



Members' Newsletter

“Catalysis research is doing well”

The year 2021 is nearing its end and the world is still struggling with the Covid-19 pandemic after two years. As a result, many scientific events, symposia, and conferences have been cancelled and postponed to the coming years. However, despite lack of presentations in international symposia and conferences, the activity of the Finnish catalysis research has been good. Several new doctors have defended their dissertations during the summer and autumn 2021, and eight abstracts are included in this Newsletter. Researchers have also been nominated as new members in the scientific communities and awarded for their remarkable achievements. Congratulations to all of you!

Many dissertations have been held fully or partly remotely and screened online. Even though the dissertations will hopefully soon be held again on-site, some might be still organized as hybrid form and delivered also online. From the Finnish Catalysis Society webpages, you can now find the tab where coming catalysis related doctoral dissertations with www-links are listed. Please, check the page and find interesting topics. Kindly send information of coming dissertations to the board members and we'll update the events on the page.

One remarkable news in the catalysis field was the Nobel Prize in Chemistry 2021 which was awarded jointly to Ph.D. Benjamin List (Germany) and Professor David W.C. McMillan (USA) for discovery and development of third type of catalysis - asymmetric organocatalysis. Their work give

concepts and new tool to produce environmentally friendly, greener, and cheaper small molecule catalysts without metals or enzymes. These can be used for reactions from pharmaceuticals to molecules capable to capture light in solar cells.

The organization of the 19th Nordic Symposium on Catalysis to be held in Espoo, in June 6-8, 2022 is progressing well. The registration and important dates can be found from the conference website (19nsc.fi). The abstract submission is open, and it is encouraged the researchers from all fields of catalysis to submit their abstracts to the 19NSC. The next Finnish Young Scientist Forum on Catalysis (FYSFC) will take place in April 2022 in Åbo/Turku with the Annual meeting of the Finnish Catalysis Society.

Hoping to see many of you in the 19th Nordic Symposium on Catalysis, the FYSFC and the Annual meeting.

Wishing you all happy and relaxing holidays, and prosperous year 2022.

Mika Huuhtanen

Chairman



Update on 19th Nordic Symposium on Catalysis



The Finnish Catalysis Society cordially invites you to join the 19th Nordic Symposium on Catalysis in Espoo, Finland 6–8 June 2022.

The Symposium will cover catalysis broadly and will be organized with plenary lectures, Berzelius award lecture and parallel sessions with Nordic keynote lectures and accepted oral contributions as well as a poster session.

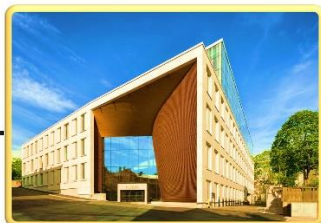
The themes of the current symposium are:
Catalysis in the climate change mitigation
Catalysis in the Nordic Countries

Registration and submission of abstracts open on 15.11.2021.

Please follow the progress of event organization at the website: <http://19nsc.fi>, and Twitter: [@19thNSC](https://twitter.com/19thNSC), [#NordicSympCat](https://twitter.com/NordicSympCat).

Save the date for Young Scientist Forum 2022

SAVE-THE-DATE! 08.04.2022



YSF2022



YOUNG SCIENTIST FORUM

- The Young Scientist Forum will take place on **8th of April** 2022 in Turku, Åbo
- Address: Henriksgatan 2, 20500 Åbo
- The preliminary programme is as follows:
 - 09:00 Breakfast and roundwalk in the new **Aaurum** Building
 - 11:30 Scientific programme, lunch and poster session at **Kakolan Ruusu**
 - 19:00 Dinner at restaurant **Rantakerttu** including sauna
 - More information and registration will come in end of January 2022
 - **SAVE THE DATE!**



Professor Johan Wärnä elected to Svenska Tekniska Vetenskapsakademien i Finland

Svenska Tekniska Vetenskapsakademien i Finland (STV), the oldest academy of technological sciences in our country celebrates its 100 years 1921-2021. New members with high merits in the development of technology have recently been nominated to this very prestigious academy. Among them is the internationally recognized scientist, TkD Johan Wärnä, professor in chemical reaction engineering at Åbo Akademi. Johan is known for his numerous contributions to the mathematical modelling of catalytic processes; his work has been published in top journals in chemical engineering and catalysis, such as Journal of Catalysis, Chemical Engineering Journal and Chemical Engineering Science. Johan is also co-author of two textbooks (Chemical Reaction Engineering and Reactor Technology, 2019 and Chemical Reaction Engineering. A computer-Aided Approach, 2020). Cordial congratulations to the very friendly co-worker and great scientist!



