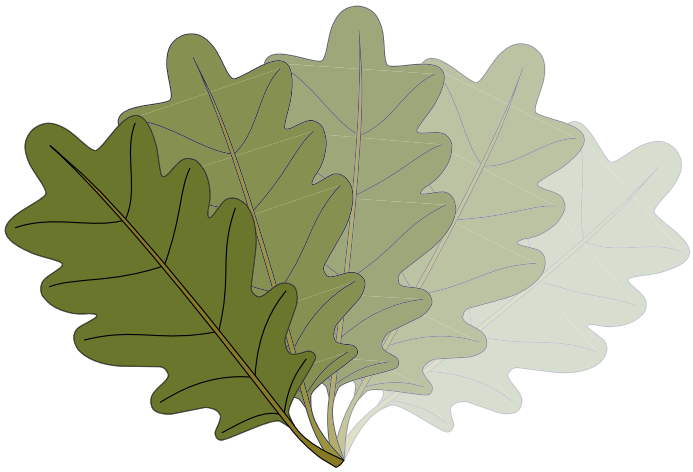
Åbo Akademi University
Science and Engineering

Annual Report 2016-2017



Johan Gadolin

Process Chemistry Centre

Johan Gadolin Process Chemistry Centre

at

Åbo Akademi University

Annual Report 2016-2017

Edited by

Henrik Grénman,
Rose-Marie Latonen, Päivi Mäki-Arvela,
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Åbo
Finland

2017

http://www.abo.fi/pcc/

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*Picture from the **PCC** annual meeting in August 2016*
Photo: Atte Aho

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PCC logo: Linus Silvander
Painosalama, Turku/Åbo

2017

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1. Introduction to the activities in 2016-2017

Background and news

The Johan Gadolin Process Chemistry Centre (***PCC***) began its journey already 1998 as a centre with common objectives and research strategy. After two periods with the status of a Centre of Excellence (CoE) in research granted by the Academy of Finland 2000-2011, and a period between 2012 and 2014 with activities in a new research program and some additional strategical funding from our university, we have now worked for nearly three years with the status of Centre of Excellence at Åbo Akademi University for the period 2015-2018. This also guarantees some CoE funding from the university.

The core of our current research plan, "**Future Refining of Forest Biomass – the Molecular Process Technology Approach**" is built on our strengths in experimental and modelling capabilities to explore chemical details in novel processes and products that use biomass-based raw materials. The focus is on modification of the biomass components and their use in high-value applications such as structural biocomposites, 3D biomaterials in biomedical applications, immunostimulatory glycoclusters, and various fine and specialty chemicals. The weight is not only on polysaccharides but very much also on lignin and trace elements, both utilization and fate in a modern biorefineries. We have continued emphasizing the incorporation of all researchers into the core activities and our Work Package leaders Chunlin Xu, Pasi Virtanen, Patrik Eklund, Nikolai DeMartini, have coordinated this well. However, the direct CoE funding being only a small share of the total funding we have also very intensive Complementary Research Activities coordinated by the newly chosen WP leaders Tom Lindfors and Patrik Yrjas.

Our Johan Gadolin Scholarship Programme has also continued to be successful and is well integrated to our research plan. The role of our Forum for Society (FS) chaired by Lars Gädda is important to help us interact with society and industry and this cooperation will be intensified as *PCC* looks forward towards our future after 2018.

PCC is active in two out of the three research profile areas Åbo Akademi University has in its current strategy, namely "Molecular Process and Material Technology (MPMT)" and "Drug development and diagnostics". The university also supports these areas with special funding and in consequence, to this we have Professor Thomas "Rosi" Rosenau from the University of Natural Resources and Applied Life Sciences (BOKU), Vienna, Austria, as an Adjunct Professor at PCC. Professor Rosenau's area of expertise is very broad and includes e.g. oxidation chemistry, cellulose chemistry, lignin chemistry, chemical synthesis and analytics. Furthermore, we also congratulate Henrik Grénman from *PCC* who got one of the tenure track professorships, Associate Professor in Molecular Process and Material Technology 1.10.2016-30.9.2020 at the Faculty of Science and Engineering, supported by the university in conjunction to the MPMT profile area.

Our cooperation with the Turku Centre for Biotechnology (CBT), Biocity Turku, and the newly established Health Campus Turku has been very successful. Biocity Turku has seven research programs, where ***PCC*** and its members are active in three and have cooperation with also some of the others. The main program where ***PCC*** is active is the Advanced Bioresources and Smart

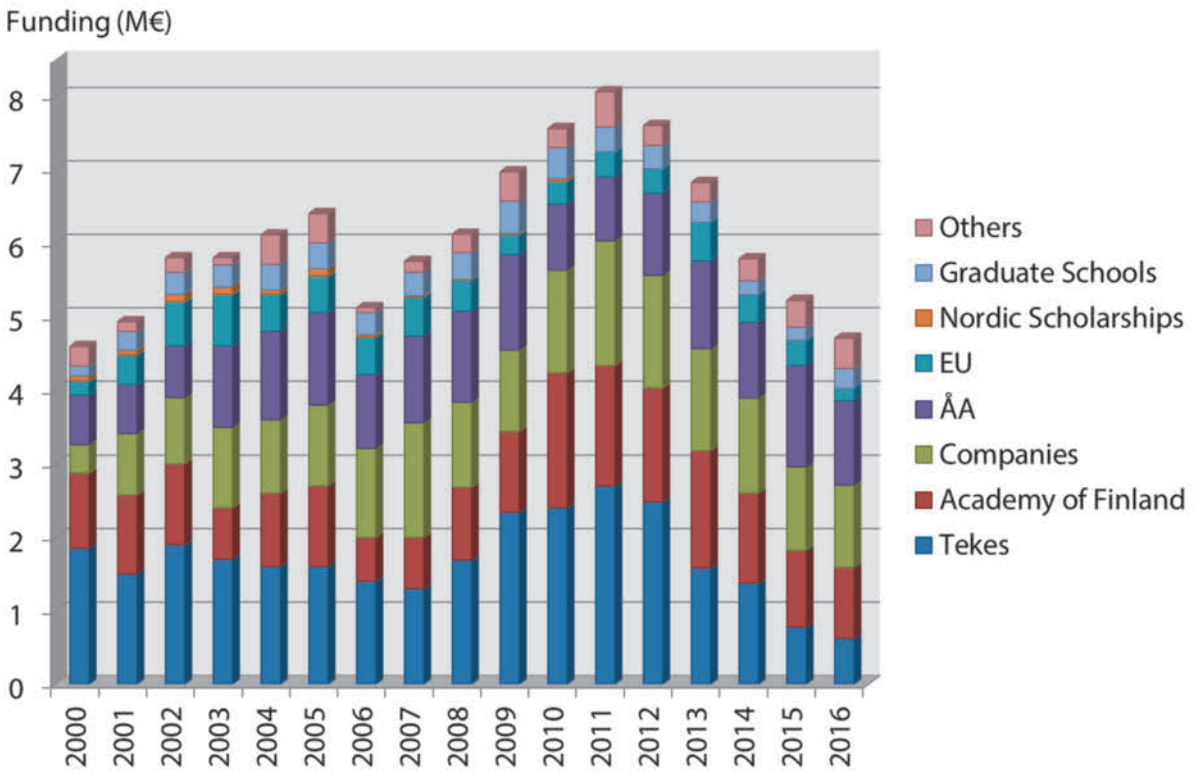
Bioproducts – Towards Sustainable Bioeconomy, "Smartbio"(director: Academy Professor Eva-Mari Aro, University of Turku (UTU), vice-director: Professor Stefan Willför). In addition to several joint courses and other activities within this program, we also arranged a seminar "From Bio-invention to the Market – Possibilities and Challenges" that got appreciably much attention also outside the universities. Then our groups are also members or associated members of the Biomaterial and Medical Device Research Programme (director: Professor Pekka Vallittu, University of Turku, vice-director: Professor Leena Hupa) and Diagnostic Technologies and Applications (directors: Professor Tero Soukka, UTU, and Jessica Rosenholm (ÅA), vice-directors: Professor Johan Bobacka and Pekka Hänninen, UTU).

As always, ***PCC*** and its members have been very active in applying for funding on both national and international level. Unfortunately, we were not successful in the call of Academy of Finland for the Centre of Excellence Programme 2018–2025, but that led to a new brain storming activity and a new idea for the period 2019 onwards. *PCC* thus decided to build a new research plan and establish an industrially relevant CoE aiming at cutting-edge scientific research where we offer a unique environment combining science and engineering in cooperation with the industry. We want to solidify and strengthen our knowledge-based industrial platform with a molecular and methodological approach with the scope going from renewable biomass to green products. The detailed planning together with the industry will continue during 2017 and 2018.

The year 2016 in numbers

In 2016, about 70 senior researchers and more than 45 full-time PhD candidates worked in the research projects of the Centre. In addition, a number of shorter term visitors, Master's students and support personnel participated in our activities.

The figure below shows the funding of the Centre since the year 2000. The key external funding sources in 2016 were Åbo Akademi University, the Academy of Finland, and Tekes – the Finnish Funding Agency for Innovation together with Industrial Companies. Especially the decrease in funding from Tekes, but also from Academy of Finland, has raised the demand level of the Centre to maintain its high-level productivity of research. This situation is a consequence of the overall funding situation for research in Finland, and ***PCC*** is convinced our high-level research, excellent output, and the new research strategy from 2019 onwards will change this negative trend. It is noteworthy that although the funding is back at the level we had when PCC first started, our production is excellent and thus the production per invested euro is better than ever. However, in order to evolve our activities further, we need to increase the funding in the future.



The funding of the Johan Gadolin Process Chemistry Centre 2000-2016

From the academic point of view, the year 2016 was again very productive. The table below gives some key numbers of our academic activities in 2016. Once again, the Centre kept a very high production rate and reached an all-time record by publishing 168 papers in scientific publication series with the full referee system. The number of theses decreased somewhat, which was to be expected considering the decreasing trend in funding, but is still on a satisfying level.

Theses and peer reviewed journal articles by the Johan Gadolin Process Chemistry Centre.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016
Doctoral Theses	5	7	8	2	11	8	8	8	9	7	6	10	10	15	16	12	6
Masters' Theses	21	23	27	26	17	15	20	23	19	17	15	11	14	12	16	25	10
Journal Articles	60	70	94	77	106	109	113	116	101	118	138	143	145	154	145	164	166

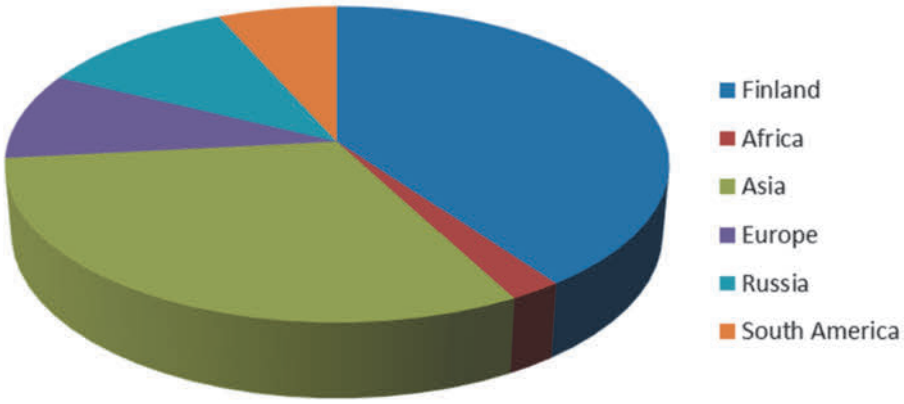
Besides the technical publications, the ***PCC*** has its Newsletter and our researchers wrote also popular texts in daily newspapers and journals and appeared on several radio and TV programs.

Organization of seminars, workshops, and courses

Our series with internal workshops and also work package meetings continued during 2016. PCC was also one of the main organizers for the course "Wood Biopolymer Science for "*New materials from trees*" - Finnish-Swedish Joint Summer School 2016" that was organized on the Åland island together with Wallenberg Wood Science Centre and Chalmers from Sweden and the Nordic PolyRefNorth researcher network. The course had 47 participants from Sweden, Denmark, and Finland – although the nationalities were much broader. This was now the second time such a joint course was organized and this fresh tradition will probably be continued in a few years. The traditional annualsSeminar was held on August 28, 2016.

Doctoral students

A central part of our research activities is done as doctoral theses works. Altogether 45 PhD thesis projects are actively underway at the Centre. Our doctoral students are very international (see the graph below). More detailed information of the background of our PhD students is given ion Chapter 6 in this Annual Report.



Nationality of PhD students at Johan Gadolin Process Chemistry Centre.

In addition to projects, CoE funding, and grants, the Åbo Akademi doctoral network program and therein the Graduate School in Chemical Engineering (GSCE) and Doctoral Network of Materials Research (DNMR) are important sources of funding for the PhD students in ***PCC***.

Johan Gadolin Scholarship Program

Our Johan Gadolin Scholarship Program was founded in 2007. It was funded by the Åbo Akademi Foundation during the years 2007-2011 and continued for 2012- 2013 on other sources of funding, after which the Åbo Akademi Foundation decided to continue funding for the Johan Gadolin Scholarships Program for at least the period 2014-2017.

In the Johan Gadolin Scholarship Program we have been able to invite PhD students and post doctoral researchers to join ***PCC*** for a period between 3 to 9 (earlier 3-12) months. So far, 62 fellows from 23 different countries and 50 different universities worldwide have participated in the

program. The visitors have participated in on-going research projects at the Centre. The cooperation between the ***PCC*** and the Johan Gadolin fellows has so far produced more than 160 scientific articles and more than 120 conference proceedings.

Boards and Task Forces

In 2016 the ***PCC*** is led by an executive board consisting of the five research group leaders: Professors Stefan Willför, Johan Bobacka, Tapio Salmi, Reko Leino, and Leena Hupa. In 2016 the board met nine times. Dr. Otto Långvik works with the coordination of the ***PCC*** and functions as secretary of the board.

Since the very beginning, the ***PCC*** board has been supported by two important Advisory Boards; the Scientific Advisory Board (SAB) and the former Industrial Advisory Board, which now is called the Forum for Society. 2015-2017 our Scientific Advisory Board consists of the Professors *Jiri Janata* from the Georgia Institute of Science and Technology in Atlanta, USA, *Raimo Alén* from the University of Jyväskylä, Finland, *Lars Pettersson* from the Royal Institute of Technology in Stockholm, Sweden, *Andreas Seidel-Morgenstern* from Max Planck Institute, Germany and *Jan-Erling Bäckvall* from Stockholm University, Sweden.

Our Forum for Society (FS) consists of representatives of the key industrial companies, as well as members of the society co-operating with the Centre. The members of the FS are listed in Chapter 2 in this Annual Report.

In 2016, the ***PCC*** had one lecture in its Distinguished Lecturer Series:
March 14, 2016: Prof. JunYong (J.Y.) Zhu . Fulbright - Distinguished Chair, Aalto University; US Forest Service R&D, Forest Products Laboratory, Madison; Dept. of Biological Systems Engineering, University of Wisconsin-Madison: "Recent Progress in Woody Biomass Conversion to Biofuel and Cellulose Nanomaterials"

Acknowledgements

This report will be published at the Annual Symposium of the ***PCC*** held on August 22, 2017 at Åbo Akademi University Arken Building in Turku. The report gives an overview of the recent activities at the Centre. It has a complete list of the journal articles, theses and other publications produced by the Centre in the calendar year 2016. It also has an activity calendar listing the main events where members of the Centre have contributed or participated during the year.

The report and layout is edited by an editorial team consisting of Henrik Grénman, Rose-Marie Latonen, Päivi Mäki-Arvela, Tiina Saloranta-Simell, Anna Sundberg, and Johan Werkelin with the assistance of Mia Mäkinen.

We want to thank all our collaborating partners in Finland and all over the world for another year of interesting and inspiring work together.

On behalf of the Board of the Johan Gadolin Process Chemistry Centre,

Stefan Willför
Chairman

1.1 Experiences of the Johan Gadolin Scholarship researchers

Barbara Kovács

My name is Barbara Kovács and I am from Hungary. I am working in the Pharmaceutical Institute of Szeged as a PhD student. In the enzymatic laboratory, I managed to separate the enantiomers of secondary amines through a lipase-catalyzed enantioselective N-acylation. Here, in Finland, our aim has been to develop a new method for the racemization of these secondary amines. I investigated these processes with the use of metal catalysts. The project was carried out successfully. This six-month scholarship gave me a lot of experiences, including work and private life. I have developed a lot within synthetic chemistry and I have learned how to use some new instruments. I met many other foreigners here and I managed to get to know different cultures. Being alone abroad for six months has changed my character completely; I have become much stronger and more confident. If you have a chance to receive a scholarship, it would be worth applying for it. I am sure, you wouldn't regret it. I appreciate for the opportunity to take part in this program.

Silvia Palano

I am Silvia Palano and have a master's degree in Chemical and Process Engineering from the University of Padova (Italy). I have a genuine interest in research and a firm determination to explore new fields of science and technology. My training is based on the design capability and management of conventional chemical and process plants (petrochemical and pharmaceutical) and industrial safety. It was a great opportunity and a pleasure to work in the Laboratory of "Teknisk kemi och reaktionsteknik". I carried out many experiments and tested different catalysts in a trickle bed reactor of direct synthesis of hydrogen peroxide. The advantage is the lack of hazardous products, but there is one drawback to keep in mind: the wide range of flammable limit of the reactant mixture H_2/O_2. The peculiarity of this work is to introduce for the first time a new structure for the metallic catalyst, carbon foam derived from melamine. The catalytic tests showed the ability of the new catalyst to be tailored for the H_2O_2 direct synthesis. The Johan Gadolin Scholarship program is well structured and functional. It allows both intercultural and scientific exchange. The city and the university make you feel comfortable here in Finland.

Benouadah Nacera

My name is Benouadah Nacera, a PhD student in eco-materials science engineering at the University of M'Hamed Bougara (Boumerdès, Algeria). I have a MSc degree in organic and macromolecular process engineering and also an engineering degree in chemical analysis from the same university. I have received a scholarship at the Johan Gadolin Process Chemistry Center (PCC) for a period of nine months, under the supervision of Docent Andrey Pranovich. My primary research interest is the characterization of hemicelluloses from different Algerian wood species (Pinus Halepensis, Eucalyptus Camaldulensis, and Date Palm Phoenix-dactylifera-L). As a result, we studied extractives and chemical composition of wood using modern and sophisticated equipment, involving at the same time the strong background of my supervisor in dealing with different aspects of wood chemistry. Turku is a good place to live; it is pleasant, peaceful setting offering a wide range of accommodations and amenities. Åbo Akademi University is the best place to get the information which enables scholars to take advantage of their advanced acquired know-how.

Jonathan Barnsley

I am Jonathan Barnsley, a PhD Candidate at the University of Otago New Zealand. I grew up on a small family farm in a southern part of the South Island. At high school, I found an interest in science, particularly physics and chemistry. At university, I studied chemistry and computer science where I found an excellent group of fellow students and mentors. My honours' project entailed spectroscopy of organic dyes for use in organic photo-voltaics under the supervision of Professor Keith Gordon. My time at university was highly enjoyable for a multitude of reasons the most prominent being an utter open-mindedness to new ideas and possibilities. After a break, I signed up for a PhD continuing my organic dye work with Keith, of which I currently have 11 months left. My background is in Raman spectroscopy and computational chemistry, the latter of which has been used to investigate ion binding energies for a number of polymer and porphyrin systems. This work has been conducted in conjunction with electrochemistry carried out by Grzegorz Lisak and Narender Joon at the PCC. I felt fortunate to have spent an extended stay at Åbo Akademi, where I met a number of very intelligent and friendly fellow scientists. The level of science is well reflected in the excellent Åbo divisional meetings, which I recommend to anyone. I can't wait to go back!

Thomas Zweckmayer

I am Thomas Zweckmayer coming from BOKU University Vienna, Austria where I have been working as a PostDoc in the field of cellulose chemistry as well as analytical chemistry over the last couple of years. I was joining the Johan Gadolin Process Chemistry Centre, Institute of Wood- and Paper Chemistry in April 2016. At PCC, I worked on the isolation of TEMPO-oxidized GGM-oligomers and analytical methods was developed to analyze the compounds isolated. PCC appears as an integral disguise which bundles all activities in the field of process chemistry at Åbo Akademi University. It is equipped with state-of-the-art infrastructure such as NMR-instruments which allows scientists to work almost independently. PCC serves as a common platform which facilitates brisk exchange between all the groups participating as well as the international scientific community. Living in Åbo, Finland was a very nice experience. Student apartments are available in walking distance at an affordable price. All essential infrastructure such as shops etc. is located in the city center of Åbo. Nice restaurants and bars are available as well. I highly recommend visiting PCC at Åbo Akademi University as a scientist where nice infrastructure is available to conduct cutting-edge research.

Vincenzo Russo

My name is Vincenzo Russo and I was born in Naples, Italy, on 2nd of May 1985. On the 9th of May 2014, I got my PhD title in Chemical Sciences in the Chemical Sciences Department of the University of Naples "Federico II", with a thesis entitled Kinetic and Catalytic Aspects in Propene Oxide Production. It dealt with the synthesis of propene oxide subject, from propene and hydrogen peroxide in the presence of TS-1 catalyst, by investigating both the kinetic and catalytic aspects. As a Post-Doctoral Researcher at the same university a few more years after my graduation, I won a scholarship at Åbo Akademi University (Turku, Finland) working on multiphase reactors modelling. The Johan Gadolin Scholarship gave me the opportunity to grow in the Chemical Engineering Science field, because of the contact with an excellent research group. The cooperation with the researchers was great and fruitful, and of course it is far to be ended. In fact, the side and very positive effect of this period was to establish and strengthen the cooperation between my research group in the University of Naples Federico II and the Laboratory of Industrial Chemistry and Reaction Engineering, heading to Åbo Akademi.

Zdenka Jarolimova

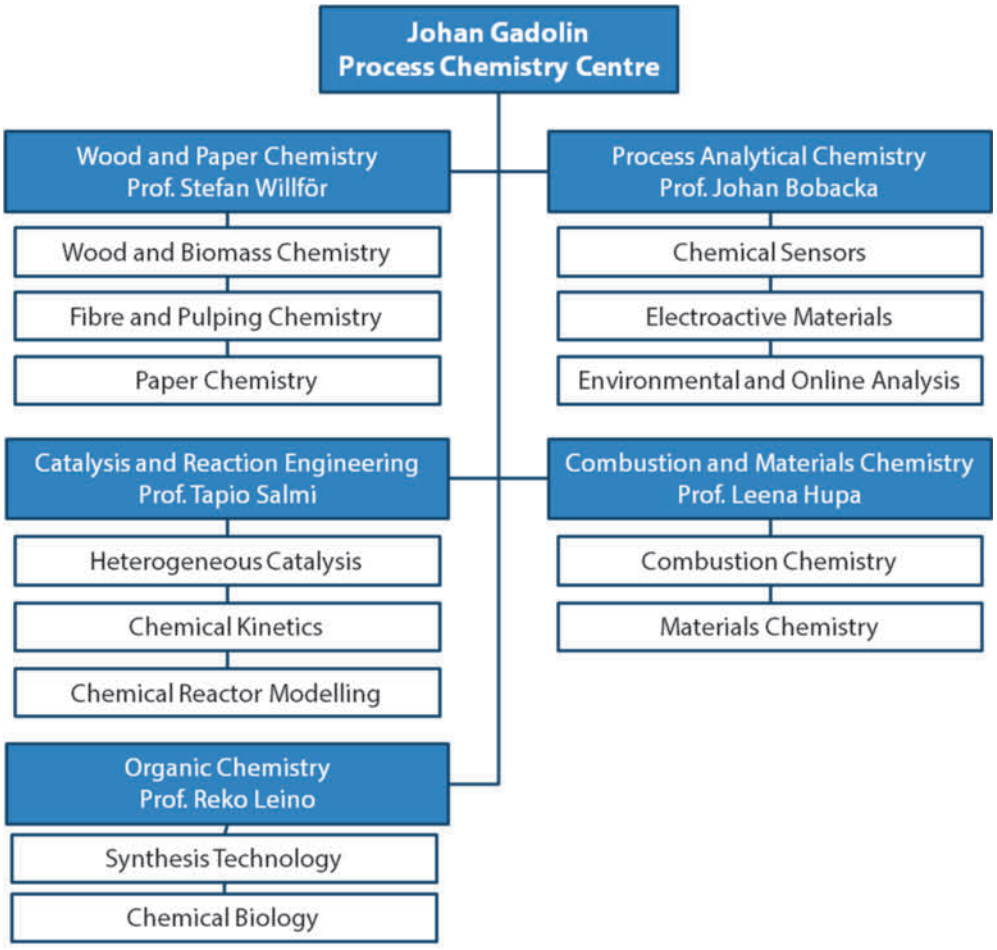
My name is Zdenka Jarolimova and I am currently a PhD student in the group led by Professor Eric Bakker at the University of Geneva (Department of Inorganic and Analytical Chemistry), Switzerland. My main research interest focuses on the development of chemical sensors based on the Solid-Contact Ion-Selective Membrane electrodes and Ionophore-based Ion Selective Optical Nanosensors. During my stay at the Johan Gadolin Process Chemistry Center, my work was focused on the experimental study of a novel signal transduction principle for SC-ISEs introduced by Professor Johan Bobacka in 2014. The novel technique is based on constant potential coulometry and uses the redox capacitance of the internal solid-contact of the ion-selective membrane electrode to convert changes in ion activity into an electrical current (and charge) readout. It was an unforgettable experience to live in Finland. I was working with nice, friendly and helpful people. I appreciate their help, support and great advices. It was a pleasure to work in such a friendly environment that was reigning at workplace. Do not hesitate to apply, you will enjoy every single moment and you will not regret it.

Zuzana Vajglová

My name is Zuzana Vajglová and I am from the Czech Republic. I recently graduated with a PhD degree from the University of Chemistry and Technology Prague in Czech Republic. My scientific focus is in microreactor technology and I have worked at the Institute of Chemical Process Fundamentals of the Czech Academy of Science already for 9 years. I applied for the JG scholarship at Åbo Akademi, because I wanted to gain new experiences, a much broader view of current events and new approach to solving the issues that interest and fulfill me (heterogeneous catalysis, microreactor technologies, kinetics, transport phenomena...). All of this was fulfilled. My postdoc fellowship in Finland confirmed that personal practical work experience abroad is invaluable. I gained knowledge and new skills that I would like to use for further research work in my home country. Moreover, a postdoctoral fellowship can be the first step to open a space for the further mutual cooperation. In my opinion, Åbo Akademi University in Finland is the perfect place for the scholarship. I met a lot of people who were very helpful and kind. I have only positive memories from my stay.

2. Organization and personnel

2.1 Organization of *PCC*



Executive board

- Professor Stefan Willför (chairman)
- Professor Johan Bobacka (vice chairman)
- Professor Leena Hupa
- Professor Reko Leino
- Professor Tapio Salmi

Coordinator

- Dr. Otto Långvik

Scientific Advisory Board (SAB)

- Professor Raimo Alén, University of Jyväskylä
- Professor Jan-Erling Bäckvall, Stockholm University
- Professor Jiri Janata, Georgia Institute of Technology
- Professor Lars J Pettersson, KTH
- Professor Andreas Seidel-Morgenstern, Max Planck Institute Magdeburg

Forum for Society (FS)

- Lars Gädda, FS Chairperson
- Örjan Andersson, Novia
- Ilmo Aronen, Raisio
- Stig-Erik Bruun, Chemigate
- Kenneth Ekman, Crisolteq
- Heidi Fagerholm, Kemira
- Linda Fröberg-Niemi, Turku Science Park
- Christine Hagström-Näsi, CLIC Innovation
- Patrik Holm, Orion Pharma
- Bertel Karlstedt, Valmet
- Kari Kovasin, Metsä Fibre
- Björn Lax, Chemec
- Timo Leppä, Chemical Industry Federation of Finland
- Lars Peter Lindfors, Neste
- Pia Nilsson, UPM-Kymmene
- Karri Mikkonen, Turku Future Technologies
- Leena Paavilainen, Luke
- Jarkko Partinen, Outotec
- Leena Sarvaranta, VTT
- Mathias Snåre, Nordkalk
- Kenneth Sundberg, Tikkurila
- Kari Toivonen, Elomatic
- Petri Vasara, Pöyry
- Stefan Wallin, Member of Parliament

2.2 Wood and Paper Chemistry

The mission of our laboratory is to *promote sustainable and multipurpose use of wood for high-value biomaterials and biochemicals and for fibre products*. We strive towards creating and publishing novel and significant scientific findings and to educate students and scientists with excellent skills and creative problem-solving ability for the needs of industry and the society.

Our research is directed towards promoting sustainable, resource efficient, and multipurpose use of wood and other renewable raw materials in products including pulp, paper, fibre, and wood products, but also for novel biomaterials, biocomposites, biochemicals, and bioenergy. Advanced analytical techniques are our tools to obtain knowledge at the molecular level on the various components of different natural raw materials and their reactions, interactions, and functions in different processes and products. Our biorefining approach aims at utilizing forest or other renewable resources as wide-ranging as possible, thus minimizing the amount of waste in the end. For example, selective extraction and recovery of hemicelluloses, cellulose, lignin, or polyphenols from wood, bark, or process waters is followed by functionalization and utilization in different value-added end-uses. A strong research approach is the utilization of nanocellulose, modified hemicelluloses, and lignin for hydrogels and materials in biomedical applications, especially through 3D bioprinting. We also work on understanding the fibre-fibre joint structure and molecular level interactions between fibre surfaces to obtain high extensibility of the fibre networks for novel mouldable packaging. Furthermore, we provide analytical services and support in process problem solving to the industry in the forest and bioeconomy sectors.

External research support during 2016 was obtained mainly from Academy of Finland and the industry and Tekes. We also have close cooperation with e.g. KTH and Chalmers in Sweden with researcher exchange and joint research and courses. Other important partners are University of Wollongong in Australia, University of Helsinki, LUKE, and groups affiliated to the Turku Centre for Biotechnology in Finland.

Link

http://www.abo.fi/institution/traochpapperskemi

Personnel of the Laboratory of Wood and Paper Chemistry in May 2017

Personnel

Professors

Stefan Willför
Bjarne Holmbom (Emeritus)

Docents

Andrey Pranovich
Annika Smeds
Anna Sundberg
Chunlin Xu

Senior and early stage researchers

Nacera Benouadah
Jarl Hemming
Victor Kisonen
Ekaterina Korotkova
Otto Långvik
Linda Nisula
Dmitrii Riabukhin
Frida Sjögren
Anders Strand
Mattias Strandberg
Sebastian von Schoultz
Wenyang Xu
Yongchao Zhang

Secretary

Marika Ginman

2.3 Process Analytical Chemistry

Our view of *process analytical chemistry* is not limited to *industrial processes*, but includes also *environmental* and *biochemical* processes, that may all benefit from *on-line analysis*. Our current research is focused mainly on the development of *chemical sensors* for on-line analysis in various fields of applications, including industrial process analysis, environmental monitoring and health diagnostics. The ultimate goal is to develop novel chemical sensors and analytical methods that can provide reliable chemical information for long times without any need for calibration or maintenance. Achieving this extremely challenging goal would open up an unlimited range of applications of benefit for industry and society.

Within the field of chemical sensors, solid-contact ion-selective electrodes (SC-ISEs) and solid-state reference electrodes continue to be major research topics in our group. In order to achieve calibration-free and maintenance-free ion sensors we conduct fundamental research on sensor materials, such as conducting polymers and graphene, and new sensing principles. Further progress was achieved in the area of printable ion sensors suitable for cost-effective mass production, wearable sensors, as well as electrochemical sensors for mutational analysis of DNA. As an alternative to classical potentiometry, the coulometric signal readout method allowing precise measurements of small concentration changes was developed further. Research on our new multisensor platform with wireless signal tranmsmission was continued in collaboration with industry in the form of a prestigious (Tekes – Challenge Finland) project.

Our research on SC-ISEs has traditionally been focused on analytes such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cd^{2+}, Pb^{2+}, Cl^-, pH and some organic cations. Extending the range of analytes towards various anions has been challenging due to the lack of ionophores (receptor molecules) that would be selective enough for the anions of interest. In order to improve the selectivity, paper-based sampling and separation was evaluated as a method to decrease the interference from salicylate anions during potentiometric determination of Cl^-. However, in order to obtain truly selective anion sensors, our recently established collaboration with a research group that synthesizes new ionophores for anions will be particularly valuable for future progress in this field.

Other research activities include dynamic extraction and on-line determination of heavy metals (Pb) from soil by using atomic spectroscopy (ICP-OES) and conversion of greenhouse gases via electrocatalytic reduction of CO_2 to CO.

We collaborate closely with national and international partners from academia and industry. Externa funding support from the Academy of Finland, Tekes, Jane and Aatos Erkko Foundation, Magnus Ehrnrooth Foundation, Otto A. Malm Foundation, Walter Ahlström Foundation, Kone Foundation, TES and TECNIOSpring (Spain) are gratefully acknowledged.

Links

http://www.abo.fi/institution/analytisk_kemi

Personnel of the Laboratory of Analytical Chemistry in May 2017.

Personnel

Professors

Johan Bobacka
Ari Ivaska (Emeritus)
Andrzej Lewenstam (Emeritus)

Docents

Leo Harju
Carita Kvarnström
Rose-Marie Latonen
Tom Lindfors
Li Niu
Tomasz Sokalski
Di Wei

Senior researchers

Zhanna Boeva
Kim Granholm
Jussi Kauppila
Grzegorz Lisak
Zekra Mousavi
Ulriika Mattinen

Laboratory manager

Tor Laurén

Early stage researchers

Jesus Arroyo
Tingting Han
Ning He
Narender Joon
Sara Lund
Minh Nguyen

Secretary & coordinator

Britt-Marie Haahti
Mia Mäkinen

Technicians

Sten Lindholm

Computer support

Peter Ekholm

2.4 Organic Chemistry

The Laboratory of Organic Chemistry strives for excellence in research and education, training students and researchers on all levels for successful careers in industry and academia.

The laboratory operates in two of the main research profiling areas of Åbo Akademi University: Molecular Process and Materials Technology; and Drug Development and Diagnostics. Within these areas, the main research efforts of the laboratory are focused on 1) Development of sustainable chemical synthesis technologies using both homogeneous and heterogeneous transition metal catalysts, organocatalysts and biocatalysts with special emphasis on understanding of reaction mechanisms and kinetics; 2) Synthetic carbohydrate chemistry and glycobiology; 3) Natural product chemistry, with particular focus on wood extractives such as lignans and hemicelluloses and lignin. All these key research areas rely heavily on utilization and understanding of advanced NMR spectroscopic techniques.

Other research activities of the laboratory range from energy research to environmental organic chemistry including studies on the environmental fate of pharmaceuticals, antibiotics and endocrine disruptors.

External research support during 2016 was obtained from Tekes, the Academy of Finland, industrial partners and foundations. The laboratory closely collaborates with several national and international partners and actively participates in research networks.

Link

http://www.abo.fi/organiskkemi

Personnel of the Laboratory of Organic Chemistry in May 2017.

Personnel

Professors

Reko Leino
Jorma Mattinen

Docents

Filip Ekholm
Patrik Eklund
Leif Kronberg
Tiina Saloranta-Simell
Rainer Sjöholm
Annika Smeds

Senior researchers

Ramesh Ekambaram
Jan-Erik Lönnqvist
Risto Savela

Early stage researchers

Ewelina Kortesmäki
Matilda Kråkström
Lucas Lagerquist
Robert Lassfolk
Ida Mattsson
Axel Meierjohann
Jani Rahkila
Sabine Rendon
Patrik Runeberg
Mathilda Råberg

Technicians

Päivi Pennanen
Peter Holmlund

Computer support

Peter Ekholm

Secretary

Mia Mäkinen

Economy secretary

Chritina Luojola

2.5 Combustion and Materials Chemistry

Our research strategy is based on detailed knowledge of chemistry in high-temperature processes and properties of the high-temperature materials. Our main research endeavours are in bioenergy, cleantech, circular economy, and biomedicine.

