

Johan Gadolin
Process Chemistry
Centre

Åbo Akademi University

Annual Report 2014-2015

Edited by Hanna Lindqvist, Anders Brink, Rose-Marie Latonen,
Päivi Mäki-Arvela, Tiina Saloranta, Anna Sundberg

Åbo, Finland
<http://www.abo.fi/pcc/>

Johan Gadolin Process Chemistry Centre (PCC) at Åbo Akademi University

The PCC is a Centre of Excellence in scientific research at Åbo Akademi University for the years 2015-2018. The PCC was also a National Centre of Excellence in Research appointed by the Academy of Finland for the years 2000-2005 and 2006-2011.

The PCC consists of the teams:

- *Combustion and Materials Chemistry (led by Prof. Leena Hupa)*
- *Wood and Paper Chemistry (Prof. Stefan Willför)*
- *Catalysis and Reaction Engineering (Prof. Tapio Salmi)*
- *Process Analytical Chemistry (Prof. Johan Bobacka)*
- *Organic Chemistry (Prof. Reko Leino)*

The PCC conducts research in detailed physico-chemical processes in environments of industrial importance, in order to meet the needs of tomorrow's process and product development. This approach, with the focus on the detailed understanding of the process chemistry, we have called Molecular Process Technology.

The PCC Forum for Society (2015) consists of: Örjan Andersson (Novia), Ilmo Aronen (Raisio), Stig-Erik Bruun (Chemigate), Kenneth Ekman (Crisolteq), Heidi Fagerholm (Kemira), Christine Hagström-Näsi (FIBIC), Patrik Holm (Orion Pharma), Jarkko Kaplin (Nordkalk), Bertel Karlstedt (Valmet), Kari Kovasin (Metsä Fibre), Björn Lax (Chemec), Timo Leppä (Chemical Industry Federation of Finland), Lars Peter Lindfors (Neste), Leena Paavilainen (Luke), Jarkko Partinen (Outotec), Leena Sarvaranta (VTT), Bengt-Johan Skrifvars (Top Analytica), Kenneth Sundberg (Tikkurila), Kari Toivonen (Elomatic), Petri Vasara (Pöyry) and Stefan Wallin (Member of parliament).

The PCC Scientific Advisory Board (2015) consists of: Professor Raimo Alén (University of Jyväskylä), Professor Jan-Erling Bäckvall (Stockholm University, Stockholm), Professor Jiri Janata (Georgia Institute of Science and Technology, Atlanta), Professor Lars J. Pettersson (Royal Institute of Technology (KTH), Stockholm) and Professor Andreas Seidel-Morgenstern (Max Planck Institute, Magdeburg, Germany).

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1. Introduction to the Activities in 2014-2015

Background and news

The Åbo Akademi Process Chemistry Centre (PCC) was formed in 1998 by joining four research groups at the Department of Chemical Engineering at Åbo Akademi into one research centre with common objectives and research strategy. PCC has won the status of a Centre of Excellence (CoE) in research granted by the Academy of Finland for two consecutive six-year periods: 2000-2005, and 2006-2011, respectively. 2012-2014 the Centre continued its activities with a new research programme working in close collaboration with a number of industrial companies and research organizations around the world, with 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. Another important change is that the Laboratory of Organic Chemistry now also is a full partner in PCC. After receiving the good news of the CoE status, we also decided to refresh the name of PCC to Johan Gadolin Process Chemistry Centre and to introduce a new logo, designed by Linus Silvander from our Centre. This logo was chosen after a competition with several good suggestions.

Our former Chairman of the Board, Professor Mikko Hupa, was elected Rector of the university for the period 2015-2018 and thus had to step aside from PCC. Professor Stefan Willför was then elected as new Chairman of the Board. Furthermore, the university once again did structural rearrangements and from the beginning of 2015 we have four faculties altogether. PCC belongs to the Faculty of Science and Engineering and Professor Tapio Salmi was chosen Dean of this new faculty for the period 2015-2018.