Finnish Chemical Society scholarship to Wilhelm Wikström

Karl-Wilhelm Wikström obtained a student scholarship from Suomalaisten Kemistien Seura (Finnish Chemical Society) for his very successful studies and particularly for his excellent bachelor thesis Tillämpning av halvkontinuerlig reaktorteknologi till homogent katalyserade konsekutiva reaktioner (Application of semibatch reactor technology on homogeneously catalyzed consecutive reactions). The thesis was accepted with the highest mark 5/5 at Åbo Akademi.

Determination of rate constants for a composite system consisting of rapid and slow reactions is a challenge because the primary reactions are typically rapid whereas the secondary and tertiary reactions can be much slower. By starting with a very small amount of catalyst and adding it gradually to the reactor system, the primary reactions can be slowed down and the subsequent reactions can be enhanced. This approach guarantees the best possible approach for the determination of the rate constants. The applicability of the approach was illustrated with experimental data obtained for the formation of mono- and diesters from carboxylic acids and dialcohols in the presence of homogeneous strong acid catalysts. Acetic acid and ethylene glycol were used as reagents in the experimental work and aqueous hydrogen chloride was the homogeneous catalyst. Rate equations for this reaction systems were derived based on molecular mechanisms and the kinetic parameters in the rate equations were estimated with regression analysis. Simulation of the esterification model illustrated the benefits of the proposed experimental semibatch approach for complex reaction systems.



It is not very common that a Bachelor work is published internationally, but thanks to Wilhelm's skillful work we were able to do that (Application of semibatch technology on the investigation of homogeneously catalyzed consecutive and parallel-consecutive liquid-phase reactions: kinetic measurements and modelling, Chemical Engineering Science 233 (2021) 116397).

Best doctoral thesis award to Dr Adriana Freites Aguilera



Rectora Magnifica of Åbo Akademi (ÅA), professor Moira von Wright gives annually an award, Elvings legat to the best doctoral thesis at our multidisciplinary university. This year the prize was given to Dr Adriana Freites Aguilera who defended the thesis in the subject Teknisk kemi och reaktionsteknik (TKR) at Åbo Akademi in January 2020. The title of the thesis was Epoxidation of vegetable oils – Process intensification for biomass conversion. The monumental work consisting of a summary and eight (8) journal articles was approved by the Faculty of Science and Engineering with the highest mark med beröm godkänt (with distinction). The evaluation was based on the statement of the faculty opponent, Directrice de recherche Doctor Carine Julcour (Université de Toulouse ENSIACET CNRS). The research was conducted in a very active and fruitful collaboration between Université Normandie – INSA-Rouen and Åbo Akademi. The work was supervised by Academy

Professor Tapio Salmi (ÅA), Professor Sébastien Leveneur (INSA-Rouen) and Docent Pasi Tolvanen (ÅA).

The topic of the thesis was epoxidation of fatty acids which appear in the domestic and very valuable renewable source, tall oil. The epoxidized products can be used as intermediates for the production of biolubricants, polyols, glycols, olefinic compounds as well as stabilizers for polymers. Epoxides are reactive with carbon dioxide and can after aminolysis form polyurethanes. Hydrogen peroxide is used in the process as a green oxidant. The reaction system is a complex solid-liquid-liquid system, which was studied experimentally and modelled mathematically. Dr Freites Aguilera could demonstrate that the process can be intensified (enhanced) by application of microwave technology and heterogeneous catalysts. The work culminated in very advanced mathematical modelling of the multiphase reaction system. All the manuscripts included in the thesis have been published in the most prestigious journals in industrial chemistry and chemical engineering, such as Chemical Engineering Science, Chemical Engineering journal and Industrial and Engineering Chemistry Research.

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Award lecture

The award (3000 euro and a diploma) was announced at the inscription ceremony of Åbo Akademi on 8th of September 2021. On the same day, Laboratory of Industrial Chemistry and Reaction Engineering (TKR) organized a scientific seminar in honour of Dr Adriana Freites Aguilera. The seminar took place in the brewery restaurant Koulu (Skolan, l'Ecole). Lunch and refreshments were served.



Receiving the congratulations at Koulu restaurant

Cordial congratulations to the award winner!