Within the bioenergy field, our research includes characterising the composition and behaviour of different biomasses and waste-derived fuels, modelling of combustion processes, measurement of emissions to the atmosphere, and development of a generic understanding of the interactions between the materials in the combustion devices, the fuels and their ashes. We utilise thermodynamic equilibrium calculations to describe high-temperature processes, especially in various ash and slag forming systems. For this, we develop thermodynamic databases of the high-temperature systems through thermal analysis in ambient and pressurised atmospheres containing different gases. Several complimentary experimental tools (single particle reactor, thermogravimetric analyser/differential scanning calorimeter – both atmospheric and pressurised and lab-scale fluidised bed) are used to understand the release of inorganic elements and their role in fouling and emissions in thermochemical conversion of biomass and waste. We also develop submodels that describe the chemistry in high-temperature processes, such as NOx formation reactions in various fuels to be adapted to the modelling of combustion-related processes with computational fluid dynamics. One distinctive attribute of our research activities is the development of cleaner and more efficient combustion technologies using fuels that are known as "difficult". The research is carried out not only in laboratory scale but also as measurements and sampling campaigns in full-scale combustion processes. Some of our core competence areas are exploring the high-temperature corrosion and erosion mechanisms of steam tubes and ceramic refractories induced by bed materials and various ashes that contain alkalis, chlorides, bromides, fluorides, etc. Recently, we have developed totally new techniques to accurately measure and understand the corrosion and reaction mechanisms of the materials in their target environments. Management of material streams and emissions, treatment and recycling of different waste streams that contain inorganic materials in energy efficient and environmentally friendly manner are essential topics in our research.

Within the medical field, development of composites containing bioactive glasses for wound-healing and tissue engineering scaffolds are our main research focuses. Over the years, our strategy has been to understand thoroughly the influence of the oxide composition of the bioactive glasses on various cellular responses. One key goal is to develop detailed knowledge of the reaction and dissolution kinetics of the bioactive glasses when they are used in various biomimetic devices in hard and soft tissue regeneration applications.

Our research is done in collaboration with national and international universities and research centres. The research is financed by Tekes, Academy of Finland, the EU, NordForsk, industry and small to medium-sized enterprises. In addition to novel generic knowledge and competence, our research gives the industry partners new strategic scientific information and tools for innovations, new products and business concepts for the global market.

Link

http://www.abo.fi/fakultet/ook

Personnel of the Laboratory of Inorganic Chemistry in May 2017

Personnel

Professors

Leena Hupa
Mikko Hupa, rector of Åbo Akademi University 2015-2019

Docents

Rainer Backman
Anders Brink
Kaj Fröberg
Daniel Lindberg
Christian Mueller
Laeticia Petit
Bengt-Johan Skrifvars
Heimo Yländen
Patrik Yrjas

Senior researchers

Dorota Bankiewicz
Nikolai DeMartini
Markus Engblom
Oskar Karlström
Tooran Khazraie Shoulaifar
Juho Lehmusto
Siim Link
Fiseha Tesfaye
Emil Vainio
Xiaoju Wang
Johan Werkelin
Maria Zevenhoven

Laboratory engineer

Tor Laurén

Early stage researchers

Laura Aalto-Setälä
Leena Björkvik
Nina Bruun
Meheretu Dirbeba
Jan-Erik Eriksson
Elisa Hupa
Hanna Kinnunen
Niklas Koivunen
Timo Lehtonen
Na Li
Jonne Niemi
Varun Rai
Joni Rantala
Patrik Salminen
Paulo Santochi
Christoffer Sevonius
Anna Sergeeva
Polina Sinitsyna
Jingxin Sui
Maria Sundqvist
Berndt Södergård

Technicians

Peter Backman
Luis Bezerra
Jaana Paananen
Linus Silvander

Computer support

Peter Ekholm

Economy secretary

Eva Harjunkoski

Secretary

Mia Mäkinen

2.6 Industrial Chemistry and Reaction Engineering

The core competence of Industrial Chemistry and Reaction Engineering is in catalysis, kinetics, chemical reactor technology as well as exploring new reaction environments and development of green process technology. Process intensification is a vital part of our research effort. Our approach is strongly methodological, but the main application area is the transformation of biomass, particularly forest biomass, to valuable chemical components. Our know-how is continuously developed on catalyst preparation, characterization and screening as well as in new approaches to chemical kinetics and reactors.

The research on reactive solids, mainly solid-liquid reactions has been expanded, because they have numerous industrial applications, from pharmaceuticals to valorization of biomass. New theoretical concepts have been developed and applied on non-ideal reactive solids and they have received a lot of international attention. New catalytic systems have been taken in use, particularly supported mono- and bimetallic catalysts, which are developed in a close collaboration with universities in Padova, Umeå, Kiev, Novosibirsk and Tver. Silicon carbide, carbon nitride as well as various mesoporous materials are active researched and used by us.

Several new processes based on molecules originating from biomass are under investigation, for example amination and epoxidation of fatty acids as well as catalytic transformation of furfural. The research collaboration in the catalyst characterization is very intensive with University of Turku, University of Oulu and University of Umeå. Molecularly oriented kinetic studies are conducted in several applications, particularly in the homogeneously and heterogeneously catalysed hydrolysis of hemicelluloses as well as hydrogenation and oxidation of mono- and disaccharides, preparation of epoxidized vegetable oils. Microwave technology is used to enhance the epoxidation fatty acids and carbonation of fatty acid epoxides (in collaboration of INSA-Rouen).

We approach reaction mechanisms and reaction kinetics from first principles, i.e. quantum chemical calculations, which can elucidate the adsorption states and adsorption stoichiometry on solid metal surfaces. In this field, the collaboration with the University of Palermo is very intensive. The complex interaction of reaction and diffusion in porous media is studied experimentally and with sophisticated simulations including particle-size distributions. The concept is applied to catalytic two- and three-phase systems as well as to solid-liquid reactions. New computational tools have been taken in use in the simulation of kinetics, diffusion and flow patterns, the most applications are in the fields of structured reactors and milli- and microreactors. The group obtained an international prize for modelling efforts applied to microreactors; the work was a collaborative effort with University of Naples (Vincenzo Russo, José Hernández Carucci, Teuvo Kilpiö and Tapio Salmi).

Microwave and ultrasound equipment are used to explore the possibilities to process intensification. The leading principle is multiscale modelling: to achieve real reaction intensification, the modeling efforts should cover the approaches from quantum chemistry to computational fluid dynamics (CFD). New kinds of structured catalysts are under investigation, such as solid foams, which are developed together with Inorganic Chemistry (PCC), Technical University of Dresden, Helmholtz-Zentrum Dresden Rossendorf and Umeå University. The aim is process intensification by minimizing the diffusion resistance and pressure drop in catalyst structures.

The progress of green process technology is visible in many fields, particularly in the development of new continuous processes for sophisticated chemicals, such as bio-degradable surfactants, platform chemicals, bio-lubricants and chemical intermediates. This is in many cases done in micro- and milliscale reactors, which provide a real technology jump; we use them for catalyst development, kinetic screening and continuous production of chemicals in gas and liquid phases. All the experimental efforts are coupled to advanced mathematical modelling of chemical phenomena in batch, semibatch and continuous systems. Completely new research efforts have been commenced in catalytic destruction of pharmaceuticals in wastewaters by using ozone as the oxidation agent.

The collaboration with several universities from EU countries is extensive and the interaction with Latin America has been expanded and deepened. Finnish-Brazil and Finnish-Chile projects are in progress in the field of microalgae as sources for biofuels and health-promoting chemicals and the student exchange with Czech, French, German, Italian, Russian, Spanish and Venezuelan universities is flourishing. We were happy to receive a record number of foreign researchers to the Laboratory in 2016. Within the framework of research profiles approved by Academy of Finland, a new tenure-track professorship in Molecular Process and Material Technology was established (Henrik Grénman). The industrial collaboration increased considerably during 2016.

Personnel of the Laboratory of Industrial Chemistry and Reaction Engineering in May 2017

Link

https://www.abo.fi/fakultet/tekniskkemi

Personnel

Professors

Tapio Salmi (20%, Dean of Faculty)
Dmitry Murzin
Johan Wärnå
Jyri-Pekka Mikkola (20%, joint professor with Umeå University)
Associate professor (tenure track) Henrik Grénman

Docents

Atte Aho
Kalle Arve
Matias Kangas
Narendra Kumar
Sébastien Leveneur
Päivi Mäki-Arvela
Fredrik Sandelin
Esa Toukoniitty
Pasi Virtanen

Laboratory manager

Kari Eränen

Senior researchers

Ikenna Anugwom
Pierdomenico Biasi
Valérie Eta
Sigmund Fugleberg
Olatunde Jogunola
Teuvo Kilpiö
Arto Laari
Jun Liu
Jussi Rissanen
Doris Ruiz
Vincenzo Russo
Eero Salminen
Juan Garcia Serna
Luis Miguel Sanz Moral
Anton Tokarev
Pasi Tolvanen
Zuzana Vajglova

Early stage researchers

Shekoufeh Adhami
Cesar de Araujo Filho
Andrea Baccini
Erfan Behravesh
Louis Bomont
Yiran Chen
Adriana Freites Aguilera
Lidia Godina
Imane Hachemi
Shuyana Heredia
Thomas Hornbogen
Ekaterina Kholkina
Ali Najarnezhadmashhadi
Hoang Nguyen
Silvia Palano
Andrea Perez Nebreda
Ricardo Pezoa Conte
Maria Pinilla de Dios
Soudabeh Saied
Farhan Saleem
Jonah Schaaf
Vladimir Shumilov
Robert Slotte
Stefano Sterchele
Frans Storgårds
Sakari Teerikoski
Zusana Vajglova
Nemanja Vucetic

Technicians

Elena Murzina

Economy secretary

Per Backman

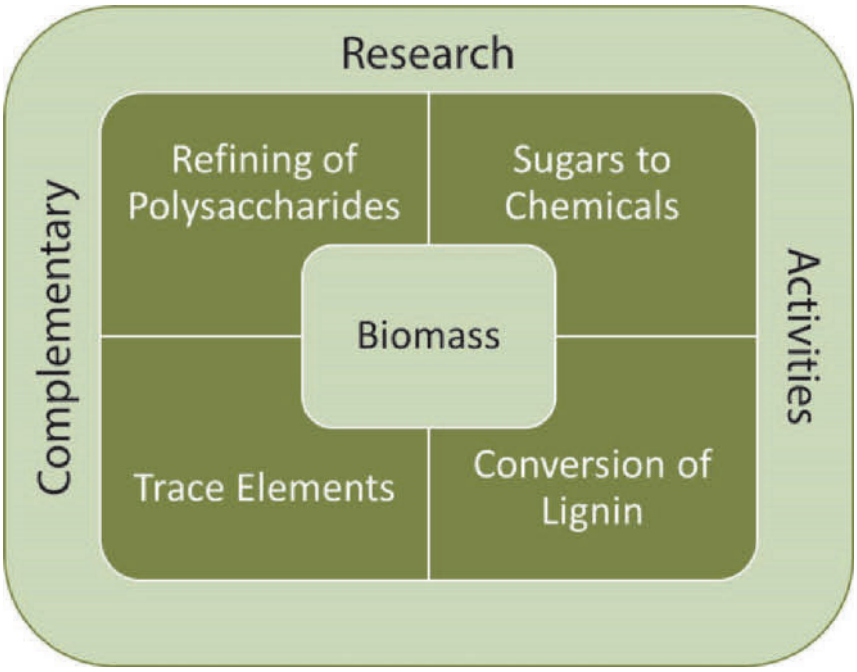
Computer support

Peter Ekholm

3. Research

Our research plan "PCC – Future Refining of Forest Biomass" is in the core of the Finnish Bioeconomy, Circular Economy, and Cleantech areas. Finland can become one of the pioneers in a global perspective in the evolutionary development of forest biomass, because 70% of our territory consists of forest, which is rich in lignocellulosic biomass. Finland actually has the largest amount of forest per capita in the whole of Europe and this biomass has a yearly growth that is larger than what we utilize. Forest biomass is potentially a very rich source of molecules, which can be further refined to new materials, chemicals and fuel components. The challenge is big, because the molecules appearing in biomass deviate substantially from those in fossil sources. Molecules from biomass have a high degree of functionality and high oxygen content compared to the molecules appearing in fossil sources. This implies that many of the current technology solutions cannot be applied directly to molecules originating from biomass and therefore new chemical technology is needed.

The development of new technologies should be based on a very deep-going understanding of the underlying chemical and physical processes, which we call Molecular Process Technology. PCC merges chemistry and chemical engineering to provide industrially relevant solutions for the future. The goal is to develop new, sustainable technologies for making selected platform chemicals, fine and specialty chemicals, as well as health promoting materials and chemicals. The research is mainly focused on two important types of molecules appearing in forest biomass, namely polysaccharides (hemicelluloses and cellulose) and lignin. The research programme is materialized in four work packages (WP): Refining and utilization of polysaccharides (WP1), Conversion of sugars and sugar derivatives to chemicals (WP2), Refining options of lignin (WP3) and Trace elements in refining of biomass (WP4).



***PCC** research areas.*

3.1 WP1 - Refining and utilization of polysaccharides

WP1 Leader, *Docent Chunlin Xu*
chunlin.xu@abo.fi

Due to an emerging urge to find natural alternatives to petro-based chemicals and synthetic materials, research in 'biorefinery' dealing with biomass-based energy, materials, and chemicals has become particularly important. However, great challenges and bottlenecks, e.g. complexity of the structure of plant cell wall components and more importantly lack of innovative approaches to develop high-value products, are limiting the technology development and the feasibility of biorefinery process. A novel extraction and fractionation process for pure hemicelluloses (pat. appl. WO2014009604 (A1)), which is in the course of being commercialized, presents PCC with a unique availability and possibility to perform application research and develop new applications based on pure hemicelluloses. The resulted cellulose can be used to prepare high quality cellulose products and nanocellulose. Our interest is currently mainly to utilize the fractionated polysaccharides for the development of high-performance products. For example, polysaccharides as polymers (in combination with conducting polymers and graphene) or other compounds such as bioactive glass for different high-value applications, including water purification, chemical sensors, 3D-printed electronics, biomedical treatment, functional barriers in packaging and films, and in biocomposites for various applications including but not limited to novel packaging materials. Moreover, the polysaccharides are excellent sources of monosaccharides for further valorization.

The ultimate goal of WP1 is to develop novel technology platform for high value applications of polysaccharides. More specifically, the objectives are:

To efficiently isolate hemicelluloses of high purity, which will then be used in WP1 and to selectively hydrolyze the polysaccharides to monosaccharides, which can be utilized in WP2;

To prepare hemicellulose-based adsorbents for removal or inactivation of dissolved hazardous compounds;

To investigate the capability of hemicelluloses as stabilizers in technical emulsions; and

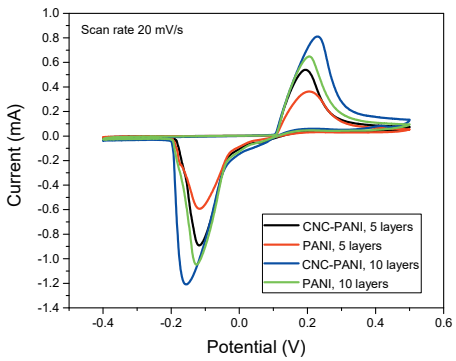
To tailor polysaccharide-based structural composites can be novel bio-based fiber-based materials for packaging. Moreover, by incorporating other composite component such as conducting polymer or other carbon material (e.g. graphene), applications in (bio) sensors and wound healing promotion are aimed. Another option of other composite component is bioactive glass aiming at the application as scaffolds in tissue engineering.

Composites Based on Conjugated Polymers and Nanocellulose

Main funding: Åbo Akademi University, Johan Gadolin Scholarship, Academy of Finland

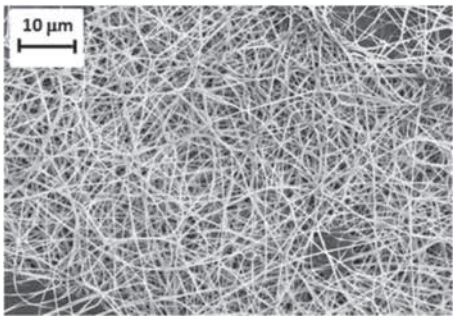
Wenyang Xu, Rose-Marie Latonen, Chunlin Xu

A water-based environmentally friendly electrically conducting ink composed of cellulose nanocrystals (CNC) and polyaniline (PANI) was prepared. PANI was synthesized by the emulsion polymerization approach using dodecylbenzenesulfonic acid (DBSA) as the dopant to induce spherical nanoparticulate formation. The ink is intended for use as a substrate for a gas sensor as such, as a conducting ink for use in paper electronics or for a chemical sensor after functionalization of CNC with suitable chemical groups. Glycerol was used to adjust the viscosity of the ink. The inks were successfully printed on Metso paper with the flexographical printing method. The ordered nano-sized crystal structure and high surface charge made CNC as suitable additive for the ink formulation of the spherical nanoparticles of PANI(DBSA). A stable nanoparticulate CNC containing ink with an electrical conductivity of the printed films with ten layers between 30 and 60 S cm^{-1} was obtained which was more than an order of magnitude higher than for the corresponding film without CNC.



Cyclic voltammograms of CNC-PANI(DBSA) and PANI(DBSA) inks with different numbers of printed layers.

The electrospinning method was used for preparation of water-resistant composite fibers based on cellulose nanofibrils (CNF) and poly(3,4-ethylenedioxythiophene):polystyrene-sulfonate (PEDOT:PSS). The fibers are intended for use as stimuli responsive materials as growth matrix for nerve cells. Polyethyleneoxide (PEO) was used as the carrier polymer to assist the electrospinning process and poly(ethyleneglycol)diglycidyl ether (PEGDE) as a cross-linker to make water-resistant fibers which are easier to handle. The electroactivity of the electrospun fibers have been characterized by cyclic voltammetry and the structure before and after the cross-linking reaction by FTIR spectroscopy.



A scanning electron microscopy micrograph of the water-resistant electrically conducting electrospun fibers made of cellulose nanofibrils and PEDOT:PSS.

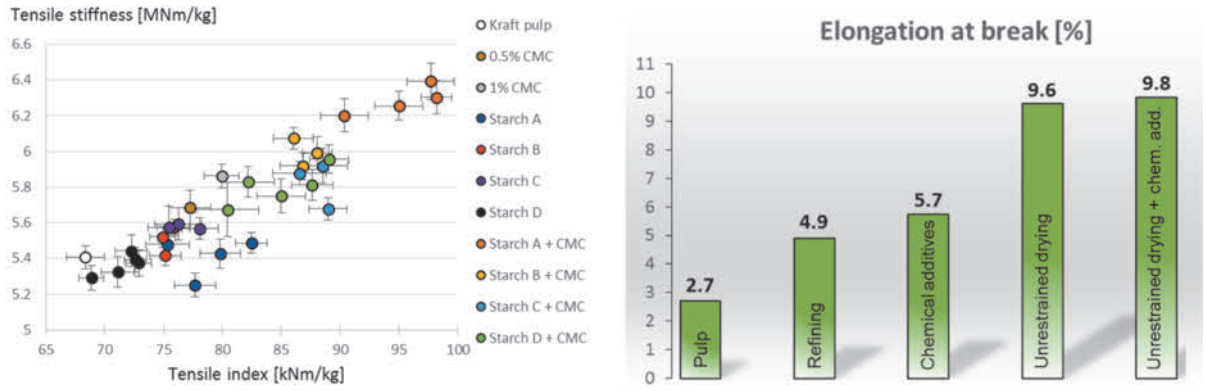
Cooperation: Centre for Functional Materials, Åbo Akademi University

Tailored Fibre-Fibre Interactions for Boosted Extensibility of Bio-based Fibre Networks - ExtBioNet

Main funding: Academy of Finland

Anders Strand, Chunlin Xu, Anna Sundberg

This project is targeted towards the development of new types of renewable fibre-based paper with high deformation potential, which is needed to obtain novel, bio-based packaging material for the use in forming processes. In order to form a 3-D structure with high quality, the extensibility of the fibre networks must be increased to a new level by mechanical and chemical means. However, increased paper extensibility is generally coupled with decreased paper strength and significantly decreased paper stiffness. High paper stiffness is important in most packaging applications. Hence, crafting a fibre network with high elongation at break and sufficiently high stiffness may be the key for the packaging applications of the future.



A wide array of paper properties can be obtained by optimized combinations of commercially available papermaking additives (left). The elongation at break of the fibrous network can be increased significantly by mechanical refining of the fibres in combination with an unconventional drying technique; i.e. unrestrained drying (right).

The effect of wet end additions of cationic starches and/or carboxymethyl cellulose (CMC) on the tensile index, tensile stiffness, elongation at break, and paper shrinkage during unrestrained drying, was determined by papermaking trials. The aim of the study was to mitigate some of the distinctive decrease in strength and stiffness due to unrestrained drying by addition of wet end additives, while maintaining the extraordinarily high elongation at break of papers after unrestrained drying.

Overall, addition of the different polysaccharides increased the tensile index and density of the paper. The largest increases in tensile index and tensile stiffness were seen when combining certain cationic starches with CMC. With certain combinations of cationic starch and CMC, it was possible to increase the tensile index and stiffness of the paper, while maintaining the high elongation at break after unrestrained drying. To complement the results from the papermaking trials, adsorption of cationic starches and CMC onto cellulose nanofibril model surfaces was studied by QCM-D and SPR techniques. It was seen that the additives adsorbed onto cellulose surfaces as soft gels, containing a large amount of coupled water. Adsorption of soft and malleable polysaccharide layers in the fiber-fiber joints were shown to enhance the paper properties significantly on a macroscopic level. The most swollen and softest layers of adsorbed polysaccharides resulted in the largest increases in tensile index and stiffness of the paper.

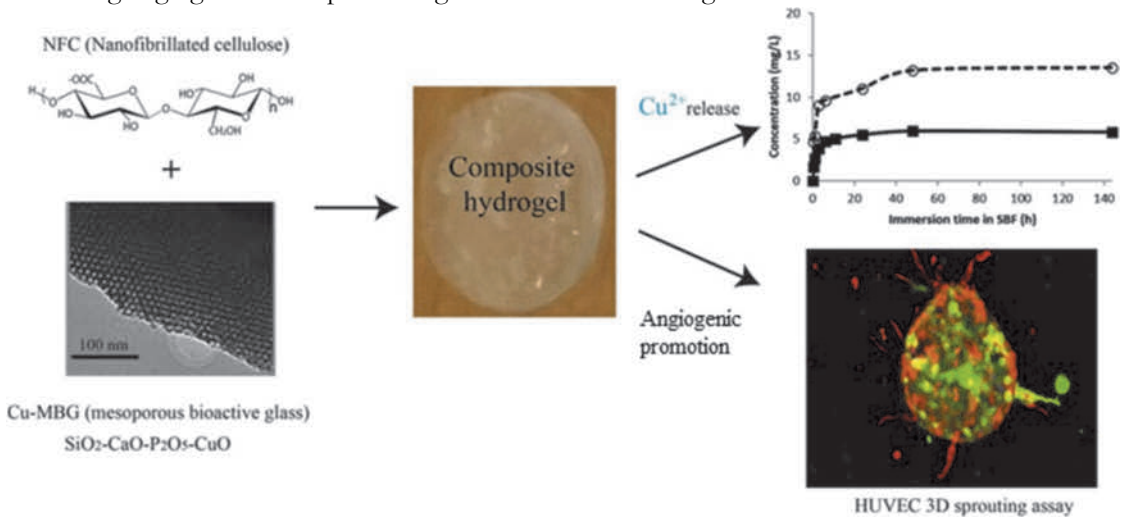
Cooperation: VTT Technical Research Centre of Finland, Finland

Biocomposites of Nanocellulose and Bioactive Glass for Biomedical Applications in Chronic Wound Healing

Main funding: PCC, Academy of Finland

Xiaoju Wang, Fang Cheng, Chunlin Xu, Leena Hupa

Chronic wounds cause patients severe emotional and physical stress and create a significant financial burden on patients and the whole healthcare system. To address an urgent need in clinics on developing a new generation of therapeutic dressings with advanced functionalities, biocomposites consisting of copper-doped mesoporous bioactive glass and wood-based nanocellulose have been developed and bio-assessed through joint efforts within PCC and Cell Biology of Åbo Akademi. Owing to excellent material properties of nanocellulose and an intriguing role of Cu^{2+} as therapeutic ions in wound healing cascades, this composite dressing integrates the therapeutic functionalities on site, including moisture retention, angiogenic promotion, and antimicrobial capacity. The developed Cu-containing wound dressing holds great promise on stimulating angiogenesis and promoting chronic wound healing in clinics.



Flow chart of the project containing material development, fabrication of composite hydrogel, in vitro ion dissolution study from the composite, and the angiogenesis assay on the composite in 3D spheroid culture system of human umbilical vein endothelial cells (HUVECs).

The synthesized Cu-MBG possesses hexagonally-packed and ordered mesopores, which endow it with a high *in vitro* bioactivity in SBF in terms of hydroxyapatite precipitation. The release of Cu^{2+} from Cu-MBG is preferential compared with the dissolution of Si network. A dose-dependent cytotoxicity of Cu^{2+} on 3T3 fibroblast was found. More importantly, a critical biological level of Cu^{2+} below 10 mg/L was suggested for the survival and growth of 3T3 fibroblasts. Due to the biological role of Cu^{2+}, the composite hydrogel showed angiogenic promotion in the angiogenesis assay of HUVECs and it also greatly enhanced the gene expression of Vegfa, Vegfc, Pdgfb and Fgf2 (bFgf) in 3T3 fibroblasts culture. Furthermore, in 3D spheroid culture, the composite (NFC:MBGSi75Cu5 = 10:1) significantly induced HUVEC sprouting and promoted the fibroblast-endothelial cell interaction and ECM production. In addition, the Cu^{2+} released from the composites of NFC and Cu-MBG also inhibited the growth of *E. coli.*

Extraction and Hydrolysis of Marine Carbohydrates

Main funding: National Commission for Scientific and Technological Research – CONICYT

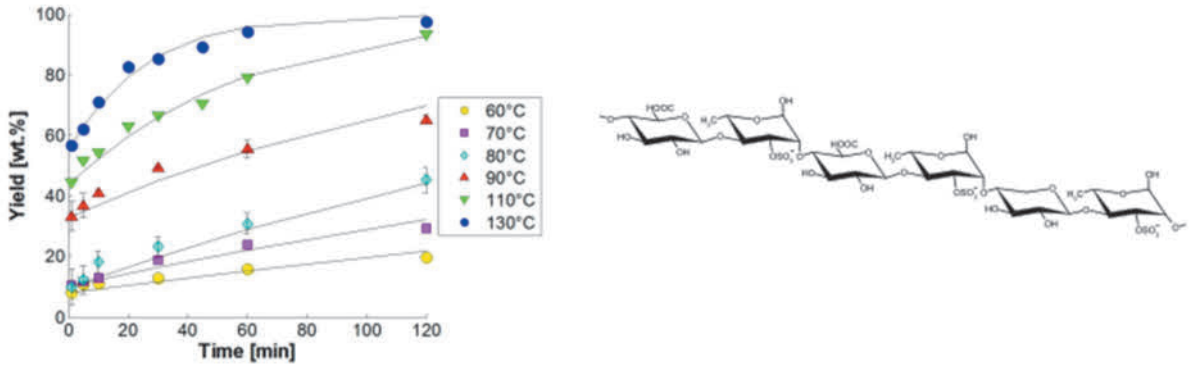
Ricardo Pezoa-Conte, Allison Leyton, Cristina Ravanal, Andrea Baccini, Päivi Mäki-Arvela, Henrik Grénman, María Elena Lienqueo, Paolo Canu, Jyri-Pekka Mikkola

In the recent years, the use of different types of biomass has become more and more important for the production of biofuels. Still the old concept of biomass processing has been evolved to a biorefinery, where most of the biomass is utilized to produce fuels, chemicals and materials.

Algae are considered the most efficient ecosystem on earth. Estimations calculate that algae comprise almost half of the total biomass on earth. Furthermore, algae grow at much higher rates compared to land plants, they do not compete for the use of land for food production, they completely lack lignin and contain substantial amount of carbohydrates. Among these, cellulose and starch are important constituents of algae, although different polysaccharides such as ulvan, carrageenan, agar and alginate are of huge importance. Consequently, these facts render them attractive under any biorefinery concept.

In this project, we have studied the extraction of marine constituents from green and brown algae. Particularly, we have studied the extraction of the green algae polysaccharide ulvan, which is constituted by l-rhamnose, d-glucuronic and l-iduronic acids residues, mainly unbranched with molar mass between 300 – 700 kDa. Ulvan is partially sulfated in O3 of l-rhamnose residues, providing ionic properties to the molecule. L-rhamnose is a rare sugar which is scarce in nature. However, l-rhamnose has gained a lot of attention in the present years due to its uses in the pharmaceutical and cosmetic industries. Our results show that ulvan is relatively easily extracted in 2 h aqueous processing at temperatures between the range 60 – 130°C with yields up to 99 wt.%. Further hydrolysis of this polysaccharide to obtain l-rhamnose monomers by processing with homogeneous and heterogeneous catalysts have been studied. Processing with Smopex-101 rendered yields of up to 90 wt.% of l-rhamnose at temperatures between the range 90 – 120°C after 48 h of reaction. A mathematical modelling of the kinetics of the extraction and the hydrolysis of ulvan have been proposed to model the experimental data.

In our work, we have also studied the extraction of phlorotannins from brown algae, which are compounds with high antioxidant activities of interest for the pharmaceutical and food industries. Different solvents and temperature conditions have been tested to optimize the extraction of phlorotannins from algae, as well as, identification of molecules using high precision liquid chromatography mass spectrometry. Additionally, we have studied the hydrolysis of alginate using alginate and oligoalginate lyases, observing yields up to 110 mg of uronic acid/g of algae.



Kinetics of the extraction of ulvan at different temperatures (left). Molecule of ulvan (right).

Cooperation: University of Chile; University of Padua, Italy

Design of Biobased Extracellular Matrix-Mimicking Scaffolds for Biomedical Applications

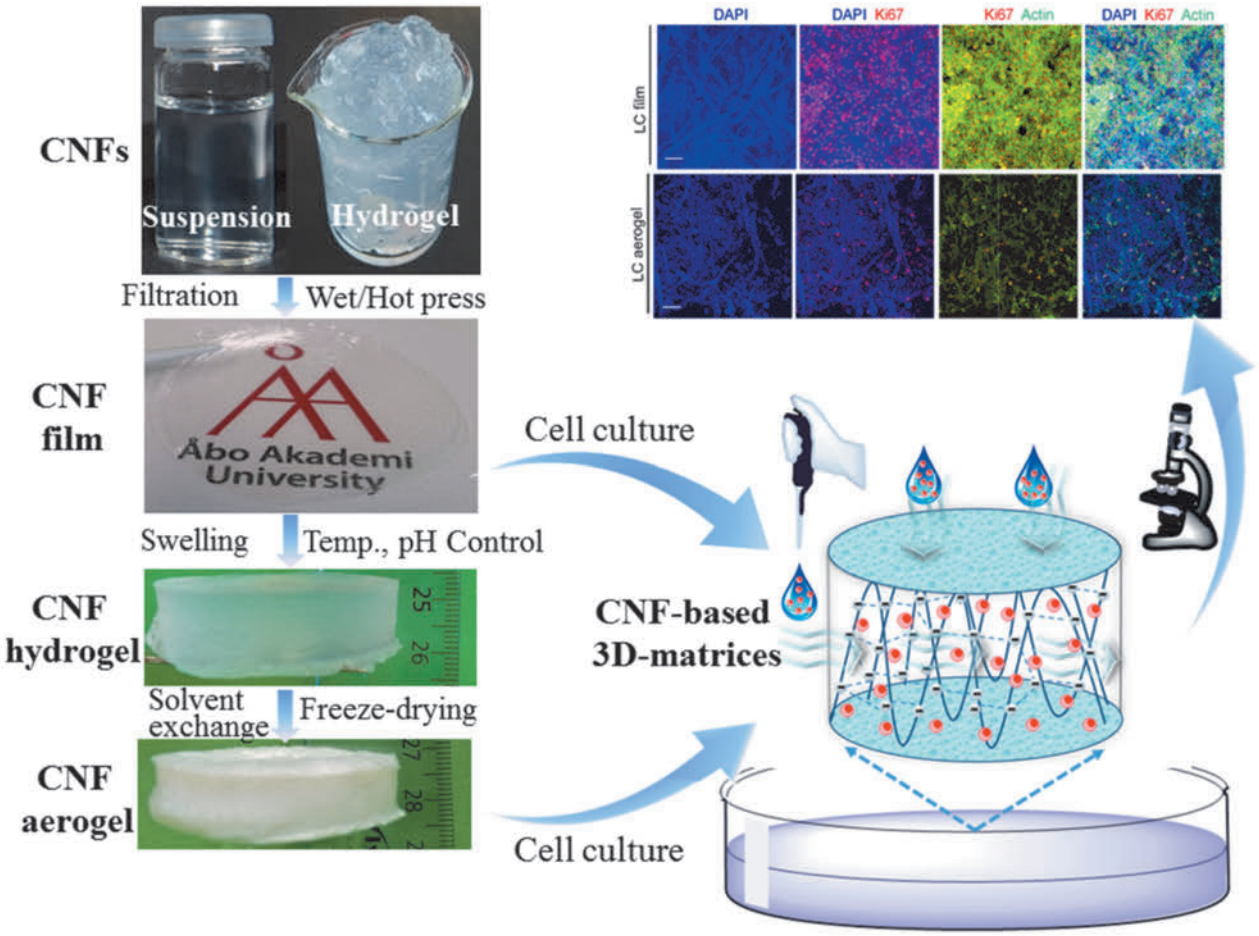
Wood-based polysaccharides, especially cellulose, which are the most abundant biorenewable materials with their promising properties such as excellent mechanical strength and flexibility, biocompatibility, and environmentally friendly nature has found their potential applications in medical treatments, e.g. cell culture and tissue engineering. To truly mimic the natural extracellular matrices (ECM), the most critical issue in all tissue-engineering approaches is the man-made scaffolds or matrices that need to have innate structural similarities with the physiological matrices in body tissues and support crucial cellular activities. Thus, we aim to design ECM-mimicking scaffolds from biobased polymers with tuneable structural properties that will satisfy various biomedical applications. Moreover, biocompatibility of biopolymers and thus-tailored scaffolds is evaluated.

