Johan Gadolin
Process Chemistry Centre

at

Åbo Akademi University

Annual Report 2015-2016

Edited by

Otto Långvik,
Rose-Marie Latonen, Päivi Mäki-Arvela,
Tiina Saloranta, Anna Sundberg, Johan Werkelin

Åbo
Finland

2016

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

The annual ***PCC*** *picture in April 2016*

Photo: Atte Aho

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PCC logo: Linus Silvander
Painosalama, Turku/Åbo

2016

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1. Introduction to the Activities in 2015-2016

Background and news

The Johan Gadolin Process Chemistry Centre (***PCC***) began its journey already 1998 as a centre with common objectives and research strategy. ***PCC*** had the status of a Centre of Excellence (CoE) in research granted by the Academy of Finland 2000-2011, while 2012-2014 the Centre continued its activities with a new research programme and some additional strategical funding from our university. For the period 2015-2018, ***PCC*** obtained the status of Centre of Excellence at Åbo Akademi University as one of four groups out of 20 that applied for the status. This also guarantees some CoE funding from the university.

We are now on the second year of our new research plan, "**Future Refining of Forest Biomass – the Molecular Process Technology Approach**". The core of the plan 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 somewhat shifted focus towards 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 have worked out well. We have emphasized the incorporation of all researchers into the core activities and our Work Package leaders Chunlin Xu, Pasi Virtanen, Patrik Eklund, and 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.

Our Johan Gadolin Scholarship Programme has also continued to be successful and is well integrated to our research plan. ***PCC*** also welcomes some new members of our Forum for Society (FS). FS now also has a chairperson, Dr Lars Gädda, who will work with intensifying our interactions with the FS, and industry and society in general, as well as suggest new ways of cooperation to benefit all parties.

Our newly established deeper cooperation with the Turku Centre for Biotechnology (CBT) and Biocity Turku has been very successful. Biocity Turku announced this year (2016) seven new 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 (director: Academy Professor Eva-Mari Aro, University of Turku (UTU), vice-director: Professor Stefan Willför). Then our groups are also members or associated members of the Biomaterial and Medical Device Research Programme (directors: Professor Tero Soukka, UTU, and Jessica Rosenholm (ÅA), vice-directors: Professor Johan Bobacka and Pekka Hänninen, UTU) and Diagnostic Technologies and Applications (director: Professor Pekka Vallittu, University of Turku, vice-director: Professor Leena Hupa). Furthermore, our cooperation has also led to several project applications and projects in the areas of biomedical applications of biopolymers and drug development.

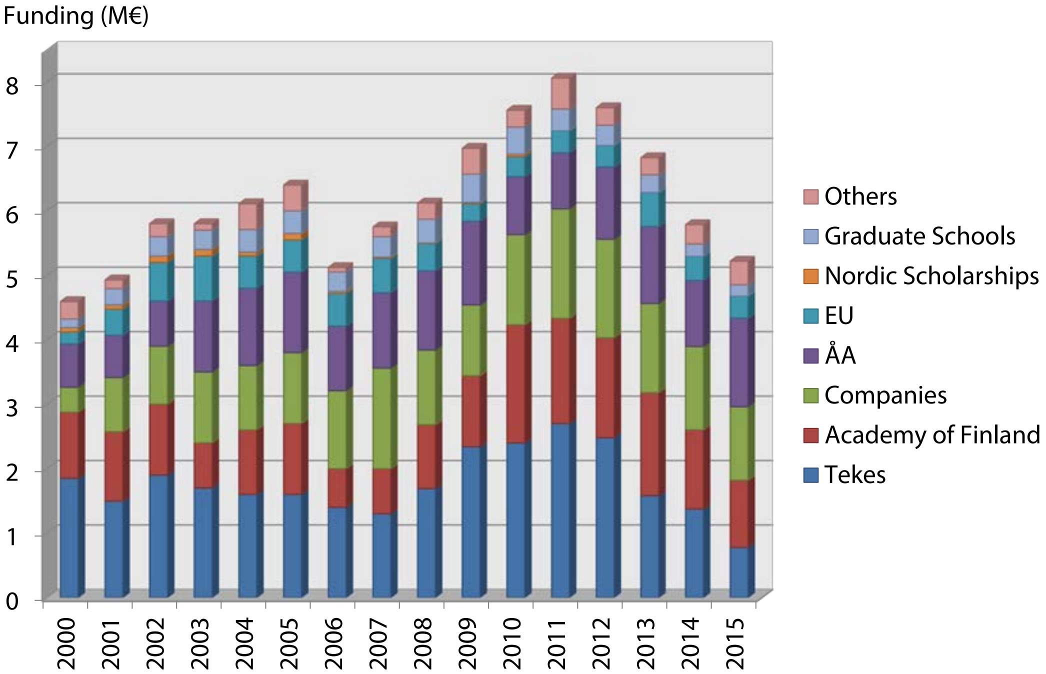
As always, ***PCC*** and its members have been very active in applying for funding on both national and international level. One of the bigger applications was most certainly the letter of intent we submitted to Academy of Finland for the Centre of Excellence Programme 2018–2025 call. The research leader for this application is Professor Dmitry Murzin.

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" and "Drug development and diagnostics". The university also supports these areas with special funding and in consequence to this we can now welcome 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. In line with this strategy of the profile areas, we have also initiated discussions with the Center for Functional Materials (FunMat) to find ways of closer cooperation and a future common research strategy.

The Year 2015 in Numbers

In 2015, more than 30 senior researchers and more than 45 full-time PhD candidates worked in the 55 major 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 2015 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 and excellent output will change this negative trend.



The funding of the Johan Gadolin Process Chemistry Centre 2000-2015

From the Academic point of view the year 2015 was very productive. The table below gives some key numbers of our academic activities in 2015. Once again, the Centre kept a very high production rate by publishing 164 papers in scientific publication series with the full referee system. It is also gratifying to note that the numbers of masters' theses show a positive trend, while the number of doctoral theses remains high.

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
Doctoral Theses	5	7	8	2	11	8	8	8	9	7	6	10	10	15	16	12
Masters' Theses	21	23	27	26	17	15	20	23	19	17	15	11	14	12	16	25
Journal Articles	60	70	94	77	106	109	113	116	101	118	138	143	145	154	145	164

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.

Organizing seminars and workshops

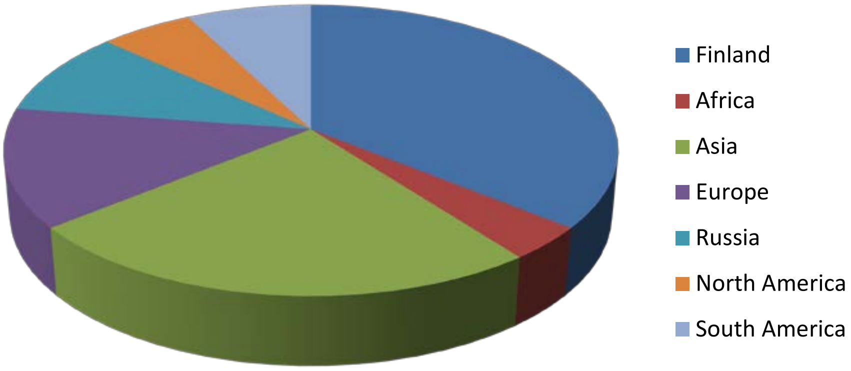
Our series with internal workshops was continued during 2015. On December 16, a MS-MS seminar on mass spectrometry was organized. Further, November 12-13, both ***PCC*** and the national chromatography association arranged, with joined forces, a national seminar on chromatography, in Naantali. In addition, the research groups i.e. Work Packages (WPs) have started to organize ***PCC*** internal seminars. More about the different research projects within ***PCC*** is found in chapter 3 in this Annual Report.

PCC annual Seminar in August 2015 (Photo: Hanna Lindqvist)

The traditional Annual Seminar was held on August 20, 2015. As part of our new research plan we also organised a joint seminar with the Turku Centre for Biotechnology (CBT) in January 2015. This seminar was strategically important for both ***PCC*** and CBT and some outcome were the abovementioned Biocity Turku programs we participate in and a number of joint project applications.

Doctoral Students

A central part of our research activities is done as doctoral theses works. Altogether about 50 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 the this Annual Report. At the moment, 45% of the ***PCC*** doctoral students are female.



Nationality of PhD students at Johan Gadolin Process Chemistry Centre 2015.

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. The Åbo Akademi Foundation decided to continue funding for the Johan Gadolin Scholarships Program for at least the period 2014-2016.

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 12 (now maximum 9) 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 2015 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 2015 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, *Raimo Alén* from the University of Jyväskylä and *Lars Pettersson* from the Royal Institute of Technology in Stockholm, Sweden, Prof. *Andreas Seidel-Morgenstern* from Max Planck Institute, Germany and Prof. *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 2015, the ***PCC*** had three lectures in its Distinguished Lecturer Series:

- November 11, 2015: Professor Thomas Rosenau, University of Natural Resources and Life Sciences, BOKU, Vienna, Austria: "Insights into the molecular mechanisms of cellulose swelling, dissolution and regeneration"
- October 6, 2015: Academy Professor Olli Ikkala, Aalto University, Finland: “Functional Glycomaterials Based on Dendronic, Supramolecular and Nanocellulosic Motifs”
- March 9, 2015: Prof. Katsuaki Konishi, Hokkaido University, Japan: “Uniqueness of Tiny Metal Objects beyond Nano: Not Just with the Sizes”

Acknowledgements

This report will be published at the Annual Symposium of the ***PCC*** held on August 25, 2016 at the Åbo Akademi Gadolinia 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 2015. It also has an activity calendar listing the main events where members of the Centre have contributed or participated during the year.

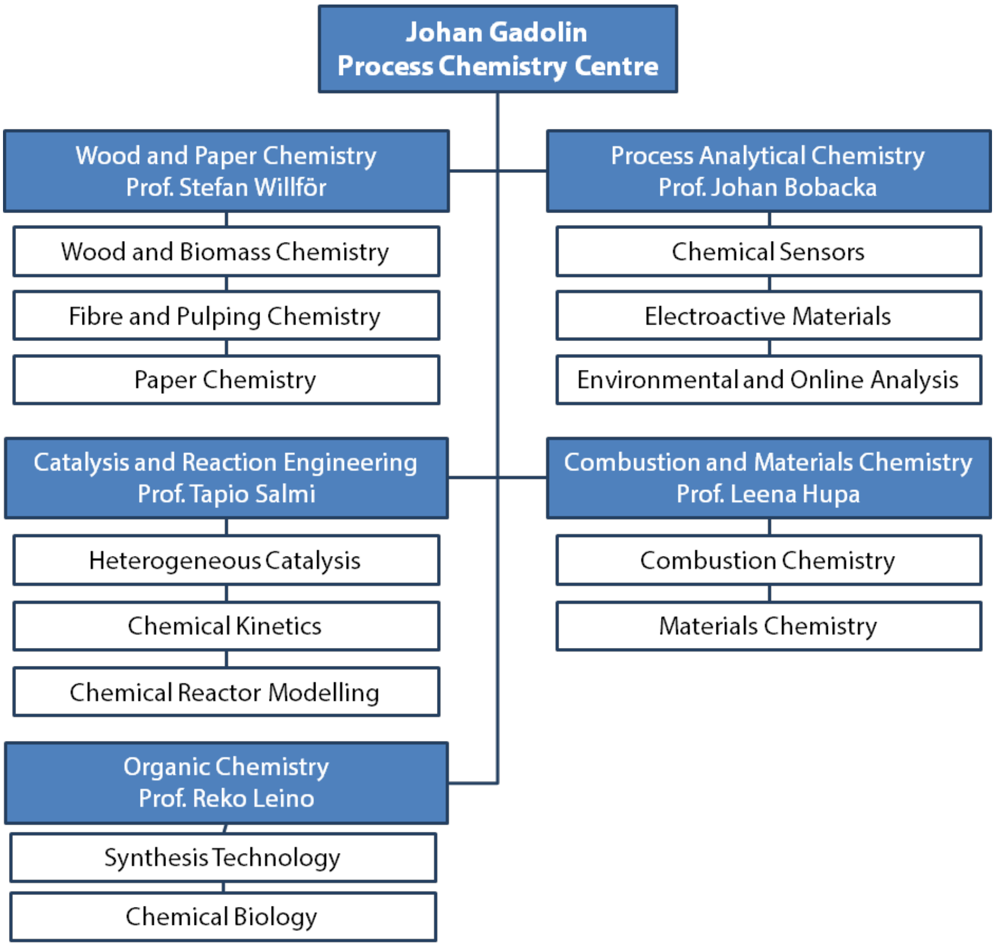
The report and layout is edited by an editorial team consisting of Otto Långvik, Rose-Marie Latonen, Päivi Mäki-Arvela, Tiina Saloranta, Anna Sundberg, Johan Werkelin with the assistance of Mia Mäkinen.

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

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 (until 31.8.2016)

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
- 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

Johan Gadolin Process Chemistry Centre has a vital role in Åbo Akademi University and its overall strategy, as it forms one essential part of the decided profiling area, Molecular Process- and Material technology.

Forum of Society, FS, was established to enhance the dialogue and cooperation between ***PCC*** members (professor, research leader and researchers) and external important stakeholders as industry, financers and other important interest groups.

This is an excellent initiative and fully supports and is in accordance with the overall Åbo Akademi University strategy. ***PCC*** is very grateful that the FS members are willing to participate in seminars and discussions with the academic researchers.

The members of FS appreciate the opportunity to participate in the well-prepared annual meeting and enjoy to take part of the high quality presentations of the ***PCC*** researchers. The FS members get a good overall view of the conducted research within ***PCC*** and can based of this knowledge draw conclusions about the applicability of research results for their companies and businesses. The cooperation between ***PCC*** and the FS members will be deepened and improved by e.g. a more active dialogue between the parties. Joint discussions and brainstorming's sessions during the coming annual meetings is a new opportunity.

Dr. Lars Gädda
PCC-FS Chairperson

2.2 Wood and paper chemistry

The mission of our laboratory is to *promote sustainable and multipurpose use of wood for fibre products and for high-value biomaterials and biochemicals*. 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, 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, including biorefining, pulping, and papermaking. 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. Remaining wood substances can then further be recovered or utilized as energy. A strong research approach is the utilization of nanocellulose and modified hemicelluloses for hydrogels and materials in biomedical applications. 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 2015 was obtained mainly from Academy of Finland and the industry. We also have close cooperation with e.g. KTH and the Wallenberg Wood Science Centre in Sweden with researcher exchange and joint research. Other current important partners are University of Wollongong in Australia, University of Helsinki, and Turku Centre for Biotechnology in Finland.

We are partners in the “Refining lignocellulosics to advanced polymers and fibers” Nordforsk researcher network and in the Loura – Platform for Water Expertise network (Intercity Collaboration of South-West Coast of Finland).

Personnel of Laboratory of Wood and Paper Chemistry in April 2016

Personnel

Professors

Stefan Willför
Bjarne Holmbom (Emeritus)

Docents

Andrey Pranovich
Annika Smeds
Anna Sundberg
Chunlin Xu

Senior researchers

Victor Kisonen
Otto Långvik
Anders Strand
Thomas Zweckmair
Lari Vähäsalo

Doctoral students & researchers

Jarl Hemming
Ekaterina Korotkova
Jun Liu
Linda Nisula
Sebastian von Schoultz
Klaus Söderback
Wenyang Xu

Technician

Leif Österholm

Secretary

Marika Ginman

Link

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

2.3 Combustion and materials chemistry

Our research strategy is based on detailed knowledge of chemistry in high-temperature processes and behaviour and properties of the high-temperature materials. Our main research efforts are in the fields of bioenergy, biomedicine, cleantech, and circular economy. Managing and treatment of the material streams and wastes to recover resource elements and valuable chemicals in the manufacture of new additional value products is an essential topic in all our research efforts. Manufacture and characterisation of inorganic materials to medical devices belong to our core research activities.

We characterise in detail the composition and behaviour of different biomasses and waste-derived fuels, model combustion processes in energy generation, measure emissions to the atmosphere, and study the interactions of the fuels and their ashes with materials in the combustion devices. Our modelling efforts range from high-temperature thermodynamic equilibrium calculations to kinetic modelling of flue gases and single particle fate in combustion processes. One typical feature of our research activities is the development of cleaner and more efficient combustion technologies using “difficult” fuels. The research is carried out not only in laboratory scale tests but also as measurement and sampling campaigns in full-scale combustion processes. One of our core competence areas is the high-temperature corrosion and erosion mechanisms of steam tubes and ceramic refractories induced by bed materials and various ashes containing chlorides, bromides, fluorides, etc. Within the medical and well-being fields, development of devices for wound-healing and skin care, tailoring of bioactive glasses for tissue engineering scaffolds and biosensors are the main research focuses. Over the years, our strategy has been to understand in detail the influence of the oxide composition on the cellular responses of the bioactive glasses. Tailoring the glass compositions for biomimetic 3D structures to various hard and soft tissue regeneration applications is a central research topic.

Our research is done in collaboration with national and international universities and research centres. The research is financed by Tekes, Academy of Finland, EU, NordForsk, industry and small to medium 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 to the global market.

Personnel

Professors

Leena Hupa
Mikko Hupa, rector at Åbo Akademi University 2015-2018

Docents

Rainer Backman (external)
Anders Brink
Edgardo Coda Zabetta (external)
Kaj Fröberg
Christian Mueller (external)
Laeticia Petit (external)
Bengt-Johan Skrifvars (external)
Heimo Ylänen (external)
Patrik Yrjas

Senior researchers

Dorota Bankiewicz
Shuo Cui
Nikolai DeMartini
Siamak Eqtesadi
Markus Engblom
Oskar Karlström
Tooran Khazraie Shoulaifar
Juho Lehmusto
Daniel Lindberg
Fiseha Tesfaye
Emil Vainio
Xiaoju Wang
Johan Werkelin
Maria Zevenhoven

Doctoral students & researchers

Laura Aalto-Setälä
Leena Björkvik
Nina Bruun
Meheretu Dirbeba
Jan-Erik Eriksson
Hanna Kinnunen
Na Li
Jonne Niemi
Magnus Perander
Varun Rai
Paulo Santochi
Christoffer Sevonius
Jingxin Sui
Maria Sundqvist
Berndt Södergård
Hao Wu

Technicians

Tor Laurén
Peter Backman
Luis Bezerra
Jaana Paananen
Linus Silvander

Computer support

Peter Ekholm

Economy secretary

Eva Harjunkoski

Secretary

Mia Mäkinen

Link

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

Personnel of Laboratory of Inorganic Chemistry in 2016

2.4 Process analytical chemistry

Our research is focused on the development of chemical sensors based on advanced electroactive materials and new sensing principles for future applications in on-line analysis and health diagnostics. In the field of chemical sensors, solid-contact ion-selective electrodes (SC-ISEs) continue to be a major research topic in our group. We are continuously developing new concepts to further improve the performance of SC-ISEs. By utilizing the unique features of conducting polymers, we are now able to electrochemically control the standard potential of SC-ISEs and obtain SC-ISEs with reproducible standard potentials. We have also developed a new signal readout principle for SC-ISEs, allowing amplification of the analytical signal. Further advances were also made in the area of paper-based chemical sensors. Our research in this area has been supported mainly by the Magnus Ehrnrooth Foundation and Åbo Akademi University (***PCC***, GSCE).

Recently, we entered into research collaboration with the National Centre for Microelectronic (IMB-CNM-CSIC) in Barcelona, Spain. The goal of this new project is to develop durable and low-cost ion sensors on printed platforms.

A unique combination of SC-ISEs with a solid-state reference electrode has resulted in a universal sensor platform that has been adapted to a unit for wireless transmission of the sensor signals. This approach was funded by Tekes and it has a great potential for practical applications and commercialization.

A scientifically very challenging research project related to electrochemical sensors for personalized medicine was recently started with funding from the Jane and Aatos Erkko Foundation.

In our materials research, we have developed composites from conducting polymers and carbon nanomaterials, such as graphene oxide (GO) and reduced graphene oxide (RGO), that show excellent electrochemical stability. Our research on graphene is part of an interdisciplinary collaboration project (FennoFlakes) funded by the Academy of Finland.

A water-based electrically conducting ink based on crystalline nanocellulose (CNC) and polyaniline (PANI) was prepared. Interestingly, printed films of CNC-PANI showed a higher electrical conductivity than films based on PANI alone. Composite fibers based on nanofibrillated cellulose (NFC), poly(3,4-ethylenedioxythiophene) (PEDOT), polyethylene oxide (PEO) and poly(ethyleneglycol)diglycidyl ether (PEDGE) were prepared by electrospinning.

Electrochemical oxidation of cellulose was studied further by utilizing electrodes modified by gold nanoparticles. This is a unique approach to electrochemical modification and functionalization of polysaccharides derived from cellulosic biomass, and this work was funded by the Kone Foundation.

In our sensor research we participate in the EU-funded International Research Staff Exchange Scheme (IRSES), IBS-Network: "*Network for Sensor Knowledge Transfer*", 2014–2017. Concerning education in analytical chemistry we are a partner of the Erasmus Mundus international joint master degree programme EACH – Excellence in Analytical Chemistry (www.ut.ee/EACH/).

Personnel at the Laboratory of Analytical Chemistry in 2016.

Personnel

Professors

Johan Bobacka
Ari Ivaska (Emeritus)
Andrzej Lewenstam (part-time)

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
Cristina Ocaña
Yasuhito Sugano
Ulriika Vanamo

Laboratory Manager

Paul Ek

Doctoral students & researchers

Jesús Arroyo
Tingting Han
Ning He
Elisa Hupa
Narender Joon
Sara Lund
Minh Nguyen
Erika Rajasalo
Ville Yrjänä
Kai Yu

Secretary & coordinator

Lotta Alho (part-time)

Technicians

Sten Lindholm
Lassi Väinölä (part-time)

Links

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

2.5 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 2015 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.

Personnel at the Laboratory of Organic Chemistry in 2016.

Personnel

Professors

Reko Leino
Jorma Mattinen

Docents

Filip Ekholm
Patrik Eklund
Leif Kronberg
Rainer Sjöholm
Annika Smeds (Wood and Paper Chemistry)

Senior Researchers

Mikhail Kondrashov
Jan-Erik Lönnqvist
Tiina Saloranta
Risto Savela

Doctoral students & researchers

Yury Brusentsev
Ewelina Kortesmäki
Matilda Kråkström
Lucas Lagerquist
Ida Mattsson
Axel Meierjohann
Jan-Erik Raitanen
Jani Rahkila
Sabine Rendon
Patrik Runeberg
Heidi Sundelin
Andreas West

Laboratory Technician

Päivi Pennanen

Link

http://www.abo.fi/organiskkemi

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. 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, Novosibirsk and Tver.

The research in biomass fractionation with ionic liquids has given revolutionary results, concerning the efficiency and selectivity of fractionation; with the aid of ionic liquids, a completely new fractionation technology has been developed. Intensive collaboration is carried out in this field with University of Umeå and Technical University of Tallinn. Supported Ionic Liquid Catalysts (SILCA) are used for transformation of fine chemicals – the catalytic effect is based on immobilized metal nanoparticles; the most recent application concerns the preparation of terpene derivatives on SILCA.

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, as well as enantioselective hydrogenation processes combined to chromatographic separation 8in collaboration with University of Porto). 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). The award for the best thesis in chemistry and chemical technology in

Finland was given to Sabrina Schmidt for the development of microreactor technology for hydrochlorinated chemical intermediates.

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 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. The Nordic-Baltic network POKE (Sustainable chemistry and process technology in the Northern Baltic Sea Region) continued its activities in form of workshops organized in Turku and Mariehamn. The network has played an important role in the education of PhD students at Turku, Stockholm, Tallinn, Oulu and Umeå. We were happy to receive a record number of foreign researchers to the Laboratory in 2015.

Personnel of Laboratory of Industrial Chemistry and Reaction Engineering in April 2016

Personnel

Professors

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

Docents

Kalle Arve
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Matias Kangas
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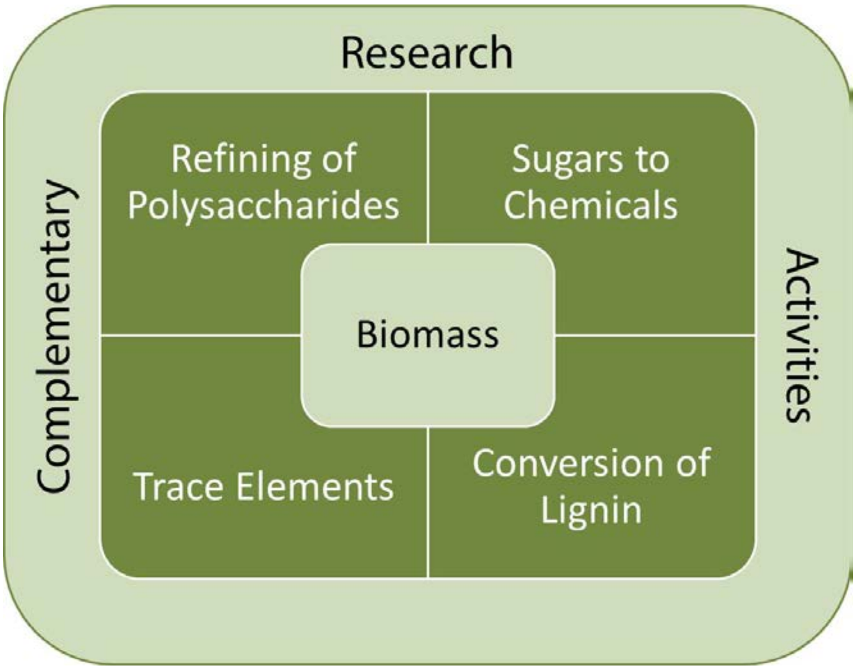
3 Research

Our research pan "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 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 nanocellulose. Our interest is currently mainly to utilize the hemicelluloses as polymers (in combination with conducting polymers and graphene) or other bioactive compounds such as bioglass 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.

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

- To isolate hemicelluloses with a large amount and of high purity which will be used in WP1 and WP2;
- To prepare hemicellulose-based adsorbents for removal or inactivation of dissolved hazardous compounds; and
- To tailor polysaccharide-based structural composites. Other composite component can be conducting polymer or other carbon material (e.g. graphene) aiming at applications in (bio)sensors and wound healing promotion. Another option of other composite component is bioactive glass aiming at the application as scaffolds in tissue engineering. The 3D printing technology will be applied by research visit to the Intelligent Polymer Research Institute at the University of Wollongong, Australia and in collaboration with the Pharmaceutical Group of Åbo Akademi University.

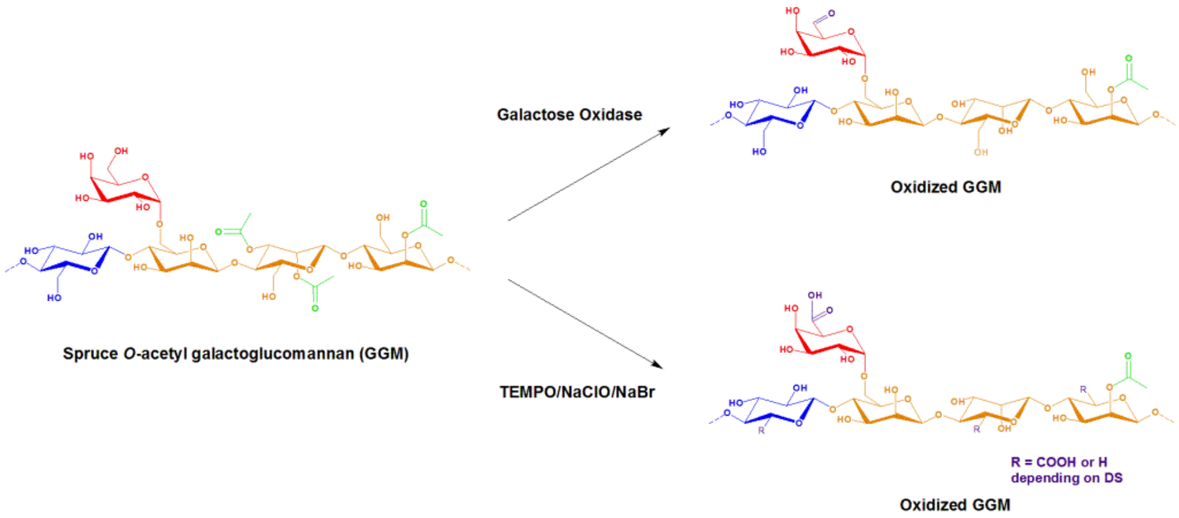
Chemical Modification of Water-Soluble Spruce O-Acetyl Galactoglucomannan

Main funding: Johan Gadolin Foundation, ***PCC***, Graduate School for Biomass Refining (BIOREGS), Knut and Alice Wallenberg Foundation

Wenyang Xu, Abhijit Sau, Ann-Sofie Leppänen, Chunlin Xu, Tiina Saloranta, Patrik Eklund, Stefan Willför

From a biomimetic perspective, the intrinsic affinity of cell wall hetero-polysaccharides, or hemicelluloses, for cellulose has inspired their use to alter the surface chemistry and mechanical properties of cellulosic materials. A particular advantage of such "indirect" modification is that issues of limited reactivity of insoluble cellulose and the need to carefully control direct chemical modification to prevent loss of fiber integrity are circumvented. Therefore, targeted functionalization is applied to activate the polysaccharides for further anchoring desired functional groups and thereafter the functionalized hemicelluloses can be sorbed onto cellulose surfaces. This approach enables the assembly of (bio)chemically active cellulose surfaces for applications in tailoring functional biocomposites with untapped potentials.

GGM is the major hemicellulose type in softwoods and a water-soluble polymer. It is a potential raw material for natural biochemicals and biomaterials. GGM has a high affinity onto cellulose fibers. By regioselective modification, i.e. on the primary alcohol of the galactose side groups or to other free hexose units, the high affinity to cellulose is preserved and modified GGM can be used for the functionalization of cellulose. Moreover, the utilization of aqueous systems as solvents is a step towards more environmentally friendly synthetic procedures.



Selective oxidation of GGM in water.

One way of performing selective modification of galactose units in GGM is to use enzymatic modification in combination with chemical reactions. The primary alcohol of galactose can be selectively oxidized to its aldehyde form, which is more reactive and ready for further chemical functionalization, e.g. indium mediated allylation and reductive amination. Thus, a broad spectrum of functional groups can be introduced.

Another approach is to use a regioselective chemical approach, i.e. 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation, which can selectively oxidize the free primary alcohols of hexoses. The formed uronic acids are then further modified by a carbodiimide-mediated amidation reaction, which opens up a window for introducing various functionalities selectively on C6 of hexoses. The affinity of the modified polysaccharides to cellulose surfaces has also been investigated.

The uronic acid derivative of GGM was also applied in the synthesis of conducting polyaniline where the GGM derivative was used as synthesis template. Furthermore, carboxylates of GGM uronic acids are ready for anchoring crosslinking agents thus the functional GGM derivatives can be used to tune the rheological properties of nanocellulose.

Lately, we have also been focusing on developing an approach to selectively activate C6 position of GGM with thiol. Model compounds of monosaccharides and disaccharides were studied. The approach will be applied to GGM. The targeted applications are biodiagnostics and biosensing.

Cooperation:
University of Helsinki; ***PCC*** and FUNMAT at Åbo Akademi University; KTH, Wallenberg Wood Science Center, Sweden

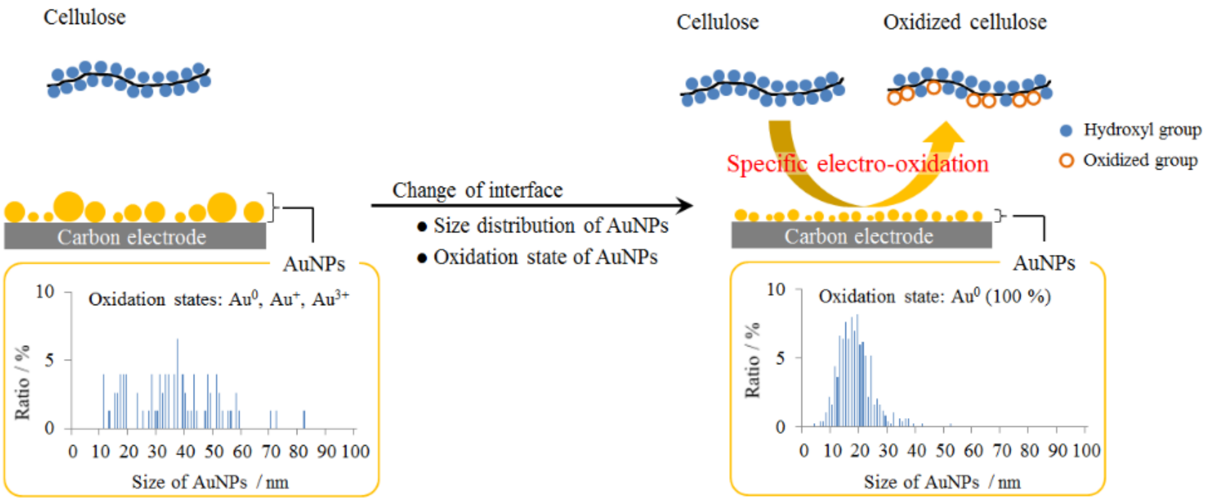
Electrochemistry of Polysaccharides Derived from Biomass

Main funding: KONE Foundation

Yasuhito Sugano, Johan Bobacka, Jyri-Pekka Mikkola

Cellulosic biomass is an environmentally-friendly and alternative resource that is expected to play an important role for a sustainable society in the future. Particularly, the production of functional materials derived from the main components of biomass (i.e. cellulose and hemicelluloses) can be an alternative to the use of petrochemicals. Functional materials and their physical properties can be designed by modifying the chemical groups of the macromolecules, e.g. by oxidation of cellulose. Cellulose can be oxidized chemically by 2,2,6,6,-tetramethylpiperidine-1-oxyl radical (TEMPO) and the reaction product has been reported to be more hydrophilic than the original cellulose. In this project, we have investigated a new reaction pathway from cellulose to functional materials that is based on electrochemical oxidation of cellulose at an electrode surface. Moreover, we found a new specific electro-catalytic oxidation phenomenon of cellulose at an electrode surface modified by Au nanoparticles, which was not observed earlier at a polycrystalline Au electrode. This is the first systematic study on the electrochemistry of polysaccharides that was initiated by Y. Sugano in 2007. This research activity has offered a new unique approach for electrochemical modification, functionalization and innovative utilization of polysaccharides derived from cellulosic biomass.

