDROLYSIS AND ESTERIFICATION*

Donato Aranda¹, Layla Rocha¹, André Ramos², and Nelson Antoniosi-Filho³

¹GREENTEC/EQ/UFRJ, Brazil, donato@eq.ufrj.br

²DEQ/UFS, Brazil

³LAMES/UFG, Brazil

Biodiesel is a biofuel with several advantages compared to petroleum diesel [1]. The most used route to produce it is the homogeneous basic catalytic transesterification of triglycerides [2], but this process has some inconvenients, as the rigorous control of raw materials and several post-reaction separation steps [3]. This work deals with an alternative process: the use of a heterogeneous acid catalyst (Nb_2O_5) to promote both hydrolysis of triglycerides (soybean and castor oils) and esterification of the produced fatty acids. Reactions were performed in a stainless steel batch reactor with controlled stirring and heating. A experimental design was performed to optimize temperature–T (250-300°C for hydrolysis, 150-200°C for esterification), water/oil and methanol/fatty acid molar ratios-R (5-20 for hydrolysis, 1.2-3 for esterification) and catalyst concentration-C (0-20% w/w for both reactions). Conversion was measured by acid-base titration and gas chromatography. Kinetic and molecular modeling was also performed. Tables 1 and 2 show some conversions obtained in both reactions at 60 min, being clear the effect of temperature and catalyst concentration. Cracking was detected as side reaction at higher temperatures. The kinetic modeling has shown different kinetics without and with catalyst, being the hydrolysis inhibited by water and zero order for the other reactants without catalyst, while second order in relation to the reactant which was not in excess was observed in catalyzed reactions. The higher reactivity of liloleic acid compared to ricinoleic acid was justified by energy differences of homo and lumo orbitals.

Table 1
Hydrolysis of soybean oil

Conditions (t=1 h)	Conversion (%)
T=250°C, R=20, C=0	46.89
T=250°C, R=20, C=20	66.83
T=300°C, R=20, C=20	85.08

Table 2
Esterification of fatty acids from soybean oil

Conditions (t=1h)	Conversion (%)
T=150°C, R=1.2, C=0	51.63
T=150°C, R=1.2, C=20	63.83
T=200°C, R=1.2, C=20	82.79

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* Prof. Aranda will present the plenary lecture «TRANSESTERIFICATION AND HYDROESTERIFICATION: THEORETICAL AND EXPERIMENTAL ANALYSIS OF BIODIESEL PRODUCTION USING HETEROGENEOUS CATALYSIS» based on the materials of his two presentations.

THEORETICAL AND EXPERIMENTAL ANALYSIS OF JATROPHA OIL TRANSESTERIFICATION BY HETEROGENEOUS BASIC CATALYSTS

Donato A. G. Aranda¹, Neyda C. O. Tapanes¹, José. W. Mesquita Carneiro²

¹*Chemical School, Federal University of Rio de Janeiro, RJ, Postal code: 21945-970, Brazil, Fax: (5521) 2562-7567, neydaom@yahoo.com, donato@eq.ufri.br*

²*Chemical Institute/Federal Fluminense University, Rio de Janeiro, Postal code: 24.020-150, Brazil*

The heterogeneous transesterification reactions have been studied for many vegetable oils. Although biodiesel of Jatropha oil have been produced in commercial scale in India, there are no published kinetics reports with this raw material. In this paper the reaction of alkali-catalyzed transesterification of jatropha oil using Mg–Al hidrotalcites as heterogeneous catalyst were studied using computational chemistry methodologies relating with the experimental kinetic results.

The kinetic modeling was carried out with Origin and Statistica softwares, to determinate the mechanism and determining step of the reaction. Uncalcined and calcined hidrotalcites at 200°C, 400°C and 600°C were used as heterogeneous catalysis. The reactions were studied with quantum method rb3lyp/lanl2dz, using Titan and Gaussian packages. In the experimental results, the good correlation between kinetic constant and the reaction yield demonstrate that Langmuir-Hinshelwood Hougen-Watson mechanism occur and the theoretical calculations confirm this result, due to the decrease of the energy difference between the HOMO of alcohol and LUMO of glyceride when the reaction occurs on the catalyst surface. The transesterification using hidrotalcite without calcinate illustrate lows reaction yield. Calcined Mg–Al hidrotalcite at 400°C was found the most effective catalyst for the transesterification of jatropha oil, obtaining conversion of jatropha oil of 96%. Theoretical calculations and experimental procedures demonstrated that the reactions of transesterification of jatropha oil using catalyst of hidrotalcite are not affected with use of ethanol or with presence of water in the reaction. In both case were obtain excellent conversion.

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ADVANCEMENT OF CATALYTIC FISCHER-TROPSCH SLURRY BUBBLE COLUMNS VIA ADVANCED MEASUREMENT TECHNIQUES FOR RENEWABLE ENERGY AND CHEMICALS PRODUCTION

Dr. Muthanna Al-Dahhan

Missouri University of Science and Technology (Missouri S&T) Rolla, MO 65409

Gas to Liquid Fischer Tropsch (FT) synthesis is an acknowledged catalytic route for production of clean fuels and chemicals from synthesis gas (a mixture of hydrogen and carbon monoxide) obtained from renewable resources such as biomass and biogas, and from natural gas and coal. Gas-catalyst fixed fluidized and circulating fluidized beds, gas-liquid-catalyst trickle beds and slurry bubble columns and gas-liquid-catalyst monolith beds have been developed and used. These catalytic processes will be outlined and the catalyst types, development and the needed advanced systems and techniques that integrate molecular to reactor scales will be discussed. FT conversions are associated with high exothermic heat for which an efficient mean of heat removal is needed. Therefore, slurry bubble column reactors operated in churn turbulent flow regimes are the reactor of choice for such conversions and for high capacity throughput. Successful commercialization of these reactors needs thorough understanding of prevailing hydrodynamics of phases (catalyst, liquid, gas) and transports for proper design, scale up, performance and operation. Therefore, detailed analysis will be given to three phase slurry bubble columns for catalytic FT conversion for clean renewable fuels and chemicals production.

Advanced measurement techniques have been used and developed which provide the needed fundamental understanding of these complex reactors. These techniques are: Radioactive particle tracking (RPT) and multiple radioactive particle tracking (MRPT) techniques for the measurement of 3D flow structure, velocity, turbulent parameters, residence time, etc. of multiple phases; computed tomography (CT) and dual source computed tomography (DSCT) for the measurement of the cross sectional phases distribution along the reactor height; gamma ray densitometry for flow pattern identification; 4-point optical probe for bubble dynamics measurements (bubble size, velocity, local gas holdup and interfacial area); overall gas dynamic tracer technique; optical probe for mass transfer measurement and overall mass transfer coefficient measurement; heat transfer probe that mimicked the

heat exchanging internals; dynamics pressure transducers. A number of achievements have been made due to such advanced fundamental understanding of bubble/slurry bubble columns. These are: advanced mechanistic reactor scale models; non-invasive technique for flow regime identification, new methodology for scale up bubble column, new methodology to measure FT gases mass transfer coefficients; true and accurate tracer response for the liquid and slurry; accurate characterization of the gas phase extent mixing; detailed flow behavior and transport parameters mapping in a mimicked FT conditions system; advanced neural net work based correlations were developed based on a large size and range of data; reliable benchmark data for evaluating CFD models and closures and development of advanced CFD models and closures.

In the presentation, FT synthesis and the type of multiphase reactors used will be overviewed, the technical issues of slurry bubble columns and the needed advanced techniques will be outlined. Among the many achievements made, the newly developed methodology for scale up of bubble column reactors and identification of the flow pattern by the newly developed noninvasive technique will be discussed. In addition, the advanced methodology and techniques that integrate molecular scale for catalyst development to process scales will be outlined.

KEY-NOTE PRESENTATIONS

CATALYTIC CRACKING OF SUNFLOWER SEED OIL

Strizhak P.E., Tripolskyi A.I., Eremenko V.E., Ivashchenko T.S., Busko A.O.

*L.V. Pisarzhevsky Institute of Physical Chemistry
National Academy of Sciences of Ukraine
pr. Nauki 31, Kiev, Ukraine, 03039
pstrizhak@hotmail.com*

Heterogeneous catalytic cracking of vegetable oil produces valuable raw materials, which can be used in the chemical and petrochemical industry. Here we report a study of catalytic cracking of sunflower seed oil over various solids, particularly, alumina or zeolites supported metals and metal oxides. Catalytic cracking has been performed in batch at atmospheric pressure in temperature range of 320-420°C. Products were analyzed by a gas chromatograph (HP-1MS, 25 m x 0.2 mm x 0.33 μ m) coupled to Shimadzu mass spectrometer.

We found that depending on a catalyst a yield of liquid phase that contains products of cracking reaches 80%. The liquid phase contains more than 200 different chemical compounds. Among those compounds approximately 50 were found at concentrations more than 0.1% in liquid phase. Mixture of linear hydrocarbons is the main product of catalytic cracking. The yield of linear hydrocarbons reaches 60%. The liquid phase contains 5-30% of oxygen containing species. Using alumina as a catalyst support leads to a decrease of oxygen containing species in products of cracking. Yield of cyclic compounds is in the range of 5-15%. It is slightly lower for metal containing catalysts comparing to pure γ -Al₂O₃ or zeolites. Yield of aromatic compounds was found less than 2% for all catalysts.

We discuss possible chemical reactions responsible for catalytic cracking of vegetable oil. Our studies highlight pathways of the vegetable oil cracking indicating how properties of catalyst affect yield of various products of the process.

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GROUP IV COMPLEXES FOR ESTERIFICATION AND TRANSESTERIFICATION REACTIONS

**Simoni M. P. Meneghetti¹, Yariadner Costa Brito¹, Vinícius Moreira Mello²,
Caio César S. Macedo², Mario Roberto Meneghetti¹, Paulo A. Z. Suarez²**

¹*Instituto de Química e Biotecnologia, Universidade Federal de Alagoas, Av. Lourival de Melo Mota, s/ nº, Maceió-AL, Brazil – 57072-970, simoni.plentz@gmail.com*

²*Instituto de Química, Universidade de Brasília, CP 4472, Brasília-DF, Brazil – 70919-910*

Two series of complexes exhibiting general formula $M(n\text{-butoxide})_{4-x}(\text{maltolate})_x$, where $M = \text{Ti}$ or Zr and $x = 0$ to 4 , were studied as catalyst for transesterification and esterification, in order to obtain methyl esters [1]. All the complexes were evaluated as catalyst for soybean oil methanolysis and reactions yields below 10 % were achieved, indicating a very low catalytic activity of these complexes when compared with other Lewis acid metal complexes in similar conditions [2,3]. In the sequence, all the complexes were evaluated in the esterification of soybean fatty acid and methanol (Figure 1).

All complexes, containing maltolate as ligand, were very efficient as catalyst in esterification, mainly those based in zirconium. The presence of maltolate ligands leads to complexes which are more stable to moisture and the complexes, bearing at least one maltolate as ligand, proved to be very efficient catalysts for esterification and the most active systems were those based on zirconium.

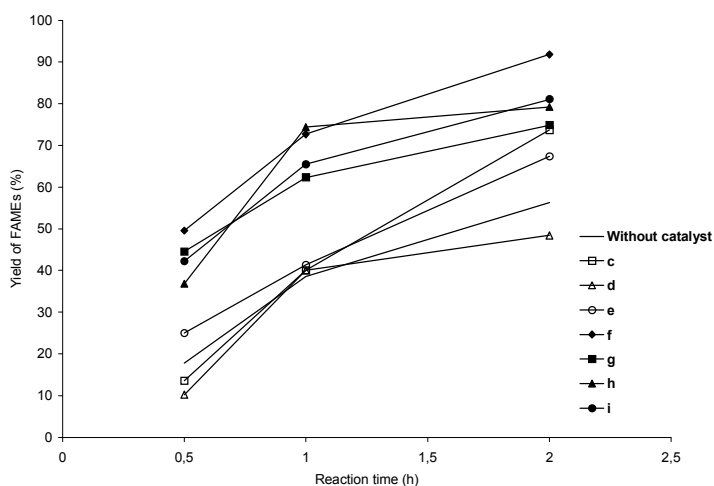


Figure 1: Production of FAMES (percentage yield) by the esterification in the presence of Ti (c to e) and Zr (f to i) catalysts. The reaction conditions were: molar proportions of fatty acid:MeOH:catalyst = 100:400:1; temperature = 140 °C.

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CONVERSIONS OF WOOD AND CELLULOSE TO GLUCOSE AND LEVULINIC ACID UNDER THE ACTION OF ACIDIC CATALYSTS

Kuznetsov B.N.^{1,2}, Sharypov V.I.¹, Baryshnikov S.V.¹

¹*Institute of Chemistry and Chemical Technology SB RAS,
K. Marx str., 42, Krasnoyarsk, 660049, fax: +7(391)2439342, e-mail: inm@icct.ru*

²*Siberian Federal University, Svobodny pr., 79, Krasnoyarsk, 660041*

The actual problem in chemical processing of renewable biomass is connected with the development of improved methods of acid-catalyzed conversions of lignocellulosic materials into valuable chemicals.

The influence of conditions of preliminary activation of wood and parameters of acidic hydrolysis process on the yield, composition and structure of obtained products was studied.

It was found that the mechanical treatments of wood in water medium increase the rate and degree of wood acidic hydrolysis to monosugars. Methods of wood activation (cuttery, jet, vibratory rod mills and mechanochemical activator) define the time of treatment, needed for maximal hydrolysis rate. The mechanochemical treatment of wood in a centrifugal-planetary activator mill AGO-2 gives the highest effect. The used method of wood treatment results in changes of wood structure. Wood fibers fibrillation influences on the rate of hydrolysis in the higher degree than that of fibers length reduction.

The efficiency of next methods of wood treatment, which reduce the content of hemicelluloses in wood was compared: shot-time treatment by steam at 220-240 °C, catalytic oxidation by H₂O₂ at 120-130 °C and prehydrolysis with 2 % HCl at 100 °C. The following complete hydrolysis of treated wood by H₂SO₄ makes it possible to produce glucose syrups without impurities of C₅-sugars, which inhibit the biotechnological synthesis of ethanol.

The influence of nature of acidic catalysts (H₂SO₄, Al₂(SO₄)₃, Fe₂(SO₄)₃), wood raw material (aspen, birch, abies, cellulose) and steam thermolysis process conditions on the yield of levulinic acid (LA) was studied. The maximal yield of LA was observed at 200-240 °C with catalysts H₂SO₄ and Al₂(SO₄)₃. Wood nature has the low influence on LA yield (reaches to 15-16 % mas.). Acidic conversion of cellulose with H₂SO₄ catalyst gives LA yield up to 25 % mas. Possible areas of levulinic acid application are synthesis of new polymers, high-octane additives and other valuable chemicals.

POLYOXOMETALATES AS CATALYSTS FOR SUSTAINABLE ORGANIC SYNTHESIS

Ivan Kozhevnikov

University of Liverpool, Liverpool L69 7ZD, UK, E-mail: kozhev@liverpool.ac.uk

Among numerous applications of polyoxometalates (POMs) catalysis is by far the most important, offering significant economical and environmental benefits. The aim of this presentation is to discuss recent results of the author's group on the application of POMs as acid and bifunctional acid-metal catalysts for chemical synthesis using renewable feedstocks such as terpenes, glycerol and acetone.

Heteropoly acids (HPAs) are demonstrated to be efficient and environmentally friendly catalysts for acid-catalyzed terpene transformations such as hydration, acetoxylation, cyclization and isomerization in homogeneous and heterogeneous systems. These reactions can provide clean routes to valuable ingredients and intermediates for the fragrance and pharmaceutical industries.

Recent development of biodiesel production has made a large amount of glycerol available as a renewable feedstock for the synthesis of chemicals. One of the most important directions for the utilisation of glycerol is its dehydration to acrolein. POMs are amongst the most efficient catalysts for this reaction. We have found that the acidic heteropoly salt, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW), is a very active catalyst for glycerol-to-acrolein dehydration in the gas phase. Doping CsPW with platinum group metals and co-feeding hydrogen reduces coke deposition thus enhancing catalyst performance.

POM-based multifunctional catalysts can effectively carry out multistep reactions in one pot (one catalyst bed) without separating intermediate products. Discussed examples include one-step hydrogenolysis of glycerol to 1,2-propanediol and synthesis of methyl isobutyl ketone from acetone using POMs doped with platinum group metals as catalysts.

CATALYTIC FUEL-GAS CLEANING IN A STAGED BIOMASS GASIFICATION PROCESS

L. van de Beld, E.J. Leijenhorst

*BTG Biomass Technology Group B.V. Josink Esweg 35, 7545 PN Enschede,
The Netherlands, E-mail: vandebeld@btgworld.com*

Biomass gasification systems are investigated and developed for a long period with some emphasis on tar and tar reduction. The presence of tar in the fuel gas hampers troublefree operation of prime movers, and tar removal is of prime importance. Additionally, it would be advantageous if systems are able to convert a wide range of feedstocks, i.e multi-fuel systems. Worldwide, huge amounts of biomass residues and waste streams are available like e.g. agricultural residues. Typically, these streams have a low bulk density and contain significant amounts of minerals. These minerals may cause ash-melting problems or result in high emissions.

The first step in BTG's staged gasification process is the conversion of biomass at low temperature into an organic vapour. This low temperature step is based on a fast pyrolysis process. The second step shows large similarities with an Autothermal Catalytic Reformer (ACR) system. In such system organic vapour is mixed with air or oxygen to increase the temperature and to supply the energy required for the reforming reactions. Subsequently, the resulting mixture (including tar) is further reformed over a catalyst bed. Furthermore, ammonia originating from fuel nitrogen will be converted to nitrogen and hydrogen in case a Ni catalyst is applied.

The process has been tested at BTG (1-5 kg/hr) to demonstrate the feasibility of the proposed system, and to test the performance of several commercial and dedicated catalysts. A clean fuel gas can be produced without additional gas cleaning. Tar concentrations below 25 mg/Nm³ and cold-gas efficiencies over 75% were obtained. The system has a high potential to convert a wide range of feedstock's into clean fuel gas at high energetic efficiency for CHP applications.

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**PALLADIUM-CATALYZED AEROBIC OXIDATION
OF BIOMASS-BASED ALKENES AS A ROUTE TO VALUABLE
FRAGRANCE AND PHARMACEUTICAL COMPOUNDS**

Elena V. Gusevskaya, Luciana A. Parreira, Luciano Menini

Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, MG, Brazil

Fax: (+55)-31-3409570; e-mail: elena@ufmg.br

The functionalization of naturally occurring special olefins can provide oxygenated compounds valuable in the fine chemicals industry. For several years, we have been interested in oxidative transformations of terpenes and substituted allyl benzenes, which are easily available from biomass and represent an important renewable feedstock for pharmaceutical and flavor&fragrance industries. In the present communication, we will review our new and recently published results in this field.

A palladium-catalyzed selective oxidation is one of the more versatile methods to introduce an oxygen-containing functionality in organic molecules. These reactions are especially attractive when molecular oxygen is involved as a final oxidant, which is usually achieved by using CuCl_2 as co-catalyst (Wacker catalyst). However, the Wacker process requires large amounts of chloride ions and acid to maintain a catalytic cycle; therefore, the system is highly corrosive and often causes the formation of chlorinated side products. Although the systems with various alternative halide-free co-catalysts, such as $\text{Cu}(\text{OAc})_2$, heteropoly acids, nitrates, and benzoquinone, have been intensively studied in attempts to reduce an environmental impact of these processes, the reoxidation of palladium(0) during the catalytic cycle under more friendly conditions remains a critical challenge.

We have studied the palladium catalyzed aerobic oxidations of a number of terpenic (limonene, camphene, myrcene, linalool, dihydromyrcene, nerolidol, etc) and allyl aromatic (eugenol, safrole, estragole, etc) natural compounds and developed various efficient methods for the synthesis of industrially important oxygenated products. A special attention has been given to chloride-free catalytic systems and the systems in which palladium (II) chloride is used as the sole catalyst in the absence of co-catalysts or stabilizing ligands.

BIO4ENERGY – THE SWEDISH QUEST FOR SUSTAINABLE SOCIETY

Jyri-Pekka Mikkola^{1,2}, Leif Jönsson¹, Stellan Marklund¹

¹Umeå University, Department of Chemistry, Technical Chemistry,
Chemical-Biological Center, Jyri-Pekka.Mikkola@chem.umu.se

²Åbo Akademi University, Department of Chemical Engineering, Laboratory of
Industrial Chemistry and Reaction Engineering, Process Chemistry Centre

As a symbiosis of universities, research institutes and industry a unique collaboration has been launched between researchers and industry. In particular, the combination of basic research in key areas and applied research resulting in the interaction of biorefining and energy supply, in symbiosis with a very strong industrial networks, provide for unparalleled new opportunities. The new centre (Bio4Energy¹), unfolding the biggest ever Swedish R&D investment in CleanTech, consists of seven research platforms, each with a strong research profile; together a complete system is encompassed merging all tools needed to achieve environmentally, societally and climatically sound energy-focused biorefineries based on non-food, lignocellulosic biomass. In the *feedstock* platform, modern biological and biotechnological tools are implemented to improve for a qualitative and quantitative characterization of the biomass intended as raw material for the subsequent processes. In the *biochemical* platform, enzymatic and microbial routes coupled to fermentation processes are developed, and in the *thermochemical* platform, processes based on gasification in collaboration with *catalysis and separation* platform evolve for the conversion of raw materials to products. For maximum efficiency and yield of the processes developed in these platforms, the *pretreatment and fractionation* platform designs procedures to make the constituents in the biomass maximally available for further processing. The overall efficiency of the processes are subject to optimization in the *process integration* platform and the research in the *environmental* platform.

The geographical area possesses large forest resources and extensive forest industry in technological transition to convert low-cost forest biomass into high-value products. To achieve this goal, it is critical to have a flexible set of technologies for each biorefinery that can be adapted to specific needs. The concept will be explained.

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Acknowledgements. The Swedish Energy Agency, Kempe Foundations, Knut & Alice Wallenberg Foundation, Umeå University, the Academy of Finland and Åbo Akademi University are gratefully acknowledged for financial support.

VALUE ADDED CHEMICALS FROM GLYCEROL: SYNTHESIS OF GLYCEROL CARBONATES USING SOLID BASE CATALYSTS

N. Lingaiah, K. Jagadeeswaraiyah, M. Balaraju and P.S. Sai Prasad

*Catalysis Laboratory, I&PC Division,
Indian Institute of Chemical Technology, Hyderabad-500607, India*

In recent time, synthesis of biodiesel by transesterification of vegetable oils and fats is identified as one of the important conversion process of renewable feedstock. Glycerol is the by-product in biodiesel synthesis and identified as one of the top ten building blocks in the bio refinery feed stocks. Conversion of glycerol into valuable chemicals by green catalytic process is a challenging area of research [1]. Glycerol is a synthesis intermediate for the preparation of a large number of compounds via hydrogenolysis, oxidation, etherification, esterification, transesterification and polymerisation, etc [2]. One important glycerol derivative is glycerol carbonate, which is widely used as protic solvent, additive and also as chemical intermediate.

Glycerol carbonates can be prepared by reacting glycerol with CO₂ or urea and also by dimethyl carbonate [3]. Transesterification reaction is one of the simplest method for producing glycerol carbonate from glycerol and dimethyl carbonate. The preparation of glycerol carbonate by transesterification of glycerol with dimethyl carbonate has added advantages due to easy separation of products. In the present work. transesterification of glycerol with dimethyl carbonate was carried over a series of Mg-Al-La based trimetallic base oxides. The mixed metal oxides were prepared by varying molar ratios of constituent metal oxides. The effect of catalyst treatment and their molar ratios are explored. The activity of the catalysts will be discussed based on the changes in the composition of the catalysts. The catalytic activities are correlated with the observed structural and surface characteristics of the catalysts. The role of basicity of the catalysts was evaluated for the transesterification of glycerol.

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ORAL PRESENTATIONS

Section 1.

CATALYSIS FOR BIOFUEL PRODUCTION

NOVEL MnCeO_x CATALYSTS FOR BIODIESEL PRODUCTION BY TRANSESTERIFICATION OF VEGETABLE OILS WITH METHANOL

Cannilla C.², Bonura G.¹, Spadaro L.¹, Di Blasi O.¹, Arena F.² and Frusteri F.¹

¹CNR-ITAE «Nicola Giordano», Salita S. Lucia 39, I-98126 Messina, Italy

²Dip. di Chimica Industriale ed Ing. Materiali, Università di Messina,
Salita Sperone 31, I-98166, Messina, Italy

Biodiesel is an environmentally friendly, non-toxic, biodegradable mixture, which can be used either as alternative pure fuel or for blending with conventional oil-derivate fractions [1]. The kinetics of the transesterification reactions can be efficiently promoted by either basic or acid catalysts, while high temperature (350-400°C) and pressure (100-250 bar) are required to get reasonable yields in supercritical methanol [2]. The nature of the catalyst depends upon feedstock composition, reaction conditions and post-separation steps. Although low-cost basic catalysts, such as potassium or sodium hydroxide, can be used, more than half of the current manufacture processes are catalyzed by sodium methoxide [3].

In the perspective to develop a heterogeneous process to produce FAME, this work was aimed to investigate a new class of ceria-manganese composite oxide systems in the transesterification of sunflower oil with methanol in comparison to solid acid and basic catalysts commonly used. The behaviour pattern of MnCeO_x catalysts synthesized via the redox-precipitation route in the transesterification reaction of sunflower oil with methanol was compared with that of supported heteropolyacids, acid resins and bulk oxides. The MnCeO_x system features a superior activity allowing oil conversion values higher than 90% (5h) at 140°C for a catalyst/oil mass ratio as low as 1 wt%. An unchanging MnO_x dispersion results in a straight-line rise of reaction rate with the Mn loading in the range of 9-35 wt%. NH_3 -TPD and CO_2 -TPD measurements indicate that the MnCeO_x system possesses a prevailing concentration of surface basic sites, though experimental data signal that the transesterification performance likely depends on both availability and accessibility of basic sites, the latter being related to the textural properties of the system.

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METHANOLYSIS OF VEGETABLE OILS IN THE PRESENCE OF ALKYL TIN(IV) CATALYST: INFLUENCE OF TEMPERATURE AND REACTION CONDITIONS ON THE CATALYST ACTIVITY

Mario R. Meneghetti, Tatiana Maciel Serra, Daniel R. de Mendonça, Jhosianna P. Vilela da Silva, Simoni M. P. Meneghetti

Instituto de Química e Biotecnologia, Universidade Federal de Alagoas, Av. Lourival de Melo Mota, s/ nº, Maceió-AL, Brazil – 57072-970, mrmeneghetti@gmail.com

The complex dibutyltin dilaurate, $(C_4H_9)_2Sn(C_{12}H_{23}O_2)_2$, was used as catalyst for the methanolysis of soybean and castor oils, in different reaction conditions (temperature, open or close reactor). The catalytic system was active for methanolysis of soybean oil and castor oil, and display an increment of the reaction yield, measured in terms of % FAMEs formed, at higher reaction temperatures (Table 1). The reactions conducted in pressurized container (close reactor) show better results and this observation can be associated to a favorable change in phase equilibrium, with consequent increase in the concentration of methanol in the liquid phase [1].

Table 1. Yield of FAMEs (%) by the methanolysis of soybean and castor oil

T (°C)	Reactor	Yield in Biodiesel (FAMEs %) from	
		Castor Oil	Soybean Oil
80	Reflux	4	13
80	Pressurized container	9	48
120	Pressurized container	53	77
150	Pressurized container	64	98

We suggest that the difference of yields observed between for the methanolysis of the two oils can be related at two factors: i) due to the atypical chemical composition of castor oil, that is comprised almost entirely (ca. 90%) of triglycerides containing the unusual fatty acid ricinoleic acid (12-hydroxy-*cis*-octadec-9-enoic acid). The hydroxyl group at C-12 of ricinoleic acid can interact with Lewis acid catalytic site decreasing the reaction yield; ii) due to mass transfer problems, since the high viscosity of castor oil and the biodiesel formed input difficulties of diffusional nature [1].

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MAGNESIA SUPPORTED STRONTIUM CATALYSTS FOR SOYBEAN OIL METHANOLYSIS: STUDY OF THE OIL ACIDITY EFFECT

Ana Paula Soares Dias¹, Joana Bernardo¹, Pedro Felizardo²,
Joana Neiva Correia², Oksana Turchanina³

¹ICEMS-UQUIMAF-GRECAT, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, s/n, 1049-001 Lisboa, Portugal, apsoares@ist.utl.pt

²Centre of Chemical Processes, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

³Donetsk National Technical University, 48 Artema str., Donetsk 83000, Ukraine

Road transportation is the fastest growing sector of greenhouse gas emissions today. Thus it seems imperative to find sustainable alternative fuels like bioethanol and biodiesel. First generation biodiesel is usually produced through a transesterification reaction (alcoholysis) between a lipid source (vegetable oils and fats) and an alcohol (mainly methanol) to produce a mixture of esters (FAME-fatty acid methyl esters) and a by-product, glycerol. The reaction occurs in presence of acid or basic catalysts but basic catalysis is generally preferred since the reaction is faster. Conversely, basic catalysts deactivate in the presence of low quality and cheaper raw oils due to the oil acidity and water content [1].

Magnesia supported strontium catalyst (Sr/Mg=0.2 atomic ratio) was prepared by contacting the commercial magnesia with an aqueous solution of Sr nitrate. The resulting suspension was evaporated at around 80°C until dryness under vigorous stirring. The SrO/MgO sample was dried, calcined and then tested for the methanolysis of soybean oil (food grade) at methanol reflux temperature and atmospheric pressure.

The effect of the oil acidity was studied. The oil was acidified by adding oleic acid. In the tested conditions, with the raw oil, the SrO/MgO catalyst presented interesting initial rate of methanolysis and no soap formation was observed. The oil acidity has, as expected, a negative effect on the catalytic performances (Fig.1). The catalyst, with $H_{\text{cat}} < 15$ is almost inactive when oil present acidity higher than 1%.

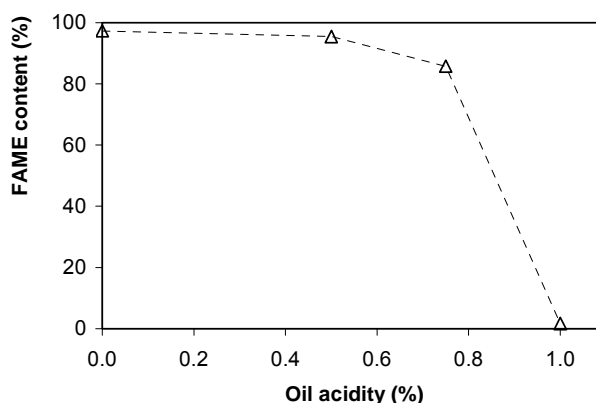


Fig. 1. Effect of oil acidity on the FAME yield. ($W_{\text{cat}}/W_{\text{oil}}=5\%$; Methanol/Oil=9; reaction time 3h).

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SYNTHESIS, CHARACTERIZATION AND USE OF Nb₂O₅ BASED CATALYSTS IN PRODUCING BIODIESEL BY ESTERIFICATION OF FATTY ACIDS

Paulo A. Z. Suarez, Vinicius M. Mello, André P. Tavares, Flávia Guinhos and Joel C. Rubim

Laboratório de Materiais e Combustíveis, Instituto de Química, Universidade de Brasília, CP 4472, Brasília-DF, Brazil – 70919-910, psuarez@unb.br

Nb₂O₅/HX (X = HSO₄⁻, H₂PO₄⁻, NO₃⁻) compounds were obtained from the treatment of niobium acid (Nb₂O₅·xH₂O) with sulfuric, phosphoric, and nitric acids as well as Nb₂O₅ and Nb₂O₅·xH₂O have been investigated as catalysts for the esterification of fatty acids. The compounds were characterized by thermal analysis (DTA-TGA), spectroscopy (DRX, FT-IR and FT-Raman), surface area (BET) and the acidity (H₀) determined by *n*-butylamine titration using the Hammett's indicator method. It was observed that after the acid treatment both the surface area and the acidity decreased as compared to the starting Nb₂O₅·xH₂O. The only exception was a higher acidity verified when nitric acid was used. As can be depicted from Table 1, except for the solid Nb₂O₅·xH₂O, all solids were active to esterify carboxylic acids, yielding selectively methyl fatty acids esters. Nb₂O₅/H₃PO₄ and Nb₂O₅/H₂SO₄ showed better activity than and Nb₂O₅. The mechanism of these reaction may be probably the usually accepted for esterification catalyzed by Lewis acid solids.⁶⁶ As proposed in Figure 8, niobium oxides reacts with methanol accepting electrons from the alcohol, affording a hydroxyl and a methoxy groups. Thus, the fatty acid reacts with the hydroxyl group leading to a carboxylate coordinated group. After a nucleophilic attack by the methoxy group to the carbonyl, the fatty acid ester is formed and the active oxide is recovered.

Table 1. The esterification of soybean fatty acids with MeOH catalyzed by the niobium solids.*

Catalyst	Reaction Yield (%)
without catalyst	32
Nb ₂ O ₅ ·H ₂ O	32
Nb ₂ O ₅	36
Nb ₂ O ₅ /HNO ₃	40
Nb ₂ O ₅ /H ₃ PO ₄	57
Nb ₂ O ₅ /H ₂ SO ₄	57

*Conditions: 10 g of soybean fatty acids, 4 g of MeOH, 1 hour, 160 °C.

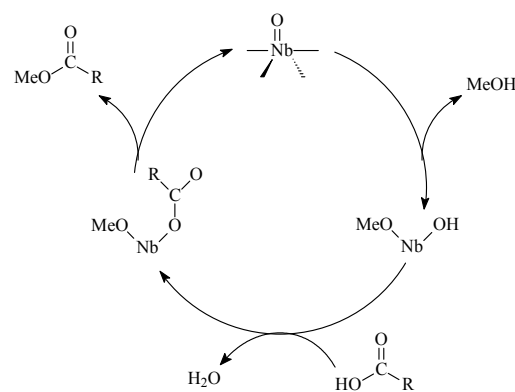


Figure 1 – Proposed mechanism for esterification using niobium based catalysts.

Acknowledgements: CNPq, FAPDF.

DEOXYGENATION OF TALL OIL FATTY ACIDS TO BIOFUEL

**Päivi Mäki-Arvela¹, Bartosz Rozmysłowicz¹, Siswati Lestari¹,
Olga Simakova^{1,2}, Tapio Salmi¹, Dmitry Yu. Murzin¹**

¹*Åbo Akademi University, Process Chemistry Centre, FI-20500 Turku, Finland,
pmakiarv@abo.fi*

²*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

Crude tall oil (CTO), which is a side product from pulp industry, is produced in relatively large quantities, e.g. in year 2004 the tall oil production only in United States was 845 thousand tons. CTO, which contains about 45% free fatty acids, undergoes distillation leading to so-called TOFA (Tall oil fatty acids). The latter could serve as a feedstock for diesel-like fuel containing long-chained hydrocarbons. Catalytic deoxygenation of fatty acids and their derivatives was demonstrated to occur at 300 – 350°C in the liquid phase using Pd/C or Pt/C as catalysts in a batch and a semibatch reactors. The aim of this work was to test applicability TOFA as a feedstock in catalytic deoxygenation. This reaction with the initial concentration of 0.15 – 0.6 mol/l in dodecane was performed in a semibatch reactor in a temperature range of 300 - 350°C under 17 bar of 1% H₂ in argon or in pure hydrogen. The

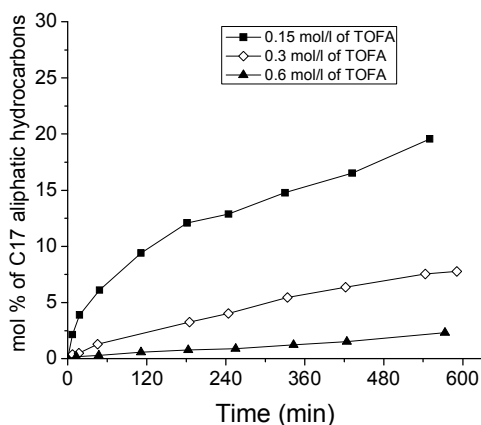


Fig. 1. Formation of n-heptadecane using different initial concentrations of TOFA at 300°C using $m_{\text{cat.}} = 0.5$ g and $V_L = 100$ ml, respectively. Solvent dodecane.

primary products were C18 fatty acid isomers and oleic acid, which were hydrogenated further to stearic acid. Thereafter, stearic acid was deoxygenated to the desired product, n-heptadecane (Fig. 1). The conversion of fatty acids to hydrocarbons increased when decreasing the initial concentration of TOFA as well as by decreasing the reaction temperature, which means that higher temperatures and initial concentration promote side reactions

stronger side reactions than deoxygenation *per se*. In the final work the effect of different parameters on reaction kinetics will be discussed.

THE PRODUCTION OF MOTOR FUEL AND CHEMICAL COMPOUNDS FROM THE PRODUCTS OF THERMAL PROCESSING OF COMBUSTIBLE SCHISTS

Lapidus A.L.¹, Strizhakova Yu.A.²

¹*N.D. Zelinsky Institute of Organic Chemistry RAS, Moscow, Leninsky Pr., 47, tel. (fax): (499)1355303, e-mail: albert@server.ioc.ac.ru*

²*Samarsky State Technical University, Samara, ul. Molodogvardeiskay, 144, e-mail: nich@samgtu.ru*

Qualified using of some solid combustible minerals with low metamorphism extent: combustible schists and peat and wood for production of fuel and chemical products is a very actual problem for our country because of their large resource. It is possible to carry out two principal different ways of their use: thermal processing and gasification with following processing of gas products. Production of synthesis gas with composition $\text{CO}:\text{H}_2=1:2$ (vol.) is possible at gasification of combustible schists. This gas is converted into the mixture of hydrocarbons over cobalt catalysts at 170-280°C at 1-30 atm. The hydrocarbons can be used as motor, including diesel, or reactive fuel. We proposed the effective catalysts at which conversion of synthesis gas in liquid products equals 80-90%.

The questions connected with production «mixed» diesel fuels containing 5-15% of $\text{C}_5\text{-C}_{10}$ *n*-paraffins and obtaining from synthesis gas over Co-systems will be elucidated in the report. These fuels are characterized by high ecologies because of low CO , CO_2 and C_nH_m contents in worked gas. The results of there fuels tests in engine of interior combustion are given in the report.

DEOXYGENATION OF FATTY ACIDS AND THEIR ESTERS OVER PALLADIUM ON CARBON CATALYST: INVESTIGATION OF REACTION MECHANISM

Bartosz Rozmyslowicz, Anton Tokarev, Päivi Mäki-Arvela, Dmitry Yu. Murzin

*Process Chemistry Center, Åbo Akademi University, 20500 Turku, Finland,
dmurzin@abo.fi*

Production of biodiesel via deoxygenation of fatty acids and their esters have been of high interest over the last years [1]. It was shown that the best deoxygenation conversion and selectivity can be achieved over palladium on carbon catalyst at 300°C under hydrogen rich atmosphere, in which deoxygenation reaction could proceed through three different pathways: decarboxylation, decarbonylation and hydrogenation of carboxylic group (Fig. 1). To investigate, which of these mechanisms is predominant, depending on hydrogen presence, series of experiments with lauric acid, lauric aldehyde and dodecanol as well as with methyl and ethyl esters of fatty acids, were carried out in hydrogen rich and in inert atmosphere.

The experiments were performed in semibatch reactor at 300°C, over 5% Pd/C catalyst using hexadecane as a solvent. Catalyst was characterized by nitrogen adsorption and TEM leading to 380 m²/g of specific surface area and 2.4 nm of average palladium clusters size. Liquid phase products were analyzed by GC and GC-MS, while gas phase products were analyzed with micro-GC.

In the final work the effect of gas atmosphere on catalytic deoxygenation as well as the reaction network will be discussed.

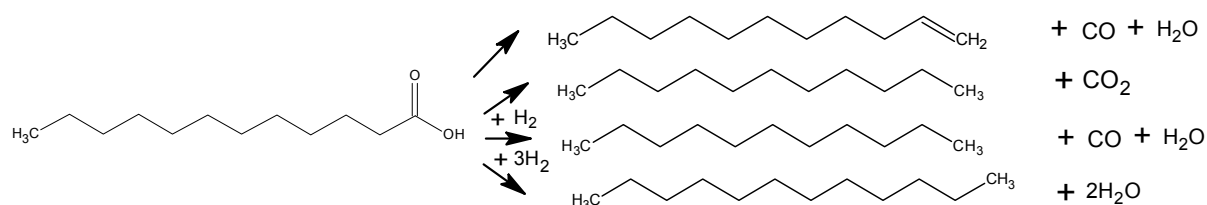


Fig. 1. Simplified reaction network for the catalytic deoxygenation of fatty acids.