Wood Polysaccharides for Biomedical Applications

Main funding: Johan Gadolin Process Chemistry Centre (**PCC**), Graduate School of Chemical Engineering (GSCE), Chinese Council Scholarship (CSC)

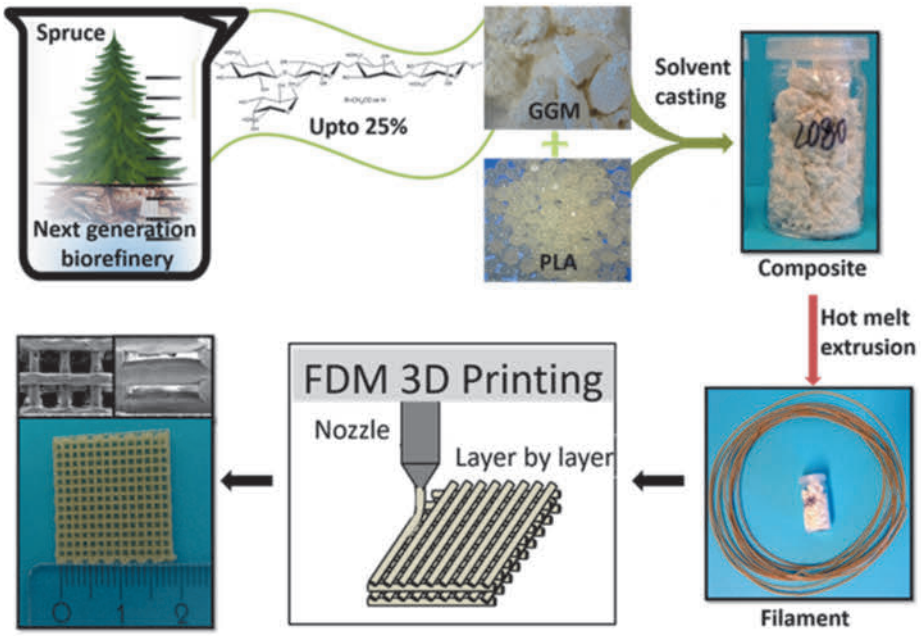
Chunlin Xu, Jun Liu, Wenyang Xu, Stefan Willför

Owing to the intrinsic non-toxicity, biocompatibility, and biodegradability, nanocellulose (cellulose nanofibrils, CNF) and its biocomposites are increasingly studied for biomedical applications, such as tissue engineering, wound healing/dressing, medical implants, and drug delivery. The scheme illustrates the preparation of CNF-based 3D matrices towards tissue engineering scaffold and 3D cell culture study. To mimic the cell attachment and proliferation in the 3D ECM scaffold *in vivo* for potential 3D cell culture application, this work proposed a novel approach to encapsulate and distribute the cells in the formed CNF-based matrices, and the encapsulated cells are supposed to grow and proliferate in the CNF 3D network as *in vivo*. The structural and mechanical properties of the matrices are tuned by judiciously controlling the intrinsic properties of the CNFs (charge density and aspect ratio) and the material processing parameters (swelling media conditions and film processing techniques) to meet the requirements for potential 3D cell culture and 3D scaffold construction in tissue engineering. Furthermore, inspired by plant cell wall in nature where hemicelluloses have high affinity onto cellulose and act as binders between mechanically strong cellulose fibrils, we incorporated hemicelluloses to reinforce the CNF scaffolds and investigated how the cell behavior responses.



Scheme for the preparation of CNF-based matrices for 3D cell culture.

In the second sub-project, 3D printing techniques are applied to tailor wood polysaccharide-containing composite scaffolds. This is the first study on the applicability of woody hemicellulose in the feedstock material for fusing deposition melting (FDM) 3D printing technique. The biocomposite incorporating up to 25 % GGM with poly-lactic acid (PLA) was developed. 3D scaffold prototypes were successfully printed from the composite filaments by FDM 3D printing.



Schematic Illustration of preparation of composite of GGM and PLA, filaments, and thereof scaffolds by FDM 3D printing.

In the third part, hydrogels with tunable mechanical properties based on spruce GGM functionalized with tyramine were developed. Gel formation was induced by enzymatic crosslinking at the addition of horseradish peroxidase and hydrogen peroxide to the modified GGMs. Such hydrogel can be used as in 3D printing ink to construct ECM mimicking scaffold.

Cooperation: Åbo Akademi University, Finland; Norwegian University of Science and Technology, Norway; Chalmers University of Technology, Sweden

Design of Biobased Extracellular Matrix-mimicking Scaffolds with Tuneable Rigidity for 3D Cell Culture and Potential Tissue Engineering (TuneScaffold)

Main funding: Academy of Finland

Chunlin Xu, Wenyang Xu, Stefan Willför

The goal of this project is to tailor wood biopolymers to scaffolds with different rigidity for *in vitro* cell culture and tissue engineering. Both wood nanocellulose and hemicelluloses will be applied. The rigidity of resulted polymeric scaffolds can be tuned by chemical modifications of the biopolymers or by incorporating other composite components. The scaffolds will be subjected to cell tests to study the mechanism of biological responses of the scaffolds with different properties.
In collaboration with University of Wollongong, Australia, 3D printing approaches of biopolymer hydrogels have been established. Further study on modifying the 3D printing approaches and on the printed subjects will be carried out.

Cooperation: Åbo Akademi University, Finland; University of Turku, Finland; University of Wollongong, Australia.

Effect of Lignin Residual in Cellulose on the Cell Behavior in Cell Culture into the Cellulose-based Hydrogels (LigECell)

Main funding: UPM Oyj

Mattias Strandberg, Chunlin Xu, Wenyang Xu, Stefan Willför

Wood-derived cellulose becomes promising for applications in the development of medical materials and devices. However, other compounds such as residual lignin and hemicelluloses, as well as possible further generated substances may occur in the cellulose-based products for medical applications. This project is to investigate the effect of residual lignin on the cell behavior in cell culture into the cellulose hydrogels.

Cooperation: Åbo Akademi University

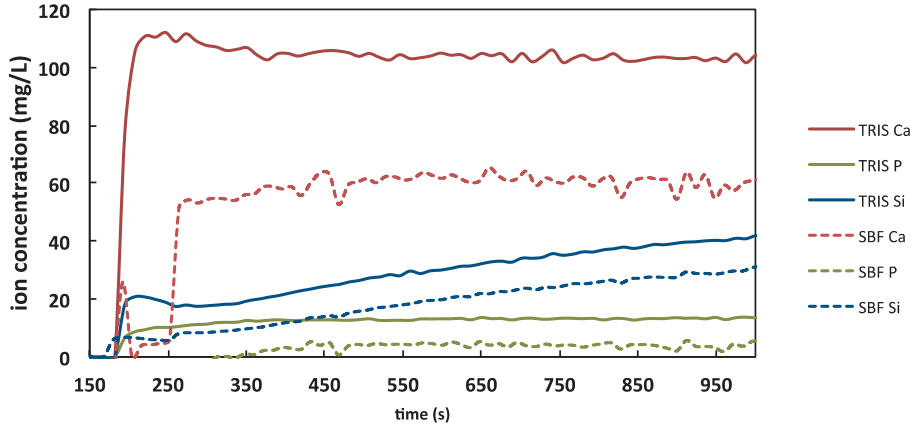
Bioactive Glasses for Tissue Engineering Devices

Main funding: Doctoral Educational Network in Materials Research (DNMR), Johan Gadolin Scholarships, Academy of Finland.

Laura Aalto-Setälä, Siamak Eqtesadi, Xiaoju Wang, Leena Hupa

We characterise the in vitro properties of bioactive glasses for medical devices in soft and hard tissue engineering. We also study the influence of the oxide composition of the glasses on their hot working properties when applied as coatings on metal prostheses or fabricated into porous products through free-form sintering, additive manufacturing and template sintering.

Controlled, predetermined ion release and gradual total dissolution of the glass are critical characteristics for the bioactive glass –based devices. Ideally, after implanting the device inside the human body, the inorganic ions are released in concentrations needed to stimulate and support the regeneration of damaged or diseased tissue. We compare the dissolution of the ions in various *in vitro* conditions with the cellular responses of the same glasses in cell culture and *in vivo* studies done by the experts in medicine, cell and molecular biology. Our research strives for achieving detailed knowledge of dissolution kinetics and the molecular level reaction mechanisms of bioactive glass –based implants in living tissue. This information is crucial for tailoring the glasses for controlled performance in the target application.



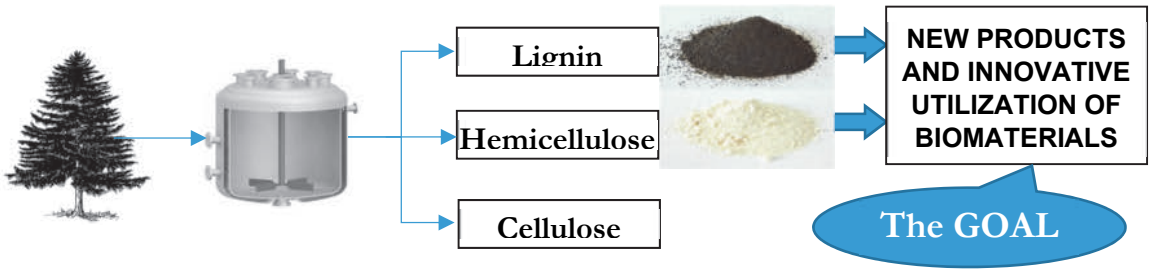
Average initial dissolution of Ca, P and Si from 300-500 m granules of bioactive glass S53P4 into continuously flowing (0.2 mL/min) Tris-buffer solution (dashed line) and simulated body fluid (solid line). The ion concentrations were measured on-line using ICP-OES.

Our recent prolonged experiments with the continuous flow-through reactor suggest that the fate of the bioactive glass in contact with bone can be estimated from dissolution experiments using simulated body fluid as the solvent. In contrast, the experiments with Tris-buffer give a possibility to compare the initial ion release pulses from different glasses.

Cooperation: University of Turku, Finland; University of Tampere, Finland; Tampere University of Technology, Finland; University of Helsinki, Finland; Friedrich-Schiller University Jena, Germany; University of Erlangen-Nuremberg, Germany; University of Extremadura, Spain; Central Glass & Ceramic Research Institute, Kolkata, India; nLight Corporation.

Novel Biomass-Based Solutions for Technical Emulsions and Industrial Applications

Cellulose has for long been the only major product from biomass for different applications. Commercialization of hemicelluloses and lignin has been far underestimated due to the lack of feasible technologies for efficient fractionation. Recent Finnish breakthrough in wood fractionation technology, the BLN process, has brought hemicelluloses and sulfur-free lignin fractions available for novel products and applications. The following two projects are aimed to offer novel biomass-based solutions for technical emulsions and industrial applications.



The projects goals are novel utilization of the biomaterial fractions: 1) lignin and; 2) hemicellulose, in everyday consumer products.

Novel Biomass-based Solutions for Technical Emulsions (BITE)

Main funding: Tekes, Industries

Andrey Pranovich, Jarl Hemming, Chunlin Xu, Stefan Willför

The BITE project aims to develop novel, highly biobased technical emulsions for paints and for emulsion polymerization of latex for paper coating utilizing domestic forestry industry fractions: hemicelluloses and lignin, as stabilizers.
Industrial partner of the BITE project, CH Bioforce, emphasizes the need to develop the expertise on the end use of wood fractionation products. The wood-based hemicelluloses (water-soluble, naturally acetylated softwood galactoglucomannans and hardwood xylans) and the low-molar-mass lignin (Mw<800 Da) were prepared from the BLN process. The capacity of BLN hemicelluloses to emulsify alkyd resins (o/w and w/o), as well as their long-term stability is under study. Emulsions using BLN lignin as stabilizers for synthesis of latex is under investigation.

Cooperation: University of Helsinki, Finland; Tikkurila Oyj; CH-Polymers Oy; CH-Bioforce Oy; Lumene Oy; St1 Oy; Fortum Oyj; Forchem Oy

Industrial Utilization of the Lignocellulosic Feedstock – (LiFe)

Main funding: PoDoCo program / Jenny and Antti Wihuri Foundation

Otto Långvik, Patrik Eklund, Stefan Willför

The LiFe project aims to: 1) investigate and define some biomaterials to be used in adhesive products. The introduction of new components is envisioned to enhance the possibilities to tailor chemical and mechanical properties of the adhesives studied and used in the construction of flexible abrasives and; 2) to introduce new biomaterial-based components, such as hemicelluloses and their derivatives, to be used as binders in abrasive products. The goal is to hereby enhance the performance and extend the lifetime of the products.

Cooperation: Mirka Ab; CH-Bioforce Oy

Development of Novel Biomass Fractionation Approaches and New Raw Materials for Lignocellulosic Biorefinery

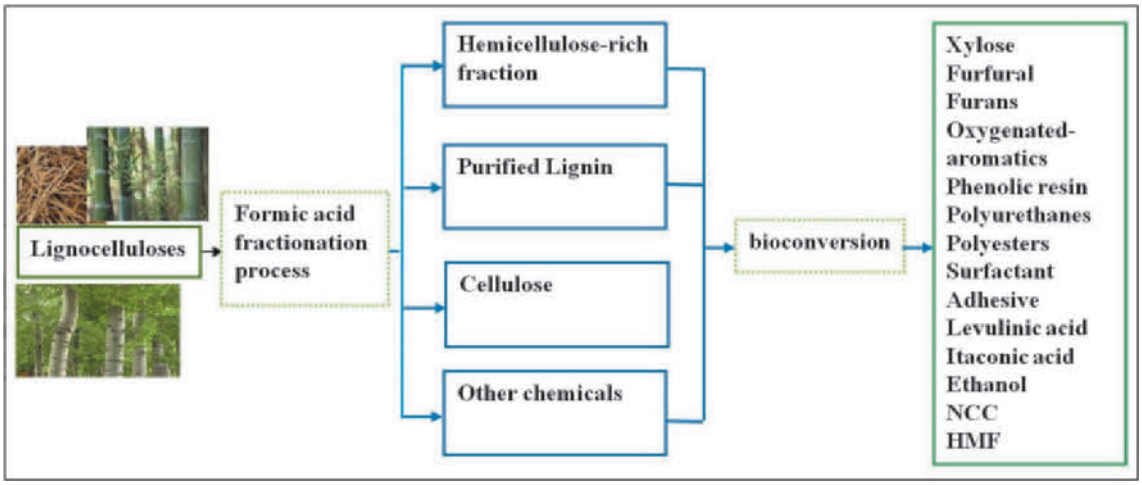
There are two sub-projects under this work task. One is to develop a formic acid fractionation approach towards integrated lignocellulosic biorefinery. The other is focused on sequential fractionation based on Algerian tree species.

Development of Novel Biomass Fractionation Approaches

Main funding: Graduate School of Chemical Engineering (GSCE), Chinese Council Scholarship (CSC)

Yongchao Zhnag, Chunlin Xu, Stefan Willför

Formic acid fractionation is regarded as one of the most promising organosolv fractionation techniques. The objective of this research is to develop a novel biomass fractionation approach using formic acid hydrolysis towards integrated lignocellulosic biorefinery. Nanocellulose (CNF) will be prepared using formic acid pulp, and the morphological features and its films will also be analyzed. The other objective is to develop and demonstrate the feasibility of the approach to integrate production of aromatic chemicals (lignin-to-liquid oils) and lignin-based high performance materials by depolymerization and modification of formic acid lignin. In addition, sugars, furfural, hydroxymethylfurfural (HMF), organic acids and other chemicals will also be separated and purified for the production of green chemicals.



Scheme of formic acid fractionation process to develop highly value-added products from.

One-step fractionation by formic acid-based organosolv process under pressure has been developed for converting bamboo into cellulose pulp, lignin, and hemicellulose-rich fraction. The process demonstrated a high selectivity for delignification, resulting in a satisfying yield (42.2% of dry bamboo) and viscosity of the cellulose pulp, which could easily be bleached to a high brightness of over 87% ISO with a short bleaching sequence. This pulp has been used to prepare cellulose nanocellulose. Additionally, the recovered lignin fraction (31.5%) had a relatively high purity and contained only a small amount of carbohydrates. High pressure formic acid lignin (HPFL) obtained with GSH type, medium molecular weight, a higher phenolic hydroxyl and carboxylate group content, relatively high purified and yield is promising feedstock to replace petroleum chemicals.

Cooperation: Tianjin University of Science & Technology, China; Taishan University, China; Qilu University of Technology, China

Hemicellulose Extraction and Utilization from Algerian Tree Species

Main funding: Ministry of Higher Education and Scientific Research of Algeria

Nacera Benouadah, Andrey Pranovich, Djamel Aliouche, Jarl Hemming, Stefan Willför

Hemicellulose is the second most abundant polysaccharide in the world and includes xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan. The efficient use of hemicelluloses requires extraction from wood and characterization to determine their possible use for suitable products. The composition and amount of hemicelluloses varies a lot depending on the wood species, methods of isolation and purification.

The main objectives of the present work are:

to obtain efficient extraction of hemicelluloses from different Algerian wood species for specific applications, e.g. biodegradable films and hydrogels-based nanocomposites. And

to characterize the chemical composition and molar mass distribution of the hemicelluloses from Algerian *Pinus Halepensis* and *Eucalyptus Camaldulensis*.

Cooperation: Université M'Hamed Bougara, Boumerdès, Algeria

Cellulose Derivatives in Ionic Liquids

Main funding: KAW Foundation - Wallenberg Wood Science Center, Kempe Foundations

Linn Berglund, Ikenna Anugwom, Mattias Hedenström, Yvonne Aitomäki, Kristiina Oksman, Evangelos Sklavounos, Alistair King, Pasi Virtanen, S. G. Khokarale, Ikenna Anugwom, Päivi Mäki-Arvela., Valerie Eta, Olatunde Jogunola, Ola Sundman, Tapio Salmi, Jyri-Pekka Mikkola

A biorefinery converts different low-value renewable biomass materials whereupon biomass is transformed, in multiple steps including fractionations, separations and conversions, to several higher-value bio based products. These products can range from food, feed and fine-chemicals to fuels, heat and electricity. A biorefinery can be formed by a single unit or can combine several facilities targeted for single purpose that further process products as well as by-products or wastes of combined facilities. According to the International Energy Agency "Biorefineries" will contribute significantly to the sustainable and efficient use of biomass resources, by providing a variety of products to different markets and sectors.Solvents are an integral part and in the center of the chemical transformations which induce the actual interactions of the reagents to the desired products. Many chemical processes, especially in organic synthesis, usually involve multiple steps (reactions, extractions, and/or separations) and each step is, in general, accompanied with various solvents having different properties.

Nordic hardwood (*Betula pendula*) was fractionated in a batch autoclave equipped with a custom-made SpinChem® rotating bed reactor, at 120°C using CO_2 and CS_2-based switchable ionic liquids systems. Analyses of the non-dissolved wood after treatment showed that 64 wt% of hemicelluloses and 70 wt% of lignin were removed from the native wood. Long processing periods or successive short-time treatments using fresh SILs further decreased the amount of hemicelluloses and lignin in the non-dissolved fraction to 12 and 15 wt%, respectively. The cellulose-rich fraction was partially dissolved in an organic superbase and an ionic liquid system for further derivatization. Homogeneous acylation of the dissolved cellulose in the presence or absence of catalyst resulted in cellulose acetates with variable degree of substitution(DS), depending on the treatment conditions. By varying the reaction conditions, the cellulose acetate with the desired DS could be obtained under mild conditions.Cellulose acetate was synthesized under homogeneous conditions. Cellulose was first dispersed in acetone, acetonitrile, 1,5-diazabicyclo(4.3.0)non-5-ene (DBN) or dimethyl sulphoxide (DMSO) and the resulting suspension was dissolved in an ionic liquid, 1,5-diazabicyclo(4.3.0)non-5-enium acetate [HDBN][OAc] at 70°C for 0.5 h. It was possible to dissolve more than 12 wt% cellulose with a degree of polymerization in the range of 1000–1100. The dissolved cellulose was derivatized with acetic anhydride (Ac2O) to yield acetylated cellulose. The cellulose acetates produced were soluble in organic solvents suchas acetone, chloroform, dichloromethane and DMSO which is essential for their further processing.

Switchable ionic liquids enable efficient nanofibrillation of wood pulp: Use of switchable ionic liquid (SIL) pulp offers an efficient and greener technology to produce nanofibers via, ultrafine grinding. We have demonstrated that SIL pulp opens up a mechanically efficient route to the nanofibrillation of wood pulp, thus providing both a low cost and chemically benign route to the production of nanocellulose fibers. The degree of fibrillation during the process was evaluated by viscosity and optical microscopy of SIL treated, bleached SIL treated and reference pulp. Furthermore, films were prepared from the fibrillated material for characterization and tensile strength testing. It was observed that substantially improved mechanical properties were attained as a result of the grinding process, thus signifying nanofibrillation. Consequently, both SIL treated and bleached SIL treated pulps were fibrillated into nanofibers with fiber diameters below 15 nm thus forming networks of hydrophilic nature with a high crystallinity index. Notably, it was found that the SIL pulp could be fibrillated more efficiently than traditional pulp since nanofibers could be produced with more than 30% less energy when compared to the reference pulp. Additionally, bleaching further reduced the energy demand by additional 16 %. The study demonstrated that switchable ionic liquid treatment has considerable potential in the commercial production of nanofibers due to the increased efficiency in fibrillation.

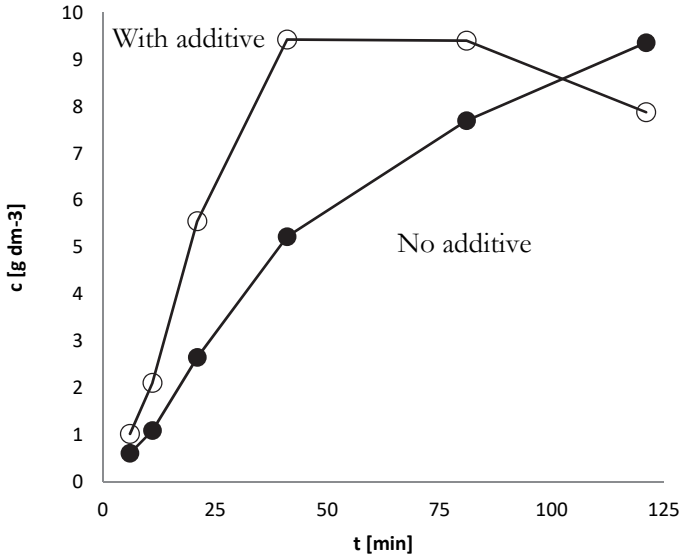
Intensified Extraction of Hemicelluloses from Biomass

Main funding: Spanish Economy and Competitiveness Ministry, Erasmus Mundus Programme Eurotango II, Academy of Finland

Jussi Rissanen, Maria Anderez Fernandez, Wenyang Xu, Chunlin Xu, Kari Eränen, Juan Garcia Serna, Stefan Willför, Dmitry Murzin, Tapio Salmi, Henrik Grénman

The main focus of the work is in the intensification of the extraction kinetics of hemicelluloses from wood. In addition, the possibility to influence the properties of the extracted carbohydrates in a controlled way is of interest. The extraction was studied in the temperature interval 120 °C – 170 °C in a batch reactor system. Selected additives were used to accelerate the extraction rate and the extraction kinetics was precisely determined quantitatively. The results demonstrate that the fractionation can be considerably enhanced with the use of selected additives compared to traditional pressurized hot water extraction and that the properties of the extract can be adjusted in the process. Moreover, the separation of the utilized additive was studied and it was concluded to be easily separable from the reaction mixture.

The main focus of the work has been on spruce; however, the project focuses also on selected hard woods e.g. on birch as a substrate and plans include studies on agricultural feed stocks. This work contributes significantly to understanding the mechanisms involved in the extraction of hemicelluloses and the influence of the extraction parameters, especially the concentration of the additives, on the process. Overall, when optimized properly, pressurized hot water extraction of hemicelluloses can give very good results, but the process can be even further advanced with applying selected additives.



The liquid phase concentration of hemicellulosic carbohydrates as a function of extraction time.

Cooperation: ***PCC***; University of Valladolid, Spain

Hydrolysis of Hemicelluloses for Obtaining Sugar Monomers

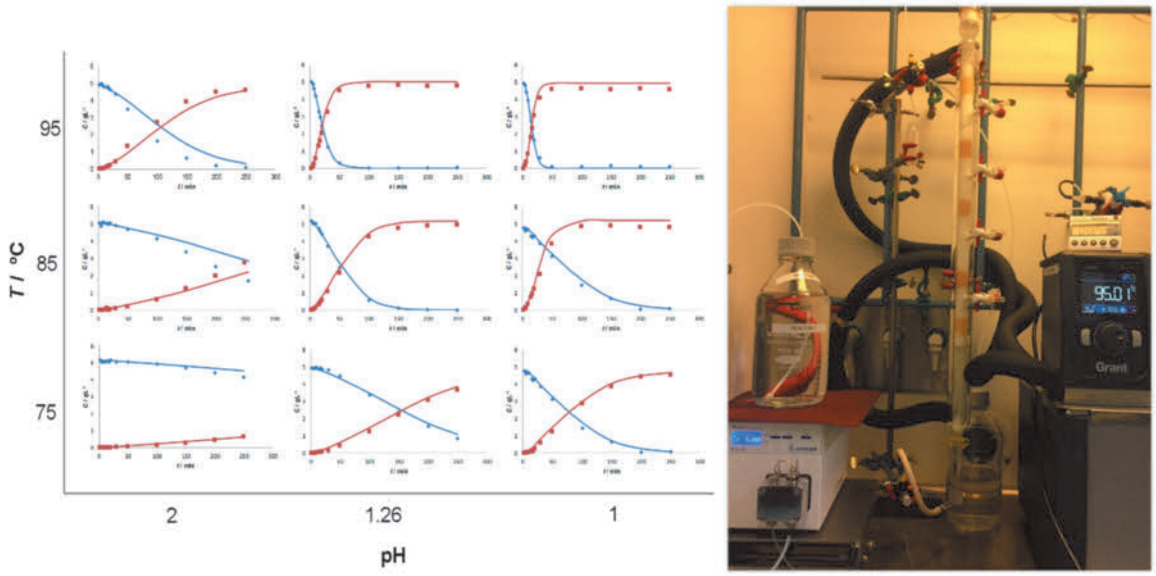
Main funding: Raisio Research Foundation, Erasmus Mundus Programme Eurotango II, Academy of Finland

Andrea Pérez Nebreda, Jonah Schaaf, Thomas Hornbogen, Kari Eränen, Chunlin Xu, Jarl Hemming, Juan Garcia Serna, Stefan Willför, Dmitry Murzin, Tapio Salmi, Henrik Grénman

The current work focuses on bridging the extraction of hemicelluloses and the conversion of sugars to chemicals, which is the main focus in WP2. The aim is to be able to sufficiently convert the hemicelluloses extracted from wood and agricultural biomass to sugar monomers employing actual extracts instead of model compounds, in order to complete the production chain from biomass to chemicals. The final goal is to be able to utilize heterogeneous catalysis combined with continuous reactor technology for enabling the elegant conversion and integration of the hydrolysis step into the overall production scheme without the need for excessive purification steps.

The project is currently in a stage where the knowledge of hydrolyzing certain model compounds, such as galactoglucomannan and inulin, is well understood, also with selected heterogeneous catalysts. Actual extracts are being studied in order to evaluate the conditions and process requirements needed in the hydrolysis. A continuous reactor setup utilizing heterogeneous catalyst was developed based on knowledge gained from batch reactor results including detailed modeling of the kinetics. The system was successfully employed in the hydrolysis of inulin and high conversion to monomers was obtained in optimized conditions. Other substrates have also been tested and the process is being optimized.

Overall, the results demonstrate that the continuous hydrolysis of hemicellulosic polysaccharides utilizing heterogeneous catalysts is feasible if the catalysts and process conditions are optimized. This enables the further development of efficient biomass processing technologies.



Modeling results of the autocatalytic hydrolysis of inulin in a batch reactor and the continuous reactor setup with het. catalyst.

Cooperation: ***PCC***; University of Valladolid, Spain; TU Dresden, Germany

3.2 WP2 - Conversion of sugars and sugar derivatives to chemicals

WP2 Leader, *Docent Pasi Virtanen*
pasi.virtanen@abo.fi

The research in WP2 is inducted by the general interest on chemicals produced from bio-based raw-material instead of fossil resources. More precisely, WP2 focuses on one hand on the chemistry and technology needed in biorefinery concept for preparation of high value chemicals from monomeric sugars obtained by carefully controlled hydrolysis of hemicelluloses and cellulose and on the other hand on synthesis and studying of specialty chemicals and functionalized materials utilizing carbohydrate derivatives. Recent research by us and other groups has shown that rare monomer sugars can be obtained in high yields from hemicelluloses. Furthermore, platform, fine and specialty chemicals can be obtained from the monomers of hemicelluloses and cellulose. WP2 combines different research areas, such as, organic chemistry, catalyst preparation, characterization, kinetic and mass transfer studies, continuous reactor technology and process intensification. The group has experts on catalysis, chemistry and analysis of biomass, as well as on chemical kinetics and reaction engineering. Advanced catalyst characterization and reactor equipment as well as various analytical chemistry tools are at our disposal (batch autoclaves, parallel screening reactors, SEM, TEM, XRD, XPS, FT-IR, NMR). Many of the projects include also national as well as international collaboration between different universities and companies in all over Europe.
The main targets of the research in WP2 are to develop applications to prepare high value chemicals from cheap renewable sugars. More precisely we are focused on:

Studying of immunostimulatory glycocluster adjuvants in allergy treatment as well as potential application of the mannoside glycocluster also in immunotherapy of cancer;

Developing new catalytic materials and reactor technology as well as kinetic model for production of high value chemicals from monomeric sugars in different reactions. These reactions include interconversion of aldoses to ketoses, oxidation of furfural and aqueous phase reforming of sugar alcohols;

Synthesizing of functional materials by utilizing carbohydrate derivatives, such as functionalized polymers;

Developing mild, selective and environmentally benign oxidation methods for wood-based compounds.

Heterogeneous Catalysis

Main funding: EU, Academy of Finland, Tekes, foundations.

Atte Aho, Lidia Godina, Anton Tokarev, Elena Murzina, Päivi Mäki-Arvela, Kari Eränen, Farhan Saleem, Pia Mueller, Johan Wärnå, Frans Storgårds, Henrik Grénman, Tapio Salmi, Dmitry Murzin

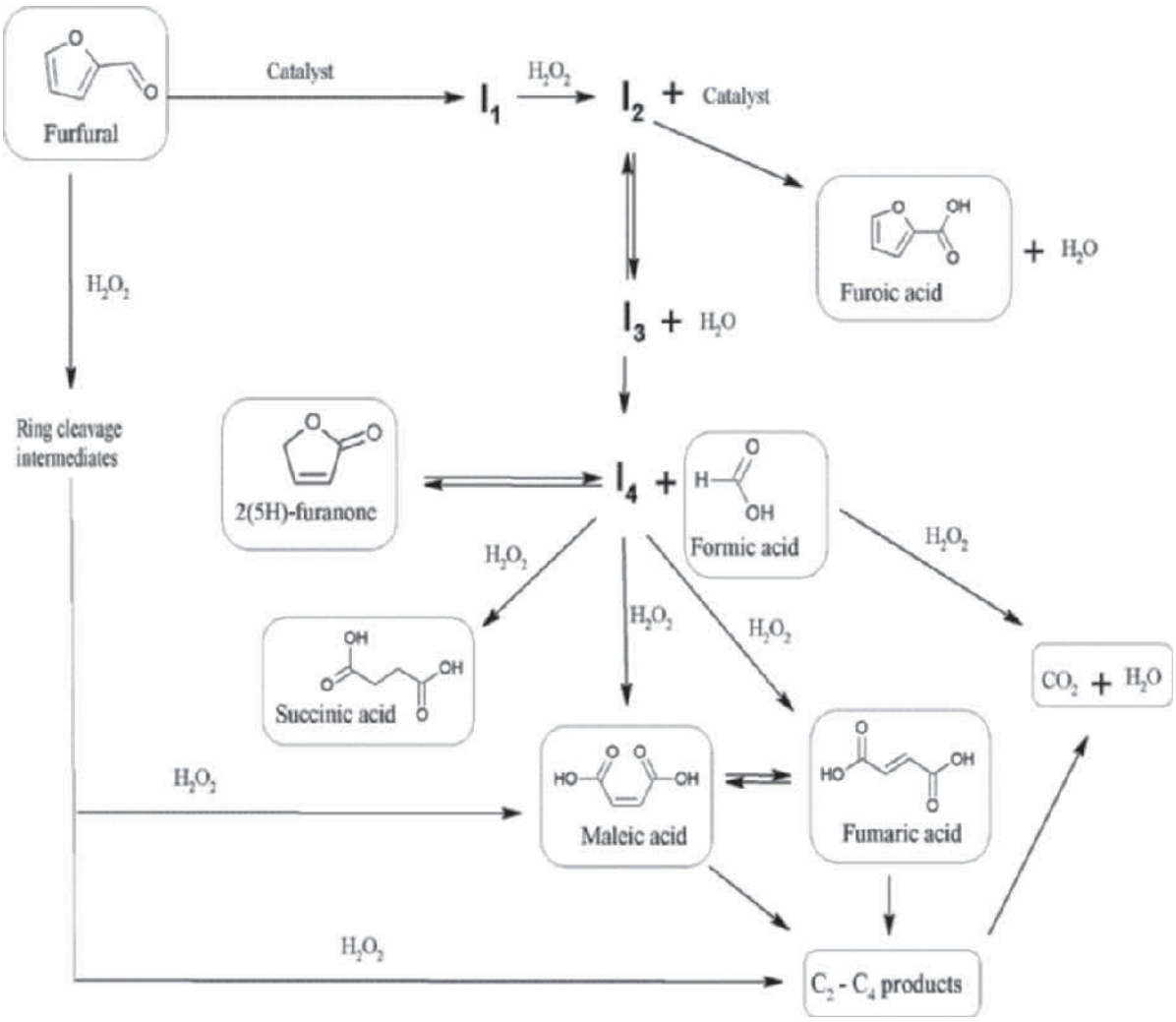
Lignocellulosic biomass originating from wood is an abundant non-food alternative feedstock for chemical and petrochemical industries. However, the conversion processes of lignocellulose to fuels and chemicals are at the moment often ineffective and unprofitable. On the contrary, catalytic processes can provide the more selective routes from biomass to the desired products. Several reactions are in focus of this subproject, devoted to catalytic transformations of sugars and their derivatives.

Sugar alcohols, known also as polyols or alditols, are compounds obtained through **hydrogenation** of the carbonyl group present in a sugar molecule either by means of chemical agents (such as sodium borohydride) or by molecular hydrogen in the presence of homogeneous or heterogeneous catalysts. The use of molecular hydrogen and heterogeneous catalysis is preferred from the viewpoint of green process technology, since the formation of stoichiometric co-products is avoided and the separation of a heterogeneous catalyst from the reaction mixture is rather straightforward.

The most common solid catalysts used for sugar hydrogenation to sugar alcohols in industrial scale are based on nickel, such as sponge nickel (Raney nickel), but recently the use of ruthenium has benefited from a growing interest, since Ru affords good activity and excellent selectivity. Thus, it is expected that Ru will replace Ni as a sugar hydrogenation catalyst, particularly because of the toxic properties of Ni. In this project different types of ruthenium catalysts on various supports have been tested in batch and continuous reactors.

Interconversion of aldoses to ketoses has attracted a lot of attention recently as research efforts have been focused on valorization of carbohydrates derived from lignocellulosic biomass within the framework of the biorefinery concept. Besides homogeneous bases (alkali or alkaline earth hydroxides) heterogeneous base catalysts are high interest being devoid of the apparent drawbacks of their homogeneous counterparts, such as low selectivity, and challenges with separation. Isomerization of several aldoses (arabinose, galactose, glucose) was performed at 100-120 °C using a range of base catalysis including magnesia, hydrotalcites, magnesium aluminates with a varying Mg/Al ratios and mixed oxides containing magnesia and alumina. Experiments with different aldose showed that the sugar structure did not influence the catalytic properties. The apparent activation energy for all sugars obtained for a mixed oxide catalyst containing in addition to magnesia and alumina also cobalt and manganese oxide was close to 99 kJ/mol. There was a linear correlation between the catalytic activity in galactose isomerization and the molar content of MgO in magnesium aluminates covering a broad range of Mg/Al ratios.

Furfural is an important compound which is obtained from acid-catalyzed dehydration of pentoses (xylose). Currently, the worldwide annual production of furfural is about 250-700 kt/a. This furan derivative can be converted into a range of chemical intermediates and products, including succinic acid. The latter is considered as a replacement for a large number of intermediates that are currently derived from non-renewable resources. A variety of industrially relevant compounds, such as γ-butyrolactone (GBL), 1,4-butanediol (BDO) and tetrahydrofuran (THF) can be produced from succinic acid. We were studying **oxidation of furfural** in the aqueous phase with hydrogen peroxide as an oxidant. Extensive catalytic screening was performed with aim to improve the yield of succinic acid in furfural oxidation, which is quite challenging as many side reactions can also happen giving a range of by-products.



Scheme : A simplified reaction scheme of furfural transformation to products.

It turned out that Smopex-101, a fibrous non-porous material with sulphonic acid functional groups grafted on poly (ethylene-graft-polystyrene) is a very promising catalyst for this reaction. Sufficient surface area provided by this fibrous catalyst with strong acidic surface functional groups (SO_3H) on the surface significantly diminished the internal mass transfer limitations, normally present in porous catalysts, affording high catalytic efficiency. The catalyst which is suitable for processing of such biomass derived molecules as furfural, can be utilized in different operation modes. Moreover, Smopex-101 has typical benefits of heterogeneous catalysts, such as easy reusability and recovery, contributing thus to principles of sustainable and green chemistry.