Notification: *The research projects related with electrochemistry of polysaccharides were finished in March 2016. From April 2016, the projects are continued by Y. Sugano at the University of Helsinki in collaboration with J. Bobacka and J-P. Mikkola with financial support from the KONE Foundation.*



Scheme of specific electro-catalytic oxidation of cellulose (dissolved in NaOH) at an electrode surface modified by Au nanoparticle with different size distributions and oxidation states.

Cooperation: Umeå University, Chemical-Biological Centre, Umeå, Sweden

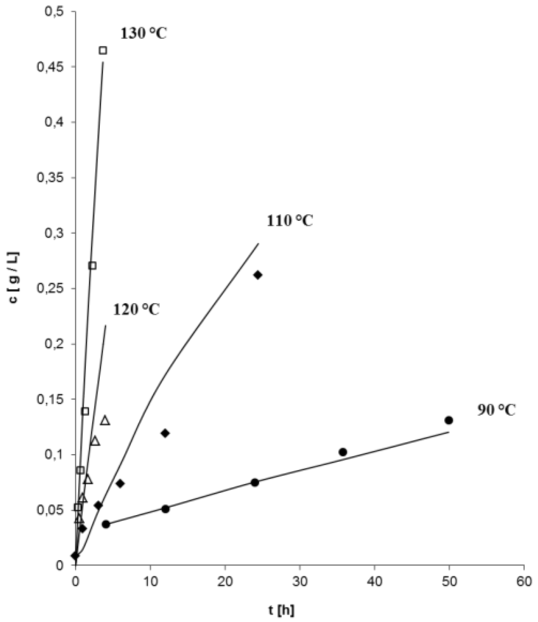
Controlled Extraction of Hemicelluloses with Hot Water

Main funding: Tekes (Fibic Oy), ***PCC***, Academy of Finland, Spanish Economy and Competitiveness Ministry, Erasmus Mundus Programme Eurotango II

Jussi Rissanen, Florencia Yedro, Kari Eränen, Chunlin Xu, Juan Garcia Serna, Stefan Willför, Dmitry Murzin, Tapio Salmi, Henrik Grénman

The main focus of the work was in the extraction kinetics and the properties of the extracted carbohydrates. The extraction was studied in the temperature interval 90 °C – 170 °C with different chip sizes, utilizing a cascade and a batch reactor system. The extraction kinetics was precisely determined quantitatively and the obtained results were successfully modeled in the whole temperature range with a simplified overall model for the extraction kinetics. The results demonstrate for the first time that the reaction mechanisms in the extraction are the same in a very broad temperature interval, despite changes in the morphology of the wood at elevated temperatures. It was also confirmed that the liquid phase pH does not influence significantly the extraction rate, in the pH range obtained in the PHWE without additives. Moreover, detailed experimental results showed that the molar mass of the hemicelluloses (2-60 kg/mol) of the obtained hemicelluloses can be radically influenced by the experimental parameters, mainly temperature and time. The main focus of the work has been on spruce; however, also holm oak and stone pine, which are abundant in the Mediterranean region, were studied. The results show that the extraction kinetics and also the properties of the extracted compound differ significantly depending on the species. This work contributes significantly to understanding the mechanisms involved in the extraction of hemicelluloses and the influence of the extraction parameters on the process.

The fractionation studies have also involved enhancing the yields and influencing the properties of the extracted hemicelluloses by using selected additives. The work is ongoing with more to come. Some focus has also been directed to the selective recovery of hemicelluloses in wood fractionation utilizing ionic liquids. The preliminary results show that the selective recovery could be significantly enhanced.



The extraction rate of hemicelluloses and model the prediction at low temperatures.

Cooperation:
PCC; University of Valladolid

Hydrolysis of Hemicelluloses for Obtaining Sugar Monomers

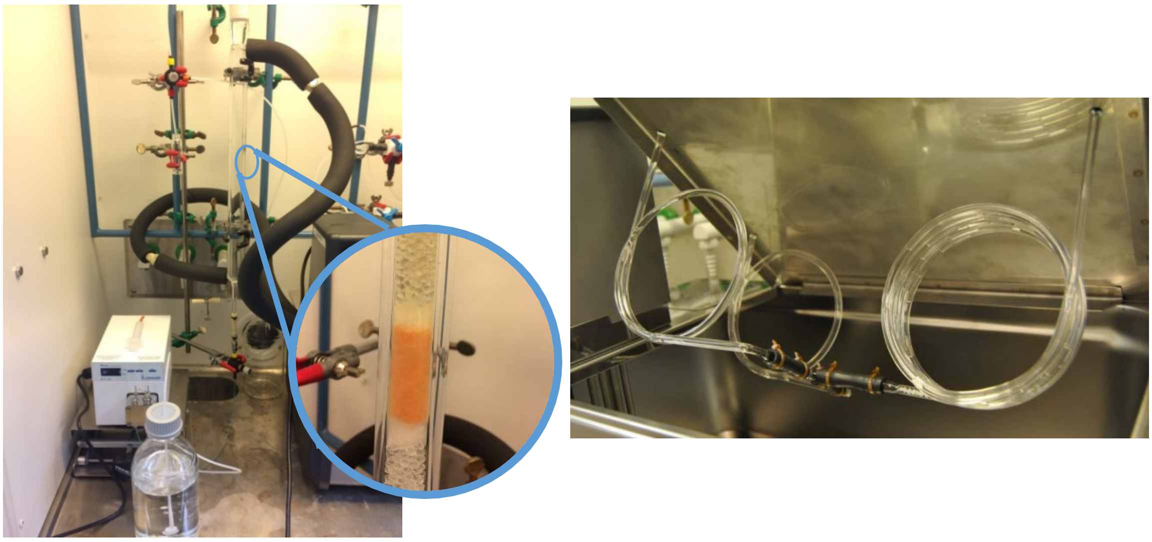
Main funding: Raisio Research Foundation, Erasmus Mundus Programme Eurotango II, Academy of Finland

Andrea Pérez Nebreda, Victor Perez Martinez, Kari Eränen, Päivi Mäki-Arvela, 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 to sugar monomers employing actual extracts instead of model compounds, in order to complete the production chain from wood 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 rather well understood especially with homogeneous catalysis. Continuous reactor technology has been developed and successfully utilized in the process with almost 100% conversion to monomers being obtained in optimized conditions. Good results have also been obtained with heterogeneous catalysis in batch mode with conversions comparable with the ones obtained with homogeneous catalysis. Novel continuous reactor technology is being developed for studying the process in more detail.

The first experiments with actual extracts from Norway spruce, scots pine and holm oak have also been tested in batch reactor experiments. The results prove the feasibility of performing the hydrolysis directly on the extracts obtained in controlled conditions, without the need for costly intermediate purification of the feed. The work is being continued on all the development fronts described above.



Continuous reactors for the hydrolysis of hemicelluloses.

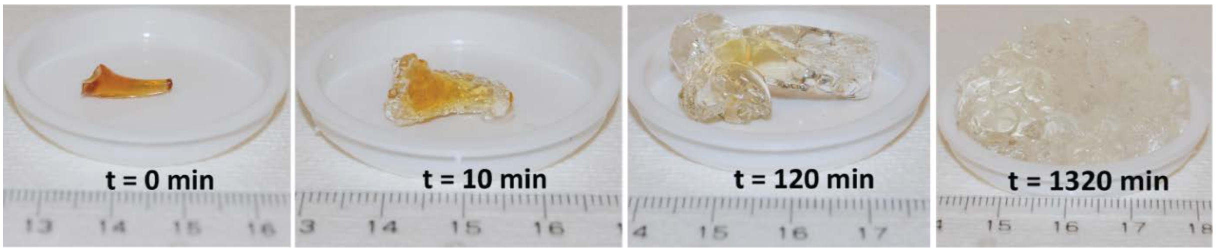
Cooperation:
PCC; University of Valladolid

Design of Hemicellulose-based Hydrogels for Wastewater Treatment

Main Funding: Aides à la formation recherche (AFR)

Daniel Dax, Chunlin Xu, Stefan Willför

GGM from Norway spruce (*Picea abies*) is a water-soluble and biodegradable polysaccharide with a high industrial potential and can be extracted from spruce wood by pressurized hot-water extraction (PHWE) or isolated from mechanical pulp wastewaters. Due to its relatively low molar mass and its availability in large quantities, GGM represents an interesting starting material for the synthesis of functional materials. In this study GGM (7 kDa or 28 kDa) was implemented in a transesterification reaction with glycidyl methacrylate using DMAP as a catalyst. The reaction conditions were investigated using different amounts of DMAP and different solvents. The GGMs with different degrees of substitution were in a second reaction used as cross-linker in a free radical polymerization. Methacrylate monomers bearing a quaternary ammonium group with chlorine as counter ion were applied. The physical properties of the GGM-based hydrogels could be tailored by adjusting the polymerization parameters. Ascribed to the potential of the used synthetic cationic polymers to act as ion exchange substrates, the produced GGM hydrogels were applied to remove toxic metal species from water. Furthermore, incorporation of CNF in the hydrogels can increase their material properties, such as mechanical strength.



Photographs of a GGM-based hydrogel in dry form (left) and fully swollen form (right).

Cooperation:
Centro de Biotecnología, University of Concepción, Chile; Polymer Department, University of Concepción, Chile

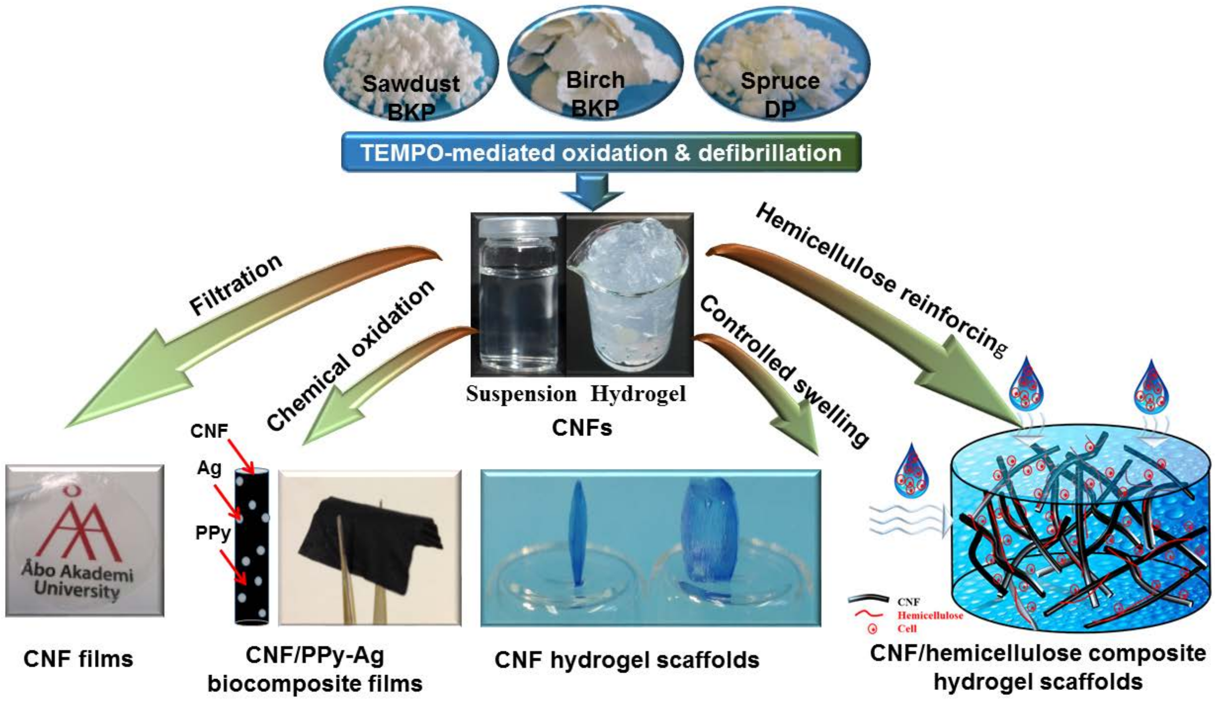
Nanocellulose Preparation

Main funding: ***PCC***, Graduate School of Chemical Engineering (GSCE), Chinese Council Scholarship (CSC), Johan Gadolin Foundation, Knut and Alice Wallenberg Foundation

Chunlin Xu, Jun Liu, Wenyang Xu, Bin Li, Risto Korpinen, Henrik Grénman, Stefan Willför

Nanocellulose represents a group of cellulosic nanomaterials. Cellulose nanofibrils (CNF), also termed as nanofibrillated cellulose (NFC), are usually manufactured by mechanical treatments or with a combination of enzymatic or chemical and mechanical treatments. Cellulose nanocrystals (CNC) or nanocrystalline cellulose (NCC) can be extracted by acid hydrolysis from a wide variety of natural sources. Our aim is to develop economically feasible processes to prepare nanocellulose.

For the first time, the applicability of sawdust has been explored to develop CNF from the biorefinery concept. The residual cellulose of wood processing waste, sawdust, which was leftover after sequential hot-water extraction processes to isolate hemicelluloses and lignin in a novel forest biorefinery concept, was explored as the starting material for the preparation of a highly value-added polymeric material, CNF. The residual cellulose in sawdust was converted to a transparent CNF suspension in water through the TEMPO/NaClO/NaBr oxidization approach. The resultant CNF with a dimension of 5-10 nm in width and hundreds of nanometers in length were further processed into CNF films. This study has demonstrated the feasibility of producing CNF and its films with high mechanical properties from a wood waste – birch sawdust, by a process incorporated into a novel biorefinery platform recovering also polymeric hemicelluloses for other applications.



Schematic illustration of the preparation of CNF and biomaterials thereof.

We have lately developed acid hydrolysis approaches using carboxylic acids, i.e. formic acid and oxalic acid to extract CNCs. These acids cause less corrosion compared to concentrated inorganic acids and they can be easily recovered and reused. CNCs thus prepared have comparable fiber morphology to those prepared from mineral acid hydrolysis.

Cooperation: University of Helsinki; KTH, Wallenberg Wood Science Center, Sweden; Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, China

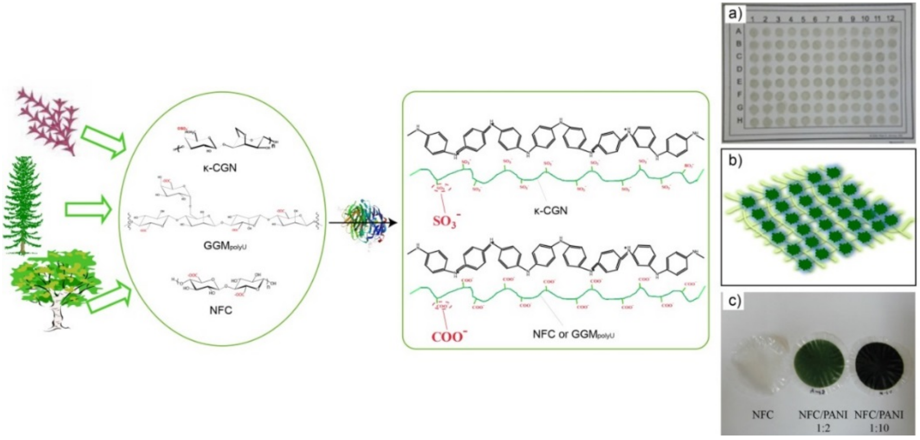
Development of Biocomposites

Main funding: Graduate School of Chemical Engineering (GSCE), Graduate School for Biomass Refining (BIOREGS), Chinese Council Scholarship (CSC), Johan Gadolin Foundation, Knut and Alice Wallenberg Foundation

Chunlin Xu, Jun Liu, Ann-Sofie Leppänen, Risto Korpinen, Bin Li, Hanna Lindqvist, Xiaoju Wang, Patrycja Bober, Tom Lindfors, Rose-Marie Latonen, Stefan Willför

The objective of this research is to develop novel advanced materials from biorenewable sources. Biocomposites and new materials based on wood components offer a huge potential in a large variety of applications. With the use of chemo-enzymatic and chemical tools, the product characteristics can be vastly improved and also designed to meet demanded purposes. They may find such applications as functional fibers, packaging, bioactive and stimuli-responsive materials, medical treatments, and other 'smart' materials.

We have developed a novel approach for fabricating PANI-biocomposites. Firstly, we developed chemo-enzymatic processes to utilize natural polysaccharides as templates instead of conventional synthetic polymers for laccase-catalyzed polymerization of aniline. Various polysaccharides and their derivatives, including naturally anionic ϰ-carrageenan (ϰ-CGN), native spruce GGM, TEMPO-oxidized cellulose derived nanocellulose (NFC or CNF), and GGM (GGMPolyU) were assessed as anionic templates. Moreover, these templates could be directly processed with PANI and utilized as construction matrix of the final PANI-composites. Notably, the resulted composite hydrogel could be directly processed to a flexible film or other forms of composites with good mechanical strength, which may find potential applications in biosensors and biomedical engineering.



Schematic illustration of the synthesis process of conductive polyaniline using anionic polysaccharides as templates.

Moreover, CNF was also used as a template in the polymerization of pyrrole and thus the composites of CNF/polypyrrole and CNF/polypyrrole/silver nanoparticle were prepared. The resulted conducting composite were directly processed to flexible free-standing films with good mechanical strength and antimicrobial properties, which may find potential applications in biosensors and biomedical engineering.

In addition, composites of CNF with other compounds such as hemicelluloses and inorganic pigments were also investigated both for the fundamental understanding of the structure-property relationship of different composite compounds and for the development of structural composites for broader application potential.

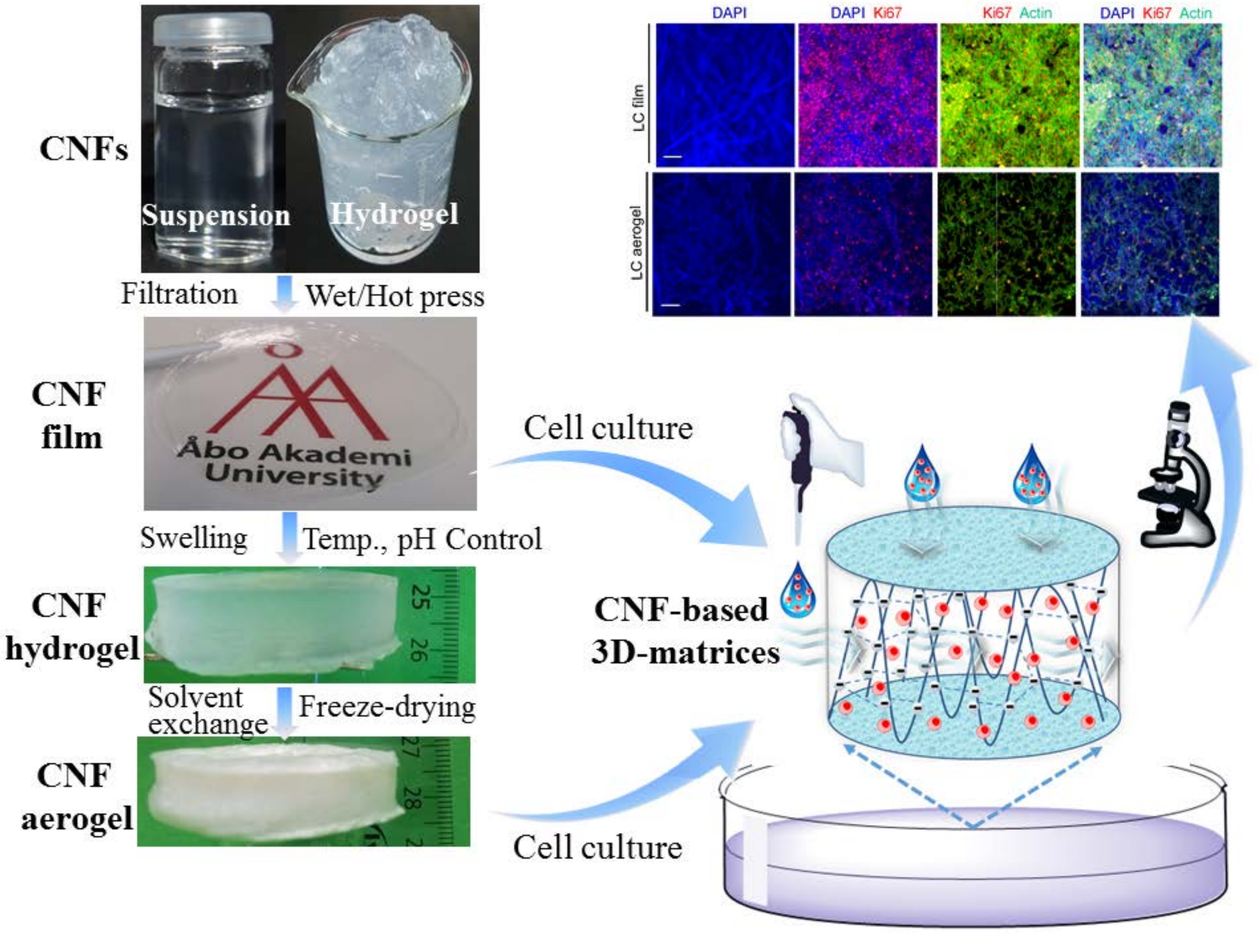
Cooperation: ***PCC*** and FUNMAT at Åbo Akademi University; University of Eastern Finland; KTH, Wallenberg Wood Science Center, Sweden

Nanocellulose-based Scaffolds for Biomedical Applications

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

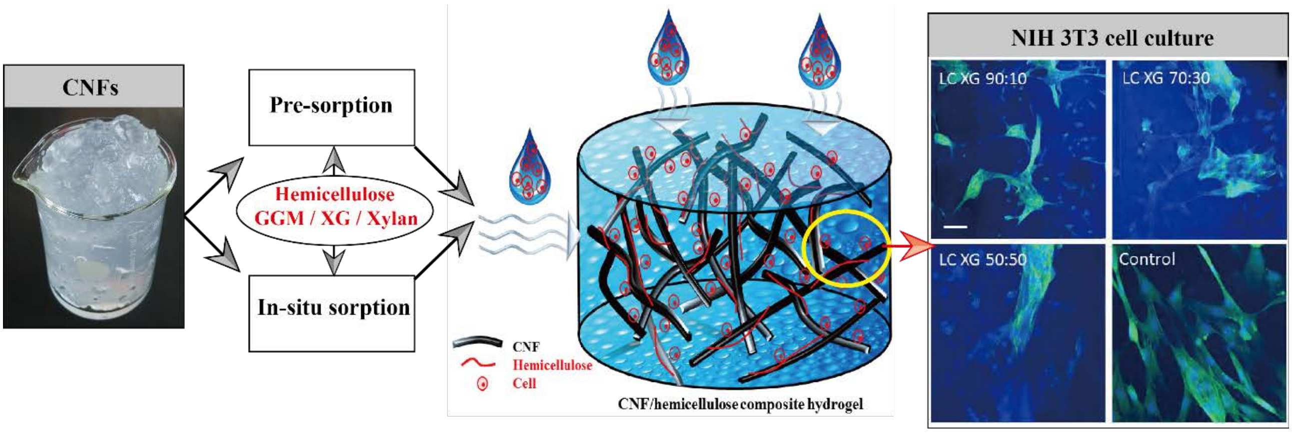
Chunlin Xu, Jun Liu, Wenyang Xu, Stefan Willför

Owing to the intrinsic non-toxicity, biocompatibility, and biodegradability, 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 extracellular matrix (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.



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

Furthermore, the mechanical and structural properties of a scaffold in biomedical application are believed to play crucial roles in the cellular behavior, e.g. cell proliferation, gene expression, maintenance of phenotype, and biosynthetic activity in tissue engineering; and therefore hemicelluloses (e.g. spruce GGM, brich xylan, and xyloglucan) have been incorporated to tune the mechanical and structural properties of CNF-based composite hydrogels, and further to investigate how the biocompatibility of the composite hydrogels is influenced by the mechanical and structural properties of the scaffolds. This work was inspired from the mechanical integrity of plant cell walls, in which the cellulose and hemicelluloses are closely associated and hemicelluloses are supposed to adsorb on the nanocellulose surface to reinforce the mechanical properties of the nanocellulose hydrogel. As depicted in the scheme, different hemicelluloses with various ratios were incorporated into the CNF hydrogel network in two approaches to tune the microscopic and mechanical properties of the composite hydrogels, thus making it possible to control properties that are important for biomedical applications like wound healing and tissue engineering.



Scheme for the preparation of hemicellulose-reinforced CNF hydrogels for wound healing.

Cooperation:

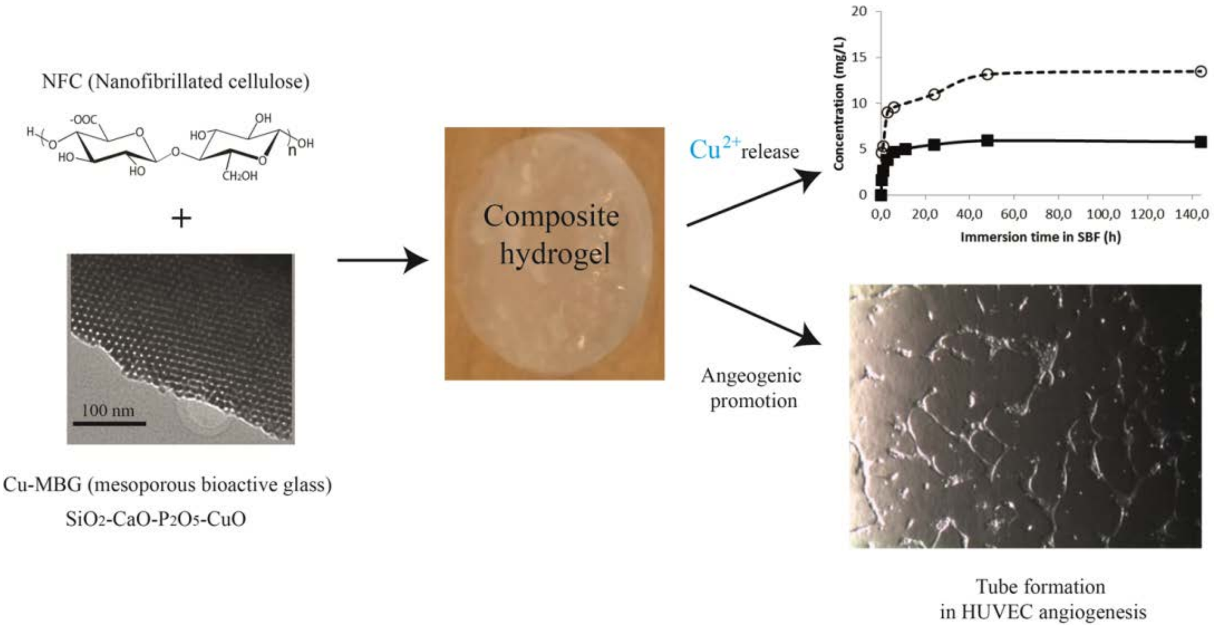
Department of Biosciences, Åbo Akademi University, Finland; Paper and Fibre Research Institute (PFI) and Department of Chemical Engineering, Norwegian University of Science and Technology, Norway.

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

Main funding: ***PCC***, Academy of Finland

Xiaoju Wang, Jun Liu, 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 with this joint project within ***PCC***. 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.



Research highlights of material development, in vitro assessment in SBF and bioassay of angiogenesis.

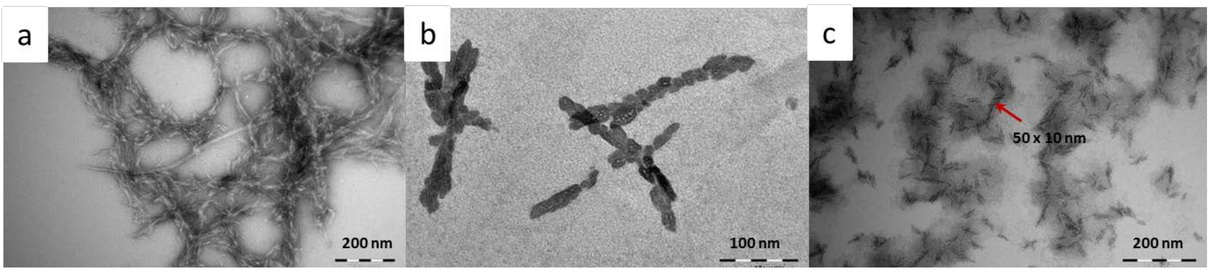
Cooperation:
Department of Biosciences, Åbo Akademi University, Finland.

Composites Based on Conjugated Polymers and Nanocellulose

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

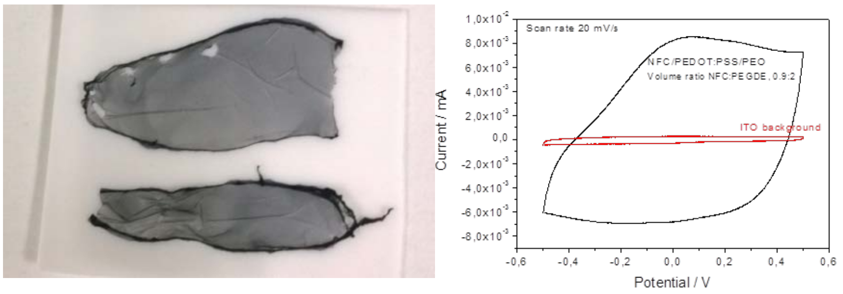
Jun Liu, Erika Rajasalo, Wenyang Xu, Muhammad Zubair, Tom Lindfors, Rose-Marie Latonen, Chunlin Xu

A water-based electrically conducting ink composed of crystalline nanocellulose (CNC) and chemically polymerized polyaniline (PANI) doped with dodecylbenzenesulfonic acid (DBSA) has been prepared using glycerol to adjust the viscosity of the ink. The ink is intended for use as a substrate for a gas sensor as such or for a chemical sensor after functionalization of CNC with suitable chemical groups. The ink has been successfully deposited on a coated paper substrate by the flexographic 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). The relative surface coverage of printed PANI(DBSA) and CNC-PANI(DBSA) films has been both found to increase rather linearly as a function of increasing number of printed layers with a steeper slope for the CNC containing ink. The electrical conductivity of the printed films with ten layers of the CNC containing ink was between 30 and 60 S cm^{-1} which was more than an order of magnitude higher than for corresponding films without CNC.



Transmission electron micrographs of a) CNC, b) PANI(DBSA) and c) CNC-PANI(DBSA) inks.

The electrospinning method has been used for preparation of water-resistant composite fibers based on nanofibrillated cellulose (NFC) and poly(3,4-ethylenedioxythiophene):polystyrene-sulfonate (PEDOT:PSS). Polyethyleneoxide (PEO) has been 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. The fibers are intended for use as a substrate for an electrochemical gas sensor or for cell growth.



(Left) A photograph of water-resistant electrospun fibers made of nanofibrillated cellulose and PEDOT:PSS. (Right) The cyclic voltammogram of NFC/PEDOT:PSS fibers on an ITO-glass electrode compared to pure ITO electrode in 0.1 M KCl electrolyte, scan rate 20 mV/s.

Cooperation: Åbo Akademi University, Centre for Functional Materials, Laboratory of Physical Chemistry, Finland

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

Main funding: Academy of Finland

Anders Strand, Chunlin Xu, Jun Liu, Anna Sundberg

This project is targeted towards the developments of new types of renewable fiber-based paper with high deformation potential, which is needed to obtain novel, bio-based packaging material for the use in forming processes (see figure below). In order to form a 3-D structure with high quality, the extensibility of the fiber networks must be increased to a new level.