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HYDROTREATMENT CATALYSTS DESIGN FOR BIO-FUELS PRODUCTION

Yakovlev V.A.¹, Khromova S.A.¹, Bykova M.V.¹, Yermakov D.Yu.¹,
Heeres H.J.², Venderbosch R.H.³, Parmon V.N.¹

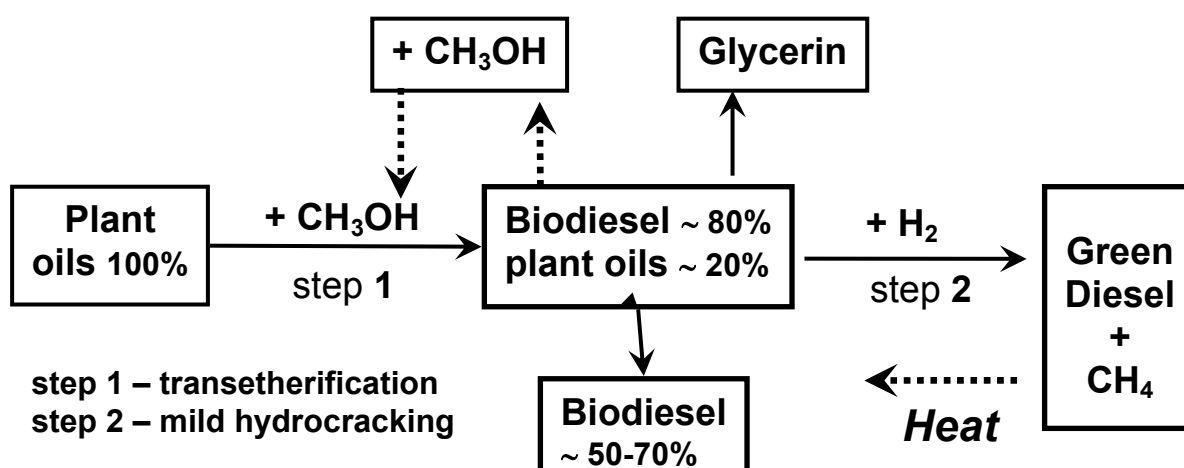
¹*Borekov Institute of Catalysis SB RAS, Novosibirsk, Russia*

E-mail: yakovlev@catalysis.ru

²*University of Groningen, the Netherlands*

³*BTG Biomass Technology Group BV, the Netherlands*

Biomass is a renewable alternative to fossil raw materials in the production of liquid fuels and chemicals. The objective of this work is to develop two-stage technology for biodiesel and green diesel production from lipidic renewables (plant oils, animal fats, algae lipids). The specificity of the work is development of new effective catalysts, adjusted to renewable feedstock. The technology is based on conjugated catalytic processes of transesterification and mild hydrocracking represented on the scheme below:



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 transesterification 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

OP-1-8

conditions (300-340°C and 2.0 MPa H₂) and possibility of green diesel production with different cetane number via hydroisomerization catalysts application.

Thus, developed transesterification and mild hydrocracking processes allow to obtain high-clean biodiesel and green diesel with high cetane number, which can be used as improving additive to traditional fossil diesels. Developed new effective catalysts can be used in processing of non-food lipidic renewables.

CATALYTIC HYDROTREATING OF FAST PYROLYSIS OIL WITH NiCu/ δ -Al₂O₃ CATALYSTS

Ardiyanti A.R.¹, Khromova S.A.², Yakovlev V.A.², Venderbosch R.H.³, Heeres H.J.¹

¹*Chemical Engineering Department, University of Groningen, Nijenborgh 4, Groningen, The Netherlands, e-mail: A.R.Ardiyanti@rug.nl*

²*Boriskov Institute of Catalysis, Pr. Akad. Lavrentieva, 5, Novosibirsk, Russia*

³*Biomass Technology Group B.V., Josink Esweg 34, Enschede, The Netherlands*

Lignocellulosic biomass can be converted efficiently via fast-pyrolysis into pyrolysis oil, an attractive liquid energy carrier [1]. However, the application of pyrolysis oil (e.g. as feedstock for existing refinery units) is limited due to its limited thermal stability, high acidity, and high viscosity. To enhance the application range of pyrolysis oil, catalytic hydrotreating of the pyrolysis oil has been proposed [2]. The major objectives of catalytic hydrotreating are a reduction of the oxygen content, and to achieve a product with improved stability and lower viscosity. Here we report our studies on catalytic hydrotreatment of pyrolysis oil using NiCu/ δ -Al₂O₃ catalysts with a range of Ni/Cu ratios in a batch set-up. Good deoxygenation levels were observed, though distinct differences in the performance were present (Figure 1).

This study clearly indicates that NiCu/ δ -Al₂O₃ catalysts have high potential for the catalytic upgrading of pyrolysis oils. Further studies in dedicated continuous set-ups are in progress

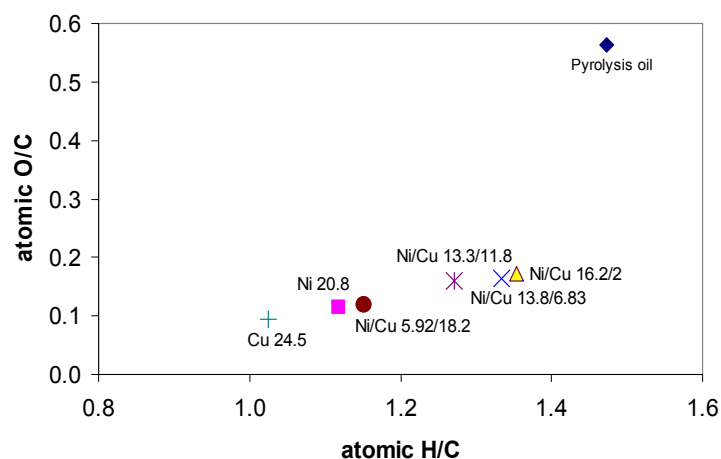


Figure 1. Van Krevelen plot of hydrotreated oils.

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Acknowledgements

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REACTION BETWEEN CO₂ AND COKE: A COMPARISON OF THE COKE FROM CATALYTIC CRACKING OF BIO-OIL AND GASOIL

Luciana T. Santos¹, Ana Paula S.S. Estevão², Fabiana M. Santos²,
Leonardo F. Mello³, Yiu Lau Lam³ and Marcelo M. Pereira²

¹Nacional Agency of Petroleum, Av. Rio Branco, 65, CEP 20090004, RJ, Brazil

FAX 55-21-2112-8389, lsantos@anp.gov.br

²Federal University of Rio de Janeiro, CT, bloco A, 7º an., CEP 21941909, RJ, Brazil

³Cepes - Petrobras, Av. Horácio Macedo 950, RJ, Brazil

The scenario of CO₂ emissions and the climatic changes are events highlighted in the world today [1]. The Fluid Catalytic Cracking Process (FCC) is a central point of this problem [2]. It is one of the major individual sources of CO₂ emission in a refinery due to large amount of coke formed during cracking reactions. To process biomass as alternative to fossil fuels can impact the energy transformation, furthermore will cause an increase in the amount of coke formed on the catalyst. So, CO production (an input for the chemical industry) and CO₂ sequestration can be simultaneously improved through the coke/CO₂ reaction [3]. The previously coked catalysts (in conventional gasoil and a bio-oil from sugarcane bagasse) were regenerated under CO₂ flux. The reaction was accompanied on line by a Mass Spectrometer and the catalysts were characterized by ¹³C NMR, LECO, AA and BET.

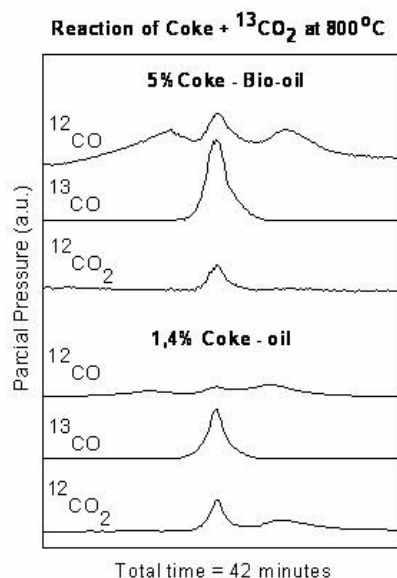


Figure 1. MS profiles of catalysts oxidation at 800°C.

Independently of the nature of coke, the CO₂ reacts in the presence of oxygen mainly at the beginning of the reaction. Simultaneously with the consumption of the label CO₂ (m/z=45), CO (m/z=29) is formed and coke is oxidized, Figure 1. The increase of the temperature facilitates the CO (m/z=28) formation. Despite the differences on coke functionality, the same range of reaction temperature was observed, both in the presence of oxygen and CO₂. The reaction kinetics was approximated by a pseudo first order with respect to CO₂ obtaining an E_{app}=87 kJ/mol to the reaction with gasoil. The calculation of the activation energy for the bio-oil is in development.

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BIOMASS' PRODUCTS TREATMENT INTO HYDROCARBONS AND HYDROGEN-CONTAINING GAS OVER NANOSIZED CATALYSTS AND MEMBRANE-CATALYTIC SYSTEMS

Tsodikov M.V.¹, Chistyakov A.V.¹, Gekhman A.E.², Moiseev I.I.²

¹A.V. Topchiev Institute of Petrochemical Synthesis, RAS, Moscow,
tsodikov@ips.ac.ru

²N.S. Kurnakov Institute of General and Inorganic Chemistry, RAS, Moscow

Results of the present paper relate to research of catalytic and membrane-catalytic processes based on alcohols, methane and carbon dioxide feed that allow obtaining fuel compounds and petrochemical substrates.

Nanosized catalysts that possess high activity and selectivity in new reactions of alkanes and olefins formation from bioalcohols were prepared with using of heterometallic alkoxide and acetic precursors containing metals of II, VI-VIII groups. It was shown the possibility of selectivity adjustment in one-step process directed on branched alkanes, olefins and alkane – olefin fractions formation. With use of kinetic and structural methods the genesis of applied catalysts was characterized and possible routes of studied reactions were found.

New approaches to high rate dry and vapor-phase reforming of bio-products lead to hydrogen-containing gas formation over membrane-catalytic systems modified with nanosized active components were developed.

Principal possibility of high effective cellulose conversion over nanosized catalysts impregnated directly on the substrate surface was demonstrated.

On the basis of developed approaches principal scheme was proposed that demonstrated the possibility to obtain a wide range of industrial important processes based on renewable raw materials.

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TUNING SELECTIVITY IN CATALYTIC CELLULOSE CONVERSION BY CONTROLLING THE Ni PARTICLE SHAPE AT THE TIP OF CARBON NANOFIBERS

Stijn Van de Vyver¹, Jan Geboers¹, Michiel Dusselier¹, Hans Schepers¹, Tom Vosch², Liang Zhang³, Gustaaf Van Tendeloo³, Pierre Jacobs¹, Bert Sels¹

¹Center for Surface Chemistry and Catalysis, K.U. Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium, stijn.vandevyver@biw.kuleuven.be

²Department of Chemistry, K.U. Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium

³Center for Electron Microscopy for Materials Science, University of Antwerp
Groenenborgerlaan 171, 2020 Antwerp, Belgium

With the world's focus on reducing our dependency on fossil carbon, one of the main challenges faced by future biorefinery processes will be the development of efficient catalysts for selective transformations of cellulose [1]. The entitled contribution demonstrates the production of sugar alcohols in excellent yields (up to 70%) from cellulose in a one-pot catalytic process over reshaped Ni particles attached at the tip of carbon nanofibers. While previous studies in this area focus on cellulose cracking with expensive transition metals dispersed on porous support materials [2-3], the basic concept of our catalyst design relies on the entanglement of threadlike carbon nanofibers around the water-insoluble cellulose matrix. Sterically accessible Ni particles allow fast hydrogenation of glucose units, released after acid-catalyzed hydrolysis of cellulose. Despite the well-documented role of Ni as an unselective hydrogenolysis catalyst, it will be shown that sorbitol is surprisingly stable towards C–C and C–O bond breaking under the applied reaction conditions. Results from batch experiments and extensive characterization studies support the idea that this bond-breaking selectivity is based on a synthesis-induced reshaping of Ni particles during the carbon nanofiber growth process. Thanks to its structure-sensitive nature, undesired hydrogenolysis behaviour of the Ni catalyst can thus be suppressed.

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Acknowledgements:

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PRODUCTION OF ACTIVE ALUMINA – SELECTIVE HYDROGENATION CATALYST CARRIER

Reznichenko I.D., Tselyutina M.I., Posokhova O.M., Kiseleva T.P.

*JSC Angarsk Catalyst and Organic Synthesis Plant, 665830, Angarsk,
Irkutsk region, Russia. E-mail: azkios@yukos.ru*

Analysis of the existing trends in new selective hydrogenation catalyst developments shows that the progressing performance level of industrial catalysts is based on optimization of structural, textural (specific surface area and porous structure) and acid properties of a carrier.

The aim of this work was to study the influence of the method of active alumina modification, used as a selective hydrogenation catalyst carrier, on its physical and chemical properties. It was revealed that introduction of the structure-forming additives at the stage of carrier preparation allows carrier pore structure to be intentionally adjusted thereby changing its physical and chemical characteristics. Properties of the industrial carrier samples obtained using structure-forming additives are given in the following table vs. typical carrier produced by double-flow precipitation (A-64).

Table - Physical and chemical properties of industrial carriers

Property	A-64	Sample 1	Sample 2	Sample 3
Specific surface area, $S_{sp,BET}$, m^2/g	270	246	200	146
Crush strength, kg/mm	1.0	2.0	2.3	2.5
Bulk weight, kg/dm^3	0.62	0.73	0.74	0.75
Pore radius distribution, pore share in total pore volume, %:				
- less than 18 Å	4	3	2	1
- 18-60 Å	34	55	88	80
- 60-100 Å	20	32	6	14
- more than 100 Å	42	10	4	5

It can be seen from the table that carrier modification with a structure-forming additive leads to changed porous structure parameters and notably increased carrier strength factor. Modified alumina carriers were used to produce industrial catalyst batches for selective hydrogenation of butane-butadiene cut from acetylenes and inert gases from oxygen and hydrogen impurities.

BIO-ETHANOL – PETROCHEMICAL RAW MATERIAL

**Tretiyakov V.F.¹, Isa Y.M.¹, Frantsuzova N.A.¹, Torkhovskii V.N.¹,
Tretiyakov K.V.²**

¹*Lomonosov Moscow State Academy of Fine Chemical Technology, Moscow*
e-mail: tretiyakov@ips.ac.ru

²*A.V. Topchiev Institute of Petrochemical Synthesis RAS, Moscow*

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 CO₂ emission, since, the carbon in these materials on combustion gives off carbon dioxide. The only, known way of absorbing atmospheric CO₂ 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 Lebedev'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.

The presented facts confirm that catalytic conversion of ethanol, is an alternative to the traditional process of crude oil refining; the process is capable of making headway for the production of synthetic fuels and raw materials for petrochemical industry at the same time preventing the increment of anthropogenic CO₂ in the atmosphere.

USING BIOMASS-BASED FUELS FOR DECENTRALISED POWER PRODUCTION

Valeriy Kirillov¹, Vadim Yakovlev¹, Bert van de Beld²

¹*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia,*
vak@catalysis.ru

²*BTG biomass technology group BV, Enschede, the Netherlands*

The Bioliquids-CHP project was set up to break down the technical barriers preventing the use of biomass-based fuels in engines and turbines for small-scale (50 to 1000 kW_e) decentralised combined heat and power generation. It aims to adapt a micro gas turbine and a diesel engine to operate on a variety of biomass-based fuels, including straight vegetable oil, FAME (biodiesel) and pyrolysis liquids.

On the one hand, the project will modify the design of these prime movers so that these can run efficiently on bioliquids like biodiesel, vegetable oil and pyrolysis oil. On the other hand, bioliquids will be upgraded and blended in order to facilitate their use in engines and turbines. In addition, the project will develop methods to control exhaust emissions (NO_x, CO, particulates) and will carry out technical, economic and environmental performance assessments.

Catalysts are developed and tested in various steps in the biomass-to-power chain, including: biomass pyrolysis, catalytic upgrading of pyrolysis oil, reforming fossil diesel and bio-liquids to synthesis gas, and controlling exhaust emissions (NO_x, CO, particulates). So, it is offered that biofuels adaption has to realize by two cross-ways: on the one hand catalytic upgrading of bio-liquids and on the other hand minimum modernization of energy generation equipment (gas turbine, diesel engine and so on).

The project is a joint cooperation between Russia and the European Union. The paper will focus on the development and testing of catalysts used in the project, and the effect on the properties of the resulting fuel.

Acknowledgements:

The authors like to thank the European Commission (FP7, Grant No. 227303) and the Federal Agency for Science and Innovation (FASI) of the Russian Federation for supplying funds and all partners involved in the BIOLIQUIDS-CHP project for their scientific contributions.

ORAL PRESENTATIONS

Section 2.

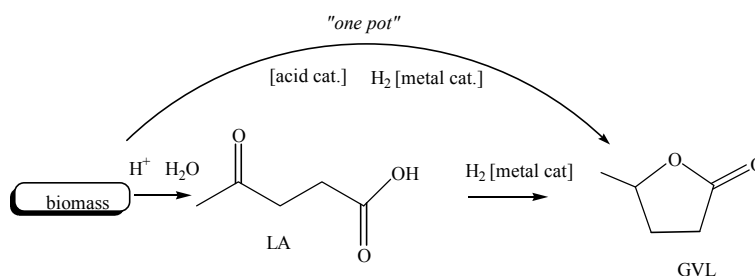
CATALYSIS FOR BIOCHEMICAL GENERATION

COMBINATION OF METAL AND ACID CATALYSIS FOR THE CONVERSION OF CARBOHYDRATE BIOMASS INTO CHEMICALS

Claudia Antonetti, Anna Maria Raspolli Galletti, Valentina De Luise,
Marco Martinelli

Department of Chemistry and Industrial Chemistry, University of Pisa,
Via Risorgimento 35, 56126, Pisa, Italy, claudia.antonetti@ns.dcci.unipi.it

Metal and acid catalyses play a strategic role in the catalytic conversion of biomass into chemicals because of the growing interest in using bio-renewable feedstocks as source of bio-fuels as well as of chemicals and fine chemicals [1]. Biomass provides security of supply and economical advantage, in particular when inexpensive or, indeed, waste or residue raw materials are employed as starting materials. In this context, the acid hydrothermal conversion of renewable resources to 5-hydroxymethyl-2-furaldehyde (HMF) or directly to levulinic acid (LA) has been studied [2] and patented [3]. The direct conversion of the carbohydrate raw biomass to LA results preferable employing homogeneous acid catalysts in water and the yield of LA can be enhanced by the proper selection of the main reaction parameters, in particular reaction time and acid type and concentration. LA can be successively hydrogenated to γ -valerolactone (GVL) which is not only a sustainable liquid but also a precursor for biomass-derived acrylic monomers and a valuable fuel additive [4].



The bi-functional (acid and hydrogenating) performances of Ru, Pd and Pt based heterogeneous catalysts and the optimization of the reactions conditions have been studied. In fact, the aim of this research is the development of the inexpensive production of GVL directly from renewable biomass with an «one pot process». In this perspective the employment of heterogeneous catalytic systems as well as of mild reaction conditions represents a challenging target.

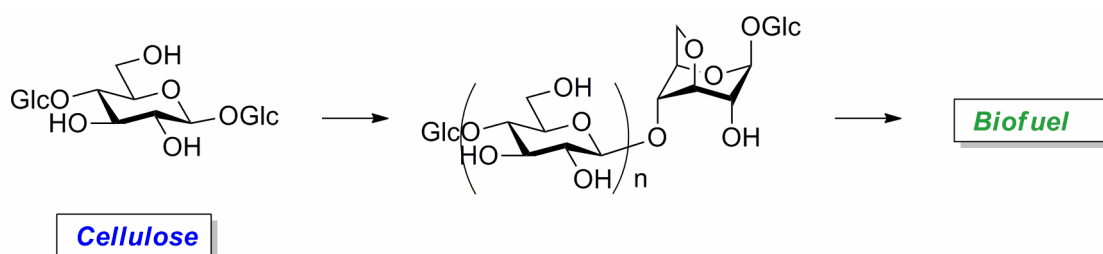
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3,6-ANHYDROCELLULOSE. A MODIFIED CELLULOSE FOR IMPROVED CATALYTIC DEGRADATION

Mikael Bols, Vrushali Jadhav

*Department of Chemistry, University of Copenhagen, Universitetsparken 5,
2100 Copenhagen Ø, Denmark, e-mail: bols@kemi.ku.dk*

Cellulose is the primary constituent of biomass and the most important potential source of biofuel. However acidic hydrolysis of cellulose is a comparatively difficult reaction, because the polysaccharide chains of cellulose hydrogen bond very strongly to each other. This means that the catalytic degradation of cellulose require strong conditions not necessarily compatible with biofuel preparation.



Recently we discovered that the rate of glucoside bond hydrolysis is several hundred times higher when glucose is forced into the 1C_4 chair conformation[1]. This led to the idea that a similar conformational change, in cellulose, might lead to a readily degradable cellulose. We here present work where we have investigated celluloses containing 3,6-anhydro residues and show that these polysaccharides are much more reactive towards acidic hydrolysis.

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Acknowledgements. We thank the Danish research council for production and technology (FTP) for financial support.

CELLULOSE HYDROTHERMAL CONVERSION PROMOTED BY HETEROGENEOUS BRØNSTED AND LEWIS ACIDS: REMARKABLE EFFICIENCY OF SOLID LEWIS ACIDS TO PRODUCE VALUABLE MOLECULES

Nadine Essayem¹, Flora Chambon¹, Franck Rataboul¹, Amandine Cabiac², Catherine Pinel¹, Emmanuelle Guillon²

¹*IRCELYON, Institut de recherche sur la catalyse et l'environnement de Lyon, CNRS, UMR 5256, 2 avenue Albert Einstein, F-69626 Villeurbanne, France*

²*IFP-Lyon, BP 3, F-69360 Solaize, France*

Introduction

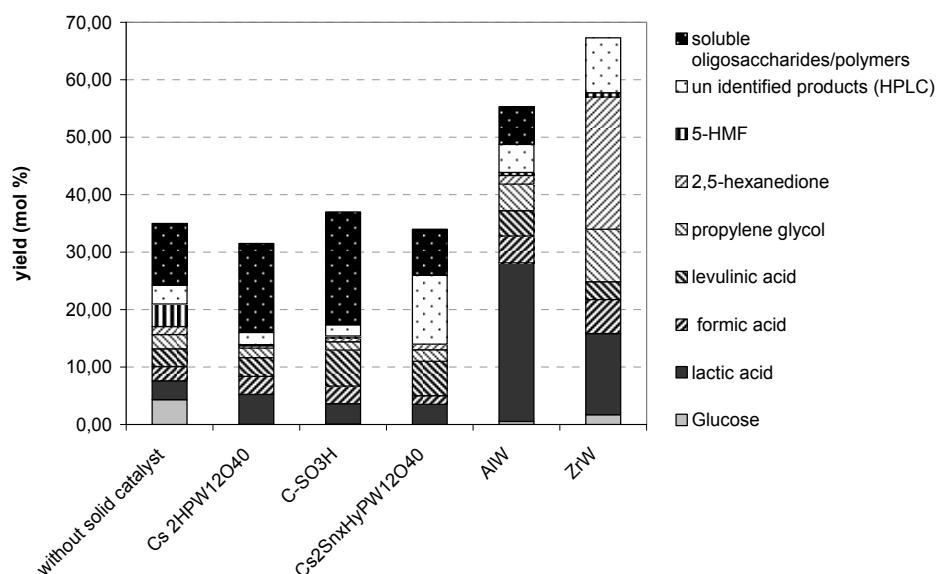
Over the past few years, the transformation of cellulose into valuable organic chemicals has attracted a growing interest. Indeed, cellulose is a widely available and non edible polysaccharide, which makes it a promising resource for the production of bio-products and bio-fuels. Liquid acids catalyzed hydrolysis of cellulose is a process known for more than 80 years. This process present drawbacks as a poor selectivity, problems of corrosion and production of large volume of waste acidic water. Recent studies reported the feasibility of cellulose depolymerization by mean of solid BrØnsted acids. In particular, sulfonated carbon based catalysts were reported to be active in the depolymerization of grinded cellulose. The present study reports investigations of hydrothermal conversion of crystalline cellulose, aimed to compare the efficiency of solid BrØnsted acids to solid Lewis acids.

Results and Discussion

In this study, the results of cellulose hydrolysis in hydrothermal conditions, that means in the absence of solid catalysts were used as a reference experiment. Indeed, in a previous study, we have shown that crystalline cellulose may be significantly depolymerised in hydrothermal conditions, depending on temperature and duration conditions; at T=190°C, in the absence of solid catalyst, a conversion of 35wt% was achieved after 24 h of reaction and glucose and HMF were detected only in poor yield [1]. It was shown by combining HPLC, TOC and MALDI TOFF analysis that mainly water soluble oligosaccharides/polymers were formed (Figure 1). In the presence of pure BrØnsted catalysts such as an acidic cesium salt of tungstophosphoric acid or sulfonated carbon, the extent of cellulose depolymerization was not changed. However, the product distribution was deeply modified; the proportion of water soluble polymers was improved at the expense of the pool of

products detected by HPLC (Figure 1). These results suggest that the Brønsted acidity brought by the solid catalyst is rather responsible of secondary transformations of water soluble polymers and/or glucose derivatives as HMF. On the opposite, solid Lewis acids such as tungstated zirconia or tungstated alumina exhibited a remarkable catalytic effect on the cellulose conversion which was increased from 30wt% to more than 55wt% and the proportion of water soluble polymers was strongly reduced. Yields of 27mol% in lactic acid and of 30mol% in 2,5,hexanedione were achieved on AlW and ZrW respectively [2]. The beneficial effect of solid Lewis sites was checked via partial exchange of the Brønsted sites of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ with Sn cations: the proportion of the polymeric products was reduced by half in presence of the Sn exchanged cesium salt.

As a concluding remark, we have demonstrated the remarkable efficiency of solid Lewis acids to produce valuable compounds from cellulose hydrolysis initiated by water autoprotolysis.



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CATALYTIC CONVERSION OF CONCENTRATED CELLULOSE FEEDS TO HEXITOLS WITH HETEROPOLY ACIDS AND Ru ON CARBON [1]

**Jan Geboers, Stijn Van de Vyver, Kevin Carpentier,
Kevin de Blochouse, Pierre Jacobs and Bert Sels**

*Center for Surface Chemistry and Catalysis; Katholieke Universiteit Leuven,
Kasteelpark Arenberg 23, 3001 Heverlee;
fax: +3216/321998, tel.: +3216/321463, Jan.Geboers@biw.kuleuven.be*

Several authors have reported on the bifunctional catalytic conversion of cellulose diluted in water (up to 2 wt%) [2] and catalyst loadings up to 0.4 wt%, achieving yields around 30-73 %, typically in 24 h. However, the need remains for a catalytic system that is capable of more rapidly and selectively transforming concentrated cellulose feeds into hexitols in high yields. Furthermore, heteropoly acids such as $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ have been shown to be efficient catalysts in several acid catalyzed reactions [4].

We combined heteropoly acids with a hydrogenation catalyst (Ru/C) which immediately converts all of the formed glucose into hexitols like sorbitol. Because these hexitols are more thermally stable than glucose, this approach enables us to increase the reaction temperature, leading to a highly selective and more complete cellulose conversion.

By careful adjustment of the reaction conditions, we were able to quantitatively convert cellulose into hexitols in 1 h. Furthermore, concentrated cellulose feeds of up to 10 wt% were converted into hexitols with high selectivity (95%) in 20 min, corresponding to an unprecedented hexitol volume productivity of $249 \text{ g L}^{-1} \text{ h}^{-1}$. As the recovery of heteropoly acid catalysts from aqueous solutions has been reported via simple recrystallisation or ether extraction [3], the development of fully recyclable HPA-Ru/C systems is within reach.

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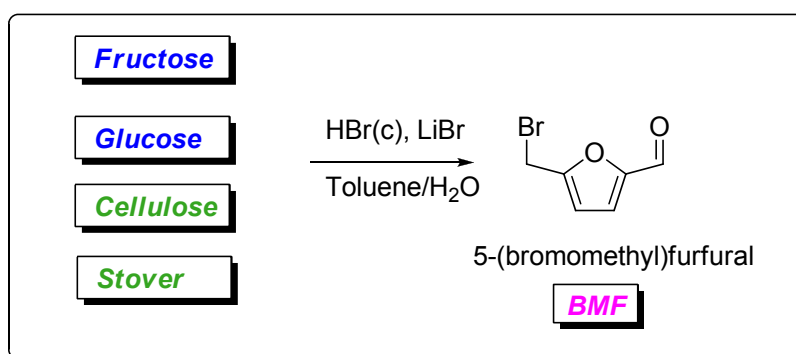
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EFFICIENT CONVERSION OF SACCHARIDES IN TO 5-(BROMOMETHYL)FURFURAL

Mikael Bols, Nitee Kumari

Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
E-mail: nitee@kemi.ku.dk

Furan based organic liquids obtained from renewable biomass resources have been found as potential substitutes for the petroleum-based building blocks which are currently used in the production of plastics and fine chemicals [1]. Mascial and coworkers [2] have recently reported that the 5-(chloromethyl)furfural (CMF) can be directly synthesized from cellulose using concentrated HCl/LiCl and a continuous extraction procedure, however CMF itself is not suitable as fuel due to the chlorine content but it can readily be reacted with ethanol to a useful biofuel. In the present work we have synthesized 5-(bromomethyl)furfural (BMF) from fructose, glucose, cellulose and straw in moderate to good yields, using HBr/LiBr. Owing to properties associated with bromo compounds, BMF can serve as a direct precursor of 2,5-dimethylfuran (DMF), which is the only liquid biofuel with highest research octane number [3]. Further we utilized the BMF in the conversion to ethoxymethylfurfural (EMF) and methoxymethylfurfural in excellent yields under very mild conditions.



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KINETICS OF SELECTIVE OXIDATION OF SUGARS OVER GOLD CATALYSTS

**Bright T. Kusema¹, Betiana Campo¹, Olga Simakova^{1,2}, Päivi Mäki-Arvela¹,
Tapio Salmi¹, Dmitry Yu. Murzin¹**

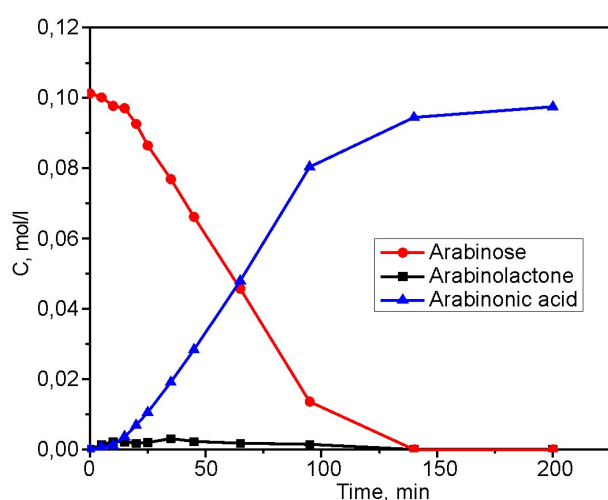
¹Laboratory of Industrial Chemistry and Reaction Engineering Process Chemistry
Centre, Åbo Akademi University, FI-20500 Åbo/Turku, Finland

E-mail: bright.kusema@abo.fi

²Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

Chemicals derived from various renewable sources have drawn great interest due to their features such as their ability to produce biodegradable and biocompatible new products as well as value-added chemicals. Arabinogalactans (AG) are hemicelluloses found in large quantities in larch species and they account for 15-25 weight % of dry wood material. The average ratio of galactose, arabinose and glucuronic acid in AG is about 5:1:0.08. AG can be converted into valuable products by a two step approach, which includes hydrolysis of AG to monomers and catalytic transformation of the sugars into bio-based valuable products having many applications in the food, detergent, pharmaceutical and cosmetic industries [1,2].

The focus of this research was on kinetics of selective oxidation of arabinose and galactose to arabinonic and galacturonic acid respectively over supported gold nanoparticles. Au samples were prepared by direct ion exchange, deposition with urea and impregnation. The influence of reaction parameters such as oxygen flow rate (2.5–5.0 ml/min), pH (6–10) and temperature (60–90°C) was investigated. The



activities and initial rates of the catalysts studied showed a strong dependence on the pH of the reaction medium with slightly alkaline conditions and moderate temperatures exhibiting high conversion and selectivity. Figure 1 shows the kinetic curves of arabinose oxidation by 2% Au/Al₂O₃ at pH 8 and 60°C.

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CHARACTERISATION AND DEPOLYMERIZATION OF SOLID HUMIN BY-PRODUCTS

Rasrendra C.B.¹, Windt M.², Meier D.², Heeres H.J.¹

¹Chemical Engineering Department, University of Groningen, Nijenborgh 4 9747 AG Groningen, the Netherlands, h.j.heeres@rug.nl

²vTI-Institute of Wood Technology and Wood Biology, Leuschnerstr. 91 D-2103 Hamburg, Germany

Biomass has been identified as an important future source for biobased chemicals. For example, lignocellulosic biomass like wood chips and agricultural residues (e.g. straw) may be converted to platform chemicals like acetic acid, hydroxymethylfurfural and levulinic acid. However, the conversion of C6-sugars to HMF and levulinic acid in acidic aqueous systems invariably leads to the formation of large amounts (up to 40 wt%) of insoluble brown solids, also known as humins (Figure 1) [1]. Given the fact that future biorefineries will process large amount of C6-sugars, it is highly relevant to identify possible high value outlets for these humin substances. We here report our studies on the characterization of humins (SEM, CP-NMR, FT-IR, GPC, TGA, DSC and XRD) and exploratory studies to depolymerise the humins using fast-pyrolysis and catalytic hydrotreatments. The fast pyrolysis of humins in micro-devices showed the presence of a range of furanics, phenolics and organic acids in the product phase. The catalytic hydrogenation of humins with Ru/C as the catalyst mainly yielded organic acids (acetic-, propionic-, pentanoic- and hexanoic- acid) and furanics.

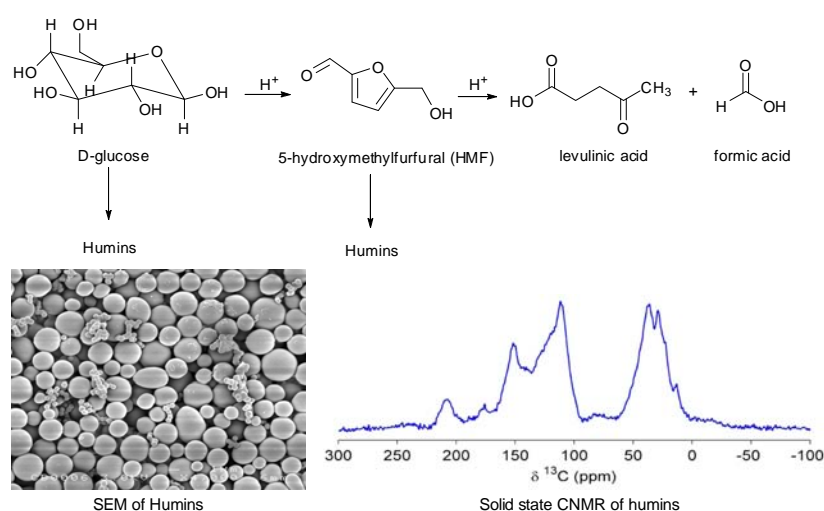


Figure 1. Humins formation from acid catalysed hydrolysis of D-glucose.

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PROCESS FOR THE PRODUCTION OF BUTYL LACTATE

**Prokhorov Alexiy¹, Shvets Valeriy¹, Suchkov Yuriy¹, Kozlovskiy Ivan¹,
Kozlovskiy Roman¹, Kapustin Alexey²**

¹*D. Mendeleev University, Moskow, Miuskaya sq., 9, proxorov.al@mail.ru*

²*Azov State University, Mariupol, 87500, Ukraine*

Butyl lactate (BL) is high-boiling, nontoxic and biodegradable substance and because of its properties BL is widely used as a solvent for nitrocellulose, oils, dyes, natural gums, many synthetic polymers etc., supplanting traditional toxic solvents and reagents (aromatic and chloroorganic compounds). Besides BL is a key intermediate for production of many chemicals such as, lactide, propylene glycol, herbicide, medicine, food or cosmetic additive, etc.

The periodical method of processing of a solution of ammonium lactate produced by fermentation to lactic acid esters by reaction of an aqueous ammonium L-lactate solution (68%) with alcohol is known. Preferably, the reaction is carried out in the bath reactor under reflux. The eliminated ammonia and water together with alcohol (azeotropic mixture) remove from system. Reaction time for noncatalytic reaction is from 10 to 17 hours.

In present work the influence of different catalysts on the rate of esterification of ammonium lactate with butanol was investigated. Estimation of efficiency of catalysts was carried out by comparison of rates of elimination of water.

Also, influence of different methods of cleaning of solutions of ammonium lactate (by using of different absorbents, coagulants and others substances), produced by fermentation, on the yield of ester has been examined.

Carrying out of reaction of ammonium lactate with butanol in the presence of the catalysts allows to reduce process duration by 25-30%.

The use of adsorbents on the clearing stage (various types of bentonites and the active carbon) allows to increase the yield of ester from 60 % to 75 %.

GOLD CATALYSTS IN THE SELECTIVE ARABINOSE OXIDATION: SIZE EFFECT

Olga A. Simakova^{1,3}, Bright Kusema¹, Betiana Campo¹, Päivi Mäki-Arvela¹,
Anne - Riikka Leino², Krisztián Kordás², Dmitry Yu. Murzin¹

¹Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Faculty of Technology, Åbo Akademi University, FIN-20500 Åbo/Turku, Finland, e-mail: olga.simakova@abo.fi

²Microelectronics and Materials Physics Laboratories, EMPART Research Group of Infotech Oulu, University of Oulu, FIN-90014 Oulu, Finland

³Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

Arabinose is one of the products of cellulose degradation, which can be transformed via selective oxidation to arabinonic acid valuable for pharmaceutical, cosmetic and food industry [1]. Since gold catalysts are well-known to be active and stable in the reactions of selective sugars oxidation, high activity in this reaction was anticipated.

Gold catalysts on different supports were tested in the selective oxidation of arabinose to arabinonic acid at mild conditions. Activity was found to be strongly dependent on the support type (Al₂O₃, TiO₂, C). The most active catalyst was obtained by supporting gold on alumina. In order to study the size effect, gold catalysts on this support with different dispersion of Au particles were prepared using different methods: deposition-precipitation with urea [2], impregnation and direct ion exchange (DIE) [3]. Catalysts prepared by DIE undergo calcination at different temperatures in the range of 300 - 600°C. Catalysts were characterized by TEM, XPS, XRD, ICP-MS techniques. Obtained catalysts have average diameter of the particles in the range of 1 - 20 nm, possessing the same metal loading and the oxidation state of gold, the only difference being the size of gold clusters.

Catalysts were applied in the arabinose oxidation at pH 8. The TOF dependency on the gold particle size was obtained, exhibiting a maximum typical for the structure-sensitive reactions.

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BIODERIVED LACTIC ACID AND LACTATES AS ALTERNATIVE SOURCES FOR PROPYLENE GLYCOL SYNTHESIS**Simonov M.N., Simakova I.L., Minyukova T.P., Khassin A.A.***Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, simakova@catalysis.ru*

Propylene glycol commercial production is currently petroleum-based and involves the high pressure and high temperature hydrolysis of propylene oxide manufactured by either chlorohydrin's process or the per-oxidation process. A catalytic method starting from lactic acid obtained by fermentation of crude biomass is perspective way of propylene glycol synthesis. However it is well known that catalytic hydrogenation of carboxylic acid to corresponding alcohols is very difficult process, which requires high pressure and temperature. For example, the hydrogenation of lactic acid to propylene glycol over Ru-containing catalyst was carried out at 145 bar and 423 K to reach necessary for noticeable lactic acid conversion and selectivity to propylene glycol [1]. According to [2] silica-supported copper prepared by incipient wetness impregnation is a high selective catalyst to convert lactic acid carboxylic group to 1,2-propanediol hydroxyl one. To decrease the pressure the preliminary esterification may be used, because the hydrogenation of corresponding esters is usually conducted in milder conditions [3,4].

The target of the present work is to elaborate vapour phase hydrogenation of lactic acid and hydrogenolysis of methyl- and butyl lactates in order to develop high selective catalytic process of propylene glycol synthesis in mild reaction conditions over silica-supported copper catalysts.