The desired product (succinic acid) has been obtained in high yields substantially exceeding published in the literature, when furfural was added in a semi-batch mode.This subproject was focused on **aqueous phase reforming** (APR) of biomass resources. The products aimed by APR, viz. hydrogen or, preferably, a combination of hydrogen and alkanes, are of high potential for sustainable fuel production. The sustainable produced hydrogen can be used either as fuel directly and is mandatory in a bio refinery for sustainable liquid fuel production. A major advantage of APR is the use of aqueous or water-soluble feedstocks at limited temperatures and slightly elevated pressures, enabling processing without energy intensive drying while hydrogen can be in situ generated from biomass by the APR reaction and in parallel from the water content by the water gas shift (WGS) reaction. Hence, APR is one of the most promising techniques for sustainable liquid and gaseous fuels production from biomass feedstocks, while the catalyst involved is the heart of the process.

In particular nanoparticles of a predefined size were synthesized, immobilized on carbons supports and tested in aqueous phase reforming of various polyols, including sorbitol, xylitiol, diols, etc. Well defined colloidal solutions of nanoparticles containing (Ru, Re, Pt, Ni, Pd, Co were synthesized in collaboration with the partners in a EU FP7 project using the polyol or micro-emulsion techniques. The influence of upscaling the colloidal synthesis method on the cluster sizes was studied. Methodologies for immobilization of well-defined nanoparticles in supports, either through post immobilization or in situ synthesis was established. A special effort was put on efficient removal of the capping agents employed in colloidal solutions and its influence on the cluster size. Colloidal synthesis routes were compared to classical impregnation routes.

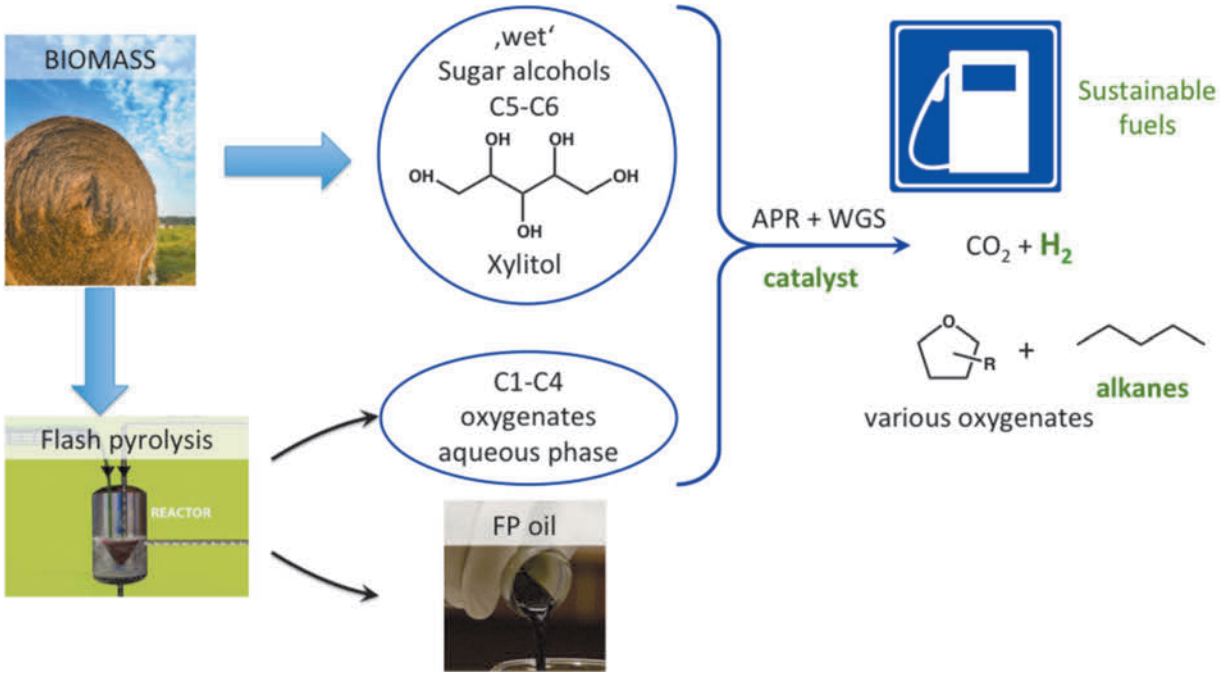


Illustration of sustainable fuel production from wet biomass feedstocks and intermediates by APR (APR = Aqueous Phase Reforming, WGS = Water Gas Shift, FP = Flash Pyrolysis)

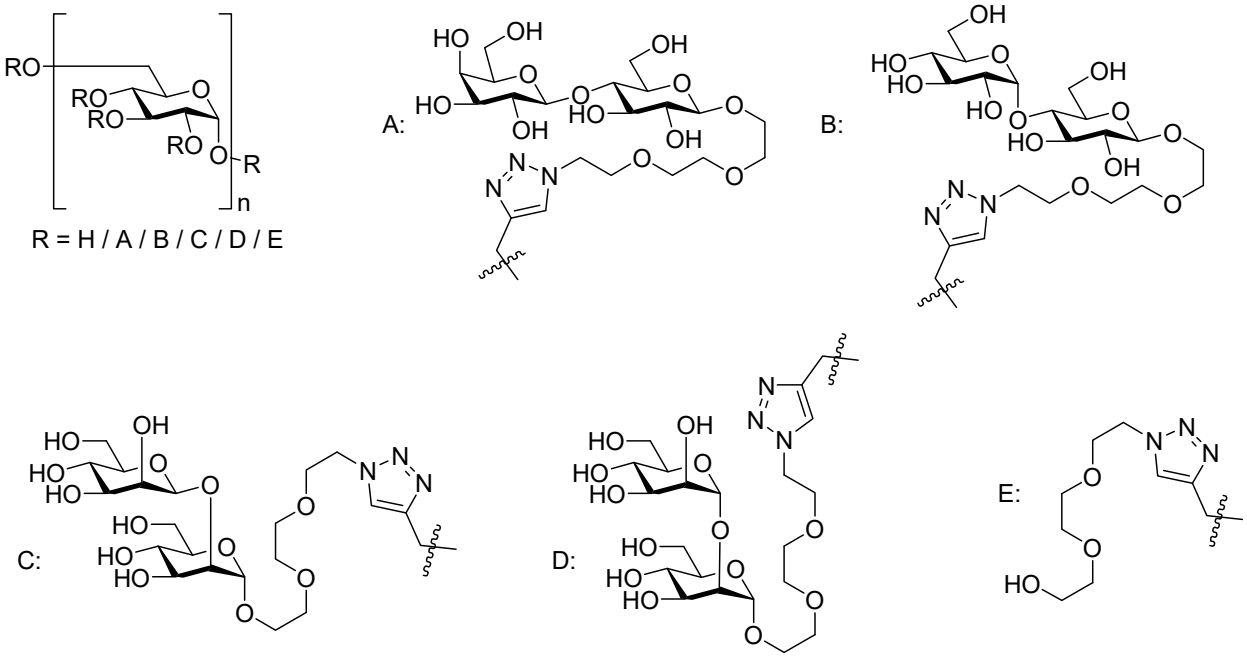
Cooperation: Autonomous University of Madrid, Spain; Boreskov Institute of Catalysis, Russia; Technical University of Darmstadt, Germany; Twente University, The Netherlands; Johnson Matthey.

Binding of Mannans to Galectin-3

Main funding: Magnus Ehrnrooth foundation.

Jani Rahkila, Filip Ekholm, Ana Ardá, Jesús Jiménez-Barbero, Johannes Savolainen, Reko Leino

Galectin-3 (Gal-3) is a galactose-binding lectin possessing important biological functions in for example cell differentiation, growth, and apoptosis as well as in inflammatory responses. While lectins are typically highly selective towards their target ligands, Gal-3 has been suggested to also bind the cell-wall polysaccharides of *Candida albicans* which contain β-(1→2)-linked mannosides. To investigate this, we have designed polysaccharides that mimic the *C. albicans* cell wall by attaching β-(1→2)-linked mannobioses to a dextran based backbone. To further assess the possibilities of using polysaccharides as scaffolds for biomolecular probes we are also investigating lactose and maltose analogues of the dextran polymer. As a negative control dextran can be modified with only the linker part used in the other derivatives.



Structures of the modified dextrans

It has been suggested that β-(1→2)-linked mannosides would bind to a non-canonical binding site on the opposite side of the carbohydrate recognition domain of Gal-3, rather than the canonical binding site responsible for β-galactoside binding.

To investigate this hypothesis and in order to verify whether β-(1→2)-linked mannosides do, in fact, bind to Gal-3 in an unusual way we are currently applying advanced NMR spectroscopic techniques. NMR spectroscopy is a powerful tool for determining binding sites which would be difficult to detect using other commonly applied methods for receptor-ligand interaction studies. For example, ^{1}H-^{15}N HSQC allows to determine exactly which amino acids in the protein are located close to the potential binding site.

Cooperation: University of Helsinki, Finland; University of Turku, Finland; CIC bioGUNE in Bilbao, Spain.

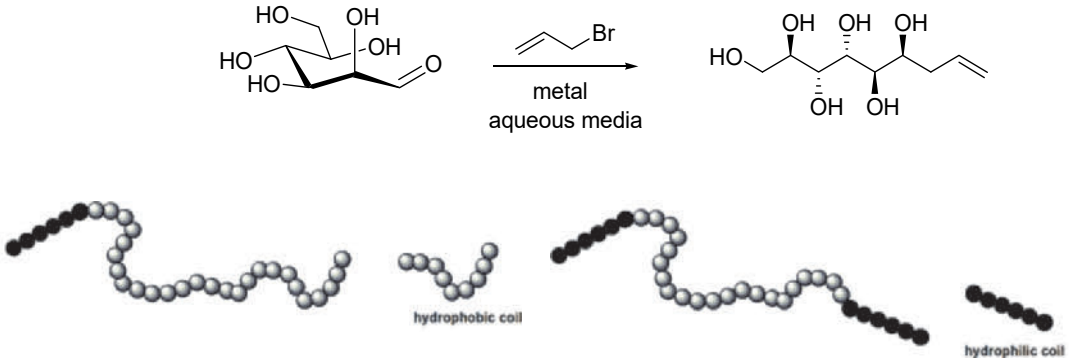
Smart Materials from Sweet Molecules

Main funding: Graduate School of Chemical Engineering, Ålands Lagtings kanslikommission

Ida Mattsson, Tiina Saloranta-Simell, Manu Lahtinen, Anssi Peuronen, Reko Leino

Utilization of unprotected carbohydrate derivatives in the synthesis of fine chemicals and functional materials is highly desirable. Such synthesis protocols are typically characterized by high efficiency and minimal waste production. As the functional groups are targeted selectively, there is typically no need for protective group manipulations and the reactions can thus be carried out in aqueous media minimizing the use of organic solvents. Ultimately, the synthesis routes start from unprotected monosaccharides utilizing the presence of different tautomeric forms, where especially the open chain aldehyde form is of interest. A representative example of a reaction that targets the aldehyde functionality selectively is the metal (typically In and Sn) mediated allylation of unprotected monosaccharides that efficiently yields alkene-terminated polyols.

Earlier, our research group found that diastereomerically pure allylated D-mannose forms rod-like, hydrogen bonded packings which aggregate in water. The self-assembling property of the polyol was found to originate from the highly ordered linear conformation of the molecule. The main diastereomer which forms upon allylation of D-mannose can easily be isolated by recrystallization from ethanol.



Top: metal mediated allylation of D-mannose and the resulting major diastereomer. Bottom: schematic presentation of rod-coil copolymers.

The terminal carbon-carbon double bond can be coupled to various small molecule thiols by UV induced thiol-ene coupling. Recently, we have discovered that the thiol-ene coupling can successfully be applied to alkene-terminated polyols without the use of protective groups. In the current project, the aim is to apply the thiol-ene click approach to various functionalized polymers, colloids and surfaces, hence giving access to highly interesting materials and applications. Furthermore, the propargylated analog is also available, opening up the possibility to utilize the Huisgen 1,3-cycloaddition click reaction in order to obtain various new compounds and materials.

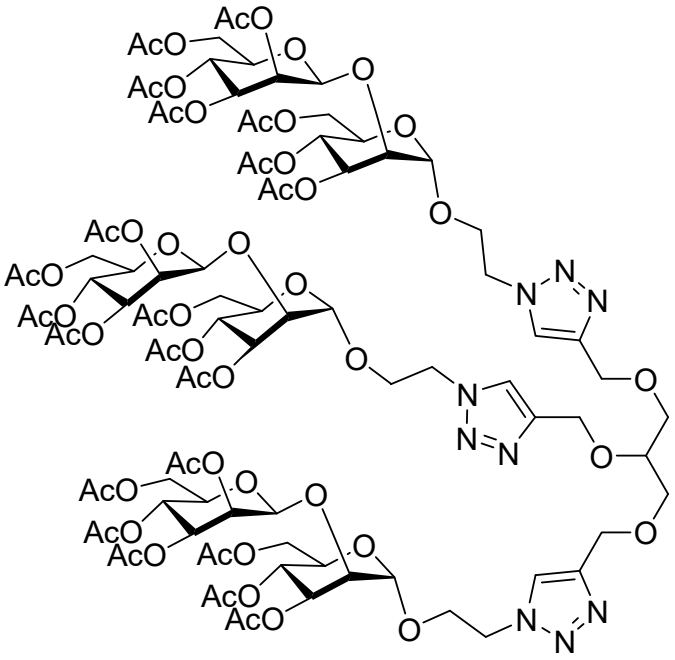
Cooperation: Aalto University, Finland; University of Jyväskylä, Finland

Immunostimulatory Glycocluster Adjuvants

Main funding: Tekes

Reko Leino, Johannes Savolainen, Ramesh Ekambaram, Jani Rahkila, Risto Savela, Tiina Saloranta-Simell

In recent work, inspired by microbial cell surface oligosaccharides of *Candida albicans*, shown in several earlier studies to be potential inducers of immune responses, we have designed and identified a highly potential immunostimulatory adjuvant lead molecule based on fully acetylated, synthetic trivalent □-(1→2)-mannobiose derived glycocluster.



In the initial *in vitro* studies using peripheral blood mononuclear cell (PBMC) samples of atopic subjects, this single compound, out of a larger library of mannoside derived clusters, was shown to be an unusually strong inducer of IFN- and IL-10. In birch stimulated PBMC from 20 allergic subjects immediately after the birch pollen season, the new compound suppressed the birch-induced production of all three Th2 cytokines (IL-4, IL-5, IL-13). In a murine model of ovalbumin (OVA) induced allergic asthma, administration of the glycocluster decreased the OVA-specific IgE and suppressed the mRNA levels of IL-4, a Th2 cytokine, in the lung tissue of mice, demonstrating *proof-of-principle* also *in vivo*. Two analogous compounds, sharing the same key structural features, have also in recent work been prepared and shown to possess *in vitro* activities similar to the earlier discovered lead compound in the PBMC model.
In an *in vivo proof-of-concept* study, the effects of the synthetic glycocluster have also been investigated in a murine model of timothy induced chronic allergic inflammation, where the administration of the lead molecule inhibited the development of eosinophilic inflammation of respiratory tract in mice with superior performance compared to known adjuvants CpG-ODN and monophosphorylated lipid A, which in the same study instead induced a neutrophilic inflammation.

In the Tekes-supported commercialization driven project, preclinical proof-of-concept is now sought in the potential application of the mannoside glycocluster also in immunotherapy of cancer. In addition, up-scaling and optimization of the lead molecule synthesis is researched for possible transfer to a GMP-level laboratory required for clinical testing.

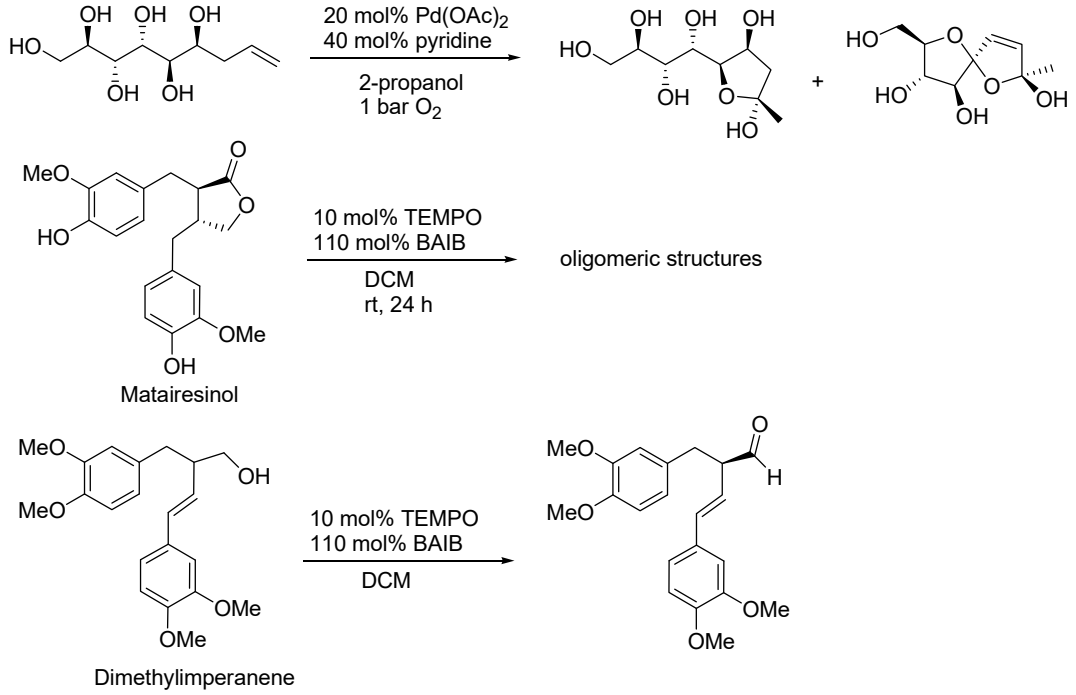
Cooperation: University of Turku, Finland

Selective Oxidation of Unprotected Carbohydrates, Polyols and Phenolic Structures from the Biorefinery Feedstock

Main funding: Academy of Finland

Patrik Eklund, Patrik Runeberg, Stefan Willför, Reko Leino, Dominique Agustin

In recent years, the use of wood in lignocellulose-feedstock based biorefineries has become more and more important. Still much attention is focused on the use of lignin and cellulose for the production of fuels and materials. However, more sophisticated methods for isolation and purification of single compounds, or mixture of specific compounds, have emerged. In many cases, wood based compounds may need further chemical modification to meet the requirements of different applications. Oxidation is one of the most important and frequently used reactions in this context. However, selective oxidations of complex wood based compounds from the biorefinery feedstock are much more difficult compared to oxidations of hydrocarbons from the petrochemical feedstock. Often, modern catalytic transition metal based oxidation reactions is not compatible with the polyolic structures of unprotected carbohydrates and polyphenols. The objective of this research is to find and develop new mild, selective, and environmentally benign oxidation methods for wood-based compounds. The oxidations will be based on catalytic methods, oxidation by molecular oxygen, oxidations by ozone, and oxidations by oxo-molybdenym catalysts, preferably in aqueous solution. Due to our previous research activities and knowledge in the field, hemicelluloses, lignans, norlignans, stilbenes and carbohydrates from the biorefinery feedstock, will be used as model substrates for the oxidations.



Some example of selective oxidative transformations of biorefinery derived products.

Recent result has shown that selective oxidations of different biorefinery based substrates can be achieved by for example TEMPO-mediated oxidations, hypervalent iodine reagents and with Pd-catalysts in aerobic conditions.

Cooperation: Institut Universitaire de Technologie Paul Sabatier, France

3.3 WP3 - Refining options for lignin

WP3 Leader, *Docent Patrik Eklund*
patrik.c.eklund@abo.fi

Characterisation of novel lignin raw material

The valorisation of lignin from various biorefinery processes, including traditional pulping, for something else than simple burning is a continuous challenge. The increased interest in producing liquid transportation fuels from cellulosic biomass, together with bioengineering efforts, has also increased the potential lignin reserves outside the common Kraft and sulphite lignin currently available (Ragauskas et al. 2014). Potential value-added products include carbon fibres, plastics, thermoplastic elastomers, foams, and membranes and naturally a multitude of biochemicals that all could replace part of the current oil-based products used. It is also evident that other lignin sources than the above-mentioned hydrolysis lignins are emerging. So-called organosolv and steam explosion lignins are examples of such. Lignins from various sources and processes have distinct characteristics that may render them useful for different applications. However, in most cases some chemical or enzymatic modification is needed to achieve the functional design appropriate for a certain product. At the PCC we have studied water-soluble Sulphur-free lignin, which can be obtained by isolation from process waters from thermomechanical pulp production (TMP) or by a novel method using extraction of wood with pressurised hot water (PHWE). PHWE lignin has recently been thoroughly characterised by our centre and it is a more potential source than Kraft lignin. Nevertheless, the most promising approach is in combination with the abovementioned hemicellulose fractionation process, where the lignin is sequentially removed from the fibre fraction using a milder alkaline process in comparison to traditional Kraft pulping. This approach also processes the biomass at lower temperatures (< 150°C) than in traditional pulping, which seem to result in a scarce introduction of LCC. Lignins obtained from different extraction processes will be carefully characterized (including classical wet chemistry derivatization followed by reductive cleavage (DFRC) and Klason lignin, GC-MS, RP-HPLC, HPSEC, 13C NMR, 1H NMR, FT-IR, UV spectrometry, Py-GC-MS, THM-GC-MS, and thermal decomposition methods such as thermogravimetry (TG) and differential scanning calorimetry (DSC)) and possibly further fractionated into groups of specific properties (e.g. according to molar mass, reactive groups, or solubility).

Adhesives, biocomposites and barrier material

Isolated mild alkali-extracted lignin can be used as novel eco-friendly adhesives and as a part of biocomposites, which may solve typical problems such as moisture stability or decrease the extensive use of phenol formaldehyde resins. The usability of the composites for adhesives, wood

protection applications, insulation materials for buildings, and as specialty chemicals will also be evaluated in cooperation with other research groups (e.g. Wallenberg Wood Science Centre, Stockholm, Sweden).

Good adhesive function, which is required from biocomposites, demands crosslinking of the lignin molecules, and furthermore attachment to the wood or other material. This may be achieved through chemical generation of radicals, e.g. by Fenton´s reagent, i.e. hydrogen peroxide and ferrous ions. Glyoxalation will also be tried. Radical formation by physical methods such as ultrasonic treatment and other irradiation will also be evaluated. The aromatic structures also have antioxidative properties, hence protecting the formed glue from oxidative degradation. Interestingly, aromatic structures can stabilize/store radicals, which in glue could act as an internal curing agent for further polymerization of dry glue. We will also test and evaluate a new idea for glue formation related to pitch deposits. Pitch deposits in Kraft pulp mills usually contain free fatty acids, sterols, and triterpenyl alcohols as major components. Recent work at our centre has, however, shown that the deposits also contain large amounts of esterified fatty acids and sterols. These esters are not in the form of typical esters between fatty acids and sterols, but instead they are esterified to other compounds. These "pitch ester" molecules have varying molar mass, typically a few thousand Daltons. During alkaline hydrolysis, the polymers decompose into free fatty acids, sterols and triterpenols as the hydrophobic part, and to various short chain hydroxy acids such as gamma-hydroxybutyric acid and other still unidentified hydroxy acids, apparently from previously oxidized aromatic structures. The basic formation mechanisms are still not clear, but research indicates that the sticky polymers are formed under acidic and oxidative conditions. Apparently the aromatic structures are oxidized to alcohols and carboxylic acids, which under acidic conditions form esters with pitch. These recently identified polymers could be used as a good starting point for natural glue production. Other selected derivatization to work as internal plasticiser to control the glass transition temperature (Tg) and 11 brittleness of biocomposites will also be tested. Hardening/coupling agents other than formaldehyde will be evaluated. Distinct barrier material properties, desired in wood protection applications, would furthermore be introduced by esterification with fatty acids, which has proved to be a good approach for fibreboard and packaging.

Spruce Lignin as a Plant Growth Regulator

Main funding: International Doctoral Programme in Bioproducts Technology, Johan Gadolin Process Chemistry Centre

Ekaterina Korotkova, Andrey Pranovich, Stefan Willför

Lignin is one of the most abundant natural polymers. Due to its phenolic structure, lignin has great potential in different areas such as producing of fertilizers, adhesives, composites, biodegradable films, resins, polymer additives, surfactants, and as base material for the various other biochemicals. Efficient fractionation of lignocellulosic biomass is a prerequisite for an economic lignocellulosic biorefinery. Nowadays lignin can be isolated mainly as a by-product in pulp and paper industry. The composition of lignins varies a lot depending on the wood species, way of isolation and purification. New techniques are needed for efficient extraction of lignin from wood in intact form. Our biorefinery concept includes a sequential separation of spruce wood into its main components with pressurised hot water.

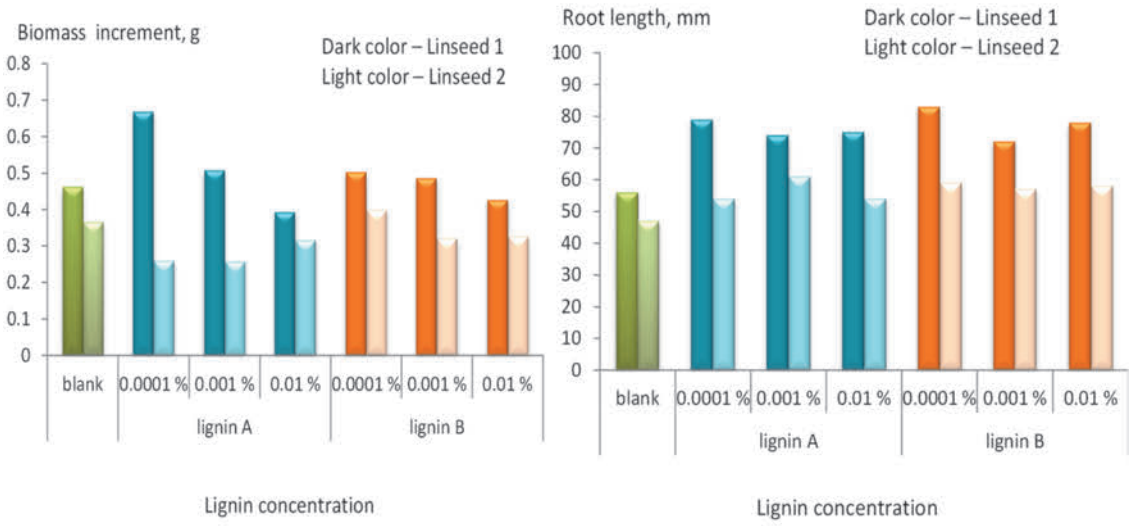
Lignin extraction from wood in an Accelerated Solvent Extractor (ASE) using hot water with small addition of alkali was performed in our work. The work so far was concentrated on obtaining a thorough understanding of how different parameters, such as sequential extraction, alkali concentration, and pre-extraction affect the extraction and purification of lignin from spruce sapwood. The extraction sequence as well as alkali concentration has great influence on the process – shorter extraction times extracted up to 10 times more lignin compared to longer extraction times. The average molar mass of lignin increased with the extraction time and concentration of alkali.

The aim of this part of work is to use mild-alkaline extracted spruce lignin as a plant growth regulator. The lignin samples used in this study were isolated from spruce sapwood with ASE using 2% aqueous NaOH as a solvent. The extraction of lignin was performed at 170°C and 10.3 MPa. Eight sequential extraction cycles per 20 minutes static time were performed and extracts from cycles 1 to 4 (combined extract A) and cycles 5 to 8 (combined extract B) were obtained. Lignin was precipitated from the extracts A and B, washed, and freeze-dried. As a result 2 samples of lignin were obtained - low molar mass lignin – Lignin A and high molar mass lignin – Lignin B.

Both lignins were tested as plant growth regulators. *Linum usitatissimum L.* seeds were used in the experiments. Lignin was added to the germination medium in different concentrations from 0.0001 to 0.01 wt%. Plain distilled water was used as a blank. The germination tests were performed for 7 days. The total biomass increment and the length of the roots were measured on seventh day (Figure 1).

Two breeding lines of *Linum usitatissimum L.* were used in the experiments. The seeds were provided by All-Russian Research and Engineering Institute of Flax Growing Mechanization, Russian Academy of Agriculture Science. In Figure 1 the Linseed 1 breeding line is shown in dark color and the Linseed 2 breeding line is shown in light color. Breeding lines respond differently to growth regulators, concentrations suitable for one line are less suitable for other. Low molar mass lignin A promoted the increase in biomass up to 44% for Linseed 1 (Figure 1 a), while its effect on Linseed 2 was not so distinct. Added in higher concentrations, lignin has shown inhibitory action on seed growth. Low molar mass lignin easier penetrates the seed coat and has more pronounced growth regulator effect compared to high molar mass lignin

Addition of lignin to germination medium has significantly improved formation of the easy-to-root shoots and their elongation (Figure 1 b). It is well known that plant hormones auxins promote root initiation. Most likely lignin has auxin-type activity and its influence on plant body development has similarities to root proliferation induced by auxins.



a b

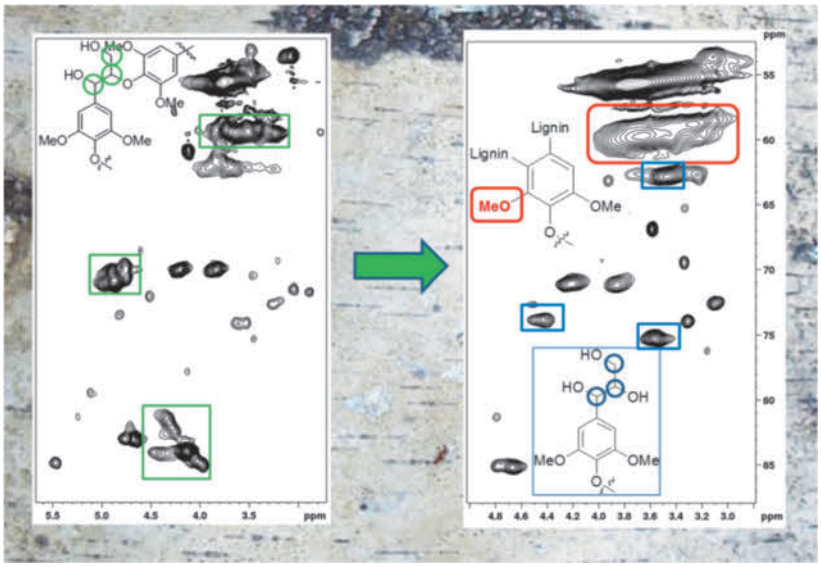
Influence of lignin addition to the germination media on a) biomass increment and b) root length on 7th day of germination.

Exploring the Structure and Reactivity of a Novel Type of Mild Alkali Pressurized Hot-Water Extracted Lignin

Main funding: Suomen Luonnonvarain Tutkimussäätiö

Lucas Lagerquist, Andrey Pranovich, Rasmus Kempe, Annika Smeds, Jani Rahkila, Stefan Willför, Patrik Eklund

In this project we have worked with lignin obtained from a novel bio-refinery process. The process, developed by CH-Bioforce Oy, separates the hemicelluloses from the biomass by pressurized hot-water extraction, followed by separation of the cellulose from the remaining fibers by mild alkali pulping. Both steps in oxygen starved conditions. As both of the carbohydrate fractions are isolated in both high purity and yields it is of importance to determine the condition of the lignin fraction for possible future utilization. The process is currently being up-scaled to a facility being able to process up to 100 k ton biomass annually.



Degradation of traditionally occurring lignin linkages and formation of new structures illustrated by the 2D NMR spectroscopy.

Structural characterization was initially performed on birch lignin. The lignin was analyzed with the spectroscopic methods ^{13}C NMR, ^{13}C DEPT experiments, ^{31}P NMR, 2D HSQC, and FTIR as well as orthogonal methods such as size exclusion chromatography (SEC), elemental analysis, pyrolysis-gas chromatography-mass spectrometry (*py*-GC-MS), methoxy group determination and carbohydrate determination after methanolysis. It was concluded that the lignin is fragmented during the process but that re-condensation is also occurring and we also identified multiple structural anomalies caused to the lignin by the process. A similar type of study has been performed on the softwoods spruce and pine, and similar type of degradation could be observed in the softwoods, even though the structure and reactivity is different compared to the hardwood. Initial studies of the reactivity of the lignin have been performed by mild hydrogenation, ozonation, oxidations and simple chemical modifications. Further modifications and valorization of this lignin is ongoing

Cooperation: VTT Technical Research Centre of Finland Ltd; University of Helsinki, Finland; CH-Bioforce Oy

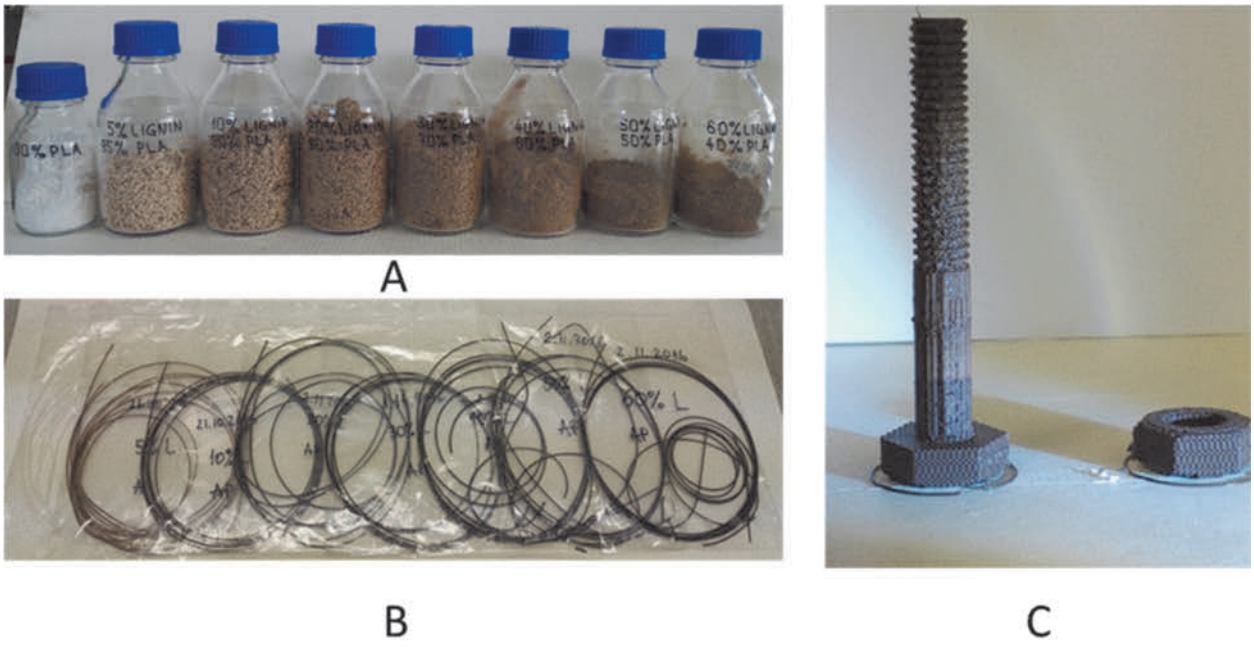
Lignin-PLA Biopolymer Composite for 3D printing

Main funding: Johan Gadolin Process Chemistry Centre (**PCC**)

Andrey Pranovich, Wenyang Xu, Stefan Willför, Chunlin Xu

Lignin is renewable and the second most abundant polymer in nature. In contrast to carbohydrates' plant polymers, this aromatic substances have not got its proper position in the material science yet and its practical importance still needs to be explored.

Using new BLN process, it is possible to obtain near natural and sulfur-free biodegradable lignin from spruce wood. This BLN spruce lignin has low negative impact factor on environment. It is a very promising constituent in different polymeric blends, particularly in blends for 3D printing. It can substitute a part of expensive polylactic acid (PLA) in polymeric blends without destroying filaments' and 3D printed final products physico-chemical properties. Since both lignin and PLA are biodegradable substances, these 3D products will also be biodegradable in contrast to the ones based on petroleum chemistry.