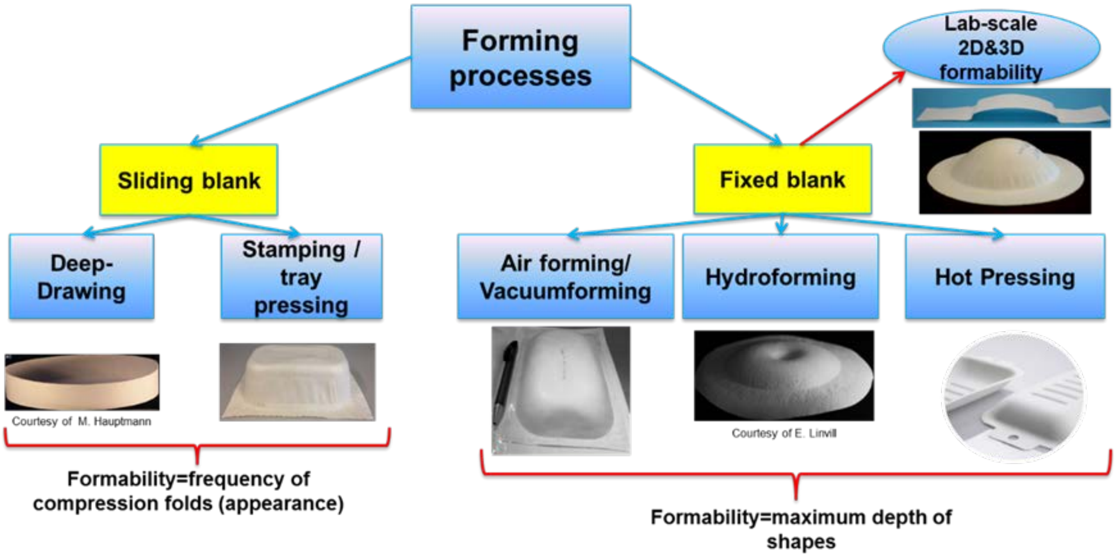


Figure: Classification of different forming processes according to the type of blank holding (Vishtal, PhD thesis, VTT Science 94, 2015).

By tailoring the fiber-fiber joint structure and molecular level interactions over the interface between fiber surfaces, it is possible to control the mechanical properties of the fibrous network on a macroscopic level. The gel-like layer at fiber surfaces affects the fiber-fiber interaction, the joint strength and flexibility. This layer and fiber joint design can be modified through chemical and enzymatic treatment or by addition of polysaccharides and polymers. The deformation properties of the fibrous network with suitable fiber joint properties and tailored drying shrinkage will also be studied. The strength and deformation mechanisms on the microscopic level are then connected to the deformation behavior of the fibrous network by numerical modelling. The strong partnership between Johan Gadolin Process Chemistry Centre and VTT Technical Research Centre of Finland is strengthened; the knowledge of fiber and paper physics at VTT is combined with the wood and wet-end chemistry expertise at ÅAU to form a unique consortium capable of solving the presented challenges.

Cooperation:
VTT

Future Biorefinery II Joint Research (FuBio)

Main funding: Tekes, FIBIC Ltd

Ikenna Anugwom, Jesús Arroyo, Johan Bobacka, Valerie Eta, Henrik Grénman, Jens Krogell, Petri Kilpeläinen, Ekaterina Korotkova, Jarl Hemming, Patrik Eklund, Tingting Han, Bjarne Holmbom, Ari Ivaska, Victor Kisonen, Ann-Sofie Leppänen, Jyri-Pekka Mikkola, Dmitry Murzin, Päivi Mäki-Arvela, Andrey Pranovich, Markku Reunanen, Jussi Rissanen, Tapio Salmi, Annika Smeds, Tao Song, Anna Sundberg, Maunu Toivari, Pasi Virtanen, Risto Korpinen, Jan-Erik Raitanen, Chunlin Xu, Stefan Willför

The FuBio project was a five-year, top-down planned research program to lay the foundation for a new knowledge-based forest biorefinery platform in Finland. The core of the program was to study and develop 1) new ways to fractionate wood into different material streams and 2) processing of these streams to generate material solutions for existing and new value chains. The first part of the project (FuBio Joint Research 1, 2009-2011) ended in 2011 and the continuation was split into two programs, namely the FuBio Joint Research 2 and the FuBio Cellulose (Products from dissolved cellulose) program that both ended in 2014.

The Fubio JR2 program created new insight into wood chemistry and promoted broad competence in hemicellulose separation technologies. Specifically it also improved understanding of the phenomena of hot water extraction of hemicelluloses.

FuBio JR2 was divided in different research work packages, where PCC was involved in WP1 (Hot water extraction and separation), WP2 (Novel biomass fractionation), WP4 (Improving traditional fiber products), and WP5 (Health-related applications). In FuBio Cellulose, PCC was involved in WP3 (New products). The main research areas considering PCC are hot water, as well as ionic liquid fractionation of wood components, hemicelluloses and there especially spruce galactoglucomannans (GGM) as barriers in papermaking, extractives in health products, and cellulose bead application technology.

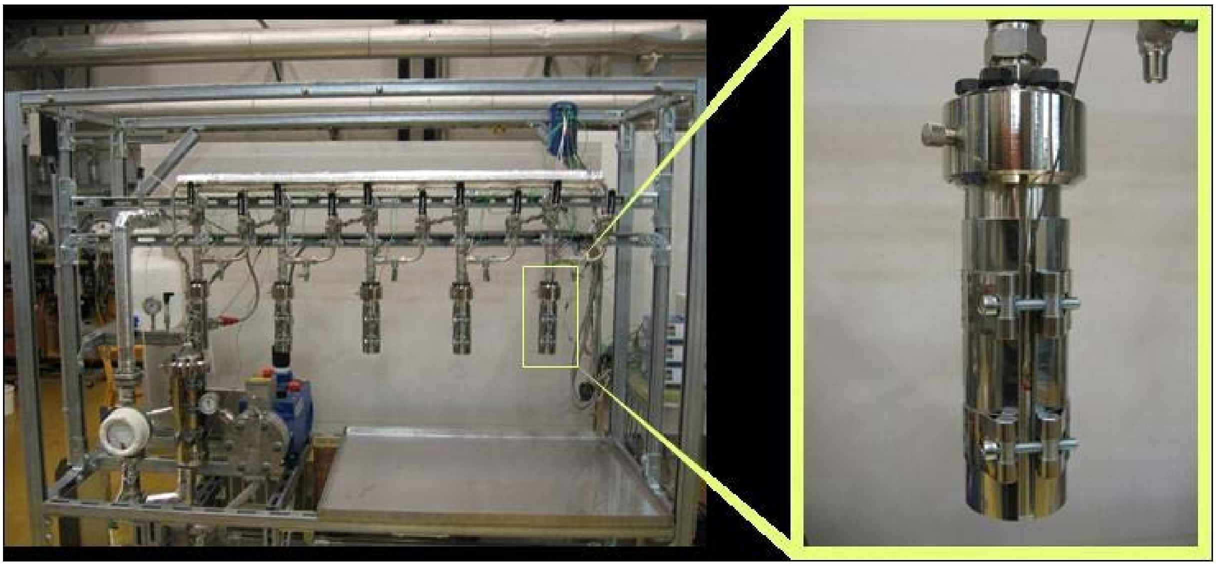
For hot water extraction, our ultimate objective was to develop a series of consecutive extractions for fractionation of wood into its main polymeric compounds: hemicelluloses, lignin, and cellulose, preferably with water and appropriate additives.

An entire new family of ‘switchable’ ionic liquids capable of selective removal of hemicelluloses, lignin and extractives from wood were synthesized. This technology enables separation of essentially pure cellulose to be used for other applications from industrial size chips. The search to optimize conditions for selective fractionation of woody biomass into its various fractions was continued by using an alkanol amine (MEA) and an organic superbase (DBU) derived SIL. The Short-Time-High-Temperature (STHT) approach involves the addition of large amounts of water thus rendering saline solvent systems for pulping. The aqueous SIL-wood mixture was kept at 160°C for two hours without stirring. While the mixture was still hot, the undissolved wood fraction was separated using vacuum filtration. The chip weight was reduced by 35 wt-% and 30 wt-% for the birch and spruce chips, respectively. Upon addition of isopropyl alcohol, the precipitated solid materials contained mostly lignin and about 10 wt-% and 25 wt-% hemicelluloses were recorded for spruce and birch, respectively. The results presented indicate selective lignin removal in a short time using SIL as the solvent, resulting in a hemicelluloses rich pulp as product.

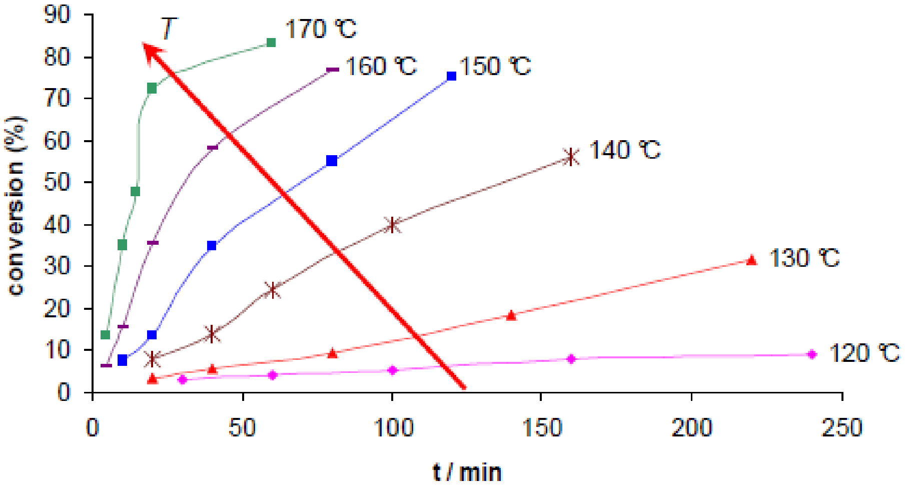
Different reactor operation modes were investigated in wood chip fractionation, such as recirculating loop reactor, SpinChem® aided stirring reactor and batch reactor.

The main aims of our work during the FuBio JR2 project were
- High-yield extraction of high-molar-mass (polymeric) GGM from spruce wood and kinetic modelling of the extraction process
- pH measurement and inline pH control in the extraction reactor
- With plain water and without buffer addition if possible
- providing as small as possible chemical altering of the residual material, which is important to a following extraction of lignin (lignin extraction)
- Purification (delignification) and also hydrolysis by heterogeneous catalysis of obtained hemicellulose fractions
- To study the influence on mass-transfer limitations: internal cell wall diffusion, effect of particle size and shape, surface, challenges with simultaneous extraction and hydrolysis, measuring and controlling the pH in the reactor at high temperatures during the extraction
- Chemical modification of spruce galactoglucomannans (GGM) to obtain hydrophobic barrier properties for coating of paper and board
- Chemical characterization for the use of wood extractives for health-related applications and final proof-of-concept studies. Special emphasis was laid on understanding the polymerization process and products that certain compounds seem to undergo.
- Study metal ion affinities of cationic cellulose beads that are prosperous materials for analytical separations and drug release and were prepared in the program

More detailed results have been reported in earlier yearbooks and will not be repeated here. However, it is important to point out that the except a large number of peer-review publications, four invention disclosures or patents, and reports, the Fubio program for PCC's part also directly generated two MSc theses and six PhD theses, as well as several theses that benefitted greatly from collaboration with the program.



Cascade reactor system for extraction of components from biomass.



The conversion of hemicellulose extraction as a function of time at different temperatures for 1.25-2 mm chips.

Cooperation:
FIBIC; VTT; Metla; Lappeenranta University of Technology; Aalto University; University of Jyväskylä; University of Helsinki; University of Turku; University of Tampere; University of Eastern Finland; Metsä Fibre; Metso; Kemira; Andritz; Pöyry; Stora Enso; UPM-Kymmene; Orthotopix; Pharmatest Services; Arbonova; Separation Research; Royal Institute of Technology (KTH), Wallenberg Wood Science Centre, Sweden; University of Valladolid, Spain

Renewable Materials as Barriers for Functional Packaging

Main funding: Tekes (Fibic Oy), Graduate School for Biomass Refining (BIOREGS), Knut and Alice Wallenberg Foundation

Victor Kisonen, Chunlin Xu, Stefan Willför

The objective of this research is to develop functional derivatives of GGM for applications in packaging. Different amphiphilic GGM derivatives, e.g. benzoate, succinate, and phthalate esters were prepared and evaluated as barriers, e.g. for grease, oxygen, water, and aroma compounds using carton board as a model packaging substrate. As obtained from non-food based side-stream resources, GGM and its esters project a sustainable and modern conception for barrier purposes in food packaging. Moreover, the composites of GGM esters and cellulose nanofibrils were also tested for the study of barrier properties.

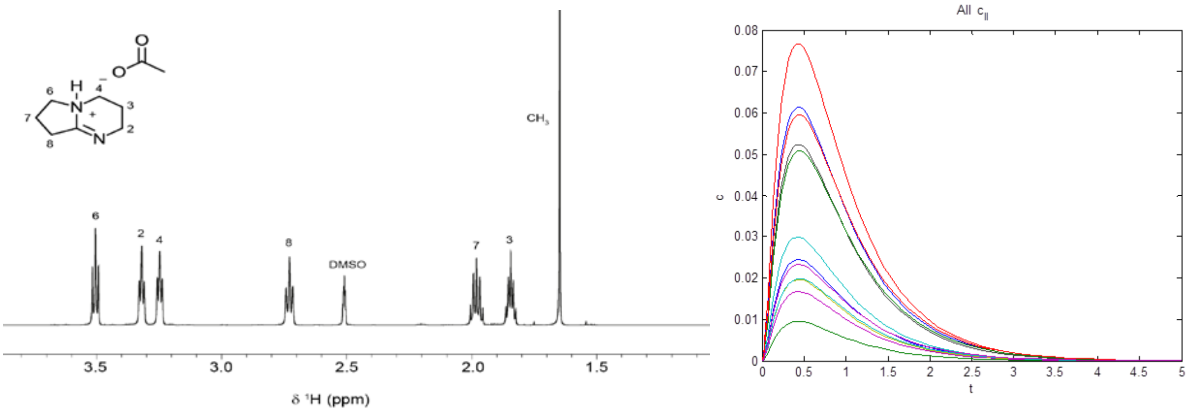
Cooperation:
KTH, Wallenberg Wood Science Center, Sweden; University of Helsinki; Aalto University

Cellulose Derivatives in Ionic Liquids

Main funding: Åbo Akademi University, Umeå University

Jyri-Pekka Mikkola, Olatunde Jogunola, Sakari Teerikoski, Tapio Salmi

Ionic liquids are excellent non-toxic, non-volatile reaction media for cellulose derivatives syntheses. This homogeneous process implies a big technology leap compared to the classical methods for preparing commercial cellulose derivatives, which are based on the use of suspended cellulose in a solvent/reagent, with all its cumbersome mass transfer limitations. In a dissolved state, cellulose reacts readily and cellulose derivatives with different functionalities are produced. The focus of the research project is on the etherification and esterification of cellulose. Breakthroughs have been made in the selection of suitable ionic liquids for cellulose acetylation and carboxymethylation. Cellulose acetates with different characteristics (DS range of 1.2 – 3.0) have been successfully produced in less than 0.5 h using an hybrid of ionic liquid, 1,5-diazabicyclo(4.3.0)non-5-enium acetate [HDBN][OAc] and co-solvents such as DMSO, acetonitrile and even acetone, which has been known to precipitate cellulose in solution. Special attention was paid to the development of a detailed scheme for the substitution kinetics of cellulose. Detailed kinetic modelling based on probabilistic theories and rate retardation was carried out. The new model is able to describe the detailed substitution kinetics even in cases when several substituents are added to the anhydroglucose unit of cellulose or hemicellulose. Furthermore, both water and organic soluble hydroxypropyl cellulose (HPC) used for artificial tears was synthesized in the ionic liquid/DMSO solution. Presently, the focus is on the synthesis of ionic liquid technology-based ethyl hydroxyethyl cellulose (EHEC) in the absence of NaOH or catalyst.



^{1}H NMR analysis of synthesized [HDBN][OAc] and theoretical simulation disubstituted anhydroglucose unit as a function of reaction time.

Cooperation:
Umeå University

3.2 WP2 - Conversion of sugars to chemicals

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

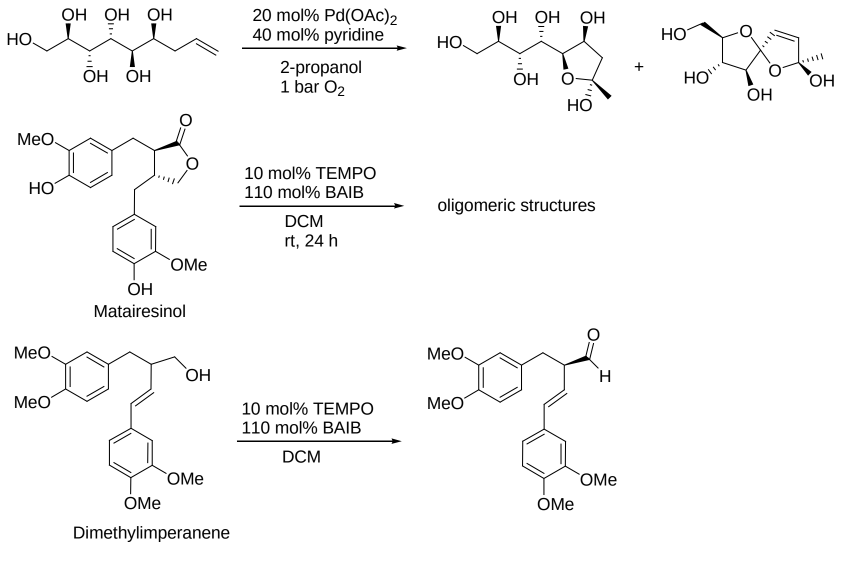
WP2 focuses on the chemistry and technology for making chemicals from monomeric sugars obtained by carefully controlled hydrolysis of hemicelluloses and cellulose. Recent research by us and other groups has shown that rare monomer sugars can be obtained in high yields from hemicelluloses. Furthermore, platform, fine and specialty chemicals can be obtained from the monomers of hemicelluloses and cellulose. WP2 combines organic chemistry, catalyst preparation, characterization, kinetic and mass transfer studies, continuous reactor technology and process intensification. The group has the experts on catalysis, chemistry and analysis of biomass, as well as on chemical kinetics and reaction engineering, needed for this subproject. 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.

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:

Laboratoire de Chimie de Coordination, Institut Universitaire de Technologie Paul Sabatier, France

Nanocatalysis in Transformation of Sugars

Main funding: EU SusFuelCat project

Atte Aho, Kalle Arve, Tapio Salmi, Elena Murzina, Dmitry Yu. Murzin

The aim is to make a breakthrough in the application of nanotechnology to synthesis of heterogeneous catalysts for biomass valorization, namely hydrogenation of sugars. In the current work colloidal Ru nanoparticles were immobilized on different carbon materials focusing on the development of effective approaches for capping agent removal for further application in catalysis. Several different carbon materials, such as mesoporous Sibunit, carbon nanofibers of platelet structure and TiC carbide-derived carbon, were used. To remove PVP both chemical washing and thermal treatment under different conditions were applied. The effect of preliminarily support modification, additional colloidal Ru nanoparticles washing with acetone prior to its immobilization and PVP removal procedure on catalytic properties and behavior in galactose hydrogenation was studied. TEM, XPS, XRF, and nitrogen physisorption were applied to characterize the carbon supports and synthesized catalysts. Chemical washing and thermal treatment of catalysts resulted in significant enhancement of catalytic activity in galactose hydrogenation. The optimal procedures of PVP removal for Ru NPs immobilized on Sibunit, TiC-CDC and CNF-Pl were determined based on their catalytic activity in galactose hydrogenation.

The key influence of Ru cluster size on catalytic activity was recently demonstrated by PCC researchers in hydrogenation of glucose. The highest turnover frequency (TOF) was obtained with a catalyst bearing average ruthenium particle size of ca. 3 nm. It is especially interesting to explore if other sugars display the same behaviour as glucose. Two model compounds were selected. One is galactose, an epimer of glucose, having the same number of carbon atoms but is different in orientation of -OH group at carbon in position 4. Another substrate selected for this study is arabinose, which is a pentose sugar.

Hydrogenation of arabinose and galactose was performed in semi-batch mode at 110°C and 20 bar hydrogen pressure over several Ru/C catalysts with different cluster size ranging between 1 and 8 nm. A clear maximum in the dependence of TOF on cluster size was found for ruthenium nanoparticles of ca. 3 nm. While the size of metal clusters had a clear influence on the reaction rate the obtained dependences were almost the same for both sugars bearing a different number of carbon atoms. A mathematical model of Langmuir-Hinshelwood type with cluster size dependent rate constants was proposed being able accurately describe a maximum in the turnover frequency at a specific the cluster size.

Cooperation:
Boreskov Institute of Catalysis, Technische Universität Darmstadt

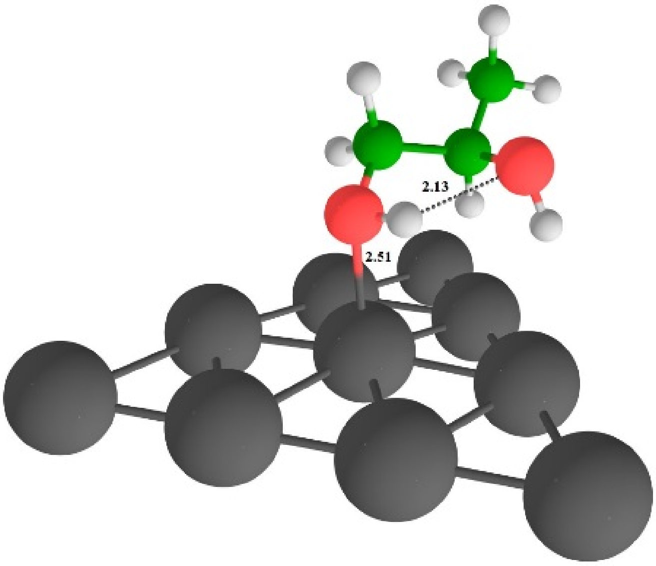
Sustainable Fuel Production by Aqueous Phase Reforming

Main funding: EU FP7

Lidia Godina, Alexey Kirilin, Anton Tokarev, Elena Murzin, Dmitry Murzin

The project aims at using biomass as a sustainable source for the production of hydrogen by the catalytic aqueous-phase reforming (APR). Besides direct hydrogen production APR is also seen as a route for making sustainable fuels. Promising hydrothermal stable catalytic materials for this reaction are noble metals supported on carbon nanomaterials. Main challenge for a successful optimization of the catalysts is the low level of understanding of this liquid/solid phase reaction as well as of hydrothermal degradation mechanisms. As supports various carbon nanostructures and tunable carbide-derived carbons in nano- and macrosize are used. The active metals Pt (Ni, Re) are deposited in a size/ shape controlled way by the colloidal synthesis. Combined efforts of theoretic calculations, synthesis of highly defined nano- and macroscopic model carbon supports and active species, advanced in-situ analytics and catalytic studies are done in this project to raise the level of insight for this important process.

Cooperation:
Friedrich-Alexander-University Erlangen-Nürnberg, Boreskov Institute of Catalysis, Novosibirsk; Biomass Technology Group, the Netherlands; FutureCarbon GmbH, Germany; Universidad Autonoma de Madrid, Spain; Università di Palermo, University of Twente



Adsorption geometry of 1.2-PDO on the Pt_{30} (111) surface.

Interconversion of aldoses to ketones on heterogeneous catalysts

Atte Aho, Elena Murzina, Tapio Salmi, Dmitry Yu. Murzin

Interconversion of aldose to ketose 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. Formation of fructose from glucose in fact is a well-known reaction practised at million-tons- per-year scale in the production of high-fructose corn syrup (HFCS) using an immobilized enzymatic catalyst – glucose isomerase This enzyme can be also used for interconversion of C5 sugar – xylose to xylilose. The final equilibrium mixture of fructose and glucose contains ca. 55% of the former.

Chemical conversion of glucose to fructose can be also done under alkaline conditions and at temperature higher than typically used (55-60°C) for the enzymatic process. Transformations in alkaline environment following the so-called Lobry de Bruyn-Alberda-van Ekenstein rearrangement are nonspecific leading to formation of side products. Conversion is typically limited resulting in fructose concentration of 40%. Aldose-ketose rearrangement is accompanied by epimerization which occurs in parallel to the main reaction. Other reactions, such as aldolization/retro-aldolization, elimination and benzylic rearrangement also contribute to formation of side products. Homogeneous bases such as NaOH, KOH, sodium aluminate etc. are frequently used for the isomerisation of glucose to achieve 30-50% of fructose yields. The aim of the current project is to investigate heterogeneous catalytic isomerization of aldoses to ketoses using heterogeneous base catalysts using galactose, xylose and arabinose as examples.

Cooperation:
Boreskov Institute of Catalysis, Bayer AG

From Carbohydrates to Valuable Bi- and Multifunctionals (CAVA)

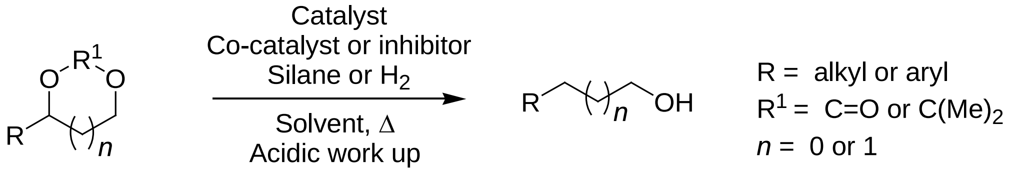
Main funding: TEKES

Atte Aho, Dmitry Yu. Murzin, Risto Savela, Tiina Saloranta, Reko Leino

In a collaborative effort between the University of Jyväskylä (Professor Petri Pihko and Dr. Karoliina Honkala) and Åbo Akademi University, the project aims at rational development of novel selective catalytic technologies for transformation of polyfunctional biomass derived compounds into valuable products and building blocks of industrial relevance. For this purpose, state-of-the art methods in molecular modeling, organic synthesis, heterogeneous catalysis and surface science are combined.

While many biomass based molecules possess potentially valuable intrinsic chirality resulting from multiple secondary alcohol functionalities, this may also be considered as a drawback in the use of such compounds as feedstock for base chemicals. Consequently, lowering of the oxygen content via cleavage of C-O bonds in biomass is of topical interest. One particularly prominent method is hydrodeoxygenation, often a combination of catalytic hydrogenation and catalytic dehydration.

The present project investigates robust and economic catalysts, such as iron. Also, the use of group IV metal precursors as catalysts or co-catalysts is under investigation. Of particular interest here is hafnium(IV) trifluoromethanesulfonate due to its long shelf life and moisture tolerance. The catalyst and co-catalyst combinations are being investigated for hydrodeoxygenation using silanes or hydrogen as the reducing agent, as illustrated in Scheme 1.



Deoxygenative reduction of organic carbonates and acetals.

The direct hydrodeoxygenation of diols and polyols usually requires high temperatures and pressures to function via removal of water, followed by subsequent reduction of ketone or aldehyde. Thus, it was postulated that derivatization of the diol to carbonate or acetal could enable lower reaction temperatures and pressures. Initial investigations using silanes as reducing agents, utilizing both iron and hafnium based catalysts as well as their combinations yielded promising preliminary results. While the use of hafnium alone functions for benzylic derivatives, addition of iron catalysts is required for aliphatic compounds. Unfortunately, the applications using iron based catalysts appear to suffer from significant purification problems.

Cooperation:
University of Jyväskylä (Professor Petri Pihko and Dr. Karoliina Honkala)

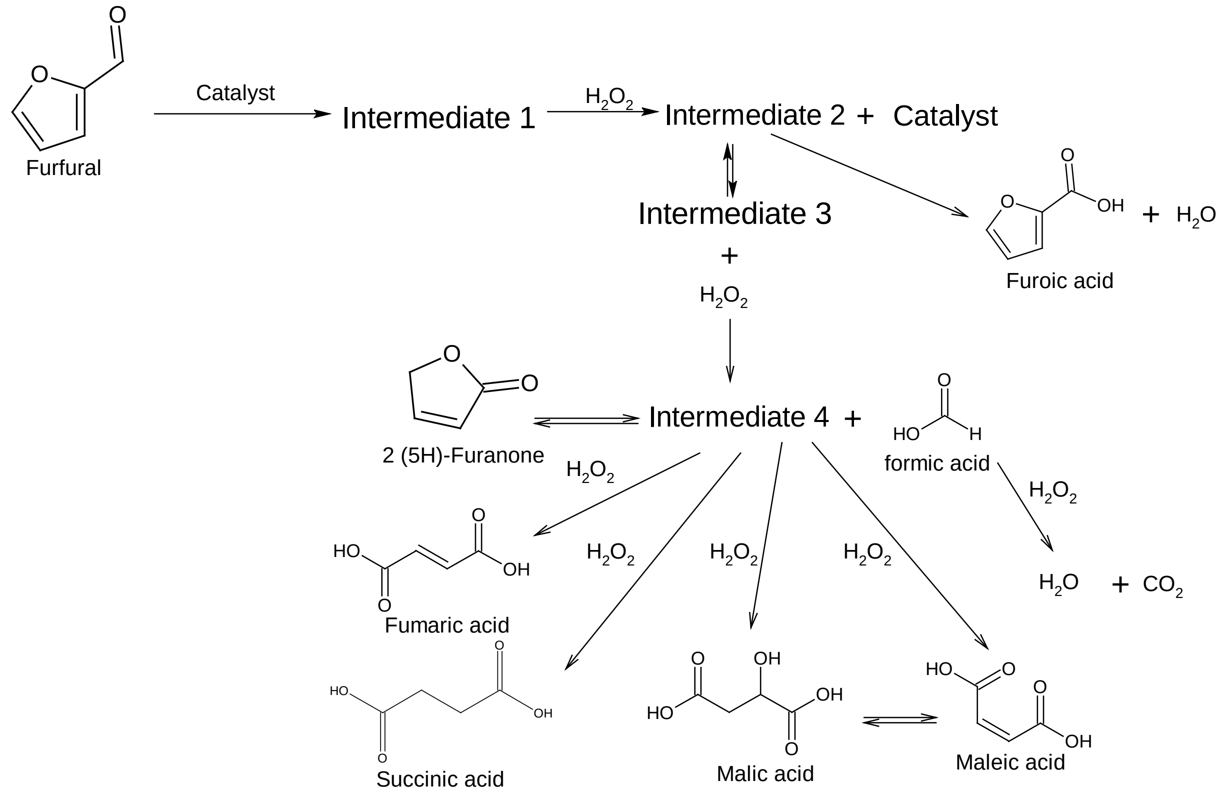
From Pentoses to Chemicals: Oxidation of Furfural

Main funding: TEKES, Magnus Ehrnrooth Foundation

Farhan Saleem, Yiran Chen, Dmitry Yu. Murzin, Tapio Salmi

Furfural is an important compound which is obtained from acid-catalyzed dehydration of pentoses (xylose), present in hemicellulosic part of biomass. This furan derivative can further be converted into valuable chemicals, such as succinic acid via oxidation with hydrogen peroxide. A variety of industrially relevant compounds, such as γ-butyrolactone (GBL), 1,4-butanediol (BDO) and tetrahydrofuran (THF) can then be derived from this acid. Furthermore, the use of hydrogen peroxide as a green oxidizing agent is more environmentally friendly compared to the conventional oxidizing agents such as nitric acid and molecular oxygen, which forms toxic wastes and requires high safety procedures in case of molecular oxygen. Secondly, the reaction proceeds directly in liquid phase under mild conditions at low temperature and atmospheric pressure after distillation of aqueous furfural solution from dehydration process.

An extensive series of kinetic experiments were conducted to reveal the velocity of the oxidation process and to elucidate the reaction mechanism. Rate equations were derived, based on the reaction mechanisms and the kinetic parameters were determined by regression analysis.



Simplified reaction mechanism

Production of Bioethanol from Macroalgae via Photo-Chemo-Enzymatic Processing

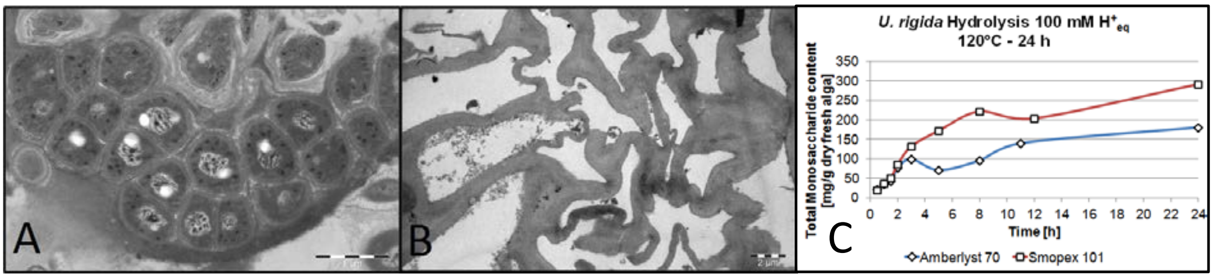
Main funding: Academy of Finland, National Commission for Scientific and Technological Research (CONICYT)

Ricardo Pezoa Conte, Andrea Baccini, Allison Leyton, Cristina Ravanal, Áron Dombovári, Melinda Mohl, Sari Hyvärinen, Päivi Mäki-Arvela, María Elena Lienqueo, Krisztián Kordás, Jyri-Pekka Mikkola

In the recent years, the use 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 for the production of fuels, chemicals and materials by means of different processes. The use of crops for bioethanol production has concerns related to the utilization of land for energy production instead of food for mankind. In turn, the use of lignocellulosic material for bioethanol production requires the addition of pretreatments with harsh conditions to assess lignin cleavage.