The main products of lactic acid hydrogenation were propylene glycol and propanoic acid, while hydrogenolysis of alkyl lactates leads to propylene glycol, hydroxyacetone and corresponding alcohol, methanol or butanol. Also in reaction mixture were presented 1-propanol, 2-propanol, 2-hydroxypropanal in total amount less than 2 wt. %. To study the activity of Cu/SiO₂ catalysts the copper loading in catalyst was varied from 14.2 wt. % to 45.5 wt. %. Conversion of substrate is monotone increasing with grow of copper content, while selectivity to propylene glycol decreases slightly. Precursor of the catalyst 45.5 wt. % Cu/SiO₂ has a structure of mineral chrysocolla with Cu:Si atomic ratio of one to one. Reduction of chrysocolla leads to formation of highly dispersed metallic copper particles, which take part in hydrogenation process. Further experiments were conducted over the most active 45.5 wt. % Cu/SiO₂ catalyst.

To estimate the optimal reaction conditions the temperature effect was studied. It was obtained, that increase of temperature leads to increase of substrate conversion as well as overall reaction rate grow, but selectivity to desired propylene glycol decreases due to increase of byproducts formation.

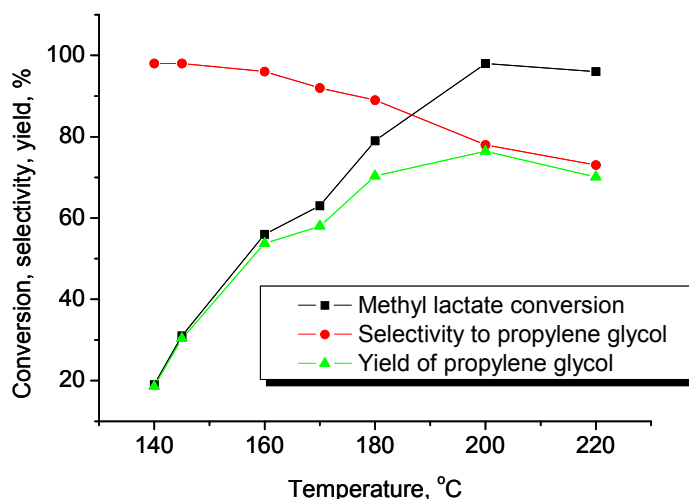


Fig.1. Effect of temperature on the catalytic performance of Cu/SiO₂ catalyst for the hydrogenation of methyl lactate, WHSV=0,18 h⁻¹

Effect of residence time on composition of reaction mixture

was studied. It was found, that concentration of substrate is decreased and concentrations of main products are increased with increasing residence time. It is noteworthy, that ratio between propylene glycol and propanoic acid in the case of lactic acid hydrogenation and propylene glycol and hydroxyacetone in the case of alkyl lactate hydrogenolysis was not depending on residence time. The data obtained allow assuming that formation of propylene glycol and propanoic acid passes through parallel independent pathways while hydroxyacetone is thermodynamically equilibrated with 1,2-propanediol.

The optimal conditions for propylene glycol synthesis were found. The most active catalyst is 45.5 wt. % Cu/SiO₂ at 473 K that provides 98% methyl lactate conversion with 78% selectivity on propylene glycol (Figure 1) while in similar conditions lactic acid conversion and propylene glycol selectivity were 95% and 65% correspondently.

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Acknowledgements:

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CATALYTIC CONVERSION OF HEMICELLULOSIC MONOSACCHARIDES TO FURFURALS

K. Vilonen, R. Karinen, J. Linnekoski, M. Veringa Niemelä

Department of Biotechnology and Chemical Technology, Faculty of Chemistry and Materials Science, Aalto School of Science and Technology, Espoo, Finland

kati.vilonen@tkk.fi

Integrated biorefinery concepts are seeking improved ways to separate and utilize the hemicellulosic fraction of lignocellulosic raw materials while the cellulose part is still used for pulp production. Dehydration of hemicellulosic monosaccharides to furfurals offers one route to substitute petroleum based building blocks in production of biobased transportation fuels and chemicals [1,2].

Water phase dehydration reactions of monosaccharides to furfurals are catalyzed by both homogeneous and heterogeneous acid catalysts. Thermal reactions also start to play a more important role in the reaction temperature of 200°C or higher. Furfurals react further producing organic acids and carbonaceous deposits, called humins, thus causing losses in yield and deactivating heterogeneous catalysts [3,4].

The key question in dehydration reactions is the optimization of reaction conditions and catalyst composition in a way to achieve the highest possible conversion still preserving an attractive selectivity to furfural. In this study, different acid catalysts, both homo- and heterogeneous, are studied using model compound sugars, such as xylose and glucose, in order to gain more understanding on the combined effect of reaction conditions and the character of the acid catalyst. Studies include also the characterization of the surface sites of the heterogeneous acid catalysts using temperature programmed desorption of methanol and pyridine as probe molecules.

The experimental results and conclusions will be discussed in more detail in this contribution. Particular emphasis is given to reaction rate, conversion and selectivity versus the composition of the catalyst when aiming to optimize both the reaction conditions and catalyst composition.

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Acknowledgements:

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SELECTIVE OXIDATION OF SUGARS USING NANODISPERSED Pt, Pd AND Au SUPPORTED CATALYSTS

Taran O.P.¹, Delidovich I.V.¹, Matvienko L.G.^{1,2}, Simonov A.N.^{1,2},
Moroz B.L.^{1,2}, Pyrjaev P.A.^{1,2}, Simakova I.L.¹, Kholodovich A.N.¹,
Bukhtiyarov V.I.^{1,2}, Parmon V.N.^{1,2}

¹*Boreskov Institute of Catalysis*, ²*Novosibirsk State University*,
Novosibirsk, Russian Federation, E-mail: oxanap@catalysis.ru

Carbohydrates constitute the major part of the renewable feedstock for chemical industry. Polyoxoacids being sugar oxidation products are widely used for synthesis of pharmaceuticals, food additives, cleaning agents, and other demanded products.

This work was aimed on the revealing the correlations between the catalytic performance of monometallic Pt, Pd and Au catalysts towards oxidation of sugars and nature of active metal, its oxidation state and dispersion. Sugars with different structure and positions of functional groups (glucose, sorbose, lactose) were used as model substrates.

The Pt/Sibunit, Pd/Sibunit, Au/Al₂O₃ and Au/Sibunit catalysts were synthesized, characterized and tested for the oxidation of sugars in aqueous solutions.

Common tendencies were revealed for the oxidation of aldoses (glucose and lactose). The catalytic activity increases in the order: Pt < Pd < Au, at the selectivity to corresponding acids up to 98% at total substrate conversion. Specific catalytic activity of Pt and Au does not depend on the metal mean particle size in the 1-5 nm range for Pt and 2-20 nm for Au. It was found that finely dispersed Pd/C catalysts (<d_{Pd}>=3 nm) are easier deactivated than samples with larger metal particles (<d_{Pd}>=6 nm) under kinetic controlled conditions. The stability of Pd nanoparticles increases under diffusion control. The dependence of catalytic activity and stability against deactivation on Pd oxidation state was studied by XPS.

The catalytic activity of Pt towards selective oxidation of sorbose exceeds those of Pd and Au. The selectivity of formation of 2-keto-gulonic acid never exceeds 20%. The reaction pathways of catalytic sorbose oxidation were proposed basing on the results of HPLC-MS analysis of the reaction mixture.

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Cu CATALYSTS FOR HYDROGENOLYSIS OF GLYCEROL TO PROPYLENE GLYCOL

Vasiliadou E.S., Lemonidou A.A.

Chemical Engineering Department, Aristotle University of Thessaloniki and Chemical Process Engineering Research Institute, Thessaloniki, Greece

evasili@cperi.certh.gr, alemonidou@cheng.auth.gr

Catalytic hydrogenolysis of glycerol is an innovative process route for the production propanediols [1]. Ru-based catalysts proved to be very active for glycerol hydrogenolysis, but the selectivity to propylene glycol was not satisfactory [2]. In this work glycerol hydrogenolysis is investigated over Cu and bimetallic Ru-Cu supported catalysts in order to achieve high activity and improved propylene glycol selectivity. More specifically, the effect of the support morphological characteristics, different Cu loadings and stability of the best performing catalyst was examined.

Mono-(Cu:5&20wt%) and bimetallic (Ru:4.13,Cu:0.87wt%) catalysts supported on silicate (SiO₂ and mesoporous HMS) were prepared using the wet impregnation method. The catalytic samples were characterized by various methods: BET, XRD, ICP, TPR. The tests were conducted in an autoclave reactor at 240°C and 80bar H₂ employing pure glycerol.

The evaluation the low Cu loading monometallic and bimetallic Ru-Cu catalysts supported on commercial SiO₂ and the as-synthesized HMS on glycerol hydrogenolysis showed that in the presence of Cu metal, the selectivity to propylene glycol increases due to the ability of Cu to hydro-dehydrogenate C-O bond and suppress C-C cleavage. The high surface area (970m²·g⁻¹) of the HMS mesoporous support stabilizes high metal loadings increasing their dispersion. The 20wt%Cu/HMS catalyst exhibited both high activity (43%) and excellent propylene glycol selectivity (91%) for 5h reaction time. Tests using spent catalyst for two times, resulted in an activity decrease of almost 50% probably due to metal aggregation, but the selectivity to propylene glycol remains constant in high levels.

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NANOSIZE CATALYSTS' STRUCTURE AND ACTIVITY IN THE PROCESSES OF BIOALCOHOLS AND CELLULOSE TREATMENT INTO HYDROCARBONS

Chistyakov A.V.¹, Yandieva F.A.¹, Kugel V.Ya.¹, Drobot D.V.², Tsodikov M.V.¹

¹*A.V. Topchiev Institute of Petrochemical Synthesis, RAS, chistyakov@ips.ac.ru*

²*M.V. Lomonosov Moscow State Academy of Fine Chemical Technology*

The present work relates to synthesis of catalytic systems based on alkoxide and acetylacetonate precursors and investigation of its structure and activity in the reactions of alcohols and cellulose conversion into fuel oil components.

Non-additive increase of W and Ta modified rhenium-contained catalytic systems activity has been found to occur in the reactions of bioalcohols conversion into olefin fraction. It was shown that when employing monometallic alkoxide based catalysts the reaction selectivity cardinally changes that results in oxygenates formation instead of olefins.

Using XPS, XAFS and TPD (ammonia) methods genesis and acidic properties of catalytic systems were studied.

The effective method of cellulose liquation in hydrogen donor medium was found. The characteristic feature of this process consists in direct deposition of Fe-Mo catalyst on the cellulose surface. Such approach allows to one-step production of cellulosic oil free from oxygen-containing compounds and increases hydrogen content in products with elemental composition C = 85-89; H = 7,1 – 7,9. First alkylcyclopentane and alkylcyclohexane were found in cellulosic oil formed with yield ~ 70 %.

Fe-Mo catalytic systems genesis was characterized using Mossbauer spectroscopy. It was found that Fe state depends on precursor nature. When catalyst was formed from Fe acetylacetonate and ammonium paramolybdate mixture, the water-methanol solution of Fe complex undergoes partial destruction followed by formation of superparamagnetic clusters with nonstoichiometric oxide structure. Fe-Mo bimetallic complex was not affected any failure after impregnation of the cellulose surface. It's important that both type of catalyst after treatment processes are in the same state – ferric oxide superparamagnetic clusters and nonstoichiometric magnetite.

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Cu-CONTAINING CATALYSTS FOR FATTY ACID TRIGLYCERIDS HYDROGENATION: RELATION OF CATALYTIC ACTIVITY TO THE MECHANISM OF COPPER REDUCTION

Shtertser N.V., Khassin A.A., Minyukova T.P., Filonenko G.A.

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, 630090, Russia,
Pr. Lavrentieva, 5. E-mail: nat@catalysis.ru
Novosibirsk State University, Novosibirsk, 630090, Russia, ul. Pirogova, 2*

Vegetable oils are a very promising source of fuel and various hydrocarbon products. Direct hydrogenation is one of prospective methods of vegetable oil processing because of its comparative technical simplicity and its possibility to obtain a wide variety of different products.

In the present work we study relations between physicochemical properties of copper containing catalysts and their catalytic performance in hydrogenation of fatty acid triglycerides.

The investigation was carried out using model catalysts which were thoroughly studied earlier: copper hydrosilicate ((Cu,H)₂[Si₂O₅](OH)₄ chrysocola) [1], copper chromite (CuCr₂O₄ tetragonal distorted spinel) [2] and a solid solution of Cu²⁺ in ZnO ((Cu,Zn)O wurtzite-like structure) [3]. Our results allow to suppose that hydrogenation of triglycerides occurs by three main reactions: (1) triglyceride + H₂ → ester of fatty acid and 1,2-propanediol + fatty acid; (2) triglyceride + H₂ → diglyceride + fatty alcohol; (3) triglyceride + H₂ → diglyceride + aldehyde. These steps are followed by hydrogenation of acids to alcohols and further – to hydrocarbons. Esterification reactions result in C₁₈-C₃ and C₁₈-C₁₈ esters formation.

(Cu,Zn)O catalyst was found to be the most effective of catalysts investigated in the reaction of hydrogenolysis of ester groups in triglycerides; however its activity in the hydrogenation of OH groups and double bonds was less than that of CuCr₂O₄ sample. (Cu,H)₂[Si₂O₅](OH)₄ catalyst was found to be less active in comparison to the patterns of CuCr₂O₄ and (Cu,Zn)O.

The catalytic studies were analyzed together with our recent studies on structural evolution and kinetics of reduction in hydrogen of the model catalysts. Copper ions reduction of CuCr₂O₄ and (Cu,Zn)O catalysts occurs without removal of lattice O²⁻ anion according to the reaction Cu²⁺ + H₂ → Cu⁰ + 2H⁺_{abs}. The generated protons are absorbed by the oxide structure in the form of OH⁻ and HOH groups [2,3]. (Cu,H)₂[Si₂O₅](OH)₄ catalyst reduction occurs according to traditional mechanism

with water formation. Therefore, according to our data the most active catalysts in the reaction of direct oil hydrogenating are that demonstrating proton stabilization during copper reduction.

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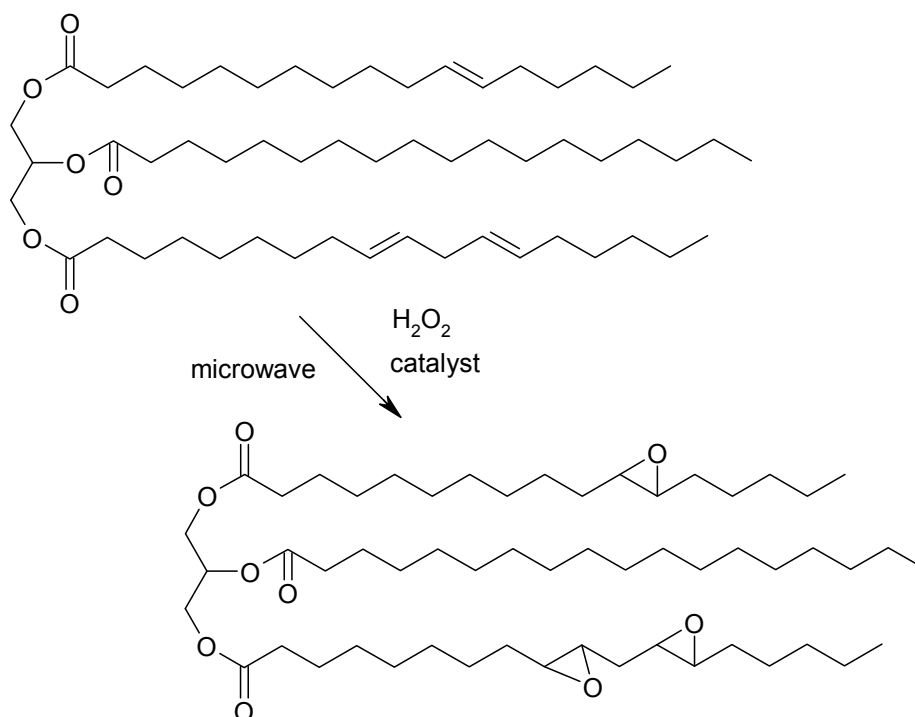
MICROWAVE-ASSISTED EPOXIDATION OF VEGETABLE OILS IN THE PRESENCE OF HYDROGEN PEROXIDE

Bogdal D., Prociak A., Michalowski S., Pala G.

*Chair of Polymer Chemistry and Technology, Cracow University of Technology
Ul. Warszawska 24, 31-155 Krakow, Poland*

e-mail: pcbogdal@cyf-kr.edu.pl

A two-step process was applied for the preparation of rapeseed and linseed oil-based polyols. In the first step, unsaturated fatty acids in triglycerides reacted with hydrogen peroxide to form epoxidized oil. Through the epoxidation, the double bonds of the triglycerides were transformed into oxirane rings.



In the second step, the epoxidized oils were converted into the polyols using monoethylene glycol (MEG) or diethylene glycol (DEG). In the case of the polyol based on rapeseed and linseed oil and the glycols both steps of the process (epoxidation and oxirane ring opening) were carried out under microwave irradiation. It allowed to reduce the reaction time of the epoxidation step ca. 60 %, and the hydroxylation step ca. 75 % in comparison to the process realised conventionally.

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EPOXIDATION OF VEGETABLE OILS UNDER MICROWAVE IRRADIATION

Leveneur S., Salmi T., Murzin D.Yu., Kumar N.

Laboratory of Industrial Chemistry, Process Chemistry Centre, Åbo Akademi,
FI-20500 Åbo/Turku, Finland, Fax: +358 2 215 4479, E-mail: slevene@abo.fi

Key words: epoxidation, peroxyacetic acids, heterogeneous catalysts, microwave irradiation.

Lubricants are widely used in different areas from car engines to office chairs. The majority of the current lubricants are petroleum-derived, then, a greener way of production is needed. Epoxidized vegetable oils, such as soya bean or rapeseed oils, are key components in the production of bio-based lubricant.

Epoxidation of unsaturated vegetable oils is done by peroxyacetic acid, which is produced *in situ* from carboxylic acid and H_2O_2 , and catalyzed by ionic exchange resins (Figure 1).

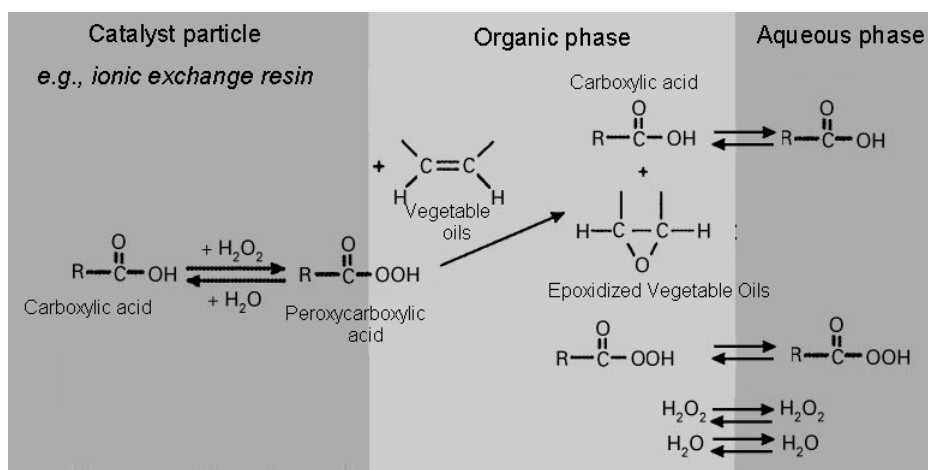


Figure 1. Reaction scheme and phases present.

Figure 1 shows that it is a liquid-liquid-solid systems, where the mass transfer phenomena play an important role. The kinetics of this system is quite slow, for instance, the conversion of ethylene unsaturated is around 80 % at 50 °C in case of jatropha oil after 10 hours of reaction [1] by using conventional heating. The purpose of this study is to show if the kinetics of such multiphase system can be increased by microwave irradiation.

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ULTRASOUND-INDUCED FORMATION OF MESOPOROUS MULTIMETAL CATALYSTS

Daria Andreeva¹, Jana Schäferhans¹, Ekaterina Skorb², Nicolas Pazos Perez¹

¹*Physikalische Chemie II, Universität Bayreuth,
Universitätstr., 30, 95444, Bayreuth, Germany
Tel.: +49(0)921552750; Fax: +49(0)921552059;*

[*Daria.andreeva@uni-bayreuth.de*](mailto:Daria.andreeva@uni-bayreuth.de)

²*Max Planck Institute of Colloids and Interfaces,
Am Mühlenberg, 1, 14476, Golm, Germany*

We study the ultrasound-driven formation of mesoporous multimetal sponges. The collapse of acoustic cavitations leads to very high temperatures and pressures on very short scales. Therefore, structures may be formed and quenched far from equilibrium. Mechanism of metal modification by ultrasound is complex and involves a variety of aspects. We propose that modification of metal particles and formation of mesoporous inner structures can be achieved due to thermal etching of metals by ultrasound stimulated high speed jets of liquid. Simultaneously, oxidation of metal surfaces by free radicals produced in water during cavitation stabilizes developed metal structures. Duration and intensity of the ultrasonication treatment is able to control the structure and morphology of metal sponges. We expect that this approach to the formation of nanoscale composite sponges is universal and opens perspective for a whole new class of catalytic materials that can be prepared in a one-step process. The developed method makes it possible to control the sponge morphology and can be used for formation of modern types of catalysts. For example, the sonication technique allows to combine the fabrication of mesoporous support and distribution of metal (Ni, Cu, Pd, Au, Pt, iron oxide etc.) nanoparticles in its pores into a single step.

THE EFFECT OF ULTRASOUND ON CATALYTIC STARCH OXIDATION BY HYDROGEN PEROXIDE

Pasi Tolvanen, Päivi Mäki-Arvela, Dmitry Yu. Murzin, Tapio Salmi

*Åbo Akademi, Department of Industrial Chemistry and Reaction Engineering
Biskopsgatan 8, FI-20500, ptolvane@abo.fi*

Oxidized starch is used in the paper industry to give the paper e.g., improved surface strength and hydrophobic properties. Conventional methods for starch oxidation use heavy metals as catalysts, and chlorites or iodates as oxidants. In this work, an environmentally friendly method for starch oxidation is developed, utilizing hydrogen peroxide as an oxidant which forms only water as a by-product, and iron tetrasulphophthalocyanine (FePcS, a metal complex) as a catalyst, of which only small amounts are needed.

The impact of ultrasound has shown to create pores and cavities on starch granules, thus increasing the surface area allowing higher oxidation degrees [1, 2]. Moreover, the effect of ultrasound on the oxidation reaction rate has not been studied before, and is in this work studied. Several different ultrasound effects were tested at different temperature. It was found out that by applying ultrasound during starch oxidation, the oxidation degree was significantly increased even at lower operational temperature.

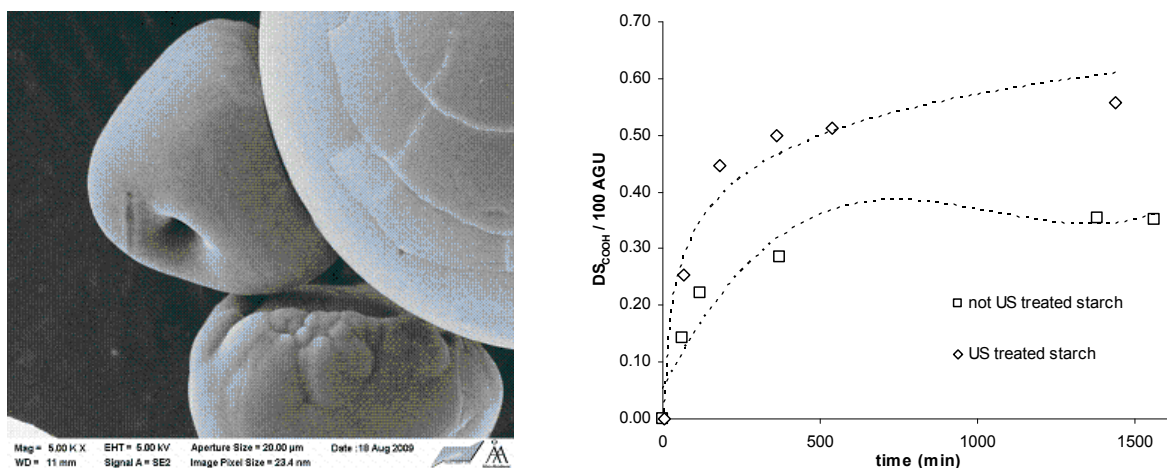


Figure 1. a) Ultrasound treated starch granules, b) kinetics of starch oxidation with or without applying ultrasound.

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EFFECT OF Ag DOPING IN La-Mn PEROVSKITES FOR THE CATALYTIC FLAMELESS COMBUSTION OF METHANE

Buchneva O.¹, Rossetti I.¹, Kryukov A.², Forni L.¹

¹*Dip. Chimica Fisica ed Elettrochimica, Università di Milano, v. C. Golgi, 19, 20133 Milano, Italy. Fax: +39-02-50314300, e-mail: ilenia.rossetti@unimi.it*

²*D.I. Mendeleev University of Chemical Technology of Russia, Miusskaya sq. 9, 125047, Moscow, Russia*

Samples with nominal composition $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$ with $x=0, 0.05, 0.1$ were prepared by flame pyrolysis (FP) and by the so-called sol-gel «citrate method» (SG). Lower specific surface area was obtained with the SG-prepared catalysts than with the FP ones. Silver introduction increased the surface area in all cases. However, no clear relationship between surface area and silver loading was observed. Due to the poor solubility of silver in the perovskite lattice, reflections of metallic silver were sometimes observed for the doped samples on XRD spectra, with increasing intensity at high Ag loading. Almost all our samples exhibited a very high activity for the catalytic flameless combustion (CFC) of methane. Indeed, under the adopted reaction conditions full methane conversion was attained below 600°C. The SG-prepared LaMnO_3 catalyst represented an exception, reaching a maximum 65% methane conversion at 600°C. The activity of FP-prepared catalyst was always higher than that of SG-prepared ones with identical nominal composition. Partial substitution of Ag for La led to increasing activity both for SG and FP prepared catalysts and the catalytic activity increased with increasing the Ag substitution.

The resistance to sulphur poisoning was checked for all catalysts, in view of their application for the CFC of biogas. Catalyst poisoning [1,2] was done *in operando* at 450°C by injecting several doses of tetrahydrothiophene. All samples lost part of their initial activity after poisoning. Silver substitution did not change the resistance to poisoning for FP prepared samples, whereas a more severe activity loss was observed for the poisoned Ag-doped samples than for the unsubstituted one when prepared by SG. However, due to the great positive effect of Ag on the initial activity, the residual conversion after poisoning of all the doped samples was still higher than for undoped LaMnO_3 .

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SURVIVAL OF *SACCHAROMYCES CEREVISIAE* CELLS IN SUPERCRITICAL CARBON DIOXIDE

Habulin M., Ajtnik M., Primožič M., Knez Ž.

*University of Maribor, Faculty of Chemistry and Chemical Engineering
Laboratory for Separation Processes and Product Design*

Smetanova 17, SI-2000 Maribor, Slovenia

tel. +386 222 94 462, fax: +386 225 27 774,

e-mail: maja.habulin@uni-mb.si

The present contribution shows the effect of supercritical carbon dioxide on cells of *Saccharomyces cerevisiae*. Yeast *S. cerevisiae* contains many different enzymes. Over the past twenty years, the use of high-pressure carbon dioxide was among others proposed as an alternative non-thermal pasteurization technique in food industry. SC CO₂ can also serve as a solvent for the extraction of intracellular components from microbial cells or for isolation of products from the reaction mixture in the production of biomass. The characteristics of SC CO₂ extraction fit very well with the biotechnological production conditions requirements. Water in contact with pressurized CO₂ becomes acidic and the decrease in the extra-cellular pH weakens microbial resistance to inactivation, by inhibiting microbial growth [1].

The effect of different incubation times and constant temperature of yeast cells *S. cerevisiae* suspended in universal liquid medium or Sodium Pyrophosphate Buffer, incubated in the SC CO₂ on the cells was studied. Before the incubation, the number of viable cells was determined. Nucleic acid concentration and alcohol dehydrogenase activity were determined before and after incubation of the cells in SC CO₂. Protein concentration in the suspension of cells was determined, as well. The suspension of culture of *S. cerevisiae* was incubated in SC CO₂ at different pressures and at constant temperature. Incubation time was changed regarding to the survival of the yeast *S. cerevisiae*.

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INSIGHTS IN GLYCEROL REFORMING IN SUPERCRITICAL WATER

Van Bennekom J.G.¹, Venderbosch R.H.², Heeres H.J.³

¹University of Groningen, Nijenborgh 4, 9747 AG, Groningen, the Netherlands,
tel.: +31 50 363 44 79, j.g.vanbennekom@rug.nl

²BTG Biomass Technology Group, Enschede, the Netherlands,
venderbosch@btgworld.com

³University of Groningen, Groningen, the Netherlands, h.j.heeres@rug.nl

The production of every ton biodiesel roughly consumes 100 kg methanol and produces the same amount of crude glycerol. Therefore, glycerol is also a product of a biodiesel producer [1]. An interesting option addressing this glycerol is the production of syngas, which can be used in different follow-up processes (e.g. methanol synthesis) [2].

Glycerol reforming in supercritical water yields a gas rich in H₂, CO and CO₂, and smaller amounts of methane and higher hydrocarbons. The composition of the gas is important as the follow-up processes all have their optimal syngas compositions. The gas composition depends on the operating conditions and is influenced by temperature, residence time, and feedstock concentration.

The research study presented here focuses on the gas composition as a function of reforming process conditions. Furthermore, the influence of different catalysts (both homogeneous and heterogeneous) on the gas composition is studied. Experiments were carried out in a bench scale unit with a throughput of 1 kg/hr of a 10-20% solution of feed in water. Pure glycerol as well as crude glycerol (derived from the biodiesel production process) are used as feedstocks. The experimental results will be presented for both catalytic and noncatalytic reforming and will be critically evaluated in terms of gas yield, glycerol conversion, catalytic effects and gas composition.

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ORAL PRESENTATIONS

Section 3.

CATALYTIC GASIFICATION OF BIOPRODUCTS

APPLICATION OF NOVEL CATALYST IN BIOMASS GASIFICATION PROCESS

Mania Abdollahi Neisiani, Jamal Chaouki

*Department of Chemical Engineering, Ecole Polytechnique de Montreal,
P.O. Box 6079, Station Centre-Ville, Montreal, Quebec, Canada H3C3A7,
mania.abdollahineisiani@polymtl.ca*

With diminution of fossil fuel resources, very high and unstable prices of oil as well as the global warming issues; utilization of biomass had gained a lot of attention as a potential source of renewable energy. One of the possible transformation routes of biomass to energy and valuable chemical products is gasification process. The gas product formed from biomass gasification consists of major components, like CO, H₂, CO₂, CH₄, H₂O and organic impurities (tars) and inorganic impurities (H₂S, HCL, NH₃, alkali metals). The organic impurities include low molecular weight hydrocarbons to high molecular weight polymer hydrocarbons. The higher molecular weight hydrocarbons, known as tar, are problematic in biomass gasification systems. They can condense in exit pipes, certain filters and other downstream processes resulting in blockages and clogged filters. Therefore, the tar removal from the gas product stream is very important before further utilization of gasification products. Several approaches for tar reduction have been reported in the literature. There are some sophisticated options available, which have claimed to reduce the tar level significantly. Depending on where the tar is removed, all the methods can be categorized into two main groups; either inside the gasifier itself (known as primary methods) or after exiting the gasifier (known as secondary methods). Although secondary methods had proven to be effective, primary methods are gaining more attention because of economical benefits. One of the most important methods in primary issues is using catalyst additives during gasification. To be able to use the catalyst on a commercial scale, its availability and price are critical factors. Many catalysts have been developed in recent years for this purpose [1]. These catalysts include Ni-based catalysts, calcined dolomite and magnesites, calcite, olivine and iron catalysts. Among all these only a few have been tried as catalyst inside the gasifier itself during gasification because most of them are not very robust and undergo attrition in fluidized bed reactors, while some undergo rapid deactivation [2-4]. Therefore, still there is a great interest in discovering a gasification catalyst which

should be efficient in terms of tar removal, economically feasible, but more importantly, it should not affect the formation of useful gaseous products.

In this paper a novel and cheap catalyst is introduced for the gasification process. This catalyst acts as a suitable bed material promoting char gasification reactions, changing the product gas composition, increasing its heating value and reduces the tar yield. Claim has been approved by thermogravimetry analysis coupled with gas chromatography tests and by comparing results with pure biomass and also other tar cracking catalysts. Biomass gasification also have been done in fluidized bed reactor with application of novel catalyst which results show significant improvement in gasification process. A kinetic model was presented for the pyrolysis step and it was fitted to experimental results in order to find its parameters. Kinetic model has been used for modeling catalytic gasification in fluidized bed employing previous developed hydrodynamic models [5]. Modeling results are comparable with experimental results. This new catalyst can be known as a breakthrough in order to improve gasification process for industrial purposes.

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REDUCING CONVERSIONS OF GLYCEROL OVER Ni-CATALYSTS

Korolev Yu.A., Greish A.A., Kustov L.M.

*N.D. Zelinsky Institute of Organic Chemistry, 119991, Moscow, Russia,
Leninsky prosp., 47, lmk@ioc.ac.ru*

Last years a search of renewable natural resources of fuel is of great importance because of the world oil reserve depletion and increased attention to the environmental protection. Producing of biodiesel fuel by means of transesterification of plant oil or animal fat with methanol can become one of such directions. Glycerol is produced in the mentioned process as a general by-product. In this connection there is a big problem of glycerol utilization. From this point of view catalytic hydrodehydroxylation of glycerol in H₂ atmosphere followed by formation of such valuable products as propanediols and ethylene glycol is perspective direction of processing of glycerol stocks.

In the flow setup it was studied the influence of temperature and hydrogen pressure on glycerol conversion and the products yield on Ni-Cr₂O₃ and Ni Raney taken as the catalysts.

During the runs H₂ / glycerol ratio was varied also.

Ni-Cr₂O₃. It was found a rise in temperature increased the yield of a target products. Particularly, at 220 °C glycerol conversion and the yield of 1,2-propanediol are equal to 47 % and 21 % respectively, while at 260 °C these values are close to 97 % and 31 %.

Ni Raney. Studying of temperature effect on hydrodehydroxylation of glycerol at 20 at pressure showed the most yield of 1,2-propanediol (32 %) to be obtained at 220 °C, at that time glycerol conversion was close to 80 %. The highest selectivity to 1,2-propanediol, more than 61 %, is reached at 180 °C.

At 240 °C a complete conversion of glycerol is observed. In these conditions several by-products are formed, e.g. lower alcohols; the yield of methanol and ethanol are of 17 % and 51 %, respectively. Noteworthy, in reaction conditions considerable quantity of methane is formed also. During temperature rise to 260 °C the yield of methane increases up to 90 %.

Increase in H₂ pressure from 5 to 50 at results in decrease in the yield of acetol from 12 % to 0,4 %. When using of Ni Raney, there is no sharp fall of glycerol conversion during increasing of H₂ pressure, as opposite to Ni-Cr₂O₃ catalyst.

LOW-TEMPERATURE CATALYTIC PYROLYSIS OF ORGANIC RAW MATERIALS

Kosivtsov Yu., Sulman E.

Tver Technical University, Tver, Russia, sulman@online.tver.ru

The search of new sources of power supply is in great demand due to the solution of one of the important problems of the modern economy, sciences and technology – the necessity of conversion and use for energy production of both available natural organic materials and wastes. Application of catalytic technologies in the manufacture of traditional fuels allows intensifying refinement processes and valorization of low-grade raw materials. From the point of view of the simplicity of the process; level of pollutants control and high yield of the final products pyrolysis is considered the best method for biomass conversion. In spite of their variety modern technologies of pyrolysis are far from perfect as a series of problems hasn't been solved (e.g. low yield of pyrolysis oil, blocking of pipe-lines with coal, quick deactivation of the catalyst). Part of these difficulties can be overcome when applying stable catalytic systems and technologies.

We have found that the use of catalytic systems does not only decrease the temperature of the pyrolysis process but intensifies the processes of refining and ennobling of low-grade natural raw material. For example during peat pyrolysis it was found that in the presence of catalysts (i.e., natural aluminosilicates or synthetic zeolites) the amount of alkanes and alkenes in gaseous mixture noticeably increased. Thus the average value of the specific heat of combustion was higher approximately by twofold in comparison with the data obtained for non catalytic process. Another trend of our investigations is low-temperature catalytic pyrolysis of polymeric cord of used automobile tyres in the presence of iron subgroup metal chlorides, which result in increase by twofold of the rate of hydrocarbons formation.

It is noteworthy that the unique express-method of analysis of the heat of combustion as well as the individual compounds of gaseous mixture on the base of GC was developed.

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LOW-TEMPERATURE CONVERSION OF ETHANOL OVER Ni-Cu/SiO₂ CATALYST

Lapin N.V., Bezhok V.S.

*Institution of Russian Academy of Sciences
Institute of Microelectronic Technology and High-Purity Materials, RAS,
Chernogolovka, Russia
Fax: (495)962-8047, E-mail: lapin@iptm.ru*

Hydrogen is promising fuel for various power plants, low-power devices (1-50W) 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 case ethanol has a number of advantages over methanol such as low cost, low toxicity, ease of transporting, exploitation, and production from renewable sources (bioethanol). When hydrogen is used to supply portable fuel cells, integration of a fuel cell and a fuel microchannel converter seems most perspective. In this case, the catalyst should be placed on the channel walls, where highly developed catalyst surface can hardly be obtained. 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.

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 CO₂ 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.

HIGHLY SENSITIVE HYDROGEN GAS SENSORS SEMICONDUCTING NANO WIRES GRAFTED WITH Pd NANOPARTICLES

Seonghwa Ju¹, Jun Min Lee², Ha-Yeong¹, Eunsongyi Lee², Ji-eun Park¹,
Wooyoung Lee², Sung-Jin Kim¹

¹*Department of Chemistry and Nano Science, Ewha Womans University,
11-1 Daehyun-Dong, Seodaemun-Gu, Seoul 120-750, Korea, sjkim@ewha.ac.kr*

²*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749*

We have investigated the hydrogen gas sensing performance of Pd nanoparticle grafted single-walled carbon nanotubes (SWCNTs) and tin dioxide NWs. The SWCNTs were modified with dendrimers and then Pd nanoparticles were grafted on the dendrimers. The SWCNTs grafted with Pd nanoparticles resulted in high response (25%), a fast response time (7 sec) at 10,000 ppm hydrogen gas, and an ultra-low concentration H₂ detection of 10 ppm in room temperature. Also, we have successfully investigated hydrogen gas (H₂) sensors Pd nanoparticle-decorated tin dioxide NWs. The SnO₂ network sensors were found to show ultra-high sensitivity ($\sim 1.2 \times 10^5$ %) and a fast response time (~ 2 s) upon exposure to 10,000 ppm H₂ at room temperature. The hydrogen sensing mechanism in the SnO₂ network sensor showing «ON–OFF switching» is mainly based on changes in the electrical conductance as the H atoms dissociated from H₂ due to the catalytic activity of Pd NPs and «spill-over» effect with oxygen ions at the surface of SnO₂. Further details related to the mechanisms of the SnO₂ network sensors will be discussed in the presentation. This fabrication method using Pd nanoparticles as a catalyst for H₂ molecules allows the production of highly-sensitive H₂ sensors that exhibit a broad dynamic detection range, a fast response time, and an ultra-low detection limit.

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H₂ PRODUCTION BY STEAM REFORMING OF BIOETHANOL**Ilenia Rossetti, Cesare Biffi, Gian Franco Tantardini, Lucio Forni**

Dip. Chimica Fisica ed Elettrochimica, Università degli Studi di Milano, v. C. Golgi 19, I-20133 Milano, Italy. Fax: +39-02-50314300, e-mail: ilenia.rossetti@unimi.it

Ni-based catalysts have been produced by flame pyrolysis (FP) and tested for the steam reforming (SR) of ethanol. The catalysts have been supported on Al₂O₃ (for comparison with commercial samples), TiO₂ and La₂O₃, with metal loading between 5 and 15 wt%. Two sets of samples have been prepared: the former by impregnation of a Ni precursor on the FP-prepared support, the latter by direct FP synthesis. The catalysts were characterised by XRD, N₂ adsorption-desorption, TPD-TPR-TPO, SEM. The activity tests were performed at atmospheric pressure and at three different temperatures (500-750°C) in a continuous tubular reactor on 0.5 g of catalyst, pre-activated at 800°C in H₂ flow. Water and ethanol have been fed in 3:1 molar ratio, with variable VHSV. Data have been collected for up to 100 h on-stream on each sample, to check for catalyst deactivation.