Different lignin-PLA blends (A), corresponding filaments made for 3D printing (B) and a 3D printed sample (C).

Collaboration: Åbo Akademi University

Novel Biomass-based Solutions Using Lignin for Technical Emulsions and Industrial Applications

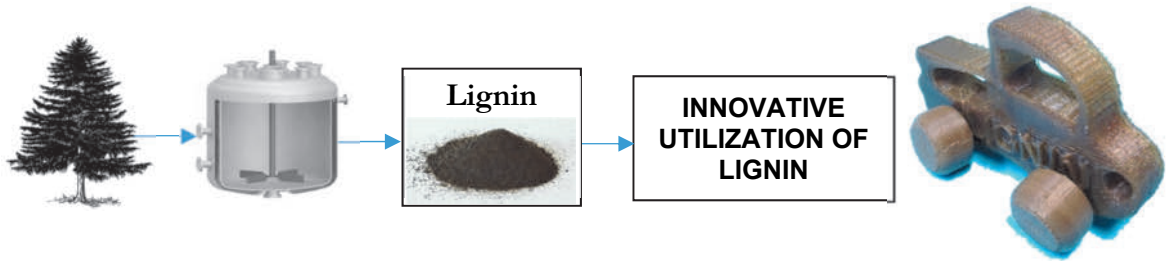
Main funding: Tekes, Industries, PoDoCo program

Andrey Pranovich, Otto Långvik, Jarl Hemming, Chunlin Xu, Patrik Eklund, Stefan Willför

In WP1, the project on 'Novel Biomass-based Solutions for Technical Emulsions and Industrial Applications' has described the objectives to utilize hemicelluloses. In the same project, we also aim to offer novel biomass-based solutions for technical emulsions and industrial applications using lignin stream.

In the project 'Novel Biomass-based Solutions for Technical Emulsions (BITE)', we have planned to develop an emulsion polymerization approach to use BLN lignin as stabilizers for synthesis of latex. The latex prepared using the new approach will be tested together with industrial partner CH-Polymers.

The PoDoCo project aim to investigate and define some specific lignin, lignin based or other biomaterials to be used in adhesive products. The introduction of new components is envisioned to enhance the possibilities to tailor chemical and mechanical properties of the adhesives studied and used in the construction of flexible abrasives.



The projects aims are to utilize lignin in an innovative manner for various applications.

Cooperation: Mirka Ab; University of Helsinki, Finland; Tikkurila Oyj; CH-Polymers Oy; CH-Bioforce Oy; Lumene Oy; St1 Oy; Fortum Oyj; Forchem Oyj

3.4 WP4 - Trace elements in refining of biomass

WP4 Leader, *Dr. Nikolai DeMartini*
nikolai.martini@abo.fi

Inorganics invariably play a role in the refining and processing of biomass and biomass residues. They enter the process with the biomass and may also be added to aid in the fractionation of biomass as is done in chemical pulping. The inorganic elements in the biomass can create challenges for industry such as calcium carbonate and calcium oxalate scaling in bleach plants and the precipitation and removal non-process elements such as Mn, Mg, Si, Al and Cl from the chemical recovery cycle in kraft pulp mills. Until relatively recently, these inorganic elements have been primarily seen as a source of problems – for ex. scaling, corrosion, etc. As more biomass is utilized, there is increased interest also in the recovery of key elements so that they can be returned to the land as fertilizer or utilized in other ways rather than being landfilled.

Within this project, we have three areas of focus:

- Selective leaching analysis
- Anionic species
- Modelling of the fate of metals

Selective leaching is the step-wise leaching of biomass with water, ammonium acetate, and acid to remove water soluble salts, organically bound metals and acid soluble salts respectively. This provides a basic understanding of the distribution of the inorganic elements in different biomass samples. This in turn gives some preliminary information of how the elements will partition in the processing of biomass.
Anionic species in biomass includes both the anions in salts, organic anions such as oxalate and anionic sites such as carboxylic and phenolic groups in biomass. These groups not only enter the process with the biomass, but they also can be formed during the processing. An example of this is oxalate formation during chemical pulping from the degradation of organics. The concentration and form of anionic species, combined with solution pH in the processing of biomass influences how the cationic species are distributed during the refining of biomass.
Modeling of the distribution of inorganics in the refining of biomass is a useful tool in helping industry realize new refining technologies. A core element of this work is to incorporate the experimental knowledge within the Johan Gadolin Process Chemistry Centre into predictive models.

Fuel and char characterization:

CLIFF WP 1, FA-Fate of fuel bound nitrogen, FA-Chemistry of biomass impurities

Main funding: Tekes, Academy of Finland, Industrial partners

Patrik Yrjas, Mikko Hupa, Leena Hupa, Anders Brink, Maria Zevenhoven, Nikolai DeMartini, Johan Werkelin, Daniel Lindberg, Markus Engblom, Tor Laurén, Oskar Karlström, Juho Lehmusto, Hao Wu, Dirbeba Meheretu, Dorota Bankiewicz, Emil Vainio, Christoffer Sevonius, Tooran Khazraie, Jonne Niemi, Paolo Santochi, Jingxin Sui, Fiseha Tesfaye

Thermochemical conversion continues to be an important part of many industrial and societal solutions, from high-efficiency recovery boilers in pulp mills to waste gasification followed by gas cleaning and gas combustion for higher electrical efficiency than traditional waste incineration. Finland is a hotbed of activity in the development and demonstration of new technologies as well as improving older technologies for more challenging solutions.

Understanding the behavior of inorganics during thermal conversion is one important part of the industrial application of these technologies. Inorganic chemistry affects thermal efficiency, capital costs and emissions in these processes. The study of this chemistry requires both careful experimental studies and the detailed modeling of complex systems. While the Combustion and Materials group has a long history of expertise in areas like ash deposition and corrosion, the interactions within the Johan Gadolin Process Chemistry Centre and its international contacts have allowed for deeper studies into such topics as organic-inorganic interactions and integration of catalysts in thermochemical conversion processes.

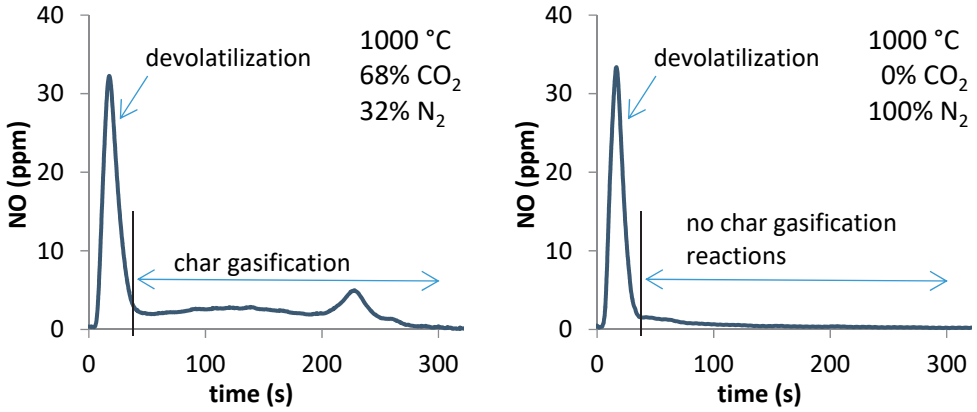
The development of new experimental data and integration into modeling is needed together to understand what is happening in the fuel and the char during thermal conversion. This approach has helped lead to significant improvements in combustion processes. Now, as the industry moves towards demonstrating gasification and pyrolysis as industrial solutions, new knowledge is needed for these gaseous environments. Below are short descriptions of a few of the projects that are ongoing in the area of thermochemical conversion.

CLIFF WP 1

CLIFF - Clustering Innovation Competence of Future Fuels in Power Production- is a three-year joint project between seven industrial partners operating in the area of biomass and waste to energy, and Finnish universities and VTT. A part of the project (WP 1 Fuels and feedstock; see also PCC WP 5 for other CLIFF tasks) is largely focused on testing new techniques for both laboratory and fuel scale applications. Examples of these techniques include: the application of XRF directly to biomass analysis; testing of a MWIR camera for combustion and gasification applications; development and utilization of a laser technique for the measurement of the release of alkali salts during combustion; development of a method to measure bed agglomeration and alkali capture; and application of a new method for measuring trace amounts of H_2SO_4 in flue gases from combustion systems. In addition to testing these different approaches, new data is being generated in the form of inorganics in biomass and waste as well as their behavior and release during combustion. The close collaboration with industry is an important element in the ultimate application of this knowledge in the improvement of existing technologies and development of new technologies.

Fate of fuel bound nitrogen

The project Fate of fuel bound nitrogen in biomass gasification is financed by the Academy of Finland as a postdoctoral researcher funding. In the past decades, large reductions in nitrogen oxide emissions from combustion have been achieved through a better understanding of nitrogen chemistry, particularly the gaseous NO chemistry. This has led to changes in boiler technology and operation. Gasification of biomass is a technology that is increasingly being applied as a means of reducing fossil fuel utilization, such as the gasification of bark to replace natural gas or fuel oil in lime kilns in pulp mills. For biomasses with high nitrogen contents, such as annual crops, high nitrogen emissions may become an issue. In biomass gasification, the formation of harmful nitrogen emissions originates from the fuel bound nitrogen (fuel-N). Around 70-90% of the fuel-N is released during devolatilization with the remaining part, around 10-30%, remaining in the char (char-N). During devolatilization, the nitrogen is released as e.g. NH_3, HCN, HNCO, NO, N_2O, N_2 and tar-N. The product distribution depends on the nitrogen content of the fuel, volatile matter, heating rate, final temperature, and surrounding gas atmosphere. Base on a review of the literature, the conversion of biochar-N has not been investigated under gasification conditions.



Measured concentration of NO from a 6 mm straw particle experiment at 1000 °C either in a CO_2-rich atmosphere or in 100 % N_2.

The figure shows NO emissions from a biomass pellet gasified in CO_2/N_2 and in N_2. The figure shows for the first time that NO is a reaction product from biomass char gasification by CO_2. This surprising observation is important in understanding the formation of nitrogen emissions in thermal gasification of biomass. Different types of biomass chars, as well as chars from demineralized biomass, are being studied in different gas atmospheres (mixtures of CO_2, H_2O, O_2) to understand the role of inorganics and gas composition. These results are being used in the continued model development for the prediction of the NO release profile during the char gasification.

Chemistry of biomass impurities

The Academy of Finland is also financing the project Chemistry of biomass impurities at reducing conditions in future thermal conversion concepts. Finland is a world leader in the development of new technologies to increase the efficiency of thermal conversion of biomass and waste for electricity and heat production, as well as, producing feedstocks for liquid fuels and chemicals. Gasification and pyrolysis are both technologies that are being demonstrated at an industrial level, which is leading to new questions. In this project we are studying the corrosion of metals in a reducing environment; the chemistry of the important fuel impurities, such as sulfur, halogens, alkalis, lead and zinc; and, their effects on deposition formation and emissions. Both experiments and thermodynamic modeling are being utilized to study these

phenomena specifically for reducing conditions. The results from the project will support solving specific industrial problems, such as prevention of potentially harmful emissions and materials corrosion and fouling in future thermal conversion concepts.

Cooperation: Amec Foster Wheeler Energia Oy, Andritz Oy, Valmet Power Oy, UPM-Kymmene Oyj, International Paper Inc., Clyde Bergemann GmbH Research partners: Tampere University of Technology, Lappeenranta University of Technology, Aalto University and VTT Technical Research Centre of Finland Ltd

3.5 Complementary research activities

Although the PCC research plan has a certain focus, our activities are much broader and most of our funding actually comes from other sources than the CoE funding. We have therefore gathered the most important activities and results under the term Complementary Research Activities (CRA). The CRA naturally falls well under the Molecular Process Technology area and the cooperation with industry is excellent.

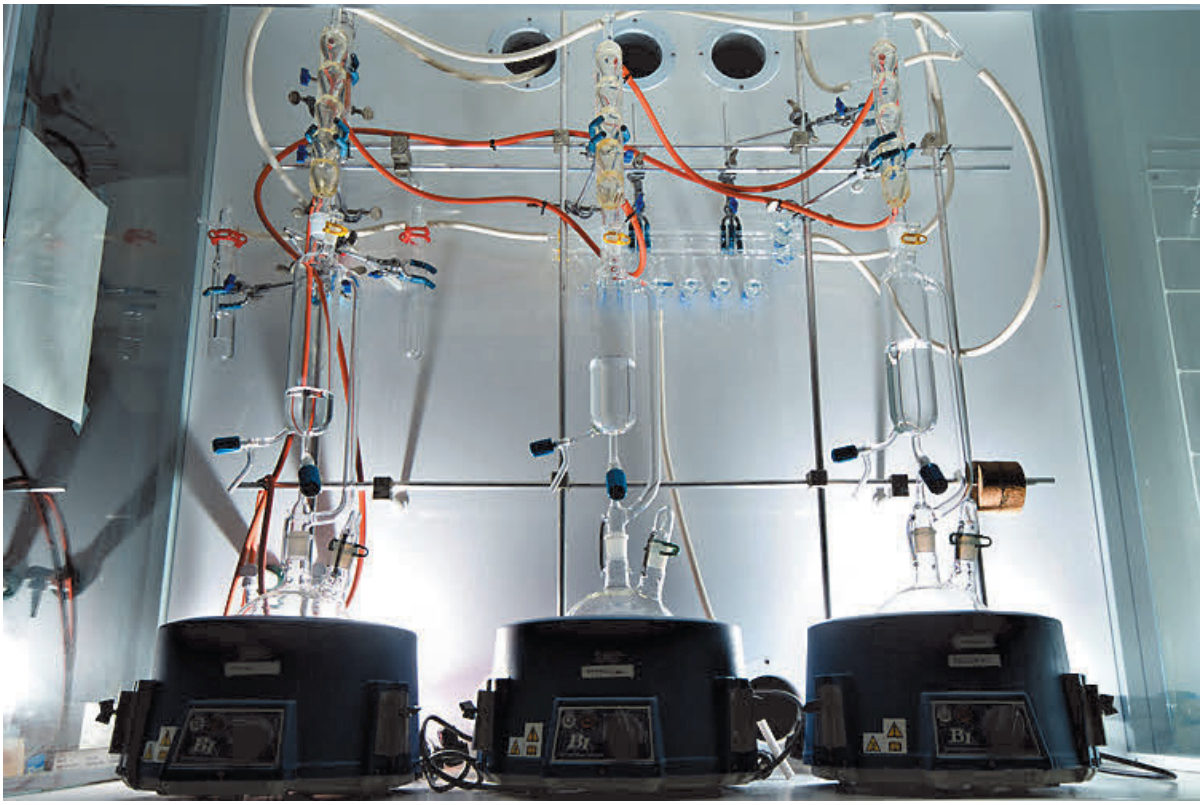


Photo: Denys Mavrynsky

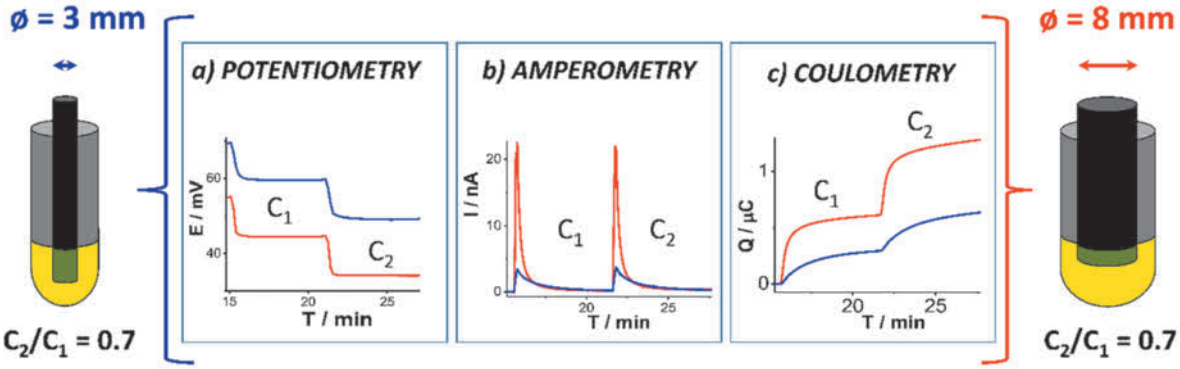
Equipment for solvent distillation over Na under Argon.

High-Performance Solid-Contact Ion-Selective Electrodes for Clinical and Environmental Applications

Main funding: Academy of Finland, Johan Gadolin Process Chemistry Centre, Magnus Ehrnrooths Foundation, Otto A. Malms Foundation, Walter Ahlströms Foundation, Åbo Akademi University

Zhanna Boeva, Tingting Han, Ning He, Ngoc Minh Nguyen Huynh, Ari Ivaska, Narendra Kumar, Rose-Marie Latonen, Tom Lindfors, Grzegorz Lisak, Ulriika Mattinen, Ville Yrjänä, Kai Yu, Jiawang Ding, Zdenka Jarolimova, Aleksei Kubarkov, Róbert Gyurcsányi, Eric Bakker, Kerli Martin, Ivo Leito, Johan Bobacka

The **novel signal readout principle for solid-contact ion-selective electrodes (SCISEs)** based on constant potential coulometry has been further explored since last year in this project. Importantly, the selectivity of the ion-selective membrane is retained even if the signal readout principle is unconventional for ISEs. The new signal readout principle enables amplification of the signal by increasing the capacitance of the electrically conducting polymer (ECP) solid-contact. Recently we showed that spreading the ECP of a given capacitance over a larger electrode area improves the response time of the SCISEs as shown in the figure below.

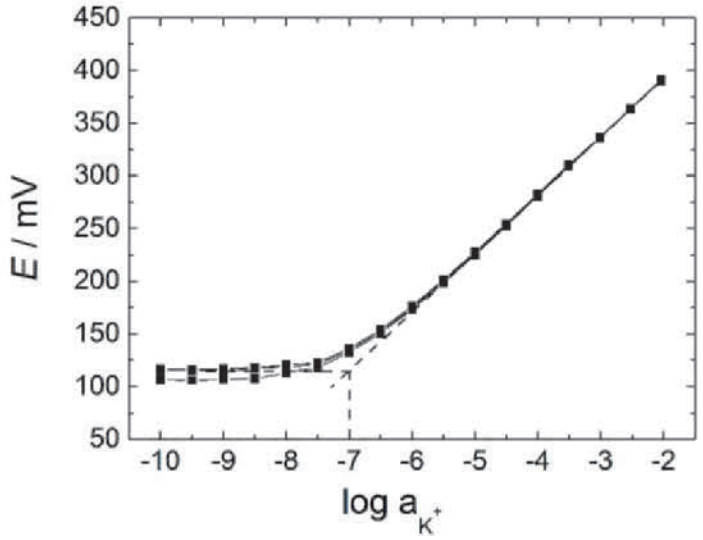


In classical potentiometry, a change in the activity (concentration of free ions) of the analyte ($C_1 \rightarrow C_2$) causes a change in the potential at the ion-selective membrane (ISM) | sample interface (a). In our new method, the potential of the electrode is forced to be constant, and the change in the primary ion activity in the sample phase results in a measurable redox current (b) from oxidation/reduction of the electrically conducting polymer (ECP) solid-contact giving a potential change of the solid contact that exactly compensates for the potential change at the ISM | sample interface. Integration of this current gives the total charge (c) that is proportional to the change in the activity in the sample phase. Increasing the electrode area shortens significantly the response time of the solid-contact ion-selective electrodes (SCISEs) when utilizing the novel coulometric signal readout method (red curve in b and c).

Combining the conducting polymer polypyrrole (PPy) with zeolites was also studied in this project in order to obtain a new type of solid-contact material for ion-selective electrodes. PPy/zeolite composites were electrodeposited on Pt electrode substrates and evaluated as solid-contact materials in K^+-selective electrodes (K^+-SCISEs). The redox capacitance of the PPy/zeolite composite was higher than for PPy doped with chloride after coating with a plasticized PVC-based K^+-selective membrane. After long-time conditioning (6 days), the detection limit of the K^+-SCISEs was significantly improved when using the PPy/zeolite composite as the ion-to-electron transducer. The results indicate that the combination of an organic electroactive material such as polypyrrole with inorganic zeolites results in materials with interesting new properties.

The project has also put considerable efforts during the last year in developing **potentiometric SCISEs with hydrophobic ion-to-electron transducers** to prevent the water layer formation between the electrode substrate and the transducer. The water layer formation results in long-term instability (drift) of the electrode response. We have successfully shown that the reproducibility of the standard potential (E^0) was improved by using both polyazulene doped with hexafluorophosphate and polypyrrole (PPy) doped with perfluorooctane sulfonate ($PFOS^-$) as transducer materials. Especially with the PPy-PFOS transducers

we obtained a very good E^0 reproducibility of only ±0.7 mV that is the best reproducibility reported for ECP based SCISEs. The project continues on focusing on fundamental interdisciplinary aspects to understand the factors governing the E^0 reproducibility and the long-term stability of SCISEs. The ultimate goals is the fabrication of conditioning- and calibration-free SCISEs.



Left: Calibration graphs of PPy-PFOS based K^+-SCISEs (n=3) showing their very good E^0 reproducibility. The dashed lines illustrate the determination of the detection limit.

The research in this project has also strongly focuses on **different types of graphene materials**. We have applied composite materials of polyaniline and few-layer graphene as transducers in Ca^{2+}-selective SCISEs. The incorporation of graphene into the conducting polymer matrix increases the capacitance and the hydrophobicity of the transducer. Both factors improves the potential stability of the SCISEs. We have also very recently prepared N-doped graphene films by electrochemical reduction of graphene oxide. Due to their pronounced electrocatalytic effect, we were able to separate the analytical signals of ascorbic acid, uric acid and dopamine (with square wave voltammetry) that were present in the same sample solution. Usually their analytical signals overlap because of their rather small difference in oxidation potentials. In autumn 2017, a PhD thesis about N-doped graphene will start within this project. We have also two very interesting ongoing projects in which we are studying the water and gas barrier properties of thin reduced graphene oxide films and polylactic acid films coated with amorphous hydrogenated carbon.

Since paper is a readily available and low-cost material that can be used for spontaneous transport of aqueous solutions via capillary forces, it has given rise to a new field of research in analytical chemistry, i.e. microfluidic paper-based analytical devices (μPADs). We have used **paper as a sampling and separation platform** allowing potentiometric sensing of chloride in presence of strongly interfering salicylate ions. Separation of salicylate prior to detection of chloride was achieved by allowing the sample to pass through a filter paper containing Fe^{3+} ions that bind salicylate but allow chloride ions to proceed to the detection zone. In the detection zone the concentration (activity) of chloride was determined by a solid-contact chloride-selective electrode. This system represents a low-cost, simple and disposable microfluidic sampling and separation platform that may broaden the range of analytes that can be determined by potentiometric ion sensors.

Furthermore, **SCIENCEs for anions** are being developed based on receptor molecules synthesized at theh University of Tartu, Estonia.

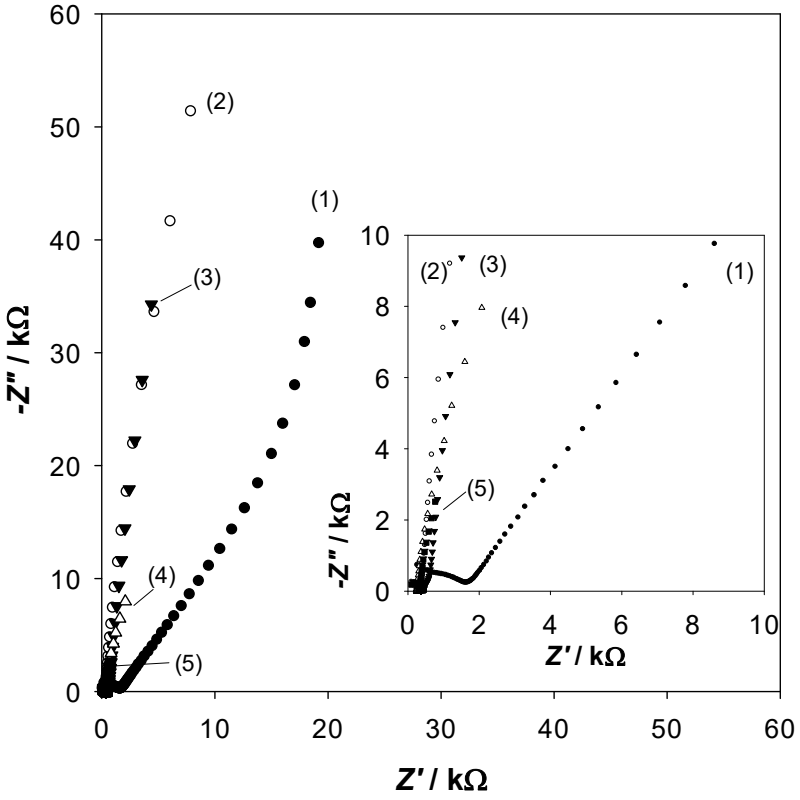
Cooperation: Budapest University of Technology and Economics, Hungary; University of Geneva, Switzerland; M.V. Lomonosov Moscow State University, Russia; University Koblenz-Landau, Germany; Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), China; University of Tartu, Estonia.

Durable and Low Cost Solid-Contact Ion Sensors

Main funding: TECNIO Spring (Spain), Johan Gadolin Process Chemistry Centre

Cristina Ocaña, Natalia Abramova, Andrey Bratov, Tom Lindfors, Johan Bobacka

Durable and low cost solid-contact ion sensors are developed for use in various applications such as clinical analysis of ions, monitoring of water quality and the control of processes in food and chemical industry. In this project poly(3,4-ethylenedioxythiophene) (PEDOT) functionalized with methacrylate groups was used as a solid-contact material allowing chemical bonding (cross-linking) to a polyurethane-acrylate-based Ca^{2+}-selective membrane. The electrodes were characterized by cyclic voltammetry, electrochemical impedance spectroscopy and potentiometry.



Impedance plots for screen-printed PEDOT-based electrodes in 0.1 M KNO_3. The PEDOT-based films also contain: (1) 0 wt % MWCNT/cMWCNT (carboxylated MWCNTs), (2) 0.2 wt% MWCNT, (3) 0.5 wt% MWCNT, (4) 0.2 wt% cMWCNT and (5) 0.5 wt% cMWCNT. E_{dc} = open-circuit potential, ΔE_{ac} = 10 mV and f = 100 kHz – 10 mHz.

Solid-contact Ca^{2+}-selective electrodes were prepared by solution-casting on screen-printed electrode substrates that are suitable for cost-effective mass production. The analytical performance of the ion sensors was improved by addition of multiwall carbon nanotubes (MWCNTs) and carboxylated MWCNTs (cMWCNTs) into the solid contact layer. The figure above illustrates the positive effect of MWCNT and cMWCNT on the impedance of the screen-printed PEDOT-based electrodes. The optimized screen-printed Ca^{2+} sensors showed Nernstian response and a life-time of three months upon continuous contact with an aqueous solution.

Cooperation: Instituto de Microelectrónica de Barcelona the Agencia Estatal Consejo Superior de Investigaciones Científicas (IMB-CNM-CSIC), Barcelona, Spain.

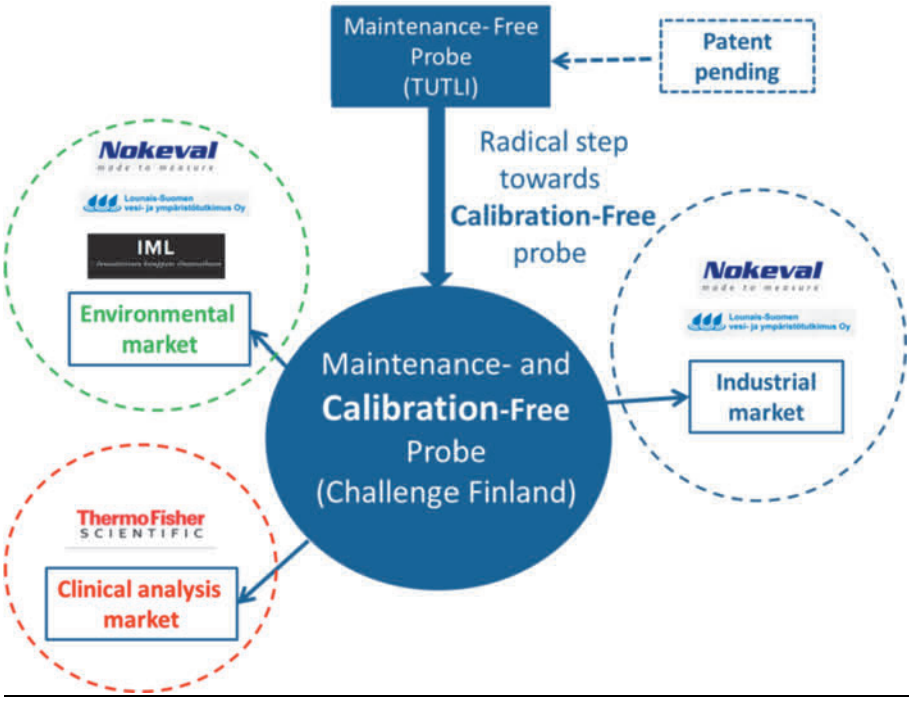
Calibration- and Maintenance-Free Multi-Sensor Probe for Wireless Monitoring (CaMaFree)

Main funding: Tekes (Challenge Finland)

Kim Granholm, Zekra Mousavi, Tomasz Sokalski, Johan Bobacka, Andrzej Lewenstam

Chemical analysis in industrial processes and environmental monitoring is mainly done by manual sampling and subsequent determination in the laboratory. The main reason for this approach is that most measuring equipment needs maintenance and frequent calibration. Such an approach (sampling and laboratory analysis) is labor-intensive, expensive, time-consuming and does not give real-time information. As a result, important trends or short-time changes of the measurement parameters will go unnoticed.

A simple, reliable and real-time monitoring system with wireless transmission which does not need calibration or other maintenance, and which can be used on-site, would therefore fill a big gap in the market. Our CaMaFree probe will revolutionize the monitoring technology and find applications in national and global markets such as the environmental, process and food industry, clinical analysis, health and well-being, and consumer markets.



CaMafree project - market potential.

During stage 1, the important task of developing, extending, and strengthening a consortium was carried out.

Cooperation: Nokeval Oy; Ilmastointimittaus Lind Oy (IML); Lounais-Suomen vesi- ja ympäristötutkimus Oy; Thermo Fisher Scientific Oy; Defour Oy; AGH-University of Science and Technology, Cracow, Poland; Warsaw University, Poland.

New Electrochemical Sensing Platforms for Personalized Medicine

Main funding: Jane and Aatos Erkko Foundation

Zhanna Boeva, Kalle Levon

The project aims to develop an easy-to-use technique for mutational analysis of the DNA sequence for clinical diagnostics and personalized medicine.

The technique developed within this project relies on basic principle of electrostatic interactions of single stranded DNA with conducting polymers as a source of the analytical response. This detection technique utilizes inexpensive single-use electrodes made of conducting polymers with immobilized single stranded DNA oligomer arrays as disposal sensing chips for *in vitro* analyses. These chips woriking in the potentiometric mode require only a basic potentiostat affordable to every clinical and chemical laboratory. The development of the technique used in this project is very promising for increasing the cost efficiency in medical and clinical diagnostics. Moreover, it has a strong potential to increase the competitiveness of the Finnish and European Union's biomedical diagnostic systems in the world market of innovations.

Cooperation: M.V. Lomonosov Moscow State University, Russia; Polytechnic Institute of New York University, U.S.A; Instituto de Microelectrónica de Barcelona the Agencia Estatal Consejo Superior de Investigaciones Científicas (IMB-CNM-CSIC), Barcelona, Spain.

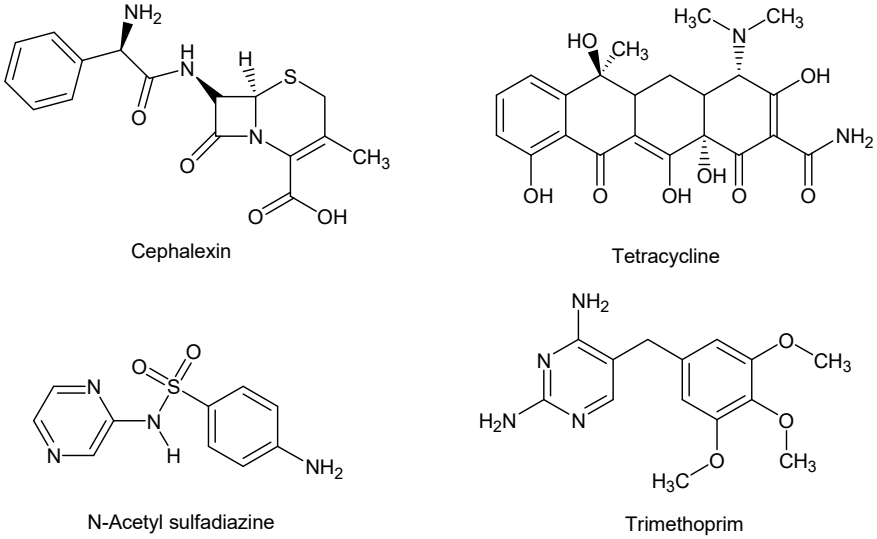
The Occurrence of Antibiotics in Wastewaters, Recipient Waters and Sediments

Main funding: Kone Foundation, Maa- ja vesitekniikan tuki ry, CIMO

Ewelina Kortesmäki, Axel Meierjohann, Leif Kronberg, Patrik Eklund

In recent years, the occurrence of antibiotics in the environment has generated a major concern among the public and decision makers because of their possible impact on the aquatic ecosystem and possible development of antibiotic resistant bacteria. Antibiotics have been shown to enter the environment through target organisms' excretion mainly *via* discharges from wastewater treatment plants (WWTPs), through the use of animal manure in agricultural fields and through direct discharge from aquaculture. It has been shown that even the relatively low concentrations of antibiotics found in WWTPs and in the environment can give rise to the selection of antibiotic resistant bacteria. However, more data on the occurrence and fate of antibiotics is needed before an actual risk assessment of their impact can be done. The overall objective of the work was to determine the occurrence and fate of 17 most used antibiotics in Finland in WWTPs, in recipient waters and sediments. Twenty-four hour composite samples were collected from the influent and effluent waters in the WWTPs in three consecutive days. WWTPs were chosen to represent different profiles by their working efficiency, characteristics of their incoming wastewater and size. Additionally, surface and bottom water samples as well as sediment samples were taken from the discharge points of the WWTPs and from the Archipelago Sea (which is rich in fish farming industry).The analytical method developed for the analysis of 17 antibiotics and 3 metabolites (tetracyclines, β-lactams, macrolides, quinolones and sulfonamides) in this study combines on-line solid-phase extraction (SPE) extraction and LC-MS/MS identification and quantification (an existing pre-treatment technique of SPE with liquid chromatography mass spectrometry triple quadrupole through on-line connection). An anti-epileptic drug carbamazepine was used as a tracer for wastewater contamination. Isotopically labeled isomers of the analyzed compounds were used for quantification.

Obtained results show that nine antibiotics could be detected frequently at concentrations ranging from over 1 μg l^{-1} in the influent to low ng l^{-1} in the effluent waters. Clarithromycin, erythromycin, erythromycin enol ether, roxithromycin and trimethoprim were found close to the discharge point (at the nearest sampling location from the discharge point) at average concentrations ranging from 26 to 132 ng l^{-1}. Preliminary results also show that some antibiotics can be detected in sediment samples taken from the Archipelago Sea.