Tapio Salmi



Catalysis related dissertations

M.Sc.(Chem.) Annu Rusanen University of Oulu Graduate School, Faculty of Technology, Research Unit of Sustainable Chemistry November 12, 2021. Linnanmaa, auditorium L5. The title of his thesis is

“Catalytic conversion of sawdust-based sugars into 5-hydroxymethylfurfural and furfural”

Opponent: Prof. Janne Jänis, University of Eastern Finland

Custodian: Ulla Lassi, University of Oulu

developed at the work. In particular, solid activated carbon catalysts were found to significantly improve the selectivity of key chemical production reactions over conventionally used catalysts.

Overall, the dissertation increased knowledge about the utilization of sawdust and introduced greener alternatives to the traditional methods used in chemical production.

Abstract:

Sawdust can be used as a raw material in chemical production. This conclusion was reached in the PhD study that succeeded in producing two key chemicals (5-hydroxymethylfurfural and furfural) from the sugars contained in sawdust. These chemicals play a key role in the manufacture of many biomass-based products and are therefore an important link between biomass resources and biomass-derived products.

The forest industry generates large amounts of sawdust each year as a by-product, which is currently mainly burned for energy. In this doctoral thesis, a suitable approach for biorefineries was used to convert the hemicellulose fraction of the sawdust to key chemicals, while the cellulose fraction, used traditionally in pulp manufacture, was left as pristine as possible.

In the chemical production itself, attention was paid to the sustainability of manufacturing processes through new catalytic solutions



M.Sc.(Chem.) Riikka Kupila University of Oulu Graduate School, Faculty of Technology, Research Unit of Sustainable Chemistry December 3, 2021. Ulappa auditorium of Kokkola University Consortium Chydenius (Talonpojankatu 2B, Kokkola) The title of his thesis is

“Catalytic conversion of furfural and glucose over activated carbon-supported metal catalysts”

Opponent: Prof. Henrik Grénman, Åbo Akademi University

Custodian: Ulla Lassi, University of Oulu

Abstract:

Forest-based sectors such as sawmills and pulp and paper play an important role in Finnish industry. Lignocellulosic side stream fractions from these activities, such as wood sawdust and lignin, are primarily used for energy. However, these fractions could be used more efficiently in biorefinery concepts like the production of value-added bio-based materials and chemicals instead of energy production.

In biorefinery concepts, catalysis is an important tool for creating more sustainable processes. Efforts to develop novel catalytic systems for biomass valorization to obtain platform chemicals from biomass feedstock are worth pursuing. In catalytic applications, novel bio-based activated carbon catalysts could be used to replace the non-renewable catalytic materials currently used.

In this thesis, the application of lignocellulose-based side stream materials as a raw material for activated carbon catalysts and their use in catalytic applications are studied. Catalysts prepared for catalytic conversion reactions to

produce value-added chemicals for biorefinery applications are investigated: specifically, the conversion of the biomass-based molecules furfural and glucose into 2-methylfuran, 5-hydroxymethylfurfural, lactic acid and its ester, ethyl lactate.

This research provides new insights into the preparation of lignocellulose based activated carbon catalysts and their suitability for catalytic conversion reactions to produce important value-added chemicals for industrial applications. The present study found that lignocellulosic side stream materials can be used in preparing high-quality activated carbon catalysts or supported catalysts. Prepared carbon-based catalysts showed promising results in the conversion reactions studied, indicating that tailored catalyst supports for specific applications are needed.



M.Sc.(Chem.) Nemanja Vucetic Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR) Thursday, December 16, 2021, Auditorium Ringbom, Biskopsgatan 8, Turku/Åbo The title of his thesis is

“Mizoroki-Heck cross coupling - Palladium based catalysts and operation modes”

Opponent: Prof. Mihkel Koel, Tallinna Tehnikaülikool

Custodian: Academy Professor Tapio Salmi

Abstract:

Present market trends in the sector of fine chemicals along with the need for rapid commercialization and less expensive production technologies boosts extensive research in this area. Mass-production of fine chemicals imposes a requirement to simplify and shift the production from traditional batch and semi-batch processes to continuous operation mode. It is important to maintain the purity of the produced compounds since the biggest share of synthesized chemicals are used in pharmaceutical industry. Impurities of any kind are not tolerated in the final products implying that the production processes have to be truly efficient and selective.

Different cross-coupling reactions are an integral part of the production of fine chemicals. Among them, palladium catalyzed Mizoroki-Heck reaction is one of the most utilized ones due to its flexibility towards various functional groups. The evident shortcomings of this reaction such as inefficient reactant conversion, catalyst instability and metal leaching are often the bottlenecks of the whole process. The current

study tackles these issues through the development of sufficiently active and stable catalysts for Mizoroki-Heck reaction in batch and continuous flow reactors.