Algae are considered the most efficient ecosystem on earth. Estimations calculate that algae comprise almost half of the total biomass on earth. 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 containing sulfates such as ulvan, carrageenan, agar, as well as, pectins such as alginate are of huge importance.

The use of ionic liquids is of great importance because of their proved abilities to disrupt the biomass matrix and its properties to dissolve carbohydrates. Some interesting results have been obtained using novel ionic liquids for the dissolution of carbohydrates contained in green algae and for the pretreatment of brown algae for the enhancement of subsequent enzymatic hydrolysis of cellulose and alginate. We focus on the extraction of sulfated polysaccharides using hot water systems, studying the kinetics of the process, and subsequent hydrolysis of these algal carbohydrates using novel processes such as solid acid resins. The project pursues a tight collaboration with Chilean researchers, who are mostly focused on the finding of novel enzymes from marine microorganisms to hydrolyze alginate, and in substituting metabolic routes on traditional fermentative microorganisms to be capable to produce bioethanol from uronic acids. The Chilean researchers have focused on the identification and extraction of novel molecules from brown algae such as phlorotannins, which are of huge interest for the pharmaceutical industry.



A: TEM image from fresh Ulva rigida biomass. B: TEM image from IL processed U. rigida biomass. C: Hydrolysis kinetics of polysaccharides contained in U. rigida biomass.

Cooperation: University of Chile, University of Oulu

Chlorella Microalgae as Feedstock for the Production of Biofuels

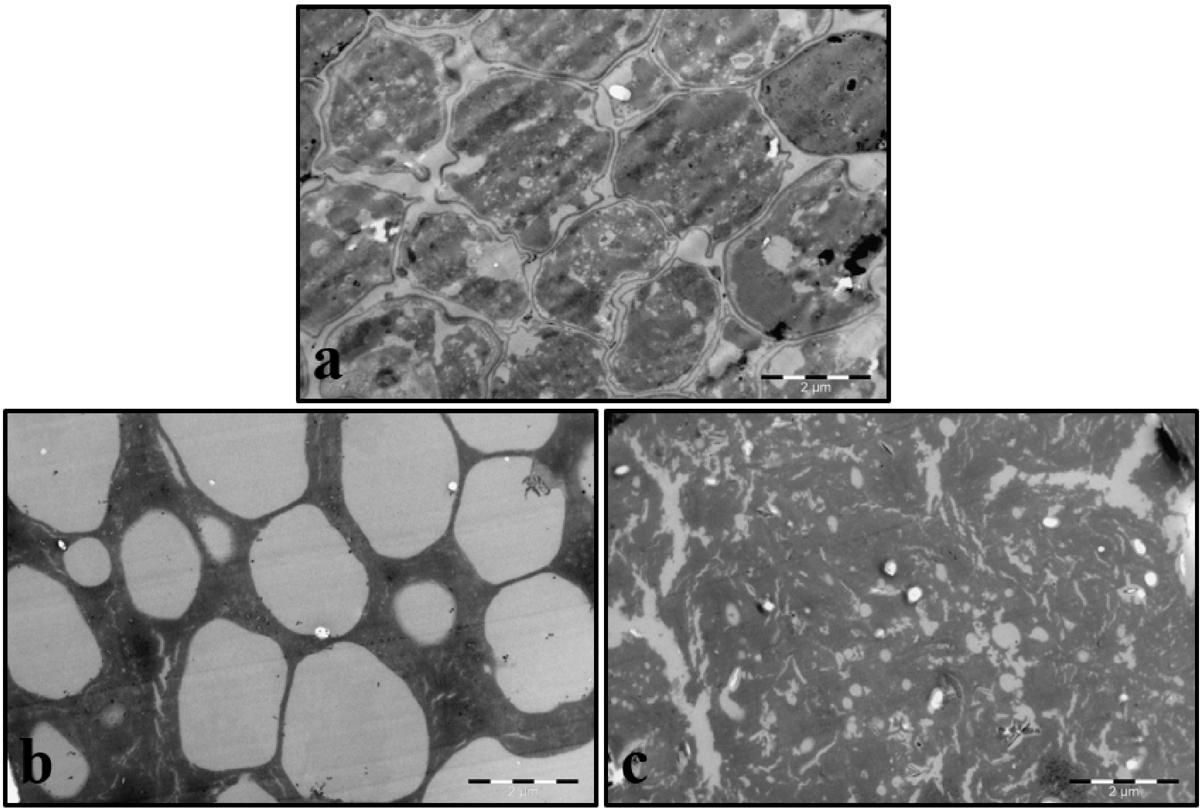
Main funding: Academy of Finland

Imane Hachemi, Päivi Mäki-Arvela, Hoang Nguyen, Narendra Kumar, Donato Alexandre Gomes Aranda, Dmitry Yu. Murzin

In order to process microalgae to fuels, lipids were extracted with supercritical hexane and treated in the presence of hydrogen to produce green diesel. Several Ni and Pd catalysts were tested in hydrodeoxygenation of algal oil.

The catalytic HDO of algal oil into green-diesel was performed in semi-batch reactor at mild conditions of temperature and hydrogen pressure. The conversion of lipids yielded to free fatty acids and C15 – C18 hydrocarbons (n-heptadecane and n-octadecane).

Nickel-supported catalysts were synthetized by wet-evaporation impregnation method and characterized by N_2-desorption, SEM, EDXA, TEM, TGA, NH_3-TPD, CO_2-TPD, ICP-OES, CO-chemisorption, and TPR.



Transmission electron microscopy images of Chlorella samples (a) Fresh Chlorella, (b) and (c) Treated Chlorella by supercritical hexane at 300 rpm for 2 h.

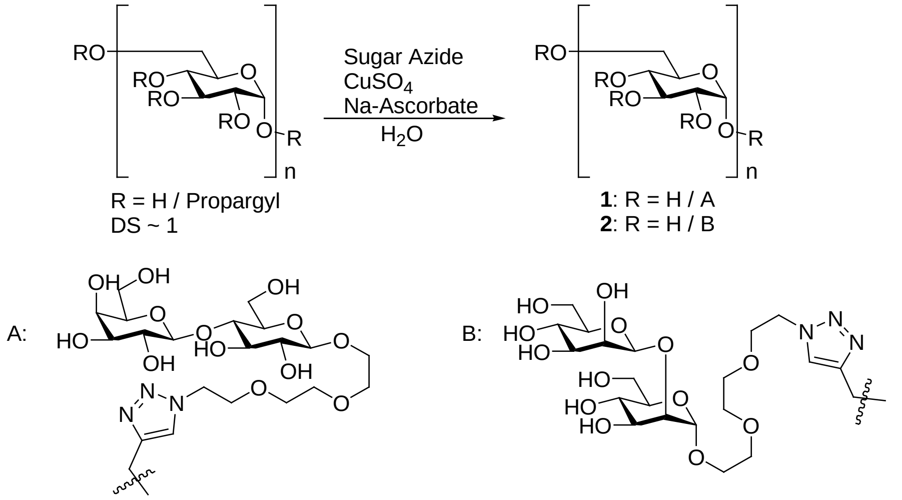
Cooperation:
Federal University of Rio de Janeiro

Investigating the Binding of Mannans to Galectin-3

Main funding: Magnus Ehrnrooth Foundation

Jani Rahkila, Reko Leino

Galectin-3 (Gal-3) is one of the 10 known human galectins. It is, as the name suggests a galactose-binding protein and plays important roles in for example cell-cell adhesion, angiogenesis, apoptosis as well as other biological systems. The protein is known to bind the cell wall polysaccharides of *Candida albicans* an opportunistic fungal pathogen. It does not, however, bind the cell wall polysaccharides of *Saccharomyces cerevisiae*, i.e. baker's yeast. The main difference in the polysaccharides is that the cell wall of *C. albicans* contains, in addition to a backbone of α-(1→6)-linked mannose with α-(1→2) and α-(1→3) branches, some branches terminating in β-(1→2) linkages. It has been suggested that Gal-3 binds to these rather unique structures.



Azidofunctionalized lactose and β-(1→2)-linked mannobiose will be attached to a propargyl-functionalized dextran backbone via click chemistry which provides the target compound in good yield without formation of byproducts.

To probe this binding, we have prepared a polysaccharide structure that imitates the *C. albicans* cell wall. The structure consists of a dextran (i.e. α-(1→6)-linked glucose polysaccharide) backbone with lactose units attached via a triethylene glycol linker connected to the dextran by a triazole moiety. A similar analogue containing β-(1→2)-linked mannobiose instead of lactose will also be prepared and the binding to Gal-3 will be investigated using binding assays and NMR spectroscopic methods.

Cooperation:

This project involves cooperation with the research group of Jesús Jiménez-Barbero at the CIC-bioGUNE in Bilbao, Spain, professor Hans-Joachim Gabius at the Ludwig Maximilian university of Munich, Germany, and Dr. Filip Ekholm at the University of Helsinki.

Highlighted Publications:

Rahkila, J.; Panchadhayee, R.; Ardá, A.; Jiménez-Barbero, J.; Savolainen, J.; Leino, R. **Acetylated Trivalent Mannobioses: Chemical Modification, Structural Elucidation, and Biological Evaluation** *ChemMedChem,* **2016**, *11*, 562–574. (Issue front cover).

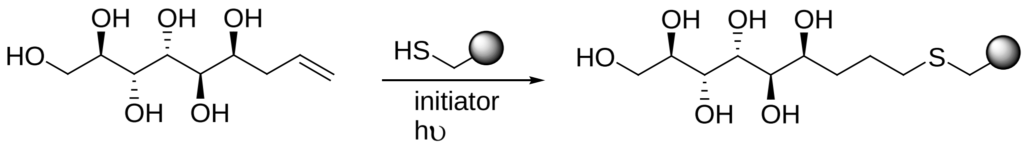
Smart Materials from Sweet Molecules

Main funding: Johan Gadolin Process Chemistry Centre

Ida Mattsson, Tiina Saloranta, Reko Leino

The use 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 and especially the open chain aldehyde form. A representative example of a reaction that targets the aldehyde functionality selectively is the metal mediated (typically In och Sn) allylation of unprotected monosaccharides that yields effectively alkene-terminated polyols. However, literature examples capitalizing on the potential of these polyols in material applications are still scarce.

In earlier work from our group, it was shown that when the monosaccharide allylation procedure is applied to D-mannose, the major diastereomer formed can be isolated by simple precipitation from ethanol. Furthermore, the D-mannose derived alkene-terminated polyol was shown to form hydrogen bonded packings that aggregate from water due to highly ordered linear conformation of this particular substrate. The perfectly linear conformation was proved by combined NMR spectroscopic, computational and X-ray crystallographic methods.



UV-induced thiol-ene coupling of D-mannose derived polyol with various thiols.

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.

Cooperation:

Academy professor Olli Ikkala, Department of Applied Physics, Aalto University School of Science

Highlighted Publications:

Saloranta, T.; Peuronen, A.; Dieterich, J.; Ruokolainen, J.; Lahtinen, M.; Leino, R. **From Mannose to Small Amphiphilic Polyol: Perfect Linearity Leads to Spontaneous Aggregation** *Cryst. Growth Des.* **2016**, *16*, 655-661.

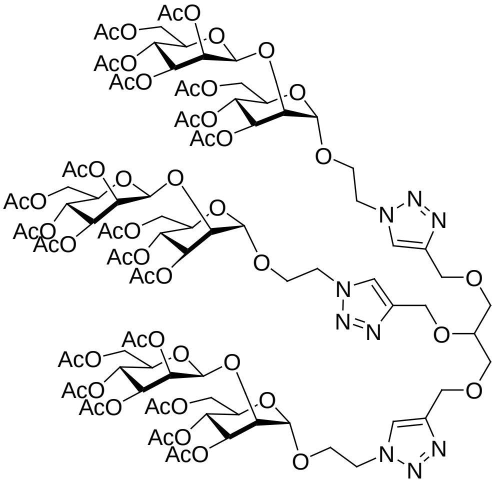
Gunell A. Från kolhydrater till finkemikalier: **Syntes av mannosbaserade polyolderivat.** *MSc Thesis*, Åbo Akademi University, Turku, Finland, **2015**

Immunostimulatory Glycocluster Adjuvants

Main funding: Tekes TutLi - New Knowledge and Business from Research Ideas: Synthetic oligosaccharide adjuvant for treatment of allergies (2014-16) and Synthetic glycocluster for immunotherapy of cancer (2015-17)

Reko Leino, Johannes Savolainen, Denys Mavrynsky, Jani Rahkila, Risto Savela, Tiina Saloranta

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 a fully acetylated, synthetic trivalent β-(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-γ 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 now been investigated also 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 these two Tekes-supported commercialization driven projects, preclinical proof-of-concept is sought in the potential application of the mannoside glycocluster as such or as adjuvant in Allergen specific immunotherapy (SIT), and preclinical proof-of-principle 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:
Both projects are jointly funded and carried out in close collaboration with the University of Turku, Professor Johannes Savolainen and other collaborators.

3.3 WP3 - Refining options of lignin

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

The valorization 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 sulfite lignin currently available. Potential value-added products include carbon fibers, 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 lignin, 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 sulfur-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 pressurized hot water (PHWE). PHWE lignin has recently been thoroughly characterized 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 fiber fraction using a milder alkaline process (patent pending) in comparison to traditional Kraft pulping. This approach also processes the biomass at lower temperatures (< 150°C) than in traditional pulping.
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. Good adhesive function, which is required from biocomposites, demands crosslinking of the lignin molecules, and furthermore attachment to the wood or other material.

Lignin will also be studied as an environmentally friendly corrosion-inhibitor additive. Lignin from softwoods is a relatively low-molar-mass product and with guaiacyl units as the main structural element, which is expected to be particularly favorable for use as a corrosion inhibitor additive. Traditional corrosion inhibitors are in some cases toxic and/or carcinogenic. Therefore, there is a growing interest in finding new natural components to replace traditional corrosion inhibitors for use in surface-protection products (coatings and paints) on metals, and as solution additives in process environments.

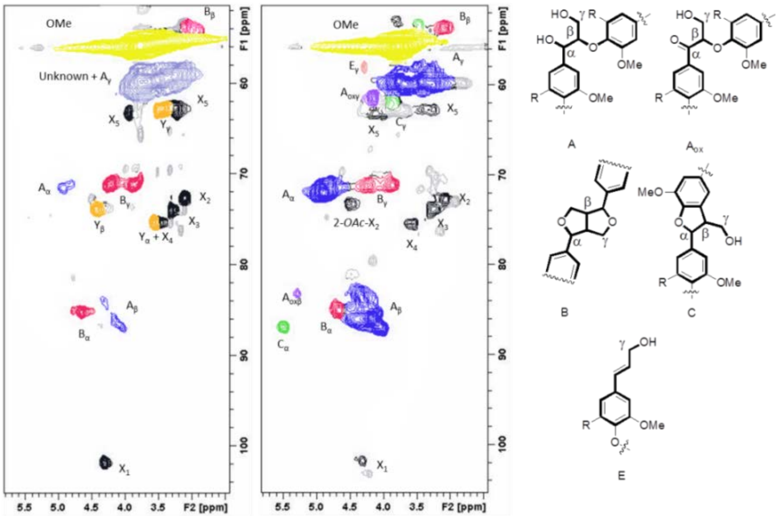
Exploring the Structure and Reactivity of a Novel Type of Mild Alkali Pressurized Hot-Water Extracted Lignin (BLN-lignin)

Main funding: Suomen Luonnonvarain Tutkimussäätiö

Patrik Eklund, Lucas Lagerquist, Stefan Willför, Tarja Tamminen, Marjatta Louhi-Kultanen

Research at Åbo Akademi University has shown that wood can be fractionated by pressurized hot-water extraction. However, very recently, our collaborator (Ab BLN-woods Ltd.) has developed a new optimized way of isolating lignin in addition to cellulose and hemicelluloses, by pressurized hot-water extraction under mild alkaline conditions. In comparison to traditional pulping or to previously known pressurized hot-water extractions, this process is operated at lower temperature using oxygen starved conditions together with a suitable additive.

The aim of this project is to characterize the lignin isolated by the BLN-process and to compare it with the previously known lignins. Both classical wet chemistry and more detailed structural analyses by different instrumental methods will be performed In addition, the chemical properties and reactivity will be studied by oxidative and reductive modifications. During this project, the structural difference of the BLN-lignin compared to other types of lignins, is expected to be determined. Based on the structural properties and reactivity more tailored functionalization of this lignin will be investigated.



HSQC spectra showing the difference between BLN-lignin (left) and MWL (right).

A method for isolation and purification of the BLN-lignin (Birch) from the black liquor has been developed and the structure and properties were compared to a birch MWL by different techniques. Based on the results the structure of BLN-lignin was shown to be "kraft-like" with most of the β-O-4 bonds cleaved. However, is seems to contain more arylglycerol endgroups and it is more defined and pure than most technical kraft lignins. The M_w was determined to be approximately 3100 (M_n 20147) and the total free hydroxyl group content 4.73 mmol/g.

Cooperation:

Technical Research Centre of Finland (VTT), Espoo; Department of Chemical Technology, Lappeenranta University of Technology (LUT), Lappeenranta; Ab BLN-Woods Ltd.; University of Tuscia, Viterbo, Italy; BLN-Woods Ltd

Spruce lignin as a renewable source for novel biomaterials

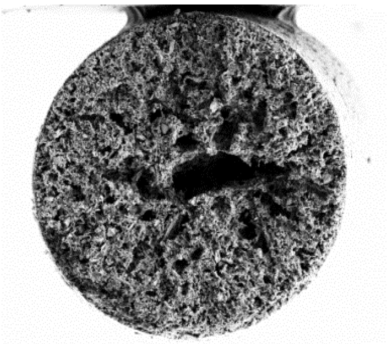
Main funding: International Doctoral Programme in Bioproducts Technology, Johan Gadolin Process Chemistry Centre

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.

A great number of research nowadays is dedicated to usage of lignin in different areas from energy recovery to fine chemicals production. One of the promising directions of lignin use is as adsorbents. Lignin represents a promising feedstock for carbon material production by its carbonization and copolymerization with synthetic polymers. The possibilities to obtain adsorbents based on spruce lignin isolated with low concentration alkali solution and polyacrylonitrile (PAN) were studied in this work.

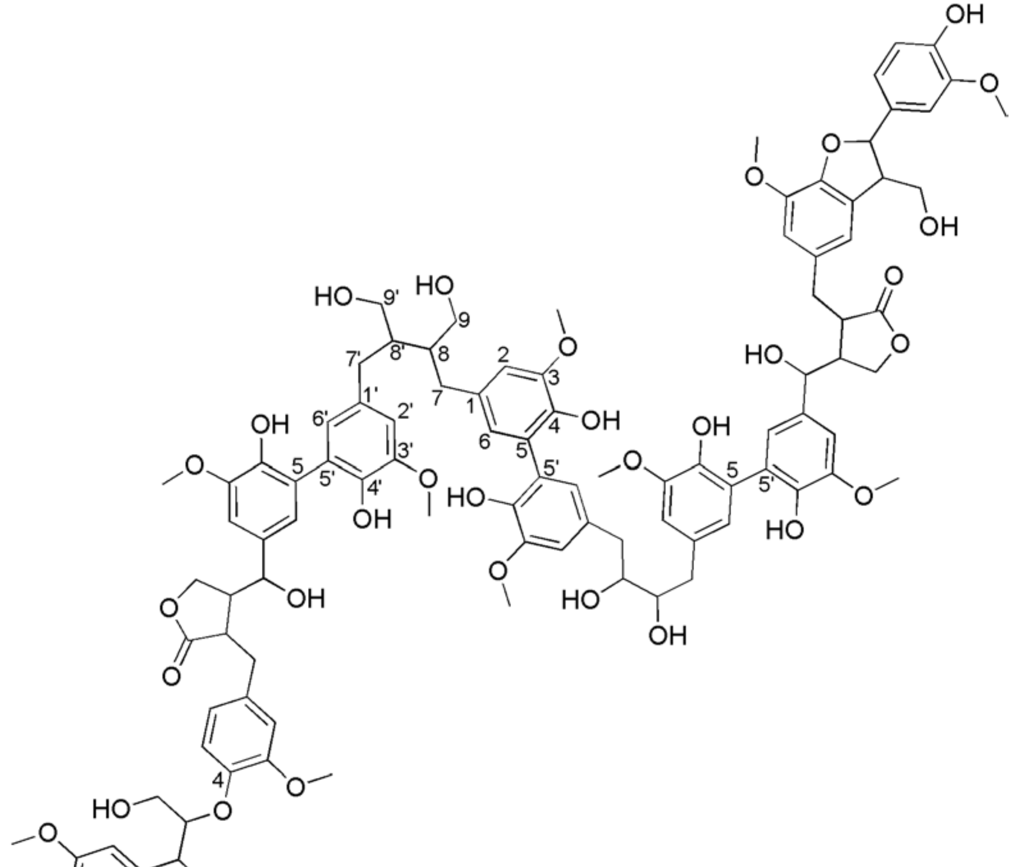


It was possible to obtain fiber-precursors with 50 wt% content of lignin and suitable mechanical strength for the further carbonization step. The resulting fibers have promising properties as precursors of carbon fibers for adsorbents with controlled porosity. The advantages of precursors with high lignin content are lower carbonization temperature in comparison with PAN-fibers. The carbonization is accompanied by significant formation of low toxicity volatile lignin thermal destruction products. Results obtained by TGA of the fiber-precursors in oxidizing atmosphere showed that destruction started at 114°C. Residual weight of sample after thermal analysis was 29.41%. Weight loss takes place due to removal of volatile fragments from lignin, mainly guaiacol; 4-methylguaiacol; 4-vinylguaiacol; trans-isoeugenol; and polyacrylonitrile fragments: pentanedinitrile-2-methyl, 4-ethyl-2-pentenedinitrile, butanedinitrile and others, as determined by Py-GC-MS.

Chemical Characterization of High-molar-mass Fractions in a Norway Spruce Knotwood Ethanol Extract

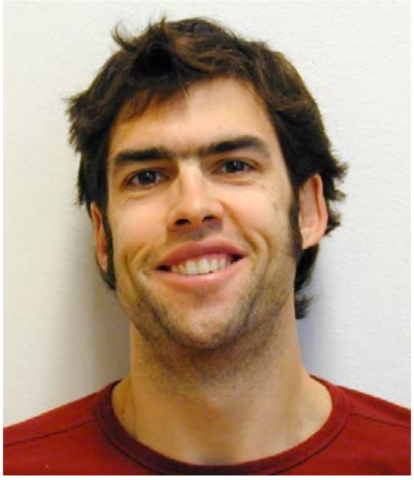
Annika Smeds, Patrik Eklund, Stefan Willför

The low-molar-mass (LMM) fraction, only, *i.e.*, the GC-eluting compounds, which are mainly lignans, has been characterized in Norway spruce knotwood hydrophilic extracts previously. In this work, dilignans and the GC non-eluting compounds (the high-molar mass fractions, HMM) were characterized in a 7-hydroxymatairesinol-reduced knotwood ethanol extract of Norway spruce by using several fractionation and analytical techniques. An MTBE insoluble fraction of the extract contained mainly HMM material, of which the main part was shown to consist of oligolignans with a molar mass up to approximately 3700 Da. They are suggested to consist of one or two different lignans that are linked by 5−5´ bonds, some of them containing one or two guaiacylglycerol ether units linked to the lignans by β−O−4 or β−5 bonds.



Tentative molecular structure of a tetralignan consisting of two 7-hydroxymatairesinol and two secoisolariciresinol units, with one guaiacylglycerol unit linked by a β−O−4 bond and the other by a β−5 bond.

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.

Chemistry of Biomass impurities at Reducing Conditions in Future Thermal Conversion Concepts

Main funding: Academy of Finland
1.9.2013-31.8.2017

Mikko Hupa, Daniel Lindberg, Fiseha Tesfaye, Hao Wu

New technologies are being developed to increase the efficiency of thermal biomass conversion for electrity and heat production as well as for producing new chemicals, such as various gasification or pyrolysis-based technologies However, many aspects of the chemistry of the fuel impurities are not fully understood at reducing conditions. In the present project we will study corrosion of construction materials of future thermal conversion technologies, the chemistry of the important fuel impurities, such as sulfur, halogens, alkalis, lead and zinc and their effects on deposition formation and emissions. Various experimental and modeling tools are utilized to study these phenomena specifically for reducing conditions. The results from the project will support solving specific industrial problems, such as prevention of potential harmful emissions and materials corrosion and fouling in future thermal conversion concepts, such as gasifiers and different types of furnaces.

Sustainable Utilization of Ash, Slag and Pyrolysis Residuals – TUULI

Main funding: Ekokem Oy , Stora Enso Oyj, Jyväskylän Energia Oy, Helsingin Energia, Fortum Power and Heat Oy, Rovaniemen Energia Oy, Kemira Chemicals Oy, Ruukki Metals Oy, Boliden Harjavalta Oy, Metsäliitto Osuuskunta, Metso Power Oy, Nordkalk Oy Ab, Paroc Oy Ab and Tekes.

Patrik Yrjas, Daniel Lindberg, Tor Laurén, Mikko Hupa

The project started in late 2012 and ended in March 2015. The target of the project was to create a viable business ecosystem between ash and slag producers, handlers and utilizers. The aim was to study how ash and slag properties can be developed by means of mechanical and chemical processing as well as by optimizing incineration conditions. The utilization potential of processed ash fractions was examined in a range of applications.

The role of Åbo Akademi was to test, analyse and predict the risks for the combustion process when changing fuel input to improve ash quality. Combustion tests were done in Piteå, Sweden within the EU-BRISK project. ÅA also evaluated the behaviour of ash minerals by thermodynamic equilibrium modeling. Also, a literature study on heavy metal separation from ashes has was done.

Cooperation:
University of Oulu, Ekolite Oy, University of Lapland, VTT Technical
Research Centre of Finland Ltd., Oulu University for Applied Sciences

Clustering Innovation Competence of Future Fuels in Power Production - CLIFF

Project coordinator: Top Analytica Oy
Research coordinator: Åbo Akademi

Main funding (and partners): Tekes, 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

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, Paulo Santochi, Jingxin Sui

CLIFF is a three year (July 2014– June 2017) joint research project between several industrial companies operating in the area of biomass and waste to energy. These are Amec Foster Wheeler Energia Oy, Valmet Power Oy, UPM-Kymmene Oyj, Andritz Oy, Top Analytica Oy Ab, 3motion Oy, Clyde Bergemann GmbH and International Paper Inc. The activities within CLIFF include confidential company-specific tasks and a common activity part, the CLIFF Common Platform Activity Program, which is to a large extent research, development and innovation tasks subcontracted from several research organizations in Finland. The Common Platform, which is coordinated by Åbo Akademi, is done by Tampere University of Technology, Lappeenranta University of Technology, Aalto University and VTT Technical Research Centre of Finland Ltd. The CLIFF project is coordinated by Top Analytica Oy Ab.

The topics of the Common Platform activities are focused on selected physical and chemical phenomena and processes which are found to be important when new solutions and products are being developed to the global market by the partners. The topics are not directly connected to any specific novel products being developed, but rather focus on generic, deeper understanding of aspects of strategic importance to the partners in their next generation of business concepts and products.

The activities within the Common Platform will to a large extend be realized as parts of Academic Theses (Masters, Doctoral). The results will this way be public domain after the end of the program. The Common Platform is divided into five work packages, which in turn contains a number of tasks. The work packages are:

WP 0. Scientific co-ordination
WP 1. Fuels and feedstock
WP 2. Theoretical and modelling
WP 3. Materials
WP 4. Information

Material Value Chains – ARVI

Main funding: Tekes and 18 Finnish companies

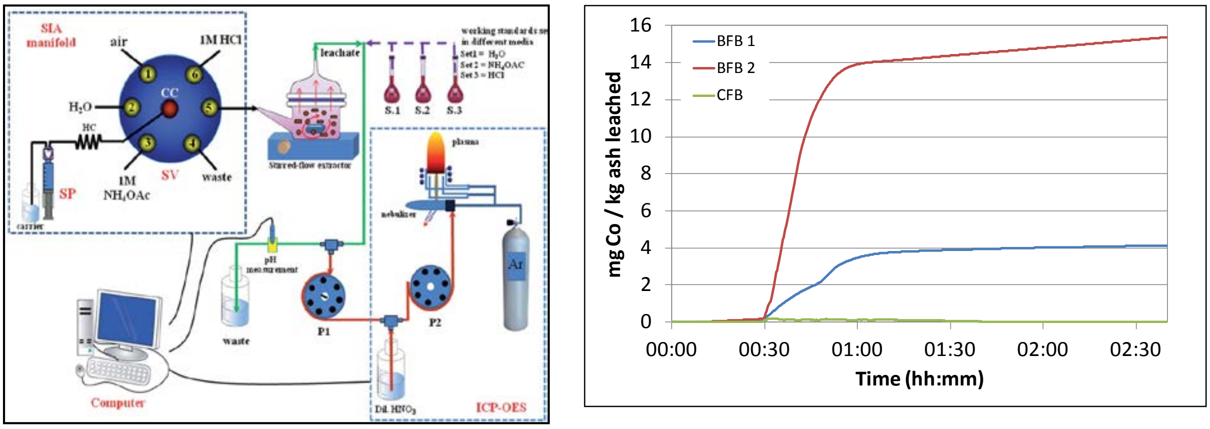
Patrik Yrjas, Emil Vainio, Daniel Lindberg, Mikko Hupa

Timetable of whole program: 1.1.2014 – 31.12.2016
Duration: 48 months

The program, coordinated by CLEEN Ltd., consists of a consortium of 29 organisations out of which 18 are companies and 11 research organisations. The research in ARVI program focuses on systemic assessment of material recovery and recycling opportunities. Attention is very much laid on studying recycling of such materials and elements. 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 sopficated overall analyses of material value chains. The program is divided into four work packages:

WP 1: Systemic evolution of business and its local environment
WP 2: Improved knowledge of material flows - analyses and foresight
WP 3: Systemic resource efficiency - concept building, modelling and optimisation
WP 4: Case Studies for Plastics, WEEE, MSW and Ashes

Within the four work packages the work is devided into different themes: plastics, electronic waste, municipal waste and ashes. The work by Åbo Akademi is focused on ashes and the elemental behaviour and leachabilites. 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.)



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

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.

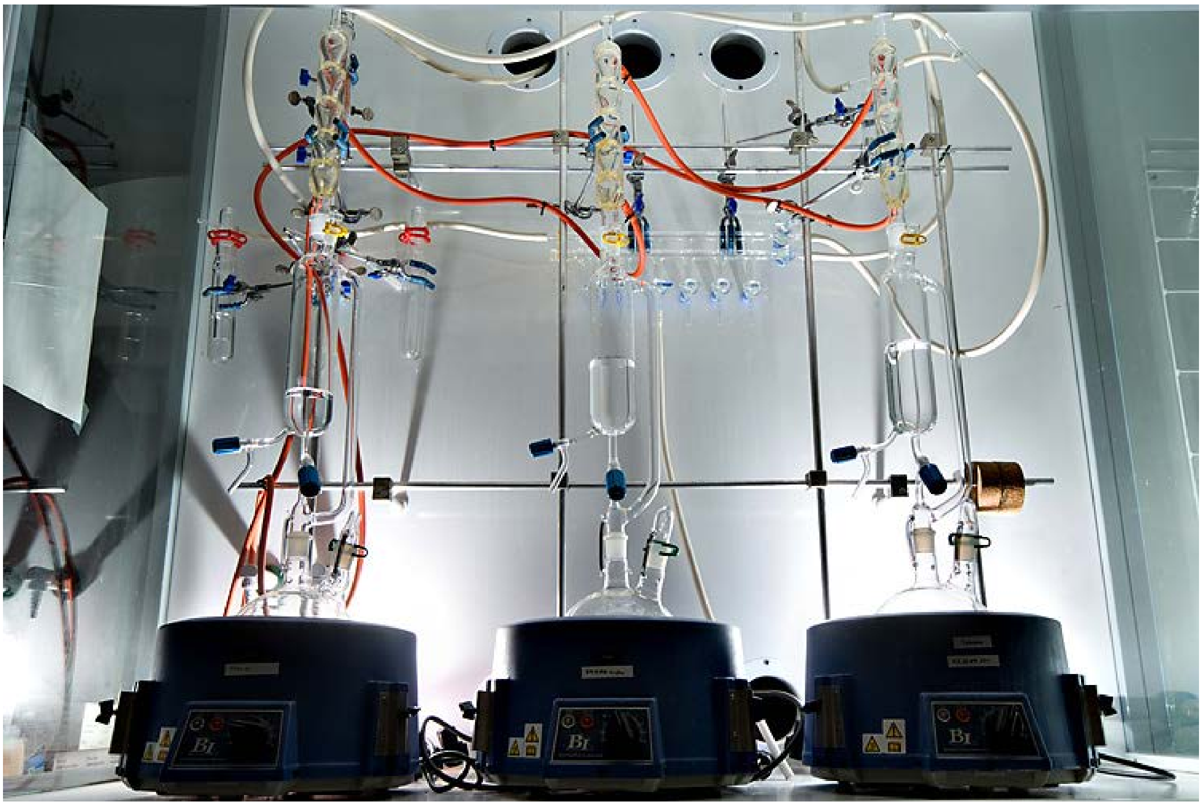


Photo: Denys Mavrynsky

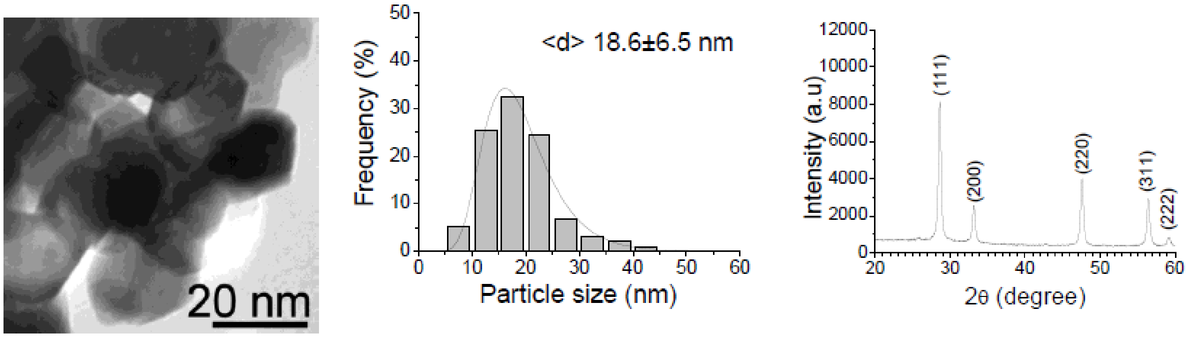
Equipment for solvent distillation over Na under Argon.