The FP synthesis led to nanosize particles (20-60 nm), characterised by suitable thermal resistance for this high temperature process. Independently of the preparation route, all the samples showed higher reducibility with respect to literature data. The activity tests showed full ethanol conversion at 750°C, with carbon balance closing to ±6 mol%. H₂ molar fraction in the products was usually higher than 0.70, whereas CO and CO₂ were strongly dependent on the operating conditions and catalyst formulation. At low temperature a contribution of the water gas shift reaction is indeed expected, increasing H₂ yield and lowering CO concentration in the outlet gas. This is especially desired for two reasons. On one hand, a low operating temperature decreases the thermal input to the process. On the other hand, if H₂ is to be fed to fuel cells, careful purification from CO is required, particularly if a PEM-FC is used, so that the lowering as much as possible the CO concentration in the reformat gas is welcome.

Some undesirable by-products such as acetaldehyde and methane were observed occasionally at low temperature only and their concentration was virtually absent when increasing contact time. By increasing again reaction temperature a full recovery of activity and optimal carbon balance were always obtained.

HYDROGEN AND SYNGAS PRODUCTION BY ETHANOL STEAM REFORMING OVER COMPOSITE CATALYSTS COMPRISED OF Ni/YSZ AND COMPLEX OXIDES

Mezentseva N.¹, Alikina G.¹, Krieger T.¹, Ishchenko A.¹,
Smorygo O.², Sadykov V.^{1,3}

¹*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, mnv@catalysis.ru*

²*Powder Metallurgy Institute, Minsk, Belarus*

³*Novosibirsk State University, Novosibirsk, Russia*

Transformation of biofuels into syngas or hydrogen via steam reforming is now considered as one of the most important task of catalysis in the energy-related fields. However, due to a high reactivity of oxygenates a heavy coking is observed leading to the catalyst deactivation. To deal with this phenomenon, active components comprised of complex oxides with a high lattice oxygen mobility (favors efficient gasification of coke precursors) promoted by precious metals (responsible for oxygenates activation) are suggested [1]. Ethanol is one of the major components which are present in biofuels and hence, ethanol steam reforming (ESR) is a suitable reaction for the development of an efficient bio-oil processing via SR.

In the present work, the nanocomposite catalysts based on Ni/YSZ (20-90wt.%) cermets co-promoted with SmPrCeZrO or LaPrMnCrO oxides (80-10wt.%) and Pt or Ru were synthesized by modified Pechini method. Samples were characterized by BET, XRD, TEM with EDX, C₂H₅OH (1% in He) TPR and their subsequent TPOx by H₂O (1% in He). The catalytic properties of nanocomposite catalysts were studied in the SR of ethanol in diluted and realistic feeds at short contact time.

Applied preparation procedures result in pronounced interaction between nanocrystalline active components including decoration of NiO/Ni particles by oxidic fragments, epitaxial intergrowth between particles of different phases, incorporation of Ni, Pt and Ru cations into perovskite or fluorite particles directly revealed by EDX and reflected in variation of lattice spacings and particle sizes. All studied samples demonstrate a high and stable performance in the steam reforming of ethanol in the intermediate temperature range (500-600°C). For samples with the low (20%) Ni/YSZ content promotion by Pt or Ru does not improve performance determined mainly by the oxygen mobility in fluorite or perovskite oxides and accessible Ni surface decorated by oxidic species. Performance of best compositions supported as porous strongly adhering layers on crofer/fechraloy nonporous/porous monolithic substrates was demonstrated to be also high and stable in ESR ensuring reformat composition close to equilibrium.

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CATALYTIC STEAM REFORMING OF BIOMASS-DERIVED OXYGENATES

Soykal I.¹, Mirkelamoglu B.¹, Song H.¹, Bao X.², Hadad C.M.², Ozkan U.S.¹

*The Ohio State University, Department of Chemical and Biomolecular Engineering¹
and Department of Chemistry², 140 W 19th Avenue, Columbus, Ohio 43210-USA*

Fax: (1) 614-292-3769, E-mail: ozkan.1@osu.edu

Significant research efforts are being devoted to development of catalytic processes for utilizing renewable resources for energy. One such process is catalytic steam reforming of biomass-derived oxygenated hydrocarbons, such as ethanol, dimethyl-ether (DME) and methanol. Catalyst deactivation arising from metal sintering and/or deposition of carbonaceous species during steam reforming of oxygenated hydrocarbons is a commonly cited problem over various catalytic systems. The development of active and stable catalytic systems based on non-noble metals is important for making the technology economically viable. At the same time, understanding of the nature of the active sites and reaction pathways is vital for tailoring the catalysts for improved activity and stability. Previously, we have shown that supported cobalt catalysts constituted active catalysts for ethanol steam reforming [1-6], achieving high hydrogen yields and high stability. A wide array of techniques including, X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, thermogravimetry, and scanning calorimetry were utilized to characterize the catalysts. Operando Raman spectroscopy with isotopic labeling was used to demonstrate oxygen exchange properties of the catalysts and the effect of oxygen mobility of the support on the catalyst activity. More recent studies include in-situ X-ray absorption fine structure spectroscopy (XAFS) and in-situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) to study the state of active cobalt species and formation of surface intermediates. Computational simulation studies will also be discussed to derive mechanistic models of steam reforming of oxygenated hydrocarbons, over Co-based catalysts.

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HYDROXYAPATITE AS A NEW CATALYST SUPPORT FOR HYDROGEN PRODUCTION VIA GLYCEROL STEAM REFORMING

Zahira Yaakob^{1,2}, Lukman Hakim¹, Manal Ismail^{1,2}, Wan Ramli Wan Daud^{1,2}

¹*Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia, zahira@eng.ukm.my*

²*Department of Chemical & Process Engineering, Faculty of Engineering & Environmental, Universiti Kebangsaan, Malaysia*

The need and development of cleaner and greener alternative technologies using truly heterogeneous catalytic system in the synthesis of fuel is very important. In this work hydrogen production via steam reforming of glycerol (C₃H₈O₃) was carried out over nickel supported on hydroxyapatite [Ca₅(PO₄)₃(OH)] as biomaterial catalyst. The reaction is carried out in a fixed-bed reactor for 240 minute at 600 °C (atmospheric pressure) and water-to-glycerol feed ratio 8:1. Catalysts were prepared by mean of wet impregnation and sol-gel methods with nickel loadings varied from 3-12% on hydroxyapatite. It is found that the 3 wt% nickel loading prepared by sol-gel method shows higher hydrogen production rate (41.19 % - 61.22 %) compare to the other nickel loadings. The catalysts were characterised by BET surface area, X-ray diffraction, and SEM-EDX techniques. It is shown that Ni/HAP catalyst surface area and morphology of the catalysts played an important role in the hydrogen production.

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CATALYTIC GAS PHASE CONVERSION OF GLYCERIN**Suprun W., Gläser R., Papp H.**

*Institut für Technische Chemie, Universität Leipzig, Germany,
Fax: + 49 341 97 36349; e-mail: suprun@chemie.uni-leipzig.de*

As a sustainable alternative, acrolein can be synthesized by the double dehydration of glycerol. Therefore, during the last decade, the catalytic dehydration of glycerol to acrolein and hydroxyacetone has gained big scientific and industrial interest. Different solid acid catalysts including zeolites (H-form) and Al_2O_3 , TiO_2 , ZrO_2 and SiO_2 impregnated with phosphates and heteropoly acids have been proposed for glycerol dehydration in gaseous or liquid phases.

The aim of the present work is to get more insight into the effect of different transition metal oxides supported on acidic $\text{Al}_2\text{O}_3\text{-PO}_4$ on the performance of catalytic gas phase conversion of aqueous solution of glycerine. In particular Cr, Cu, Ce, Fe, Mn, Mo, V and W oxides were investigated to elucidate their role in different mechanism pathways and thus, formation of main and by-products. This will then have repercussions for the deactivation and long-term stability in the selective conversion of glycerol to C_2 - C_3 products. Bifunctional catalysts $\text{Al}_2\text{O}_3\text{-PO}_4$ modified by Cu-, Cr-, Fe-, V-, Mo-, W-oxides and SAPO (11, 34) were synthesized and characterized by N_2 pysisorption, XRD, NH_3 - and H_2 -TPD analysis. Catalytic conversion of glycerol was investigated at the constant reactions conditions in presence of water. Glycerol conversion and summary selectivity to acrolein and hydroxyacetone depended strongly on the total acidity and redox properties. The influence of temperature and GHSV on the selectivity of dehydrations products was also evaluated. In comparison to acidic catalysts, the $\text{Al}_2\text{O}_3\text{-PO}_4$ donated with W-, Mo-, Cr- and Cu -oxide showed complete glycerol conversion and excellent long time stability. The SAPO samples showed high acrolein selectivity only at the shot time of stream. The properties of the used catalysts were studied by TPD- NH_3 and DTA-TG, TPO, DRIFT and XPS analysis. Relatively low deactivation rate of $\text{MeOx-Al}_2\text{O}_3\text{-PO}_4$ catalyst could be due to oxidative cleavage of carbonaceous deposits. Moreover, the mechanism of products formation and catalyst deactivation by glycerol dehydration was proposed [1].

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DEMANDS FOR CATALYSTS SUITABLE FOR A WGS MEMBRANE REACTOR WITH GAS FEED FROM GASIFIERS

Krzysztof Gosiewski, Marek Tanczyk

Institute of Chemical Engineering, Polish Academy of Sciences, Gliwice, Poland

A conventional WGS plant consists of two-stage process with the high temperature reactor followed by the cooler and the low temperature reactor. The conventional reactor is usually fed with a gas with relatively high H₂/CO ratio (2 to 5), while for processing of coal-derived or biomass gasification gas H₂/CO is around 0.5 and rarely exceeds 1. Thus, the total adiabatic temperature rise in WGS reactor for such a feed gas is much higher than that when WGS reactor is fed with syngas from SR or POX. For membrane reactor (MR) the single-stage tube in tube or multi-tubular configuration is usually proposed. The tube and shell zone in the MR are separated by a membrane. In conventional plants the total temperature rise not exceeding 300 °C can be adjusted using 2 separate stages, usually from 300 to 500 °C for high temperature catalyst and from 180 to 280 °C for low temperature catalyst.

Mathematical simulations of the MRs with H₂ selective membranes were done to estimate operating conditions for industrial application of MR with coal-derived gas feed. It was found that for MR the temperature rise in the reaction zone can be as high as 350 °C for S/C ratio below 2.0. Existing commercial catalysts will not survive, however, such a temperature rise cf. [1]. Thus, a catalyst with operational temperature range of 200 – 600 °C is expected as a reasearch target for 2015 [2].

To adjust the temperature in MR to the present catalyst operation range an economically not attractive high S/C ratio should be applied. On the other hand, heat exchange to the cold sweep gas becomes to be very important. A discussion of coal-derived gas processing in MRs at pressures up to 2.6 MPa is given. Finally, it is concluded that the future of the WGS membrane technology will depend on the development of new catalysts with adequately wide range of operating temperatures.

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ORAL PRESENTATIONS

Section 4.

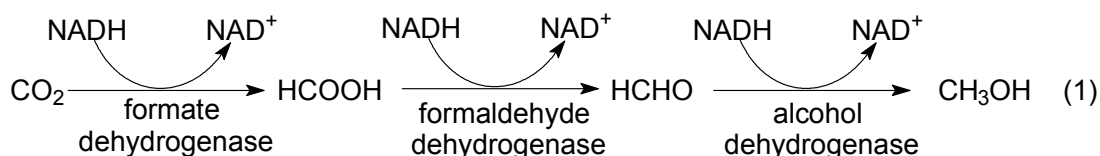
BIOCATALYSIS FOR BIOMASS PROCESSING

ENZYMATIC CARBON DIOXIDE REDUCTION TO METHANOL IN WATER AT ROOM TEMPERATURE: REGENERATION OF THE REDUCING AGENTS

Aresta M., Dibenedetto A., Giannoccaro G. and Stufano P.

*Department of Chemistry and CIRCC University of Bari, Via Celso ulpiani,
27 – 70126 Bari – IT. E-mail: m.aresta@chimica.uniba.it*

In this paper the conversion of carbon dioxide to methanol will be discussed. In particular, we will consider the CO₂ reduction into methanol at room temperature in an aqueous environment by using a cascade of reactions catalysed by enzymes under electron transfer conditions. (Eq. 1)



CO₂ is first reduced to HCOOH, which is converted into formaldehyde (CH₂O), and eventually into methanol [1,2]. (Obert, 1999; Jiang *et al.*, 2003) This research is in its infancy, but it has been demonstrated that the three enzymes can be encapsulated and used together for an easy conversion of CO₂ into methanol [2,3]. (Jiang *et al.*, 2003, Xu *et al.*, 2005)

The limiting factor is the electron source: the NADPH⁺/NADP couple has been used so far. Cheap reducing agents or solar energy should be used [4,5] to generate the electrons necessary for the reduction of CO₂ into methanol. A couple of options will be discussed.

The process above would be of great importance as the production of methanol under such conditions would represent the solution to recycling CO₂ and using it as source of carbon in the energy and chemical industry.

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Acknowledgements. This work was supported by University of Bari and MiUR.

THE EFFECT OF OXYGEN MASS TRANSFER INTENSITY ON BIOCATALYTIC PHENOL OXIDATION RATE

Borovkova I.S., Kazakov D.A., Volhin V.V.

Perm State Technical University, 614990, Perm, Komsomol pr., 29
[borovkova irina s@mail.ru](mailto:borovkova_irina_s@mail.ru)

Phenolic compounds are applied widely in the chemical industry and in some cases significant amounts of these compounds get to water ecosystems and cause an essential damage to environment.

There are many degradation methods of phenol, however most of them are ineffective and have essential lacks: high cost, incomplete purification. Biocatalytic oxidation by microorganisms is one of the most effective and economically expedient methods of wastewater treatment for phenol removal. However, for the effective use of this process for environmental biotechnology it is important to know its kinetics, which has been insufficiently studied. The phenol biooxidation proceeds in a heterogeneous system «gas-liquid-quasisolid (cell)» and includes the stage of oxygen mass transfer from the gas phase to a liquid, which proceeds quite slowly and can limit the rate of the process. The available literature data don't allow to estimate the impact of this stage to the overall process rate. According to the foresaid the aim of the research was to study the effect of gas - liquid oxygen mass transfer intensity on phenol biodegradation rate.

Mixed bacterial culture isolated from activated sludge of treatment facilities LLC «LUKOIL-Permnefteorgsintez» has been chosen as the object of the research. This bacterial culture utilizes phenol as the source of carbon and energy. Volumetric mass transfer coefficient (K_La) was used as the characteristic of oxygen mass transfer rate.

It was shown that an increase of the liquid phase agitation rate resulting in K_La value growth led to increase of phenol degradation rate. At agitation rate 600 and 800 rpm average phenol degradation rate was 7.74 and 8.84 mg/(L·h) respectively, while at 1200 rpm the degradation rate rose to 10.03 mg/(L·h).

Thus, obtained data show that the intensity of gas - liquid oxygen mass transfer makes essential impact on the phenol biodegradation rate. The intensification of the degradation process can be carried out by the hydrodynamic conditions change and using of interphase transfer activators.

THE PRACTICAL APPLICATION OF MECHANICALLY ACTIVATED ENZYMATIC HYDROLYSIS

Bychkov A.L.^{1,2}, Lomovsky O.I.¹

¹*Institute of Solid State Chemistry and Mechanochemistry, Kutateladze, 18, Novosibirsk, 630128, Russia, e-mail: bychkov.a.l@gmail.com*

²*Research and Education Centre «Molecular Design and Ecologically Safe Technologies», Novosibirsk State University, Pirogova, 2, Novosibirsk, Russia*

It's known that mannanooligosaccharides (MOS) are a perspective replacement for antibiotics in animal husbandry [1, 2]. Modern technologies of MOS-containing preparations production are very complicated and require big inputs. In this work the use of mechanical activated enzymatic hydrolysis to get the antibacterial preparation containing mannanoproteins and mannanooligosaccharides is examined. The processes effectiveness from the point of view of bioavailability of mannanooligosaccharides for chemical and biochemical processes was estimated. The morphological changes of cell wall which take place during mechanical treatment and enzymatic hydrolysis were studied.

As a result of mechanical activation of yeast biomass the reactivity of cell wall polysaccharides increases in relation to enzymatic hydrolysis. That effect is based on cell wall supramolecular structure disordering. Due to this the diffusion limitations are cancelled and the effectiveness of enzymatic hydrolysis of structural forming component (β -glucan) increases considerably. The combination of mechanical treatment and further enzymatic hydrolysis allows to significantly increase (2,9 times) the bioavailability of yeast mannanooligosaccharides.

The introduced approach seems perspective in the area of prophylactic antibacterial preparations production for poultry keeping. The preliminary results which were achieved are the evidence of successful use of the product.

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VALORIFICATION OF FERMENTATION BUTANOL FOR ALCOHOLIC FUELS

Vasile Georgescu

*Institute of Physical Chemistry «Ilie Murgulescu», Romanian Academy,
Spl. Independentei 202, Bucharest, Romania, e-mail: vgeorgescu@icf.ro*

Introduction

Alcohol-based fuels have been important energy sources.

Butanol is a chemical that has excellent fuel characteristics. It contains approximately 22% oxygen, which when used as a fuel extender will result in more complete fuel combustion. Use of butanol as a fuel will contribute to clean air by reducing smog-creating compounds, harmful emissions (CO) and unburned hydrocarbons in the tail pipe exhaust.

The value of octane boosting is dependent of isomers content of butanol.

In this work $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$ catalyst was prepared and studied. The catalyst possessed high catalytic activity and stability in the dehydration and isomerization of butanol

The highest activity in the transformations of butanol was observed after treating the catalyst with plasma [1].

Experimental

$\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$ catalyst was prepared by solid state synthesis.

The composition of the surface layer of the samples was characterized by X-ray photoelectron spectroscopy, UV-VIS spectrophotometry and electronic microscopy.

The acidity of the surface was determined spectrophotometrically from pyridine adsorption.

The plasma chemical technology for obtaining catalysts is based on the character of plasma action on solids [2,3].

Catalytic experiments were performed at 100-500°C in a flow unit. The products were analyzed chromatographically.

The activity of $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$ in butanol transformations was studied for initial samples and after plasma chemical treatment in oxygen, hydrogen and argon.

Discussion

The results obtained in studying the surface of $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$ show that the binding energies of chromium, phosphorus, and oxygen do not change after plasma chemical

treatments. The results of testing surface acidity in experiments with pyridine adsorption show that the numbers of pyridine adsorption centres at 25°C were equal for the samples subjected to plasma chemical treatment in O₂ and H₂. After treatment in argon, this number increased approximately threefold.

The results of the catalytic tests show that:

- After plasma chemical treatment in oxygen, reaction products contained isomers of butanol only. The activation energy was $E = 63$ kJ/mol.
- After plasma chemical treatment in hydrogen was obtained 90% isomers of butanol and 10% n-butanol.
- After plasma chemical treatment in argon was formations 15% ketone, 25% n-butanol and 60% isomers of butanol.

Conclusion

We are led to conclude that the surface state after plasma chemical treatment in Ar is unstable and changes after catalytic experiments. Reactivity changes and the number of dehydrogenation centers increases under the action of the reaction medium whereas dehydrogenation centers return to their initial state.

The modification of the surface of catalysts and their regeneration under the action of a plasma in oxygen and hydrogen causes the appearance of a new surface structures, which increase activity, selectivity and operation stability.

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MECHANISM OF ULTRASOUND-ASSISTED ENZYME HYDROLYSIS OF CELLULOSE

Olga V. Golyazimova, Anatoly A. Politov

*Institute of Solid State Chemistry and Mechanochemistry, Kutateladze, 18,
Novosibirsk, 630128, Russia, e-mail: o.golyazimova@gmail.com*

Enzyme hydrolysis of cellulose is heterogeneous reaction, and to improve this process it is necessary to accelerate mass transfer. To this effect it may be used ultrasound treatment of reagents. As it is known, acceleration of chemical reactions in ultrasound field may be because of cavitation phenomena. Local growth of temperature and pressure, appearance of radicals and more rapid mass transfer are in reaction medium because collapses of cavitation bubbles take place. This physicochemical phenomena account for enzyme denaturation and decreasing of enzyme activity. So it is necessary to study the mechanism of influence of ultrasound treatment on enzyme hydrolysis of cellulose.

To determine the mechanism of ultrasound-assisted acceleration of enzyme hydrolysis, influence of US-treatment on enzyme activity and sorption properties of cellulose substrate was studied. Also it was found that preliminary ultrasound treatment accelerates this enzymatic reaction. It is interesting that ultrasound treatment of cellulose in water without enzymes is ineffective, fig. 1 (graph 2). The possible mechanism of reaction acceleration by ultrasound is its influence on enzyme sorption processes through the acoustocapillary effect.

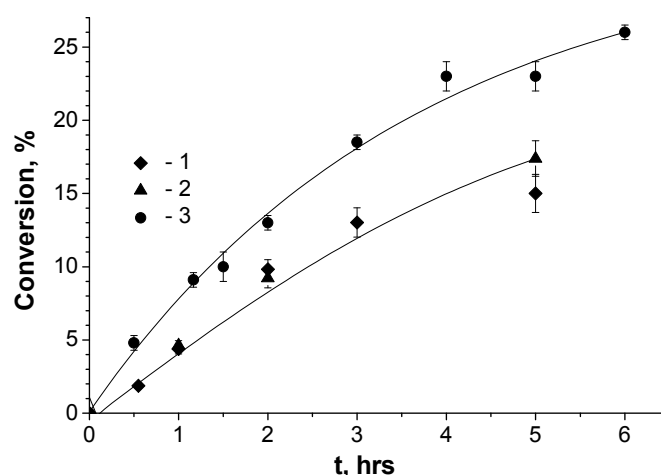


Fig. 1. Hydrolysis kinetics of cellulose: 1 – untreated cellulose, 2 – after ultrasound treatment without enzymes, 3 – after ultrasound treatment with enzymes.

This work was supported by CRDF (RUX0-008-NO-06) and ISTC № 3235 and Russian Academy of Science Presidium Program “Chemical aspects of energy” 19.6.

POSTER PRESENTATIONS

THE ORTHO – PARA CONVERSION OF PROTIUM ON THE NANOS-PARTICLES OF PLATINUM AS THE CATALYST

Antonov A.Yu.¹, Boeva O.A.², Revina A.A.³, Shaymukhametova G.R.¹, Sergeyev M.O.¹, Zhavoronkova K.N.¹

¹*D.I. Mendeleev University of Chemical Technology of Russia, Moscow, Russia*

²*«Engineering center «Russian gas centrifuge»», Moscow, Russia*

³*Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Moscow, Russia*

An importance of hydrogen as a source of energy will increase owing to its high heating capacity, inexhaustible resources and ecological purity of products of burning. Using of liquid hydrogen in energetic, aviation and cosmic techniques puts forward the problem of its storing and transportation. This problem is connected with ortho-para conversion of hydrogen. It is known that H₂-molecules exist in two modifications: o-H₂ and p-H₂ with different nuclear spins. Spontaneous ortho-para conversion in liquid hydrogen leads to losses of product due to the heat of reaction which is more than the heat of evaporation. These losses may be about 7% weekly [1] and 70% of all losses [2]. That's why it is necessary to carry out this reaction in gas phase previously at 77K and 20K with help of catalyst.

The aim of this work is to find an active catalyst for o-p conversion at low temperatures.

The method of synthesis of Pt-nanos-particles in inverted micellar solution and preparation of highly dispersed catalyst – Pt^{mic}/ γ -Al₂O₃ have been developed. Formation of nanos-particles of Pt in solution, their stability in time and their adsorption on the surface of the carrier (γ -Al₂O₃) were controlled by spectrophotometer. Sizes of inverted micelle in solution were determined by the power microscope. Surface of adsorbed nano-particles on the carrier was determined by chemisorption of hydrogen at 77 K. The full surface of catalyst was measured by physical adsorption of nitrogen.

The catalyst was found to have high specific catalytic activity for ortho-para conversion at 77K. This activity does not depend on temperature (activation energy about 0). They may be recommended to carry out this reaction in practice at 77K and more low temperatures.

PRODUCTION OF MOTOR FUELS COMPONENTS ON THE BASE OF XYLOSE

Arinicheva J.A., Dzyubenko A.A., Maximov A.L., Nekhaev A.I.

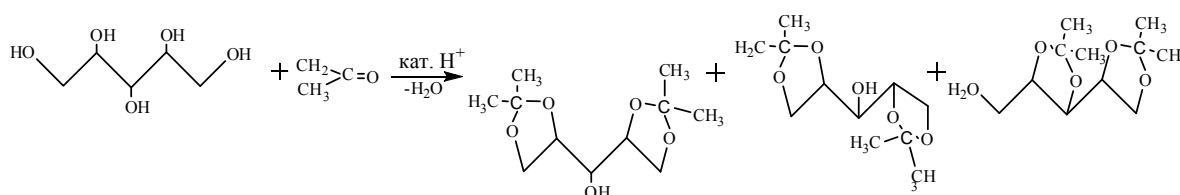
*A.V. Topchiev Institute of Petrochemical Synthesis RAS, 119991 Moscow,
Leninsky prospect, 29, nekhaev@ips.ac.ru*

One of the ways for producing of motor fuel components is based on the modification of polyols (monosaccharides and their derivatives) for the production of ketals. Ketals are able to increase considerably the octane number of petrol and a number of them can be used as components of diesel fuel. Usually, sulphuric acid is applied as a catalytic agent for ketal synthesis, which reduces the attractiveness of the process from an industrial point of view.

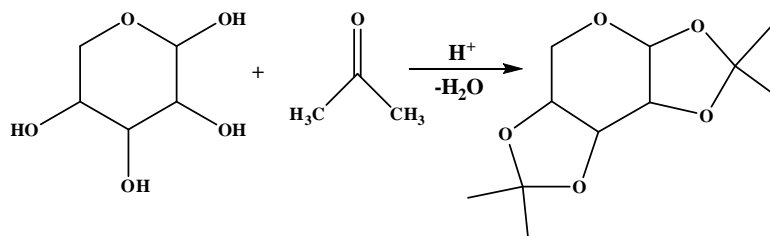
We have shown that heterogenic catalysts, such as zeolite β , cationite KU-2 and Nafion, can successfully be used as substitutes for sulphuric acid.

Xylite und xylose were used as substrates for production of ketals in this work.

Xylite is produced using hardwood or maize sources, by hydrogenation of xylose, which converts the sugar (an aldehyde) into a primary alcohol.



In the case of xylite the best results were achieved using Nafion (a product yield of about 30%) followed by zeolite β and cationite KU-2 respectively. However with all the catalysts increase in product yields was observed when the temperature was increased from 40°C to 50°C.



In the case of xylose the best yields were obtained with zeolite β (40%) followed by Nafion and KU-2. Significant influence of temperature was observed. The experiments were conducted in temperature interval of 45-55°C. According to combined gas chromatography mass-spectrometry data the only product was obtained.

THREE-STAGE WASTE-FREE PROCESS OF ALKYL PETROL PREPARATION FROM METHANOL ON ZEOLITE CATALYSTS BASE**Bachurikhin A.L.**

*N.D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Science,
Russia, Moscow 119991, GSP - 1, the Leninsky av., 47,
E-mail: SECRETARY@ioc.ac.ru*

Constant toughening of requirements to structure and properties of automobile gasolines results in introduction of the new standards forbidding or limiting use aromatic and olefinic hydrocarbons, O-, S-, N- and metallic connections in structure of gasolines. One of alternative ways of an exit from this situation is the increase in manufacture of a share of non-polluting automobile fuel components motor, such as alkylates and isomerizates. The limiting factor on this way is absence of enough of a source of raw materials and optimum technological decisions.

The method of alkyl petrol preparation by a three-stage catalytic conversion from accessible raw material - methanol with use of heterogeneous catalysts such as SAPO, PdLaCa (Mg) X (Y) - Faujasite and some Al₂O₃-modifications is developed.

The method differs presence of the following stages:

1) Methanol conversion in dimethyl ether (DME) with use of catalysts SAPO and γ -Al₂O₃ at speeds 2÷10h⁻¹ and temperatures 300÷400°C. Thus there is practically 100 %-s' methanol conversion in DME.

2) Subsequent conversion DME on zeolite catalysts such as SAPO at speeds 2÷4h⁻¹ and temperatures 400÷450°C in a mix olefinic and iso-/n-parafinic hydrocarbons of the following structure: ethylene - 1÷5 weights of %, propylene - 1÷4 weights of %, isobutylene - no more than 0,5 weights of %, n-butylene-1 and n-butylenes-2 - no more than 0,5 weights of %, isobutane - 10÷30 weights of %, n-butane - no more than 5 weights of %, the rest a mix of methane, ethane, propane, hydrogen, carbon monoxide and traces of formaldehyde.

3) Fluid-phased alkylation of iso-/n-butane by C₂-C₄-olefines in zeolite catalysts presence such as PdLaCa (Mg) X (Y) - Faujasite at speeds 2÷4 h⁻¹ and temperatures 50÷100°C with preparation of alkyl petrol components, mainly, trimethylpentanes and dimethylhexanes with the following characteristics: Total conversion of olefines - about 99 %, the output of liquid products from theoretical counting upon olefines - about 95 %, the contents of fractions C₈ - 80÷85 weights of %, C₉₊ - no more than 8 weights of %, C₅-C₇ - no more than 9 weights of %, trimethylpentanes - 65÷70 weights of %, the mass relation trimethylpentane/dimethylhexane - 5÷5,5.

COMPLEX WASTE-FREE TECHNOLOGY OF ANILINE AND N-MONOMETHYLANILINE PREPARATION WITH USE HETEROGENEOUS Cu-BASED CATALYSTS

Bachurikhin A.L.¹, Golosman E.Z.²

¹*N.D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Science,
Russia, Moscow 119991, GSP - 1, the Leninsky av., 47,*

E-mail: SECRETARY@ioc.ac.ru

²*LLC "NIAP-KATALIZATOR", Novomoskovsk, Russia*

Aniline and N-monomethylaniline are the major products of the chemical industry, world which total manufacture annually increases approximately for 5 % and now is at a level about 5 million tons one year. Aniline is strategic raw material in manufacture of dyes, medical products, explosives, N-monomethylaniline and diphenylmethanediisocyanate - a component for manufacture polyurethanes. N-monomethylaniline - an antidetonation additive for easy updating octane numbers automobile fuels.

Technological process of preparation of aniline and N-monomethylaniline is developed and is at a stage of preparation of pilot tests on the basis of use nitrobenzene and methanol as initial products. Process is characterized by use of catalysts on the basis of Al₂O₃ and Fe₂O₃, modified CuO (6÷60 weights of %) and Cr, Mn (III, IV)-oxide (0÷1 weights of %), tubular reactor systems with the multizone control of temperature profile. Process differs an opportunity of joint and separate preparation of aniline and N-monomethylaniline, absence of necessity of use of hydrogen as separate initial component, high efficiency and absence of harmful waste products.

The work cycle is characterized by presence of the following stages:

1) Fluid-phased nitrobenzene hydrogenation at speeds up to 10 h⁻¹ in fluid-phased catalytic hydrogenation battery, consisting of the several, consistently connected reactors, with consistently growing temperature of hydrogenation in an interval 100-300°C

2) Alkylation aniline with methanol and re-alkylation in system aniline - N,N-dimethylaniline, proceeding at speeds up to 10 h⁻¹ in a temperature interval 250-300°C

3) Sequence of transformations of the easy gaseous products including a) Decomposition residual of methanol; b) Disproportion reaction of mixes CO, H₂ and

PP-4

H₂O with formation superfluous H₂ and CO₂; c) Absorption of CO₂ in the device of CO₂-absorption-desorption. Working temperatures - 500-700°C.

Norms of raw material consumption on 1 kg of the aniline/N-monomethylaniline received make (kg): nitrobenzene - 1,32/1,15, methanol - 0,34/0,60.

Planned capacity of the pilot block on initial nitrobenzene - 1 tons/day, Rough expenses of energy - 15 KWt×h/day.

NANOSTRUCTURED CARBON FROM SIBERIAN PINE NUTSHELL

**Chingiz Barnakov¹, Alexey Kozlov¹, Svetlana Seit-Ablaeva²,
Vladimir Anufrienko³, Zinifer Ismagilov³**

¹*Institute of Coal and Coal Chemistry SB RAS, Kemerovo, Russia,
e-mail: han@kemnet.ru*

²*Kemerovo Technological Institute of Food Industry, Kemerovo, Russia*

³*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

Siberian pine nutshell is forest biomass which has not yet been utilized or processed to useful products. The annual volume of this forestry waste is about one million tons per year only in Siberia. The major part of pine nutshell is not processed, similar to apricot nutshell. Recently, it was reported that Kazakhstan and Japan scientists have developed in cooperation a method of apricot nutshell carbonization. Using this method, it is possible to produce carbon anodes for lithium-ion accumulators with improved (3-5 times) characteristics in comparison with the graphite ones. In literature, there is a set of criteria of a «good» carbon anode. One of them correlates with the surface area of a carbon but does not correlate with either interplanar distance or graphitization degree and has weak particle size dependence [1].

Nanostructured carbon materials have the highest surface area. One of such materials is KEMERIT[®] [2].

The use of Siberian pine nutshell as a raw material in producing carbons like KEMERIT[®] resulted in the synthesis of a nanostructured carbon material with high surface area (up to 3500 m²/g) and high pore volume (up to 1.7 cm³/g). Is it possible to use this carbon for production of lithium-ion accumulator anodes? To answer this question, the development testing must be done. Both a standard test bench and an interested customer are requirements for carrying out such testing.

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HYDROGEN FROM FORMIC ACID DECOMPOSITION FOR BETTER UTILISATION OF BIOMASS HYDROLYSIS PRODUCTS. Pd AND Au CATALYSTS

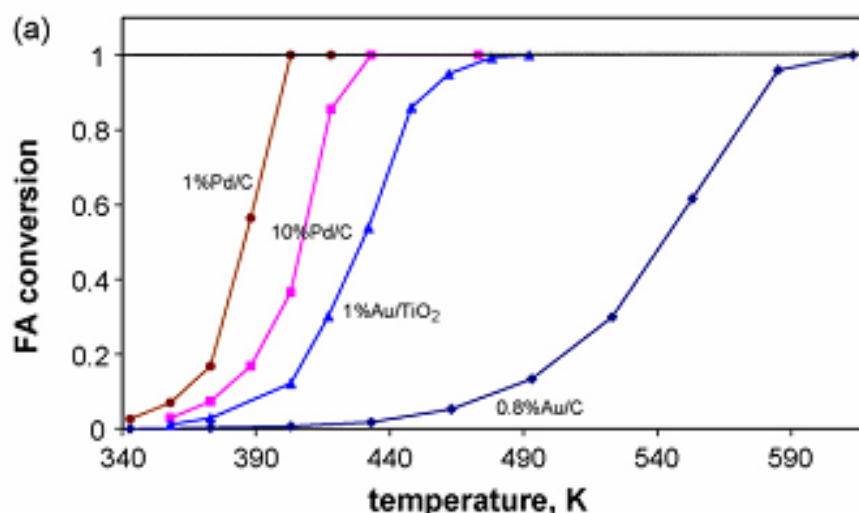
Dmitri A. Bulushev¹, Sergey Beloshapkin², Julian R.H. Ross¹

¹Charles Parsons Initiative, Chemical & Environmental Sciences Department,
University of Limerick, Limerick, Ireland

²Materials & Surface Science Institute, University of Limerick, Limerick, Ireland
E-mail: serguei.belochapkin@ul.ie, fax:+353-61-213529

Dilute-acid hydrolysis of cellulosic biomass to levulinic acid is one of the economically valuable options for the utilisation of biomass feedstock. Formic acid is one of the byproducts of hydrolysis process. The yield of formic acid during the hydrolysis can be comparable with the yield of target product levulinic acid. Formic acid can be used as a source of hydrogen for the subsequent hydrogenation of levulinic acid to more valuable products such as γ -valerolactone.

Vapour phase decomposition of formic acid has been studied over range of catalysts: 1.0 and 10wt.% Pd/C, 0.8wt.% Au/C and 1.0wt.% Au/TiO₂. The metal particle size distribution of the catalysts was estimated by TEM technique. The Au/C catalyst was found to be least active in the decomposition reaction. The Pd/C catalysts demonstrated the highest activity with the performance up to 0.04 moles of H₂ per minute per gram of metal at 400K. The selectivity of Pd/C catalysts was in range of 95-99 %. Temperature dependences of the steady-state conversions are presented on the following graph.



TRANSITION METAL OXIDES IN CATALYTIC PROCESSING OF BIOFUEL

Boykov E.V., Vishnetskaya M.V.

*Gubkin Russian State University of Oil and Gas, 65 Leninsky Av., Moscow, 119991
Russian Federation, e-mail: ev-boykoff@yandex.ru*

Forthcoming transfer auto transport on fuel with the low sulphur content – down to 15 ppm challenge a problem of low sulphur fuel for diesel engines. Production of biofuel from renewable raw materials represent an alternative to desulphurization of primary oil processing products. The sulphur content in plants amounts 0.3-1.2 wt %, it is in animal organisms of 0,5-2 %, and in sea products even more. Therefore at wood pyrolysis, for example, yields a fuel liquid with the sulphur content of about 1000 ppm [1] which makes it necessary to remove S down to acceptable level.

We report here a novel approach to catalytic oxidative desulfurization of organic raw materials using both individual V and Mo oxides and mixed $V_2O_5 \cdot MoO_3$ oxides with molar ratios of 3:1, 3:2, 1:1, 2:3 and 1:3. V_2O_5 and MoO_3 samples were prepared via thermal decomposition of ammonium metavanadate and metamolybdate. Mixed $V_2O_5 \cdot MoO_3$ oxides were prepared by coprecipitation of saturated aqueous solutions of ammonium metavanadate and metamolybdate followed by calcination of obtained precipitates at 400°C. Catalytic tests were performed using a plug flow-type reactor at 200-350°C and 0.101 MPa. Benzene with 2 wt.% of thiophene as a most oxidation resistant compound was used as a model feed.

Thiophene conversion was found to decrease with Mo oxide content in catalysts. The sample with molar V-to-Mo ratio of 3:1 gives complete thiophene conversion. However, complete conversion over 3:2 $V_2O_5 \cdot MoO_3$ sample does not occur even at 350°C. Under optimal conditions, namely, molar ratio of V:Mo = 3:1, 310°C and $WHSV=0.8 \text{ hr}^{-1}$, thiophene conversion is 100%, while that of benzene does not exceeds 8 wt.%.

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VALORIZATION OF GLYCEROL BY CONDENSATION WITH ACETONE OVER HETEROPOLYACIDS IMMOBILIZED IN SILICA

Ferreira P.¹, Fonseca I.M.², Ramos A.M.², Vital J.², Castanheiro J.E.¹

¹*Centro de Química de Évora, Departamento de Química, Universidade de Évora, 7000-671 Évora, Portugal, E-mail: jefc@uevora.pt*

²*REQUIMTE, CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*

Glycerol is the by-product of biodiesel production by transesterification of triglyceride with methanol or ethanol. For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol is formed. An increase of glycerol production and a price decrease becomes the glycerol a promising low-cost feedstock for producing value-added chemicals or materials [1,2]. A possible solution to the problem, it is the condensation of glycerol with acetone, which provides a branched oxygen-containing compound. These compounds could be used as an additive in the biodiesel formulation. The products of glycerol acetalisation are (2,2-Dimethyl-[1,3]dioxan-4-yl)-methanol (solketal) and 2,2-Dimethyl-[1,3]dioxan-5-ol [3,4]. Heteropolyacids (HPAs) with the Keggin structure are known to be highly active heterogeneous

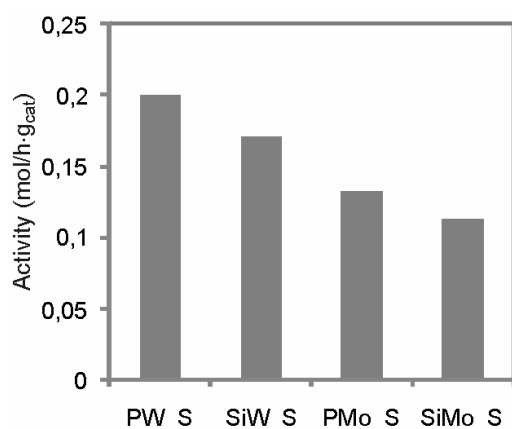


Fig. 1. Acetalisation of glycerol over heteropolyacids.

catalysts in acid type reactions. A great variety of supports have been used as support to immobilize HPAs [5]. In this work, we report the acetalisation of glycerol over silica-included heteropolyacids. The tungstophosphoric acid (PW), molybdophosphoric acid (PMo), tungstosilicic acid (SiW) and molybdosilicic acid (SiMo) were immobilized in silica by sol-gel method, according to Y. Izumi et al. [6]. It was observed that the catalytic activity decreases

in the series: PW_S > SiW_S > PMo_S > SiMo_S (Fig. 1). All catalyst exhibited good values of selectivity to solketal (about 98% near complete conversion).