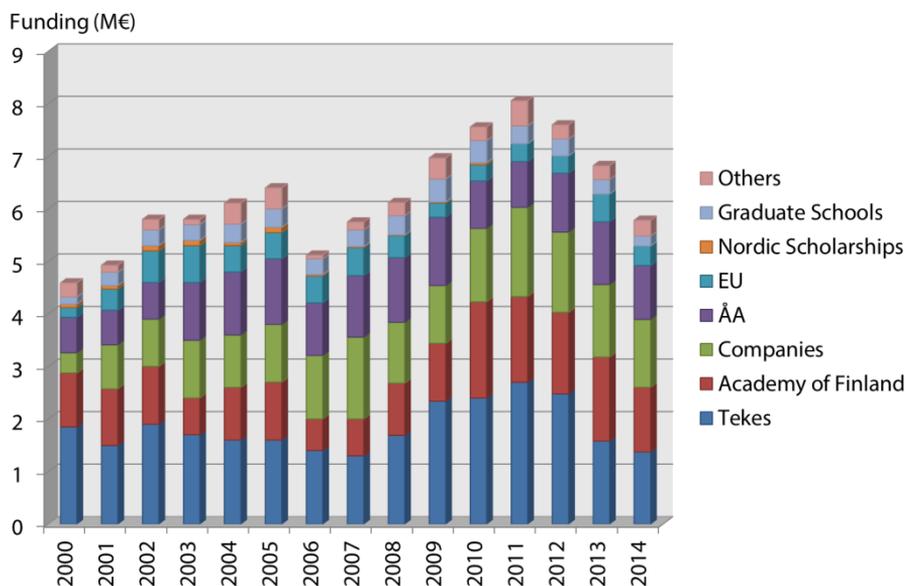
From the year 2015 we thus follow a new overall research plan, “Future Refining of Forest Biomass – the Molecular Process Technology Approach”, where our activities are divided into four Work Packages and Complementary Activities. The core of the new plan is still built on our strengths in experimental and modelling capabilities to explore chemical details in novel processes and products that use biomass-based raw materials. The focus has shifted a bit from fractionation of biomass towards modification of the biomass components and their use in high-value applications such as structural biocomposites, 3D biomaterials in medical applications, immunostimulatory glycoclusters, and various fine and specialty chemicals. Our Johan Gadolin Scholarship Programme has continued stronger than ever and we are also establishing new cooperation with the Turku Centre for Biotechnology within the scope of the new research plan.

Emeritus Professor Bjarne Holmbom, former board member and currently Scientific Advisor to PCC, has been recognized for having made preeminent contributions to the paper industry worldwide and thus he will be inducted into the Paper Industry International Hall of Fame (<http://www.paperhall.org>) in October this year. Their mission is “To recognize people who have made preeminent contributions to the paper industry, worldwide, by inducting them into the Paper Industry International Hall of Fame. To foster a greater understanding of the paper industry, its heritage, its impact on our quality of life, its challenges and its opportunities through educational programs and interpretive exhibits”. PCC congratulates Prof. Em. Holmbom for his outstanding achievements.

The Year 2014 in Numbers

In 2014 more than 20 senior researchers and 50 full-time PhD candidates worked in the 50 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 2014 were Tekes – the Finnish Funding Agency for Innovation together with Industrial Companies, and the Academy of Finland. Since 2012 the Centre has no longer received the Centre of Excellence funding from the Academy of Finland. However, this decrease in funding was partly compensated by a special strategic support from Åbo Akademi University and also from other sources, and this made it possible for the Centre to continue its activities with full capacity.



The funding of the Åbo Akademi Process Chemistry Centre 2000-2014.

From the Academic point of view the year 2014 was extremely productive. The table below gives some key numbers of our academic activities in 2014. Once again, the Centre kept a high production rate by publishing 145 papers in scientific publication series with the full referee system. Further, another remarkable record was achieved in 2014: 16 PhD theses were defended during the year.

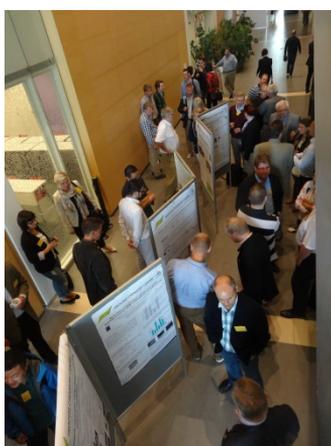
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Doctoral Theses	5	7	8	2	11	8	8	8	9	7	6	10	10	15	16
Masters' Theses	21	23	27	26	17	15	20	23	19	17	15	11	14	12	16
Journal Articles	60	70	94	77	106	109	113	116	101	118	138	143	145	154	145
Other Pubs.	105	86	96	86	111	148	157	169	195	204	191	168	220	155	n.d.