Novel Functional Materials

Main funding: Åbo Akademi University

Narendra Kumar, Sabrina Schmidt, Kai Yu, Alexandra Torozova, Irina Simakova, Jyri-Pekka Mikkola, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

Synthesis of new materials, such as different micro- and mesoporous materials as well as supported metals has been carried out. These materials are intended to be used in catalysis, drug delivery and building construction. The effect of ultrasonic treatment on zeolite crystallization has been studied. *In situ* metal modification has been applied in preparation of metal modified zeolites and molecular sieve catalysts. The prepared catalysts are characterized with modern techniques, such as XRD, SEM, TEM, AFM and TPD. The catalysts are applied in many projects, for instance in hydrocarbon transformations as well as in preparation of fine chemicals. The deactivation and regeneration of zeolite materials is investigated. Sensor materials and microreactor coatings have been synthesized and successfully applied. Quantum chemical calculations, FTIR and solid state NMR have been used to characterize the active sites on zeolites.
Cooperation:
Estonian National Institute of Chemical Physics and Biophysics, Tallinn, University of Turku; Åbo); Hungarian Academy of Sciences, Budapest, Hungary; Jagiellonian University, Kraków, Alexander von Humboldt-Universität, Berlin, Boreskov Institute of Catalysis, Novosibirsk



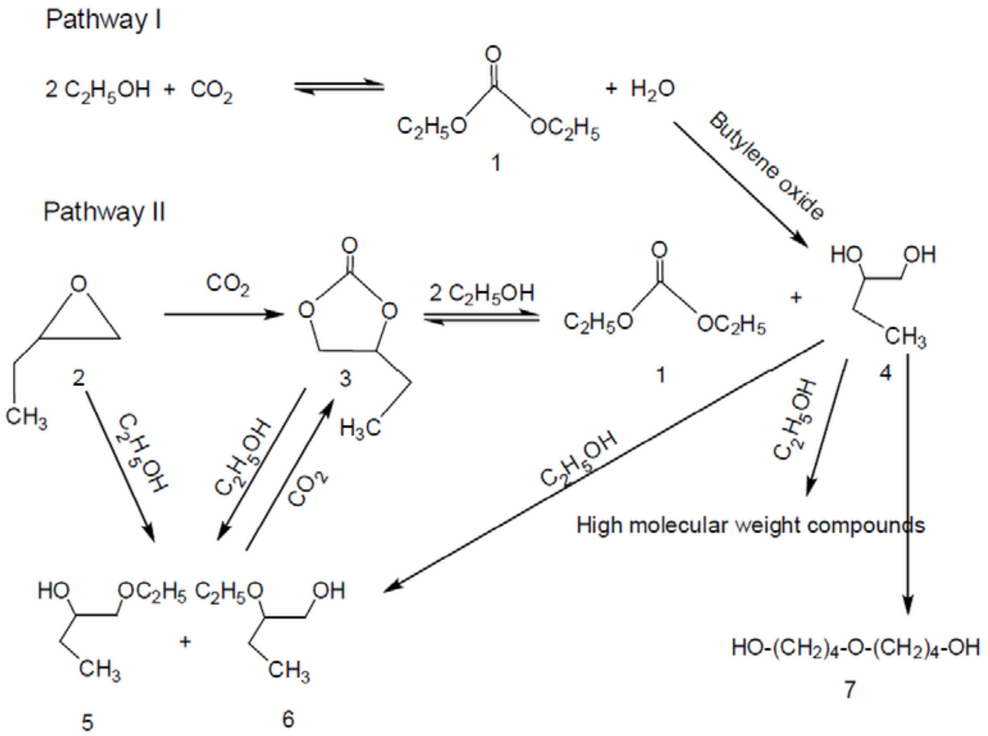
TEM images, metal particle size distribution and XRD patterns of the CeO2 catalysts prepared within different synthesis.

Complex Reaction Kinetics and Thermodynamics

Main funding: Graduate School of Materials Research (GSMR), CIMO, Neste

Johan Wärnå, Jyri-Pekka Mikkola, Valerie Eta, Ewelina Leino, Karolina Maduna Valkaj, Antonina Kupareva, Anastasia Tkacheva, Simon Bridier, Eero Salminen, Soudabeh Saeid, Maria Pinilla de Dios, Sergio Perez, Frans Storgårds, Andreas Franz, Pasi Tolvanen, Päivi Mäki-Arvela, Tapio Salmi, Dmitry Murzin

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 were esterification, oxidation of aldols, various catalytic hydrogenations, aldol condensation, CO_2 utilization and reactions between solids and liquids, as well as production of pharmaceuticals. Both conventional and microreactors are used. New catalyst concepts and new kinetic models were used for the alkyl carbonate synthesis (CO_2 utilization). 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 new sub-project was started with the aim to destroy rests of pharmaceuticals in wastewaters. The approach is to use ozonation combined to heterogeneous catalysts.



The reaction pathway in the synthesis of diethyl carbonate from ethanol and CO_2 using butylene oxide as the dehydrating agent.

Cooperation:
VTT; Recoil; Forchem; Université de Bourgogne, France; University of Oulu; INSA Rouen, France

Solid Foams as Structured Reactors

Main funding: Graduate School in Chemical Engineering (GSCE), Fortum Foundation

Tapio Salmi, Jyri-Pekka Mikkola, Teuvo Kilpiö, Ali Najarnezhadnashhadi, Vladimir Shumilov, Erfan Behravesh, Kristoffer Lindfors, Leena Hupa, Johan Wärnå, Kari Eränen, Dmitry Murzin, Markus Schubert

Fibers, solid foams and monoliths provide an attractive alternative for traditional catalyst technologies, since they combine the immobility of the catalyst to a short diffusion path, which guarantees a minimized mass transfer resistance. Fiber catalysts and monoliths enable a continuous operation for processes, which traditionally have been carried out batchwise, particularly synthesis of fine chemicals. Three kinds of fiber catalysts have been investigated: polymer-based fibers as well as silica and carbon fibers. The former ones have applications in esterification, etherification and aldolization reactions, while the latter ones are used after metal impregnation in oxidation and hydrogenation reactions. Hydrogenation of aldehydes and ketones has been used as model reactions. Compared to conventional catalysts, a clearly improved performance has been achieved, since the internal mass transfer limitation is suppressed. Ruthenium-impregnated carbon cloths showed a high activity in the hydrogenation of various sugars, such as arabinose and galactose to corresponding sugar alcohols. A breakthrough was achieved in the preparation and use of solid foams based on ceramic structures. The foam structures are applied in sugar hydrogenation as well as hydrogenation of other aldehydes and ketones. The work is done as a collaboration between industrial chemistry and inorganic chemistry. The solid foams are characterized with tomographic techniques available at Helmholtz-Institut at Dresden-Rossendorf.

A structured catalyst, open-cell Aluminum foam after polymerization step (left) and after activation (right).

Cooperation:
Helmholtz-Institut Dresden-Rossendorf, TU Dresden, University of Tver

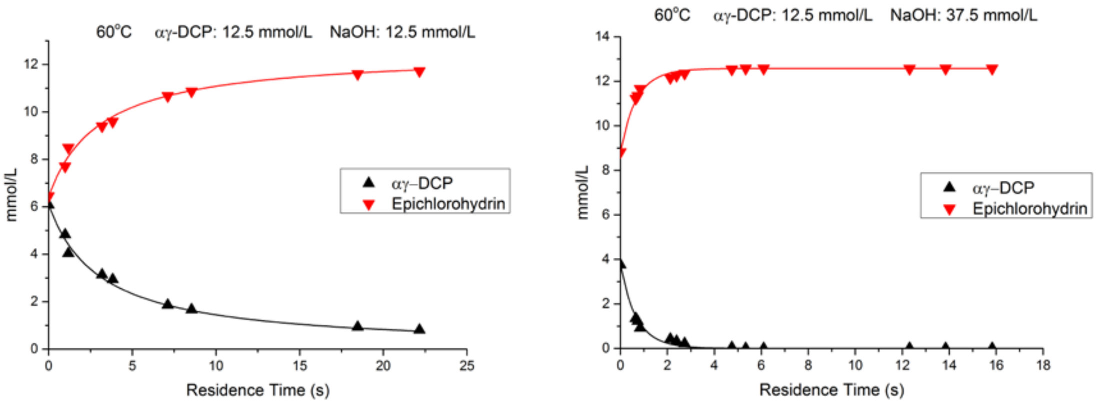
Micro- and Milliscale Reactor Technology

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

Kari Eränen, José Rafael Hernández Carucci, Sabrina Schmidt, Zuzana Vajglova, Quentin Balme, 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 Gas-phase microreactors have been successfully implemented to prepare chemical intermediates, such as ethylene oxide, methyl chloride and ethyl chloride. 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. The catalyst materials showed a high activity and selectivity in the halogenation process and very high yields and selectivities of methyl and ethyl chloride were obtained. 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 precily 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.



Reaction kinetics and mathematical modelling of epichlorohydrin formation in a millireactor.

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

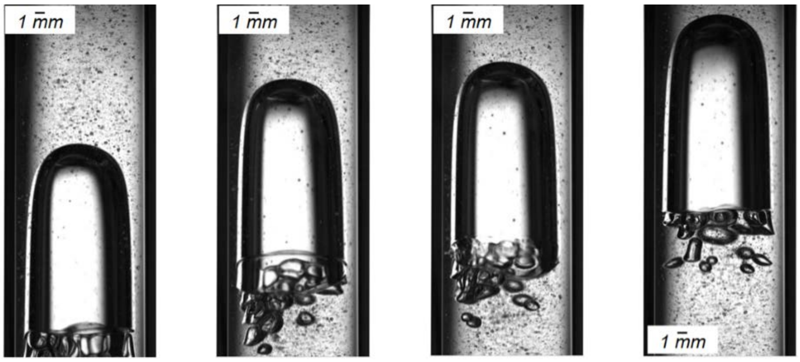
Multiphase Reactors

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

Johan Wärnå, Teuvo Kilpiö, 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, Irene Huerta, Paolo Canu, Lionel Estel, 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 a very successful both in semibatch 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.



t*= 0 ms t*= 66 ms t*= 86 ms t*= 140 ms

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

Cooperation:
Università di Napoli, Università di Padova, INSA Rouen, Universidad de Valladolid

Batch and Semibatch Reactors for Reactive Solids

Main funding: PCC, FIBIC

Henrik Grénman, J-P. Mikkola, Jussi Rissanen, Andrea Perez Nebreda, Pasi Tolvanen, Claudio Carletti, Vincenzo Russo, Daniel Valtakari, Päivi Mäki-Arvela, Johan Wärnå, Dmitry Murzin, Tapio Salmi

Kinetics and morphology of reactive solids is a fascinating area of chemical reaction engineering. In recent years, we have performed an extensive research programme concerning many liquid-solid reactions, from mineral leaching to selective extraction of hemicelluloses. Batch and semibatch reactors are frequently used in the production of fine and specialty chemicals through solid-liquid reactions. The aim of the project is to develop experimental equipment and procedures for obtaining very precise kinetic data and to carry out advanced modelling of chemical kinetics and mass transfer in (semi)batch reactors. Typical case studies are reactions of solid materials with organic compounds in liquid phase as well as decomposition of organic materials in liquid phase. A new theoretical approach was presented for the starch oxidation process, where an interesting two-stage reaction sequence was discovered. Solid particles change their morphology during the reaction; for instance, craters appear on the surface. Furthermore, the solid particle distribution changes as the reaction progresses. A new mathematical model was developed to describe these effects: morphology change, change of porous layer thickness change as well as change of the particle size distribution. The new theory for solid-fluid kinetics has been presented at numerous conferences and articles in the best journals in chemical engineering.

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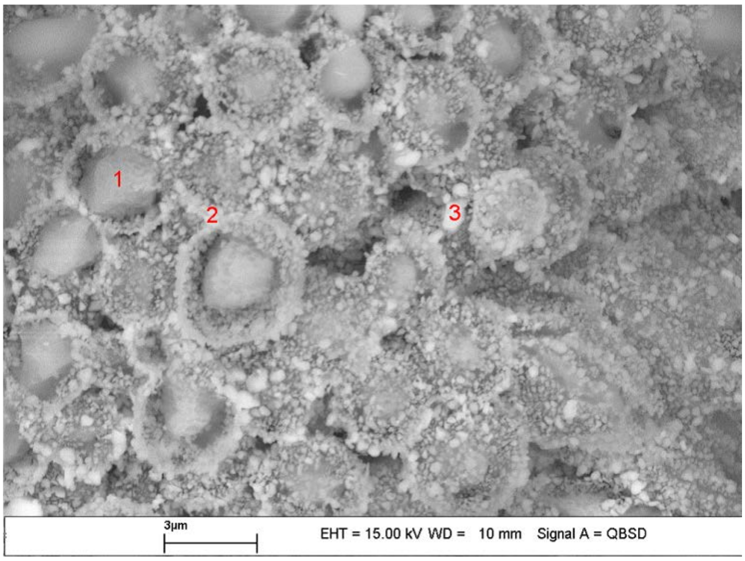


Elemental sulphur particles were formed during the dissolution process with zinc sulphide.

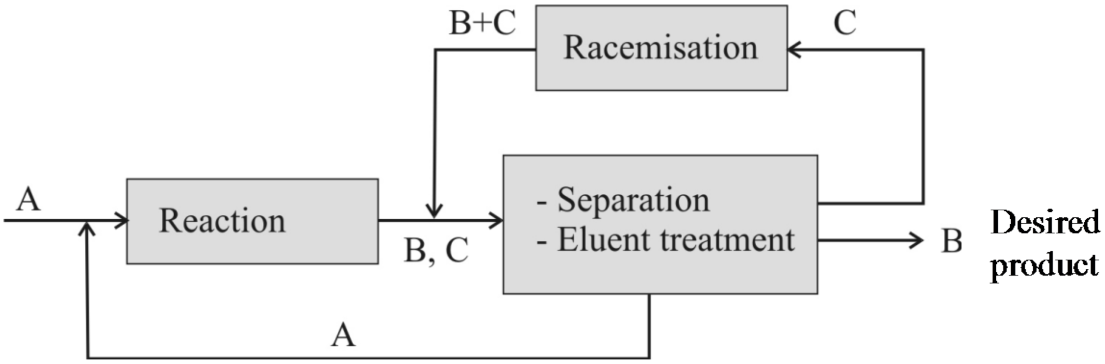
Cooperation:
Università di Napoli, Università di Bologna

Asymmetric Catalysis and Chromatographic Separation

Main funding: Åbo Akademi University

Gerson Martin Curvelo, Carla Pereira, Päivi Mäki-Arvela, Rainer Sjöholm, Reko Leino, Henrik Saxén, Frank Pettersson, Alirio Rodrigues, Dmitry Murzin, Tapio Salmi

Enantioselective catalytic hydrogenation of ketones provides a pathway to a cleaner synthesis of optically active compounds, which are used as intermediates for pharmaceuticals. The aim of the project is to develop new catalytic technologies for the production of enantiomerically pure compounds through selective catalytic hydrogenation in the presence of catalyst modifiers. Molecular modelling is used as a tool to increase the understanding in enantioselective hydrogenation. New multicentered adsorption models have been applied to enantioselective hydrogenation. The enantioselective hydrogenation has been performed in a batch and in a continuous reactor and the transient behavior of the system has been modelled quantitatively. The work is mainly focused on the combination of enantioselective hydrogenation and chromatographic separation in order to elaborate a green process concept, which minimizes waste production and maximizes the production of desired enantiomers. The experimental work gave proof that it is possible, and a completely new technology for enantioselective hydrogenation was developed, based on the use continuous fixed bed reactors and chromatographic separation. Advanced mathematical modelling was applied on the enantioselective hydrogenation and chromatographic processes, in close collaboration with University of Porto.



Schematic illustration of the proposed clean and continuous process for preparation of optically active chemicals

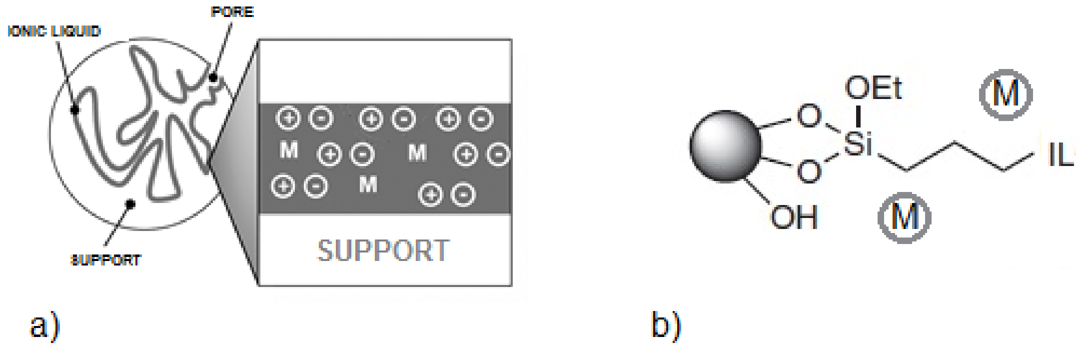
Cooperation:
University of Porto, Portugal

Preparation of Valuable Organic Chemicals – from Homogeneous Catalysis to SILCA and Batch to Continuous Technology

Main funding: Graduate School of Chemical Engineering (GSCE)

Nemenja Vucetic, Pasi Virtanen, Eero Salminen, Jyri-Pekka Mikkola, Dmitry Yu. Murzin, Tapio Salmi

The aim is to make a breakthrough in the transformation of selected organic compounds (alkenes and halides) to valuable products through Heck reaction by palladium-based catalysts in micro reactors. A new catalyst heterogenization concept, supported ionic liquid catalyst (SILCA) will be applied. In first part of a project the work will be focused on development and tuning of a semi-continual and continual process in tubular flow reactor (mesoscale). Different particle sizes of silica as a support for IL will be used. Unofficially the plan is to test reaction in one batch reactor. This will provide us valued data for further work on micro reactor level. In micro reactor a SILCA catalyst will be prepared by coating the reactor walls with a thin layer of a carrier (silica) and catalytically active compound. Durability and selectivity of the catalyst is strongly dependent on catalyst preparation and solvent that is used in reactor system. Water as a greenest solvent draw our attention and at this level it is studied as a possible solution. Two main approaches in catalyst synthesis can be stated here: physisorption methodology wherein ionic liquid layer is bounded to support by van der Waals interaction and chemisorption approach where ionic liquid is covalently anchored to surface of the carrier. Both approaches are studied in this work and there are schematically represented below. Different reaction conditions, reactants and ionic liquids will be tested.



(a) Supported ionic liquid catalyst made by physisorption and (b) chemisorption technique.

Later on, the flow pattern in the reactor will be characterized by tracer experiments under chemically inert conditions. Four different approaches to flow modelling will be used: simple flow models based on the concept of plug flow, laminar flow and dispersive flow (axial dispersion model) and the most advanced flow modelling based on Navier-Stokes equations (computational fluid dynamics, CFD). Also, a systematic kinetic study will be carried out by changing the residence time in the reactor, the reaction temperature and the reactant concentration. Systematic planning of experiments will be applied to obtain the best possible efficiency in the experimental work. These data will be used in kinetic modelling.

The European Research Infrastructure for Thermo-Chemical Biomass Conversion (BRISK)

Main funding: European Commission Seventh Framework Programme

Anders Brink, Oskar Karlström, Maria Zevenhoven, Mikko Hupa

The overall objective of BRISK (1.10 2011 to 31.9 2015) is to integrate leading European research infrastructures for advancing fundamental and applied research in thermochemical biomass conversion. The BRISK network links 25 leading centers of biofuel research located in 14 different countries and well spread over the entire European region. Feedstocks like woody biomass, crop residues, sewage sludge, municipal solid waste and other traditional and novel biogenic sources will be employed for a wide spectrum of powerful and, in many cases, unique laboratory-based and pilot-scale equipment. The project is devided into three different types of activities. The Networking activities will foster cooperation and interrelation between project participants, between the project and the scientific community at large, and between the project and other clusters or related projects: this will ensure broad dissemination of results, human resources exchange and ultimately the enhancement of the scientific and technical quality of the services provided by BRISK itself. In the Joint Research Activities, activities are to further enhance targeted, critical services offered by the facilities included in the BRISK network. JRA WP1 focuses on the development of methodologies for characterization of new feedstocks, 2nd generation biofuels, and residues. JRA WP2 deals with the development of advanced measurement methods and operational procedures in thermochemical biomass conversion JRA WP3 will improve methods for advanced testing, examination, and optimization of catalytic conversion processes of biosyngas conversion to 2nd generation liquid or gaseous biofuels. The core of the project is the Transnational Access activities. Within this frame work European researchers will have free access to a larger number of installations. The BRISK project is creating new opportunities via the equivalent of around 3400 experimental days for Transnational Access for an expected 220 user-visits over a 4 year period, BRISK will enable users to conduct high quality research.

PCC is involved in two of the three Joint Research Activities. “Task 6.1 Methods for characterisation of feedstocks, 2nd generation fuels and residues based on small batch reactors” , “Task 7.1 Particle sampling system for lab scale fluid bed”. In addition two facilities for second generation biofuel characterization is offered within the Transnational Access framework. The project period of the BRISK project is 1.10 2011 -30.9 2015.

Cooperation:
Kungliga Tekniska Högskolan – Coordinator (Sweden), Åbo Akademi University Finland, Aston University (United Kingdom), BIOENERGY 2020+ GmbH (Austria), Cardiff School of Engineering (United Kingdom), Centre for Research and Technology Hellas (Greece), Danmarks Tekniske Universitet (Denmark), Delft University of Technology (The Netherlands), Energitekniskt Centrum i Piteå (Sweden), Energy Center of the Netherlands (The Netherlands), Fundacion Ciudad de la Energia (Spain), INERCO Ingeniería, Tecnología y Consultoría (Spain), International Flame Research Foundation (Italy), L'Agenzia ENEA (Italy), Norges Teknisk-Naturvitenskapelige Universitet (Norway), PALL Filtersystem Corporation (Germany), Paul Scherrer Institute (Switzerland), Stiftelsen for Industriell og Teknisk Forskning (Norway), Technische Universität München (Germany), Technische Universität Wien (Austria), TUBITAK MRC Energy Institute (Turkey), Universidad de Zaragoza (Spain), Università degli Studi di Napoli Federico II (Italy), Wroclaw University of Technology (Poland)

Negative CO_2 - Negative CO_2 Emissions with Chemical-Looping Combustion of Biomass

Main funding: Nordic Energy Research

Anders Brink, Maria Zevenhoven, Leena Hupa

Negative CO2 is a multi-partner and cross-disciplinary project funded by Nordic Energy Research. The project runs from November 2015 to October 2019. The research topic is CO2 capture during biomass combustion by means of an innovative and potentially revolutionary technology. The ultimate goal of the Negative CO2 project is the development of new competitive technology that:

- enables CO2 capture and negative CO2 emissions with the lowest possible cost and energy penalty
- is able to produce power and/or steam for industrial and other applications
- utilizes Nordic expertise and competence in fluidized bed technology
- eliminates thermal NOx emissions and has potential to achieve more efficient fuel utilization compared to ordinary biomass combustion.

The technology capable of achieving these goals is Chemical-Looping Combustion of biomass (Bio- CLC), a unique and innovative combustion technology that will be studied and developed in the project. 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 gas separation can be avoided. Because of this, CLC is expected to have at least 50% lower energy penalty and cost than any other CO2 capture technology. In this project Åbo Akademi University focus on the interaction between ash forming matter and oxygen carrier material as well as on corrosion in Chemical-Looping Combustion.

Cooperation

The project partners are Chalmers University of Technology (coordinator), the Bellona Foundation, Sibelco Nordic AB, SINTEF Energy Research, SINTEF Materials and Chemistry, VTT Technical Research Centre of Finland Ltd and Åbo Akademi University. Associated with the project is also an advisory board, consisting of industrial stakeholders with interest in the project: Alstom Power AB, Andritz Oy, AKZO Nobel, Elkem AS, E.ON Sverige AB, Fortum Oyj, Foster Wheeler Energia, Göteborgs Energi, Titania A/S.

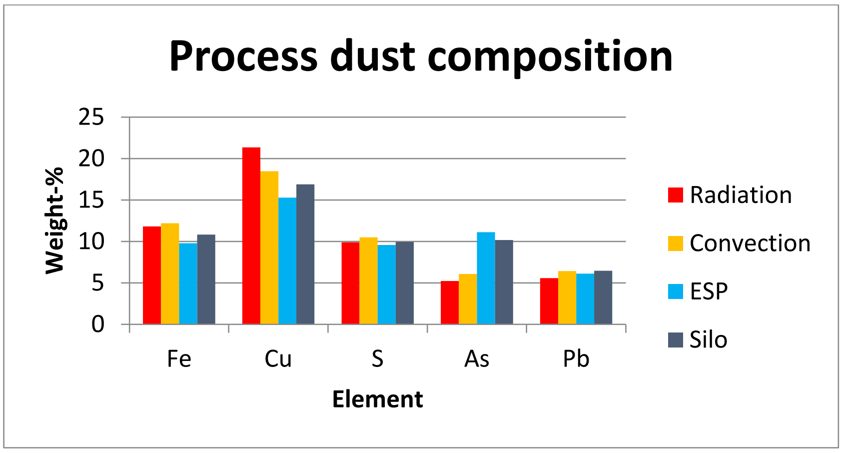
In-Furnace Measurements of Deposit Build-Up and Corrosion in a Copper Flash Smelting Heat Recovery Boiler

Juho Lehmusto

Flash smelting is a method used for extraction of primary copper and nickel from sulphide ores through a continuous process, which can be considered to be nearly auto thermal and thus, very cost-effective. The reaction heat originating from the feedstock is utilized as an energy source for the smelting process, obviating the necessity of an external fuel. One characteristic of the process is a large amount of unburned inorganic material, such as oxidic flue dust, entering the heat recovery boiler, where the temperature of the process gas is decreased from around 1400 °C to 350 °C. In this temperature range, metallic sulphates become thermodynamically stable and since the process gas typically contains around 40 vol% SO_2, sulphation of the oxide-containing flue dust occurs. The sulphation reactions are highly exothermic, resulting in sintering of the flue dust particles, which might then adhere to the heat-transfer surfaces in the heat recovery boiler, resulting in decreased heat-transfer efficiency and blockages of the gas flow path. In addition to the high SO_2 content, process gas also contains water vapor and excess air, enabling the formation of sulfuric acid (H_2SO_4). The H_2SO_4 formation originates from the presence of catalytic vanadium and/or other metals in the flue dust, enabling the oxidation of SO_2 to SO_3, which can then further react with water vapor to H_2SO_4. The formed H_2SO_4 might then condense on the heat-transfer surfaces, resulting in corrosion and severe material degradation. The aim of the project was to improve the understanding of deposit formation and corrosion in a copper flash smelting plant through full-scale in-furnace measurements. This was executed by collecting flue dust samples and determining corrosion rates at different locations of the plant.

The samples for dust analyses were taken from the dust silos in the radiation part, convective part, electrostatic precipitator (ESP), and dust recycling silo. The chemical composition of the samples was determined with SEM/EDX (see image below). Based on the corrosion rate tests, the main corrosion mechanism appears to be sulfuric acid dew point corrosion.

The results of this project can be used for developing the heat recovery process in a flash smelter and improving the productivity of the whole smelter process since broader understanding about the build-up chemistry and corrosion behavior will surely save the process operators from unexpected shutdowns.



The chemical compositions of process dust at different locations of the process line

Online Corrosion Monitoring for the Combined Combustion of Coal and Chlorine-Rich Biomasses in Pulverised Fuel and Circulating Fluidised Bed Systems - OnCord

Main funding: Research Fund for Coal and Steel (EU-RFCS)

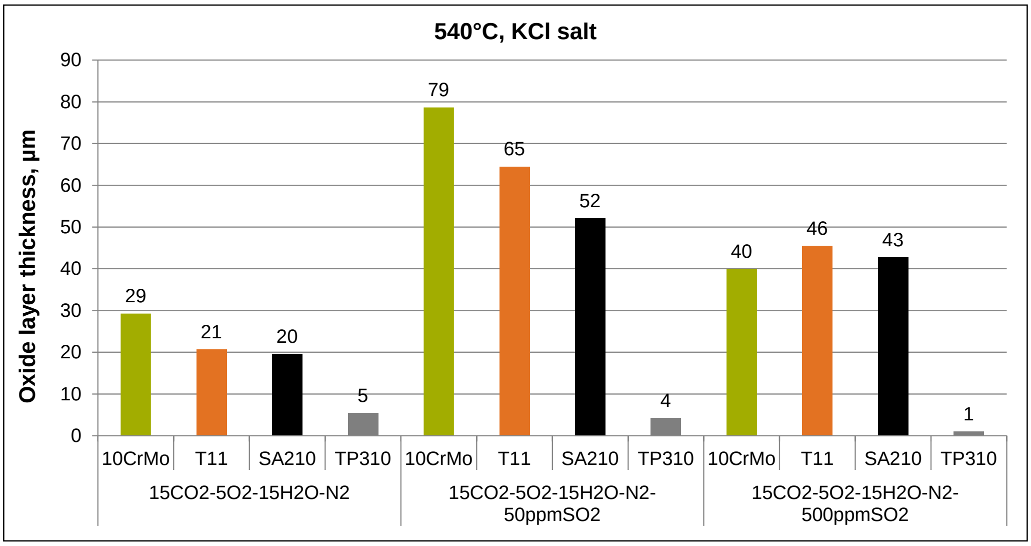
Partners: Technische Universität München (coordinator), VTT Technical Research Centre of Finland Ltd., Universität Augsburg, International Flame Research Foundation, Bilfinger (Germany), Enel (Italy), Doosan (UK), Valmet Power Oy

Patrik Yrjas, Dorota Bankiewicz, Mikko Hupa

Project time: 01.07.2014-31.06.2017
Duration: 36 months

The emerging trend towards renewable energy sources leads to an increased share of biomass used in solid fuel fired power plants. This development and the demand for increasing live steam temperatures result in severe operational problems, such as high temperature corrosion which can lead to unscheduled power plant shut downs and a decreased boiler availability. Co-firing biomass is often limited to high quality wood materials in order to ensure safe combustion without the risk of corrosion. It has been observed that the proper combination of coal and chlorine-rich biomass significantly reduces corrosive deposits. Often, these observations could not be explained properly and further research was recommended. Within the project co-firing of chlorine-rich biomasses at high shares and with elevated steam temperatures is enabled by using coal and its ash as a protective agent. Coal and its inorganic constituents such as sulphur and alumina-silicates are able to prevent the formation of alkali chlorides, and consequently chlorine-rich deposits. Two online corrosion sensors are developed and used in combination with online measurement techniques yielding gaseous and solid phase composition to monitor corrosion. Both sensors are tested under aggressive conditions and long-term exposure tests in pulverised fuel and fluidised bed systems of varying size and in combination with material loss probes. Experiments will start in small scale and proceed with increasing plant size. By this approach corrosion rates can be correlated to the fuel composition and process conditions in order to understand observed phenomena. Modelling will support the understanding of corrosion attack and its mechanisms. The project will provide strategies for setting up fuel blends and 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 this project, Åbo Akademi focuses on advanced fuel characterisation, fuel mix calculations, alkali absorption laboratory tests, ash behaviour evaluation, corrosion tests of sensor material with synthetic salts and real ashes from pilot and/or full scale tests and SEM/EDX analyses of deposits and corrosion layers from the fluidized bed tests done within the project.