Various amorphous silica supported ionic liquid catalysts (SILCAs) with a double ionic liquid layer loaded with palladium were designed and compared with other catalysts, such as grafted ordered mesoporous silica and metal-organic frameworks (MOFs) deposited with palladium. Throughout the work, the dynamic nature of the metal catalysis of this reaction via a release-and-catch mechanism was observed. This required a special attention on both operation modes, however, naturally it was more detrimental under continuous operation. High catalyst activity and stability that guarantee complete reactant conversion in a single flow pass is a prerequisite for implementing continuous operation policy. To reach this goal, all the synthesized materials were first tested in Mizoroki-Heck reaction of methyl or butyl acrylate with iodobenzene in batch mode under optimized conditions.

During the optimization of the reaction conditions, it was confirmed that the catalysts were mostly active in polar aprotic solvents and at increased reaction temperatures. Use of tertiary amines as a base is the most favorable option and they should be used in excess because the lack of it can lead to rapid catalyst deactivation. An excess of acrylate is also necessary due to its volatility.

The study of potential catalysts that are suitable for the reaction with methyl acrylate showed that the bis-layered supported ionic liquid catalysts composed of covalently anchored imidazolium bromide and pyridine-carboxylate balanced with tetramethylguanidinium displays extremely high activity and stability in five to six cycles.



The existence of N-heterocyclic carbenes, carbon monoxide and nitrogen rich tetramethylguanidine (TMG) in the structure of the ionic liquid layer was mostly important for palladium stabilization. The activity of SILCA was higher by order of magnitude compared to the palladium deposited ordered mesoporous silica which was grafted with melamine ligands SBA-15/Pr-NH-CH₂-melamin-Pd(0), amino-functionalized metal-organic framework IRMOF-3 and magnetized MOF catalysts Fe₃O₄-NH₂@MIL-101-NH₂-Pd(OAc)₂ tested in the batch reactor under the optimized conditions. A high catalytic activity that enables good conversion at a relatively short residence time is crucial for the application of continuous processes.

In order to upgrade designed bis-layered SILCA, different grafting molecules i.e. carboxylic acids, bases and metal sources were used to modify the surface of SiO₂ and the catalytic effect of obtained SILCAs were studied in the reaction with the less reactive butyl acrylate. The impact of the ionic liquid layer structure on the catalyst activity and stability was observed. The rigidity of the ionic liquid layer was attributed to the existence of imidazole ring, while the carboxylic group in the layer coordinated the TMG cations that are most efficient in stabilizing palladium nanoparticles. Fine-tuning of the layer structure resulted in a SILCA with propyl imidazolium bromide-tetramethylguanidinium pentanoate modified SiO₂ and loaded with PdCl₂ as an optimal choice for the use in the continuous reactor.

Low SILCA loadings were used in simple and long-lasting process in a continuous packed bed reactor for the reaction with butyl acrylate. In contrary to what was observed in the batch reactor, excessive amounts of the catalyst did not result in deactivation caused by metal

agglomeration. Catalyst leaching was verified with on-line UV-VIS spectrometry, and the catalytic behavior was rationalized to certain extent elucidating the catalytic cycle within the ionic liquid layer. Poisoning was adopted as the main reason for the catalyst deactivation and leaching, which was resolved by the catalyst washing sequences. The new packed bed reactor concept was competitive and even outperforming the commercially available concepts showing the real potential of the designed SILCA and its use for production of fine chemicals in continuous operation mode.



M.Sc.(Chem.) Eveliina Mäkelä Aalto University, Department of Chemical and Metallurgical Engineering. October 8, 2021. The title of his thesis is

“Hydrotreatment of lignocellulose-derived molecules to renewable fuels and chemicals”

Opponent: Prof. Anders Riisager, Technical University of Denmark, Denmark

Custodian: Prof. Riikka Puurunen, Aalto University School of Chemical Engineering

Abstract:

Lignocellulose is an abundant, non-edible source of biofuels and biochemicals. It can be processed into several platform molecules, such as furfural, levulinic acid (LA), and phenols. In this thesis, the hydrotreatment of lignocellulose-derived molecules to obtain biofuels and renewable chemicals was studied using batch reactors. Instead of traditional hydrotreatment catalysts (sulfided NiMo and CoMo on γ -Al₂O₃) and toxic copper chromite (industrial furfural hydrotreatment), noble and base metal catalysts on metal oxides as well as on bio-based carbon supports were used.