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METHOXYLATION OF α -PINENE USING TUNGSTOPHOSPHORIC ACID SUPPORTED IN SILICA

Pito D.S.¹, Fonseca I.M.², Ramos A.M.², Vital J.², Castanheiro J.E.¹

¹Centro de Química de Évora, Departamento de Química, Universidade de Évora, 7000-671 Évora, Portugal, E-mail: jeffc@uevora.pt

²REQUIMTE, CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

α -Pinene is a renewable raw material usually obtained from pine gum or as a waste from the Kraft process. Its acid catalysed methoxylation yields a complex mixture of monoterpenic ethers, being α -terpinyl methyl ether the main product. The α -terpinyl methyl ether smells grapefruit-like and might be used as flavour and fragrance for perfume and cosmetic products [1]. The use of solids as catalytic materials in liquid-phase reactions as replacement for homogeneous catalysts has been a major goal in catalysis research. Beta zeolite [2] and sulfonic-modified mesoporous silica [3] have been used for the α -pinene alkoxylation. Heteropolyacids have gained application as catalysts in industrial practice both in acid catalysis and

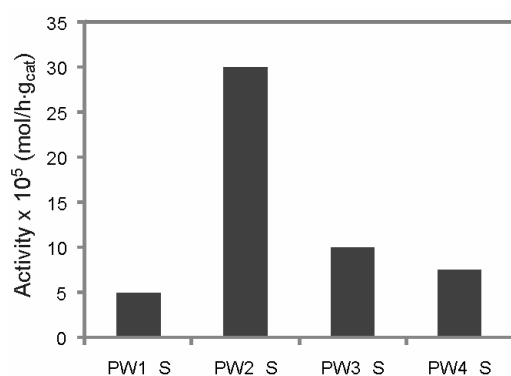


Fig. 1. Methoxylation of α -pinene over PW supported in silica.

oxidation reactions [4]. In the present work, we report the methoxylation of α -pinene over tungstophosphoric (PW) acid immobilized in silica. The catalysts were prepared according to Y. Izumi et al. [5]. Fig. 1 shows the activity of catalysts. It was observed that the initial catalytic activity increases with the HPA content until a maximum. However, with high heteropolyacid loading on silica, a decrease in the catalytic activity is observed. At a low

PW loading on silica, the increase of the heteropolyacid amount leads to the increase of activity, probably, due to the kinetic effect. However, the high amount of heteropolyacid on silica leads to a decrease of the catalytic activity. This behaviour can be explained probably, due to a decrease of the accessibility to the active sites.

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BIODIESEL PRODUCTION FROM WASTE COOKING OIL OVER SULFONATED CATALYSTS

Tropecêlo A.I.¹, Fonseca I.M.², Ramos A.M.², Vital J.², Castanheiro J.E.¹

¹*Centro de Química de Évora, Departamento de Química, Universidade de Évora, 7000-671 Évora, Portugal, E-mail: jeffc@uevora.pt*

²*REQUIMTE, CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*

Biodiesel is an alternative fuel for diesel engines that is made from renewable biological sources, such as vegetable oils and animal fats. The use of cheap low quality feed stocks such as waste cooking oil (WCO) will help in improving the economical feasibility of biodiesel. Biodiesel production from WCO have been carried out over solid catalysts, such as zeolites [1], ion-exchange resins [2] and carbohydrates-derived solid acid catalysts [3]. This work reports the biodiesel production from WCO with methanol over sulfonic acid functionalized on poly(vinyl alcohol), polystyrene and MCM-41. PVA catalyst was prepared by dissolving PVA in

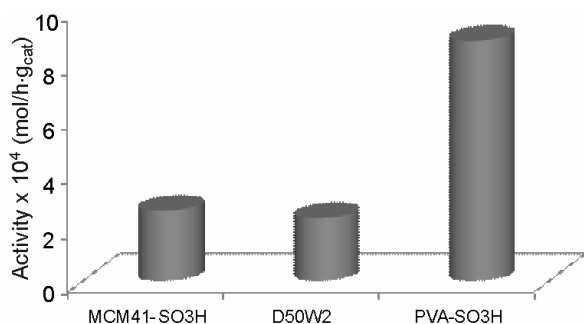


Fig. 1. Transesterification of WCO with methanol over sulfonated catalysts. Initial activities taken as the maximum observed reaction rates.

water at 90°C, with the appropriate amount of sulfosuccinic acid (SSA) 10wt% solution, according to Rhim et al. [4]. MCM-41-SO₃H was prepared as described by I. Díaz et al. [5]. Commercial resin (Dowex D50W2) was also used in the reaction.

The catalytic experiments were carried out in a stirred batch reactor at 60°C. In a typical experiment, the reactor was loaded with 30 ml of methanol, 0.2 g of polymer. Reactions were started by adding 2.5 mL of WCO. Fig. 1 shows the initial activity of the catalysts in the transesterification of WCO with methanol. It was observed that the initial catalytic activity PVA-SO₃H is higher than the activity of the MCM-41-SO₃H and D50W2, probably, due to the high amount of sulfonic acid groups.

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CHEMPAK: OPTIMIZATION OF THE CHEMICAL REACTION KINETICS OF CATALYTIC PROCESSES WITH USING OF COMPUTER SIMULATION

Chernykh I.G.

*Institute of Computational Mathematics and Mathematical Geophysics SB RAS,
Novosibirsk, Russia, chernykh@ssd.sccc.ru*

At present, mathematical modeling is successfully used to support decision making in the development and modernization of chemical processes and reactors. Note that modernization of chemical processes and reactors is the interdisciplinary problem, which requires the involvement of experts in physics, chemistry and mathematical modeling. Determination of kinetic scheme of chemical reactions is a key stage in devising a mathematical model of reactor

In this paper CHEMPAK software package presented. CHEMPAK package makes possible to generate a set of ordinary differential equations corresponding to the scheme of chemical reactions. This set with relevant kinetic and heat parameters is automatically included in the model computations. The main features of CHEMPAK software package are an easy-to-use interface adapted for modification and evaluation of kinetic scheme of a chemical process, an automatic solver of chemical kinetic tasks, a network chemical database for storage of chemical reaction systems and other chemical data, the possibility of using the reactor models with chemical reaction models. There are some software plugins included in CHEMPAK. These plugins gives possibility of preparing and using data to/from FLUENT and CHEMKIN. The CHEMPAK architecture is shown schematically in Figure 1. CHEMPAK can be used for different purposes such as an optimization of kinetics of sugar synthesis or optimization of homogeneous pyrolysis of C₂-C₃ hydrocarbons. Computer simulation of kinetics of homogeneous pyrolysis of C₂-C₃ hydrocarbons was used in FLUENT for complex task of CFD modeling with chemical reactions. More detailed description of usage of CHEMPAK is in [1-5]. Also CHEMPAK should be used for the optimization of kinetics scheme of catalytic processes for chemical production of biofuels.

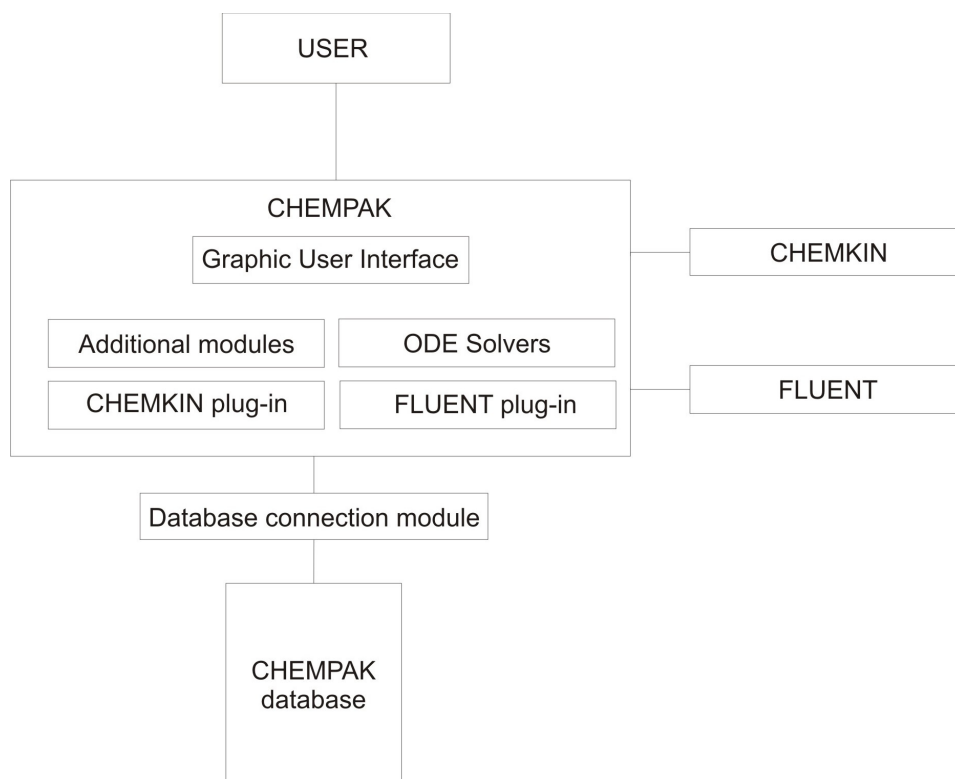


Figure 1. CHEMPAK architecture scheme.

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CATALYTIC ACTION OF MOLTEN ALKALI IN CONVERSION OF BIOMASS TO POROUS CARBONS

Chesnokov N.V.^{1,2}, Mikova N.M.¹, Ivanov I.P.¹, Kuznetsov B.N.^{1,2}

¹*Institute of Chemistry and Chemical Technology SB RAS,
K. Marx str., 42, Krasnoyarsk, 660049, fax: +7(391)2439342, e-mail: inm@icct.ru*

²*Siberian Federal University, Svobodny pr., 79, Krasnoyarsk, 660041*

As known, the molten salts are in catalytic processes of coal and biomass gasification and liquefaction. Catalytic action of molten KOH and NaOH in thermal conversions of wood, lignin and cellulose was studied in this work.

It was shown that the molten hydroxides of alkaline metals promote the significant development of solid raw material porous structure. The specific surface area, total volume and size of the pores depend on the nature of raw material and alkali hydroxide, ratio raw material/alkali hydroxide and on the temperature of activation treatment. The optimal conditions of alkaline activation of various raw materials were selected which allow to provide the maximal development of nanoporous structure of produced active carbons.

When wood biomass is used as a raw material, the carbonization with KOH increases by 5-10 times the specific surface area of produced active carbons in the comparison with traditional carbonization process. It was found that the wood nature influences on the texture characteristics of active carbons produced by alkaline thermal treatment. The maximal surface area of active carbons from birch-wood reaches 2050 m²/g, when the same for aspen-wood active carbons is no more than 1350 m²/g.

The specific surface area of nanoporous carbons obtained by carbonization of cellulose and wheat-straw lignin in the presence of molten KOH goes through a maximum with the increase of KOH/raw material ratio. The maximal surface area of carbons from cellulose reaches to 1700 m²/g and for wheat-straw lignin – to 2040 m²/g.

Sorption properties of active carbons prepared by alkaline activation of different types of natural raw material were studied. They are active in sorption of molecular hydrogen and different hydrocarbons (trichlormethane, benzene, alcohols etc.). Aside from the nature of initial raw material the sorption capacity for H₂ increases with the growth of micropores volume of prepared active carbons.

HYDROCONVERSION OF VEGETABLE OILS INTO HYDROCARBON-BASED BIODIESEL OVER NONSULFIDED CATALYSTS: A COMPARATIVE STUDY OF METAL CATALYSTS SUPPORTED ON BORATED ALUMINA

Chumachenko Yu., Lavrenov A., Skorpluk A., Drozdov V.,
Gulyaeva T., Arbuzov A., Buyalskay K., Kudrya E.

*Institute of Hydrocarbons Processing of SB RAS, Russia, Omsk,
Neftezhavodskaya, 54, Fax +7-3812-64-61-56, E-mail: lavr@ihcp.oscsbras.ru*

Hydrocarbon diesel fuels produced from vegetable oils do not yield to the best samples of oil origin fuels in combustion value and low-temperature properties. They greatly surpass them in cetane characteristics and environmental safety at the expense of practically full absence of sulfur compounds and aromatic components. The employment of sulfided catalysts by hydroconversion of neat vegetable oils requires the addition of sulfur-containing compounds in the process for keeping of the catalyst activity and lifetime. In the framework of this paper for development of catalyst of vegetable oils processing into hydrocarbon diesel fuels it is first suggested to examine bifunctional catalytic compositions based on Pt, Ni, Co, Mo, W-containing systems with $B_2O_3-Al_2O_3$ as a solid-acid support. The catalysts were characterized by BET method, XRD, FTIR, UV, TPR H_2 , TPD NH_3 , CO chemisorption. The catalyst screening is carried out in fixed-bed reactor in H_2 atmosphere under constant temperature ($400^\circ C$), pressure (4 MPa) and WHSV of sunflower oil ($5 h^{-1}$). It is shown, that on all catalysts, including initial support, decomposition of vegetable oil proceeds with yield of liquid products about 70-85 wt%. Hydroconversion of triglycerides, containing in vegetable oil most efficiently proceeds on Pt and Ni containing catalysts. For both catalysts heavy cycloalkanes and arenes, and also alkanes with number of carbon atoms in molecule up to 35 are found in liquid hydrocarbon products. They are products of side reactions of cyclization, aromatization and condensation. Thus, established level of jet and diesel fuel in liquid products does not exceed 63 wt%. Selective conversion of vegetable oils into alkanes is achieved at $350^\circ C$ and 4 MPa over a 0.5 wt% Pt catalyst. The results show that platinum catalyst gives a 78% yield of liquid products. It is determined that liquid products contain mostly alkanes C_{17} and C_{18} (up to 53 and 35.3 wt.% respectively). Furthermore, the gas-phase analysis demonstrates that the decarboxylation and decarbonylation reaction are more profound over this catalyst.

THE EFFECT OF HYDROLYSIS TREATMENTS ON SUGARCANE BAGASSE

**Josilaine A. Cunha¹, Alessandra V. Silva¹, Ligia M. M. Valente¹,
Marcelo M. Pereira¹, Pilar Ramírez de la Piscina², Narcís Homs^{2,3},
Luciana T. Santos⁴, Margareth Rose L. Santos¹**

¹*Federal University of Rio de Janeiro, CT, bloco A, 7º andar, CEP 21941-909, RJ, Brazil, FAX 55-21-2562-7240, josi@iq.ufrj.br*

²*Departament de Química Inorgànica and Institut de Nanociència i Nanotecnologia, Universitat de Barcelona, C/ Martí i Franqués 1-11, Barcelona, Spain*

³*Catalonia Institute for Energy Research (IREC), C/ Josep Pla 2, Barcelona, Spain*

⁴*Nacional Agency of Petroleum, Av. Rio Branco, 65, RJ, Brazil*

The use of agricultural residues for reducing greenhouse gas emissions and fossil fuel dependence by applying thermochemical methods (such as direct combustion, pyrolysis or gasification) has proved to be a potential resource of renewable energy. In this context, sugarcane bagasse is a typical example of an agricultural by-product that is available in abundance worldwide [1-3]. This work reports the influence of the hydrolysis pretreatment on both sugarcane bagasse composition and its LTC pyrolysis derivative bio-oil. The sugarcane bagasse (BC) was submitted to acidic (BCA), base (BCB) or sequential acid/base (BCS) hydrolysis at 25°C-100°C. Acid hydrolysis were carried out in the range from 0.001 to 2M of HCl with or without microwave assistance at different residence times (15 min to 60 min). It is possible highlight that microwave irradiation improves fibers hydrolysis, while 46% wt/wt of the BCA sample was removed during regular hydrolysis (60 min and 1M) this value was increased to 58%wt/wt with microwave assistance. However the bio oil yield (in LTC) obtained from the microwave assistance hydrolysis was lower than that obtained from regular hydrolysis since most part of cellulose and hemicellulose were previously removed. The BCA samples presented the largest fibers disorganization (showed by SEM characterization) and also the highest bio-oil yield. It was possible to correlate both bio-oil yield at LTC and fibers organization. The main pyrolysis products were levoglucosan and 5-hydroxymethylfurfural as showed in ¹³C NMR and ¹HNMR.

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CaO AND Al₂O₃ SUPPORT SOLID CATALYSTS FOR BIODIESEL PRODUCTION

Ana P. Dias¹, Jaime Puna², João Gomes^{2,3}, M. Joana Correia⁴, João Bordado³

¹ICEMS, Instituto Superior Técnico (IST-UTL), Lisboa, Portugal, apsoares@ist.utl.pt

²Instituto Superior de Engenharia de Lisboa, Lisboa, Portugal, jpuna@deg.isel.ipl.pt

³IBB – Institute of Biotechnology and Bioengineering, IST-UTL, Lisboa Portugal

⁴Centre for Chemical Processes, IST-UTL, Lisboa, Portugal

This paper describes preliminary work done by the authors towards the development of new metallic heterogeneous catalysts that are intended to be used in the production of biodiesel. Biodiesel, is a mixture of mono-alkyl esters of fatty acids, and is currently manufactured by transesterification of triglycerides with methanol, using NaOH or KOH as liquid base catalyst. However, an important drawback related with the use of these catalysts is that, the liquid based catalyst has to be neutralized after the reaction, thus producing salt streams. Moreover, due to the presence of free fatty acids, it reacts to form soaps as unwanted by-products, hence requiring more expensive separation processes. Therefore, there is currently a drive towards the development of industrial processes for biodiesel production using solid catalysts. In addition to lower separation processes costs, the key benefit of using solid acid or basic catalysts is that, the catalysts don't have to be removed since they don't mix with the biodiesel. This work refers preliminary studies done in these field using CaO and Al₂O₃ heterogeneous support catalysts, with Li, Sr and Ca as solid precursors. Several analysis techniques were used for catalysts characterization, like MIR, SEM, XRD, TG and BET. The results obtained so far will be presented in this proceeding.

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INVESTIGATION OF THE KINETICS OF STRAW ENZYMOLYSIS

**Emelyanov V.M., Nurtdinov R.M., Mukhachev S.G., Ablaev A.R.,
Valeeva R.T., Gadelshina G.A.**

*Kazan State Technological University, K. Marks Street, 68, Kazan, Russia,
phone: +7(843)2314049, fax: +7(843)2314042, e-mail: Emelianov@front.ru*

One of the promising renewable resources of plant raw materials are straw and green mass of other crops. In Russia, this type of resource is not used efficiently. There are several works in the field of utilization of straw hydrolyzates and enzymolyzates in fodder production and as growth media for the processes of microbiological synthesis. However, enzymatic hydrolysis of cellulose has not yet mastered in industrial biotechnology in Russia.

The processes of enzymatic hydrolysis of straw by liquid enzyme preparations from Genencor International PS AO3329-1.OEN GC-440 (with cellulase activity of 1470-1800 units/g), PS AO3143-1.1EN Optiflow RC 2.0, PS AO3131-1.OEN GC-220 and PS AO3197-1.OEN Acellerase CB100 (with cellulase activity of 6200-7580 units/g) are carried out. Model experiments for studying of enzymolysis kinetics are carried out using paper and cotton as a source of cellulose. Further grinded and sifted through a sieve with 1 mm mesh rye straw was used. Experiments were carried out at varying liquor ratio and concentrations of enzyme preparations. Straw was steamed in an autoclave with excess pressure 0,07 - 0,1 MPa for 0,5 - 1 hour. Change in the total content of sugars in hydrolyzate during the process lasting up to 8-10 hours is determined. A kinetic model of the process of straw enzymolysis is developed. The values of kinetic constants are determined.

CATALYTIC CRACKING OF GLUCOSE OVER ZSM-5 ZEOLITE AT DIFFERENT TEMPERATURES

Alyne da S. Escobar¹, Margareth Rose L. Santos¹, Luciana T. Santos²,
Marcelo M. Pereira¹

¹Federal University of Rio de Janeiro, CT, bloco A, 7º andar, CEP 21941-909, RJ, Brazil FAX: 55-21-2562-7240, alyneescobar@iq.ufrj.br

²Nacional Agency of Petroleum, Av. Rio Branco, 65, CEP 20090-004, RJ, Brazil

Bio-oils derived from biomass have been used as alternative sources of fuels and chemicals [1]. The direct use of bio-oils as fuels presents some difficulties due to their viscosity, poor heating value, corrosiveness and instability [2]. Those compounds could be cracked in order to produce hydrocarbons [3]. The catalytic cracking of glucose by ZSM-5 zeolite is reported in this work. Before evaluation, all catalysts were heated under N₂ from room temperature (10 K/min) to the reaction one. The experimental apparatus consist of a «U» type reactor made of quartz. Gas fraction was measured on line by CG-MS and the condensed products were recollected and analyzed after reaction. The products were separated into organic and aqueous phase and characterized by CG-MS and LC-MS respectively. Coke was quantified by

Table 1 - %wt/wt of products after catalytic cracking of glucose.

%wt/wt	Temperature (K)			
	673	743	793	853
Gas	3	7	28	38
Coke	21	32	20	20
Organic Phase	12	5	7	20
Aqueous Phase	64	56	45	24

LECO. The catalysts showed deactivation and the gas values (%wt/wt) presented in Table 1 is an average of 15 and 60 minutes of time on stream. Coke and organic phase were less affected by temperature while gas remarkable increased and aqueous phase decreased. The main

products in the gas phase were CO, ethylene and propylene, the organic phase consisted of mainly phenol and 5-hydroxymethylfurfural and aqueous phase is under investigation. The blank tests produced less gas and more aqueous fraction than the catalytic cracking.

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CONVERSION OF METHANE AND LIGHT HYDROCARBONS INTO HYDROGEN CONTAINING GAS ON MEMBRANE CATALYTIC SYSTEMS

Fedotov A., Tsodikov M., Moiseev I.

*A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
Leninsky pr., 29, Moscow, 119991, Moscow, Russia, alexey.fedotov@ips.ac.ru*

This work is devoted to study of original membrane catalytic systems (MCS) [1], high active in dry and steam reforming of methane and light hydrocarbons into hydrogen containing gas that can be used in petrochemical industry or in compact electric generators.

MSC represent porous ceramic membranes prepared by self-propagating high-temperature synthesis from high dispersive Ni-Al powder and modified by nano size metal oxide La-Ce, Pd-Mn, Pd, Mn [2] and Au-Ni containing precursors using sol-gel method. Experiment conditions: $T = 350 - 800^{\circ}\text{C}$; $P = 1.5 - 30 \text{ atm}$; $W_{\text{feed}} = \text{up to } 25000 \text{ h}^{-1}$; $\text{C}_1\text{-C}_5/\text{CO}_2/\text{H}_2\text{O}$ in various proportions.

By using MCS in dry methane reforming (DMR) process we have achieved the following syngas productivities: 10500 for La-Ce and $7500 \text{ l/h}\cdot\text{dm}^3_{\text{membr.}}$ for Pd-Mn containing MCS; syngas composition (H_2/CO) was 0,63 and 1,25, respectively; conversion of initial gas mix ($\text{CH}_4/\text{CO}_2=1$) was $\sim 50\%$ in both cases. We have found that on MCS, dry methane reforming is in one order more intensive at moderate temperatures ($350 - 650^{\circ}\text{C}$) than in a traditional reactor with a fixed bed layer of the same catalyst [3]. We have proposed an energy production method using MCS as a syngas generator in a compact integrated scheme based on solid-oxide fuel cells in which methane and light hydrocarbons ($\text{C}_2\text{-C}_4$), contained in gases of incomplete combustion of hydrocarbon fuels, convert into syngas at high feed rate ($\sim 25000 \text{ h}^{-1}$) by dry-steam reforming process.

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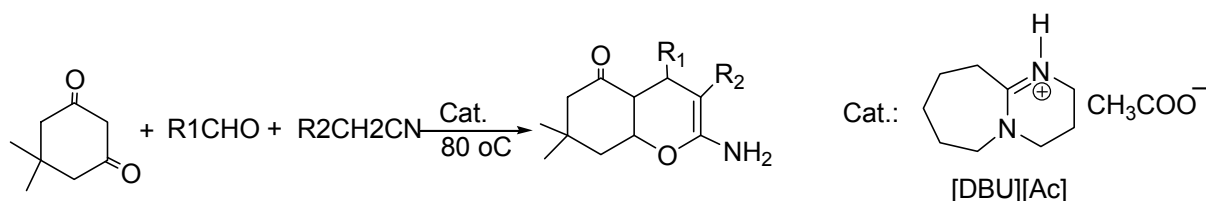
This work was supported by Grants RFBR 08-03-92496-NCNIL_a and 09-03-12060-ofi_m.

[DBU][Ac]: A TASK-SPECIFIC IONIC LIQUID FOR THE SOLVENT-FREE SYNTHESIS OF TETRAHYDRO BENZO[b]PYRANS

Alireza Hasaninejad, Nooshin Golzar, Maryam Rasekhi

Chemistry Department, Faculty of Sciences, Persian Gulf University,
Bushehr, 75169, Iran. E-mail: hasaninejad@pgu.ac.ir

Ionic liquids have received considerable attention due to their interesting chemical and physical properties, such as wide liquid range with melting point around room temperature, good stability in air and moisture, high solubility including inorganic, organic, and even polymeric materials, and negligible vapor pressure [1]. The use of ionic liquids as reactions medium may offer a convenient solution to both the solvent emission and catalytic recycling problem. Development of 4H-pyrans synthesis has been of considerable interest in organic synthesis, because of their wide biological and pharmaceutical activities [2]. Consequently numerous methods have been reported from the synthesis of 4H-pyrans. However, some of the reported methods have the following drawbacks: for example use of expensive reagents; long reaction times; low yields of products and use of an additional microwave oven. Because of their wide range of biological, industrial and synthesis applications, the preparation of 4H-pyrans as been received renewed interest of researchers for the discovery of reproved protocols and still awaits further developments of mild and high-yielding processes. Herein, we wish to disclose a green protocol for the synthesis of a variety of biologically important 4H-pyrans using a catalytic amount of [DBU][Ac] under solvent-free condition (Scheme 1).



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PREPARATION OF Pd/ γ -Al₂O₃ CATALYST FOR SELECTIVE HYDROGENATION OF ACETYLENE IN EXCESS ETHYLENE

Karim H. Hassan

Department of Chemistry, College of Science, University of Diyala, Iraq
e-mail: drkarim1953@yahoo.com

In petrochemical industry, and mainly in ethylene production plants, acetylene presents in trace amount in ethylene gas and causes a serious problems owing to its higher activity and being explosive at certain concentration limits with air, so it has to be converted to ethylene in selective hydrogenation.

The selective hydrogenation catalyst Pd / Al₂O₃ used in a selective acetylene hydrogenation was prepared. Three catalysts with 0.03 %, 0.05% and 0.07 % wt of palladium loaded on activated alumina were prepared by impregnation method. The catalysts were then characterized and the physical and chemical properties were determined. The activities of these catalysts were tested in a laboratory unit at 150 °C and atmospheric pressure and compared with the commercial one.

It has been observed from the results that the prepared catalyst of 0.05 % Pd shows a very good conversion and selectivity if compared with the commercial catalyst, as its activity in the hydrogenation of acetylene exceeds 97.5 % calculated as total acetylene hydrogenated to ethylene, in addition of being operated at lower temperatures. With this catalyst it is possible to operate for longer times and it is possible also to increase the operation time by raising the temperature as the activity declined.

SELECTIVE CONVERSION OF CARBON OXIDES TO METHANE OVER NiO-Al₂O₃ CATALYST

Karim H. Hassan

*Department of Chemistry, College of Science, University of Diyala, Iraq
e-mail: drkarim1953@yahoo.com*

In petrochemical industry, and mainly in ethylene production plants, carbon monoxide and carbon dioxide present in trace amount in ethylene gas and causes a serious problems owing to it is being a poison material to all the catalysts used in the following stages, so it has to be converted to non poison material, methane in selective catalytic hydrogenation.

The selective hydrogenation catalyst NiO/Al₂O₃ used in carbon oxides hydrogenation that contains 25 % NiO, 65 % Al₂O₃, 8 % CaO and 2 % graphite was prepared by precipitation method using nickel nitrate, aluminum nitrate and aluminum oxide as a source of metal precursors Ni and Al with sodium hydroxide as the precipitating agent where precipitation is done at a pH of 7. The required amount of calcium oxide was added either to the reaction mixture before precipitation process or in the later stages after it. The catalytic materials after being filtered and washed with distilled water is then dried at 110 °C for 5 hours and calcined at 450 °C for 5 hours too, finally it is converted to a tablets 5mm x 5mm size using tablet machine or high pressure press with graphite being added as a binder and lubricant at same time.

Then the produced catalyst is analyzed and characterized and the physical and chemical properties were determined. The activity of this catalyst was tested in a laboratory unit at a temperature of 250 °C, pressure of 12 bar, space velocity of 2500 hour⁻¹ and compared with the commercial one. The analysis of CO and CO₂ as methane was done using a gas chromatograph where they have been converted catalytically to methane in a small methanation reactor.

It has been observed from the results that the prepared catalyst shows a very good conversion and selectivity if compared with the commercial catalyst, as its activity in the hydrogenation of CO and CO₂ to methane exceeds 95 % calculated as total oxides hydrogenated, in addition to that, the prepared catalyst was thermally stable and can be operated for longer time with a reasonable and stable activity.

PRODUCTION OF TRANSPORT FUELS FROM BIO-ETHANOL

Isa Y.M.¹, Tretiyakov V.F.¹, Torkhovskii V.N.¹, Antanyuk S.N.¹,
Trushin A.A.², Tretiyakov K.V.²

¹*Lomonosov Moscow State Academy of Fine Chemical Technology, Moscow*

²*A.V. Topchiev Institute of Petrochemical Synthesis, Moscow*

e-mail: tretjakov@ips.ac.ru

Carbon materials have been used as fuels for a very long time. Despite the wide variety of the raw materials used in their production, not all fuels are able to meet their universal need. This shortcoming has to do with their nature and composition which reflects their efficiency. Most plant materials have the potentials of producing energy that could be used across a wide area, however due to the relatively low energy density of solid fuels, liquids and gaseous fuels are preferred. Hence, the need to convert the plant solid fuels into a form that could be utilized more efficiently.

A possible route of augmenting to the global liquid and gaseous transport fuel supply is by converting the available energy in plants to liquid and gases that could later be liquefied or upgraded to meet transportation fuel standards. Fermentation makes it possible to obtain ethanol from plant materials. However, the nature and origin of the fermented material makes it difficult for the liquid to be easily exploited for transportation purposes.

Using modified zeolites, propane- butane fractions and liquid hydrocarbons have been produced from ethanol. The liquid fraction contains a wide range of hydrocarbons ranging from alkanes to aromatic compounds. By hydrogenating the obtained liquid from fermentation, the high aromatic content in the liquid could be reduced to levels acceptable for fuels, further more, the benzene content could be reduced to 0%.

From our work, a three staged process of obtaining transport fuels from plant materials has been developed i.e; fermentation, conversion of ethanol and hydrogenation of the conversion products.

HYDROGEN PRODUCTION BY ETHANOL STEAM REFORMING IN A PALLADIUM-ALUMINA MEMBRANE REACTOR PREPARED BY COMBINE SOL-GEL AND ELECTROLESS PLATING TECHNIQUE OVER Ni / γ -Al₂O₃ CATALYST

Manal Ismail^{1,2}, Zahira Yaakob^{1,2}, Wan Ramli Wan Daud^{1,2}, Ratna Sari¹

¹*Fuel Cell Institute, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia*
manal@eng.ukm.my

²*Department of Chemical & Process Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia*

The palladium-alumina membrane reactor has been packed with Ni/ γ -Al₂O₃ for carrying out ethanol steam reforming. The preparation of the palladium coated ceramic alumina membrane has been performed using combine sol-gel process and the electroless plating technique. Ni/ γ -Al₂O₃ catalyst was prepared by the wetness impregnation of γ -Al₂O₃ support. The H₂O/ C₂H₅OH feed molar ratio of the inlet reactant was 13:1. The reactions were conducted at various temperatures 400-450°C. The effect of pressures difference across the membrane (2x10⁴-8x10⁴ Pa) and flow rate (2.086E-4 – 4.173E-4 mol/s) toward hydrogen yield (%) have been investigated. It is shown in this study that the H₂O/ C₂H₅OH feed molar ratio 2.086E-4 mol/s produced a higher hydrogen yield in operating at 450°C and 8x10⁴ Pa.

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PROCESS FOR THE PREPARATION OF L-LACTIDE

Khlopov Dmitry¹, Shvets Valeriy², Kozlovskiy Roman³, Suchkov Yury⁴

¹*D.I. Mendeleev University of Chemical Technology of Russia, Moscow,*

hlopovd@mail.ru, +7(499)7796973

²hxc@muctr.ru, +7(499)9789554

³rakozlovskiy@mail.ru, +7(499)9789554

⁴hxc@muctr.ru, +7(499)9789554

L-Lactide is a monomer that can be polymerized into polymeric materials. Polymers made from L-lactide are particularly useful because they can be biodegraded over time under most environmental conditions into carbon dioxide and water. In the future such compounds can solve the problem of polymeric wastes.

In literature there are a lot of works devoted to synthesis of L-lactide from L-lactic acid. In the current report we present results on investigation of L-lactide synthesis from butyl lactate which can be prepared from ammonium lactate obtained by fermentation of renewable source.

The process of butyl lactate conversion to L-lactide comprises two stages:

1. butyl lactate condensation yielding to oligomer formation having an average molecular weight in a range from 100 to 5,000;
2. L-lactide synthesis by oligomer depolymerization.

The influence of reaction conditions (such as temperature, pressure, catalyst type and concentration) on conversion and selectivity for both stages of process was investigated and optimal ranges of these parameters were determined.

As a catalyst the series of compounds of metals of Groups IV, V and VII of Periodic Table were tested. It was found that most efficient catalyst was tin (II) octoate which efficiently catalyzed as oligomerization and depolymerization stages and can be recycled.

SUB- AND SUPERCRITICAL WATER AS A CATALYST FOR CELLULOSE CONVERSION

Khudoshin A.G.¹, Goryainov A.U.¹, Lunin V.V.¹, Bogdan V.I.²

¹*Department of Chemistry, Lomonosov Moscow State University, Moscow, khudoshin@kge.msu.ru*

²*N.D. Zelinsky Institute of Organic Chemistry RAS, Moscow, bogdan@ioc.ac.ru*

Sub- and supercritical water (**SCW**) has been focused on as an acid-base catalyst and as an environmentally attractive reaction media at the same time where lignocelluloses materials can be decomposed into smaller molecules. High-temperature water (**HTW**) exhibits properties that are very different from those of ambient liquid water. HTW has a lower dielectric constant, fewer and weaker hydrogen bonds, and a higher isothermal compressibility than ambient liquid water. Moreover, the ion product (K_w) for high-temperature liquid water is about 3 orders of magnitude higher than that for ambient liquid water. These properties of HTW vary with temperature and pressure (or density) over wide ranges at near critical and supercritical conditions.

Cellulose is a major component of different waste streams from industries, agriculture, forest or municipalities. Hydrolysis of these materials in ecologically benign SCW media for production of useful chemicals is very attractive challenge.

Reactions of cellulose with high-temperature water have been studied using sucrose, glucose and fructose as a cellulose monomer compounds, carboxymethylcellulose as a soluble cellulose analogue and crystalline cellulose.

Experiments are conducted in flow reactor with a temperature 200-450°C and a pressure 80-270 atm. Products of decomposition of cellulose and its model compounds are analyzed using chromatography (HPLC, GC, GC-MS), thermogravimetric analysis and viscosimetry.

Influences of pressure, temperature, concentration and flow rate on passing of reactions are investigated.

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HYBRID PLASMONIC CARBON NANOMATERIALS FABRICATED BY DIRECT CARBONIZATION OF SELF-ORGANIZED BLOCK COPOLYMER NANOTEMPLATES FOR ELEMENTS IN ENERGY DEVICES

Dong Ha Kim, Yu Jin Jang, Yoon Hee Jang

Department of Chemistry and Nano Science, South Korea, Seoul,
dhkim@ewha.ac.kr

Hybrid carbonaceous materials have been widely utilized as core elements in the field of catalysis. It has been recently reported that nanostructured carbon materials also exhibit synergetic effects on the catalytic properties when they form a composite with noble metals [1-2].

Among the numerous strategies to generate nanostructured materials, block copolymer (BCP) self-assembly have attracted a growing attention as versatile platforms for fabricating functional nanostructures with tailored composition and architecture [3].

Here, we suggest simple and viable strategies to fabricate carbon nanostructures decorated with highly ordered Pt or Pd nanoparticles based on BCP self-assembly processes. BCP acts as a structure directing agent for controlled nanostructures and a carbon source, simultaneously. By this way, hybrid carbonized nanostructures in low-dimensional configurations could be obtained. The versatile functions of the resulting hybrid nanocomposites were evaluated in terms of photocatalytic and electrocatalytic activities based on which potential applications in fuel cell or photovoltaic devices are enabled.

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THE BLENDING OF SECOND – GENERATION BIO-GASOIL WITH FOSSIL DIESEL: EFFECT ON PETROLEUM-DERIVED FUEL QUALITY

Kirichenko E.N., Dundich V.O., Bukhtiyarova G.A., Yakovlev V.A.

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

evgenia@catalysis.ru

The blending of biofuels in the diesel pool has become more and more important in the past years due to several reasons: depletion of crude oil resources, environmental protection (avoiding acid rains and greenhouse effect, etc.). One of the problem arising is to introduce a large quantity of renewable fuel into the diesel fuel market without negative impact on fuel properties, affecting engine performance and pollutant emissions. Bio-gasoil can be produced by hydroprocessing of vegetable oil with high-cetane alkanes producing [Simacek, 456].

The aim of this topic is to investigate the effect of the second generation Bio-gasoil blending (from 5 to 50 vol. %) on the properties of the fossil diesel fuel. The bio-gasoil used in this study was produced by hydroprocessing of rapeseed oil over Ni-based catalyst in the down-flow reactor at the 6.0 MPa H₂, LHSV=2 h⁻¹, H₂/oil = 300 and 350°C [1]. The samples of hydrotreated SRGO with 12 or 70 ppm sulfur as well as the hydrotreated mixture of SRGO/LCO were used as fossil derived diesel fuel.

The influence of the biodiesel addition on the boiling range distribution, specific gravity, cetane number, sulfur, nitrogen and aromatic compounds contents in the diesel fuel was considered. It was found, that parameters of blended fuel were similar to or better than those of original fossil fuel. Especially noticeable improvement in cetane number, specific gravity and decrease of polycyclic aromatic compounds content were achieved when the bio-gasoil was added to the diesel fuel produced from the SRGO/LCO mixture. Such properties as excellent stability of the prepare blends and low solubility of water in them allow to use existing logistic system. So, the properties listed above open the wide perspectives for use the second generation bio-gasoil as blending component of diesel fuel.

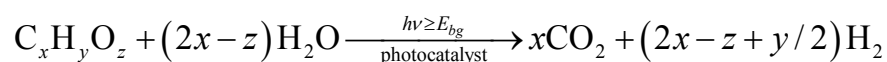
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PRODUCTION OF HYDROGEN BY PHOTOCATALYTIC REFORMING OF BIOMASS COMPONENTS AND DERIVATIVES IN AQUEOUS Pt/TiO₂ SUSPENSIONS

Panagiotopoulou P., Kondarides D.I., Verykios X.E.