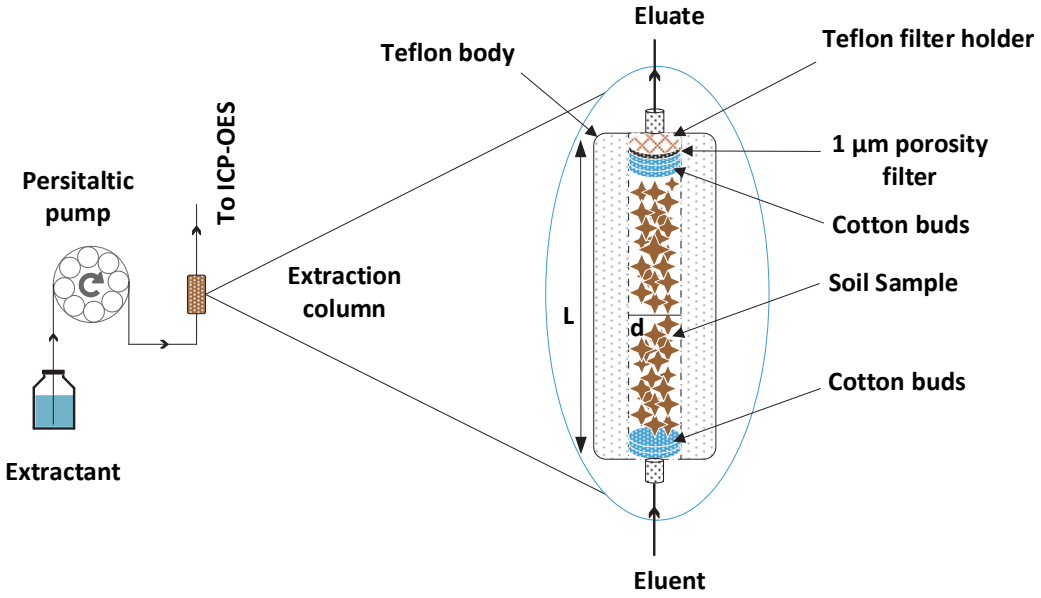
Structures of the selected antibiotics

Continuous Dynamic Extraction and On-line Determination of Metals from Solid Environmental Samples

Main funding: Johan Gadolin Process Chemistry Centre, Academy of Finland

Narender Kumar Joon, Paul Ek, Maria Zevenhoven, Leena Hupa, Grzegorz Lisak, Manuel Miró, Johan Bobacka

Contaminated soil decreases food quality and land usability and thus affects adversely environmental sustainability of the planet. Several methodologies have been used to identify and quantify toxic metals in soil, mostly by utilizing batch methods of metal extraction. However, there are several shortcomings of batch methods: (i) they are non-selective, (ii) they cause re-adsorption of extracted metals on the solid, (iii) they prevent accurate pH control, (iv) they are usually very time-consuming, and (v) they do not provide information about the kinetics of metal leaching from soil and other solid environmental samples.



Continuous dynamic extraction and on-line determination of metals by ICP-OES.

Therefore, a clear need arises for continuous dynamic extraction of heavy metals (see the figure above) in which a leaching solution is all the time delivered to the soil sample for efficient extraction of each toxic metal fraction. In such a system the concentration of the extracted metal is continuously measured by coupling the extraction column to the ICP-OES instrument. In this way, comprehensive information on the different fractions (bio-accessible and bio-available) of toxic metals present in the solid environmental samples is obtained.

Cooperation: University of the Balearic Islands, Palma de Mallorca, Balearic Islands, Spain.

Materials in Energy Technology

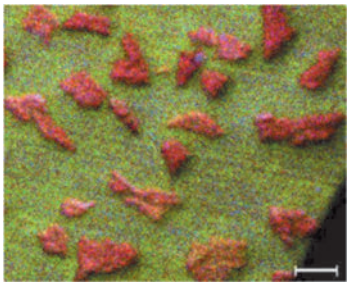
CLIFF WP 3, KME-717, EU-OnCord and others

Main funding: Academy of Finland, Tekes, Industrial partners, Swedish Energy Agency, European Union's Research Fund for Coal and Steel, Finnish Recovery Boiler Committee

Patrik Yrjas, Leena Hupa, Anders Brink, Daniel Lindberg, Maria Zevenhoven, Niko DeMartini, Markus Engblom, Oskar Karlström, Emil Vainio, Juho Lehmusto, Dorota Bankiewicz, Paolo Santochi, Tooran Khazraie, Wu Hao, Christoffer Sevonius, Tor Laurén, Jan-Erk Eriksson, Jingxin Sui, Jonne Niemi, Meheretu Dirbeba, Varun Rai

The emerging trend towards renewable energy sources has led to an increased share of biomass used in solid fuel fired power plants. However, different types of biomass fuels (forest residue, bark, demolition wood, waste, straw, husks, energy crops, etc.) contain elements that may cause corrosion and erosion of the power plant equipment. This development and the demand for increasing steam temperatures often result in severe operational problems, which can lead to unscheduled power plant shutdowns and decreased boiler availability. There are a number of ways to tackle these problems; co-firing fuels with different specifications to achieve positive chemical synergies thus avoiding the formation of harmful compounds or use chemical additives with the same goal or alternatively use better, but also more expensive materials already in the construction phase. In the projects presented here the overall goal is to minimize corrosion through understanding of the different phenomena. This is done by laboratory research on the topic under different conditions, measurements on site and also through the development of new and novel experimental methods to be able to reveal details about the corrosion reaction mechanisms.

In CLIFF, which is a three-year joint research project between several industrial companies and research organizations in the area of biomass and waste to energy, the research is divided into several work packages of which WP 3 is a part of this chapter. It is also in part closely connected the Academy of Finland funded project called "Novel Approaches to Study Corrosion Mechanisms in High-temperature Industrial Processes". In *CLIFF WP* 3 the focus is on studies concerning superheater and refractory corrosion and erosion and development of new research methods.



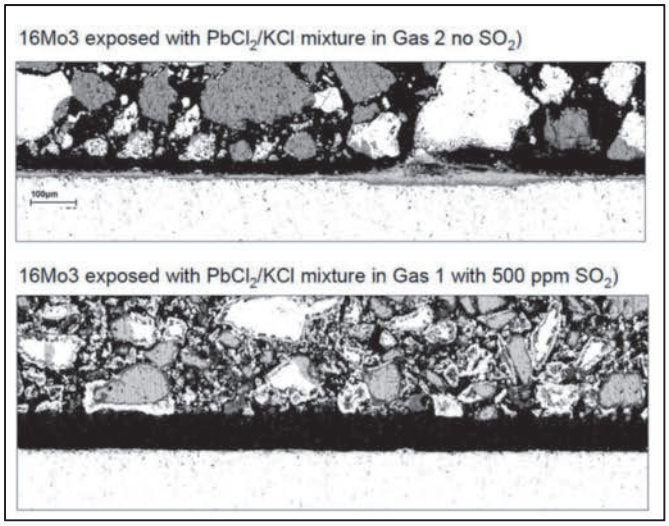
First results from a corrosion test using isotopes showing a ToF-SIMS image of a steel surface exposed to KCl at 540 °C in synthetic air ($^{16}O_2$ and N_2) in the presence of $H_2{}^{18}O$; ^{16}O appears red and ^{18}O appears green. The scale bar equals to 10 microns.

ToF-SIMS proved to be an applicable tool, providing detailed information about the distribution of the two oxygen isotopes at the sample surfaces. Highly interestingly, the preliminary results indicated that oxygen from water vapor reacts directly with the steel surface, whereas oxygen from air is involved in the formation of an intermediate corrosion product, K_2CrO_4 (the red particles).

In another project, KME-717, funded by the Swedish Energy Agency the focus has been recycled wood due to low price compared to virgin wood-based fuels. However, used wood is often contaminated with paint, plastic and metal components, leading to elevated concentrations of heavy metals, such as zinc and lead, chlorine, sodium and sometimes sulphur in flue gases and deposits relative to those from virgin wood. While much work has been conducted on high-temperature corrosion (> 450°C) caused by KCl and NaCl

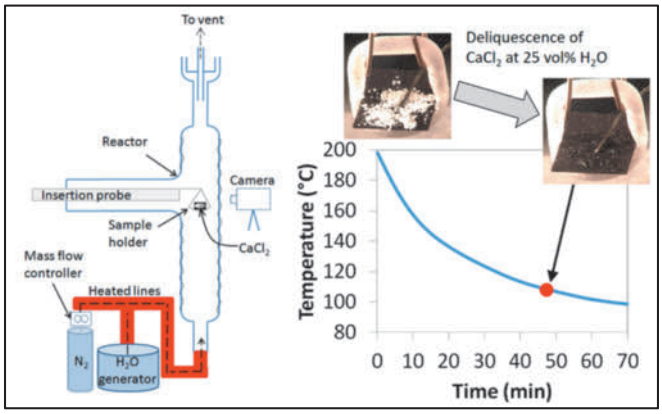
which are present in wood fuels, much less is known about corrosion in the range 150- 420°C and corrosion caused by Pb and Zn and their chlorides.

The goal of the project is to investigate if Pb and Zn and their chlorides found in used (recycled) wood, causes corrosion problem in the temperature range 150-420°C, and if the use of sulphur as a fuel additive increases the corrosion. The project includes laboratory testing, thermodynamic equilibrium modelling, and probe testing at 150-420°C in a real boiler firing used wood with and without the use of an additive.



Cross-sections of salt particles, corrosion layer and steel after tube furnace exposures in 300°C for 168 h.

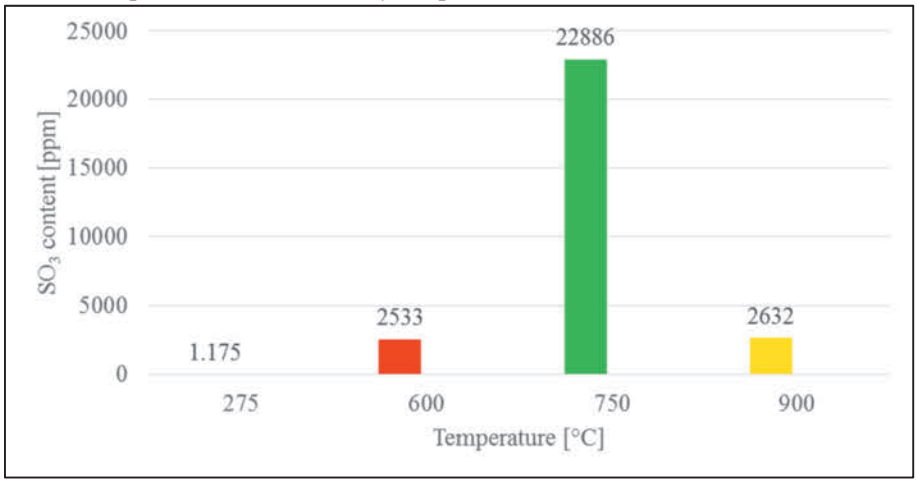
The full-scale testing will give new valuable knowledge about the importance of Pb and Zn for corrosion when firing used wood and waste fuels. From this and the results of the modelling and laboratory testing solutions for minimizing potential problems will be suggested.
While the focus in KME-717 is on salt-induced corrosion at relatively low temperatures, there are two other projects focusing on low-temperature corrosion due to hygroscopic salt deposits or/and sulphuric acid. In one of these projects "Low-temperature Corrosion in Combustion – Old Problem, New Approaches" funded by the Academy of Finland a new method to measure sub-ppm levels of gaseous H_2SO_4 in the flue gas has been developed. Previously, when burning sulphur-rich fuel the formation of H_2SO_4 was a limiting factor and to avoid condensation in the power plant the flue gas temperature was kept over 150°C. This temperature is still commonly used, although the fuels that are used have changed. The existence of H_2SO_4 in the fuel gases will be clarified within this work. Results have already shown that for example in Kraft recovery boilers there is nearly no H_2SO_4 present and in another project (Understanding Low-temperature Corrosion in BL Combustion) funded by the Finnish Recovery Boiler Committee this issue is addressed. However, corrosion may instead be caused by hygroscopic salts if the flue gas temperature is lowered too much. As soon as water is absorbed by the salts, corrosion will begin. In this research, a first mapping of the corrosion of a carbon steel as a function of salt, temperature and humidity is carried out.



A laboratory test to study the hygroscopic nature of $CaCl_2$. The red point illustrates the temperature where $CaCl_2$ starts to absorb water from the gas.

Corrosion issues are also on the agenda in the *EU-OnCord* project, which is coordinated by the Technical University of Munich. Co-firing chlorine-rich biomasses at high shares with coal at with elevated steam temperatures is enabled by using the coal ash as a protective agent. Coal and its inorganic constituents such as sulphur and aluminum silicates are able to prevent the formation of alkali chlorides, and consequently chlorine-rich deposits. Two online corrosion sensors have been developed and used in combination with on-line measurement techniques yielding gaseous and solid phase composition to monitor corrosion. Both sensors have been tested under aggressive conditions and long-term exposure tests in pulverized fuel and fluidized bed systems of varying size and in combination with material loss probes. Experiments have been done in laboratory scale, in pilot scale and in full-scale plants. By this approach, corrosion rates can be correlated to the fuel composition and process conditions in order to understand observed phenomena. The project aims at providing strategies for setting up fuel blends and to strengthen the position of solid fuel fired boilers, particularly the position of coal since it enables the use of low-grade biomass in highly efficient combustion systems.

In the *Variations in catalytic properties of the flash smelter process dusts*-project, which is done in co-operation with Outotec and Boliden, the process conditions are quite different compared to power plant combustion. Flash smelting is a continuous, nearly auto-thermal process, which is used to extract primary copper and nickel from sulfide ores. The process gas entering the heat recovery boiler of a copper flash smelter typically contains around 40 vol-% of sulfur dioxide (SO_2) and roughly 5 vol-% of water vapor. Previously, it was observed that the process dust catalytically converts SO_2 to sulfur trioxide (SO_3), which then reacts further to H_2SO_4. At latter parts of the flash smelter process line, when the temperature decreases to the dew point of H_2SO_4, the formed gaseous H_2SO_4 might condense on the heat-transfer surfaces, resulting in severe material degradation. In order to optimize the flash smelting process and to prevent corrosion, a deeper understanding of variables affecting the SO_3 formation is essential. This is now addressed by further studying the role of process dust's chemical composition in the SO_2-to-SO_3 conversion. The goal is to clarify, which species in the dust are responsible for the SO_3 formation and to what extent does the amount of these species matter. The results are expected to shed more light on the gas phase chemistry taking place in industrial-scale in the presence of solid catalytic species.



The SO_3 amount formed in the reaction catalyzed by process dust as a function of temperature.

Cooperation: Amec Foster Wheeler Energia Oy, Valmet Power Oy, UPM-Kymmene Oyj, Andritz Oy, Top Analytica Oy Ab, Clyde Bergemann GmbH, International Paper Inc., Tampere University of Technology, Lappeenranta University of Technology, Aalto University and VTT Technical Research Centre of Finland Ltd, Swerea KIMAB Ab, Energiforsk Ab, Andritz Energy & Environment, Vattenfall Ab, AB Fortum Värme, City of Stockholm, TU München, Universität Augsburg, International Flame Research Foundation, Bilfinger, Enel, Doosan, Valmet Technologies Oy, Outotec Oy, Boliden AB

Lignans and Lignins as Potential Components for Dye-Sensitized Solar Cells

Main funding: Doctoral Education Network of Materials Research (DNMR)

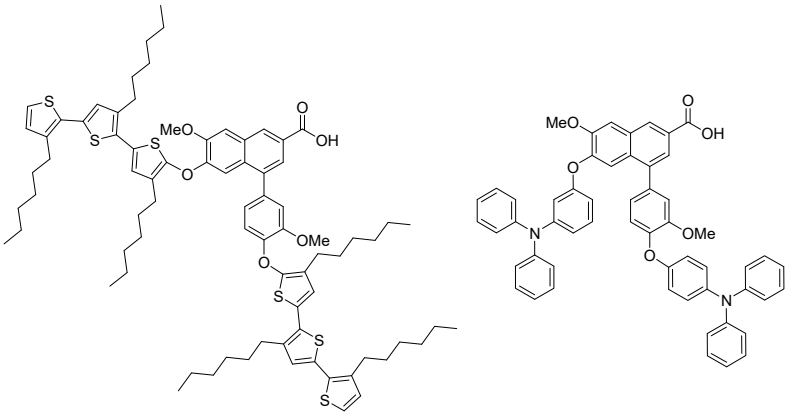
Sabine Rendon, Rose-Marie Latonen, Reko Leino

Dye-sensitized solar cells (DSSCs) belong to emerging photovoltaic technologies where the active layer contains light absorbing dyes. Currently, the most efficient DSSCs are typically based on non-abundant and expensive ruthenium dyes. Ruthenium has been proposed to be the main limiting factor for large-scale production of DSSCs. Therefore, we are currently screening and developing new dyes potentially based on cheap and readily available forest resources such as lignans and lignins.

Hydroxymatairesinol is the most abundant lignan in Norway spruce (*Picea abies*). This lignan is found in especially high concentrations in the knots of the tree, from where it can be easily isolated in large amounts. Lignans have not been investigated earlier as starting material for dyes in DSSCs. Preliminary results indicate, however, that especially conjugated lignans absorb light in the visible region, making them promising candidates for use in cheap DSSCs.

The related polyphenol lignin is highly abundant, with hardwoods typically containing 18-25% lignin and softwoods 25-35%. Due to its complex structure, random degree of polymerization and poor solubility, lignin has traditionally been a difficult substance to utilize as biomass derived feedstock. Some lignin derivatives have, however, been successfully used in DSSCs, but additional modifications would be needed in order to increase the power conversion efficiency and performance of the devices.

In this project, the electrochemical properties of selected lignans and lignins are being investigated using UV-Vis spectroscopy and cyclic voltammetry. Based on these result, suitable dye candidates will be synthesized, further modified and tested in prototype solar cells.



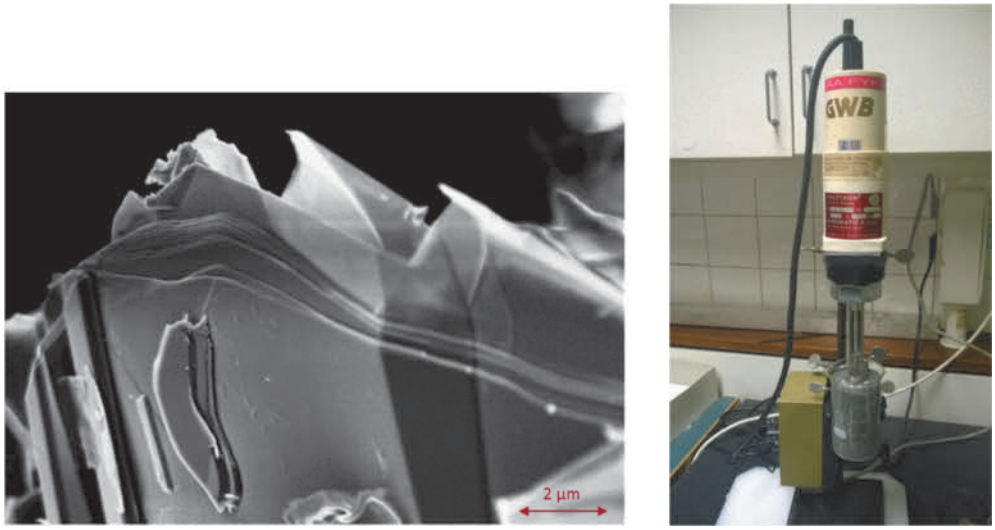
Examples of dye candidates based on lignans.

The FennoFlakes Project – From the Identification of the Potential Flake Graphite Ores in the Fennoscandian Shield to the Utilization of Graphene

Main funding: Academy of Finland (MISU Programme) and K.H Renlunds stiftelse

Sara Lund, Jussi Kauppila, Rose-Marie Latonen, Tom Lindfors, Jan-Henrik Smått, Jouko Peltonen, Jenny Palosaari, Sauli Raunio, Rasmus Blomqvist, Jukka Marmo, Olav Eklund

FennoFlakes is an interdisciplinary collaboration project between Geology and Mineralogy, Laboratory of Analytical Chemistry and Laboratory of Physical Chemistry. The project identifies and purifies Finnish flake graphite ores and aims to use the produced graphite in graphene production. The idea is to show that the domestically produced graphite has high quality so that it can be used in graphene production. Furthermore, graphene will be utilized in proof-of-concept applications to demonstrate the good quality of the produced material. The purification process is carried out in cooperation between the geologists and chemists and the idea is to study new processing routes such as electrodynamic fragmentation (SelFrag) of the mineral ore. After each processing step, the product is characterized quantitatively and qualitatively. Especially important is to monitor the carbon content, which helps to optimize the whole enrichment process.



A SEM image of flake graphite from Piippumäki area (left) and a high-shear laboratory mixer producing a graphene dispersion (right).

So far, the geologist have found and characterized flake graphite ores from several different locations in Finland. The most interesting areas seem to be located in Savonia. The enrichment of the ore is currently in its final stage where the chemists are removing the last impurities from the graphite ore by chemical methods. While the purification process of the domestic graphite has been going on, the chemists have used commercial flake graphite to optimize the exfoliation process.

The graphite exfoliation is done by high-shear mixing using a suitable dispersant, which prevents the graphene flakes from re-stacking. A traditional sodium cholate surfactant solution has been used for this purpose and as a new method; graphite has also been successfully exfoliated in a suspension of cellulose nanocrystals (CNC). Exfoliating graphite directly in CNC offers a simple and eloquent method to produce graphene/CNC composites. Different parameters for the preparation of the graphene/CNC dispersions have been investigated in purpose of preparing solid electroconductive graphene/CNC composites. Preliminary test on films prepared by drop-casting show that our graphene/CNC composites are conductive.

Cooperation: Åbo Akademi University; The Geological Survey of Finland (GTK), Beowulf Mining, Fennoscandian Resources, Haarla Group

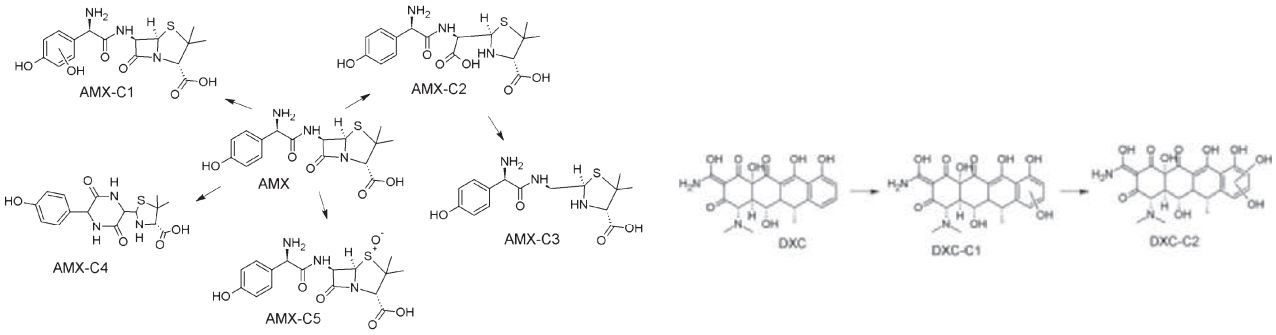
The Fate of Antibiotics in Pulsed Corona Discharge Oxidation

Main funding: Maa- ja vesitekniikan tuki

Matilda Kråkström, Alexander Sokolov, Marjatta Luohi-Kultanen, Patrik Eklund, Leif Kronberg

Antibiotics in the environment are of concern due to the development of antibiotic resistant bacteria. Conventional wastewater treatment plants are not designed to remove micropollutants such as antibiotics. Thus, a significant amount of these compounds are released into the aquatic environment. The gas-phase pulsed corona discharge process (PCD) is an effective, environmentally friendly method for removing recalcitrant organic compounds in waste water. In PCD organic compounds are transformed through reactions with hydroxyl radicals and ozone. The objective of this work is to optimize PCD oxidation for the antibiotics amoxicillin (AMX) and doxyxycline (DXC).

The experimental system comprised a pulsed corona discharge reactor and a high voltage pulse generator. The concentration of pharmaceuticals was measured by high performance liquid chromatography. The main oxidation products were characterized with liquid chromatography coupled to mass spectrometry. A preliminary structural characterization of oxidation products was performed on the basis of molecular weight determination by a time of flight mass spectrometer, and fragmentation pattern recorded by an ion trap mass spectrometer.



Proposed transformation pathways for amoxicillin and doxycycline.

The preliminary results show that AMX forms nine transformation products of which five have been tentatively identified. DXC forms two major products, both of which have been tentatively identified. The most common transformations are those where one or hydroxyl groups are added to the parent compound and ring opening of the β-lactam ring in AMX

Cooperation: Lappeenranta University of Technology, Finland.

Circular Economy

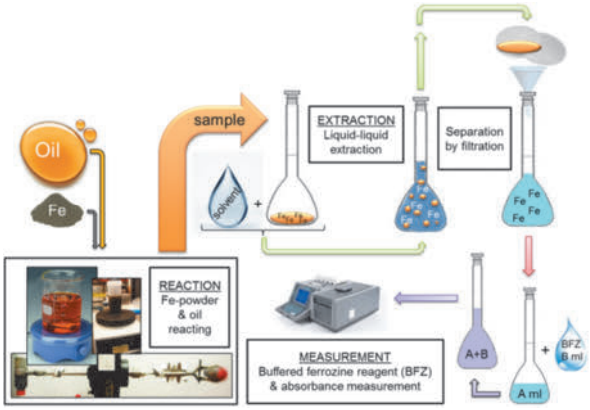
Smart research, Material value chains – ARVI, Nordic Flagship

Main funding: Tekes INKA-EAKR, Tekes and 18 Finnish companies, Nordic Energy Research.

Jan-Erik Eriksson, Nina Bruun, Jarl Hemming, Sofia Höglund, Anna Sergeeva, Joon Narender Kumar, Joni Rantala, Tooran Khazraie, Johan Werkelin, Grzegorz Lisak, Johan Bobacka, Stefan Willför, Leena Hupa, Patrik Yrjas, Emil Vainio, Daniel Lindberg, Mikko Hupa, Anders Brink, Maria Zevenhoven, Cristoffer Sevonius, Linus Silvander, Olle Holmbäck, Patrik Salminen.

A circular economy strives to minimize its resource input and waste production, emissions, and energy leakage by closing material and energy loops in society and industry. Three different projects in the PCC WP 5 can be placed under this caption: two of them financed by Tekes and one by the Nordic Energy Research.

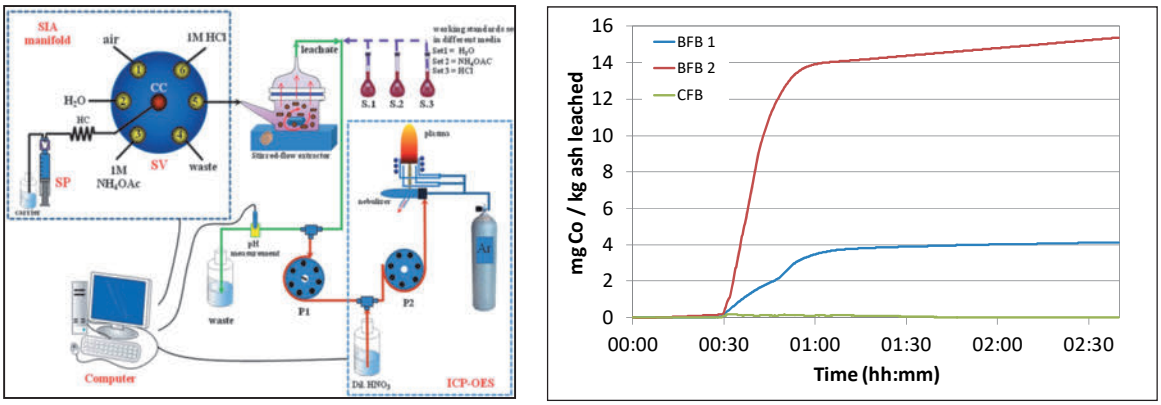
SmartResearch project is a joint effort by Åbo Akademi, Turku University of Applied Sciences, and the University of Oulu to develop and tailor reliable analytical methods and research services for participating small and medium scale enterprises (SME) working with future bio and circular economy challenges. The main effort is within refining biomasses or their ashes, recycled materials and industrial by-streams to new high-value products. One goal is to create a common innovation platform where the SME´s via mutual collaboration and together with the participating universities develop and test smart processes to produce new products for international markets. The research activities will contribute to building up the R&D&I platform in the Smart Chemistry Park business park in Raisio outside Turku. The innovation platform structure aims to develop a network and collaboration model where SME´s, industry and universities together develop smart processes and methods for sustainable cities. The development of versatile and reliable analytical methods to the research of the aforementioned materials is crucial to the R&D of the companies and is therefore in the main focus of this project.



Test method to detect corrosivity of bio-oils

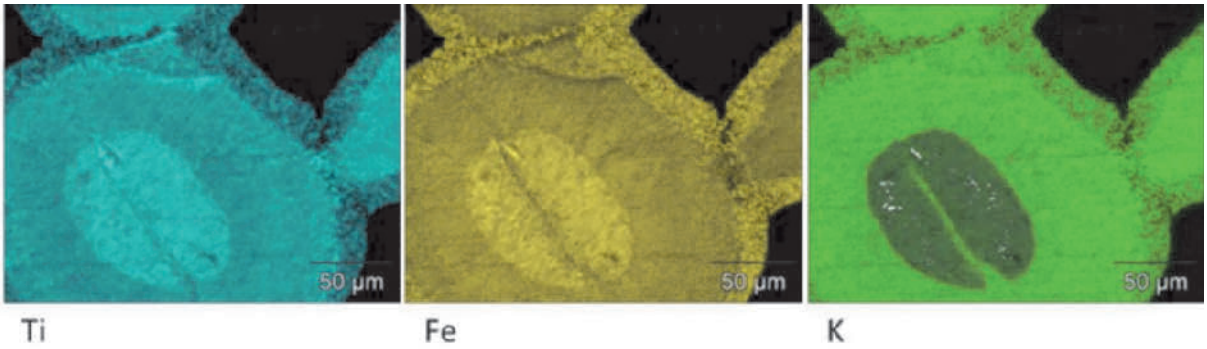
The research in the ARVI program focuses on systemic assessment of material recovery and recycling opportunities. The program, coordinated by CLEEN Ltd., consists of a consortium of 29 organizations out of which 18 are companies and 11 research institutes. The work by Åbo Akademi is focused on ashes and its elemental behavior and leachability. The objective is both to separate eventual valuable elements and simultaneously decrease the concentrations of possibly limiting elements for further use of the ash bulk (building material, agricultural use, forest use, etc.). Detailed knowhow is created on material compositions and structures, and processing technologies are studied to modify the materials for reuse purposes or to capture valuable components found in very small amounts in complex matrixes. In addition, different types of modelling and assessment methodologies for chemical, process, LCA, environmental footprint and

techno-economical calculations are combined to perform sophisticated overall analyses of material value chains.



Continuous leaching system of ashes (left) and leaching of cobalt (right) from two fly ashes from a bubbling fluidized bed (BFB) and one fly ash from a circulating fluidized bed (CFB). The first 30 min. with water and then with 5M HNO_3.

Nordic Flagship ("Enabeling negative CO_2 emissions through the use of CLC of biomass") is a multi-partner and cross-disciplinary project funded by Nordic Energy Research that runs from November 2015 to October 2019. Chemical-Looping Combustion of biomass (Bio-CLC) is a unique and innovative combustion technology that is studied and developed in the project. Negative CO_2 emissions can be achieved by CO_2 capture and storage from biomass combustion. Chemical-Looping Combustion (CLC) involves oxidation of fuels with oxygen provided by solid oxygen carrier particles rather than by air. Both the high energy penalty and the high capital cost associated with conventional gas separation needed for CO_2 capture can be avoided with this technology. Åbo Akademi focuses on the interaction between ash forming matter and oxygen carrier material as well as on corrosion in CLC.



The SEM/EDS map of the oxygen carrier material ilmenite, $FeTiO_3$, after heat treatment with K_2CO_3 from biomass ash shows that it reacts to form potassium titanate (blue and green areas) enriching the surface with iron oxides (yellow)

During 2016 the interaction of alkali salts with potential oxygen carriers, such as ilmenite ($FeTiO_3$) and manganese minerals was studied under oxidizing dry conditions. It was found that potassium carbonate interacts with ilmenite. This interaction potentially enhances the oxygen carrier capacity of ilmenite, whereas potassium dihydrogen phosphate inhibits its oxygen carrier capacity and will cause heavy agglomeration in the fluidized beds used in the CLC.

Cooperation: University of Oulu, Finland; Turku University of Applied Science, Finland; CrisolteQ, Renotech Oy, Ecomation Oy, KWH Mirka Ltd, Ab Nanol Technologies Oy, VG-Shipping Ltd, Kierto Environmental Services LTD, CLEEN Ltd., consists of a consortium of 29 organisations out of which 18 are companies and 11 research organisations, Chalmers University of Technology, the Bellona Foundation, Sibelco Nordic AB, SINTEF Energy Research, SINTEF Materials and Chemistry, VTT Technical Research Centre of Finland Ltd.

Asymmetric Catalysis and Chromatographic Separation and Combinations of Enzymatic and Organometallic Catalysis and Preparation of Pharmaceutically Relevant Fused Heterocycles

Main funding: Academy of Finland

Risto Savela

Many natural occurring lactones and lactams contain biological and pharmaceutical activities, especially chiral bicyclic lactones and lactams are found to be very versatile as intermediates and biologically interesting compounds. Thus investigation in preparation of lactones and lactams via combination of enzyme and organometallic catalysis is planned.

By extending the dynamic kinetic resolution methodology to allylic alcohols using acrylates as acyl donors a fast and efficient route to new intermediates for further derivatization, such as ring closing metathesis, can be envisioned. Most importantly, this secures the route to five membered chiral ring structures previously poorly attainable by other methodologies. Iron is a very interesting, relatively cheap and nontoxic alternative to many other noble metals used as catalysts. In addition, with the recent major improvements into iron catalyzed reactions, further derivatization using iron catalysis will be investigated.

As the compounds attained by dynamic kinetic resolution contain multiple unsaturated bonds, cycloaddition reactions are very interesting alternatives to ring closing metathesis. As cycloaddition is a very atom efficient methodology and when combined with iron catalysis it gives good grounds for environmentally beneficial reactions. Thus a cost effective route to fused 5+4 and 5+6 membered bicyclic lactones and lactams in proposed with use of [2+2] and [2+2+2] cycloaddition reaction. Furthermore, alternative cyclization methods will be investigated with the use of hydroformylation/cyclization or alcoholamination/hydroamination cascades.

Cooperation: Imperial College London, United Kingdom; University of Edinburgh, United Kingdom.

Complex Reaction Kinetics and Thermodynamics

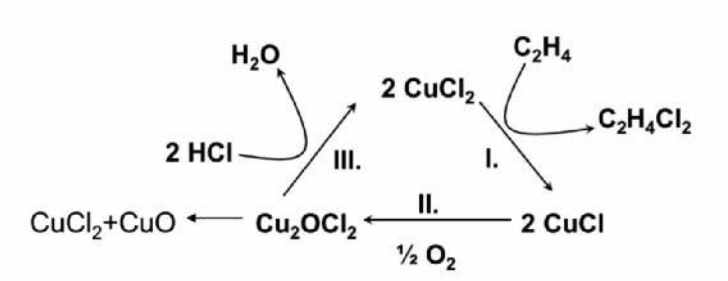
Main funding: Abo Akademi Foundation, Svenska Litteratursällskapet, CIMO, Neste Oyj

Johan Wärnå, Jyri-Pekka Mikkola, Nemanja Vucetic, Eero Salminen, Soudabeh Saeid, Maria Pinilla de Dios, Frans Storgårds, Andreas Franz, Zuzana Vajglova, Atte Aho, Pasi Tolvanen, Päivi Mäki-Arvela, Henrik Grénman, Tapio Salmi, Dmitry Murzin

A big part of industrially relevant chemical reactions consists of very complex reaction networks for which stoichiometric and kinetic analysis plays a decisive role in order to be able to design new processes and equipment. Reaction kinetics and equilibria as well as solubilities and mass transfer effects of complex reaction networks are measured experimentally and modelled quantitatively. Development of the methodology for analysis of complex reaction networks is an essential part of the project, particularly for heterogeneously and homogeneously catalyzed reactions and solid-liquid reactions. The main case studies are devoted to reaction networks of biomass components, reactions of pharmaceuticals and specific gas-phase processes. Also the preparation of valuable organic chemicals with supported ionic liquid catalysts (SILCA) is an essential part of the development work. Both conventional and microreactors are used. Environmentally friendly direct amidation of fatty acids and fatty acid methyl esters from algal oil have been performed with various alkanolamines using micro- and mesoporous catalysts for production of pharmaceuticals and surfactants. A is going on with the aim to destroy rests of pharmaceuticals in wastewaters. The approach is to use ozonation combined to heterogeneous catalysts. A new project has been started concerning the oxochlorination and oxidation of ethylene. The aim is very precise kinetic analysis and development of microreactor technology for oxychlorination.