Furfural hydrotreatment to 2-methylfuran (MF) was conducted using Pt, Ru, and Ni catalysts on wood-based activated carbons (ACs) from spruce and birch and with Cu/Ni catalysts on bio-based activated carbon foams (ACFs) from tannic acid and pine bark extracts and on spruce-based AC. The highest MF yields of 49%–58% were obtained with 1.5–3 wt.% Pt and Ru catalysts and with 5/5 wt.% Cu/Ni catalyst on ACs in liquid phase at 230–240 °C and 40 bar H₂ pressure. The suitability of ACFs as catalyst supports was also confirmed, and MF selectivity was increased

by acid treatments. The important catalytic factors affecting the MF selectivity were metal particle size and dispersion as well as the support's porosity and surface groups.

Hydrotreatment of LA dimers was first studied with a model compound, γ -nonalactone, using 3 wt.% Pt, Pd, Ru, and Rh catalysts on ZrO₂ at 280 °C and at an average pressure of 57.5 bar H₂. The highest selectivity to hydrocarbons (nearly 24%) was obtained with the Ru catalyst. The initial conversion of the catalysts (Rh \gg Ru) correlated with the amount of detected surface metal atoms. Further, the hydrotreatment of LA dimers was demonstrated with a 3.6 wt.% Ru/ZrO₂ catalyst at 250–300 °C and 47.5 bar average H₂ pressure to obtain increased carbon-chain-length (>C₆) products. Deoxygenation, the formation of volatile products, and the formation of aromatics increased at high temperature. The volatile products mainly comprised not only acids, esters, and ketones but also linear, branched, and cyclic hydrocarbons.

Hydrotreatment of 4-propylphenol to propylbenzene was studied with 3 wt.% Pt catalysts on Nb₂O₅, TiO₂, and ZrO₂ supports in liquid organic phase at 350 °C and 20 bar H₂ pressure. The highest selectivity of 77% at 98% conversion level was obtained with the Pt/Nb₂O₅ catalyst. Nb₂O₅- and TiO₂-supported catalysts had activity superior to ZrO₂-supported catalyst, which was thought to be attributable to oxophilic sites created during catalyst reduction.

In this thesis, high MF yields were obtained using catalysts on wood-based ACs. To the best of the author's knowledge, ACFs were tested as catalyst supports, for the first time. Moreover, the hydrotreatment of LA dimers with Ru catalyst was demonstrated, which

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offers a new route from lignocellulosic sugars to increased carbon-chain-length products. Finally, high selectivity to propylbenzene was obtained from 4-propylphenol; this is among the best results reported in the liquid-phase hydrotreatment of phenols.



M.Sc.(Chem.) Ali Najarnezhadmashhadi from Laboratory of Industrial Chemistry and Reaction Engineering (TKR) Åbo Akademi May 19, 2021. The title of his thesis is:

“Development of structured catalyst and reactor technologies for biomass conversion - Continuous production of sugar alcohols”

Opponent: Professor Dr. Juan Garcia Serna, Universidad de Valladolid

Custodian: Academy Professor Tapio Salmi

Abstract:

Energy-efficient technologies have been an aspiration for chemical industries, especially the design of chemical reactors. Structured catalysts play an important role to achieve this purpose. Several types of structured catalysts have been invented and investigated in recent years, such as monoliths, fibers, solid foams as well as structures prepared by three-dimensional (3D) printing. Due to the fact that solid foam catalysts provide a high porosity (75-95%) and a high specific surface area, open cell foam catalyst packings have been investigated as an alternative for catalytically active reactor packings. Enhanced mass and heat transfer, suppressed pressure drop and high specific surface area are important positive features of the solid foam packings. Furthermore, the structures of pores and struts in open cell foams allow radial liquid flow and local vigorous turbulence which result in enhanced mass and heat transfer.

Development of a structured catalyst was performed successfully and ruthenium catalysts supported on carbon-coated

aluminum foams (Ru/C) were prepared. First an active carbon support was prepared on open-cell aluminum foams. To incorporate a carbon layer into the aluminum foams, polymerization of furfuryl alcohol was carried out. The incorporation of ruthenium nanoparticles on the carbon coated aluminum foams was implemented by homogeneous deposition precipitation. Seven different characterization techniques such as SEM, TEM, XPS, TPR, ICP-MS, carbon monoxide chemisorption and nitrogen physisorption were applied on the solid catalysts.