Department of Chemical Engineering, University of Patras, 26504 Patras, Greece
Fax.: + 30 2610 991527; e-mail: dimi@chemeng.upatras.gr

Photocatalytic degradation of organic compounds in solution usually takes place in the presence of atmospheric oxygen and utilizes the strong oxidation potential of photogenerated holes to progressively degrade organic compounds into CO₂ and inorganic ions. Photogenerated electrons are believed to reduce oxygen adsorbed on the photocatalyst surface and generate additional oxidizing species, which also participate in the degradation process. However, if the reaction takes place under unaerated conditions, the reduction potential of photogenerated electrons may be utilized to generate hydrogen by reduction of water. Under these conditions, the overall process may be described by the following «photo-reforming» reaction:



In the present study we investigate photo-reforming of a variety of organic compounds in aqueous Pt/TiO₂ suspensions irradiated by a solar light-simulating source. Results show that waste biomass components and derivatives, such as alcohols, organic acids and carbohydrates, can be degraded effectively under unaerated conditions with simultaneous production of hydrogen. The rate of hydrogen evolution (r_{H_2}) depends strongly on the nature and initial concentration of the organic compound in solution and, to a lesser extend, on solution pH and temperature. Depending on the experimental conditions employed, r_{H_2} can be more than two orders of magnitude higher, compared to that obtained from pure water, rendering the process suitable for practical application. The photo-reforming process is non-selective and practically all organic compounds investigated so far may be degraded in the absence of oxygen. The process can be applied for the production of hydrogen from surplus of waste materials from biomass processing industries, practical feedstocks or glycerol-containing liquors derived from biodiesel plants, with minimum purification. It may also provide an efficient and cost effective method for cleaning up wastewaters with simultaneous production of hydrogen fuel.

STUDY ON THE PRETREATMENTS OF BIRCH WOOD SAWDUST FOR ETHANOL PRODUCTION

Kosheleva D.A., Volkhin V.V.

Perm State Technical University, Perm, Russia, E-mail: vvv@purec.pstu.ac.ru

Ethanol is one of the most important renewable fuels derived mainly from sugar cane and corn grain. The lignocellulosic biomass is a potential feedstock for low-cost ethanol production, but it must be pretreated before enzymatic hydrolysis [1-3]. Now chemical processes are considered as the most comprehensible pretreatments [4].

The effectiveness of dilute sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄) pretreatments of wood wastes for conversion of carbohydrates to fermentable sugars was investigated. Birch wood sawdust at a solid loading of 10% (w/v) were pretreated with NaOH and H₂SO₄ by autoclaving at 121 °C for 20, 40, and 60 min. H₂SO₄ pretreatment promoted the increase of soluble sugars content (the highest sugars yield was 15.8% at 60 min). The FTIR-spectra of pretreated samples proved essential solubilization of xylan due to H₂SO₄ activity and indicated the increase of lignin content. Solids from NaOH pretreatment (at 2%, 60 min, 121 °C) showed significant lignin degradation and small decomposition of xylan, but no changes in cellulose crystallinity were detected. Moreover NaOH hydrolysis resulted in the decrease of main soluble sugars yield. Probably this phenomenon was caused by the formation of phenolic and heterocyclic compounds, like furfural, during heat alkali pretreatment. Therefore, comparative analysis of the two pretreatment methods demonstrated that H₂SO₄ pretreatment is more suitable for wood splitting. Further the influence of 1% and 2% H₂SO₄ concentrations on soluble sugars yield was examined (solid loading was 10% (w/v), 121 °C, residence times of 20-360 min). The kinetic curves of the soluble sugars yield from acid concentrations were obtained. In addition, a process directed on the intensification of H₂SO₄ hydrolysis in an autoclave was studied. It can serve as a step towards the optimization of birch sawdust pretreatment.

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QUANTUM-CHEMICAL RESEARCH OF CATALYTIC COMBUSTION

Kukueva V.

Fire Safety Academy, Cherkassy, Ukraine, kukueva@yahoo.com

The conventional energy sources like fossil fuels, crude oil, natural gas etc. are dwindling fast. The world stock of non-renewable natural sources indeed have decreased. There is every necessity of going for renewable alternative resources for energy. The energy crisis of 1973 left scientists to accelerate the renewable energy programmes.

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. Biomass is the best alternative as it is available in plenty and production of energy from biomass is also less costly. The simple act of burning biomass to obtain heat, and often light, is one of the oldest biomass conversion processes known to mankind. The basic stoichiometric equation for the combustion of wood, represented by the empirical formula of cellulose, $(C_6H_5O_5)_n$. Carbon dioxide (CO_2) and water are the final products along with energy. If most biomass did not sustain its own combustion to make heat readily available in preindustrial times when and where it was needed, our historical development would not have reached its present state. The science of combustion has advanced a great deal since then and improved our understanding of the chemical mechanisms involved. There is also continued interest in developing a better understanding of the oxidation of hydrocarbon fuels over a wide range of operating conditions in order to increase efficiency and to reduce the emission of pollutant species. Thus, the development of a detailed kinetic mechanism for hydrocarbon oxidation necessary begins with a hydrogen/oxygen sub mechanism, which could be achieved by the quantum-chemical research, including the cases when additional substances can promote the combustion processes.

THERMAL CONVERSIONS OF WOOD SAWDUST TO GASEOUS FUELS IN A FLUIDIZED CATALYTIC BED

Kuznetsov B.N.^{1,2} and Shchipko M.L.¹

¹*Institute of Chemistry and Chemical Technology SB RAS,
K. Marx str., 42, Krasnoyarsk, 660049, fax: +7(391)2439342, e-mail: inm@icct.ru*

²*Siberian Federal University, Svobodny pr., 79, Krasnoyarsk, 660041*

The selection of catalytically active materials for fluidized bed was made taking into account the extreme conditions of their work in the studied high temperature pyrolysis and gasification processes. Different slag materials of metallurgy industry having a high mechanical resistance and thermal stability were tested. As it was found the Marting slag after the special activation treatment has the best catalytic properties among the other slag materials.

The studied process of syn-gas production from wood sawdust is based on the integration of carbonization and gasification stages. In the pyrolysis reactor the wood is pyrolyzed to char product and fuel-gas in fluidized bed of slag catalyst. Then the char is treated by steam in the gasification reactor for production of syn-gas. The circulation of hot char-product between carbonization and gasification reactors supplies by heat the water stage of char gasification by steam.

The optimal technological parameters of carbonization and gasification stages were selected. They synchronize the work of carbonization and gasification reactors and provide the maximal yield of syn-gas. Syn-gas produced from wood by the developed integrated carbonization – gasification process has low tar impurities.

The studied process of methane-enriched gas production from wood sawdust includes the next steps. At first the wood particles expose to thermally destruction in the heated fluidized bed of catalyst with the formation of volatile and solid char products. Some part of char reacts with steam, the finest char particles are burned in a combustion chamber. The heat for gasification process is collected from three sources: from overheated steam, from catalytic methanization of produced syn-gas and from combustion of some part of char product. The suggested one-step gasification process makes it possible to produce from waste wood the methane-containing gas with calorific value on 30 % higher in comparison with the traditional steam gasification process.

STUDY OF PRODUCTS OF LIGNOCELLULOSIC RAW MATERIALS CATALYTIC OXIDATION BY HYDROGEN PEROXIDE

Kuznetsova S.A.^{1,2}, Kuznetsov B.N.^{1,2}, Danilov V.G.¹, Petrov A.V.¹

¹*Institute of Chemistry and Chemical Technology SB RAS,
K. Marx str., 42, Krasnoyarsk, 660049, fax: +7(391)2439342, e-mail: inm@icct.ru*

²*Siberian Federal University, Svobodny pr., 79, Krasnoyarsk, 660041*

Promising directions of plant biomass wasteless processing are based on the conversion of two main components of biomass – polysaccharides and lignin to valuable products. The preliminary separation of lignocellulosic materials into cellulose and lignin makes it possible to increase the efficiency of biomass chemical processing. Method of catalytic oxidative depolymerization of plant lignin with hydrogen peroxide was used for biomass separation.

The present communication describes results obtained on the area of oxidation of lignocellulosic materials (sawdust of deciduous and coniferous wood, wheat straw, oats husk) by hydrogen peroxide in the medium acetic acid – water in the presence of acidic and oxidative-reductive catalysts.

Products of catalytic oxidation of biomass at 100-200 °C are presented by solid cellulose, low-molecular lignin and water soluble organic compounds. Their composition and structure were studied by chemical analysis, FTIR, NMR H¹ and C¹³, C.M.-G.C, XRD methods.

The optimal conditions of oxidation were selected for different types of biomass and catalysts. They make it possible to combine the stages of lignin oxidative depolymerization and acidic hydrolysis of hemicelluloses and amorphous cellulose. This allows to produce the microcrystalline cellulose (MCC) from different types of lignocellulosic raw materials by one-stage process.

The possible areas of application of microcrystalline cellulose and low molecular lignin, obtained by catalytic oxidation of plant biomass were studied. Microcrystalline cellulose can be used instead of MCC from cotton for obtaining food fibers and biologically active sulphates of MCC. Low molecular lignin is applicable for producing various valuable products: enterosorbents, binding agents for wood panels, liquid biofuels and nanoporous active carbons.

PHYSICO-CHEMICAL PROPERTIES OF TUNGSTEN CARBIDE POWDERS PREPARED FROM IONIC MELTS

Malyshev V.V.¹, Kushkhov Kh.B.², Gab A.I.³

¹*V.I. Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, 32/34 Palladin ave, Kyiv, 252680 Ukraine,*

tel./fax: +38044 4249433, e-mail: victor_malyshev@mail.ru

²*Kabardino-Balkar State University, ul. Chernyshevskogo, 173, Nalchik, 360004 Russia*

³*National Technical University of Ukraine «Kyiv Polytechnic Institute», 37 Peremoga ave, 03056, Kyiv, Ukraine, e-mail: lina_gab@mail.ru*

Prior to the removal of free carbon and adsorbed oxygen, tungsten carbide prepared by electrolysis of molten salts contained 85-90 wt % combined tungsten, 4-6 wt % combined carbon, ≤ 7 wt % free carbon, and ≤ 5 wt % adsorbed oxygen. Free and surface oxygen was removed by additional purification, after which the material contained 0.2-0.3 wt % O₂ and no more than 0.1 wt % C. The contents of Li, Na, Fe, Mo, Ti, and Mg were within 100 ppm by weight, and those of Cu, Si, Cr, and Ca within 10 ppm; the Co content was below the detection limit. The specific surface of the powders before purification was 10-20 m²/g, in part owing to the presence of fine-particle free carbon. After purification, the specific surface was 5-10 m²/g. The lattice parameters of WC were determined to be $a = 2.906 \pm 0.003$ Å and $c = 2.837 \pm 0.006$ Å, in perfect agreement with reference data.

After purification, the powders were used to fabricate ceramics. Prior to sintering, the powders were detailed studies into the corrosion behavior of WC both in electrolyzers operating under various conditions and during storage.

Potentiostatic and potentiodynamic measurements indicate that a major reason for the decrease in the electrocatalytic activity of WC during storage and service is surface oxidation, which begins at potentials above 0.2 V and prevails in the range 0.5-0.7 V; oxidation of WC in contact with an MF-4SK membrane is irreversible. Taking into account these results, we established the storage and service conditions under which the catalytic activity of WC remains intact. Oxidation can be prevented by creating a reducing atmosphere in the cathode compartment and a reducing or inert atmosphere (e.g., H₂ + N₂, N₂, or AT) in the anode compartment, thereby setting the necessary potential of tungsten carbide. Life tests show that, under such conditions, the in-use life exceeds 500 h (50 electrolysis cycles), whereas without these precautions, the service life is only 200 h.

AMINE CONTAINING COMPOUNDS AS CATALYST FOR PRODUCING OF BIODIESEL FUELS

**Mammadova T.A., Talibov A.H., Andryshenko N.K., Askerova E.N.,
Veliyev X.R., Aliyeva Z.M.**

Petrochemical Unstitute name after Mamedaliyev, Baku, Azerbaijan
mamedova.tarana@rambler.ru

For the purpose to research more efficacious catalyst for reaction of etherification of vegetable oils triglycerides, which are allowed at the same time to escape problems with soap-forming may be observed by using KOH, NaOH were researched pyridine, piperidine, tetramethylammonium hydroxide, aminoguanidin carbonat. Experiments by produce of methylesters of sunflower oil were spented at 50-80 °C, ratio methanol/oil 1:6 and reaction time 1-5 hours with various containing of catalyst.

Among the investigated compounds tetramethylammonium hydroxide has the most activity. When containing of tetramethylammonium hydroxide in reaction system is 0.1%, yield of alkyl esters is 30% and by further increasing of containing of catalyst till 0.3 - 05% (reaction time 1 hour) yield of alkyl esters increase to 76 and 98% accordingly. Further increasing of catalyst containing of is not expedient because the yield of alkyl esters in this time containing 98,3%.

Quite enough activity in reactions of etherification of vegetable oils triglycerides has the aminoguanidin carbonat, which provide the yield of esters more than 95% and at the same time it is the insoluble in spirits and oils solid powder, what is its advantage in comparison with the others catalysts as it allow to keep off separation and washing products from catalysts.

Piperidine displays enough activity by containing of it in system 3%.

Yield of alkyl esters by the using of pyridine contains no more than 54% even the containing of it more than 10%.

LOW-TEMPERATURE OXIDATION OF ORGANICS BY SINGLET OXYGEN

Vishnetskaya M.V., Vahrushin P.A., Matrosova O.V., Rufov Ju.N.

*Gubkin Russian State University of Oil and Gas, 65 Leninsky Av., Moscow, 119991
Russian Federation, E-mail: mvvishnetskaya@mail.ru*

At the present day, oxidative gasification of biomass is considered as a promising technology for biogas production. Catalytic oxidative gasification in the presence of oxides is one of the most perspective ways of vegetable biomass processing [1]. In earlier study [2], vanadium and molybdenum oxides have been shown to be able to generate singlet oxygen at the temperature as low as 200°C. This brings low-temperature alkane oxidation into effect.

In the present work, we report on peroxide groups present on the surface of vanadium and molybdenum oxides that produce singlet oxygen ($^1\text{O}_2$) when decomposed, which further participates in dodecane oxidation. Quantitative determination of low-temperature emission of $^1\text{O}_2$ from the surface of individual and mixed vanadium-molybdenum oxides $x\text{V}_2\text{O}_5 \cdot y\text{MoO}_3$ using the thermal desorption technique enable one to establish the optimum conditions of its generation and its participation in oxidation of dodecane by air oxygen as well.

Catalytic reaction was performed in a flow reactor at atmospheric pressure, 200–350°C, dodecane VHSV $\sim 3\text{--}9\text{ h}^{-1}$ and air flow $\sim 30\text{--}180\text{ ml/min}$. The principal possibility of dodecane oxidation into lauric acid by air oxygen at 200–350°C was proved. The dependence of dodecane conversion, selectivity and acid yield from temperature, feed rate of dodecane and air on different catalysts was found. Rather unexpected dependence of alkane conversion on reaction temperature was revealed. So, in the temperature range of 250–350°C the maximum of dodecane conversion was observed, at higher temperatures it trends to increase.

The suggestion was made that on removing the peroxide groups from the oxides surfaces, the oxygen vacancies are formed. These oxygen vacancies are supposed to play the main role in the activation of molecular oxygen into its triplet form and in hydrocarbon oxidation.

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SOLAR ACTIVATION AND ELECTROCHEMICAL REACTION CATALYSIS

Michael Michman

*The Institute of Chemistry, Campus E.Y. Safra,
The Hebrew University of Jerusalem, 91904 Jerusalem, Israel
Fax: 972 2 6585345, michman@cc.huji.ac.il*

The utilization of solar energy for heating and power production is gaining impetus throughout the technology prospect of the 21-century. New developments of commercially available collectors with improved efficiency and decreasing price have made the solar option practical and available. When used for power production the output is transformed to AC current yet it is principally a DC source.

Electrochemistry (EC) on the other hand is very efficient in sensing devices and analysis due to its high sensitivity but very expensive in reactions as reflected in the high value of the Faraday constant. Also low voltage and high DC currents are recognized for high loss of energy – heat loss. Therefore EC, though considered occasionally as a green method, is therefore the method of choice only in selected cases.

Using photovoltaic collectors for power generation can become an interesting option for the activation of slow reactions, low concentration processes of material treatment, water treatment, in well-known reactions such as oxidations, chlorination, metal-ion treatment, etc. Some illustration by which EC catalysis can be applied will be supported with examples of our work [1-3]. All these need specific considerations of electrodes, electrolytes and catalysis. Some examples of our previous work are considered.

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**LABORATORY EQUIPMENT FOR THE STUDY OF HYDROLYSIS
AND ENZYMOLYSIS OF PLANT RAW MATERIALS**

**Mukhachev S.G., Emelyanov V.M., Shavaliyev M.F., Valeeva R.T.,
Ablaev A.R., Nurtdinov R.M., Builin A.M.**

*Kazan State Technological University, K. Marks Street, 68, Kazan, Russia,
phone: +7(843)2314049, fax: +7(843)2314042, e-mail: Emelianov@front.ru*

Comparative research of hydrolysis and enzymolysis of cellulose raw materials are of practical importance in connection with intensive development and launching to the market new and more effective enzymes.

For this purpose a universal laboratory hydrolyser was developed, which provides intensive mixing of hydrolyzed mass of rye and wheat straw in dispersed particles not longer than 5 mm, at liquor ratio not less than 5. The device is equipped with frame stirrer and control system providing measuring of specific energy consumption. Sampling device allows sampling at an excess pressure of 0,4 MPa and temperatures up to 140 °C. This allows studying the kinetics of enzymatic or chemical hydrolysis in this equipment and evaluating specific energy consumption of sugars formation.

Estimation of biological quality of hydrolyzates and enzymolyzates was carried out by the intensity of growth and fermentation of alcohol yeast in shake flasks with the help of measuring of the optical density of culture liquid and the intensity of production of carbon dioxide.

In addition, for estimation of suitability of yielded media for growing inoculum there was developed inoculator with membranous appliance of controlled oxygen feeding, controlled devices for feeding nutrient components and titrating agents and stabilization of the volume of culture fluid.

Technical and biotechnical tests of above-mentioned equipment were carried out and design documentation for it batch production was developed.

THE PROCESSING OF ANTHROPOGENIC RAW MATERIAL FOR EXTRACTION THE NON-FERROUS AND NOBLE METALS

Narbekova T.N.¹, Krushenko G.G.²

¹Norilsk Industrial Institute, narbekova07@inbox.ru

²Institute Computational Modeling SB RAS, genry@icm.krasn.ru

The technologies of processing the mineral raw material at mining non-ferrous metallurgy plants are accompanied by the formation of waste substances in the form tails of ore-dressing, slag, fettling called «anthropogenic deposits» (AD) in connection with its considerable volumes, which contain one or another quantity of non-ferrous and noble metals so it is an important additional source of non-ferrous metals.

The scientific research on evaluation AD volumes and study AD composition with extraction non-ferrous and noble metals from it was organized at Mining-metallurgy industrial complex «Norilsk Nickel» (MMIC «NN»).

It is established that the dumps of the copper-smelting plant (slag, fettling and others) achieve considerable volumes - approximately only 3500–4000 tonnes of the converters waste fettling is thrown away to dump every year. The thickness of slag deposits amounts to 10–20 m with 1-10% copper content.

The comparison of chemical elements content in products mentioned above allows to conclude that AD included all chemical elements (except sulfur) from the MMIC «NN» production list (Cu, Ni, Co, Pt, Pd, Au, Ag, Ru, Rh, Os, Ir, Se, Te) was formed on a base of offal of the copper-smelting plant.

The waste fettling of the nickel plant thermal-electric furnaces contains g/t 0,1-2,0 Pt; 0,4-20,0 Pd; 1,0-7,0 Ag; 0,02-1,0 Au. The waste fettling of converters contains to 0,54 % Ni; to 6,5% Cu and to 0,031% Co. The waste fettling of the copper-smelting plant electrolysis baths contains to 2,0 % Cu and to 0,05 % Ni.

The technology of copper and nickel extraction from the waste fettling of electrolysis baths (bulk of it is in excess of 1200 t/year) which is consisted in the crushing and reduce samples to fragments with following leaching by mixing a grinded product and sulfuric acid was worked out and introduce in production at Mining-metallurgy industrial complex «Norilsk Nickel».

The solution was filtered after a lapse of time of experiment, the sample of filtrate was selected, so the content of copper in it was detected by titrimetric analysis iodometric method and the content of nickel was detected by gravimetric method.

FERMENTATION PROCESSES OF FREE AND IMMOBILIZED CELLS OF *CLOSTRIDIUM ACETOBUTYLICUM* ON DIFFERENT MEDIA

Nikolskaya A.B.¹, Efremenko E.N.^{1,2}, Varfolomeev S.D.^{1,2}

¹*Institute of Biochemical Physics RAS, Moscow, anickolskaya@mail.ru*

²*Chemical Enzymology Department, Chemical Faculty MSU, Moscow*

Fermentation processes using anaerobic microorganisms provide a promising path for converting biomass and agricultural wastes into fuels. Acetone-butanol-ethanol fermentation with the strict anaerobic bacterium *Clostridium acetobutylicum* was one of the most extended processes in industry but its application was limited by low yields and product concentrations. However this process allows to produce one of the most important biofuels today – hydrogen and butanol – simultaneously. From this point of view it is interesting to develop methods for increasing the productivity of *Clostridium acetobutylicum* cells. One of methods is carrying out the cell immobilization of microorganisms, which allows to create and save high cell concentrations in reactor, provides continuous operation stability of biocatalytic system and reduces power inputs for process in general. In this investigation the immobilization of cells *Clostridium acetobutylicum* into cryogel of poly(vinyl alcohol) was carried out and fermentation processes of different media were studied.

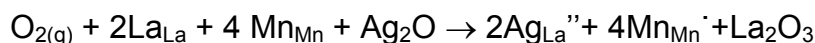
Acknowledgements. The authors gratefully acknowledge financial support from program of fundamental investigations of Presidium RAS «Chemical aspects of energetics».

La_{1-x}M_xMnO₃ PEROVSKITE-LIKE CATALYSTS FOR METHANE FLAMELESS COMBUSTION: XRPD-RIETVELD AND EPR CHARACTERIZATION

Oliva C., Scavini M., Rossetti I., Cappelli S., Allieta M.,
Sironi B., Buchneva O., Forni L.

Dip.Chimica Fisica ed Electrochimica, Università degli Studi di Milano, Italy

The performance of La_{1-x}M_xMnO₃ materials for the methane catalytic flameless combustion (CFC) is strongly dependent on the nature of M, as well as on sample preparation procedure. M = Ag, x = 0, 0.05, 0.10 catalysts prepared by «Flame Pyrolysis» (FP) showed always more active than those prepared by «Sol Gel» (SG). [Mn⁴⁺] was more abundant in the (rhombohedral) SG than in the (monoclinic) FP fresh catalysts [1]. The possible defect equilibria were:



A single Lorentzian-shaped EPR line (L) was observed at T > 300 K, as reported for x = 0 and for x ≠ 0 and M = Ca, Sr; Eu [2-4]. L was narrower with our SG than with FP fresh catalysts, probably due to the higher amount of Mn⁴⁺ ions present in the former, forming –O–Mn³⁺–O–Mn⁴⁺–O– chains, through which the Double Exchange (DE) relaxation occurs. [Ag] further contributed to the [Mn⁴⁺] increasing (as revealed by the L narrowing) and, therefore, to the increasing of catalytic activity. However, the higher [Mn⁴⁺] in SG than in FP samples seems in contrast with the lower catalytic performance of the former. This could be explained by the formation of Mn⁴⁺-rich domains in SG samples, hindering the electronic exchange involved in the catalytic process. The presence of these domains is in agreement with the ferromagnetic transition of the SG samples, revealed by L broadening at T < 290 K [2,3].

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THERMOCATALYTIC HYDROLYSIS AND ALCOHOLYSIS OF LIGNIN AS A CONVENIENT APPROACH TO BIOFUEL OF NEW GENERATION

Trofimov B.A., Oparina L.A., Vysotskaya O.V., Gusarova N.K.

*A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 Favorsky Street, RUS-664033 Irkutsk, Russia
Fax: +7(3952) 419346; E-mail: oparina@irioch.irk.ru*

The resources of hydrolysis lignin in Russia amount to about 95 million tons [1]. Only in Irkutsk region, 4 hydrolysis plants produce approximately 20 millions tons of hydrolysis lignin [1], representing severe environmental danger. At the same time, hydrolysis lignin is promising organic raw material. Therefore, over the last decade, the interest to the reprocessing of different types of lignin to liquid and gaseous hydrocarbons has dramatically increased.

For the first time we have shown that in the course of thermocatalytic hydrolysis and alcoholysis (including its combination with hydrogenolysis) lignin is almost quantitatively transformed into liquid («lignooil») and gaseous («lignogas») products. The liquid fraction contains a mixture of aliphatic alcohols and their ethers, aromatic hydrocarbons, substituted phenols and their ethers. These products are formed due to the destruction of lignin polymer matrix across the C-O and C-C bonds as well as demethoxylation and alkylation of the aromatic ring. Besides, depolymerization of lignin is accompanied by the significant decrease of oxygen content in the liquid products formed (up to 8-10%) as compared to the starting lignin (30%). In gas phase («lignogas»), carbon oxides, methane as well as other lower hydrocarbons (C₂-C₅) have been identified.

Thus, based on thermocatalytic hydrolysis and alcoholysis of hydrolysis lignin, the conditions of its quantitative transformation into liquid and gaseous products, have been elaborated. The liquid fraction obtained, «lignooil» C₁₀₋₁₄H₁₃₋₂₀O (H/C ratio = 1.3-1.4) can be used for the preparation of motor fuels of new generation.

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CATALYTIC CONVERSION OF ETHANOL INTO BUTADIENE

Ordonsky V.V., Sushkevich V.L., Ivanova I.I.

Department of Chemistry, Moscow State University, Moscow, Russia
iiivanova@phys.chem.msu.ru

Butadiene is a major product of the petrochemical industry and an important building block for many industrial products. The main applications of butadiene are connected with production of synthetic rubbers. The traditional approach for butadiene production (over 95%) based on extraction from heavy steam crackers. However, the increase of the cost of oil extraction force to search ways of butadiene production from the recovery resources like ethanol.

The first process of butadiene production from ethanol (Lebedev process) was developed and commercialized in the Soviet Union in the 1930s. This process involved two steps: dehydrogenation of ethanol to acetaldehyde and conversion of acetaldehyde into butadiene. The second step was carried out over basic catalyst containing magnesium oxide. However, acetaldehyde conversion was 35 to 37% per pass and the maximum yield of butadiene was only 60 to 64%. In addition, the life time of the catalysts between regenerations was very short (1-2 days).

In the present work different basic, acidic and acid-base catalytic systems were studied in the synthesis of butadiene from ethanol. It was found out that the process can be carried out in one step. Introduction of the metal such as copper to acid-base bifunctional catalyst was shown to give positive effect on the conversion of ethanol and selectivity in butadiene. Investigation of the reaction mechanism and active sites showed that first stage of the process can proceed via direct reaction of ethanol into crotonaldehyde on metal-acid-base site pairs without the intermediate formation of gas phase acetaldehyde. This leads to decrease of the rate of further condensation of crotonaldehyde and formation of heavy products like in the case of two step process. The study of model reaction of crotonaldehyde with ethanol pointed that the reduction of crotonaldehyde intermediate product by alcohol proceeds via Meerwein–Ponorf–Verley (MPV) mechanism over the Lewis acid sites of the catalyst.

The best catalytic performance was obtained over multifunctional catalyst which allowed for the direct transformation of ethanol into butadiene with the conversion of ethanol 44%, the yield of butadiene of 84% and high stability of work at relatively low temperature (325°C).

OBTAINING OF SYNTHETIC FUEL FROM METHANOL

Piriev N.N., Ahmedova R.G., Babayeva F.A., Rustamov M.I.

Institute of Petrochemical Processes NAS of Azerbaijan, Baku
feridan@rambler.ru

Prospects of dimethyl ether (DME) use as ecologically pure diesel fuel, and also possibilities of its transformation into low-molecular olefins C₂-C₄, aromatic hydrocarbons and components of high octane gasolines demand a sharp increase in the volume of its manufacture.

For obtaining DME commercially by dehydration of methanol or directly from synthesis-gas on a mix of catalysts for obtaining methanol, such catalysts are necessary which possess not only high activity and selectivity, but also the raised operational properties.

In the present work, we simulate and study the regularities of methanol transformation on catalysts prepared from not modified and modified by phosphoric acid industrial catalysts for cracking, containing zeolite Y and HZSM.

Samples of catalysts have been tested on flowing installation with a stationary layer, at atmospheric pressure, in a temperature interval 280-450 °C and volume speed of delivering methanol 3.5 h⁻¹ without additional dilution by inert gas-carrier.

It has been established that the industrial catalysts containing zeolite of Y type, unlike the catalysts containing ZSM-5, can be used in a mix with methanol synthesis catalysts (Cu+ZnO/Al₂O₃) and are effective as for obtaining DME in the process of methanol dehydration, and in one stage process of transformation of synthesis-gas into DME. They are characterised by high activity, stability of work and reproducibility of results.

Use of industrial catalysts with well prepared base of their manufacture can considerably simplify the decision of the problem of expansion of DME manufacture without essential additional capital investments.

EFFECT OF REDUCTION CONDITIONS OF 20%Co/(H β +50%Al) CATALYST ON THE CATALYST PROPERTIES IN HYDROCARBON SYNTHESIS FROM CO AND H₂

Potapova S.N., Mikhailova Ya.V., Svidersky S.A., Loginova A.N.

*United research and development centre, Russia, Moscow, Leninsky pr. 55/1, b.2.
research-centre@yrd.ru*

Search for new ways to use associated and natural gas is of great importance in fuel sources utilization. One of promising methods for large-scale processes is production of synthetic liquid hydrocarbons via Fischer-Tropsch synthesis over cobalt catalysts. In the presence of these catalytic systems, normal paraffins are mainly formed with yield and composition depending not only on composition of a catalyst but also on the conditions of its activation before the synthesis. Formation of active surface of cobalt catalyst is known to occur during its reduction with hydrogen. Reduction conditions have an impact on the ratio between metallic and oxide phases which, in its turn, determines catalytic properties of a system, particularly selectivity to C₅₊ hydrocarbons and methane. Large amount of hydrogen is required to reduce (activate) commercial Fischer-Tropsch catalysts. Consumption of hydrogen can be lowered by its dilution with inert gases (helium, nitrogen, argon) to provide H₂ content from 5 to 100 vol.%. However, there is a limited number of studies considering the method.

The aim of our study was to investigate the influence of 20%Co/(H β +50%Al) catalyst reduction conditions, particularly hydrogen dilution with nitrogen and helium, on its properties in hydrocarbon synthesis from CO and H₂.

20%Co/(H β +50%Al) catalyst has been prepared by the technique described in patent [1]. Hydrocarbon synthesis from CO and H₂ was performed in a flow unit with fixed-bed catalyst at P=2.0 MPa and syngas space velocity of 1000 hr⁻¹. The catalysts were activated either with pure hydrogen or with reducing mixtures (10%H₂+N₂) or (10%H₂+He) at 400°C. In all the cases the total amount of pure hydrogen passed was 7.5 l.

All the catalysts were active in hydrocarbon synthesis from CO and H₂.

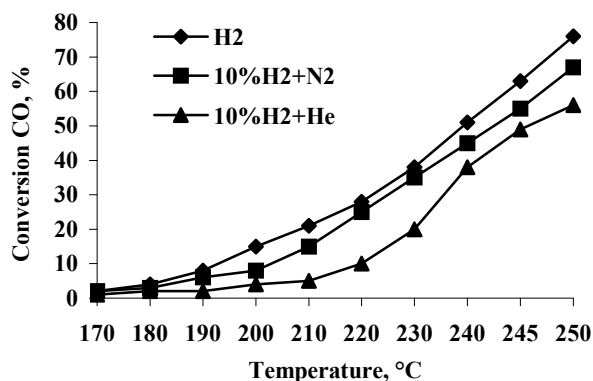
Over the whole temperature range of the synthesis the largest CO conversion and liquid hydrocarbon yield were achieved over the sample reduced with pure

PP-44

hydrogen. The highest values of the parameters were observed at $T=250^{\circ}\text{C}$ and amounted to 76% and 92 g/nm^3 , respectively (Fig. 1-2).

Over the whole temperature range studied the sample reduced with (10% H_2 + N_2) mixture demonstrated a slight decrease in CO conversion and C_{5+} hydrocarbon yield by 1.1-1.3 times, respectively (Fig. 1-2). 20% $\text{Co}/(\text{HB}+50\%\text{Al})$ catalyst activated with

Fig. 1. Effect of different reduction conditions on CO conversion of 20% $\text{Co}/(\text{HB}+50\%\text{Al})$ catalyst



contents were 7 and 28%, respectively.

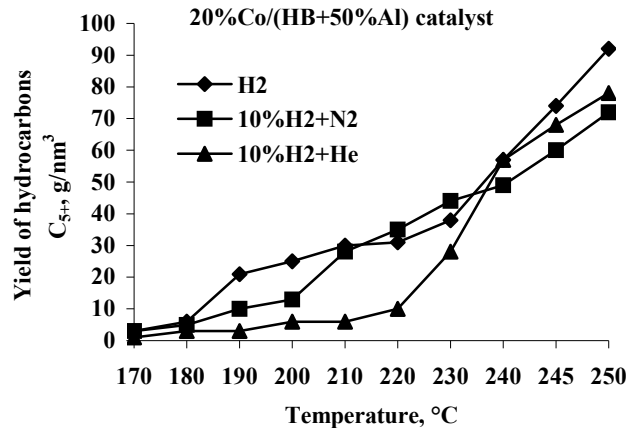
Dilution of hydrogen-containing mixture with nitrogen led to an increase in n-paraffin content in synthesis products (up to 80%), dilution with helium caused growth of olefin and isoparaffin percentages (up to 20 and 38%, respectively).

Thus, the possibility of Fischer-Tropsch catalyst activation with hydrogen diluted with inert gases has been demonstrated. The method offers a way to save expensive hydrogen as well as to control group composition of synthesis products.

helium-containing mixture exhibited a lower activity compared with the two other samples. C_{5+} hydrocarbon yield and CO conversion at all synthesis temperatures decreased by 1.2-1.4 times, respectively.

Catalysate obtained on the sample reduced with pure H_2 contained mainly n-paraffins (~65%). Olefin and isoalkane

Fig. 2. Effect of different reduction conditions on liquid hydrocarbon yield of 20% $\text{Co}/(\text{HB}+50\%\text{Al})$ catalyst



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CATALYTIC OXIDATION OF MODEL LIGNIN COMPOUNDS IN ACIDIC MEDIUM

Povarnitsyna T.V., Popova N.R., Bogolitsyn K.G., Beloglazova A.L.,
Varakin E.A.

*Arkhangelsk State Technical University, Arkhangelsk, 163002, Russia
Northern Dvina emb. 17, tpovarnitsyna@yandex.ru*

One of the ways to intensify treatment of plant biomass and lignin-containing substances is to catalysis by ions and complex compounds of metals of variable valency. One of perspective directions in this area is application polyoxometalates (POM) as catalysts, which catalytic action in process of oxidation lignin compounds was revealed during the process of search and creation of new chlorine – free technologies in bleaching [1]. The purpose of the given work is the establishment of the main rules in process of catalytic oxidations of lignin compounds by the dissolved molecular oxygen in acidic medium using POM as a catalyst. In this connection, influence of the duration of oxidation, the nature of oxidized compound and catalyst, pH of solution were investigated. Earlier we carried out the investigations about establishing of the main rules in process of catalytic oxidations of model lignin compounds [2]. Low – modified dioksanlignin and technical sulfate lignin were used as a oxidized compounds, sodium vanadomolybdophosphate (HPA-5) and Mn-contain sodium vanadomolybdophosphate (HPA-5-Mn) were used as a catalysts. Process controlled by the changing in functional structure of the allocated products of oxidation which defined by standard methods [3]. As a result, the main rules and optimal conditions of the catalytic oxidation process of lignin compounds were determined; catalytic reactivity of catalysts was detected; it was showed, that the HPA-5-Mn is more effective than HPA-5; at researching of catalytic oxidation process of lignin it is possible to use the same methods, as at studying of process of oxidation of model lignin compounds – that speaks about the same of main rules and factors, which affected on the oxidation process.

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PROBLEM OF RECEPTION OF ANTIMATTER BY MEANS OF ENERGY OF THE SUN

Prokopev E.P.

A.I. Alikhanov Institute for Theoretical and Experimental Physics, str. Bolshaya Cheremushkinskaya, 25, Moscow, Russia, 117218, e-mail: epprokopiev@mail.ru

The big interest represents an possibility of reception of intensive streams of positrons (probably and other antiparticles) at reorganization of physical vacuum in strong fields (for example, in an electric field of modern super-power laser beams) and on accelerators (<http://www.popmech.ru/part/?articleid=4803&rubricid=3>). Speech can possibly go about creation of space solar factories on the Moon or asteroids, etc. with use of the transformed energy of radiation of the Sun to electric energy and uses of a space for manufacture and storages of positrons [1-3]. The essence of a method should consist in reception by means of the transformed energy of the Sun on accelerators or any other methods of streams of fast positrons with their subsequent delay up to temperatures of the order 0,5 K in some closed area of a space. Thus, very significant stocks of positrons could be created. Gathering of such positrons in magnetic traps in conditions of a space can become rather effective method of accumulation of antimatter by means transformations of energy of the sun.

On a modern level of development of technologies about lots of received antimatter to speak it is not necessary. Besides this process of reception is very dear. Therefore probably really to speak only about tens or hundreds nanograms received antimatter. This quantity of antimatter, apparently, would suffice for creation of space vehicles (SV) with the sizes in nano-or a micron range. This fantastic assumption is not deprived sense in a context of modern development of nanotechnologies in the World. All the sizes long devices and details such SV should not exceed the sizes of nano- and micron ranges.

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ACID-CATALYZED CONVERSION OF MISCANTHUS AND GIANT REED INTO CHEMICALS

Anna Maria Raspolli Galletti¹, Enrico Bonari²,
Claudia Antonetti¹, Valentina De Luise¹, Marco Martinelli¹, Nicoletta Nassi²

¹*Department of Chemistry and Industrial Chemistry, University of Pisa,
Via Risorgimento 35, 56126, Pisa, Italy, roxy@dccci.unipi.it*

²*Scuola Superiore Sant'Anna, Piazza Martiri della Libertà 33, 56100 Pisa, Italy*

Biomass represents a sustainable alternative to fossil resources in order to produce chemicals, fuels and innovative materials [1]. In this context, the exploitation of lignocellulosic biomass from herbaceous cropping systems can represent a valuable opportunity for rural areas. In particular perennial grasses, as miscanthus (*Miscanthus giganteus*) and giant reed (*Arundo donax* L.) seem to be especially suited as feedstock due to their high productivity (about 35 and 25 t ha⁻¹ year⁻¹ of dry matter for giant reed and miscanthus respectively) and low input requirements, in terms of fertilisation and irrigation level [2]. Nevertheless very little is reported about the use of these grasses for catalytic conversion into chemicals.

Now we have studied and patented [3] a new process for the complete and efficient acid-catalyzed exploitation of the three components (hemicellulose, cellulose and lignin) of these lignocellulosic materials.

This process allows to obtain in the same time with high yields furfural and levulinic acid (4-oxopentanoic acid) using one or more proton acids working on aqueous biomass slurry.

The solid lignin residue, recovered at the end of the process, has been suitably employed for many valuable technological applications.

This study has been carried out both under traditional heating and using microwaves-irradiation: in this last case the reaction time is significantly reduced without detrimental effects on the yields.

It is remarkable that under the optimized conditions only negligible amounts of soluble by-products or polymeric black solids, which cause the reactor clogging, are detected.

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INVESTIGATION OF NEW WAYS OF BIODIESEL PRODUCTION**Romanova Anastasiya¹, Khanikyan Vago², Kustov Andrey³, Sapunov Valentin⁴**

¹*D.I. Mendeleev University of Chemical Technology of Russia, Moscow, liceistka2003@mail.ru, +7(499)7796973*

²*A.N. Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, vagokhan@rambler.ru, +7(499)7796973*

³*"VEGA-CHEM" Ltd., Moscow, koustov@muctr.edu.ru, +7(499)9789554*

⁴*"VEGA-CHEM" Ltd., Moscow, sapunovvals@gmail.com, +7(499)9789554*

Biodiesel is a renewable diesel fuel that is also known as FAME (fatty-acid methyl ester) in the European Community. Biodiesel has the advantage that it works just as well as normal diesel fuel, but the combustion process expels lower concentrations of toxic emissions. It is made from animal fats, vegetable oils or recycled restaurant greases. As is known, the traditional technologies for Biodiesel manufacture have several disadvantages. For example, there are very stringent requirements on availability of water and free fatty acids (FFA) in raw vegetable oil in case of homogeneous alkaline catalysis using. The large ratio of Methanol/ Oil, high temperature and pressure and also a relatively short lifetime of the catalyst are the main disadvantages of technology of heterogeneous catalysis. For decision of the above enumerated questions, we have carried out various studies using heterogeneous and homogeneous catalysis as well. The most interesting results we have obtain by using FA salts of lead (II) as a homogeneous catalysis. This variant of process design allows carrying out the transesterification of vegetable oil in relatively mild conditions and in presence of any quantity of FFA in the feedstock. In addition, using of lead (II) salts in contrast to the alkali catalysts excludes, practically, the problems, which associated with the stages of phase separation of the final products in case of transesterification of vegetable oils by other lower alcohols. Analysis of distribution of lead compounds in the reaction products and their comparison with the obtained kinetic regularities of the process, allowed us to offer a variant of reuse of the catalyst, which makes this technology attractive also.