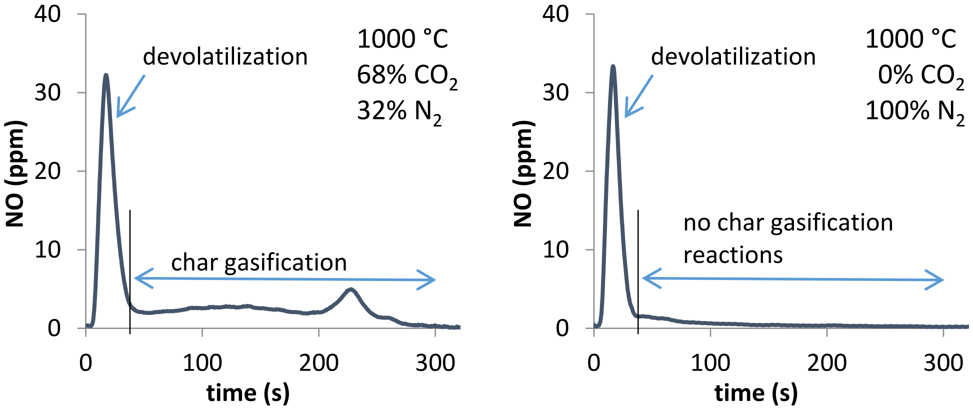
Corrosion layer thicknesses of four steels exposed to KCl at 540°C for one week under different gaseous conditions.

Fate of Fuel Bound Nitrogen in Biomass Gasification

Main funding: Academy of Finland

Oskar Karlström
Period: 01.09.2015-31.08.2018

Gasification of biomass with high nitrogen contents, such as annual crops, gives high nitrogen emissions. In biomass gasification, the formation of harmful nitrogen emissions origins mainly from the fuel bound nitrogen (fuel-N). Around 70-90% of the fuel-N is bound to the volatile matter (vol-N) and released during devolatilization. The remaining part, around 10-30%, is mostly bound to 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. On the other hand, little is known regarding the path of char-N during biomass gasification. This is surprising, since for biomass a significant amount of nitrogen, up to 30%, can be bound to the char. In the literature the conversion of char-N has not been investigated under biomass gasification conditions. Fig. 1 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. At present, more experiments are conducted to understand the formation of nitrogen species. Further, a mathematical model is under development able to predict the rather interesting NO release profile during the char gasification: although the char is gasified and reduces in size and mass, the release rate of NO increases.



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

Reliable and Efficient Combustion of Oxygen/Coal/Recycled Flue Gas Mixtures (RELCOM)

Main funding: European Commission Seventh Framework Programme

Anders Brink, Oskar Karlström, Dorota Bankiewicz, Jaana Paananen, Mikko Hupa

The RELCOM project (1.12 2011 to 30.11 2015) is designed to undertake a systematic and focused series of applied research, development and demonstration activities involving both experimental studies and combustion modelling work to enable full-scale early demonstration oxyfuel plant to be designed and specified with greater confidence as well as providing improved assessment of the commercial risks and opportunities.

The key tasks within the project are -

- Underpinning technology investigation including: fuel and combustion characterisation; flame radiation and explosion characteristics; high temperature gas-side corrosion; flue gas clean-up; and mercury emissions in oxy/coal/recycled flue gas.
- CFD simulation and validation to develop improved burner designs, flame stability assessment and scaling rules.
- Pilot-scale burner trials for assessment of novel burner designs and development of combustion monitoring and control systems.
- Medium-scale burner testing using pilot scale results and scaling criteria developed within the project.
- Detailed engineering analysis of retrofit and new-build case studies utilising the fundamental data and modelling tools developed within the project.
- Dissemination and technology transfer of findings to project stakeholders.

Åbo Akademi's main activities in this project are releated to underpinning technology investigation. Three different tasks are undertaken: "*Task 1.1 Fuel and Combustion Characterization*", "*Task 1.4 Investigation of High Tempeature Gas-Side Corrosion*", "*Task 2.1 CFD Sub-models*".

Cooperation:
University of Glamorgan – Coordinator (UK), Åbo Akademi (Finland), E.On New Build & Technology Ltd. (UK), Technische Universität München (Germany), Electricite de France S.A. (France), University of Leeds (UK), Instytut Energetyki (Poland), Universität Stuttgart (Germany), Katholieke Universiteit Leuven (Belgium), Doosan Power Systems Ltd. (UK), Enel Ingegneria e Innovazione SpA (ITALY), Fundación Ciudad de la Energía (SPAIN), International Flame Research Foundation (Italy)

Publications
A temperature-history based model for the sticking probability of impacting pulverized coal ash particles, Fuel Processing Technology, DOI: 10.1016/j.fuproc.2015.08.039.

Behavior and Properties of Molten Ash in Biomass and Waste Combustion

Main funding: Academy of Finland (Academy of Finland Research Fellow) 1.9.2013-31.8.2018

Daniel Lindberg, Fiseha Tesfaye, Markus Engblom, Jonne Niemi

Many challenges in the deeper understanding of the chemistry in a number of industrial high-temperature processes are connected to the molten phase. Behavior of systems containing molten phases is very difficult to predict by any theoretical methods. Thermodynamic properties of molten phases consisting of a number of components are not very well known. There are many indications that the presence of even small amounts of a molten phase

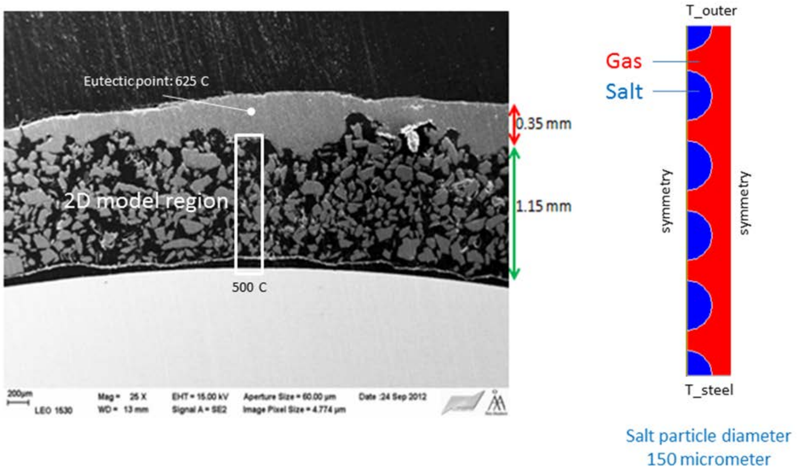
may have a dramatic importance to the kinetics of many industrially important high-temperature reaction systems. However, little systematic generic research has been published on the detailed role of composition and amount of liquid phases in reacting systems.

The present project sheds more light to the chemical phenomena of industrial significance related to the presence of a molten phase, especially connected to the role of the melt in ash deposits in biomass and waste combustion. The chemical and physical changes of partly molten ash deposits in thermal gradients are studied simulating the condition in boilers. The mobility of components in the melt phase in temperature gradients are studied to predict accumulation of corrosive or harmful species in deposits.

We will also develop new electrochemical methods to detect the formation of a melt in ionic mixtures as compliments to thermal analysis. The physical properties of the relevant molten ash components are modeled to combine these properties with other predictive tools, such as thermodynamic equilibrium modeling. These properties will also assist in modeling the thermal gradients in ash deposits in real boilers.

A variety of experimental and theoretical approaches will pave the road to more quantitative 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.

From the application point of view, the expected results from the project will support solving specific industrial problems, such as materials corrosion and fouling in reactors and furnaces.



Backscatter SEM image of a $NaCl$-Na_2SO_4 mixture with a porous inner layer and a molten outer layer in a temperature gradient, and illustration of the CFD modeling approach concerning geometry and boundary conditions.

Low Temperature Corrosion in Combustion – Old Problem, New Approaches

Main funding: Academy of Finland

Emil Vainio – Academy of Finland Postdoctoral Researcher

Low temperature corrosion is an old problem in combustion of fossil fuels with high sulfur content. The limiting factor in lowering the flue gas temperature is the sulfuric acid dew point. The cause of low temperature corrosion in biomass combustion appears to be dramatically different. The old experiences and rules of thumb seem to be completely invalid in biomass combustion. This lies in key factors of biomass combustion, such as different combustion technology, lower sulfur content, and ash composition.

The objective of this research is to better understand the causes of low temperature corrosion in combustion of various biomass fuels by using new analysis and sampling techniques, and in this way pave the road for new solutions to avoid corrosion. This would lead to an increased economy of the power production, by increased energy production and less unplanned shutdowns due to corrosion. Low temperature corrosion seen in biomass combustion is often assumed to be caused by condensation of sulfuric acid. However, this is rarely the case. In order to avoid low temperature corrosion it would be of utmost importance to understand the mechanism behind it. A novel method for measuring sub-ppm levels of H_2SO_4(g) in flue gases will be used to study the risk of sulfuric acid induced low temperature. Measurement campaigns will be conducted in several biomass combustors to clarify the risk of sulfuric acid induced low temperature corrosion.

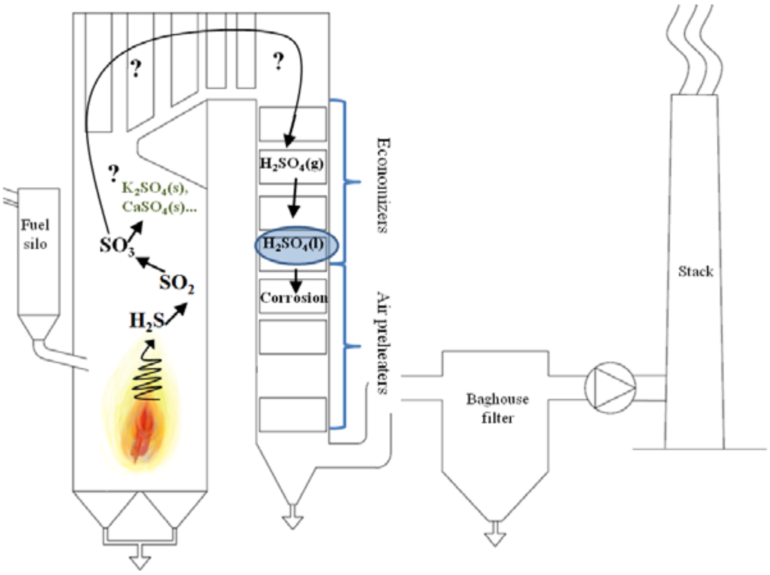


Illustration of some possible routes for SO_3 and H_2SO_4 in combustion.

Highlighted publications:

-Vainio, Emil; Laurén, Tor; DeMartini, Nikolai; Brink, Anders; Hupa, Mikko: Understanding Low-Temperature Corrosion in Recovery Boilers: Risk of Sulphuric Acid Dew Point Corrosion? Journal of Science & Technology for Forest Products and Processes, 4(6), pp 14-22, 2015.

-Vainio, Emil; Kinunen, Hanna; Laurén, Tor; Brink, Anders; Yrjas, Patrik; DeMartini, Nikolai; Hupa, Mikko: Low-Temperature Corrosion in Co-Combustion of Biomass and Solid Recovered Fuels, FUEL 2016, doi:10.1016/j.fuel.2016.03.096

Erosion of Metals and Refractories in Fluidized Bed Combustion

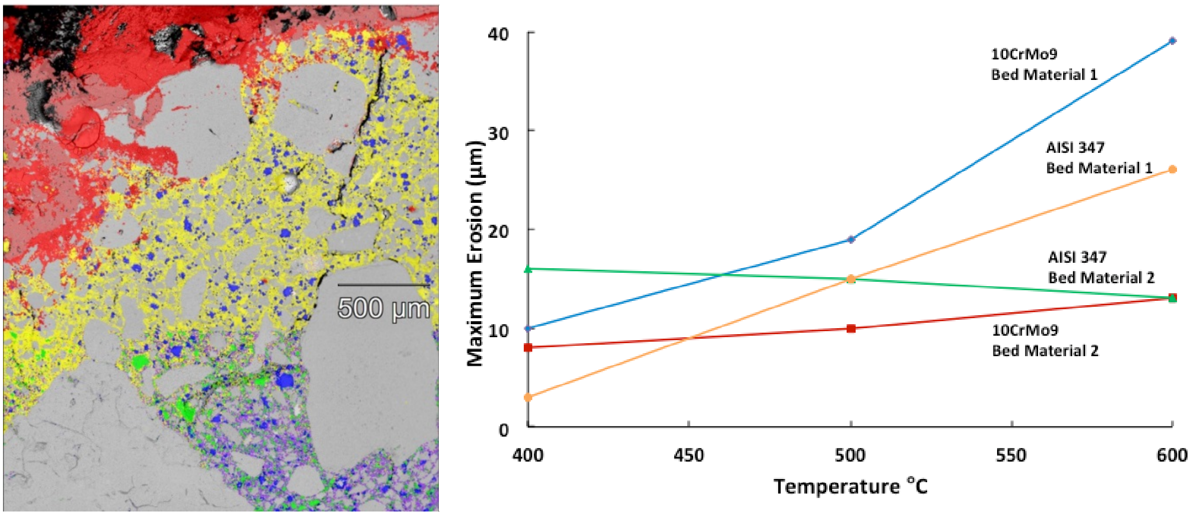
Main funding: CLIFF project partners, Academy of Finland, PCC

Varun Rai, Na Li, Emil Vainio, Patrik Yrjas, Leena Hupa

Combined chemical - mechanical durability challenges the choice of refractory metals and ceramics in boilers utilising biomass and waste derived fuels. For these fuel grades, fluidised bed combustion enables lower furnace temperatures and thus lower tendency to corrosion. Simultaneously, the collisions of the abrasive particles result in a faster degradation of the boiler materials compared to corrosion or erosion alone.

We have developed a laboratory scale procedure to evaluate, compare and predict the chemical and mechanical durability of refractory metals and ceramics in biomass combustion devices. The erosion tendency is tested using short-term experiments at demanding environments imitating the conditions in combustion devices. The effect of chemical deterioration is studied by exposing the materials for synthetic ashes at various temperatures for one week, after which the materials are eroded conditions imitating the environment in typical boilers.

The changes in the boiler material composition are studied using SEM-EDXA and XRD while the surface topography and profile changes are measured using confocal optical microscopy. This research aims to produce material selection maps for different industrial conditions.



Left: SEM-XPhase map showing infiltration of potassium into the matrix phase of an alumina refractory after a one-week exposure to typical biofuel ash at 800 °C; red high, yellow intermediate, purple and green negligible K content (Na Li). Right: the effect of temperature and bed material on the erosive wear of metals 10CrMo9 and AISI 347.

Understanding Low Temperature Corrosion in BL Combustion

Main funding: Finnish Recovery Boiler Committee

Nikolai DeMartini; Henri Holmblad; Emil Vainio; & Patrik Yrjas

Combustion is a key step in the recovery of pulping chemicals in a kraft pulp mill. In modern mills, the combustion of black liquor in a kraft recovery boiler not only results in nearly complete recovery of the pulping chemicals, but also produces enough steam and electricity to run the pulp mill and still provide green electricity to the electrical grid. The industry is starting to increase the efficiency by recovering more heat from the flue gases. The primary concern in lowering the flue gas temperature is low temperature corrosion.

The assumption has been that sulfuric acid exists in recovery boilers and that the flue gas temperature must be kept above the sulfuric acid dew point. Measurements in kraft recovery boilers by the PCC over the past couple of years have now clearly shown that there is no sulfuric acid in kraft recovery boilers and that more heat can be recovered from the flue gas. Instead, it is the absorption of water by hygroscopic salts that can lead to low temperature corrosion if the flue gas temperature is lowered too much. As soon as water is absorbed by the salts, corrosion will begin. Thus, to avoid corrosion, the flue gas temperature needs to be kept high enough that the salts don’t absorb water.

In this research, a first mapping of the corrosion of carbon steel as a function of salt, temperature and humidity was carried out. The results indicate that flue gas temperatures can be lowered to about 120 °C which would result in a 1-3% improvement in the thermal efficiency of recovery boilers depending on the current flue gas temperature. Work is ongoing in this area to both test more salt mixtures to better understand the behavior of mixtures and to extend this understanding to biomass boilers.

Intermediate Temperature Corrosion in Used-Wood Fired Boilers – the Influence of Lead, Zinc and Their Chlorides (KME-717)

Main funding: Swedish Energy Agency

Project partners: Swerea KIMAB Ab, Energiforsk Ab, Andritz Energy & Environment, Vattenfall Ab, AB Fortum Värme together with the city of Stockholm

Partik Yrjas, Dorota Bankiewicz, Hao Wu

Combustion of biomass reduces the dependence on non-renewable energy sources, and thus the CO_2 emissions. In recent years, used (recycled) wood has become a fuel of interest 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. In several cases, boilers burning used wood have experienced increased fouling and corrosion of furnace walls, superheaters and economisers, problems attributed to the content of chlorine, zinc, lead and alkali metals in the deposits. To minimize corrosion problems, the steam temperature is currently kept at a relatively low level and that limits electric power production efficiency.

Much work has been conducted on high temperature corrosion (> 450°C) caused by KCl and NaCl which are present in wood fuels. By contrast, much less is known about corrosion in the range 150-420°C and corrosion caused by Pb and Zn and their chlorides, which are found in used wood.

The goal for 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 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 use of additive. 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.

SmartResearch

Main funding: Tekes INKA-EAKR

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

SmartResearch project is a joint effort by Åbo Akademi University, 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 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 SmartChemistryPark business park. 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.

Oils based on biomasses and animal wastes and used recycled oils have different precipitating and corrosion tendencies on metals.

Collaboration:
University of Oulu, Turku University of Applied Science, CrisolteQ, Renotech Oy, Ecomation Oy, KWH Mirka Ltd, Ab Nanol Technologies Oy, VG-Shipping Ltd, Kierto Environmental Services LTD

Glasses with Functional Properties for Medical and Optical Devices

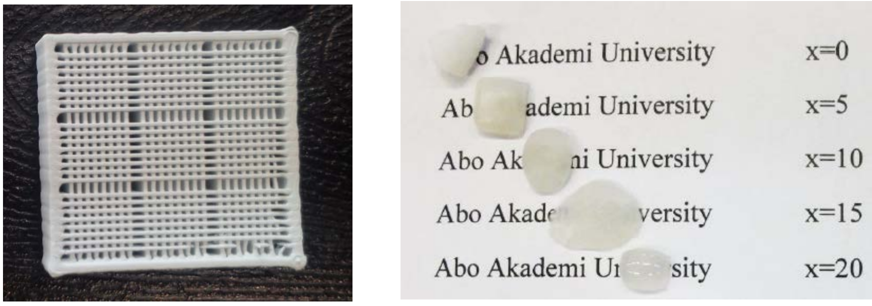
Main funding: Doctoral Educational Network in Materials Research (DNMR), Johan Gadolin Scholarships, Academy of Finland, ÅA-PCC

Laura Aalto-Setälä, Shuo Cui, Siamak Eqtesadi, Johan Sangder, Sara Kiran, Chao Gao, Xioaju Wang, Leena Hupa

In our functional glass research, we developed and characterised properties of glass and glass-ceramics for medical and optical devices. The main goal was to gain a detailed understanding of the influence of chemical composition on the physical, chemical and biological properties of the materials. This information is crucial for tailoring the materials for controlled performance both during the manufacture and more importantly, in the final application.

We studied the influence of the glass composition on the hot working properties of the glasses into various products ranging from solid devices, coatings and fibres into porous products manufactured via free-form sintering, additive manufacturing or template sintering. Typically, the so-called bioactive glasses easily crystallise during the manufacture into the desired product form. Further, nucleation and crystal growth kinetics are decisive for successful manufacture of bioactive glass-ceramics. For of optical devices, nanoparticles with controlled composition and size are of interest for enhanced mechanical and optical properties.

Controlled, predetermined ion release and dissolution of the glass network are critical characteristics for the bioactive glasses and glass-ceramics. When implanted inside the human body, the inorganic ions released from the devices stimulate and support the regeneration of tissue. We studied the ion release kinetics in various in vitro conditions and compared with the cellular responses of the glasses in cell culture and in vivo studies. Our biomaterials research done in collaboration with experts in medicine, cell and molecular biology strives for achieving enhanced knowledge of the molecular level mechanisms and reactions of bioactive glasses and glass-ceramics in living tissue.



Left: 3D porous, robocasted bioactive glass-ceramic tissue engineering scaffolds (S. Eqtesadi). Right: Gradual change from opaque (x = 0) to slightly translucent (x = 20) appearance of thermally treated optical glasses (S. Cui)

Cooperation: University of Turku, University of Tampere, Tampere University of Technology, University of Helsinki, Friedrich-Schiller University Jena (Germany), University of Erlangen-Nuremberg (Germany), University of Extremadura (Spain), Central Glass & Ceramic Research Institute, Kolkata (India), University of Rennes (France), University of Bordeaux (France), Politecnico di Torino (Italy), nLight Corporation.

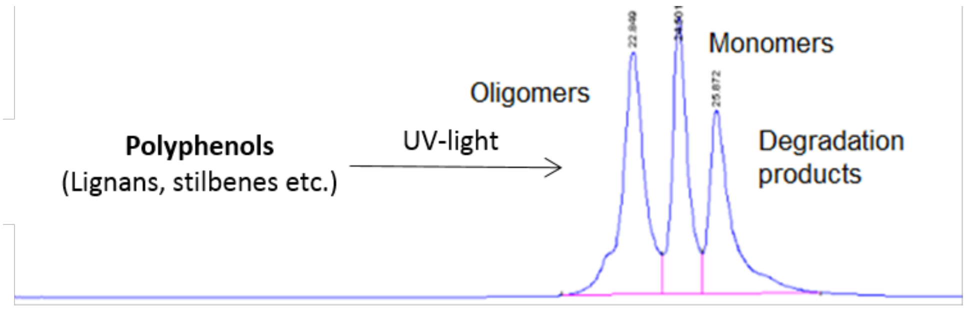
Oxidation of Food Constituents – Identification of Novel Oxidation Products and Mechanisms

Main funding: Raision Säätiö

Jan-Erik Raitanen, Patrik Eklund, Stefan Willför

Oxidation is one of the most fundamental and important reactions in organic chemistry as natural plant constituents play a key role in many foods and feed products. Polyphenols and especially unsaturated fatty acids and sterols may be oxidized during storage and can form dimers and higher oligomers, and eventually polymerize. Oxidation products may also react with each other in cross-coupling reactions to form complex heterogeneous structures. These polymerized compounds may remain in foodstuffs and can reduce the quality and shelf life of the product. Nevertheless, the rates and significance of the aforementioned reactions, the fate of the reaction products, and a deep understanding of the underlying chemistry has remained mostly unexplored and unexplained both in industry and academia.

The target of this project was to study oxidation reactions of various plant and food constituents at mild conditions. Oxidation induced by UV-light or by salts of transition metals (one electron oxidants) was performed on chosen model compounds. The studied polyphenols were shown to form dimers and oligomers (Figure 1). However, for unsaturated polyphenols, degradation to aldehydes and acids could also be observed.



HPSEC-chromatogram showing the transformation of polyphenolic compounds into both oligomeric structures and degradation products.

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

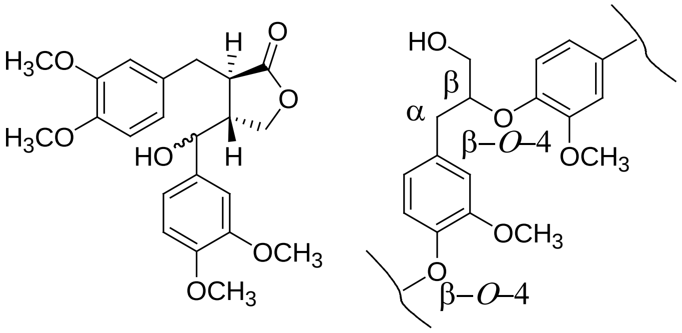
Main funding: Fortum Foundation, Doctoral Education Network in Materials Research (DNMR).

Sabine Rendon, Reko Leino

Dye-sensitized solar cells (DSSC) are electrochemical devices where light absorption and current generation occurs in dye molecules attached to a nanostructured TiO_2 electrode. Currently, some of the most efficient DSSCs contain expensive ruthenium-based dyes. For commercialization of the technology and mass production of cheap solar cells it would be valuable to be able to develop efficient cells and devices from low-cost components. Lignin is a component of the cell wall in trees and is readily available in large quantities as a side-product of the paper industry. Lignans are a group of polyphenolic compounds that are also found in plants.

In previous work we have developed a method for investigating the degradation of some common dye sensitizers for DSSCs. We also compared methods for assessing the purity of the dye and investigated what effect purification of different electrolyte components had on the performance and long-term stability of the solar cells.

In this project, electrochemical properties of selected lignans and lignins will be investigated using UV-Vis spectroscopy and cyclic voltammetry. The compounds with the most promising electrochemical properties may also be synthetically modified in order to increase their potential for use as dye sensitizers in DSSCs. Cyclic voltammetry will also be used to investigate the general antioxidant properties of lignans.



Hydroxymatairesinol

Lignin

Examples of a lignan (hydroxymatairesinol) and lignin

Highlighted Publications:

Rendon, S.; Mavrynsky, D.; Meierjohann, A.; Tiihonen, A.; Miettunen, K.; Asghar, I.; Halme, J.; Kronberg, L.; Leino, R. **Analysis of dye degradation products and assessment of the dye purity in dye-sensitized solar cells.** *Rapid Commun. Mass Spectrom.* 2015, *29*, 2245–2251.

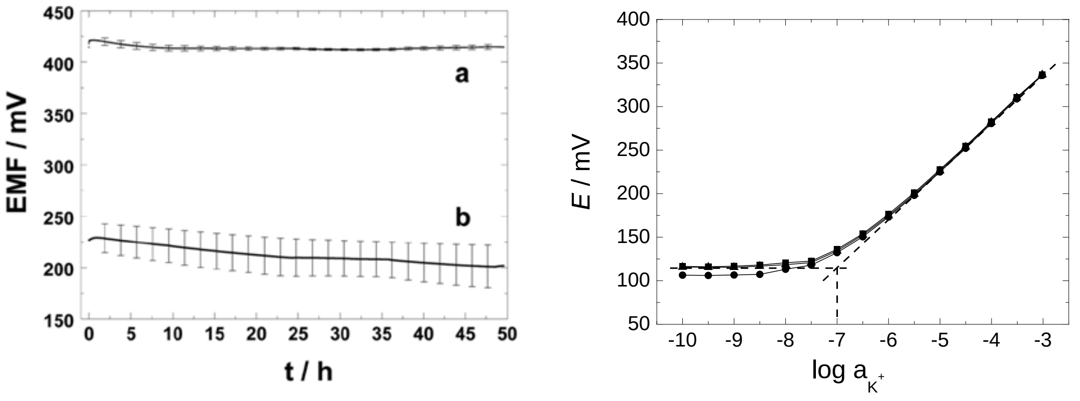
Tiihonen, A.; Miettunen, K.; Rendon, S.; Mavrynsky, D.; Halme, J.; Leino, R; Lund, P. **The effect of electrolyte purification on the performance and long-term stability of dye-sensitized solar cells.** *J. Electrochem. Soc.*, 2015, *162*, 661-670.

New Solid-Contact Materials for Ion-Selective Electrodes for High Performance Clinical and Environmental Analysis

Main funding: Åbo Akademi University, ***PCC***, Johan Gadolin Scholarship

Zhanna Boeva, Ning He, Rose-Marie Latonen, Tom Lindfors, Johan Bobacka

Our research on developing new electrically conducting polymeric materials and composites for use in solid-contact ion-selective electrodes (SC-ISEs) has continued. The main purpose has been to develop new materials for calibration-free ISEs by solving the problem with the irreproducibility of the measured standard potential. We have focused our forces on hydrophobic ion-to-electron transducers based on polyazulene and polypyrrole (PPy) doped with perfluorooctane sulfonate (PFOS). With the PPy-PFOS based K^+-selective SC-ISEs we have very recently reported, in collaboration with Prof. Gyurcsányi's research group at the Budapest University of Technology and Economics in Hungary, a superior reproducibility of the standard electrode potential (E^0) of only ±0.3 mV surpassing any previously reported E^0 reproducibilities. This is a very important step towards condition- and calibration-free SC-ISEs.



Left: Comparison of the potential response of (a) the polyazulene-based and (b) poly(3-octylthiophene)-based solid-contact K^+-selective electrodes (n=4) at their first contact (after fabrication) with a 10^{-3} M KCl solution.
Right: The calibration graphs of three identically prepared PPy-PFOS based K^+-SCISEs (n=3). The dashed line illustrates the determination of the LOD.

Together with Gyurcsányi's group we have also recently developed a new technology based on the use of polystyrene beads as template for the fabrication of 3-D hollow poly(3,4-ethylenedioxythiophene) based solid-contact materials.

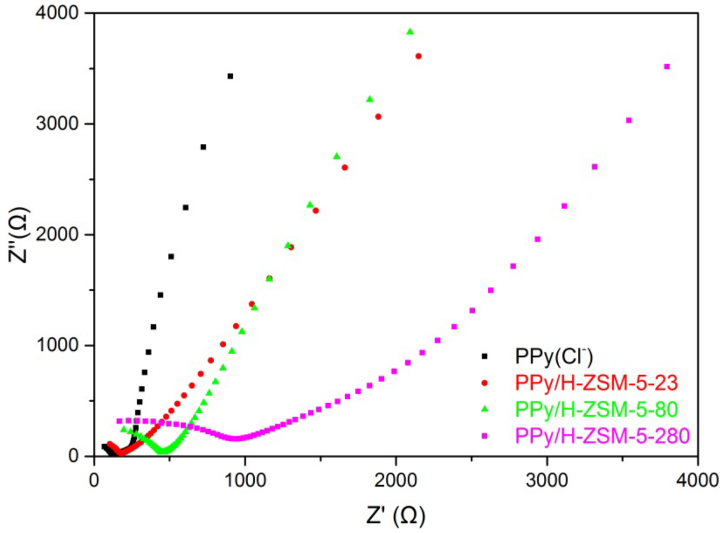
Cooperation: Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry and Research Group of Technical Analytical Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary; M.V. Lomonosov Moscow State University, Chemistry Department, Division of Polymer Science, Laboratory of Polyelectrolytes and Biopolymers; Institute of Macromolecular Chemistry of the Academy of Sciences of the Czech Republic, Dept. of Conducting Polymers, Prague, Czech Republic; Åbo Akademi University, Center for Functional Materials, Physics, Finland; University of Koblenz-Landau, Department of Physics, Institute of Integrated Natural Sciences, Germany

Electrosynthesized Polypyrrole/H-ZSM-5 Zeolite Composite as the Solid Contact in Ion-Selective Electrodes

Main funding: *PCC*

Kai Yu, Ning He, Narendra Kumar, NianXing Wang, Ari Ivaska

A novel ion-to-electron transducer composed of polypyrrole (PPy) and H-ZSM-5 zeolite has been fabricated and characterized. Integration of the two materials was achieved by electrochemical deposition on platinum substrate in aqueous solution (22±1°C). The proton forms of ZSM-5 zeolites with $SiO2/Al2O3$ ratios of 23, 80 and 280 were selected for the study. The acidity decreases but the hydrophobicity increases when the zeolite has a higher $SiO2/Al2O3$ ratio. The chemical composition (aluminum and silicon) and the density of anionic groups in the H-ZSM-5 zeolites were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and potentiometric titration, respectively. Surface and cross-section morphological analysis by SEM show that the composite layers consist of PPy and H-ZSM-5 particles and that the composite layers are much thicker compared to PPy(Cl-) which was synthesized in the same way. Impedance and FTIR-ATR measurements revealed the combination between PPy and H-ZSM-5 particles, and the anionic groups in H-ZSM-5 functioned as the counterions for PPy. Similar cyclic voltammograms were observed for all PPy/H-ZSM-5 composites and PPy(Cl-). The hydrophobicity of the composites determined by contact angle measurements was found to decrease in the order of PPy/H-ZSM-5-23 > PPy/H-ZSM-5-80 > PPy/H-ZSM-5-280. Potentiometric water layer tests indicate that the PPy/H-ZSM-5 with low hydrophobicity exhibit similar or even better potential stability than PPy(Cl-) due to the thick and compact composite layers between the conducting substrate and the polymeric ion-selective membrane.