The Ru/C foam catalysts were used in a continuously operating multiphase reactor set-up which had six tubular reactors working in parallel. Continuous hydrogenation of D-glucose, L-arabinose and a binary mixture of L-arabinose and D-galactose were studied in the experimental setup. Through investigating different reaction parameters, the temperatures 100-110°C and the liquid flow rates 0.5-1 mL/min were found suitable for catalyst screening and activity testing. The experiments were carried out at 20 bar hydrogen pressure. The continuous hydrogenation experiments were successful, the reproducibility was good, and the foam catalysts were stable. High selectivities of the desired products, sugar alcohols and sugar alcohol mixtures were obtained.

A mathematical model for open foam catalyst structures was developed. It was based on the concept of axial dispersion as the prevailing flow pattern, on liquid-solid mass transfer effects and intrinsic kinetics on the active sites of the catalyst. Rate equations were presented for the hydrogenation of individual sugars and binary sugar mixtures on Ru/C catalysts and they were implemented in the mass transfer and flow models of the open foam catalyst. The flow pattern in the foam structure was

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confirmed with step change experiments with an inert tracer.

A kinetic model for sugar hydrogenation was fitted to the experimental data obtained from open foam ruthenium catalysts. The non-competitive adsorption model was used for the adsorption of sugars and hydrogen. The effect of external mass transfer was included in the model, because it is in practice impossible to completely eliminate the external mass transfer limitations in continuous operation of the shallow foam bed: in order to obtain a high enough liquid residence time, low liquid velocities were used.

Finally, a new advanced comprehensive and transient multiphase model for a trickle bed reactor with solid foam packings was developed where axial, radial and catalyst layer effects were combined. The unique feature of this model is that the gas, liquid and solid phase mass balances include most of the individual terms such as internal diffusion, gas-liquid and liquid solid mass transfer and intrinsic kinetics.

A very powerful software (gPROMS ModelBuilder) was used for the model development and implementation which provided rapid computations and parameter estimation results at a reasonable time. Parameter estimations for both models, including the activation energies and adsorption parameters were carried out. In all the cases, the confidence intervals of the parameters remained within 10% error, indicating a good accuracy of the parameters. To investigate the model performance, a sensitivity analysis was carried out and the effect of the kinetic parameters and the operation conditions on the arabinose and galactose conversions was studied in detail. The mathematical models developed and implemented in the present work are

applicable for other three-phase research in continuous catalytic reactors with solid foam packings.



M.Sc.(Chem.) Ramakrishna Jogi from Laboratory of Industrial Chemistry and Reaction Engineering (TKR) Åbo Akademi, May 21, 2021. The title of his thesis is

“Green aviation fuel hydrocarbons from lignocellulosic biomass via hydrothermal liquefaction”

Opponent: Professor Dr. Knut Irgum, Umeå Universitet

Custodian: Professor Dr. Jyri-Pekka Mikkola

Abstract:

Hydrothermal liquefaction (HTL) of lignocellulosic biomass in primary alcohols is a novel thermochemical method to produce sustainable aviation fuel range cyclic hydrocarbons. In this method, particularly the underutilized wood fractions, hemicellulose and lignin components are dissolved to produce biocrude. The current planned process comprises of three phases, such as production of biocrude through HTL, extraction of bio-aromatics from biocrude using deep eutectic solvents (DES) and further transformation of bio-aromatics into cyclic hydrocarbons via hydrodeoxygenation (HDO). The main aim of this work was to utilize the heterogeneous catalysts in HTL method to produce biocrude at fixed temperature and under low initial hydrogen pressure in supercritical ethanol. The selection of catalysts was based on the acidity of the support material and transition metal immobilized on the support. The following catalysts were applied: 5 wt. % Fe-Beta-150 exhibiting with weak and medium Brønsted-Lewis acidity or non-acidic 5 wt. % Fe-SiO₂ and weakly Brønsted acidic NbOPO₄ or Pd/NbOPO₄ with weak Lewis acidity.

In-house prepared and characterized Fe-based catalysts were used in birch fractionation. The influence of gaseous atmosphere and catalyst acidity as well as formation of phenolic products during liquefaction was studied over 5 wt. % Fe-H-Beta-150 or 5 wt. % Fe-SiO₂. After the experiments, the liquid, solid and gaseous products were fully characterized using several analytical techniques. The obtained results show that Brønsted-Lewis acidic 5 wt. % Fe-H-Beta-150 catalyst, gave rise to around 25 wt. % of biocrude with 68 wt. % aromatic products, while non-acidic 5 wt. % Fe-SiO₂ catalyst only gave around 18 wt. % of biocrude with 38 wt. % aromatic products. A Brønsted acidic catalyst enhances the dissolution efficiency, particularly hemicellulose and lignin degradation into biocrude with increased formation of acids, esters and aromatic compounds. Relatively low amounts of gaseous products were formed and catalyst leaching during liquefaction was low. Based on X-ray diffraction measurements of the solid wood residue, amorphous cellulose transformed into crystalline state during liquefaction.