Oxychlorination of ethylene

$$C_2H_4 + \tfrac{1}{2}O_2 + 2HCl \xrightarrow{CuCl_2} C_2H_4Cl_2 + H_2O \qquad \Delta H^0_{R,298K} = -295\text{kJ/mol}$$



I. Reduction of cupric chloride (ethylene chlorination)
II. Reoxidation of the cuprous chloride
III. Chlorination of copper oxide

Cooperation: University of Valladolid, Spain; Czech Academy of Sciences, Institute of Chemical Process Fundamentals, Czech Republic; INSA Rouen, France; Umeå University, Sweden.

Thermochemical conversion of solid, liquid and gaseous biomass fuels

EU-Biofficiency, FA-Molten ash, FA-LEAN, and CLIFF WP 2

Main funding: European Union, Academy of Finland, Tekes, Industrial partners

Daniel Lindberg, Fiseha Tesfaye, Markus Engblom, Jonne Niemi, Patrik Yrjas, Anders Brink, Oskar Karlström, Leena Hupa

Three projects (one EU and two FA) and a work package from a larger Tekes project deal with thermal conversion of several types of biomass fuels by different thermochemical conversion techniques ranging from industrial recovery boilers or municipal combined heat and power plants to internal combustion engines. Many projects are concerned with the ash formed during combustion but some are also dealing with the detailed oxidation paths of hydrocarbons and nitrogen species.

EU-Biofficiency

Heating and cooling are responsible for almost half of EU's final energy demand and biomass combustion is currently responsible for more than 90% of all renewable heat. The goal of biomass-based technologies is to increase its share in the heat market in Europe from 11% in 2007 to about 25% in 2020.

Combined Heat and Power (CHP) from biomass is a suitable technology for medium- and large-scale units where many utility and industrial applications can be found in Scandinavia. The main challenge for efficient CHP and high-temperature steam production from biomass are ash-related problems, i.e. ash fouling and corrosion that limits both steam temperature and heat transfer. By solving these issues, large-scale boilers offer a huge potential for efficiency increase and emission reduction during CHP generation at cost competitive and environmental friendly conditions. In order to reach these goals and to enable a secure and almost carbon neutral heat and power generation, several measures have to be undertaken. The main objectives and goals of the Biofficiency project are to:

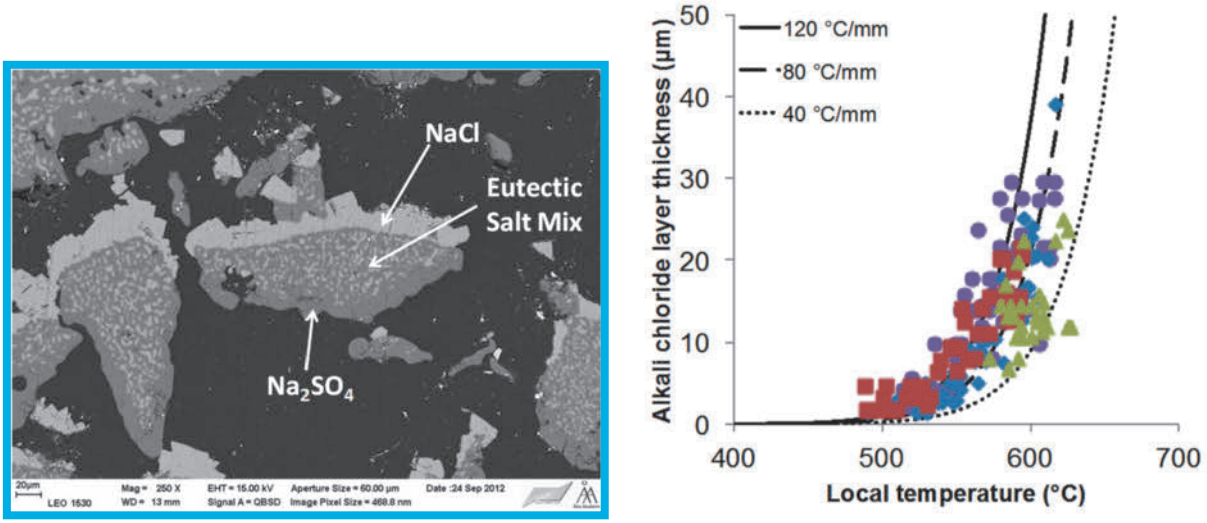
- Develop next generation, biomass-fired CHP plant at medium to large scale (10 to 200 MWth) with elevated steam temperatures up to 600 °C.
- Increase efficiency of CHP plants by elevated steam temperatures through solving and understanding of ash-related problems – slagging, fouling and corrosion.
- Reduce emissions – i.e. CO_2, particulates, CO, NO_x, and SO_2 – by efficiency gain, reduction of impurities and by intelligent plant design.
- Widen the feedstocks for pulverised fuel (PF) and fluidised bed (FB) power plants using pretreatment methods to reduce inorganic elements: chlorine, sulphur and alkali metals.
- Widen ash utilisation and nutrient recirculation and explore new ideas to the European technical regulation for future biomass ash usage.
- Design of a reference CHP plant based on detailed measurement results and modelling studies.

Power generation from biomass is unfortunately not as easy as this!

FA-Molten ash

Many challenges in a number of industrial high-temperature processes are connected to the presence of a molten phase. Even small amounts of a molten phase may have a dramatic importance to the kinetics of many industrially important high-temperature reaction systems. However, little systematic generic research has been published on the detailed role of composition and amount of liquid phases in reacting systems.
This project sheds more light on the chemical phenomena of the presence of a molten phase, especially connected to the role of the melt in ash deposits in biomass and waste combustion with the aim of solving specific industrial problems, such as materials corrosion and fouling in reactors and furnaces. Behavior of systems containing molten phases is very difficult to predict by any theoretical methods. Thermodynamic properties of molten phases consisting of several components are not very well known.
During the five year period of the AoF Research Fellowship, the goal is to:

- study the mobility of components in the molten phase in temperature gradients to predict accumulation of corrosive or harmful species in deposits.
- develop new electrochemical methods to detect the formation of a melt in ionic mixtures as compliments to thermal analysis.
- model the physical properties of the relevant molten ash components to combine these properties with other predictive tools, such as thermodynamic equilibrium modeling.
- determine the connections between the presence and composition of a molten phase and the rate of processes such as sintering, solid-gas reactions or oxidation of steels and alloys.



Intradeposit sodium chloride transport and layer growth (left) and experimental and modeled sodium chloride layer thicknesses after 24 h (right)

FA-LEAN

Åbo Akademi University is collaborating with Aalto University in the Academy of Finland funded project "New insight on the ignition of ultra-lean gas combustion". The objective is to understand the role of unavoidable variations in engine operation on the on auto-ignition in ultra-lean dual-fuel gas mixtures. These include variations in charge temperature and pressure, inhomogeneity of the charge, turbulence field and variations in the fuel spray. At Åbo Akademi University, the primary vehicle for attacking this problem is a detailed understanding of the combustion chemistry. Understanding the ignition process is essential when designing and controlling new gas combustion engine concepts with high fuel efficiency, capable of a dynamic operation.

CLIFF WP 2

CLIFF is a three year joint research project between industrial companies operating in the area of biomass and waste to energy; Finnish universities and VTT. A part of the project is largely focused on modelling the combustion process by means of process flow by the use of Computational Fluid Dynamics (CFD), multi-phase chemical equilibrium calculations and detailed gaseous kinetic scheme's modelling. Its goals are to achieve:

- Extension of models for black liquor sprays and recovery boilers for prediction of NOx formation by extending the current CFD droplet model and char bed model with experimental data on cyanate formation and destruction. The model extensions have direct implications for NOx chemistry predictions in the lower furnace and for NO release from carry-over droplets; thus affecting the overall prediction of the recovery furnace NOx formation chemistry.
- Modeling of NOx abatement techniques using CFD-based models as well as reactor based models utilizing a detailed description of the reaction kinetics. The CFD work focuses on the effects of the injection technique, i.e. as droplets or as gas. The CFD results will be compared to evaluate the reactor-network -based approach.
- 3D-visualization of CFD results to the viewer is a more effective format for presenting results and for gaining better – or even new - insight into the modeled process. An existing CFD calculation of a Kraft recovery boiler will be used as the case study and aims at developing a practical procedure for converting CFD results to 3D visualization.
- Development of single particle models for biomass char gasification and the formation of nitrogen containing species during char gasification. Detailed models and CFD-applicable single particle models will be developed. Fuel specific parameters to the models will be determined both from modeling and from detailed fuel characterization, and the models are validated by experimental measurements.
- A literature study of the combustion behavior of arsenic, beryllium, cadmium, chromium, lead, manganese, nickel and selenium in biomass firing systems that focus on in what form these elements leave the combustion

Cooperation: Technische Universität München, Germany; Dong Energy, Denmark; Technical University of Denmark, Valmet Technologies; Technical University of Athens, Greece; Energy Research Centre of the Netherlands, Mitsubishi Hitachi Power Systems Europe; Laborelec; Metsä Fibre; Amec Foster Wheeler Energia Oy; Andritz Oy; Valmet Power Oy; UPM-Kymmene Oyj; International Paper Inc.; Clyde Bergemann GmbH; Tampere University of Technology, Finland; Lappeenranta University of Technology, Finland; Aalto University, Finland; VTT Technical Research Centre of Finland

Process Intensification and Reactor Technology

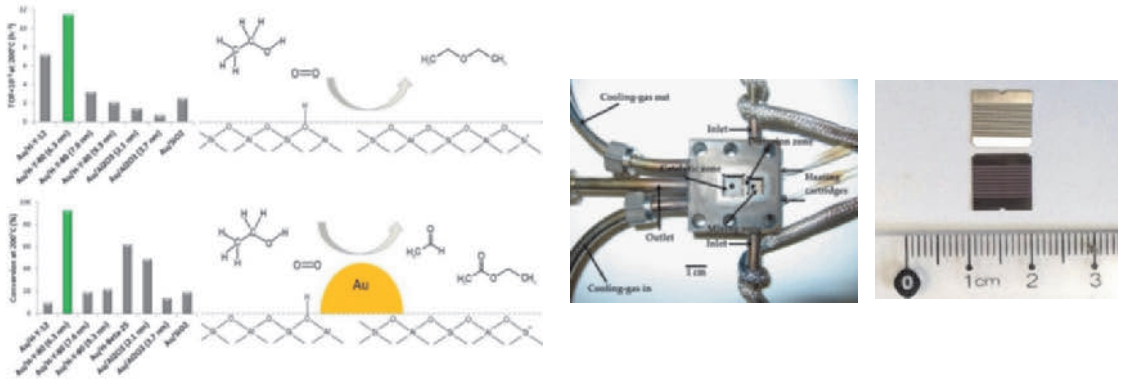
Micro- and Milliscale Reactor Technology

Main funding: Graduate School in Chemical Engineering (GSCE), Academy of Finland (MICATOX)

Kari Eränen, José Rafael Hernández Carucci, Sabrina Schmidt, Erfan Behravesh, Narendra Kumar, Teuvo Kilpiö, Vincenzo Russo, Cesar de Araujo Filho, Andrea Perez Nebreda, Shuyana Heredia, Johan Wärnå, Päivi Mäki-Arvela, Dmitry Murzin and Tapio Salmi

Micro- and millireactors enable an efficient performing of chemical processes – they provide the future technology for safe on site production of chemical intermediates. Gas-phase microreactors have been successfully implemented to prepare chemical intermediates, such as ethylene oxide, methyl chloride, ethyl chloride as well as oxochlorination products. Silver-based microreactor combined to micro-gas chromatography gave excellent results in the preparation of ethylene oxide, while zinc doped alumina turned out to be the best catalyst for preparation of methyl chloride. In general, the microreactor coating technology by using aluminium oxide as well as micro- and mesoporous materials was successfully developed; we are able to prepare catalytically active and mechanically strong coatings. Catalytic oxidation of hydroxyl and carbonyl groups in molecules from biomass using gold (Au) catalysts was performed. Monometallic and bimetallic gold nanoparticles have recently turned out to be most interesting catalysts in alcohol oxidation with environmentally friendly oxidizers such as molecular oxygen. Millireactor technology was introduced to prepare epichlorohydrin from hydrochlorinated products of glycerol. The results illustrated how the kinetics of very rapid liquid-phase reactions can be very precisely measured by using millireactors. The results were modelled mathematically. A new millireactor system was also used for liquid-phase reactions and it was successfully used for the homogeneously catalyzed hydrolysis of hemicelluloses – the work will go on in future with various hemicelluloses and extensive mathematical modelling based on the concept of laminar flow with radial and axial diffusion is in progress.

Big steps forward in the demanding field of mathematical modelling of milli- and microscale reactors were taken by introducing the modelling software gPROMS. A detailed mathematical model was developed for catalyst layers in micro- and millireactor structures. The model describes the reaction-diffusion phenomena in the porous structure very well. Our research group won an international prize for its achievements in micro- and millireactor modelling. The prize was awarded to us because of an article in Chemical Engineering Science (Vincenzo Russo et al.): PSE Model-Base Innovation Prize Runner-Up.



Oxidation of ethanol over gold catalyst.

Cooperation: Lappeenranta University of Technology, Finalnd; University of Oulu, Finalnd; Aalto University, Finalnd; Università di Napoli, Italy; Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Czech Republic; CPE Lyon, France.

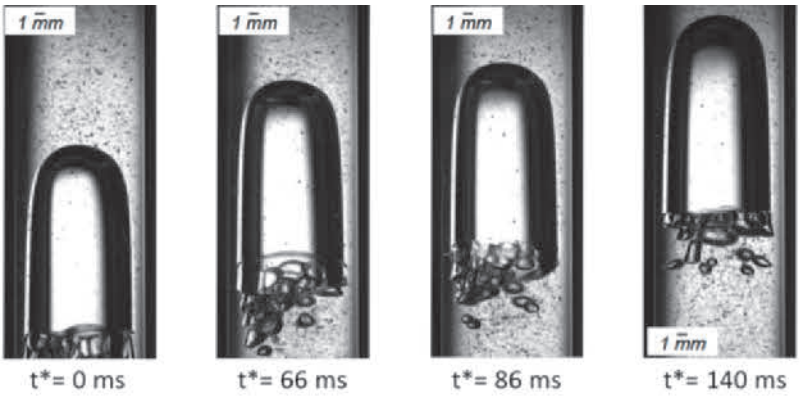
Multiphase Reactor Technology

Main funding: PCC, Academy of Finland, Magnus Ehrnrooth Foundation

Johan Wärnå, Teuvo Kilpiö, Silvia Palano, Pasi Tolvanen, Cesar de Araujo Filho, Adriana Freites, Sébastien Leveneur, Pierdomenico Biasi, Nicola Gemo, Gianluca Gallina, Stefano Sterchele, Marta Gonzalez Munos, Tina Samson, Eduardo Paiva, Fredrik Sandelin, Juan Garcia Serna, Tapio Salmi

Advanced modelling of multiphase reactors is the topic of the project, involving various flow models in the bulk phases of the reactor as well as modelling of simultaneous reaction and diffusion in porous catalyst pellets: in process scale-up, the crucial step is the shift from small particles used in laboratory experiments to large particles characteristic for fixed bed reactors. The main applications are catalytic three-phase hydrogenation and oxidation, and catalytic liquid-phase hydrochlorination. The feasibility of hydrogen peroxide direct synthesis in a continuous fixed bed was successfully demonstrated and modelled mathematically. The work was combined to kinetic studies carried out in a tailored batch reactor for hydrogen peroxide synthesis. Production of epoxidized vegetable oils under the presence and absence of microwaves was studied extensively and the results were astonishing: a considerable rate enhancement was achieved by applying microwave technology on the epoxidation process. The products are valuable chemical intermediates and bio-lubricants. Valorization of glycerol was carried out in very successfully both in semi-batch and continuous reactors. A more general and rigorous kinetic model was derived based on a consistent reaction mechanism proposed in the literature. The model was validated with experimental data reported in the literature as well as with new data of our own. A dimensionless number, called Catalyst Modulus, was proposed as a tool for corroborating the kinetic model.

A co-current bubble column was used to investigate the glycerol hydrochlorination process under continuous operation. The influence of liquid flow rate, gas flow rate, temperature and catalyst concentration on the glycerol conversion and the product distribution was studied. The fluid dynamics of the system showed a remarkable behaviour, which was carefully investigated and described. High-speed camera images and residence time distribution experiments were conducted to collect relevant information about the flow conditions inside the column reactor. A model based on the axial dispersion concept was developed and confronted with the experimental data. The kinetic and solubility parameters estimated from the semi-batch experiments were successfully used for describing the mass transfer and the fluid dynamics of the bubble column reactor.



Coalescence in a Taylor bubble in glycerol hydrochlorination in a bubble column reactor.

Cooperation: Università di Napoli, Italy; Università di Padova, Italy; INSA Rouen, France; Universidad de Valladolid, Spain.

Development of Functional Materials and Catalysts

Main funding: Foundations, Åbo Akademi University

Narendra Kumar, Jeanne Zhu, Maria Barsukova, Ekaterina Kholkina, Atte Aho, Kari Eränen, Päivi Mäki-Arvela, Tapio Salmi, Dmitry Murzin

Different kinds of functional materials and have been developed including carbon nitride, hybrid micro-mesoporous materials, metal modified zeolites and other types of supported metals.

Materials based on carbon nitride attract close attention due to their unique properties – such as high strength, low coefficient of friction, chemical inertness, stable auto-electronic emission, transparency in a wide range of optical frequencies and high water resistance. Thanks to its properties such materials are promising for technological and biological applications, such as biocompatible coatings for medical implants, as electrodes in power sources, protective coatings against corrosion, sensors for determination of moisture and composition of gas mixtures.

Nonstoichiometric carbon nitride characterized by spatial ordering, large pore volumes and specific surface areas were obtained via matrix carbonization of ethylenediamine in mesoporous molecular sieves KIT-6 and MCF as exotemplates. In contrast to nitrogen-containing carbons obtained by modification of carbon samples with nitrogen in the result of compatible thermal treatment of the initial porous carbon with melamine nonstoichiometrical carbon nitride contains much more nitrogen and increased quantity of basic nitrogen-containing groups. A substantial increase of the desorption capacity towards hydrogen and carbon dioxide in nonstoichiometric carbon nitride was observed due to incorporation of nitrogen atoms into carbon framework.

Silicon carbide (SiC) is among few unique materials with a desirable combination of characteristics including low density, high specific strength, high thermal shock resistance, superior chemical inertness, and high temperature stability. SiC based materials could be used as filters for molten metals, gas burner media, diesel particulate filters, and components in metal containing composites. High chemical stability makes SiC a promising catalyst support due to its resistance against corrosion in strong acidic solutions during catalyst regeneration. These applications undoubtedly require a material with a developed surface area, although commercial silicon carbide has a low specific surface area due to hazardous preparation conditions.

Formation of silicon carbide with distinctive morphologies in the carbothermal synthesis depending on the types of carbon and silicon sources was investigated. Mixtures of sucrose (or carbon) with aerosil and carbon-silica composites based on SBA-3, SBA-15, KIT-6 and MCF mesoporous silica were used as precursors. The investigation showed that the content of fibers in silicon carbide is increasing with an increase of mesopore surface area of carbon in carbon-silica composites. Based on the correlation found between the morphology and porosity of SiC and mesopore surface area of the carbon component in the composites a templating role of carbon in carbothermal reduction was confirmed. High hydrogen adsorption capacity of synthesized silicon carbide was obtained due to a low density of the framework atoms in the structure. The highest ever reported value among the existing porous materials was observed for specific adsorption of H_2 by SiC (specific adsorption on the pore surface, up to 15 $\mu mol/m^2$) corresponding to almost complete filling of the surface with hydrogen.

Zeolites are crystalline microporous materials which are widely used in industry for catalysis, adsorption of small molecules, separation of multicomponent mixtures. However, microporous nature of these materials limits their use in the processes of catalytic transformation of bulk organic molecules and viscous liquids which is necessary in fine chemicals, pharmaceutical industry, etc. This drawback can be avoided with **mesoporous** molecular sieves (MMS), which are characterized by uniform mesoporosity, developed surface and spatial ordering and periodicity in the nanometer range distances. However, the amorphous state of a substance of MMS walls leads to poor hydrolytic stability and acidity, which limits the use of mesoporous materials in catalysis. Mesoporosity in zeolites can be created as intracrystalline cavities in zeolite single crystals or as intercrystallite pores in aggregates of zeolite nanoparticles. Many approaches were developed for generation of secondary porosity in zeolites.

The approach of dual templating was used by us to adjust the structure and sorption properties of the catalysts. In this way **hybrid materials** were prepared that combine properties of Beta zeolite, an important industrial catalyst, and mesoporous cellular foams (MCF), which unlike other mesoporous silica (MCM-41, SBA-15) has large pores (larger than 20 nm). Microporous, mesoporous and novel hybrid materials were studied in verbenol oxide isomerization for the synthesis of biologically active substance with anti-Parkinson activity. Formation of the target product was the highest over microporous mild acidic H-Beta-300 and hybrid ZF-100, also with mild acidity and even absence of strong acid sites. Hybrid ZF-100 material showed ca. 60% selectivity towards the desired product.

Iron modified zeolites were used for synthesis of stearoyl ethanolamine by amidation of stearic acid with ethanolamine in solventless conditions. Iron containing heterogeneous catalysts supported on SiO_2, Al_2O_3, Beta (BEA), ZSM-12 (MTW) and Ferrierite (FER) were used. Sn-modified Ferrierite and H-Ferrierite were also studied for comparison. Fe-modified catalysts synthesized using solid state ion-exchange and evaporation impregnation methods, were thoroughly characterized with X-ray powder diffraction, scanning electron microscope, FTIR with pyridine, nitrogen adsorption, energy dispersive X-ray microanalysis and Mössbauer spectroscopy. The highest conversion was obtained with Fe-H-FER-20 at giving a 98% selectivity towards the desired amide. The catalytic performance in terms of turnover frequency per mole of iron was achieved with the catalyst exhibiting the largest amount of Fe^{3+} species, optimum acidity and a relatively low Brønsted to Lewis acid site ratio.

Cooperation: Institute of Physical Chemistry, Kiev, Ukraine; TU Dresden, Germany; St. Petersburg State Technical University, Russia

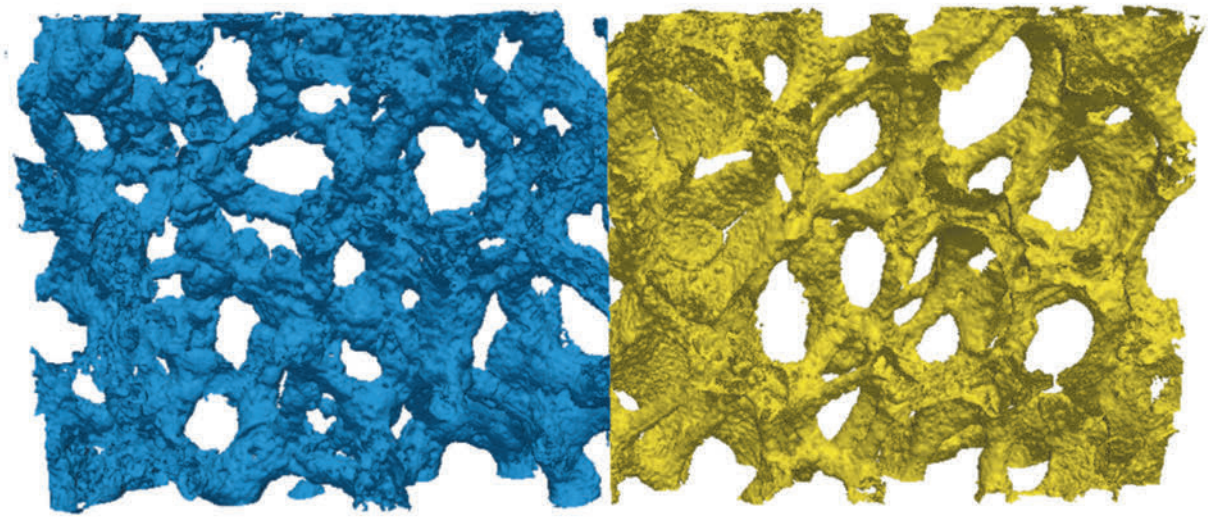
Development of Structured Catalysts

Main funding: GSCE, Fortum Foundation

Vladimir Shumilov, Ali Najarnezhadmashhadi, Luis Miguel Sanz Moral, Kari Eränen, Dmitry Murzin, Tapio Salmi

Structured catalysts such as open-cell foam catalysts offer new possibilities for process intensification. Open-cell foams have some excellent features such as very low pressure drop and high voidage despite high geometrical surface area per unit volume that favor the application as reactor packing because the foam packing increases the gas-liquid and liquid-solid interfacial area and create local turbulences by splitting and recombining the fluid that leads to enhancement of mass and heat transfer.

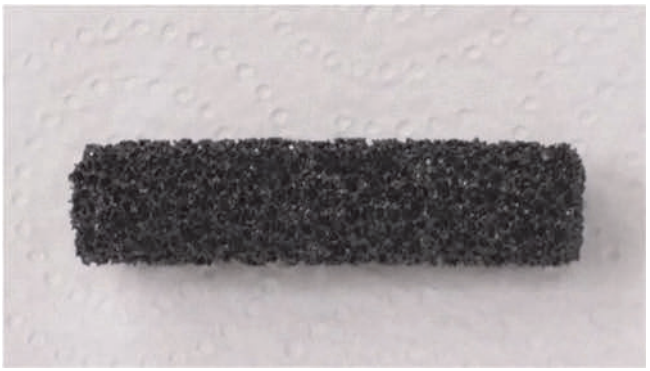
Ceramic foams have a wide range of potential applications in biomedicine, thermal insulation, filtration of molten metal alloys, absorption of environmental pollutants, catalyst supports, etc. Since the physical properties of the foams do not fully meet the requirements in some applications, improvement of conventional fabrication methods or totally new techniques are of interest. Procedure for manufacturing of ceramic foams via the replica technique with subsequent washcoating and deposition of the catalytic phase was developed. Slurries consisted of alumina powder mixed in aqueous solutions of polyvinyl alcohol (PVA) and magnesia and titania as sintering aids. The foams were produced by tuning different processing parameters to give properties suited for catalyst supports. These parameters included pore size of the polyurethane (PU) foam used as a template, parameters in the PU foam pretreatment, particle size of alumina powder in the slurry, slurry loading and drying of the green alumina coated PU foam.



High resolution X-ray computed tomography – foam 3D iso-surface visualization.

Structured **catalyst supported by carbon-coated aluminum foams** were developed and tested. Foams with a pore density of 40 PPI were applied. To attain a homogeneous polymer layer on the foam and also to avoid clogging of the foam structure, a controlled polymerization of furfuryl alcohol had to be conducted. For this purpose, the foam samples were rotated with a defined stirring speed during the whole polymerization process. After polymerization step, the sample was pyrolyzed in a tubular furnace in a nitrogen stream. To obtain a porous carbon layer, the foam samples were activated in an air stream. Figure 3 shows the Aluminum foam before and after coating.

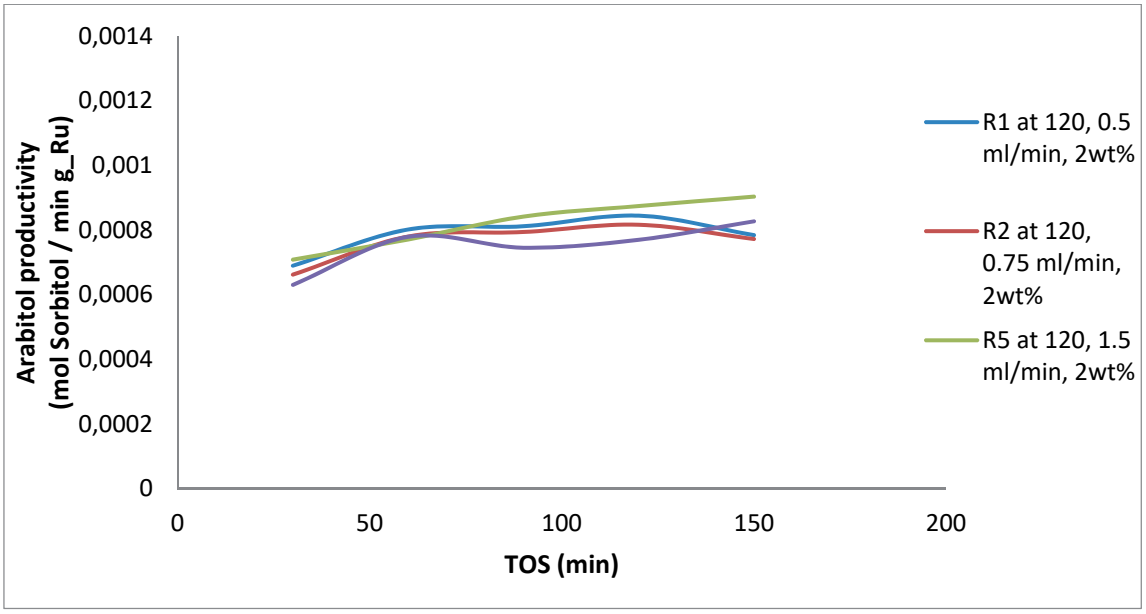
Homogeneous deposition precipitation (HDP) was chosen to incorporate ruthenium into the carbon-coated foam substrates. The HDP process was carried out by putting pre-treated carbon-coated foam in beaker filled with a solution precursor and urea with a ratio of 1:5 in distilled water.



Sample of a 40 PPI open-cell aluminum foam (a) before polymerization step after activation.

The coated foams (Ru/C/Al) were used for the valorization of sugar monomers through catalytic hydrogenation of selected sugars to sugar alcohols, such as hydrogenation of glucose to sorbitol and hydrogenation of arabinose to arabitol. Moreover, it is important to investigate the hydrogenation of sugar mixtures and to determine the interaction of sugars mixtures on catalyst surfaces. Sugar alcohols are excellent sweeteners and health promoting components with anti-caries and anti-inflammatory properties.

Sugar hydrogenation can be performed over supported metals belonging to the platinum, rhodium, and ruthenium. Supported ruthenium catalysts have been found to be the most active ones. Extensive hydrogenation of sugar and sugar mixtures experiments have been conducted and are ongoing by varying the reaction conditions. Hydrogenation was successful, the reproducibility is good and catalyst is stable and the selectivity is high. The influence of the sugar molar ratios on the hydrogenation kinetics of both sugars (L-arabinose and D-galactose) in the mixture have been studied, several experiments are ongoing and will be carried out at different molar ratios of D-galactose and L-arabinose (0.1-10).



Arabitol productivity using 0.13 mol l^{-1} aqueous L-Arabinose at different flow rates at 120 °C.

Cooperation: TU Dresden, Germany; Helmholtz-Zentrum Dresden Rossendorf, Germany; University of Tver, Russia

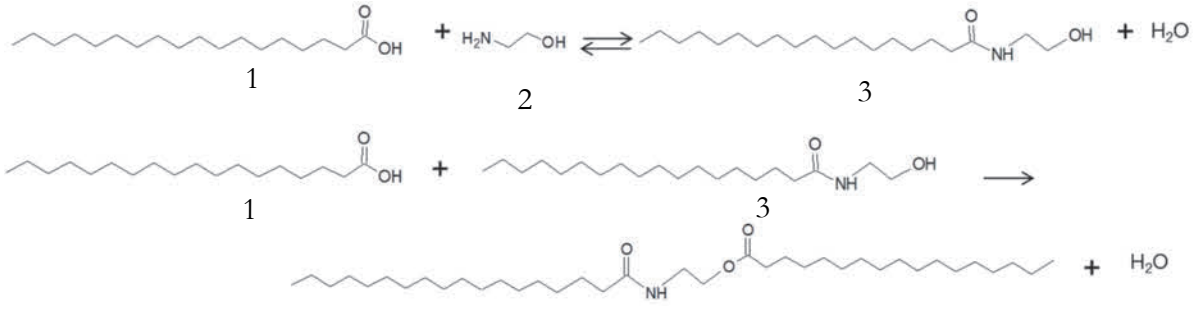
Heterogeneous Catalyst Development for Production of Pharmaceuticals and Fuels

Main funding: Åbo Akademi University

Imane Hachemi, Alexandrina Sulman, Nataliya Shcherban, Hoang Nguyen, Päivi Mäki-Arvela, Narendra Kumar, Atte Aho, Kari Eränen, Iris Winberg, Mariia Barsukova, Andre Rudnäs, Jarl Hemming, Annika Smeds, Dmitry Murzin

Different types of heterogeneous catalysts, including acidic micro- and mesoporous materials and metal modified catalysts supported on zeolites, mesoporous materials, carbon nanofibers and oxides have been prepared, characterized and tested in the production of pharmaceuticals and fuels. The aim has been to prepare tailor-made catalysts for specific applications and tune their properties.

For pharmaceutical applications, in the synthesis of monoterpenoid dioxinols, betulinic aldehyde and stearoylethanolamide have been investigated. In the production of fuel components, green diesel was synthesized starting from algal oil, stearic acid, tall oil fatty acids and animal fats. The special emphasized has been put on utilization of cost-effective metal oxides as a source for Lewis acidity, for example iron in amidation of fatty acids. In fuel production, sulfur free nickel supported on zeolite has been the most promising catalyst.



Reaction scheme for amidation of stearic acid (1) with ethanolamine (2) to stearoylesteramide (3) and esteramide (4).

Cooperation: Boreskov Institute of Catalysis, Novosibirsk, Russia; Unipetrol Centre of Research and Education, Litvinov, the Czech Republic; St Petersburg State University, Russia; University of Turku, Finland.

Electrocatalytic Reduction of CO_2 to CO over Gold Nanoparticles based 3D Networks

Main funding: Academy of Finland

Grzegorz Lisak, Rose-Marie Latonen, Dmitry Yu. Murzin, Tapio Salmi, Johan Bobacka

Human activities have led to a heavy consumption of fossil fuels and as a result overproduction of greenhouse gases, such as carbon dioxide. The accumulation of carbon dioxide is truly a huge problem, thus it is of utmost importance to develop appropriate mitigation methods for carbon dioxide. A chemical conversion has the great potential to change the fate of carbon dioxide from greenhouse gas into a valuable feedstock. Such possibility comes with the application of electrocatalysis, once the problem with high overpotentials that are needed to initiate the reduction of carbon dioxide will be solved. In order to lower the overpotentials and to control the energy pathways of reaction intermediates, highly efficient catalysts must be developed and used. New insight into carbon dioxide electrocatalysis is brought via application of metal nanoparticles. In this context, if an appropriate catalyst will be successfully developed, the electrocatalytic conversion of carbon dioxide to carbon monoxide can substantially contribute to the solution of a global problem.

This interdisciplinary project will promote scientific breakthroughs in the area of material engineering, environmental engineering and process chemistry. The project will benefit the society in form of delivering novel and potentially clean methods for removal and utilization of this problematic greenhouse gas from the environment.