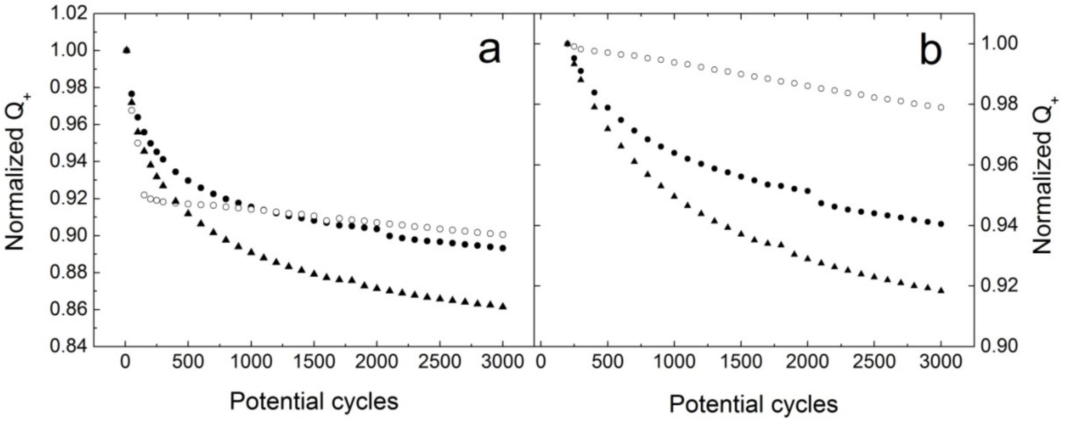
Impedance measurement of PPy(Cl$^-$) and PPy/H-ZSM-5 composites in 0.1 M KCl solution

Composite Materials of Electrically Conducting Polymers and Graphene Oxide and Reduced Graphene Oxide for Supercapacitor Applications

Main funding: Åbo Akademi University

Tom Lindfors

The supercapacitor properties of composite materials of electrically conducting polymers and GO/RGO have been studied in this project. The potential cycling stability was compared for poly(3,4-ethylenedioxythiophene) (PEDOT) composite films prepared either with graphene oxide (GO), reduced GO (RGO) or poly(styrenesulfonate) (PSS). It is shown that PEDOT-GO had reversible redox behavior and fast charging/discharging with at least equal electrochemical properties to PEDOT-PSS. 10 000 potential cycles between -0.5–0.5 V in the three-electrode cell decreased the anodic charge of PEDOT-GO with 6.2%. In the two-electrode cell, the decrease was only 5.4% between 0–0.7 V. The potential cycling stability of PEDOT-GO and PEDOT-RGO prepared electrochemically without other additives than GO has not been previously reported. It is expected that the incorporation of GO in the PEDOT matrix improves its mechanical stability which is beneficial in counteracting the mechanical stress induced on the composite film during the oxidation and reduction cycles (swelling/shrinking). All composite materials in this study had a very good potential cycling stability. Even PEDOT-RGO, which had the lowest stability, showed a loss of only 8.2 % of its anodic charge upon repeated cycling between -0.5–0.5 V (vs. Ag/AgCl/4 M KCl) in 0.1 M KCl under oxygen-free conditions in the three-electrode cell. Our results reveal that PEDOT-GO and PEDOT-RGO are suitable new materials to substitute PEDOT-PSS as the ion-to-electron transducer in SCISEs.



The normalized anodic charge (Q_+) vs. the number of potential cycles for (●) PEDOT-PSS, (○) PEDOT-GO and (▲) PEDOT-RGO measured in a three-electrode cell with 0.1 M KCl as the electrolyte. Potential cycles: (a) #10-3000 and (b) #200-3000. RE: Ag/AgCl/4 M KCl; v=0.1 V s^{-1}.

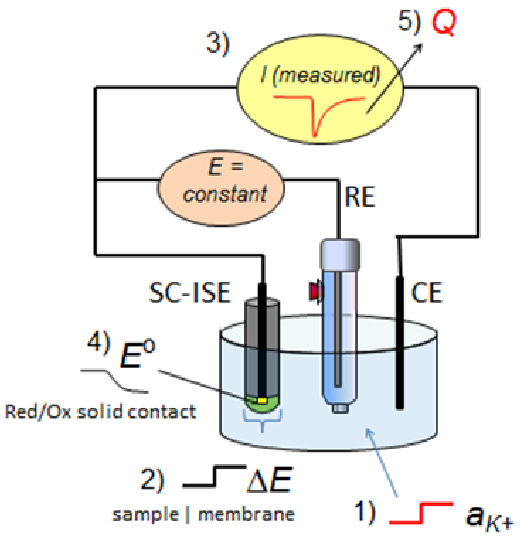
Cooperation:
Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry and Research Group of Technical Analytical Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

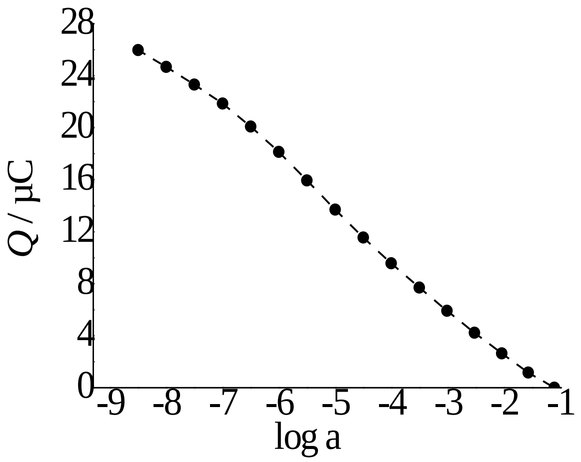
Novel Signal Readout Principle for Solid-Contact Ion-Selective Electrodes

Main funding: Magnus Ehrnrooth Foundation, Graduate School in Chemical Engineering (GSCE)

Ulriika Vanamo, Elisa Hupa, Ville Yrjänä, Johan Bobacka

A novel signal readout principle for solid-contact ion-selective electrodes (SC-ISEs) was studied further. The signal transduction mechanism utilizes the capacitance of the solid contact layer to convert ion concentration (ion activity) into an electrical current, which is then integrated to obtain the charge value. The transduction principle and a calibration plot for a K^+-selective SC-ISE is illustrated in the figure below. The calibration plot shows an impressive dynamic range, which is encouraging for further work. Furthermore, the new signal readout method allows amplification of the analytical signal for SC-ISEs, which opens up new fields of applications for ion sensors.





Left: A change in the primary ion (1) gives rise to a potential difference at the membrane-solution interface at the ion-selective electrode (2). This potential difference in turn gives rise to a current flux between the ion-selective electrode and the counter electrode (3). This current flux causes a charging or discharging of the conducting polymer layer and thereby also the potential of the ion-selective electrode (4). The current flows until the potential change at the solid-contact ion-selective electrode (4) exactly compensates for the potential difference at the membrane-solution interface of the ion-selective electrode (2). Then the current ceases to flow and the current-time transient (3) is integrated to obtain the charge (5).

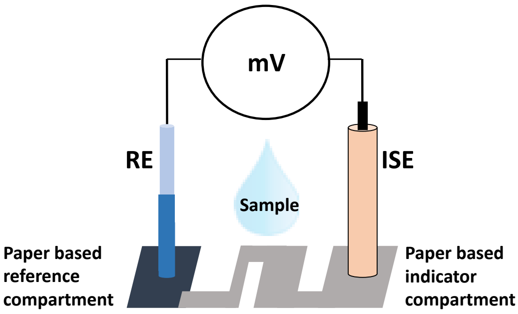
Right: Calibration plot for a K^+*-selective SC-ISE utilizing the novel signal readout principle.*

Paper-Based Chemical Sensors

Main funding: ***PCC***, Magnus Ehrnrooth Foundation

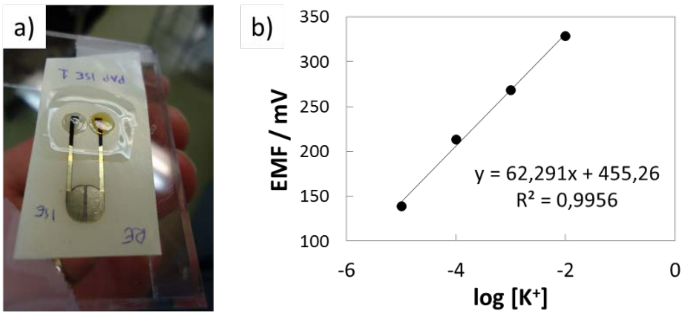
Grzegorz Lisak, Ulriika Vanamo, Tingting Han, Marta Novell, Marta Pokrzywnicka, Marta Fiedoruk, Jiawang Ding, Johan Bobacka

Paper is an interesting material both for sample transport and as a substrate for chemical sensors. A paper-based microfluidic system was developed and studied for electrochemical determination of ions in various samples. The microfluidic system consisted of two separate compartments: (i) reference and (ii) indicator compartments. The reference compartment consisted of a paper substrate containing KCl salt and an Ag/AgCl wire. Upon contact with an aqueous standard or sample solution, dissolution of KCl in the paper of the reference compartment created a saturated KCl solution that stabilized the potential of the Ag/AgCl wire. In this way, during each measurement (new paper strip) a new single-junction reference electrode was created. Due to the short measurement time, the high concentration of KCl in the reference compartment did not interfere with the measurement of ions in the indicator compartment of the microfluidic system.



Microfluidic paper-based analytical system.

Paper-based chemical sensors were also designed and fabricated in a planar format. This was accomplished via joint research efforts combining printing technology (FunMat, Laboratory of Physical Chemistry) and chemical sensor technology (***PCC***, Laboratory of Analytical Chemistry). The potentiometric paper-based sensors consisted of printed gold electrodes onto which a layer of conducting polymer, i.e. poly(3,4-ethylenedioxytiophene) (PEDOT) doped with poly(syrene sulfonate) (PSS), was electropolymerized. Thereafter, the two gold/PEDOT(PSS) electrodes were covered with a potassium-selective membrane and a reference membrane, respectively. The aim was to design simple, mass-producible and disposable sensors for rapid on-site analytics.



Left: Paper-based potentiometric K^+-selective sensor and reference electrode. Right: Calibration plot.

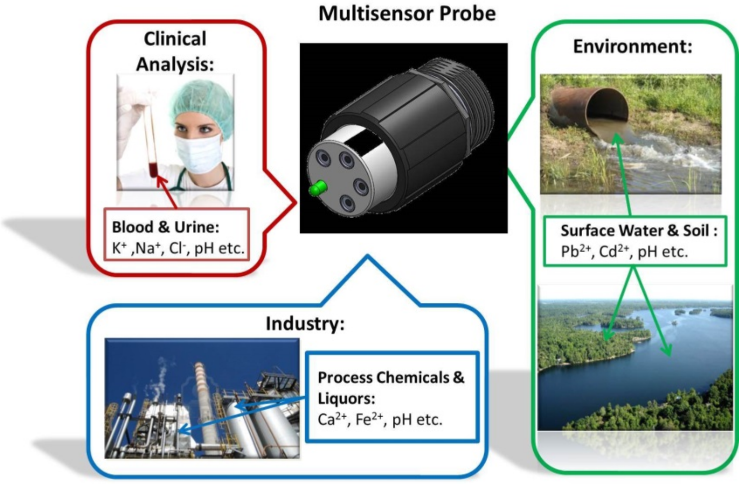
Cooperation: University of Warsaw, Warsaw, Poland; Malmö University, Malmö, Sweden; Universitat Rovira i Virgili, Tarragona, Spain; Center for Functional Materials, Laboratory of Physical Chemistry, Finland

Universal Solid Electrochemical Platform (UNISEP)

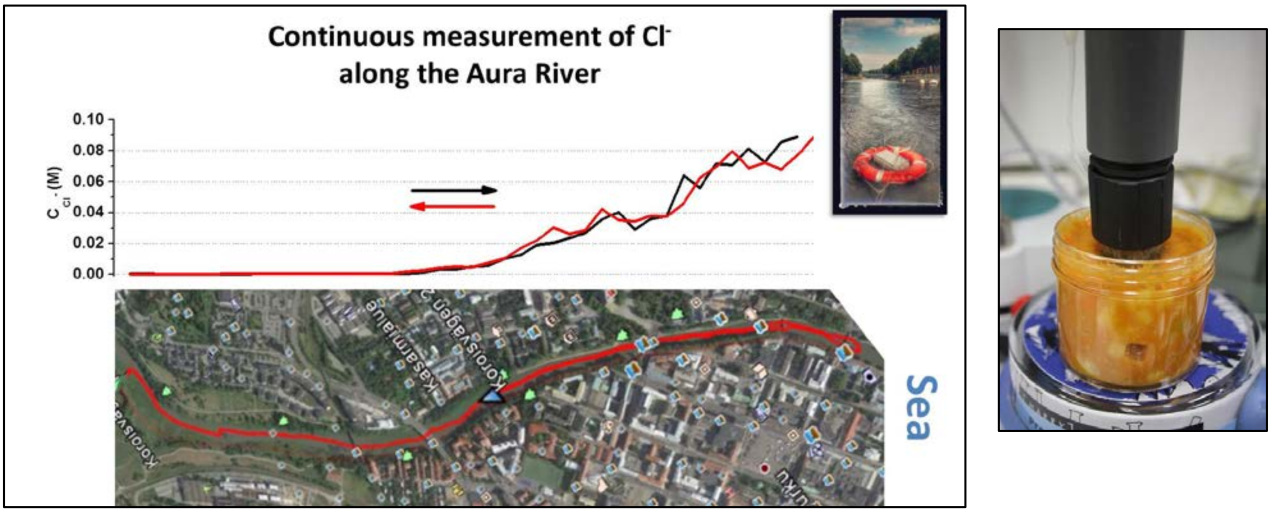
Main funding: Tekes (TUTLI)

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

Our invention is a solid-state electrochemical reference electrode which can be extended and modified to form an entire electrochemical platform that can be used in all fields of electrochemical analysis. This platform integrates the indicator electrode(s) and the solid-state reference electrode in a single body.



The main aims of the project are to obtain a customer grade product and to develop a feasible commercialization concept. The work is divided into three work packages. Two of these work packages (WP1 and WP3) are related to the commercialization activities and one (WP2) to the technology activities.



UNISEP was successfully tested in wireless mode for environmental applications (left) and in wired mode for food industry applications (right).

Cooperation: Orion Diagnostica Oy; Nokeval Oy; Peilituote Oy; LS Link Ab; Patiq Oy; Berggren Oy; Defour OY; LSVSY; AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Krakow, Poland

Durable and Low Cost Solid-Contact Ion Sensors

Main funding: TECNIO Spring (Spain), ***PCC***

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

The main objective of this recently started two-year project is the design, development and characterisation of durable and low cost solid-contact ion sensors 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 the final stage of the project a technology of the sensors production will be developed, thus being ready for technology transfer to interested industrial partners. The work will include the use of innovative composite materials for the enhancement of the stability and the durability of the sensor, which entails the study of the latest advances in the field of solid-contact ion sensors. The synergy between ***PCC*** and IMB-CNM-CSIC (Spain) will facilitate the attainment of the objectives.

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

Composite Materials of Polyaniline and Exfoliated Ggraphite for Solid-State Electrochemical Sensor

Main funding: Åbo Akademi University, ***PCC***, Johan Gadolin Scholarship

Zhanna Boeva, Ngoc Minh Nguyen Huynh, Tom Lindfors

Composites consisting of few-layered graphene and polyaniline (PANI) readily dispersible in *N*-methylpyrrolidone have been developed. Significantly improved pH stability and electrochemical behavior in aqueous electrolyte solutions at $\text{pH} \leq 8$ compared to pure PANI have been obtained. Due to the dispersibility of the composites, thin films possessing stability in water can easily be prepared by solution casting for different types of solid-state chemical sensor and ISE applications operating at neutral pH. A potential reproducibility of only ±4 mV has been obtained for the Ca-SCISEs having graphene–PANI as the solid-contact. The Ca-SCISEs in this study had a detection limit of 5×10^{-8} M Ca^{2+}, which was obtained without any sophisticated pre-treatment protocols. The improved potential reproducibility was assigned to the synergistic effect between polyaniline and the few-layer graphene, as well as to the higher hydrophobicity of the composite solid-contact compared to the pure electrically conducting polymer counterpart.

We are also currently studying the applicability of different types of graphene materials in high performance electrochemical biosensors for health diagnostics.

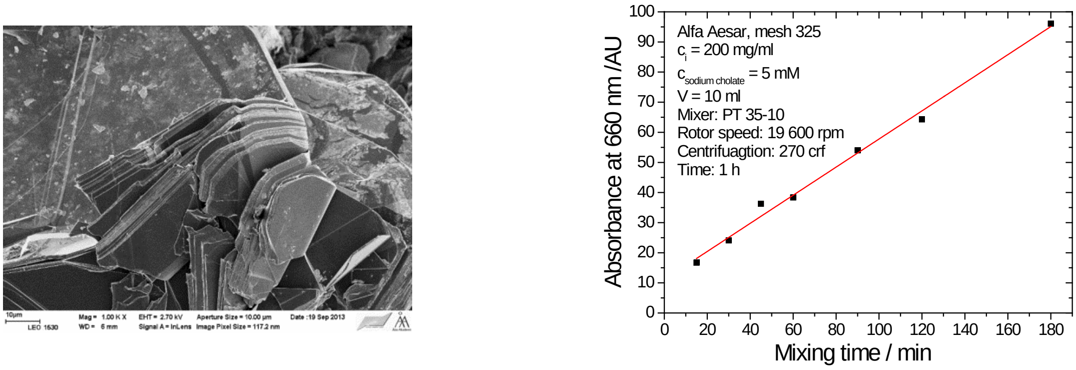
Cooperation: M.V. Lomonosov Moscow State University, Chemistry Department, Division of Polymer Science, Laboratory of Polyelectrolytes and Biopolymers

From the Identification of the Potential Flake Graphite Ores in the Fennoscandian Shield to the Utilization of Graphene (FennoFlakes)

Main Funding: The Academy of Finland (MISU-program)

Sara Lund, Tom Lindfors, Rose-Marie Latonen, Jussi Kauppila

The FennoFlakes project is an interdisciplinary collaboration project between Geology and Mineralogy and The Laboratory of Analytical Chemistry (LAC) and The Laboratory of Physical Chemistry (LPC) at Åbo Akademi University. The first part of the project aims to identify high-quality flake graphite ores in Finland and to purify the graphite ore by different enriching methods. The task for the chemists is to produce graphene from the purified flake graphite ore and to demonstrate the usefulness of the developed material in some proof-of-concept application. So far, different flake graphite ores have been identified and the focus of the project is now on the enrichment of the ore. LAC and LPC have also supported the development of the enriching process by providing many of the necessary characterizations (CHNS analysis, XRD, FTIR and Raman). The enriching process is currently in its final state where flotation tests are done on the graphite ore. The exfoliation process with commercial flake graphite is currently being optimized. The exfoliation is done in liquid phase by high-shear mixing. Different parameters have been tested to produce as highly concentrated graphene dispersions as possible. So far, concentrations up to 1.5 mg/ml have been achieved. This concentration is high enough for spray-coating on glass which has been done successfully. The results from the exfoliation tests are analyzed with UV-vis spectroscopy, AFM and Raman spectroscopy.



Left: A SEM image of flake graphite from Piippumäki.
Right: The absorbance (AU) at 660 nm of different graphene dispersions as a function of mixing time from 15 min to 180 min measured with UV-vis spectrophotometer.

Cooperation: The Geological Survey of Finland; Beowulf Mining; Haarla Group; Åbo Akademi University, Center for Functional Materials, Physical Chemistry, Finland; Åbo Akademi University, Geology and Mineralogy, Finland

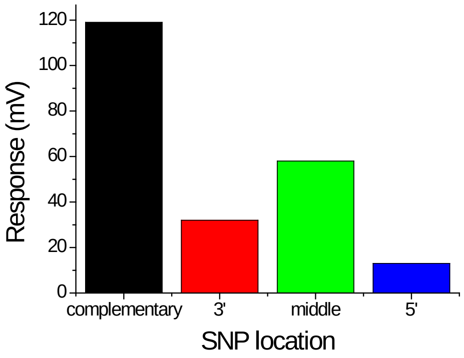
New Electrochemical Sensing Platforms for Personalized Medicine

Main funding: Jane and Aatos Erkko Foundation

Zhanna Boeva

This project is aimed to develop electrochemical sensors based on conducting polymers for an easy-to-use mutational analysis of the DNA sequence for clinical diagnostics and personalized medicine. The focus is to prepare a potentiometric biosensor for the detection of the DNA hybridization with the use of polyaniline (PANI) composite materials as indicator electrode. The composite materials are used for non-covalent immobilization of single stranded oligonucleotides (probe) with different length (20, 30, 40 and 50 nucleobases in a strand). The immobilization of the probe is monitored potentiometrically and the drop of the potential upon the probe immobilization is detected. The DNA sensor with the probe immobilized onto the PANI surface is then used for the detection of the single stranded oligonucleotide (target) with a sequence complementary to the sequence of the immobilized probe. The addition of the target to the solution containing indicator electrode with immobilized probe leads to the increase of the potential of the indicator electrode due to the formation of the double helix of target and probe (hybridization) occurring on the surface of PANI and confirmed with fluorescence spectroscopy. The potentiometric response is found to be proportional to the length of the target and probe and can be registered for the oligonucleotides having 40 and 50 nucleobases in the sequence.

The covalent immobilization of the probe onto the surface of PANI is also carried out to fabricate robust and multiple-use indicator electrodes for DNA detection. It was found that the covalent immobilization of the probe with the use of thiol chemistry causes the similar drop of the potential of the indicator electrode. Addition of the target gives the similar positive response. The response amplitude of the biosensor depends on the length of the target and probe in the similar way as it was observed for non-covalently immobilized probe. Furthermore, the response of the DNA sensor depends also on the presence of the mismatches in the formed hybrid. We have found that in case of partial complementarity of the double helix the potentiometric response is lower compared to the fully complementary target and depends on the place where the mismatch is located. The presence of the mismatch in the middle of the helix lowers the response of the biosensor twice. In case of the mismatch by the 3'-end the four-fold decrease of the response is observed and in case of the mismatch by the 5'-end the response was registered to be the lowest. The found phenomenon is very important and has a strong potential in the future for the development of electrochemical biosensors for the detection of the mutations in the genomic DNA.



The response of the electrode modified with probe to the addition of the target without SNP (black), having one mismatch by the 3' end (red), in the middle (green) or by the 5' end (blue).

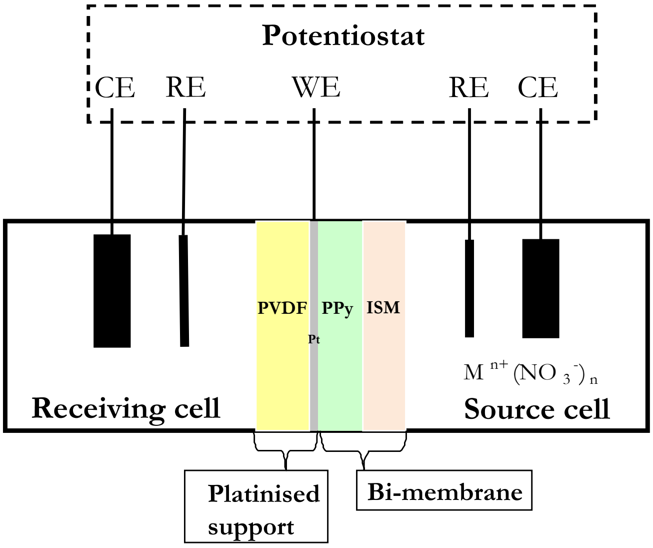
Cooperation: Moscow State University, Moscow, Russia; Polytechnic Institute of New York University, New York, USA

Electroactive Bi-Membranes for Separation of Ions

Main funding: *PCC*

Jesús Arroyo, Grzegorz Lisak, Marceline Akieh-Pirkanniemi, Rose-Marie Latonen, Ari Ivaska, Johan Bobacka

Electroactive bi-membranes were developed and studied as a selective barrier in the transport of target ions. The bi-membranes consisted of an ion-selective membrane (ISM) and a conducting polymer (polypyrrole, PPy) membrane. The conducting polymer was electrodeposited on a Pt-sputtered PVDF membrane. The ion-selective membrane acted as a selective barrier for ions while the conducting polymer acted as an electrochemically controlled barrier. Owing to the presence of the ion-selective membrane the bi-membranes demonstrated permselectivity and selectivity towards the studied target ions. Electrochemical oxidation/reduction of the conducting polymer induced an ion flux, while the ISM determined which ions can go through the membrane.



Schematic illustration of the transport cell used to study the permeation of ions across bi-membranes (ISM/PPy/PVDF). CE = counter electrode, RE = reference electrode, WE = working electrode. M^{n+} *is the cation under study, whereby the source cell contains equimolar mixture of* KNO_3 *and* $Ca(NO_3)_2$.

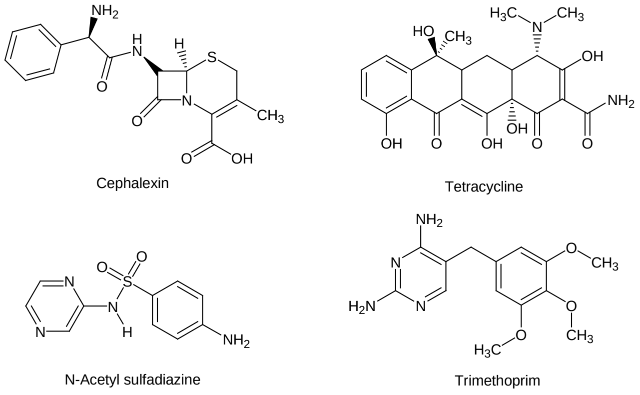
The Occurrence of Antibiotics in Wastewaters, Recipient Waters and Sedimentsroject

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

Leif Kronberg, Patrik Eklund, Ewelina Kortesmäki, Axel Meierjohann, Johnny Östman

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

The Fate of Antibiotics in Pulsed Corona Discharge Oxidation

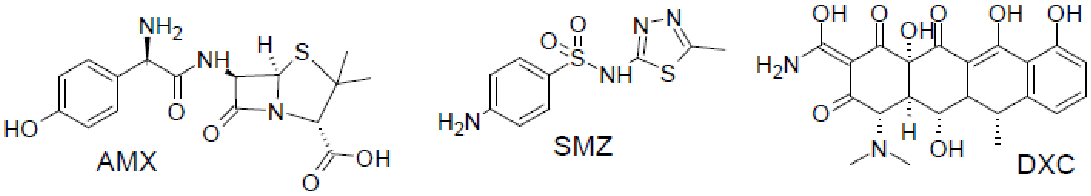
Main funding: Maa- ja vesitekniikan tuki

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), sulfamethizole (SMZ) and doxyxycline (DXC).

Quantitative analyses of the antibiotics and their oxidation products will be performed and the main oxidation products will be fully characterized. 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. Final structural determination will be performed by NMR studies (1H and 13C NMR) on isolates obtained through semi-preparative LC fractionation of reaction mixtures. Subsequently, an exact quantification of the main products will be performed with a triple quadrupole mass spectrometer using the isolated compounds as authentic standards.

The preliminary results show that AMX forms nine transformation products of which five have been tentatively identified. SMZ forms many minor products of which the structures of five products have been preliminarily elucidated. 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.



Structure of the antibiotics studied in this project.

Cooperation:
This project is a collaboration with Lappeenranta University of Technology.

4 Publications

4.1 Theses

4.1.1 Doctoral theses (12)

David Agar, The Feasibility of Torrefaction for the Co-Firing of Wood in Pulverised-Fuel Boilers
http://urn.fi/URN:ISBN:978-952-12-3321-0

Petteri Kangas, Modelling the super-equilibria in thermal biomass conversion: applications and limitations of the constrained free energy method
http://urn.fi/URN:ISBN:978-951-38-8298-3

Petri Kilpeläinen, Pressurized hot water flow-through extraction of birch wood
http://urn.fi/URN:NBN:fi-fe201503262029

Victor Kisonen, Functionalisation of spruce O-acetyl-galactoglucomannans for barrier and composite applications
http://urn.fi/URN:NBN:fi-fe2015092814123

Jens Krogell, Intensification of hemicellulose hot-water extraction from spruce wood by parameter tuning
http://urn.fi/URN:ISBN:978-952-12-3202-2

Antonina Kupareva, Silicon-containing species in used lube oil re-refining
http://urn.fi/URN:NBN:fi-fe201503111854

Ewelina Leino, Transformation of carbon dioxide to diethyl carbonate over ceria and
ceria-supported catalysts
http://urn.fi/URN:NBN:fi-fe201504237416

Otto Långvik, Bio and Chemocatalysis for Stereo and Regioselctive One-Pot Reaction Applications
http://urn.fi/URN:NBN:fi-fe2015092413971

Jussi Rissanen, Utilizing hemicelluloses - The first step: Controlled extraction with hot water
http://www.doria.fi/handle/10024/117546

Risto Savela, Iron (III) as Lewis Acid Catalyst in Organosilicon and Carbonyl Chemistry
http://urn.fi/URN:ISBN:978-952-12-3206-0

Ulriika Vanamo, Solid-State Reference and Ion-Selective Electrodes – Towards Portable Potentiometric Sensing
http://urn.fi/URN:ISBN:978-952-12-3190-2

Daniel Valtakari, The role of metal ions in selective and sustainable processes
http://urn.fi/URN:NBN:fi-fe2015092914187

4.1.2 Master´s theses (25)

Akhmetzyanova, Uliana, Synthesis and characterization of metal modified solid heterogeneous catalysts – Application of Raman spectroscopy

Bernardini, *Andrea*, Direct synthesis H_2O_2 over palladium supported on rare earths promoted zirconia (in co-operation with Universitá di Padova)

Bizzotto, *Francesco*, Application of the catalyst wet pretreatment method (CWPM) for catalytic direct synthesis of H_2O_2 (in co-operation with Universitá di Padova)

Fernández, Andérez María, Extraction of hemicelluloses from stone pine, Norway spruce and holm oak with pressurized hot water

Forsblom, *Juha*, An overview of cancer immunotherapy and oncology markets

Gao, *Chao*, Porous implants sintered of bioactive glasses

González, Munoz Marta, Microwave-assisted and acid-catalyzed epozidation of oleic acid in the presence of peracetic acid and cation exchange resin

Gunell, *Andreas*, Från kolhydrater till finkemikalier: Syntes av ett par polyolderivat

Holmblad, Henri, Low temperature corrosion in black liquor recovery boilers due to hygroscopic salts

Hussein, Abdifatah Mohamed, Characterization of novel solid-state reference electrodes

Kiran, *Sara*, Preparation of bioactive glass scaffolds via replica technique

Kosivtsova, *Anna*, Isolation of Ligning with aqueous alkali and peroxide from hot-water pre-extracted Norway spruce wood

Kotelnikova, *Aleksandra*, NFC-galactoglucomannan-based hydrogels for the removal of heavy metal ions from aqueous solutions

Kråkström, *Matilda*, Transformation av läkemedel i biologisk avloppsvattenrening

Kujanpää, *Petra*, En ny avisningsmetod

Pérez Martinez, *Victor*, Acid hydrolysis of hemicelluloses from hardwood and softwood with homogeneous and heterogeneous catalysts

Raguzina, Ekaterina, Investigation of the potential stability of ion-selective electrodes with solid-contact

Rai, *Varun*, Development of a short-term gas-blast type erosion tester for elevated temperatures

Sangder, *Johan*, Dynamisk in vitro-undersökning av bioaktiva glas med och utan zink- och strontiumsubstitution

Smirnov, *Ilia*, Bubbling fluidized bed agglomeration due to phosphorus compounds

Stenlund, *Daniel*, In-furnace measurements of deposit build-up and corrosion in a copper flash smelting waste heat boiler

Tkacheva, *Anastasia*, Pharmaceuticals and surfactants from alga derived feedstock: catalytic amidation of fatty acids and their derivatives with amino alcohols over heterogeneous catalysts

Xu, *Wenyang*, Preparation of cellulosa nanocrystals (CNCs) using oxalic acid

Zubair, Muhammad, Electrospinning of conducting polymer and nanofibrillated cellulose based composite fibers

Östman, *Johnny*, Bestämning av antibiotika i kommunala avloppsvatten med användning av fastfasextraktion och vätskekromatografi-masspektrometri

4.2 Publications

4.2.1 Articles in refereed international scientific journals and series (146)

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2. Aho, A., Roggan, S., Simakova, O., Salmi, T., Murzin, D. Yu., **Structure sensitivity in catalytic hydrogenation of glucose over ruthenium**, *Catalysis Today* 241 (2015) 195-199

3. Aho, A., Roggan, S., Eränen, K., Salmi, T., Murzin, D. Yu., **Continuous hydrogenation of glucose with ruthenium on carbon nanotubes catalysts**, *Catalysis Science and Technology,* 5 (2015) 953-959

4. Berguerand, C., A. Yarulin, A., Cardenas-Lizana, F., Wärnå, J., Sulman, E. M, Murzin, D. Yu., Kiwi-Minsker, L., **Chemoselective liquid phase hydrogenation of 3-nitrostyrene over Pt nanoparticles: synergy with ZnO support**, *Industrial and Engineering Chemistry Research,* 54 (2015) 8659–8669

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8. Blochberger, M., Hupa, L., Brauer, D.S., **Influence of zinc and magnesium substitution on ion release from Bioglass® 45S5 at physiological and acidic pH**, *Biomedical Glasses* 1 (2015) 93-107

9. Bober, P., Humpoíček, P., Pacherník, J., Stejskal, J., Lindfors T., **Conducting polyaniline based cell culture substrate for embryonic stem cells and embryoid bodies**, *RSC Advances* 5 (2015) 50328-50335

10. Bourhis, K., Massera, J., Petit, L., Ihalainen, H., Fargues, A., Cardinal, T., Hupa, L., Hupa, M., Dussauze, M., Rodriguez, V., Boussard-Plédel, C., Bureau, B., Roiland, C., Ferraris, M., **Influence of P_2O_5 and Al_2O_3 content on the structure of erbium-doped borosilicate glasses and on their physical, thermal, optical and luminescence properties**, *Materials Research Bulletin* 63 (2015) 41-50

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12. Brusentsev, Y., Eklund, P., **Synthesis and application of diphosphine ligands derived from the lignan hydroxymatairesinol**, *Catalysis Today* 241 (2015) 260-263

13. Cortese, R., Schimmenti, R., Armata, N., Ferrante, F., Prestianni, A., Duca, D. Murzin, D. Yu., **Investigation of polyol adsorption on Ru, Pd and Re using vdW density functionals**, *Journal of Physical Chemistry C.* 119 (2015) 17182-17192

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21. Granholm, K., Sokalski, T., Lewenstam, A., Ivaska, A., **Ion-selective electrodes in potentiometric titrations; a new method for processing and evaluating titration data**, *Analytica Chimica Acta* 888 (2015) 36-43

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152. Vallittu, P.K., Närhi, T.O., Hupa, L., **Fiber glass - bioactive glass composite for bone replacing and bone anchoring implants**, *Dental Materials* 31 (2015) 371-381

4.2.3 Books and book chapters (5)

153. Lewenstam, A., Gorton, L., **Electrochemical processes in biological systems***,* Wiley, 2015, pp. 1-255, ISBN: 978-0-470-57845-2

154. Mikkola, J.-P., Sklavounos, E., King, A., Virtanen, P., **'Biorefinery and green chemistry'** (chapter 1), *'Ionic Liquids in the Biorefinery Concept'*, Ed. Lukasik, R., RSC publishing, 2015, pp. 1-37, ISBN: 978-1-84973-976-4

155. Murzin, D. Yu., *Chemical Reaction Technology*, De Gruyter, **2015**. 428 p

156. Rahkila, J., Misra, A.K., Guazzelli, L., Leino, R., **Glycosylation of Phenolic Acceptors Using Benzoylated Glycosyl Trichloroacetimidate Donors**, (Chapter 12), *Carbohydrate Chemistry: Proven Synthetic Methods, Vol. 3*; CRC Press/Taylor & Francis Group, 2015, pp 97-105.