From the liquid phase analysis results as a function of time, a reaction mechanism was proposed for the lignin degradation products over 5 wt. % Fe-H-Beta-150 or 5 wt. % Fe-SiO₂ catalysts. The main lignin degradation product was isoeugenol, while some other intermediate products, i.e. coniferyl, and sinapyl alcohol, 4-propenyl syringol, syringaresinol, along with syringyldehyde rapidly reacted further. To support the proposed reaction mechanism, the thermodynamic analysis was also performed using the Joback approach and Gibbs-Helmholtz equation. In case of Nb-based catalysts, Pd/NbOPO₄ catalyst was prepared through wet-impregnation method and fully

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characterized. Reaction conditions were optimized and catalytic liquefaction over Pd/NbOPO₄ was compared with fresh and acetone extracted birch. In addition, the influence of support, and metal upon the liquefaction of birch were determined. From the liquid phase results, the main product in lignin degradation was homosyringaldehyde, opposite to 5 wt. % Fe-H-Beta-150, for which isoeugenol was the main product contrary to Pd/NbOPO₄ catalyzed hydrogenation of sinapyl alcohol to dihydroconiferyl alcohol. The fresh treated wood over Pd/NbOPO₄ resulted in the formation of 34 wt. % of phenolic monomers composed of 76.9 wt. % of dimethoxyphenols and 16.5 wt. % of guaiacol related monomers. The liquefaction of acetone extracted birch treated over Pd/NbOPO₄ gave 35 wt. % of lignin monomers containing 93.2 wt. % of dimethoxyphenols and 6.8 wt. % of guaiacol based monomers. The delignification efficiency during liquefaction of fresh and acetone-extracted birch over Pd/NbOPO₄ was also determined. Based on the liquid phase results the following reaction mechanism was proposed: Lignin degradation occurs via cleavage of ether bonds, which is catalyzed by Lewis acid sites in the solid acid catalyst. Thereafter, decarbonylation of aldehydes proceeds through Pd metal under low hydrogen initial pressure. Furthermore, a novel extraction method to extract the aromatic fraction from biocrude was developed. A deep eutectic solvent (DES) composed of choline chloride: ethylene glycol (1:4 mol) was used in a stepwise method with methyl isobutyl ketone (MIBK) and water.



M.Sc.(Chem.) Wander Perez Sena from Laboratory of Industrial Chemistry and Reaction Engineering (TKR) Åbo Akademi. Laboratoire de Sécurité des Procédés Chimiques (LSPC) Normandie Université INSA-Rouen. Cotutelle (double degree). The title of his thesis is

“Monomers from vegetable oil feedstock: kinetics, catalysis and thermal risk”

Members of the Jury: Professor Riitta Keiski (University of Oulu), Professor Laurent Falk (Université de Lorraine, Nancy), Professor Mélaz Tayakout (Université de Lyon), Professor Tuomo Sainio (LUT-University), Professor Päivi Mäki-Arvela (Åbo Akademi), Professor Lionel Estel (INSA-Rouen), Professor Sébastien Leveneur (INSA-Rouen), Academy Professor Tapio Salmi (Åbo Akademi)

Custodian: Academy Professor Tapio Salmi

Abstract:

Polyurethanes are among the most important polymers in our everyday life, they are industrially produced via the reaction of polyols and di-isocyanates. This process present multiple severe drawbacks such as high toxicity of the di-isocyanates. Furthermore, di-isocyanates are produced from petroleum-derived compounds such as phosgene, which is known to be an extremely toxic compound. In recent decades, a more environmental friendly strategy for the production of this precious polymer has emerged, that is the polymerization reaction of polycarbonates and polyamines, which takes

the advantages of bio-based and carbon dioxide feedstock.

This scientific effort is devoted to the study of the reaction pathway for the production of polyurethanes from vegetable oils based raw materials. Vegetable oils are a green source of raw materials that offer several benefits such as non-toxicity, renewable character and biodegradable products.

Each reaction step required to upgrade vegetable oils to polyurethanes was investigated separately. The epoxidation reaction was first investigated from a process safety point of view. Different epoxidation methods were compared and it was found that direct epoxidation with hydrogen peroxide in the presence of a metal oxide catalyst such as aluminium oxide gives the lowest probability of thermal runaway. Thereafter, the kinetics of the system was investigated and its efficiency was enhanced by application of semi-batch reactor technology. Mathematical modelling of the reaction system was performed, and a rather good description of the experimental data was achieved.