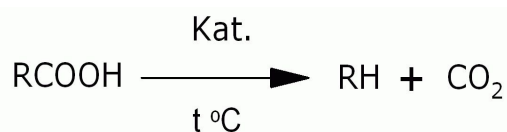
PROCESS FOR THE PREPARATION OF BIOFUEL BY DECARBOXYLATION OF NATURAL CARBOXYLIC ACIDS

Romanova Anastasiya, Shvets Valeriy, Suchkov Yury, Korneev Igor

*D.I. Mendeleev University of Chemical Technology of Russia, Moscow,
Miuskaya sq., 9, liceistka2003@mail.ru*

The world's fossil fuel resources – including crude oil, natural gas and coal – are huge, however they will be exhausted sooner or later. There is already fossil fuel deficit leading to a rise of motor fuel prices. As a result use of renewable energy sources expands steadily. Thus, the most significance acquires a biofuel produced from vegetable oils, animal fats, or its derivatives, particularly, fatty acids.

In literature there are a lot of works devoted to the process of producing the biofuel engine (biodiesel, ethanol, methanol etc.) In the current report we present results of investigation of process for production of biofuel by decarboxylation of fatty acids, which in perspective should be a key stage in obtaining hydrocarbons containing 15-21 carbon atoms. This type of fuel can be termed as biofuel II generation.



The influence of reaction conditions (such as temperature, pressure, catalyst type and feed rate of stock) on conversion and selectivity of process decarboxylation of fatty acids was investigated and optimal ranges of these parameters were determined.

As a catalyst the series of compounds from a number of industrial catalysts of hydrorefining, individual and supported zeolites and many others, were tested. It was found that the most efficient catalysts are γ -alumina and supported zeolites, which can be recycled.

DEVELOPMENT OF AN EFFICIENT METHOD OF POLYMER WASTE RECYCLING

**Rustamov M.I., Abad-zade Kh.I., Mukhtarova G.S., Gadirov Kh.G.,
Efenfdiyeva N.Kh., Farzullayev T.S., Ibragimov R.H.**

*Azerbaijan NAS Institute of Petrochemical Processes,
Azerbaijan Republic, Az1025, Baku, Khojali Aavenue, 30,
Fax: (+99412) 490-24-76; E-mail: gulermuxtarova@yahoo.com*

World production of plastics increases by 5-6% yearly, and is estimated to reach 250 million tons by 2010. Increase of volumes of polymeric products consumption leads to accumulation of non-decaying waste. Each year world population produces an enormous mountain of waste – about 400 million tons. It consists mostly of polymeric and plastic waste. Large part of polyethylene terephthalate (PET), polyethylene (PE) and other polymers waste is either buried into the ground or incinerated, which is unreasonable from financial point of view, and even harmful in terms of ecology. The issues with recycling of PET bottles and PE plastic bags are remaining unsolved due to lack of original and non-expensive technologies of reprocessing.

As a solution for the problem, we have developed a technology of different kind plastic waste recycling by means of joint hydrocracking with fuel oil in presence of catalyst, resulting in motor fuels production.

After hydrocracking of fuel oil with PE, petrol with octane number of 60-67 points, contains 0-0.3% of benzene, and acts as a high-quality raw material for reforming. Cetane number of diesel fraction is about 53.3-54 points.

As a result of hydrocracking, PE and PET are depolymerized into simpler non-toxic compounds, and their mixture is further processed in presence of catalyst, together with fuel oil products, resulting in fuel fractions output. Light fractions yield at fuel oil hydrocracking with addition of polymers reaches about 90%, as compared with 70% yield without polymers under the same conditions.

CATALYTIC COMBUSTION OF WOOD CHIPS IN CONICAL SPOUTED BED

María J. San José, Sonia Alvarez, Luis B. López, Iris García

Departamento de Ingeniería Química. Universidad del País Vasco. Aptdo 644. 48080 Bilbao. Tel. 34-946015362, Fax 34-946013500, e-mail: mariajose.sanjose@ehu.es

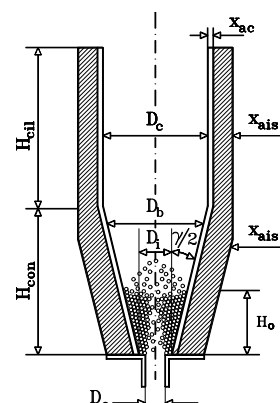
Spouted bed technology is suitable for thermal treatment of wastes. In previous papers, stable operating and non-segregation conditions of beds consisting of coarse particles [1-3]. and of sawdust and mixtures of wood wastes [4] and of catalyst solids [5] and thermal treatment by combustion of biomass [6-7] and of cork wastes [8] have been studied in conical spouted beds.

In this paper, a conical spouted bed combustor have been started up and tuned for catalytic combustion of wood chips with Pd catalyst.

The experimental unit designed at pilot plant scale basically consists of a blower, an electric resistance for preheating the air, a solid feeding system, thermocouples at several positions in the contactor and two high efficiency cyclones. The reactor utilized, at pilot plant scale, shown in the Figure, cone angle, $\gamma = 36^\circ$, is made of AISI-310S heat-resistant stainless steel, thermally insulated.

The solids used have been wood chips ($d_p = 25$ mm, $\rho_s = 540$ kg/m³, Geldart group D) and Pd/Al₂O₃ ($d_p = 0.11$ mm, $\rho_s = 378$ kg/m³, Geldart group A).

The performance of catalytic combustion of wood chips in the new combustor has been run out and results prospects an environmental improvement.



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ZEOLITE COATINGS ON SUGAR CANE BAGASSE: A WAY TO ACHIEVE ENHANCED SELECTIVITY IN ACID CATALYSIS?

Marcelo M. Pereira¹, Margareth Rose L. Santos¹, Luciana T. Santos², Fabien Ocampo³, Benoit Louis³

¹*Federal University of Rio de Janeiro, CT, bloco A, 6º andar, 628, CEP 21941-909, RJ, Brazil – FAX 55-21-2562-7251, maciel@iq.ufrj.br*

²*Nacional Agency of Petroleum, Av. Rio Branco, 65, CEP 20090-004, RJ, Brazil*

³*Laboratoire des Matériaux Surfaces et Procédés pour la Catalyse, UMR 7515 du CNRS, University of Strasbourg, 25 rue Becquerel 67087 Strasbourg Cedex 2, France*

French fries-like ZSM-5 zeolite crystals with a size ranging between 50 and 100 nm were grown on sugar cane bagasse surface. Aligned zeolite crystals were allowed to grow using a combination of supramolecular templating and conventional self-assembly of template cations and silica species. A relationship has been established between the chemical composition of the vegetal and the morphology and aggregation degree of zeolite crystals.

Zeolite nanocrystals, grown on the sugar cane substrate, allow enhanced diffusional properties in comparison with purely microporous zeolite materials. Their catalytic behavior in n-hexane cracking reaction led to a higher selectivity toward light olefins. Higher selectivities to propylene and ethylene were reached with structured mesoporous ZSM-5 zeolite. This higher selectivity toward light olefins (alkene/alkane ratio about 20% higher than conventional ZSM-5 zeolite. This result suggests that improved diffusion properties within the hierarchical porosity are induced within these nano French-fries like zeolite crystals.

The double novelty consists in the synthesis of hierarchical zeolite microspheres (diameter about 1µm) formed by the self-aggregation of many French-fries like nanocrystals (see Figure 1). In addition, a renewable vegetal source can be used as a supramolecular template in replacement of expensive polymers.

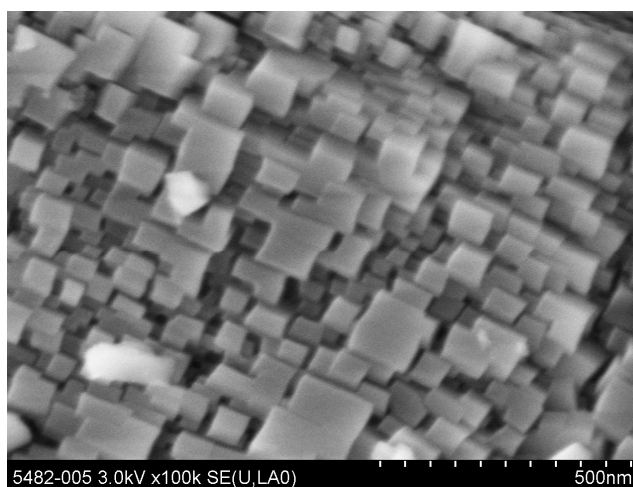


Figure 1 - Self-organized nano-French fries shaped ZSM-5 zeolite crystals.

USE OF PATENT APPLICATIONS AS TECHNOLOGICAL INDICATORS ON THE ETHANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS IN BRAZIL

**Luiz André F.S. Schlittler¹, Edelvio de Barros Gomes²,
Adelaide Maria S. Antunes³, Nei Pereira Junior⁴**

^{1,2,4}*Dep. of Biochemical Engineering – Federal University of Rio de Janeiro
Av. Athos da Silveira Ramos, 149 / bl. E – lab. 121
Rio de Janeiro – RJ – Brazil. Zip: 21.941-909 / P.O. BOX: 68542
E-mail: lafelizardo@yahoo.com.br*

³*Dep. Of Chemical Engineering – Federal University of Rio de Janeiro
Av. Athos da Silveira Ramos, 149 / bl. E – I. 2000 – SIQUIM
Rio de Janeiro – RJ – Brazil. Zip: 21.941-909*

The trends of the industry, nowadays, go towards cleaner technologies to reduce environmental pollution. Biotechnology offers environmental, social and economic advantages that can be considered important factors to develop sustainable actions, especially in rural communities. The lignocellulosic biomass is the richest source of carbohydrates in the world and, in the past, due to lack of sustainable technologies, it has not been properly exploited. Today, there are available technologies to turn the polymeric structure into building blocks for the production of biofuels and chemicals, suggesting a new conception of process integration, which has been denominated Biorefinery. This work screened the state of art of the ethanol production technologies from lignocellulosic biomass using patent applications in the Brazilian Institute of Industrial Property (*INPI*) until the year of 2009. The work is shared in three topics: Pretreatments, enzymes production and ethanol production processes. There are 36 applications of pretreatment technologies which 75% belong to American continent institutions (20 North American and 7 Brazilian) and most of it dealing with diluted acid pretreatment. On the subject of enzyme production there are 38 patent applications and, among these, 14 belong to Danish companies, focus on Novozymes with 12 applications, and 7 to North Americans. Most of these applications are related with cellulases and hemicellulases utilization on the textile industry. On the ethanol production processes from lignocellulosic biomass there are 31 patent application and, in this case, Brazil is has the majority (12 applications), followed by United States (9 applications) and Finland (3 applications). It is notorious the expertise of the Brazilian institutions on the production of first generation ethanol, which is being transferred to the second (agricultural residues) and third generations (macroalgae).

PREPARATION OF ADVANCED ADSORBENTS AND CATALYST SUPPORTS BY PROCESSING OF RICE HUSK

Shikina N.V.¹, Ismagilov Z.R.¹, Andrievskaya I.P.¹, Rudina N.A.¹,
Mansurov Z.A.², Biisenbaev M.A.², Zhandosov Zh.M.²

¹*Borekov Institute of Catalysis SB RAS, 630090, Novosibirsk, Russia,
5, Pr. Akad. Lavrentieva, zri@catalysis.ru*

²*Al-Faraby Kazakh National University, 050038, Almaty, Kazakhstan,
71, al-Faraby av.*

Rice husk (RH) is a valuable secondary material obtained during production of commodity rice. As much as 550 million tons of rice husk are accumulated annually in rice-producing countries. RH is characterized by high concentration of ashes (more than 20%) consisting mostly of amorphous SiO₂. Meanwhile, RH is a lignocellulose biomass that can be used as a precursor for synthesis of carbon materials with developed porous structure by special processing. The RH processing includes carbonization followed by physical (CO₂, water vapor) or chemical (KOH, NaOH, K₂CO₃, ZnCl₂, etc.) activation of the carbonized rice husk (CRH) at 650°C or higher temperature. The CRH activation yields microporous carbon materials with high specific surface area and pore volume. However, it is necessary to develop mesoporous structure and lift steric limitations to use them for adsorption of heavy metals, radioactive nuclides, and organic pollutants or as catalyst supports.

We developed a SiO₂ leaching method for the predominant formation of mesopores necessary for the catalyst supports or adsorbents. We studied RH carbonization in the Ar atmosphere, developed a CRH leaching method, demonstrated the formation of honeycomb monoliths from CRH and applicability of the SiO₂ leaching method for the formed monoliths. The mesoporous CRH and carbon monoliths were studied at all the synthesis stages by a complex of physicochemical methods: BET, SEM, XRD, AAS and determination of the mechanical strength. The developed method makes it possible to remove 90-95% of SiO₂ from the material matrix, increasing S_{BET} from 167 to 400 m²/g and V_Σ from 0.1 to 0.4 cm³/g, and yielding a material with the fraction of mesopores (D_{pore}=30-100 nm) about 85-90%. The prepared monoliths are characterized by S_{BET} exceeding 300 m²/g, V_Σ = 0.3 cm³/g and high mechanical strength. In the presentation we shall demonstrate examples of the tests and application of the synthesized materials.

PRODUCTION OF KETAL OF GLYCERIN – POTENTIAL MOTOR FUEL WITH HIGH ANTIKNOCK PROPERTIES

Maximov A.L., Shlyakhtitsev D.S., Nekhaev A.I.

*A.V. Topchiev Institute of Petrochemical Synthesis RAS, 119991 Moscow,
Leninsky prospect, 29, nekhaev@ips.ac.ru*

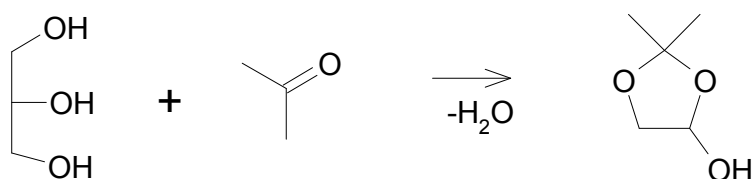
The problem of search of renewable energy sources arises because of the increasing consumption of fuels and limitedness of petroleum reserves. One of inexhaustible sources for fuel producing is vegetable biomass of our planet.

Glycerin is easily generated by hydrolysis of natural oils and also as the large-tonnage co-product of interesterification of vegetable oils with methanol for the purpose of production of biodiesel, which is a substitute for petroleum diesel fuel.

Acetone is an available and relatively cheap product of petrochemical synthesis and also the co-product of biotechnological production of biobutanol. Ketal, that is a product of reaction between acetone and glycerin, is not only a good motor fuel, but also possesses high antiknock properties.

Interaction between acetone and glycerin was led in flow reactor heated by cylindrical electrical oven. Initial products were fed into mixing junction with high-pressure pumps. Reaction products were identified by the instrumentality of chromatography-mass spectrometric method, current analyses were made with chromatograph Kristalux-4000M.

As catalytic agents were tested cationite KU-2, zeolites β , ZBM, NaX. The highest product yields were achieved by using of zeolite β .



HYDROGENATION OF CIS-METHYL OLEATE OVER PLATINUM GROUP METALS: CIS-TRANS ISOMERIZATION IMPACT

Irina Deliy¹, Nicoletta Ravasio², Rinaldo Psaro², Irina Simakova¹

¹*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia,*

E-mail: simakova@catalysis.ru

²*ISTM-CNR, Milano, Italy*

Hydrogenation of vegetable feedstocks over the platinum group metals could be carried out at the milder conditions (lower temperature and hydrogen pressure) in comparison with Ni catalysts to produce oils both for food and for industrial application [1]. In the previous work on methyl linoleate hydrogenation over Pd/MgO [2, 3] it was shown that at methyl linoleate conversion up to 95 % the reaction product is the mixture of cis- and trans-isomers of methyl oleate while methyl stearate is practically missing in the reaction mixture. The cis-trans isomerization rate increases sharply after complete methyl linoleate conversion to methyl oleate.

In the present work the monounsaturated oleic acid methyl ester was chosen as model compound for studying of competitive hydrogenation and cis-trans isomerization of unsaturated fatty acids methyl esters over carbon supported VIII group metals.

The liquid phase hydrogenation and isomerization of cis methyl oleate over Pd/C, Ru/C, Rh/C, Pt/C and Ir/C catalysts were investigated in the temperature range of 298-373 K and hydrogen pressure within 1-10 bar using n-octane as a solvent. The platinum group metals supported on carbon catalysts were prepared by the deposition-precipitation method on the carbon support Sibunit as already reported [4] and characterized by N₂ physisorption, XRD, HREM. GLC, ¹³C-NMR and FTIR techniques were employed to characterize the reaction products.

The initial hydrogenation rates of methyl oleate over Pd/C, Ru/C, Rh/C, Pt/C and Ir/C catalysts were estimated. It was shown that the most active catalysts for the cis methyl oleate hydrogenation are the Pt/C and Rh/C catalysts. The Ir/C catalyst has the low catalytic activity in hydrogenation. Over the explored catalysts the processes of cis methyl oleate double bond isomerization and hydrogenation took place concurrently. Among the studied catalysts based on Group 8 metals the highest catalytic activity in the cis methyl oleate hydrogenation with minor methyl elaidate formation is revealed over Pt catalyst.

The reaction scheme of cis methyl oleate hydrogenation and cis-trans methyl oleate isomerization was proposed for the kinetic modeling. A good agreement between the estimated kinetic curves and the experimental data for the isomerization and hydrogenation of methyl oleate over group 8 metals supported on carbon was obtained. The estimated kinetic parameters calculated for all investigated catalysts (Pd/C, Rh/C, Pt/C, Ru/C and Ir/C) and the effective activation energies, E_a^* , for the methyl oleate hydrogenation and cis-trans isomerization steps are obtained from effective kinetic constants at various temperatures using the Arrhenius equation.

The influence of the catalyst amount, stirring rate, cis methyl oleate concentration, reaction temperature, and hydrogen pressure on the cis-trans isomerization rate during methyl oleate hydrogenation were investigated. The highest catalytic activity in the cis methyl oleate hydrogenation with minor methyl elaidate formation is revealed over Pt/C catalyst. It is concluded that fatty acids methyl esters hydrogenation over platinum metals at mild conditions is the promising way for selective cis methyl oleate preparation.

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CAVITATION ASSISTED DESIGN OF CATALYSTS

Ekaterina V. Skorb¹, Daria V. Andreeva²

¹Chemistry Department, Belarusian State University, Leningradskaya, 14, Minsk 220030, Belarus, E-mail: skorb@bsu.by

²Chair of Physical Chemistry II, University of Bayreuth, Universitatstr., 30, Bayreuth 95440, Germany, E-mail: daria.andreeva@uni-bayreuth.de

Here, we explored a novel reagent-free approach to form nanoscale mesoporous composites which could be effectively used as catalytic materials in aqueous media using a high-intense ultrasound as a tool. The short-lived, localized ultrasonic cavitation microbubble in ambient conditions of the bulk solution is characterized by temperatures of roughly 5000 K, pressures of about 1000 atmospheres, lifetimes considerably below a microsecond, and heating and cooling rates above 10^9 degrees per second inside the cavitation microbubble, which allow one to perform physical and chemical processes in highly non-equilibrium conditions.

One step formation of catalytic systems (example: Al-Ni catalyst)

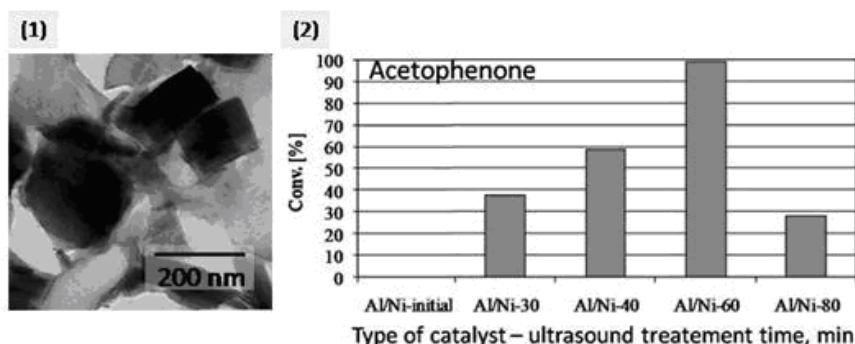


Fig. One step formation of Al/Al oxide/ Ni mesoporous system: TEM microphotograph of nickel particles distributed in the porous aluminium support (1); effect of sonication time on efficiency of Al/Al oxide/Ni catalyst in hydrogenation of acetophenone (2).

We performed the highly-intense ultrasound treatment (maximum intensity was calculated to 57 W/cm^2 at a mechanical amplitude $81 \mu\text{m}$) of aluminum-nickel alloy dispersion in aqueous medium. It leads to the formation of sponge-like structure and also results in phase segregation yielding nickel nanoparticles distributed in the pores as evidenced by TEM micrograph given in Fig. The system formed after 60 min of alloy treatment in a standard reaction of hydrogenation exhibits >99% conversion of acetophenone (Fig.) and a very high selectivity in hydrogenation of ketones due to a very narrow pore distribution in mesoporous metal system formed by ultrasound. The developed method makes possible to control the sponge morphology and can be used for formation of modern types of catalysts. For example, the sonication technique allows one to combine into the single step the fabrication of mesoporous support and distribution of metal (Cu, Pd, Au, Pt etc.) nanoparticles in its pores.

HYDROCONVERSION OF VEGETABLE OILS INTO HYDROCARBON-BASED BIODIESEL OVER NONSULFIDED CATALYSTS: APPLICATION OF SUPPORTED MOLYBDENUM CARBIDE

Skorpluk A., Lavrenov A., Chumachenko Yu., Drozdov V., Trenichin M., Gulyaeva T., Arbuzov A., Kudrya E., Leontieva N.

*Institute of Hydrocarbons Processing SB RAS, Russia, Omsk, Neftezhavodskaya 54,
Fax +7-3812-64-61-56, E-mail: lavr@ihcp.oscsbras.ru*

Vegetable oils can be hydroconverted to produce straight chain alkanes ranging from C₁₂ to C₁₈. These alkanes have high cetane numbers and can be used as an alternative diesel biofuel. Hydroconversion of vegetable oils into hydrocarbons supposes elimination of oxygen. It has been found that conventional hydrotreating catalysts, such as sulfided Co(Ni)-Mo(W) supported on porous matrix, are suitable for deoxygenation of vegetable oils. However, the application of sulfided catalysts in hydroconversion of neat vegetable oils requires the addition of sulfur-containing compounds in the process for keeping the catalyst activity and lifetime. This paper presents the results of sunflower oil hydroconversion using supported molybdenum carbide catalysts. The aim is to describe in details the effect of molybdenum content and the influence of reaction conditions on yield and composition of gas-phase and liquid products. A series of γ -Al₂O₃ – supported catalysts (5-20 nominal wt% Mo) were prepared via temperature-programmed reaction of supported molybdenum oxide with CH₄/H₂ mixture. Catalysts were characterized with BET, XRD, HREM, FTIR, TPR H₂, TPO O₂, TPD NH₃ and CO chemisorption. Catalytic experiments were carried out in fixed-bed reactor. To determine the significant factors for the hydroconversion of sunflower oil, a 2^k experimental design was used to plan the experiment. The reaction temperature, pressure and WHSV were varied in the range of 300-350°C, 2-4 MPa and 1-5 h⁻¹, respectively. The hydrogen to feedstock ratio was constant. Selective conversion of vegetable oil into hydrocarbons was achieved at 350°C and 4 MPa over the catalyst with 10 wt% Mo. The results showed that molybdenum carbide catalyst gave up to 87% yield of liquid products. It was determined that liquid products contained mostly alkanes C₁₈ (up to 66 wt.%) and alkanes C₅-C₁₇ (up to 18 wt.%). Furthermore, the gas-phase analysis demonstrated that the reduction reaction was more profound over the molybdenum carbide catalyst, while the decarboxylation and decarbonylation reactions were more evident over the sulfided and metallic catalysts.

KINETICS OF CATALYTIC GASIFICATION OF LIGNITE WITH CARBON DIOXIDE BY THERMOGRAVIMETRY

Vergel Bungay¹, Byungho Song¹, Sangdone Kim², Jungmin Sohn³,
Yongjeon Kim⁴, Gyootae Kim⁴, Sam R. Park⁴

¹Chemical Engineering Department, Kunsan National University, Gunsan, Jeonbuk 573-701, Korea, bungayvc@live.com; bhsong@kunsan.ac.kr

²Department of Chemical and Biomolecular Eng., KAIST, Daejeon 305-701, Korea
Kimsd45@kaist.ac.kr

³Department of Mineral Resources & Energy Eng., Chonbuk National University, Jeonju, Jeonbuk 561-756, Korea, jmsohn@jbnu.ac.kr

⁴SK Energy Institute of Technology, Daejeon 305-712, Korea

yikimej@skenergy.com; gtkim@skenergy.com; srpark@skenergy.com

The catalytic effect on the gasification rate of lignite with CO₂ was determined by the thermogravimetric method. The tested catalytic single salts are K₂CO₃, Na₂CO₃, K₂SO₄ and FeSO₄. The gasification experiments were carried out by using lignite coal loaded with 5-15% catalyst at temperature ranging from 600°C to 900°C and ambient pressure with N₂-CO₂ reactant gas mixture. The kinetic parameters were determined by the modified volumetric reaction model. Potassium carbonate exhibits the highest catalytic activity at the given temperature and catalyst loading. It was observed that complete carbon conversion was obtained within 10 min with the catalyst at 800°C in the following catalytic activity as K₂CO₃ > Na₂CO₃ > K₂SO₄ > FeSO₄. Enhancement of the gasification rate is found to ranged from 1.5-18 times that of the uncatalyzed reaction. Activation energy of the gasification with K₂CO₃, Na₂CO₃, K₂SO₄, and FeSO₄ are found to be 124.9, 134.6, 201.9, and 155.0 kJ/mol, respectively, as within the range reported in the literature [1-3]. The apparent reaction rate of catalytic coal gasification is proposed for each catalyst.

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EFFECT OF RESIDENCE TIME OF THE ACIDIC AND BASIC HYDROLYSIS OF THE SUGARCANE BAGASSE ON THE FEEDSTOCK AND PYROLYSIS DERIVATIVE BIO-OIL PROFILES

Matheus O. Souza¹, Marcelo M. Pereira¹, Margareth Rose L. Santos¹,
Luciana T. Santos², Josilaine A. Cunha¹ and Ligia M. M. Valente¹

¹Federal University of Rio de Janeiro, CT, bloco A, 7º andar, RJ, CEP 21941-909, Brazil, FAX 55-21-2562-7240, m.oliveira13@ig.com.br

²Nacional Agency of Petroleum, Av. Rio Branco, 65, RJ, Brazil

The use of agricultural residues as a potential resource of renewable energy has been worldwide investigated and it seems to be very attractive and opportune to utilize sugarcane bagasse for the Brazilian energy needs. This work reports the influence of the residence time of the acidic and alkaline pretreatment of sugarcane bagasse on the biomass feedstock and on the Low Temperature Conversion (LTC) pyrolysis derivative bio-oil profiles. Hydrolyses were carried out at 120°C in acidic (HCl 2M) and basic (NaOH 2M) moiety by 1, 3 and 5 h. Both non- and pretreated biomasses were analyzed by FTIR. The LTC-pyrolysis experiments were performed in a home-made «U» type glass reactor apparatus under N₂ atm at 20-120°C (5°C/min rate), 120-350°C (10°C/min) and then 350°C by 15 min. The liquid fraction, condensed at the reactor outlet, was extracted with acetone. The solvent was removed at low pressure and the oily residue was analyzed by ¹H NMR at 200 MHz in acetone-d₆. The comparative FTIR feedstock spectra profiles of the hydrolyzed and non-hydrolyzed bagasses showed, independent of the time of reaction, a strong decrease in the lignin and hemicellulose content for the alkaline hydrolyzed bagasse and just a significant decrease on the hemicellulose content for the acidic hydrolyzed bagasse. The comparative ¹H NMR bio-oil spectra profiles showed through the correlation among the peak areas at 3-5 ppm (carbohydrates) and those at 9-10 ppm (furfurals) plus those at 6-8 ppm (phenyls+furfurals) an increase of carbohydrate content after acidic hydrolysis, independent of the reaction time, and the maintenance of the carbohydrate content with a discrete increment along the increase of the reaction time after the basic hydrolysis. Thus it can be concluded that the hydrolysis pretreatment, independent of the resident time, affect the composition of both sugarcane bagasse and its pyrolysis bio-oil derivative profiles. In addition the yield % of the bio-oil obtained from the acidic hydrolyzed bagasse was 2.4 times greater than those obtained from the basic hydrolyzed bagasse.

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ORGANOSOLV LIGNIN AS CHEMICALS PRECURSOR**Ana Toledano, Araceli Garcia, Jalel Labidi**

Chemical and Environmental Engineering Department, University of the Basque Country, Plaza de Europa 1, 20018, Donostia-San Sebastian, Spain
jalel.labidi@ehu.es

Biomass is a promising source of different by-products that can be transformed into high value added products. Lignocellulosic biomass availability for 2010 in the UE is approximately 140 Mtoe and this type of biomass could assume a yearly supply of approximately 200 billion metric tons worldwide. This type of biomass is mainly composed by cellulose, hemicelluloses and lignin. Lignin is the second most abundant polymer and the only biomass constituent based on aromatic units. Lignin's native structure suggests that it could play a central role as a new chemical feedstock in the formation of supramolecular materials and aromatic chemicals. [1]

In this work under development, organosolv based biorefineries are being developed to produce high quality lignins. Organosolv treatments are considered as clean technologies with reduced environmental impact and constitute a good approach for the complete utilisation of plant biomass as a source of fibres and chemicals [2]. Organosolv lignin is industrially interesting because it is a sulphur free lignin and presents lower molecular weight. Despite the low molecular weight, organosolv lignin macromolecule, like other types of lignins, is characterized by broad molecular weight distribution. The obtaining of lignins with specific molecular weight and homogeneous properties is a key point for further transformation of the lignin. Ultrafiltration technology is an effective process to produce different fractions of lignin with specific molecular weight and uniform properties [3].

Specific lignin fractions can be catalytically transformed more easily as the obtained fractions will present homogenous properties. The lowest molecular weight fraction can be considered for the productions of chemicals such as phenols, benzene, toluene... by using selective hydrogenolysis catalyst and other catalytic reactions. Oxidative processes can be taken into consideration to produce derived aldehydes, acids. The development of efficient catalytic technologies is required to make lignin a profitable stream in the biorefinery process.

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CERAMIC MEMBRANES IN THE PROCESSES OF VAPOR CONVERSION OF ETHANOL AND ACETIC ACID AS THE MAIN PRODUCTS OF BIOMASS FERMENTATION

Uvarov V.I., Borovinskaya I.P., Malevannaya I.G.

*Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka,
Moscow region, 142432 Russia. E-mail: uvar@ism.ac.ru*

The paper is dedicated to obtaining high-temperature, corrosion-resistant, mechanically strong nano-porous structures by self-propagating high-temperature synthesis and producing efficient membranes based on the structures for vapor conversion of ethanol and acetic acid as the main products of biomass fermentation. At first the «gas-kinetic model» of porous structure formation during SHS was considered and Laplace's equation was used for determining the pore size. The metal melts in the combustion wave and spreads with a liquid layer formation. If in this case the pressure of the liquid vapor and impuritive gases in the liquid is higher than the external pressure, the open porosity of the final product (membrane) is formed at fast cooling.

The conditions of the open and closed porosity formation were defined; the zone of conversion of the closed porosity of the synthesized material to its open value was also found. It allows controlling the structure and pore size in the obtained graded nano-porous SHS materials, i.e. membranes.

Using the «gas-kinetic model», we developed the modes for synthesizing catalytically active high-porous ceramic carriers of membrane-catalytic systems based on refractory inorganic compounds Ni-Al-Co; Ni-Al-Co/NiO, Ni-Al-Mn, Ni-Al-Ti, Ni-Al/NiO with the following characteristics:

Open porosity, %	40 – 58
Pore size, μm	10 – 0.01
Bending strength, MPa	50 – 60
Specific surface, m^2/g	3 – 10

The structure of the samples was studied with an electronic microscope, the structural analysis was carried out using an X-ray microanalyser. A membrane-catalytic module with gas consumption of up to $25 \text{ m}^3/\text{h}$ was made.

The catalytic layer of metal oxides was formed inside the membrane channels by the sol-gel method using organic solutions of metal-complex precursors in toluene

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which were taken in preset quantities for obtaining oxides of the preset composition with introduction of the agents stabilizing the mother liquor.

Pipe-like microporous membranes of 15 mm in diameter and 130 mm in length were used as initial membranes.

The mother liquors of metal-complex precursors were pumped through the membrane in order to modify the internal surface of the channels. Then the membrane was blown through with the moistened heated air, dried in vacuum (1 Torr), and heated at various modes.

A membrane-catalytic module with gas consumption of up to 25 m³/h was made. The membrane-catalytic system containing palladium particles as an active component was used to study the process of vapor conversion of ethanol and acetic acid as the main products of biomass fermentation. The initial mixture composition corresponded to that of the fermentation products (a substrate/H₂O – 10-12). The specific activity in hydrogen formation was 600 l/dm³_{membr}h and 400 l/dm³_{membr}h for acetic acid and ethanol, respectively.

CONVERSION OF SACCHARIDES INTO FURANIC ALDEHYDES USING 1-ETHYL-3-METHYLIMIDAZOLIUM HYDROGEN SULFATE

Anabela A. Valente¹, Sérgio Lima¹, Margarida M. Antunes¹, Patrícia Neves¹, Martyn Pillinger¹, Nikolai Ignatyev²

¹*CICECO, Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-106, Aveiro. E-mail: atav@ua.pt*

²*PC-RL, Ionic Liquids Research Laboratory, Merck KGaA, Frankfurter Str. 250, D 64293, Darmstadt, Germany*

Carbohydrates are among the most abundant organic compounds on earth and represent the major portion of the world's annually renewable biomass. Sources of carbohydrates include conventional forestry, wood processing by-products, agricultural crops and surpluses, and plants grown on degraded soils, etc. The bulk of the carbohydrate-biomass comprises di/oligo/polysaccharides (e.g. hemicelluloses, cellulose, starch, inulin, sucrose), which by hydrolysis form sugars, such as xylose, arabinose, glucose and fructose. The partial dehydration of monosaccharides can form furfural (FUR) from pentoses (e.g. xylose) and 5-hydroxymethyl-2-furaldehyde (HMF) from hexoses (e.g. fructose, glucose). These reactions may be accelerated by the use of Brønsted or Lewis acid catalysts.

The one-pot hydrolysis/dehydration of mono/di/polysaccharides into FUR or HMF in the presence of an acidic ionic liquid, 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM][HSO₄]), at 100 °C, was investigated [1]. [EMIM][HSO₄] is promising for FUR and HMF production from xylose, fructose or related polysaccharides (e.g. 84% FUR yield at 6 h from xylose; 88% HMF yield at 30 min from fructose). Better results were achieved with [EMIM][HSO₄] than with aqueous H₂SO₄, under similar conditions. In the case of the xylose to FUR conversion, reaction/solvent extraction and reaction/evaporation systems were investigated for simultaneous reaction and product separation and for both the acidic medium could be reused.

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EXTRACTION OF HUMIC ACIDS FROM ACTIVATED SLUDGE

Vialich E.A., Ilarionov S.A., Degtev M.I., Maksimov A.S.

Perm State University, Perm, Russia, eavel@rambler.ru

Soil productivity is connected with the content of humic matter in soil. Nowadays humic acids find a wide application in different areas of human activity. These compounds are applied to produce fertilizers in agriculture; to obtain antifungal agents in medicine; to remediate oily soil and water; to accelerate and improve food industry processes (processes of fermentation in cultured dairy products, beer, wine, etc). They are also used in the product of biologically active food additives in diets of cattle and in industrial technological cycles (mining industry and oil extraction). The basic raw materials for extracting humic acids are coal, peat and sapropel. These raw materials are formed for a long time and can be used to obtain other products. Therefore, the search for a new source of raw materials to extract humic acids is a pressing problem.

For extracting humic acids, we have used waste activated sludge from treatment facilities. This activated sludge was previously filtered to remove moisture. The humic acids extraction was carried out according to a standard procedure, using a 0.1 n NaOH solution [1]. The alkaline solution was boiled for an hour to increase humic acids output. The obtained humic acids were analysed by: polyacrylamide gel electrophoresis, infrared spectroscopy and their elemental composition was determined. Humic acids extracted from sod-podzol soil were used as a control sample.

The obtained results demonstrate a close similarity humic acids extracted from sod-podzol soil and from activated sludge. The humic acids output percent determined by gravimetric methods is 50 %. According to the obtained data, one can conclude that the humic acids are similar to typical ones.

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THE EFFECT OF IMPURITIES ON THE CATALYTIC ACTIVITY OF ANTRAQUINONE IN THE PROCESS OF DELIGNIFICATION

Menshikov S.Yu.¹, Vurasko A.V.², Driker B.N.², Mikushina Yu.V.¹, Eryomin D.V.¹

¹*Institute of organic synthesis URAL Branch the Russian Academy of Science, st. S.Kovalevskoj/Akademicheskaya, 22/20, Ekaterinburg, 620219, Russia*

²*Ural state forest engineering university, Siberian highway, 37, Ekaterinburg, 620100, Russia
Fax: (343)3741189; E-mail: vurasko2010@yandex.ru*

Kinetic and thermodynamic parameters were determined in the reaction of reduction of anthraquinone (AQ) in water-alkaline solution. Reversible reaction AQ-anthrahydroquinone (AHQ) is dependent on a number of factors, basic of which are: presence a lignine-carbohydrate complex, alkaline conditions, temperature. It is obvious, that catalytic activity and ability AQ to reduction are interconnected and defined by rate and depth of transformation in AHQ. It is obvious, that the quality indicators resulted in specifications, in an insufficient degree characterize ability AQ to reduction. As objects of research used samples AQ obtained by synthesis from phthalic anhydride and benzene (AQP), AQ, received by gas-phase anthracene oxidations and AQ - withdrawal (AQW) of the same process. Interpretation of the experimental data on reduction AQ spent on the equation of formal kinetics. In spite of the fact that process of reduction AQ is homogeneous-heterogeneous reaction, it's quite well described on concentration of AHQ in a reaction mixture by the equation $C = a(1 - e^{-KT})$. On the basis of data on temperature effect on initial rate of formation AHQ are estimated kinetic and thermodynamic parameters (energy of activation, Gibbs energy, enthalpy and entropy of activation) for samples AQ various ways of reception.

Temperature, °C	Wo, mol/l·min	Energy of activation, KJ/mol	ΔG^* , KJ/mole	ΔH^* , KJ/mol	ΔS^* , KJ/deg·mole
40 AQP	0.00224	97.1247	99.6494	94.5237	-0.0161
60 AQP	0.01032		93.6315	94.3575	-
70 AQP	0.0436		94.5256	94.2744	-0.0001
50 AQW	6.1733	66.2504	68.7516	63.5663	-0.0160
60 AQW	19.325		70.9645	63.4832	-0.0225
70 AQW	26.462		73.1799	63.4001	-0.0285

THE INVESTIGATION OF ASPECTS OF TRANSESTERIFICATION HYDRODYNAMIC DURING BIODIESEL PRODUCTION

Zernina I.A., Kazakov D.A., Volkhin V.V.

Perm State Technical University, Perm, Russia

Biodiesel is attracting attention as alternative fuel for diesel engines. This fuel is renewable, non-toxic, biodegradable fuel, and it has low emissions [1]. According to chemical structure biodiesel fuel is a mixture of methyl or ethyl monoesters of fatty acids, produced from oils by transesterification reaction. The system, where the transesterification occurs, is heterogeneous, reactants are immiscible in each other. The mass transfer of reactants could limit the rate of reaction [2,3]. Enhance of the reagents transfer could intensify the biodiesel production process. The goal of work is to find out the principle aspects of transesterification reaction mechanism and the behavior of catalyst in the reaction area under various hydrodynamic conditions.

The comparison of natural and used frying oils compositions was done. It is shown, that the contents of fatty acids are similar in the natural and used oils. Experimental results showed that used frying oil has high free fatty acid level. The comparison of natural and used oil transesterification was done. Experimental data showed that the compositions of biodiesel from natural and used oil are identical.