Cooperation: University of Wollongong, Australia; Osaka University, Japan; Malmö University, Sweden

4. Publications 2016

4.1 Theses

4.1.1 Doctoral theses (6)

de Araujo Filho, Cesar, A reaction engineering approach to homogeneously catalyzed glycerol hydrochlorination

Hau, Wo, Chemistry of potassium halides and their role in corrosion in biomass and waste firing

Konwar, Lakhya, New biomass derived carbon catalysts for biomass valorization

Liu, Jun, Wood-derived biomaterials for biomedical applications

Shoulaifar, Tooran Khazraie, Chemical changes in biomass during torrefaction

Sundquist, Anna, Modelling the chemistry of metal cations in pulp and papermaking processes

4.1.2 Master's theses (10)

Chen, Yi Ran, A preliminary kinetic model for furfural oxidation with hydrogen peroxide

Deba, Shuyana Heredia, Epoxidation of fatty acids assisted by microwaves in the presence of organic acids and catalyzed by cation exchange resin

Höglund, Sofia, Different analysis methods for assesing the suitability of biofuel ash as a structural Material

Kumar Joon, Narender, Leaching kinetics of lead from contaminated soil

Lindén, Daniel, Capture of corrosive potassium chloride vapor with kaolin and coal ash – experimental studies in a laboratory reactor (in Swedish)

Lindholm, Sten, Utveckling av ett analyssystem för fotometrisk bestämning av arsenik baserat på sekventiell injektionsanalys, hybridgenerering och gasdiffusion

Nguyen Huynh, Ngoc Minh, Chemically reduced graphene oxide and its water barrier properties

Nyman, Jonas, Fouling and Corrosion in 4-stoke diesel engine exhaust gas systems

Söderback, Klaus, Träfiberskivor med BLN-lignin

West, Andreas, Utvärdering av några oxidationsmetoder för oxidering av lignanderivat

4.2 Publications

4.2.1 Articles in refereed international scientific journals and series (145)

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4.2.2 Review articles in refereed international scientific journals and series (1)

146. Haase, S., Murzin, D. Yu., Salmi, T., **Review on hydrodynamics and mass transfer in microchannel wall reactors with gas-liquid Taylor flow**, *Chemical Engineering Research and Design* 113 (2016) 304-329

4.2.3 Books and book chapters (8)

147. Behravesh, E., Hupa, L., Salmi, T., Murzin, D. Yu., **Alumina ceramic foams as catalyst support**, Catalysis-Special Periodical Reports, in "Catalysis", Royal Society of Chemistry 28 (2016) 28-50

148. Boeva, Z. A., Latonen, R.-M., Lindfors, T., Mousavi, Z., **Electrochemical Nanofabrication Principles and Applications**, Ed. Di Wei, (Chapter 11), *Electrochemical fabrication of carbon nanomaterial and conducting polymer composites for chemical sensing*, 2nd Ed., Pan Stanford Publishing Pte. Ltd., 2016, pp. 417-471, ISBN: 978-981-4613-86-6

149. Kilpiö, T., Mäki-Arvela, P., Salmi, T., Murzin, D. Yu., **Modelling of the catalytic deoxygenation of fatty acids in a packed bed reactor, In Multiphase Catalytic Reactors: Theory, Design, Manufacturing and Applications**, (Ed. Z. Ilsen Önzan, A.K. Avci), Wiley 2016, 365-376.

150. Lewenstam, A., **Postępy elektroanalizy : praca zbiorowa**, Czujniki jonowe w analizatorach klinicznych : badania podstawowe widziane z perspektywy przemysłu, ISBN: 978-83-63663-78-0

151. Mikkola, J.-P, Sklavounos, E., King, A. W. T., Virtanen, P., **The biorefinery and green chemistry**, *RSC Green Chemistry Series* 36 (Ionic liquid biorefinery concept) (2016) 1-37

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154. Rahkila, J., Saloranta, T., Leino, R., **Oligosaccharides for pharmaceutical applications, Biomass sugars for non-fuel applications**, *RSC Green Chemistry 2016*, Chapter 6, 205-227

4.2.4 Articles in refereed international edited volumes and conference proceedings (12)

155. Brink, A., Sevonius, C., Zevenhoven, M., Yrjas, P., Hupa, L., **The interaction of potassium and ilmenite in bed sintering in chemical looping combustion**, *Joint meeting of the Portuguese and Scandinavian-Nordic Sections of the Combustion Institute*, Lissabon, Portugal, 2016.

156. Demartini, N., Vainio, E., Holmblad, H., Hupa, M., **Understanding low temperature corrosion in Kraft recovery boilers – Implications for increased energy recovery**, Pulping, Engineering, Environmental, Recycling, Sustainability Conference 2016 (PEERS 2016), 1 (2016) 127-135

157. Engblom, M., Lindberg, D., Niemi, J., Hupa, M., **Mathematical modeling of intradeposit alkali chloride enrichment in biofuel boiler superheaters**, *26th international conference on Impacts of Fuel Quality on Power Production*, Praque, Czech Republic 2016

158. Kekonen, A., Bergelin, M., Eriksson, J-E., Ylänen, H., Kielosto, S., Viik, J., **Bioimpedance measurement system for evaluation of the status of wound healing**, *Proceedings of the 15th Biennial Baltic Electronics Conference, BEC* (2016), 175-178

159. Lehmusto, J., Sui, J., Bergelin, M., Skrifvars, B.-J., Yrjas, P., **Utilization of stable oxygen isotopes in high-temperature corrosion studies**, *Proceedings: the 26th international conference on Impacts of Fuel Quality on Power Production and the Environment*, September 19-23, 2016, Prague, Czech Republic.

160. Lehmusto, J., Stenlund, D., Lindgren, M., Yrjas, P., **Deposit build-up and corrosion in a copper flash smelting heat recovery boiler**, *Proceedings: 9th International Symposium on High-Temperature Corrosion and Protection of Materials*, May 15-20 2016, Les Embiez, France

161. Link, S., Yrjas, P., Hupa, L., **Ash behaviour of wheat straw blends with wood and reed**, *6th International Symposium on Energy from Biomass and Waste*, Venice, Italy, 2016

162. Lewenstam, A., **Novel multisensor platforms for biomedical analysis of electrolytes and monitoring of ion-transport through biological membranes**, *Acta Biochimica Polonica* 63 (2016)

163. Tesfaye, F., Lindberg, D., Taskinen, P., **The Cu-Ni-S system and its significance in metallurgical processes**, *2016 EPD Congress*, 29-37

164. Vainio, E., DeMartini, N., Orang, N., Tran, H., Hupa, M., **Is there sulfuric acid in flue gases in biomass combustion? Measurement techniques and results**, *International Bioenergy and Bioproducts Conference 2016 (IBBC 2016)*, 234-243

165. Vainio, E., DeMartini, N., Hupa, M., Hupa, L., **Role of ash-forming elements on low-temperature corrosion in biomass boilers**, *22nd International congress on Impacts of fuel on quality of power production*, Prague, Czech Republic 2016

166. Zevenhoven, M., Lindberg, D., Brink, A., Hupa, L., Smått, J.H., Kronlund, D., Rydén, M., Lyngfelt, A., Lagerbom, J., Langørgen, Ø., **Chemical looping combustion of biomass - Interaction of ash forming matter with bed materiál, Impacts on fuel quality on power production**, *22nd International congress on Impacts of fuel on quality of power production*, Prague, Czech Republic 2016

4.3 Edited conference proceedings and reports (1)

1. Långvik, O., Latonen, R-M., Mäki-Arvela, P., Saloranta, T., Sundberg, A., Werkelin J. (eds) Åbo Akademi Johan Gadolin Process Chemistry Centre Annual Report 2015-2016, Åbo Akademi University, 2016, ISSN: 1459-8213, Painosalama, Turku/Åbo, Finland, 2016.

4.4 Awards granted

Rahkila, Jani
Akademikerpriset, Akademiföreningen Åbo Akademiker r.f.

Sundqvist, Maria
Tekniska Föreningen i Finland: The best master's thesis of technology in the Swedish language in Finland 2015

Vanamo, Ulriika,
Alfthanska priset, "Solid-state reference and ion-selective electrodes – towards portable potentiometric sensing"

Toni Riittonen
Catalysts, Best Paper Award 2016, "One-Pot Liquid-Phase Catalytic Conversion of Ethanol to 1-Butanol over Aluminium Oxide— The Effect of the Active Metal on the Selectivity".

5. Other activities 2016

5.1 Organization of conferences/courses/meetings

Wood Biopolymer Science for New materials from trees - Finnish-Swedish Joint Summer School

Wood Extractives, PhD course

Renewable Plant Resources and Organic Chemistry (RR-2017), International Conference, St. Petersburg, Russia, Co-Chairman and co-organizer *Andrey Pranovich*

International Conference of Lithuanian Society of Chemistry – Chemistry & Chemical Technology, Vilnius, Lithuania, Member of scientific committee, *Johan Bobacka*

6th Baltic Electrochemistry Conference, Helsinki, Finland, Member of scientific committee, *Johan Bobacka*

14th International Conference on Optical and Electronic Sensors COE'2016**,** Gdansk, Poland, Member of scientific committee, *Johan Bobacka*

5.2 Participation if conferences, meetings, and courses

January

Pűhajärve, Estonia, EACH Winter School

Copenhagen, Denmark, The Torkil Holm Symposium: Visions in Chemistry

Florida, Tappi KROS, invited lecturer, *Mikko Hupa*

Daytona, Florida, 40th International Conference and Expo on Advanced Ceramics and Composites (ICACC 40), invited presentation, *Leena Hupa*

February

Kaunas, Lithuania, COST TD1203 workshop 'Green technologies for future biorefineries', invited speaker, *Stefan Willför*

Lahti, Finland, VIII Liekkipäivä 2016

March

Paris, France, Biomass conversion: Green Chemistry & Innovative Processes, invited speaker, *J.-P. Mikkola and Tapio Salmi*

Paris, France, French-Nordic Networks, invited speakers, *J.-P. Mikkola and Tapio Salmi*

Miami, USA, The 26th Biennial ORCS Meeting, 3

Atlanta, Georgia, USA, PITTCON 2016, invited lecturer *Johan Bobacka*

Reykjavik, Island, 4th Nordic Meeting on Organometallic Chemistry

April

Poznan, Poland, COST EXIL CM1206 Workshop

Berlin, Germany, Green and Sustainable Chemistry Conference

Tampere, Young Scientists' Forum for Catalysis

Stockholm, Sweden, BioEurope Spring 2016

Vilnius, Lithuania, International Conference of Chemistry & Chemical Technology

Shanghai, China, 24th International Congress on Glass, invited presentation *Leena Hupa*

Stockholm, Sweden, Askdagen / "Ash day", Svenska energiaskor

May

Albi, France, 6th International Conference Engineering for waste and biomass valorization and 2nd WasteEng Summer School, Session chairperson, keynote lecture, *N. Kumar*

Ghent, Belgium, The 12th International Conference on Renewable Resources & Biorefineries (RRB-12), invited speaker, *Bjarne Holmbom*

Nantes, France, SETAC (Society of Environmental Toxicology and Chemistry) Europe 26th Annual Meeting

Tolouse, France, HTCPM 2016 - 9th International Symposium on High-Temperature Corrosion and Protection of Materials

June

Prague, Czech Republic, EMN Meeting 2016, Energy Materials Nanotechnology, invited lecture, *N. Kumar*

Timisoara, Romania, RomCat, invited plenary speaker *J.-P. Mikkola*

Mariehamn, Finland, Wallenberg Wood Science Center Meeting

Lund, Sweden, 17th Nordic Symposium on Catalysis

Stockholm, Sweden, Wallenberg Wood science Center meeting

Strasbourg, France, Carbocat VII, plenary speaker, *Dmitry Murzin*

Odense, Denmark, NORDTEK, session chairperson, *Tapio Salmi*

Delft, the Netherlands, Delft Process Technology, Internationational Program committee, *Tapio Salmi*

Frankfurt, Germany, Zellcheming 2016, invited speaker, *Stefan Willför*

Autrans, France, European Workshop on Lignocellulosics and Pulp, invited speaker, *Anna Sundberg*

Helsinki, Finland, 6th Baltic Electrochemistry Conference

Moscow, Russian Federation, International Symposium in Polyelectrolytes 2016

Clearwater, Florida, USA, The International Technical Conference on Clean Coal & Fuel Systems

July

Beijing, 16th International Congress on Catalysis, keynote lecture, *Dmitry Murzin*

Seoul, South Korea, 36th Symposium of the Combustion Institute, plenary lecture, *Mikko Hupa*

August

Prague, Czech Republic, 22nd International Congress of Chemical and Process Engineering, (CHISA2016) session chairperson, *J.-P. Mikkola, V. Russo, T. Salmi, P. Tolvanen, N. Kumar*

The Hague, the Netherlands, 67th Annual Meeting of the International Society of Electrochemistry

September

Lyon, France, 11th international Congress on Catalysis and Fine Chemicals (*CAFC*-11), session chairperson, *Dmitry Murzin*

Mittweida, Germany, 7th Kurt-Schwabe-Symposium, plenary lecturer, *Johan Bobacka*

Stockholm, Sweden, 9th Asian-European Symposium on Metal-Mediated Efficient Organic Synthesis*,* invited lecturer, *Reko Leino*

Sheffield, United Kingdom, 13th European Society of Glass Science and Technology Conference and the Society of Glass Technology Centenary Annual Meeting, session chair, *Leena Hupa*

Montpellier, France, Eurocorr 2016, the annual event of the European Federation of Corrosion

Prague, Czech Republic, 22nd meeting for Impacts of fuel quality on power production

Jacksonville, Florida, USA, TAPPI 2016 PEERS Conference

October

Helsinki, Finland, UPM, Visions for 3D cell culture- seminar and networking event

Stockholm, Sweden, Marcus Wallenberg Prize Young Researcher Seminar

Svetlogorsk, Russia, X International Conference "Mechanisms of Catalytic Reactions" (MCR-X), invited keynote lecture, *Reko Leino*

Yokohama, Japan, BioJapan 2016 - Regenerative Medicine Japan

Turku, Finland, Åbo Akademi University Research Day

Sitges, Spain, Bioresource Technology for Bioenergy, Bioproducts & Environmental Sustainability

Turku, Finlnd, ScanBalt Forum 2016 Biomaterials' day

Tampere, Finland, Soodakattilapäivä

November

San Fransisco, USA, AIChE (American Institute of Chemical Engineers) Annual Meeting

Helsinki, Finland, Paper engineers' Association Autumn meeting

Brussels, Belgium, European Paper Week

Wroclaw, Poland, The OXO Conference - Advances in OXO Synthesis - Where the Science Meets Industry, invited lecturer, *Reko Leino*

Cologne, Germany, BioEurope 2016

Lisabon, Portugal, Joint meeting of the Portuguese and Scandinavian-Nordic Sections of the Combustion Institute

December

Göteborg, Sweden, Wallenberg Wood science Center meeting (WWSC)

Ås, Norway, Final meeting and seminar of the NordForsk funded Refining Lignocellulosics to Advanced Polymers and Fibers - PolyRefNorth – researcher network, Ås, Norway, invited speaker, *Stefan Willför*

Tokyo, Japan, 73rd IEA-FBC Meeting

5.3 Visitors and visits

Visitors

Aubert, Florian, National Institute of applied Sciences of Rouen, France, June - August

Barnsley, Jonathan, University of Otago, New Zealand, September-October

Benouadah Nacéra, M'Hamed Bougara University, Boumerdesm, Algeria, October, 2016 - June 30, 2017

Brauer, Delia, University of Jena, Germany, June

Ding, Jiawang, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, China, February

Gatarz, Sandra, University of Warsaw, Poland, August-September

Gepperth, David, University of Ulm, Germany, January–February

Gumbmann, Lorenz, Technical University of Dresden, Germany, January - August

Jarolimova, Zdenka, University of Geneva, Switzerland May-August

Link, Siim, Tallinn Technical University, Estonia, April–December

Jinze Dou, Aalto University, Finland, January

Järvinen, Mika, Aalto University, Finland, Mars–May

Konwar, Lakhya, University of Umeå, Sweden, December

Kovacs, Barbara, University of Szeged, Hungary, October-December

Kubarkov, Aleksei, Moscow State University, Russia, September-December

Litvinova, Victoria, St. Petersburg Technological University, Russia, January

López, Sara, University of Alicante, Spain, August-November

Maheswor Dev Gautam, Aarhus University, Denmark, August – September

Matveeva, Anna, St. Petersburg University of Technology, Russia, December

Mauyean, Timothé, University of École normale supérieure Paris-Saclay, France, April-July

Nguyen, Hoang, Technical University of Lappeenranta, Finland, January - May

Ocaña, Cristina, IMB-CNM-CSIC Barcelona, Spain, April-December

Ogereau, Emilie, ENSICAEN, Caen, France, April - August

Palano, Silvia, University Degu Studi di Padova, Italy, April - July

Plösser, Jutta, Technical University of Darmstadt, Germany, April

Russo, Vincenzo, University of Naples, Italy, July - December

Saina Kishani, KTH Royal Institute of Technology, Sweden, January - February

Skoglund, Nils, Umeå University, Sweden, December

Snierle, Marc, University of Stuttgart, Germany, October-December

Tairabekova, Samal, Al-Farabi Kazakh National University, Almaty, Kazakhstan, April – May

Vajglova Zuzana, Institute of Chemical Technology and Fundamentals, Prague, Czech Republic, December

Wittrup Agger, Jane, DTU, Denmark, January

Zheng, Jun Liu, January-May

Zhu, Jeanne, ENSICAEN, Caen, France, April – August

Zweckmayer, Thomas, BOKU, Austria, April – December

Visits

Bankiewicz, Dorota, Nanyang Technological University, Singapore, August – November

DeMartini, Niko, University of Toronto, Ontario, Canada, June

Joon, Narender Kumar, Malmö University, Sweden (February-March)

Karlström, Oskar, MIT Portugal Program, Lissabon, Portugal, May

Lehmusto, Juho, Chalmers University of Technology, Sweden, November

Lindfors, Tom, Budapest University of Technology and Economics, Hungary (May-June)

Lisak, Grzegorz, Malmö University, Sweden (February)

Liu, Jun, Uppsala Universitet, Sweden, June - August

Niemi, Jonne, University of Toronto, Ontario, Canada, May – July

Pranovich, Andrey, St. Petersburg Forest Technical University, Russia, April

Xu, Chunlin, University of Wollongong, Australia, December

Xu, Wenyang, Natural Resources and Life Sciences (BOKU), Austria, December

Wang, Xiaoju, University of Wollongong, New South Wales, Australia, December

5.4 External evaluations and reviews

External evaluations

Evaluation of research proposals, Mid Sweden University, Sundsvall, *Dmitry Murzin*

Evaluation of grants in Haldor Topsoe Russian PhD programme, *Dmitry Murzin*

Evaluator for research programs and projects for the Slovenian Research Agency (ARRS), J.-*P. Mikkola*

Evaluation of proposals in the EU H2020 Marie-Skłodowska-Curie Actions-IF-ST-CHE, Brussels, *Päivi Mäki-Arvela*

Evaluation of proposals in Swedish Science Council, Stockholm, *Päivi Mäki-Arvela*

Evaluation of research proposals, FONDECYT, Chile, *Päivi Mäki-Arvela.*

Evaluation of proposals in M-Era-NET, Turku, *Päivi Mäki-Arvela and Narendra Kumar*

Evaluation of two project/mobility proposal for the international postdoctoral mobility program AgreenSkills+, *Stefan Willför*

Evaluation of a research project in mechanical and process engineering (LabEx Tec 21), Laboratoire des Écoulements Géophysiques et Industriels, Grenoble, France), *Andrey Pranovich*

Evaluation of Green chemicals from forests and forest by-products, MidSweden University, *Bjarne Holmbom*

Evaluation of research proposals, Estonian Research Council, *Johan Bobacka*

Evaluation of research proposals in the EU H2020-IND-CE-PILOTS-01-2016, stage 1, *Rose-Marie Latonen*

Evaluation of research proposals in the EU H2020-IND-CE-PILOTS-01-2016, stage 2, *Rose-Marie Latonen*

Evaluation of research proposals in the EU H2020 Marie Skłodowska-Curie Actions-IF-2016, *Rose-Marie Latonen and Zhanna Boeva*

Evaluator of applications, Belgian Fund for Scientific Research - FNRS (Fonds de la Recherche Scientifique F.R.S.), *Reko Leino*

Member of Academy of Finland, Research Council for Natural Sciences and Engineering, 2016-2018, *Reko Leino*

Member of NT-6 evaluation panel, Swedish Research Council (Vetenskapsrådet), *Reko Leino*

Mid-term evaluator of H2020-MSCA-EJD project (EU Research Executive Agency - REA), *Reko Leino*

Vice-chair of H2020-MSCA-ITN Chemistry evaluation panel (EU Research Executive Agency - REA), *Reko Leino*

Vice-chair of H2020-MSCA-IF Chemistry evaluation panel (EU Research Executive Agency - REA), *Reko Leino*

Doctoral thesis evaluations

Chukwudi, Okoro, Sunday, Technical University of Denmark, opponent, *Patrik Yrjas*

Darif, *Bouchra,* University of Oulu, opponent *Tapio Salmi*

Drif, *Asmaa,* Couaib Doukkali University, El Jadida, opponent *Tapio Salmi*

Filatova, Anastasia, Technical University of Tver, opponent *Dmitry Murzin*

Hajer, Kamal Alm, KTH Royal Institute of Technology, member of the evaluation committee *Anna Sundberg*

Heikkinen, Susanna, University of Helsinki, Finland, opponent *Stefan Willför*

Kumar, Hemanathan, University of Jyväskylä, Finland, reviewer of PhD thesis, *Stefan Willför*

Liu, *Jun,* INSA-Rouen, jury member and opponent *Tapio Salmi*

Majoinen, Johanna, Aalto University, Finland, reviewer, *Reko Leino*

Marinkovic, Jelena, Chalmers University of Technology, Gothenburg, Sweden, examination committee for doctoral thesis, *Maria Zevenhoven*

Mendecki, Lukasz, Keele University, UK, examination committee (opponent), *Johan Bobacka*

Muddassar Hassa, *Raja,* Aalto University, reviewer of PhD thesis *J.-P. Mikkola*

Ngoc Pham, *Tung,* Umeå University, opponent *Dmitry Murzin*

Obadas, Nora, University of Natural Resources and Life Sciences, Vienna, Austria, external evaluator *Anna Sundberg*

Parviainen, *Arno,* University of Helsinki, Finland, reviewer of PhD thesis, *Stefan Willför*

Rasmussen, Helena, DTU, Denmark, thesis committee member *Stefan Willför*

Sasikala, Anbarasan, Aalto University, Finland, opponent *Stefan Willför*

Svensson Mouritz, Nolsøe, Aalborg University, Denmark, opponent, *Leena Hupa*

Tham, Yuen Yue, University of Tasmania, Australia, external evaluator *Anna Sundberg*

Xie, Yujiao, Luleå University of Technology, opponent *Päivi Mäki-Arvela*

Zhu, *Bicheng,* the University of Auckland, New Zealand, reviewer, *Tom Lindfors*

Evaluation of candidates

Maunula Teuvo, Aalto University, evaluation of docentship, *Dmitry Murzin*

Evaluator of lecturer position in analytical and inorganic chemistry, Aalto University, *Ari Ivaska*

Evaluator of assistant professors position in inorganic chemistry, Alborg University, *Leena Hupa*

Editorial boards

Catalysis for Sustainable Energy, editorial board member, *Dmitry Murzin*

Bulletin of Chemical Reaction Engineering and Catalysis, regional editor for Europe, *Dmitry Murzin*

Bulletin of St. Petersburg State Institute of Technology, editorial board member, *Dmitry Murzin*

Catalysis in Industry, Associate editor and editorial board member, *Dmitry Murzin*

Catalysis Letters, scientific advisory board, editorial board member, *Dmitry Murzin*

Current Catalysis, editorial board member, *Dmitry Murzin*

International Journal of Chemical Engineering, editorial board member, *Dmitry Murzin*

Journal of Engineering, editorial board member, editorial board member, *Dmitry Murzin*

Kinetics and Catalysis, editorial board member, *Dmitry Murzin*

Russian Journal of Chemical Industry, editorial board member, *Dmitry Murzin*

The Open Catalysis Journal, editorial board member, *Dmitry Murzin*

Topics in Catalysis, scientific advisory board, *Dmitry Murzin*

Catalysis today, editorial board member, *Dmitry Murzin*

Biomass Sugars for Non-Fuel Application, RSC Green Chemistry, RSC, 2016, *Editors D. Murzin, O. Simakova*

Biomedical Glasses, editorial board member, *Leena Hupa*

Journal of Applied Glass Science, editorial board member, *Leena Hupa*

Topics in Catalysis: Bridging Organic Chemistry and Heterogeneous Catalysis, 2016, 59, No.13, Editors *Reko Leino, Dmitry Yu. Murzin, Tiina Saloranta*

Chemistry of plant raw material, editorial board member, *Pranovich, Andrey*

Jacobs Journal of Materials Science, editorial board member, *Andrey Pranovich*

Wood Science and Technology, editorial board member, *Bjarne Holmbom*

Holzforschung, editorial board member, *Bjarne Holmbom*

Cellulose Chemistry and Technology, editorial board member, *Bjarne Holmbom*

O´Papel, editorial board member, *Bjarne Holmbom*

Chemistry of Plant Raw Materials, editorial board member, *Bjarne Holmbom*

Nordic Pulp and Paper Research Journal, scientific advisory board member, *Stefan Willför*

Holzforschung, editorial board member, *Stefan Willför*

Cellulose Chemistry and Technology, editorial board member, *Stefan Willför*

Journal of Wood Chemistry and Technology, editorial board member, *Stefan Willför*

Nordic Pulp and Paper Research Journal, editorial board member, *Anna Sundberg*

Cellulose Chemistry and Technology, advisory board member, *Stefan Willför*

Chemosensors (MDPI), editorial board member, *Johan Bobacka*

Sensing and Bio-Sensing Research (SBSR), editorial advisory board member, *Tom Lindfors*

Member of scientific committees and boards

Member of the scientific committee, CHISA2016, Prague, *Tapio Salmi*

Member of the scientific committee, "Chemreactor-22", London, *Dmitry Murzin*

Member of the scientific committee, "Mechanisms of catalytic reactions-X", Kaliningrad, *Dmitry Murzin*

Member of the scientific committee, "I&S Workshop: Insights and strategies towards a bio-based economy", Montevideo, Uruguay, *Dmitry Murzin*

Member of scientific committee, Unicrea Unipetrol, *Dmitry Murzin*

Member of the international scientific committee CAFC-11, 11th Congress on Catalysis Applied to Fine Chemicals, Villeurbanne-Lyon, France, *J.-P. Mikkola*

Member of Scientific committee, Workshop on Insights and Strategies Towards a Bio-Based Economy, Montevideo, Uruguay, *Andrey Pranovich and Anna Sundberg*

Member of the Publication Forum by the Finnish scientific community (JuFo), *Anna Sundberg*

Deputy member of the Management Committee of the EU COST action FP1306, "Valorisation of lignocellulosic biomass side streams for sustainable production of chemicals, materials & fuels using low environmental impact technologies", *Stefan Willför*

Board member (vice director), Biocity Turku Research Programme: Diagnostics Technologies and Applications Programme, *Johan Bobacka*

Member of the National Bioeconomy Panel appointed by the Ministry of Employment and the Economy (3.11.2015-30.4.2019), *Stefan Willför*

Member of the Scientific Advisory Board of the chemical industry, "Kemianteollisuuden tieteellinen neuvottelukunta, Kemianteollisuus ry", *Stefan Willför*

Board member, Turku Centre for Biotechnology, *Stefan Willför*

Expert Member of the Vasa Preservation Council, Stockholm, *Bjarne Holmbom*

Vice-chair of the Biocity Turku research program "Advanced Bioresources and Smart Bioproducts – Towards Sustainable Bioeconomy", 2016-2020, *Stefan Willför*

Vice-chair of Biomaterial and Medical Device Reserch Program, Biocity Turku, *Leena Hupa*

Vice-chair of the ÅA Graduate School DNMR, *Leena Hupa*

Member of steering group, Smart Chemistry Park, *Leena Hupa*

Member of the Council, International Comission of Glasses, *Leena Hupa*

5.5 Others

"Medelinsamlingen", raising funds for ÅA, *Stefan Willför*

Board member, Institute of Human Rights, AAU, *Stefan Willför*

Member of the planning committee for the 100-year celebration of AAU, *Stefan Willför*

Officers club, Åbo, Invited lecture: Skog och hälsa, *Bjarne Holmbom*

ÅAU-UPM steering group member, 2016-, *Stefan Willför*

ÅAU representative in the Shareholder Forum and in the Bioeconomy task force for Clic Innovation Ltd (innovation cluster in bioeconomy, energy, and cleantech), 2016-, *Stefan Willför*

Member of the Research Ethics Board of AAU (18.12.2015-31.7.2017), *Stefan Willför*

Promotor, Åbo Akademi University Doctoral Conferral Ceremony, 2016, *Reko Leino*

Honorary titles

Knight, First Class, Order of the White Rose of Finland, *Dmitry Murzin*

6. Doctoral theses in progress at *PCC*

Aalto-Setälä, Laura (MSc 2014, University of Helsinki): *Gradient-Structured Bio-Engineered Implant Surfaces*

Akhmetzyanova, Uliana (MSc 2013, Tver Technical University, MSc 2015, Åbo Akademi University): *Hydroconversion of Biomass Derivatives over Heterogeneous Catalytic Systems Based on Transition Metal Carbides, Nitrides, and Phosphides*

Behvarvesh, Erfan (MSc 2014, Åbo Akademi University): *Millistructured Flow Chemistry for Oxidation Processes of Molecules from Biomass*

Björkvik, Leena (MSc 2011, Åbo Akademi University): *Bioactive Glass Composites*

Brusentsev, Yury (MSc 2003, Moscow State University): *Synthetic Modifications of the Natural Lignin Hydroxymatairesinol towards Ligands for Asymmetric Catalysis* (defended 2/2017)

Bruun, Nina (MSc 1984, Åbo Akademi University): *Challenge of Bio-Oil in Marine Engines*

Dirbeba, Meheretu Jaleta (MSc 2013, Addis Ababa University): *Characterization of Biomass-Containing Industrial Byproducts for Thermochemical Conversion*

Freites, Asdriana (MSc 2015, University of Simon Bolivar): *Epoxidation of Vegetable Oils under Microwave Irradiation, Process Intensification for Biomass Conversion*

Godina, Lidia (MSc 2012, Mendeleyev University of Chemical Technology): *Understanding Catalysis and Hydrothermal Stability of Carbon Supported Noble Metals for Sustainable Fuel Production by Aqueous Phase Reforming*

Hachemi, Imane (MSc 2012, University of Sciences and Technology Houari Boumediene): *Biofuels from Fatty Acids Hydrodeoxygenation over Sulfur-Free Catalyst*

Han, Tingting (MSc 2008, Åbo Akademi University): *Novel Signal Readout Principle for Solid-Contact Ion-Selective Electrodes*

He, Ning (MSc 2009, Åbo Akademi University): *Ion-Selective Electrodes with Hydrophobic Solid-Contacts*

Hupa, Elisa (MSc 2014, Åbo Akademi University): *New Approach to Determine Initial Melting of Corrosive Deposits*

Joon, Narender (MSc 2016, Åbo Akademi University): *Doctoral thesis: Continuous Dynamic Extraction and On-Line Determination of Metals from Solid Environmental Samples*

Kinnunen, Hanna (MSc 2009, Tampere University of Technology): *Influence of Lead and Zink Compounds on Superheater Corrosion in Fluidized Beds Firing Demolition Wood*

Kråkström, Matilda (MSc 2015, Åbo Akademi University): *Evaluation of Advanced Oxidation Processes for Removal of Antibiotics in Wastewater Treatment Plants*

Korotkova, Ekaterina (MSc 2011, Åbo Akademi University): *Mild-Alkaline Extraction of Spruce Lignin and its Applications*

Kortesmäki, Ewelina (MSc 2013, University of Gdansk): *Occurrence and Fate of Antibiotics in Wastewater, Wastewater Treatment Plants and Recipient Waters*

Lagerquist, Lucas (MSc 2011, Åbo Akademi University): *Exploring the Structure and Reactivity of a Novel Type of Pressurized Hot Water Extracted Lignin*

Li, Na (MSc 2007, Åbo Akademi University): *High-Temperature Corrosion of Ceramics in Biomass Combustion*

Lindfors, Christian (MSc 2008, Helsinki University of Technology): *Quality Improvement of Biomass Pyrolysis Bio-Oil by Additives or Organic Catalysts*

Lund, Sara (MSc 2013, Åbo Akademi University) *Liquid-Phase Exfoliation of Finnish Flake Graphite in Cellulose Nanocrystals and Preparation of Electrically Conducting Composite Films for Sensor Applications*

Meierjohann, Axel (MSc 2010, Åbo Akademi University): *Application of LC-MS/MS for Environmental Analysis*

Mattsson, Ida (MSc 2015, Åbo Akademi University): *Smart Materials from Sweet Molecules: Self-Assembling Polyols Derived from Mannose*

Najarnezhasmashbadi, Ali (MSc 2015, Åbo Akademi University): *Development of New Structured Catalyst and Reactor Technologies for Biomass Conversion*

Niemi, Jonne (MSc 2014, Åbo Akademi University): *The Role of Temperature Gradient in Ash-Deposit Chemistry and Superheater Corrosion*

Nisula, Linda (MSc 2003, Åbo Akademi University): *Wood Extractives in Conifers - a Study of Stem Wood and Knots of Industrially Important Species*

Pérez Nebreda, Andrea (MSc 2013, Universidad de Cantabria): *Valuable Monomers and Oligomers from Hemicelluloses*

Pezoa Conte, Ricardo Miguel (MSc 2010, University of Chile): *Biorefinery of Macroalgae: from Extraction of Carbohydrates to Production of Sugars*

Rahkila, Jani (MSc 2012, Åbo Akademi University): *Exploring Multivalency: From Oligosaccharides to Oligovalency and Beyond*

Rai, Varun (MSc 2015, Åbo Akademi University): *High-Temperature Erosion of Boiler Materials*

Rendon, Sabine (MSc 2011, Åbo Akademi University): *Dyes in Dye-Sensitized Solar Cells*

Runeberg, Patrik (MSc 2014, Åbo Akademi University): *Selective Oxidation of Unprotected Carbohydrates, Polyols and Phenolic Compounds from the Biorefinery Feedstock*

Russo, Vincenzo (MSc 2011, Università di Napoli 'Federico II'): *Reactor Modelling for Fluid-Solid Systems*

Saeid, Soudabeh (MSc 2015, Islamic Azad University Tabriz): *Elimination of Pharmaceutical Products from Waste Water by Ozonation and Heterogeneous Catalysis - a Systematic Kinetic and Reaction Engineering Approach towards New Technology*

Saleem, Farhan (MSc 2013, Åbo Akademi University): *Furfural Valorization by H_2O_2: Synthesis of Green Dicarboxylic Acids*

Santochi, Paulo (MSc 2012, Åbo Akademi University): *Mathematical modelling of nitrogen oxide formation in black liquor combustion*

Sevonius, Christoffer (MSc 2012, Åbo Akademi University) *Agglomeration Studies in a Laboratory Bubbling Fluidized Bed in Conditions Typical for Biomass and Agrofuel Firing*

Shumilov, Vladimir (MSc 2014, Åbo Akademi University and Tver State Technical Univeristy): *Development of Structured Reactors for Transformation of Biomass Components to High-Value Products: Green Process Intensification*

Jingxin, Sui (MSc 2011, Åbo Akademi University): *An Electrochemical Approach to High-Temperature Corrosion*

Sundqvist, Maria (MSc 2015, Åbo Akademi University): *Refining of Industrial-Based Wastes to High-Value Products*

Vucetic, Nemanja (MSc 2013, Belgrade University): *Preparation of Valuable Organic Chemicals from Homogeneous Catalysis to SILCA and Batch to Continuous Technology*

Xu, Wenyang (MSc 2015, Åbo Akademi University): *Three Dimensional Printing of Wood-Based Biopolymer for Biomedical Application*

Yu, Kai (MSc 2010, Åbo Akademi University): *Synthesis, Characterizarion and Application of Polypyrrole/Zeolite Composites*

Zhang, Yongchao (MSc 2015, Qilu University of Technology): *Development of a Novel Biomass Fractionation Approach Using Performic Acid Hydrolysis towards Integrated Lignocellulosic Biorefinery*

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