157. Sokalski, T., **Transmembrane ion fluxes for lowering detection limit of ion-selective electrodes, Electrochemical processes in biological systems** (Eds. Andrzej Lewenstam, Lo Gorton), Wiley, Hoboken, 2015, pp. 23-59, ISBN: 978-0-470-57845-2

4.2.4 Articles in refereed international edited volumes and conference proceedings (7)

158. Bernhardt, D., Böhning, D., Beckmann, M., Karlström, O., Brink, A., **Experimental investigations into combustion behaviour of biomasses at single particle scale and in a 300 kW circulating fluidized bed with special focus on NO formation**, *Proceedings of the 22nd International Conference on Fluidized Bed Conversion*, Åbo, Finland (2015) ISBN: 978-952-12-3222-0
159. Brink, A., Engblom, M., Hupa, M., **Modeling of selective non-catalytic reduction system using detailed chemistry and a jet-entrainment model**, *Proceedings of the 22nd International Conference on Fluidized Bed Conversion*, Åbo, Finland (2015) ISBN: 978-952-12-3223-7
160. Kinnunen, H., Bankiewicz, D., Hedman, M., Uusitalo, M., Enestam, S., **Corrosivity of lead chloride containing salt mixtures**, *Proceedings of the 22nd International Conference on Fluidized Bed Conversion*, Åbo, Finland (2015) ISBN: 978-952-12-3223-7
161. Lehmusto, J., Yrjas, P., Hupa, M., **The effect of oxide layer thickness and morphology on KCl-induced corrosion at elevated temperatures**, *10th European Conference on Industrial Furnaces and Boilers INFUB,* Gaia, Porto (2015) eISBN: 978-972-99309-7-3
162. Niemi, J., Lindberg, D., Engblom, M., Laurén, T., Hupa, M., **Alkali chloride transport within superheater deposits due to temperature gradients**, *Proceedings of the 22nd International Conference on Fluidized Bed Conversion*, Åbo, Finland (2015) ISBN: 978-952-12-3223-7
163. Sevonius C., Yrjas P., Lindberg D., Hupa M., **Agglomeration mechanisms in a laboratory bubbling fluidized bed due to addition of different phosphate compounds**, *Proceedings of the 22nd International Conference on Fluidized Bed Conversion*, Åbo, Finland (2015) ISBN: 978-952-12-3223-7
164. Vainio, E., Laurén, T., Kinnunen, H. , Yrjas, P., Brink, A., Hupa, M., **Sulfuric acid induced dew point corrosion in BFB combustion of biomass?**, *Proceedings of the 22nd International Conference on Fluidized Bed Conversion*, Åbo, Finland (2015) ISBN: 978-952-12-3222-0

4.3 Edited conference proceedings and reports (1)

1. Lindqvist, H., Brink, A., Latonen, R-M., Mäki-Arvela, P., Saloranta, T., Sundberg, A. (eds) *Johan Gadolin Process Chemistry Centre Annual Report 2014-2015*, Åbo Akademi University, 2015, ISSN: 1459-8213, Newprint, Loimaa, Finland

4.4 Patents and invention disclosures (3)

1. Holmbom, Thomas; Holmbom, Bjarne. Hydrophobization composition, hydrophobization treatment of substrate and hydrophobic substrate. Finn. Pat 125475 (2015), 12 pp.
2. Savolainen, J., Ranta, K., Mukherjee, C., Leino, R. Multivalent β-1,2-Linked Mannose Oligosaccharides as Immunostimulatory Compounds and Uses Thereof, U.S. Patent 9,221,861, December 29, 2015.
3. Sokalski, T., Lewenstam, A., Mousavi, Z., Granholm, K., A reference electrode and an arrangement for an electrochemical measurement, WO 2014091083 A1

4.5 Awards granted (5)

Anugwom, Ikenna
Baltic University Programme (BUP) 2014 PhD Award
Winner of the 2014 BUP PhD Thesis Award is Ikenna Anugwom of Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Finland and Umeå University Sweden for his thesis Towards Optimal Fractionation of Lignocellulosic Biomass Using Switchable Ionic Liquids. The thesis is found by using the link below.
https://www.doria.fi/handle/10024/95610

Holmbom, Bjarne
Honoured as an "Inductee" at Paper Industry International Hall of Fame, Appleton, Wisconsin, USA. Bjarne Holmboms merits are characterized as follows: *"His studies are a superb combination of high –level basic and applied research. His research has had a major significance for the development of forest industry and wood-based innovations, creating new commercial fields building on the inherent chemistry of wood. Holmbom's research has made an important contribution towards making the forest products industry a biorefining industry."*

Niemi, Jonne
The 22nd FBC Best Paper Awards were given to Jonne Niemi, et al. for their paper "Alkali chloride transport within superheater deposits due to temperature gradients"

Schmidt, Sabrina
Best doctoral thesis in chemistry and chemical technology, Finska Kemistsamfundet (Association of Finnish Chemists)

Vincenzo, Russo; Kilpiö, Teuvo; Carucci, Jose Hernandez; di Serio, Martina; Salmi, Tapio
2015 PSE Model-Based Innovation Prize. The Runners up prize has been awarded to the publication entitled: "Modeling of microreactors for ethylene epoxidation and total oxidation". Among the prize winner we can find Teuvo Kilpiö and Tapio Salmi. The work is published Chemical Engineering Science and can be found using this link [Chem. Eng. Sci. 134 (2015) 563–571]. Further information about the prize can be foud here.

5 Other activities 2015

5.1 Organization of conferences, courses and seminars

April
Course in Chromatography, St. Petersburg, Russia, Andrey Pranovich

May
Session chairman, 3rd International symposium on green chemistry, La Rochelle, Dmitry Murzin

June
22nd International Conference on Fluidized Bed Conversion, Åbo/Turku, Finland
IEA-FBC meeting, Patrik Yrjas (SEE NEXT PAGE)

Workshop, New materials from trees, KTH Royal Institute of Technology, Albanova Univ Center, Stockholm, Sweden, SWE-FIN, Anna Sundberg

August
Turku, ***PCC*** annual meeting, Åbo Turku, Hanna Lindqvist

Symposium organizer (education in catalysis), Europacat-12 Congress on Catalysis, Kazan, Dmitry Murzin

Symposium organizer (novel catalysts and processes), Europacat-12 Congress on Catalysis, Kazan, Dmitry Murzin

Member of scientific committee, CRS-3: Third International Conference Catalysis for Renewable Resources. Messina, Dmitry Murzin

October
Session chairman, European Symposium in Chemical Reaction Engineering (ESCRE), Munich, Dmitry Murzin and Tapio Salmi

November
Suomen Kromatografiaseuran, Åbo Akademin ja Nesteen Syysseminaari, Biomassan jaolstus ja analytiikka – haasteet ja tulevaisuuden näkymät, Naantalin, Finland, Hanna Lindqvist

December
Modern Analytical Tools for Pulping and Papermaking, Åbo, Finalnd, Stefan Willför

The 22nd International Conference on Fluidized Bed Conversion, June 14-17, 2015 in Radisson Blu Marina Palace Hotel in Turku

Sponsors: Åbo Akademi University, City of Turku, Amec Foster Wheeler and Valmet

Mikko Hupa, Patrik Yrjas, Dorota Bankiewicz, Mia Mäkinen, Anders Brink, Maria Zevenhoven

The FBC conference series is held every third year and has almost a 50 year tradition. The 22nd FBC conference was held in June 14-17, 2015 in Radisson Blu Marina Palace Hotel in Turku and was co-organized by Åbo Akademi University, Amec Foster Wheeler and VTT. The conference covered the latest issues in fluidized bed combustion technology for power production, co-generation and waste incineration including fundamental research, equipment design, application and performance experience. During three busy conference days almost 140 papers were presented in 8 topical areas in 32 sessions. The conference gathered over 230 participants from academy, research centers and industry from 26 countries from all over the world.

Publications/Printed Proceedings:

- Proceedings of 22nd International Conference on Fluidized Bed Conversion, Vol 1, ISBN: 978-952-12-3222-0, Vol 2, ISBN: 978-952-12-3223-7

5.2 Participation in conferences, major meetings and courses

Location, meeting/organization, contribution, number of *PCC* participants

January

Florida, Tappi KROS, invited lecturer *Mikko Hupa*

Daytona, Florida USA, 39th International Conference and Expo on Advanced Ceramics and Composites (ICACC 39), invited lecturer *Leena Hupa*

Helsinki, Circulation economy symposium (SITRA), 1

February

Nelson, New Zealand, 6th International Conference on Advanced Materials and Nanotech., 1

Turku, K. Eränen symposium, Åbo Akademi

Belgrade, EPI306 COST Action, 1

Rouen, Symposium on sustainable process technology, 1

March

Petnica, Serbia, The 4th YES (Young Environmental Scientists) Meeting, 1

New Orleans, USA, Pittcon 2015, 1

Denver, USA, 249th American Chemical Society National Meeting, 1

Sitges, Spain, 4th International Conference on Multifunctional, hybrid and nanomaterials, 9-14.3.2015, 2

Turku, POKE Symposium, Åbo Akademi

April

Carvoeiro, Portugal, 4th Zing Electrochemistry Conference, 1

Bangor, UK, COST CM 1102/IBCarb Spring Training School "Synthesis for nano- and glycol-sciences", 1

Turku, Finland, I Russian-Finnish Symposium, Emerging Trends in Drug Development, 15

Turku, Finland, PET basics, 1

Gaia (Porto), Portugal, 10th European Conference on Industrial Furnaces and Boilers (INFUB 10), 1

Palermo, FineCat 2015, 2

London, Process Systems Enterprise: Advanced Process Modelling Forum 2015, 1

Erlangen-Nürnberg, Helmholtz-Allianz: Energie-effiziente Dreiphasenreaktorsysteme, 1

May

Barcelona, Spain, SETAC (Society of Environmental Toxicology and Chemistry) Europe 25th Annual Meeting, 1

Jyväskylä, Finland, Fate of Organic Chemicals in the Environment (intensive course), 1

Jyväskylä, Finland, Finnish Conference of Environmental Sciences, 1

Espoo, Finland, Carbohydrate and Bioengineering meeting, 4

Miami, Florida USA, Glass & Optical Materials Division and the Deutsche Glastechnische Gesellschaft Joint Annual Meeting (GOMD-DGG 2015), 1

Chicago, Illinois USA, 227th Electrochemical Society meeting, 1

Raisio, Inauguration Seminar of Smart Chemistry Park, 1

June

Manchester, United Kingdom, Graphene Week 2015, 2

Stockholm, Sweden, New materials from trees, 2

Madison, USA, International Symposium on Activation of Dioxygen and Homogeneous Oxidation Catalysis (ADHOC), 1

Freising, Germany, 18th IFRF International Members' Conference "Flexible and clean fuel conversion in industry", 3

Delft, Annual meeting of Delft Process Technology, 1

Reykjavik, NORDTEK conference, 1

Saariselkä, Lapland, Novel Reactors for 21st Century – Intensification in Reaction Engineering, 3rd Finnish Symposium and Summer School on Reaction Engineering, *several invited lectures*

Stockholm, SWE-FIN workshop, New materials from trees, 1

Tarragona, Chemical Engineering Department of the University Rovira i Virgili, 'Processing of Cellulosic Biomass', Invited lecturer *J.-P. Mikkola*

July

Lisbon, Portugal, Cleanair Conference, 2

August

Helsinki, Finland, Emerging targets and molecules in middle space, 2

Jyväskylä, Finland, The 25th Jyväskylä Summer School: Advanced Environmental Chemical Analysis (intensive course), 2

Sao Paulo, Brazil, The Advanced School on Glasses and Glass-Ceramics, 1

Kazan, EuropaCatXI, 5

September

Valencia, Spain, European Society for Biomedical Research on Alcoholism, 1

Kraków, Poland, 4th International Symposium on Surface Imaging/Spectroscopy at the Solid/Liquid Interface, 1

Bankok, Thailand, International Commission on Glass (ICG) Annual Meeting 2015, 1

Vienna, Austria, 18th International Symposium on Wood, Fiber and Pulping Chemistry, 2

Tulln, Austria, pre-symposium to 18th ISWFPC "Analytical Techniques in the Chemistry of Renewable Resources", 1

Novosibirsk, Chemical reagents and processes for fine chemistry XXIV, 1

Varna, 11th International Symposium on heterogeneous catalysis, plenary lecture *Tapio Salmi*, oral presentations: *Narendra Kumar*; *Yasuhito Sugano*

October

St. Petersburg, Russia, II Russian-Finnish Symposium, Emerging Trends in Drug Development, 3

Antalaya, Turkey, COST CM 1102 Multivalent Glycosystems for Nanoscience, final meeting, 2

Taipei, Taiwan, 66th Annual Meeting of International Society of Electrochemistry, Green Electrochemistry for Tomorrow's Society, 1

Copenhagen, Denmark, Nordic Flame Days 2015, 6

Vantaa, Finland, Soodakattilapäivä 2015, 1

Warsaw, Poland, 4th EPNOE International Polysaccharide Conference, 1

Nice, France, The 10th European Congress of Chemical Engineering (ECCE10), 1

Fürstenfeldbrück/München, ESCRE 2015 - European Symposium on Chemical Reaction Engineering, plenary lecturer *Dmitry Murzin*, oral presentation *Tapio Salmi*

November

Pultusk, Poland, The 7th International Workshop on Surface Modification for Chemical and Biochemical Sensing, 1

Seoul, South Korea, 71st meeting of International Energy Agency - Fluidized Bed Conversion, 1

Naantali, Finland, Suomen Kromatografiaseura, invited lecturers *Chunlin Xu, Bjarne Holmbom*, 3

Santiago, Chile, Algae Biorefinery Workshop, invited lecturer *Päivi Mäki-Arvela*

Åland, Finland, POKE seminarium, *several invited lectures*

December

Ås, Norway, Final meeting and seminar of the NordForsk funded Refining Lignocellulosics to Advanced Polymers and Fibers - PolyRefNorth – researcher network, 2

Helsinki, Graduate School of Environmental Science and Technology (EnSTe), Annual Seminar, invited lecture *Bjarne Holmbom*

Santa Cruz, US, Genomics, Metabolic Engineering and Bioinformatics in Biotechnological Applications, III Workshop CeBiB, invited lecturer *Päivi Mäki-Arvela*

Turku, Åbo Akademi University, Industrial Chemistry and Reaction Engineering 95 years

5.3 Visitors and visits

Visitors to *PCC*

Baranowska, Katarzyna, Polish Academy of Sciences, Poland (August, 2 weeks)

Bernardini, Andrea, University of Padova, Italy (January-February)

Blochberger, Max, Friedrich Schiller University of Jena, Germany

Boeva, Zhanna, **JGS*,** Lomonosov Moskow State University, Russia (January-December)

Brandt-Slowik, Juliane (September)

Bridier, Simon, ENSICAEN, France (April-July)

Chapellier, Yann, ENSICAEN, France (April-July)

Cingano, Marco, University of Padova, Italy (January-June)

Cherniakova, Natalia, St. Petersburg Technical University, Russia (August)

Cui, Shou, **JGS***, (January – September) University of Rennes, France

Czesick, Joanna, University of Warsaw (February-April)

Deryotkov, Sergei, St. Petersburg Technical University, Russia (August, 2 weeks)

Ding, Jiawang, **JGS***, Yantai Institute of Coastal Zone Research, Chine Academy of Sciences, China (December)

Dosmagabetova, Inkar, Kazakh University of Al-Farabi, Almaty, Kazakhstan (January)

Duprez, Thibault, Ecole Nationale Supérieure de Chimie de Montpellier, France (June-September)

Eqtesadi, Siamak, **JGS***, (August – December), 9 months University of Extremadura, Spain

Fakih, Ferial, Queen's University Belfast, United Kingdom (March)

Fernandez, Maria Anderez, University of Valladolid, Spain (January-May)

Gallina, Gianluca, University of Padova, Italy (April-July)

Gemo, Nicola, University of Padova, Italy (January-July)

Golets, Mikhail, **JGS***, University of Umeå, Sweden (April)

Gonzalez, Munos Marta, University of Cantabria, Spain, (January-June)

Gumbmann, Lorenz, Technical University of Dresden, Germany (December-January)

Haase, Stefan, **JGS***University of Dresden, Germany (July-October)

Ipatova, Elena, **JSG***, St. Petersburg State Forest Technical University, Russia (February-May)

Fijalkowski, Karol, University of Warsaw, Poland (March-April)

Fiedoruk, Marta, University of Warsaw, Poland (December)

Gepperth, David, University of Ulm, Germany (October-December)

Jale, Yanik, Ege University, Turkey (August)

Klunda, Tomás, Slovak Academy of Sciences, Slovakia (October)

Kramb, Jason (August) Tampere University of Technology, Finland

Maduna, Valkaj, Karolina, University of Zagreb, Croatia (January-December)

Maksymillian, Zegon, University of Warsaw (February-April)

Markstedt, Kajsa, **JGS***, Chalmers University of Technology, Sweden (September-November)

Munos Gonzales, Marta, University of Cantabria, Spain (January-May)

Müller, Pia, Technical University of Dresden, Germany (April-July)

Perez, Sergio, University of Valladolid, spain (October-December)

Pinilla de Dios, Maria, **JGS*** University of Valladolid, Spain (January-November)

Pokrzywnicka, Marta, University of Warsaw, Poland (December)

Prestipino, Mauro, (April – May) University of Messina, Italy

Ruiz Vasquez, Doris Polett, University of Conception, Chile (January-June)

Samson, Tina, INSA-Rouen, France (June-August)

Sau, Abhijit Sau, **JGS***, Bose Institule, India (January-August)

Schiller, Freidrich, University of Jena, Germany

Sugano, Yasuhito, Osaka University, Japan (January-December)

Wetzel, Roland, (September) Friedrich Schiller University of Jena, Germany

Zinnurova, Aigiza, St. Petersburg Technical University, Russia (November)

* **JGS** = Johan Gadolin Scholarship program participant

Visits by *PCC* Members

Aalto-Setälä, Laura, Friedrich-Schiller-University Jena, Germany (October)

Karlström, Oskar, Northwestern University (June-Spetbember)

Khazraie, Tooran, Lakeside University, Thunder Bay, Canada (September – October)

Lisak, Grzegorz, Malmö University, Sweden (January, March)

Lisak, Grzegorz, University of Wollongong, Australia (February)

Lisak, Grzegorz, Osaka University, Japan (September)

Liu, Jun, Paper and Fibre Research Institute (PFI), Norway (April-July)

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

Sangder, Johan, Friedrich-Schiller-University Jena, Germany (March-April)

Sokalski, Tomasz, AGH University of Science and Technology in Kraków, Poland (November)

Vainio, Emil, University of Toronto, Canada (September – November)

Wärnå, Johan, University of Dresden, Germany, 3 months

Invited Lecturers at ÅA-*PCC*

- Guest Lecturer, Professor Michio Murata, Department of Chemistry, Osaka University, Japan
- Guest lecturer Professor Janne Jänis, Department of Chemistry, University of Eastern Finland

5.4 External eveluations, reviews and tasks

Editorial boards

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 for Sustainable Energy, editorial board member, Dmitry Murzin

Catalysis in Industry, associate editor and editorial board member, Dmitry Murzin

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

Catalysis Today, editorial board member, Dmitry Murzin

Catalysis Today, guest editor 2015, Dmitry Murzin

Cellulose Chemistry and Technology, member of editorial board, Bjarne Holmbom, Anna Sundberg and Stefan Willför

Chemistry of Plant Raw Materials, journal language: Russian, member of editorial board, Bjarne Holmbom

Chemistry of Plant Raw Materials, journal language: Russian, member of editorial board, Andrey Pranovich

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

Current Catalysis, editorial board member, Dmitry Murzin

Holzforschung, member of editorial board, Bjarne Holmbom, Anna Sundberg and Stefan Willför

International Journal of Chemical Engineering, editorial board member/editor, Dmitry Murzin

Journal of Engineering, editorial board member, Dmitry Murzin

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

Kinetics and Catalysis, editorial board member, Dmitry Murzin

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

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

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

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

The Open Catalysis Journal, Dmitry Murzin

Topics in Catalysis, scientific advisory board, Dmitry Murzin

Wood Sci. Technol, member of editorial board, Bjarne Holmbom

O´Papel, member of editorial board, Bjarne Holmbom

Evaluation of candidates

Board member in evaluation of the candidates to the chair in physical chemistry at Aalto University, *Ari Ivaska*

Evaluator of docentship in chemistry, University of Jyväskylä, *Reko Leino*

Evaluator of lecturer track position in biopolymer chemistry with focus on surface and colloid chemistry, Aalto University, *Anna Sundberg*

Evaluation of tenure track positions, University of Ljubljana, *Tapio Salmi*

Evaluation of project or research proposals

Evaluator for AgreenSkills+, *Stefan Willför*

Evaluation of chemistry and chemical engineering in Czech Republic, Prague, *Tapio Salmi*

Evaluation of a research proposal, Quatar Research Council, *Ari Ivaska*

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

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

Evaluation of research proposal in nordic innovation, Norway, *Päivi Mäki-Arvela*

Evaluation of a research proposal, Chilean National Science and Technology Commission, *Ari Ivaska*

Evaluation of a research proposal, Slovak Academy of Sciences, *Tom Lindfors*

Expert evaluator of EU ERC Advanced grants, Brussels, Dmitry Murzin

External evaluator, scientific boards and honorary positions

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

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

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*

Deputy member of the Board of the Finnish Bioeconomy Cluster (FIBIC), *Stefan Willför*

Evaluator for Belgian Research Agency (FNRS), *Reko Leino*

Evaluator for the Christian Doppler Research Association 2015, *Stefan Willför*

Evaluator for Swedish Research Council (Vetenskapsrådet), *Reko Leino*

Evaluator for Slovenian Research Agency (ARRS), *Reko Leino*

Evaluator for South Africa's National Research Foundation (NRF), 2015, *Stefan Willför*

Evaluator for Hungarian Scientific Research Fund (OTKA), *Reko Leino*

Evaluator for several FP7 and H2020 evaluation tasks for EU Research Executive Agency (research proposals, mid-term evaluations of research networks, evaluation panel vice-chair tasks), *Reko Leino*

Evaluation of chemical engineering in Czech Republic, Tapio Salmi

Evaluation of the Netherlands Organization for Scientific Research, (NWO), *Tapio Salmi, J.-P. Mikkola*

Evaluation of the Netherlands Organization for Scientific Research, (NWO), *J.-P. Mikkola*

Expert for the Qatar Research Council, *Dmitry Murzin*

Full member of the Russian Akademie der Naturwissenschaft, *Dmitry Murzin*

Honorary professorship, St. Petersburg State Technological Institute (technical university), *Dmitry Murzin*

Member of international program committee of Delft Process Technology, TU Delft, *Tapio Salmi*

Member of the scientific advisory board of the chemical industry, "Kemianteollisuuden tieteellinen neuvottelukunta, Kemianteollisuus ry", *Stefan Willför*

Member of scientific advisory board, Czech Academy of Sciences, Institute of chemical Process Fundamentals, *Tapio Salmi*

Member of scientific committee, European Symposium in Chemical Reaction Engineering (ESCRE), Munich, *Tapio Salmi*

Member of scientific committee, European Congress in Chemical Engineering (ECCE), Nice, *Tapio Salmi*

Member of steering group of Helmholtz Energie-Allianz: Energieeffiziente Dreiphasen-reaktorsysteme, Germany, *Tapio Salmi*

Scientific board member for Biological and Chemical research Centre at University of Warsaw, Poland, *Andrzej Lewenstam*

Turku Future Technologies, Chairman of the steering group, *Tapio Salmi*

External PhD evaluations

Ankarfors, Mikael, KTH, Sweden, examination committee for doctoral thesis, *Anna Sundberg*

Gonzalez Arcos, Angelica, KTH, Stockholm, jury member, *Tapio Salmi*

Bäckström, Daniel, Chalmers University of Technology, Gothenburg, Sweden, examination committee for doctoral thesis, *Patrik Yrjas*

Eqtesadi, Siamak, University of Extramadura, Badjoz, Spain, opponent, *Leena Hupa*

Grund-Beck, Lina, Linnaeus University, Växjö, Sweden, opponent *Leena Hupa*

Hilli, Yulia, University of Eastern Finland, evaluator, *Päivi Mäki-Arvela*

Jefimova, Jekaterina, University of Tartu, *J.-P. Mikkola*

Jiang, Yu, University of Eastern Finland, Reviewer, *Leena Hupa*

Karppanen, Essi, Aalto University, Finland, reviewer, *Reko Leino*

Kloekhorst, Arjan, University of Groningen, opponent, *Dmitry Murzin*

Lali, Faical, TU Dresden, opponent, *Tapio Salmi*

Leveneur, Sébastien, Université de Rouen, habilitation, jury members, *Tapio Salmi* and *J.-P. Mikkola*

Li, Tian, Norwegian University of Science and Technology, Trondheim, Norway, opponent, *Anders Brink*

Mathew, Renny, Stockholm University, Sweden, examination committee for doctoral thesis, *Leena Hup*a

Mufti Azis Muhammed, Chalmers University of Technology, opponent, *Dmitry Murzin*

Niemi, Piritta, Aalto University, reviewer, *Stefan Willför*

Plaban, Bora, Tezpur University, India, evaluator, *Päivi Mäki-Arvela*

Pawar, Prashant Mohan-Anupama, Swedish University of Agricultural Sciences, Umeå, member of the committee, *Päivi Mäki-Arvela*

Peljo, Jani, Tampere Technical University, Tampere, Finland, reviewer, *Ari Ivaska*

Rautiainen, Sari, University of Helsinki, evaluator, *Päivi Mäki-Arvela*

Recasens, Marta Novell, Universitat Rovira i Virgili, Tarragona, Spain, reviewer, *Johan Bobacka*

Selin, Jukka, University of Jyväskylä, reviwer, *Anna Sundberg*

Yamamoto, Akio, Aalto University, opponent, *Stefan Willför*

Yedro, Florencia, University of Valladolid, jury member, *Henrik Grénman*

Societal evaluations and tasks

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

Publicity

D. Murzin, Läroböcker är också ett sätt att skaffa synlighet, Meddelanden från Åbo Akademi 9 (2015) 6

6 Doctoral thesis in progress at *PCC*

Students from Outside Finland (incl. part-time and external students)

- Steliana Aldea (Romania, *F*), MSc University of Bucharest, Bucharest, Romania 2006, BSc ibid. 2002
- Cesar de Araujo Filho (Brazil, *M*), MSc Federal University of Ceara, Fortaleza, Brazil 2010, defence in May 2016
- Jesús Arroyo Condori (Peru, *M*), MSc ÅAU 2011, BSc Universidad Nacional Mayor de San Marcos (UNMSM), Peru 2010
- Erfan Behravesh (Iran, *M*), MSc ÅAU 2014, BSc Azad University of Quchan (IAUQ), Iran 2010
- Yury Brusentsev (Russia, *M*), MSc Moscow State University, Russia 2003
- Meheretu Jaleta Dirbeba (Ethiopia, *M*), MSc Addis Ababa University, Ethiopia 2013, BSc ibid. 2003
- Lidia Godina (Russia, *F*), MSc Mendeleyev University of Chemical Technology of Russia, Moscow, Russia 2012
- Imane Hachemi (Algeria, *F*), MSc University of Sciences and Technology Houari Boumediene (USTHB) 2012, BSc Ibid., Algiers, Algeria 2009
- Tingting Han (China, F), MSc ÅA 2008, BSc Shandong Institute of Light Industry, China 2006
- Ning He (China, *M*), MSc ÅA 2009, BSc Shandong Polytechnic University, China 2007
- Tooran Khazraie Shoulaifar (Iran, *F*), MSc Sharif University of Technology, Tehran, Iran 2007, BSc Tehran University, Tehran, Iran 2002
- Ekaterina Korotkova (Russia, *F*), MSc ÅA 2011 & Tver State Technical University, Tver, Russia 2010 (double degree), BSc Tver State Technical University, Tver, Russia 2008
- Ewelina Kortesmäki (Poland, *F*), MSc University of Gdansk, Poland 2013
- Ron Lai (Canada, *M*), MSc University of British Columbia, Vancouver, Canada 1994
- Na Li (China, *F*), MSc ÅA 2007, BSc Shandong Institute of Light Industry, China 2005
- Jun Liu (China, *M*), MSc Tianjin University of Science and Technology, China 2012
- Donald MacNeil (Canada, *M*), MSc ÅA 2002, BEng Dalhousie University, Halifax, Canada 1994
- Axel Meierjohann (Germany, *M*), MSc ÅA 2010
- Ali Najarnezhasmashhadi (Iran, *M*), MSc ÅA 2015, BSc 2005 Azad University, Iran
- Andrea Pérez Nebreda (Spain, *F*), MSc Universidad de Cantabria, Santander, Spain 2013
- Ricardo Miguel Pezoa Conte (Chile, *M*), MSc University of Chile, Santiago, Chile 2010
- Maria Pinilla de Dios (Spain, *F*), MSc Universidad de Valladolid, Valladolid, Spain 2014
- Soudabeh Saeid (Iran, F) MSc Islamic Azad university Tabriz, Iran 2015
- Rishabh Sarna (India, *M*), MSc ÅA 2012, BSc Indian Institute of Technology, Roorkee, India 2010

- Farhan Saleem, (Pakistan, *M*), MSc. ÅA, 2013, Bachelor in Chem. Tech. University of Karachi, Pakistan 2007
- Paulo Santochi (Brazil, *M*), MSc ÅA 2012, Bachelor in Chem. Eng, University of Sao Paulo, Brazil 2010
- Vladimir Shumilov (Russia, *M*), MSc ÅA 2014 & Tver State Technical University, Russia 2014 (double degree), BSc Tver State Technical University, Russia 2012
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- Nemenja Vucetic (Serbia, *F*), MSc Belgrade University, Serbia 2013
- Hao Wu (China, *F*), MSc ÅA 2007, BSc Shandong Institute of Light Industry, China 2005
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- Kai Yu (China, *M*), MSc ÅA 2010, BSc Shandong Polytechnic University, China 2008

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- Laura Aalto-Setälä, (Kokemäki, *F*), MSc University of Helsinki 2014
- Leena Björkvik (Vasa, *F*), MSc ÅA 2011
- Elisa Hupa (Åbo, *F*), MSc ÅA 2014
- Matilda Kråkström (Pedersöre, *F*), MSc ÅA 2015
- Lucas Lagerquist (Vasa, *M*), MSc ÅA 2011
- Christian Lindfors (Helsingfors, *M*), MSc Helsinki University of Technology 2008
- Sara Lund (Åbo, *F*), MSc ÅA 2013
- Ida Mattsson (Saltvik, *F*), MSc ÅA 2015
- Sam Myllynen (Borgå, *M*), LicTech ÅA 2002
- Jonne Niemi (Somero, *M*), MSc ÅA 2014
- Linda Nisula (Vasa, *F*), MSc ÅA 2003
- Magnus Perander (Pargas, *M*), MSc ÅA 2010
- Piia Poranen (Raisio, *F*), M.Sc. Lappeenranta University of Technology, 1997
- Jani Rahkila (Karleby, *M*), MSc ÅA 2012
- Sabine Rendon (Esbo, *F*), MSc ÅA 2011
- Patrik Runeberg (Borgå, *M*), MSc ÅA 2014
- Christoffer Sevonius (Sibbo, *M*), MSc ÅA 2012
- Maria Sundqvist (Pargas, *F*), MSc ÅA 2015