The study of agitation intensity influence was done. Experimental data demonstrate that the yield of ethers increase over the range of the impeller Reynolds number between 0 and $8,7 \cdot 10^5$. But there is delay in esters formation at high Reynolds number. We suppose that at high turbulence the drop diameter becomes small. Such drops have no internal circulation, have slow rate of surface renovation and lower mass transfer. Therefore this effect has negative influences on transesterification. The reaction has an optimum of Reynolds number, which is between $6 \cdot 10^5$ and $8,7 \cdot 10^5$. Investigated optimal condition allow us to reduce the time of reaction in 1,5 times.

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STEAM REFORMING OF BIOMASS-DERIVED GLYCEROL AND ETHANOL FOR H₂ PRODUCTION

Ziyi Zhong, Shici Duan, Chang Jie

Institute of Chemical and Engineering Sciences, A-star, 1 Pesek Road, Jurong Island, Singapore 627833. Zhong_ziyi@ices.a-star.edu.sg

Bioethanol and biodiesel are two most dominant products from biomass while glycerol is the major byproduct in biodiesel production. Steam reforming (SR) of glycerol and ethanol (EtOH) for H₂ production is attractive as the two feedstocks can be directly converted into H₂, which is a clean energy carrier [1]. In this investigation, Pt/C(activated carbon) and Rh/ZrO₂ catalysts were prepared by the sonication and the impregnation method respectively. The Pt/C catalyst was applied to catalyze the SR reaction of glycerol, while the Rh/ZrO₂ catalyst to SR reaction of EtOH. High catalytic activities were observed on the two catalysts above 400°C. However, at temperatures below 400°C, a fast deactivation was observed for them due to the accumulation of surface C-species. A detailed structure-catalytic property relationship and possible reaction pathways are also discussed.

Table 1. H₂ yield (moles of H₂ yielded per glycerol or EtOH) at 400°C.

Catalyst	1%Pt/C ^a	5%Pt/C ^a	5%Pt/C(commercial) ^a	1%Rh/ZrO ₂ ^b
H ₂ yield	2.3	3.2	2.7	5.5

a: SR reaction of glycerol; b: SR reaction of EtOH.

Reaction conditions: H₂O:EtOH=10:1, GHSV= 54000h⁻¹.

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LIST OF PARTICIPANTS

Neisiani ABDOLLAHI

Ecole Polytechnique de Montral
Office A-570.2

C.P. 6079, succ. Centre-Ville
Montréal Québec, H3C 3A7

Canada

Tel.: +1 514 340 4711

E-mail: mania.abdollahineisiani@polymtl.ca

Muthanna AL-DAHMAN

Missouri University of Science and Technology
MO 65409-Rolla

USA

Tel.: +573 341 4416

Fax: +573 341 4377

E-mail: aldahhanm@mst.edu

Daria ANDREEVA

University of Bayreuth
Universitätstr., 30
95444 Bayreuth

Germany

Tel.: +49 921 55 2750

Fax: +49 921 55 2059

E-mail: daria.andreeva@uni-bayreuth.de

Claudia ANTONETTI

University of Pisa
Via Risorgimento, 35
56126 Pisa

Italy

Tel.: +39 050 2219000

Fax: +39 050 2219260

E-mail: claudia.antonetti@ns.dcci.unipi.it

Alexey ANTONOV

D.I. Mendeleev University of Chemical
Technology of Russia
Miuskaya square, 9
125047 Moscow

Russia

E-mail: zest-alant@mail.ru

Donato ARANDA

Greentec -Federal University of Rio de Janeiro
Rua Nereu Ramos, 211, Cob 02
22795-080 Rio de Janeiro

Brazil

Tel.: +55 21 25627657

Fax: +55 21 25627657

E-mail: donato.aranda@gmail.com

Agnes ARDIYANTI

Department of Chemical Engineering
University of Groningen
Nijenborgh, 4
9747 AG Groningen

The Netherlands

Tel.: +31 50 3634486

E-mail: A.R.Ardiyanti@rug.nl

Michele ARESTA

CIRCC and University of Bari
Via Celso Ulpiani, 27
70126 Bari

Italy

Tel.: +39 0805442084

Fax: +39 0805443606

E-mail: m.aresta@chimica.uniba.it

Julia ARINICHEVA

A.V. Topchiev Institute of Petrochemical
Synthesis RAS

Leninsky pr., 29

119991 Moscow

Russia

E-mail: yaarinicheva@yandex.ru

Erwan ARZEL

COST
Avenue Louise 149
1050 Brussels

Belgium

Tel.: +32 2 533 38 17

Fax: +32 2 533 38 90

E-mail: erwan.arzel@cost.eu

Farida BABAYEVA

Institute of Petrochemical Processes of
Azerbaijan NAS
pr. Khojali, 30
Az1025 Baku

Azerbaijan

Tel.: 994-124902593

Fax: 994-124903520

E-mail: feridan@rambler.ru

Alexander BACHURIKHIN

N.D.Zelinsky Institute of Organic Chemistry
RAS

Leninsky pr., 47

119991 Moscow

Russia

Tel.: +7 499 137 29 44

E-mail: Shao-kahn@yandex.ru

Chingiz BARNAKOV

Institute of Coal and Coal Chemistry SB RAS
Rukavishnikova, 21

650610 Kemerovo

Russia

Tel.: +7 384 236 81 88

E-mail: han@kemnet.ru

Alexandra BELOGLAZOVA

Arkhangelsk State Technical University
Nabereznaya Severnoj Dviny, 17
163002 Arkhangelsk

Russia

Tel.: + 7 8182 287 673

Fax: + 7 8182 287 614

E-mail: bel-aleksa@yandex.ru

Sergey BELOSHAPKIN
Materials and Surface Science Institute
University of Limerick
Limerick
Ireland
Tel.: +353 61 234131
Fax: +353 61 213529
E-mail: serguei.belochapkin@ul.ie

Chesare BIFFI
Department of Physical Chemistry and
Electrochemistry
University of Milan
Via Golgi, 19
20133 Milano
Italy
E-mail: cesare.biffi@unimi.it

Dariusz BOGDAL
Cracow University of Technology
Warszawska, 24
31155 Krakow
Poland
E-mail: pcbogdal@cyf-kr.edu.pl

Mikael BOLS
University of Copenhagen
Universitetsparken, 5
2100 Copenhagen
Denmark
E-mail: bols@kemi.ku.dk

Irina BOROVKOVA
Perm State Technical University
Komsomolskii pr., 29
614990 Perm
Russia
E-mail: borovkova_irina_s@mail.ru

Evgeny BOYKOV
I.M. Gubkin Russian State University
of Oil and Gas
Leninsky pr., 65
119991 Moscow
Russia
E-mail: ev-boykoff@yandex.ru

Olga BUCHNEVA
University of Milan
Via Golgi, 19
20133 Milano
Italy
Fax: +39 02 50314300
E-mail: olga.buchneva@unimi.it

Vergel BUNGAY
Kunsan National University
Miryong-dong, 68
573-701 Jeollabuk-do
Korea
Tel.: +82 63 469 4201
Fax: +82 63 462 5334
E-mail: vcbungay@kunsan.ac.kr

Alexey BYCHKOV
Institute of Solid State Chemistry
and Mechanochemistry SB RAS
ul. Kutateladze, 18
630128 Novosibirsk
Russia
Fax: +7 383 332 28 47
E-mail: bychkov.a.l@gmail.com

Catia CANNILLA
CNR-ITAE "Nicola Giordano"
Salita S. Lucia, 39
I-98126 Messina
Italy
E-mail: francesco.frusteri@itae.cnr.it

José CASTANHEIRO
Universidade de Évora
Largo dos Colegiais, 2
7000-671 Évora
Portugal
E-mail: jefc@uevora.pt

Jie CHANG
Institute of Chemical and Engineering Science
Pesek road, 1, Jurong Island
627833 Singapore
Singapore
Tel.: +65 6796 3878
Fax: +65 63166182
E-mail: chang_jie@ices.a-star.edu.sg

Natalia CHEPELKINA
"VEGA-CHEM" Ltd.
Miuskaya square, 9, buil. 1
125047 Moscow
Russia
Tel.: +7 499 973 50 06
Fax: +7 499 978 92 95
E-mail: natalia@vega-chem.ru

Igor CHERNYKH
Institute of Computational Mathematics
and Mathematical Geophysics SB RAS
pr. Akademika Lavrentjeva, 6
630090 Novosibirsk
Russia
E-mail: chernykh@ssd.sccc.ru

Nikolay CHESNOKOV
Institute of Chemistry and
Chemical Technology SB RAS
K. Marx str., 42
660049 Krasnoyarsk
Russia
Tel.: +7 391 2495399
Fax: +7 391 2439342
E-mail: cnv@icct.ru

Andrey CHISTYAKOV

A.V. Topchiev Institute of Petrochemical
Synthesis RAS
Leninsky pr., 29
119991 Moscow

Russia

Tel.: +7 495 954 42 22

Fax: +7 495 633 85 20

E-mail: Chistyakov@ips.ac.ru

Yulia CHUMACHENKO

Institute of Hydrocarbons Processing
of SB RAS

ul. Neftezhavodskaya, 54
644040 Omsk

Russia

Tel.: +7 3812 67 33 32

Fax: +7 3812 64 61 56

E-mail: lavr@ihcp.oscsbras.ru

Josilaine DA CUNHA

Chemical Institute
Federal University of Rio de Janeiro
Av. Athos da Silveira Ramos, 149
CEP 21941-909 Rio de Janeiro

Brazil

Tel.: +55 21 2562 7240

Fax: +55 21 2562 7240

E-mail: jalvescunha@click21.com.br

Orazio DI BLASI

CNR-ITAE "Nicola Giordano"
Salita Santa Lucia Sopra Contesse, 5
I-98126 Messina

Italy

E-mail: orazio.dibiasi@itae.cnr.it

Ana DIAS

Instituto Superior Técnico
Av. Rovisco Pais, s/n
1049-001 Lisboa

Portugal

Tel.: +351218417873

Fax: +351218499242

E-mail: apsoares@ist.utl.pt

Angela DIBENEDETTO

CIRCC and University of Bari
Via Celso Ulpiani, 27
70126 Bari

Italy

E-mail: a.dibenedetto@chimica.uniba.it

Klaus DIBLITZ

SASOL O&S
Anckelmannsplz., 1
20537 Hamburg

Germany

Tel.: +49 40 636841243

Fax: +49 40 636843626

E-mail: marlies.piotrowski@de.sasol.com

Victoria DUNDICH

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 330 62 54

E-mail: dundich@catalysis.ru

Ananastasia DZYUBENKO

A.V. Topchiev Institute of Petrochemical
Synthesis RAS
Leninsky pr., 29
119991 Moscow

Russia

E-mail: a.a.dzyubenko@gmail.com

Victor EMELYANOV

Kazan State Technological University
ul. Karla Marksa, 68
420015 Kazan

Russia

Tel.: +7 843 231 40 49

Fax: +7 843 231 40 42

E-mail: emeljanov@front.ru

Alyne ESCOBAR

Chemical Institute
Federal University of Rio de Janeiro
Av. Athos da Silveira Ramos, 149
CEP 21941-909 Rio de Janeiro

Brazil

Tel.: +55 21 2562 7240

Fax: +55 21 2562 7240

E-mail: alyne.escobar@yahoo.com.br

Nadine ESSAYEM

Institut de Recherche sur
la Catalyse et l'environnement de Lyon
2 avenue Albert Einstein
F-69626 Villeurbanne

France

E-mail: nadine.essayem@ircelyon.univ-lyon1.fr

Alexey FEDOTOV

A.V. Topchiev Institute of Petrochemical
Synthesis RAS
Leninsky pr., 29
119991 Moscow

Russia

Tel.: +7 495 955 42 22

Fax: +7 495 633 85 20

E-mail: alexey.fedotov@ips.ac.ru

Natalya FRANTSUZOVA

M.V. Lomonosov Moscow State Academy
of Fine Chemical Technology
Vernadsky pr., 86
119571 Moscow

Russia

E-mail: tretjakov@ips.ru

Morten FRØSETH

SINTEF Materials and Chemistry
Pb. 124 Blindern
0314 Oslo

Norway

E-mail: morten.froseth@sintef.no

Francesco FRUSTERI

Institute CNR-ITAE
Via S. Lucia Sopra Contesse, 5
98126 Messina

Italy

Tel.: +39 090 624233

Fax: +39 090 624247

E-mail: francesco.frusteri@itae.cnr.it

Jan GEBOERS

Katholieke Universiteit Leuven
Kasteelpark Arenberg, 23
3001 Heverlee

Belgium

Tel.: +3216321463

Fax: +3216321998

E-mail: Jan.Geboers@biw.kuleuven.be

Mark GELMONT

Technion - Israel Institute of Technology
32000 Haifa

Israel

Tel.: +972 4 8294313

E-mail: mark@tami-imi.icl-ip.com

Vasile GEORGESCU

Institute of Physical Chemistry
"Ilie Murgulescu",
Romanian Academy of Science
Independentei Splai str., 202
060041 Bucharest

Romania

Tel.: +40 213 167912

Fax: +40 213 121147

E-mail: vgeorgescu@icf.ro

Nematollah GHEIBI

Qazvin University of Medical Sciences
Shahid Bahonar Boulevard
Qazvin

Iran

Tel.: +98 281 333 6001 5

E-mail: gheibi_n@yahoo.com

Olga GOLYAZIMOVA

Institute of Solid State Chemistry and
Mechanochemistry SB RAS
ul. Kutateladze, 18
630128 Novosibirsk

Russia

E-mail: o.golyazimova@gmail.com

Krzysztof GOSIEWSKI

Institute of Chemical Engineering,
Polish Academy of Sciences
ul. Bałtycka, 5
44-100 Gliwice

Poland

Tel.: +48601 546535

Fax: +4832 2310318

E-mail: k.gosiewski@iich.gliwice.pl

Elena GUSEVSKAYA

Universidade Federal de Minas Gerais
Av. Antônio Carlos,
6627 - Pampulha
Belo Horizonte - MG

Brazil

E-mail: elena@ufmg.br

Maja HABULIN

University of Maribor
Smetanova, 17
2000 Maribor

Slovenia

Tel.: +386 2 22 94 462

Fax: +386 2 25 27 774

E-mail: maja.habulin@uni-mb.si

Lenka HANNEVOLD

SINTEF Materials and Chemistry
P.O.Box 124 Blindern
Oslo

Norway

E-mail: lenka.hannevold@sintef.no

Alireza HASANINEJAD

Persian Gulf University
75169 Bushehr

Iran

E-mail: hasaninejad@pgu.ac.ir

Karim HASSAN

Department of chemistry
College of Science University of Diyala
Diyala

Iraq

Tel.: +96407901749122

E-mail: drkarim1953@yahoo.com

Erik HEERES

University of Groningen
Department of Chemical Engineering
Nijenborgh, 4
9747 AG Groningen

The Netherlands

Tel.: +31 503634484

Fax: +31 503634479

E-mail: h.j.heeres@rug.nl

Yusuf ISA MAKARFI

M.V. Lomonosov Moscow State Academy
of Fine Chemical Technology
Vernadsky pr., 86
119571 Moscow

Russia

E-mail: yusufisa@yahoo.com;
yusufisa@mail.ru

Manal ISMAIL

University Kebangsaan Malaysia
43600 Selangor

Malaysia

Tel.: +60389216404

Fax: +60389216148

E-mail: manal@eng.ukm.my

Elena KARASKOVA

"VEGA-CHEM" Ltd.

Miuskaya square, 9, build. 1
125047 Moscow

Russia

Tel.: +7 499 973 50 06

Fax: +7 499 978 92 95

E-mail: elena_mi@mail.ru

Vaginak KHANIKYAN

A.N. Nesmeyanov Institute of Organoelement
Compounds RAS

Vavilov str., 28
119991 Moscow

Russia

Tel.: +7 499 978 95 54

E-mail: vagokhan@rambler.ru

Dmitry KHLOPOV

D.I. Mendeleev University of Chemical
Technology of Russia

Miuskaya square, 9
125047 Moscow

Russia

E-mail: hlopovd@mail.ru

Andrey KHUDOSHIN

Department of Chemistry
M.V. Lomonosov Moscow State University

Leninskie Gory, 1/9
119991 Moscow

Russia

Tel.: +7 495 93 33 22

Fax: +7 495 93 45 75

E-mail: khudoshin@kge.msu.ru

Dong-Ha KIM

Ewha Womans University
11-1 Daehyun-dong
Seodaemun-gu
120-750 Seoul

Korea

Tel.: +82 2 3277 4517

Fax: +82 2 3277 3419

E-mail: dhkim@ewha.ac.kr

Sung-Jin KIM

Ewha Womans University
11-1 Daehyun-dong
Seodaemun-gu
120-750 Seoul

Korea

Tel.: +82 2 3277 2350

Fax: +82 2 3277 3419

E-mail: sjkim@ewha.ac.kr

Evgenia KIRICHENKO

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 32-69-410

E-mail: evgenia@catalysis.ru

Valerii KIRILLOV

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 330 61 87

E-mail: vak@catalysis.ru

Dimitris KONDARIDES

University of Patras
26504 Patras

Greece

Tel.: + 30 2610 969527

Fax: + 30 2610 991527

E-mail: dimi@chemeng.upatras.gr

Yuri KOROLEV

N.D. Zelinsky Institute of Organic Chemistry
RAS

Leninsky pr., 47
119991 Moscow

Russia

E-mail: osmos7@mail.ru

Darya KOSHELEVA

Perm State Technical University
Komsomolsky, 29

614990 Perm
Perm

Russia

Tel.: +79026370492

E-mail: dasha100987@mail.ru

Yuri KOSIVTSOV

Tver Technical University
A. Nikitina str., 22
170026 Tver

Russia

Tel.: +79036307723

Fax: +74822449317

E-mail: kosivtsov@science.tver.ru

Ivan KOZHEVNIKOV
Department of Chemistry
University of Liverpool
L69 7ZD Liverpool
UK
Tel.: +44 151 794 2938
Fax: +44 151 794 3589
E-mail: kozhev@liverpool.ac.uk

Alexey KOZLOV
Institute of Coal and Coal Chemistry SB RAS
St. Rukavishnikova, 21
650610 Kemerovo
Russia
E-mail: kemerit@rambler.ru

Ivan KOZLOVSKIY
"VEGA-CHEM" Ltd.
Miuskaya square, 9, str. 1
125047 Moscow
Russia
Tel.: +7 499 973 50 06
Fax: +7 499 978 92 95
E-mail: iakozlovsky@rambler.ru

Genry KRUSHENKO
Institute Computational Modeling SB RAS
Akademgorodok
660036 Krasnoyarsk
Russia
Tel.: +7 391 290 74 98
Fax: +7 391 243 26 56
E-mail: genry@icm.krasn.ru

Nataliya KRYLOVA
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel.: +7 383 326 9784
Fax: +7 383 330 8056
E-mail: krylova@catalysis.ru

Vitalina KUKUEVA
Fire Safety Academy
Onoprienko str., 8
18034 Cherkassy
Ukraine
Tel.: +38 0 47 255 09 71
E-mail: kukueva@yahoo.com

Nitee KUMARI
University of Copenhagen
Universitetsparken, 5
2100 Copenhagen
Denmark
Tel.: +45 35 32 01 21
E-mail: nitee@kemi.ku.dk

Bright KUSEMA
Åbo Akademi University, Laboratory of
Industrial Chemistry
Biskopsgatan, 8
20500 Turku
Finland
E-mail: bright.kusema@abo.fi

Andrey KUSTOV
"VEGA-CHEM" Ltd.
Miuskaya square, 9, str. 1
125047 Moscow
Russia
Tel.: +7 499 973 50 06
Fax: +7 499 978 92 95
E-mail: kustov@vega-chem.ru

Boris KUZNETSOV
Institute of Chemistry and Chemical Technology
SB RAS
K. Marx str., 42
660049 Krasnoyarsk
Russia
Tel.: +7 391 249 48 94
Fax: +7 391 243 93 42
E-mail: bnk@icct.ru

Irina KUZNETSOVA
"VEGA-CHEM" Ltd.
Miuskaya square, 9, buil. 1
125047 Moscow
Russia
Tel.: +7 499 973 50 06
Fax: +7 499 978 92 95
E-mail: kuznetsova@vega-chem.ru

Svetlana KUZNETSOVA
Institute of Chemistry and Chemical Technology
SB RAS
K. Marx str., 42
660049 Krasnoyarsk
Russia
Tel.: +7 391 249 48 94
Fax: +7 391 243 93 42
E-mail: ksa@icct.ru; inm@icct.ru

Jalel LABIDI
University of the Basque Country
Sarriena S/N
48080 Bilbao
Spain
E-mail: jalel.labidi@ehu.es

Albert LAPIDUS
N.D. Zelinsky Institute of Organic
Chemistry RAS
Leninsky pr., 47
119991 Moscow
Russia
Tel.: +7 499 135 5303
Fax: +7 499 135 5303
E-mail: albert@ioc.ac.ru

Nikolaj LAPIN

Institute of Microelectronic Technology
and High-Purity Materials, RAS
Chernogolovka, Moscow District
142432 Moscow

Russia

Tel.: 8 (496) 524 40 15

E-mail: lapin@iptm.ru

Alexandr LAVRENOV

Institute of Hydrocarbons Processing
of SB RAS
Neftezhavodskaya str. 54
644040 Omsk

Russia

E-mail: lavr@ihcp.oscsbras.ru

Sebastien LEVENEUR

Laboratory of Industrial Chemistry
Åbo Akademi University
Biskopsgatan, 8
20500 Turku

Finland

E-mail: sleveneu@abo.fi

Armin LIEBENS

SOLVAY
Rue Du Prince Albert, 44
1050 Brussels

Belgium

Tel.: +32 2 264 33 87

Fax: +32 2 264 34 60

E-mail: pascale.tulpinck@solvay.com

N. LINGAIAH

Indian Institute of Chemical Technology
500607 Hyderabad

India

Tel.: +91 40 27193163; +91 40 27176379

E-mail: nakkalingaiah@iict.res.in

Päivi MÄKI-ARVELA

Åbo Akademi University
Biskopsgatan, 8
20500 Turku

Finland

Tel.: +358 2 215 4424

E-mail: paivi.maki-arvela@abo.fi

Alexander MALYSHEW

SASOL Germany GmbH
Anckelmannplz., 1
20537 Hamburg

Germany

Tel.: +4940636841244

Fax: +4940636841944

E-mail: alexander.malyschew@de.sasol.com

Victor MALYSHEV

V.I. Vernadskii Institute on General &
Inorganic Chemistry of NASU
32/34 Palladina Ave.
03680 Kiev

Ukraine

Tel.: +38044 4249433

Fax: +38044 4249433

E-mail: victor_malyshev@mail.ru

Tarana MAMMADOVA

Institute of Petrochemical Processes
of Azerbaijan NAS
pr. Khojali, 30
Az1025 Baku

Azerbaijan

Tel.: +99450 473 50 85

E-mail: mamedova.tarana@rambler.ru

Stellan MARKLUND

Umeå University
SE-901 87 Umeå

Sweden

Tel.: +46 (0)90 786 50 00

E-mail: stellan.marklund@chem.umu.se

Oleg Martyanov

Boriskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 32 69 745, 330 93 04

E-mail: oleg@catalysis.ru

Olga MATROSOVA

I.M. Gubkin Russian State University
of Oil and Gas
Leninsky pr., 65
119991 Moscow

Russia

E-mail: mov.86@mail.ru

Anton MAXIMOV

A.V. Topchiev Institute of Petrochemical
Synthesis RAS
Leninsky pr., 29
119991 Moscow

Russia

E-mail: max@ips.ac.ru

Mario MENEGHETTI

Instituto de Química e Biotecnologia
Universidade Federal de Alagoas
Av. Lourival de Melo Mota, s/ nº
57072-970 Maceió-AL

Brazil

Tel.: +55 82 32141373

E-mail: mrmeneghetti@gmail.com

Simoni MENEGHETTI

Instituto de Química e Biotecnologia
Universidade Federal de Alagoas
Av. Lourival de Melo Mota, s/ nº
57072-970 Maceió-AL

Brazil

Tel.: 55 82 32141703

E-mail: simoni.plentz@gmail.com

Sergey MENSHIKOV

Institute of Organic Synthesis UB RAS
str. S. Kovalevskoj/Akademicheskaya, 22/20
620219 Ekaterinburg

Russia

E-mail: kox@ios.uran.ru

Natalia MEZENTSEVA

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 330 87 63

E-mail: mnv@catalysis.ru

Michael MICHMAN

Hebrew University of Jerusalem,
Institute of Chemistry
91904 Jerusalem

Israel

Fax: +972 2 6585345

E-mail: michman@cc.huji.ac.il

Jyri-Pekka MIKKOLA

Umeå University
SE-901 87 Umeå

Sweden

Tel.: +46 (0)90 786 5284

Fax: +46 (0)90 13 63 10

E-mail: Jyri-Pekka.Mikkola@chem.umu.se

Sergei MUKHACHEV

Kazan State Technological University
ul. Karla Marksa, 68
420015 Kazan

Russia

Tel.: +7 843 2314049

Fax: +7 843 2314042

E-mail: Emelianov@front.ru

Tatiana MINYUKOVA

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 32 69 464

E-mail: min@catalysis.ru

Gulbeniz MUKHTAROVA

Institute of Petrochemical Processes of
Azerbaijan NAS
pr. Khojali, 30
Az1025 Baku

Azerbaijan

E-mail: gulermuxtarova@yahoo.com

Dmitry MURZIN

Laboratory of Industrial Chemistry
Åbo Akademi University
Biskopsgatan 8
20500 Turku

Finland

Tel.: +358 2 215 4985

Fax: +358 2 215 4479

E-mail: dmurzin@abo.fi

Inna MUTAS

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 326 96 06

Fax: +7 383 330 62 97

E-mail: mutas@catalysis.ru

Tatyana NARBKOVA

Norilsk Industrial Institute
50 year of October street, 7
663300 Norilsk

Russia

Tel.: +7 3919 421 632

Fax: +7 3919 421 741

E-mail: narbekova07@inbox.ru

Andrey NEKHAEV

A.V. Topchiev Institute of Petrochemical
Synthesis RAS
Leninsky pr., 29
119991 Moscow

Russia

E-mail: nekhaev@ips.ac.ru

Anna NIKOLSKAYA

Institute of Biochemical Physics RAS
Kosygina, 4
119334 Moscow

Russia

E-mail: anickolskaya@mail.ru

Cesare OLIVA

University of Milan
Via Golgi, 19
I-20133 Milan

Italy

Tel.: +39 0250314270

Fax: +39 0250314300

E-mail: cesare.oliva@unimi.it

Ludmila OPARINA

A.E. Favorsky Irkutsk Institute of Chemistry
SB RAS
St. Favorskogo, 1
664033 Irkutsk

Russia

Tel.: +7 3952 425931

Fax: +7 3952 419346

E-mail: oparina@irioch.irk.ru

Vitaly ORDOMSKY

Department of Chemistry
M.V. Lomonosov Moscow State University
Leninskie Gory, 1/9
119991 Moscow

Russia

Tel.: +7 495 939 20 54

Fax: +7 495 939 35 70

E-mail: vitord@mail.ru

Umit OZKAN

The Ohio State University
140 W 19th Avenue
43210 Columbus

USA

Tel.: +614 292 6623

Fax: +614 292 3769

E-mail: ozkan.1@osu.edu

Valentin PARMON

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 330 82 69

Fax: +7 383 330 4719

E-mail: parmon@catalysis.ru

Marcelo PEREIRA

Chemical Institute
Federal University of Rio de Janeiro
Av. Athos da Silveira Ramos, 149
CEP 21941-909 Rio de Janeiro

Brazil

Tel.: +55 21 2562 7251

Fax: +55 21 2562 7240

E-mail: maciell@iq.ufrj.br

Svetlana POTAPOVA

United Research and Development Centre
Leninsky pr. 55/1, b. 2
119333 Moscow

Russia

E-mail: PotapovaSN@yrd.ru

Stephen POULSTON

Johnson Matthey PLC
Hatton Garden, 40-42
EC1N 8EE London

United Kingdom of Great Britain

Tel.: +44 0 20 7269 8400

E-mail: poulss@matthey.com

Tatyana POVARNITSYNA

Arkhangelsk State Technical University
Nabereznaya Severnoj Dviny, 17
163002 Arkhangelsk

Russia

Tel.: +7 8182 218 948

Fax: +7 8182 218 948

E-mail: tpovarnitsyna@yandex.ru

Nizami PIRIYEV

Azerbaijan Methanol Company
20 Afyaddin Jalilov street, 2nd floor
AZ1024 Baku

Azerbaijan

Tel.: +994 12 598 35 40/39

Fax: +994 12 598 35 41

E-mail: aziza.seidova@azmeco.com

Wolter PRINS

Faculty of Bioscience Engineering
University of Ghent
Coupure Links, 653
B-9000 Ghent

Belgium

E-mail: Wolter.Prins@UGent.be

Aleksey PROKHOROV

D.I. Mendeleev University of Chemical
Technology of Russia
Miuskaya square, 9
125047 Moscow

Russia

E-mail: proxorov.al@mail.ru

Evgeniy PROKOPEV

A.I. Alikhanov Institute for Theoretical and
Experimental Physics (ITEP)
Bolshaya Cheremushkinskaya, 25
117218 Moscow

Russia

Tel.: +7 4997311104

E-mail: epprokopiev@mail.ru

Galletti RASPOLLI

University of Pisa
Via Risorgimento, 35
56126 Pisa

Italy

Tel.: +39 050 221 90 00

Fax: +39 050 221 92 60

E-mail: roxy@dcci.unipi.it

Irina REZNICHENKO

Angarsk Plant for the Catalyst Production
and Organic Synthesis
665830 Angarsk

Russia

Tel.: +7 3955 57 79 32

Fax: +7 3955 52 75 45

E-mail: azkios@anhk.rosneft.ru

Colin ROBERTSON

Hidden Analytical Ltd
Europa Boulevard, 402
WA57UN Warrington
United Kingdom of Great Britain

E-mail: colinr@hidden.co.uk

Anastasiya ROMANOVA
D.I. Mendeleev University of Chemical
Technology of Russia
Miuskaya square, 9
125047 Moscow
Russia
E-mail: liceistka2003@mail.ru

Ilenia ROSSETTI
Dipartimento Chimica Fisica ed Elettrochimica
Universita degli Studi di Milano
Via C.Golgi, 19
I-20133 Milano
Italy
Fax: +39 02 50314300
E-mail: ilenia.rossetti@unimi.it

Elizabeth ROWSELL
Johnson Matthey PLC
Hatton Garden, 40-42
EC1N 8EE London
United Kingdom of Great Britain
E-mail: rowsee@matthey.com

Bartosz ROZMYŚŁOWICZ
Laboratory of Industrial Chemistry
Åbo Akademi University
Biskopsgatan, 8
20500 Turku/Åbo
Finland
E-mail: brozmysl@abo.fi

Anastasiya SAMARINA
Journal "Catalysis in Industry"
Editorial Office
Lenisky pr., 4
119049 Moscow
Russia
Tel.: +7 495 955 00 29
Fax: +7 495 955 01 97
E-mail: ctls@kalvis.ru, red@kalvis.ru

Maria SAN JOSE
University of the Basque Country
Sarriena S/N
48080 Bilbao
Spain
Tel.: +34 946015362
Fax: +34 946013500
E-mail: mariajose.sanjose@ehu.es

Luciana T. SANTOS
National Agency of Petroleum
Av. Rio Branco, 65
20090-004 Rio de Janeiro
Brazil
Tel.: +55 21 21128385
Fax: +55 21 21128389
E-mail: ltsantos@anp.gov.br

Margareth Rose SANTOS
Universidade Federal do Rio de Janeiro
Av. Pedro Calmon, 550 - Prédio da Reitoria
2 andar Cidade Universitária - Rio de Janeiro
CEP 21941-901 Rio de Janeiro
Brazil
E-mail: megrose@iq.ufrj.br

Valentin SAPUNOV
"VEGA-CHEM" Ltd.
Miuskaya square, 9, str. 1
125047 Moscow
Russia
Tel.: +7 499 973 50 06
Fax: +7 499 978 92 95
E-mail: sapunovvals@gmail.com

Luiz SCHLITTLER
Department of Biochemical Engineering
Federal University of Rio de Janeiro
Av. Athos da Silveira Ramos, 149
CEP 21941-909 Rio de Janeiro
Brazil
Tel.: +21 25627644
E-mail: lafelizardo@yahoo.com.br

Max SHEPELEV
Ivanovo University of Chemistry and
Technology
pr. Engel'sa, 7
153000 Ivanovo
Russia
E-mail: vicount@inbox.ru

Nadezhda SHIKINA
Borekov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel.: +7 383 330 76 70
E-mail: shikina@catalysis.ru

Laleh SHIRAZI
Research Institute of Petroleum Industry (RIPI)
P.O. Box 14665-137 Tehran
Iran
E-mail: shirazil@ripi.ir

Daniil SHLYAKHTITSEV
A.V. Topchiev Institute of Petrochemical
Synthesis RAS
Leninsky pr., 29
119991 Moscow
Russia
E-mail: nekhaev@ips.ac.ru

Natalya SHTERTSER
Borekov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel.: +7 383 3269768
E-mail: nat@catalysis.ru

Irina SIMAKOVA
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 32 69 531

E-mail: simakova@catalysis.ru

Olga SIMAKOVA

Åbo Akademi University
Biskopsgatan, 8
20500 Turku

Finland

Tel.: +358505511184

E-mail: osimakov@abo.fi

Ekaterina SKORB

Belarusian State University
ul. Leningradskaya, 14
220030 Minsk

Belarus

E-mail: katjaskorb@mail.ru

Alexander SKORPLUK

Institute of Hydrocarbons Processing SB RAS
ul. Neftezavodskay, 54
644040 Omsk

Russia

Tel.: +7 3812673332

Fax: + 73812646156

E-mail: lavr@ihcp.oscsbras.ru

Olga SNEGURENKO

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 32 69 600

E-mail: sneg@catalysis.ru

Jung SOHN

Chonbuk National University
Deokjin-Dong, 664-14, 1GA
561-756 Jeonju

Korea

E-mail: jmsohn@jbnu.ac.kr

Byungho SONG

Kunsan National University
573-701 Jeonbuk
Gunsan

Korea

Tel.: +82 63 469 47 73

Fax: +82 63 469 47 79

E-mail: bhsong@kunsan.ac.kr

Matheus SOUZA

Chemical Institute
Federal University of Rio de Janeiro
Av. Athos da Silveira Ramos, 149
CEP 21941-909 Rio de Janeiro

Brazil

Tel.: +55 21 2562 7240

Fax: +55 21 2562 7240

E-mail: m.oliveira13@ig.com.br

Oleg SMORYGO

SSI "Powder Metallurgy Institute"
Platonov Str. 41
220005 Minsk

Republic Belarus

E-mail: smorygo@rambler.ru

Peter STRIZHAK

L.V. Pisarzhevsky Institute of Physical
Chemistry NAS of Ukraine
pr. Nauki, 31

03028 Kiev

Ukraine

Tel.: 38044 5256663

Fax: 38044 5256663

E-mail: pstrizhak@hotmail.com

Julia STRIZHAKOVA

Samara State Technical University
Molodogvardeiskaya str., 244
443100 Samara

Russia

Tel.: +7 846 278 43 17

Fax: +7 846 278 44 17

E-mail: strizhakova@mail.ru

Paulo SUAREZ

Institute of Chemistry
University of Brasilia
CP 4478

70910970 Brasilia

Brazil

E-mail: psuarez@unb.br

Wladimir SUPRUN

Universität Leipzig
Institut für Technische Chemie
Linnèstr., 3

04103 Leipzig

Germany

Tel.: +49 0341 9736309

Fax: +49 0341 9736349

E-mail: suprun@chemie.uni-leipzig.de

Sergei SVIDERSKII

United Research and Development Centre
Leninsky pr., 55/1
199333 Moscow

Russia

E-mail: research-centre@yrd.ru

Oxana TARAN

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 3307563

Fax: +7 383 3308056

E-mail: oxanap@catalysis.ru

Ana TOLEDANO

University of the Basque Country
Sarriena S/N
48080 Bilbao

E-mail: atoledano001@ikasle.ehu.es

Pasi TOLVANEN

Åbo Akademi University
Biskopsgatan, 8
20500 Turku

Finland

Tel.: +358440310790

E-mail: ptolvane@abo.fi

Valentin TRETIYAKOV

M.V. Lomonosov Moscow State Academy
of Fine Chemical Technology
Vernadsky pr., 86
119571 Moscow

Russia

E-mail: tretjakov@ips.ac.ru

Mark TSODIKOV

A.V. Topchiev Institute of Petrochemical
Synthesis RAS
Leninsky pr., 29
119991 Moscow

Russia

Tel.: +7 495 9554304

Fax: +7 495 633 85 20

E-mail: tsodikov@ips.ac.ru

Valerii UVAROV

Institute of Structural Macrokinetics and
Materials Science RAS
ul. Institut'skaya, 8
142432 Chernogolovka

Russia

Tel.: + 495 962 80 49

Fax: + 495 962 80 25

E-mail: uvar@ism.ac.ru

Pavel VAKHRUSHIN

I.M. Gubkin Russian State University
of Oil and Gas
Lenenskii pr., 65
119991 Moscow

Russia

E-mail: Ekokat@mail.ru

Anabela VALENTE

Universidade de Aveiro
Campus de Santiago
3810-193 Aveiro

Portugal

Tel.: +351 234370603

Fax: +351 234401470

E-mail: atav@ua.pt

Joost VAN BENNEKOM

University of Groningen
Broerstraat, 5
9712 CP Groningen

The Netherlands

Tel.: +31503634484

E-mail: j.g.van.bennekom@rug.nl

Bert VAN DE BELD

BTG Biomass technology Group BV
PO BOX 835
7500 AV Enschede

The Netherlands

Tel.: +31534862288

Fax: +31534861180

E-mail: vandebeld@btgworld.com

Stijn VAN DE VYVER

Katholieke Universiteit Leuven
Kasteelpark Arenberg, 23
3001 Leuven

Belgium

Tel.: +32473251261

E-mail: stijn.vandevyver@biw.kuleuven.be

Efterpi VASILIADOU

Aristotle University of Thessaloniki
541 24 Thessaloniki

Greece

Tel.: +30 2310 99.6199

Fax: +30 2310 99 6184

E-mail: evasili@cperi.certh.gr

Palligarnai VASUDEVAN

University of New Hampshire
NH 03824 New Hampshire

USA

Tel.: 603 862 2298

Fax: 603 862 3747

E-mail: vasu@unh.edu

Robbie VENDERBOSCH

BTG Biomass technology Group BV
PO BOX 835
Enschede

The Netherlands

E-mail: venderbosch@btgworld.com

Xenophon VERYKIOS

University of Patras
26504 Patras

Greece

E-mail: verykios@chemeng.upatras.gr

Elena VIALICH

Perm State University
Bukireva str., 15
614990 Perm

Russia

E-mail: eavel@rambler.ru

Kati VILONEN

Aalto University School of Science and
Technology

P.O.Box 16100
00076 Aalto Espoo

Finland

Tel.: +358 9 470 22627

E-mail: kati.vilonen@tkk.fi

Marina VISHNETSKAYA

I.M. Gubkin Russian State University
of Oil and Gas

Leninsky pr., 65
119991 Moscow

Russia

E-mail: mvvishnetskaya@mail.ru

Zahira YAAKOB

Department of Chemical and Process
Engineering

University Kebangsaan Malaysia
43600 Bangi

Malaysia

Tel.: +60389216420

Fax: +60389216148

E-mail: zahira@eng.ukm.my

Vadim YAKOVLEV

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk

Russia

Tel.: +7 383 326 9650

Fax: +7 383 330 8056

E-mail: yakovlev@catalysis.ru

Phatima YANDIEVA

A.V. Topchiev Institute of Petrochemical
Synthesis RAS

Leninsky pr., 29
119991 Moscow

Russia

Tel.: +7 495 9554347 203

E-mail: yand@ips.ac.ru

Tatiana ZAMULINA

Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5

630090 Novosibirsk

Russia

Tel./Fax: +7 383 330 62 97

E-mail: zam@catalysis.ru

Irina ZERNININA

Perm State Technical University

Komsomolskiy pr., 29
614990 Perm

Russia

Tel.: +7 342 282 70 44

E-mail: zernina88@mail.ru

Ziyi ZHONG

Institute of Chemical and Engineering Sciences

Pesek Road, Jurong Island Singapore, 1
627833 Singapore

Singapore

Tel.: +65 67963809

Fax: +65 6316 6182

E-mail: zhong_ziyi@ices.a-star.edu.sg

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