A series of heterogeneous catalysts were synthesized and tested in the carbonation process of epoxidized vegetable oils. The most important parameter to obtain a good reactant conversion and product yield was the utilization of mesoporous materials as supports and the presence of a Lewis acidity source such as a metal.

A Tian-Calvet isothermal calorimeter was used to determine the reaction enthalpies of the aminolysis system. The reaction enthalpies of aminolysis and amidation were determined, denoting a low exothermicity. Thereafter, the kinetics of the aminolysis system was explored using four amines; mathematical models for

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each amine system were developed, and a linear free energy relationship (LFER) was established linking the substituent of the amine and the estimated reaction rate.



M.Sc.(Chem.) Xiaojia Lu from Laboratory of Industrial Chemistry and Reaction Engineering (TKR) Åbo Akademi. Laboratoire de Sécurité des Procédés Chimiques (LSPC) Normandie Université INSA-Rouen, October 1, 2021. Cotutelle (double degree). The title of his thesis is

“Reductive catalytic depolymerization of industrial lignin and hemicellulose – process development and intensification”

Members of the Jury: Professor Ange Nizhou (IMT Mines Albi), Professor Ulla Lassi (University of Oulu), Academy Professor Tapio Salmi (Åbo Akademi), Professor Carita Kvarnström (University of Turku), Docent Mika Huuhtanen (University of Oulu), Professor Lionel Estel (INSA-Rouen), Professor Sébastien Leveneur (INSA-Rouen), Professor Henrik Grénman (Åbo Akademi)

Custodian: Professor Henrik Grénman

Abstract:

Modern biorefinery aims at utilizing renewable feedstocks to make a wide range of products such as chemicals, biofuels, and biomaterials while leaving as little residue as possible. Lignocellulosic biomass is a promising feedstock due to its availability, renewable nature, widespread application, and low competition with food. The fractionation of lignocellulose to its three main polymeric constituents and depolymerization of especially lignin and hemicellulose into monomers and oligomers before conversion into value-added chemicals is a key step in biorefineries. Despite a large potential, massive quantities of industrially produced hemicellulose and lignin are regularly simply burned for energy, which significantly hinders

the realization of the sustainable bioeconomy. The current work is devoted to enhancing the depolymerization of lignin and hemicellulose fractions obtained from Finnish silver birch with the help of a novel semi-industrial method.

The lignin was depolymerized in different organic solvents or solvent mixtures under a hydrogen atmosphere in the presence of a heterogeneous catalyst. The goal was to acquire small aromatic compounds for further valorization. The influences of different parameters, including lignin solubility, reaction time, hydrogen pressure, reaction temperature, basic additives, type and loading of catalyst, as well as type and composition of organic/aqueous solvent on the kinetics was investigated. Selective and efficient depolymerization to monomers and dimers was achieved by process intensification.

The research on depolymerization of industrial hemicellulose was performed in two stages. The acidic hydrolysis of xylan to xylose was first studied in both batch and continuous reactors. Several commercial heterogeneous catalysts were screened, and the reaction parameters were optimized to find a compromise between the reaction kinetics of the hydrolysis and the undesired degradation of monosaccharide products to achieve the highest xylose yield. Moreover, the reaction kinetics was modelled successfully.

One flow through hydrolysis and hydrogenation of hemicellulose was investigated in a continuous reactor equipped with two catalyst beds. The xylose produced by hydrolysis was subsequently converted to xylitol in the second bed. The reaction temperature, hydrogen pressure and residence time were varied to study the kinetics. A high yield (c. 90%) of xylitol was achieved and the

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kinetics was modelled obtaining a good fit to the experimental data.

The process of biomass valorization is typically highly temperature sensitive and it is not self-evident that isothermal processing conditions are optimal. The heat capacity of the reactor system is crucial when the process is performed under dynamic conditions and the heat capacity of catalyst support is not very well known and it was here studied in order to simulate and perform secure experimental operation in the future. The specific heat capacities of typical catalytic supports used in biorefinery applications were characterized with a Tian-Calvet micro-calorimeter. The temperature dependence was investigated for each catalytic material and polynomial expressions were successfully applied for simulating the experimental data. Significant differences were observed between the supports and the results contribute significantly to future development in valorization of biomass in dynamic conditions.

The current work contributes to the development and intensification of novel and sustainable processes for valorizing forest biomass according to the principles of green chemistry and process technology.

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Thank you.