Theses and other publications by the Johan Gadolin Process Chemistry Centre 2000-2014.

Besides the technical publications the PCC again published two Newsletters. Our researchers also wrote 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 2014 with a Winter Colloquium in March and the PCC Anders Ringbom Workshop in Flow chemistry, Microanalysis and Microtechnology in December. The traditional Annual Seminar was held on August 20, 2014. 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 has already opened up new areas of collaboration between the two strong Centres.



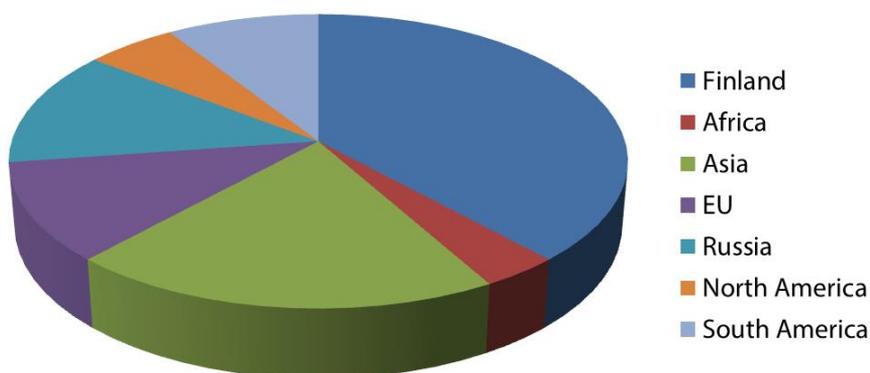
PCC Annual Seminar in August 2014 (Photo: Ari Ivaska).

Doctoral Students

A central part of our research activities is done as doctoral theses works. Altogether about 56 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 on page 148 of this Annual Report.

At the moment, 37.5% of the PCC doctoral students are female.

Many of the PhD projects have been done with support from the national graduate schools, such as the Graduate School in Chemical Engineering (GSCE), which earlier was coordinated by PCC. In 2014 GSCE received additional funding from the Åbo Akademi doctoral network program, which allowed for additional recruiting of students from the beginning of the year.



Nationality of PhD students at PCC 2014-2015. For more detailed information see page 148.

Johan Gadolin Scholarship Program

Our Johan Gadolin Scholarship Programme 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 recently decided to grant new funding for the Johan Gadolin Scholarships Programme for the period 2014-2015, with an option for two more years as well. This new funding will strongly activate the program and in the next two years we expect to have continuously 5-10 visiting Johan Gadolin fellows at our Centre.

In the Johan Gadolin Scholarship Programme we have been able to invite PhD students and post doctoral researchers to join PCC for a period between 3 to 12

months. So far, 57 fellows from 22 different countries and 47 different universities worldwide have participated in the programme. 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 130 scientific articles and more than 110 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 2014 the board met eleven times. Dr. Hanna Lindqvist works with the coordination of the PCC and functions as secretary of the board. From September 2015 Hanna will move to other tasks within the university and Dr. Otto Långvik will be the new coordinator for PCC.

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. In 2015-2016 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 2014, the PCC had three lectures in its Distinguished Lecturer Series:

- September 19, 2014: Prof. Jaap Schouten, TU Eindhoven, the Netherlands: "Process intensification with new reactors"
- December 12, 2014: Prof. Vasile Parvulescu, University of Bucharest, Romania
- December 19, 2014: Prof. Michele Maggini, University of Padua, Italy: "Recent developments in flow chemistry"

Acknowledgements

This report will be published at the Annual Symposium of the PCC held on August 20-21, 2015 at the Åbo Akademi ICT 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 2014. It also has an activity calendar listing the main events where members of the Centre have contributed or participated during that year.

The report is edited by an editorial team consisting of Hanna Lindqvist, Anders Brink, Rose-Marie Latonen, Päivi Mäki-Arvela, Tiina Saloranta and Anna Sundberg with the assistance of Mia Mäkinen. The layout was done by Hanna Lindqvist.

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

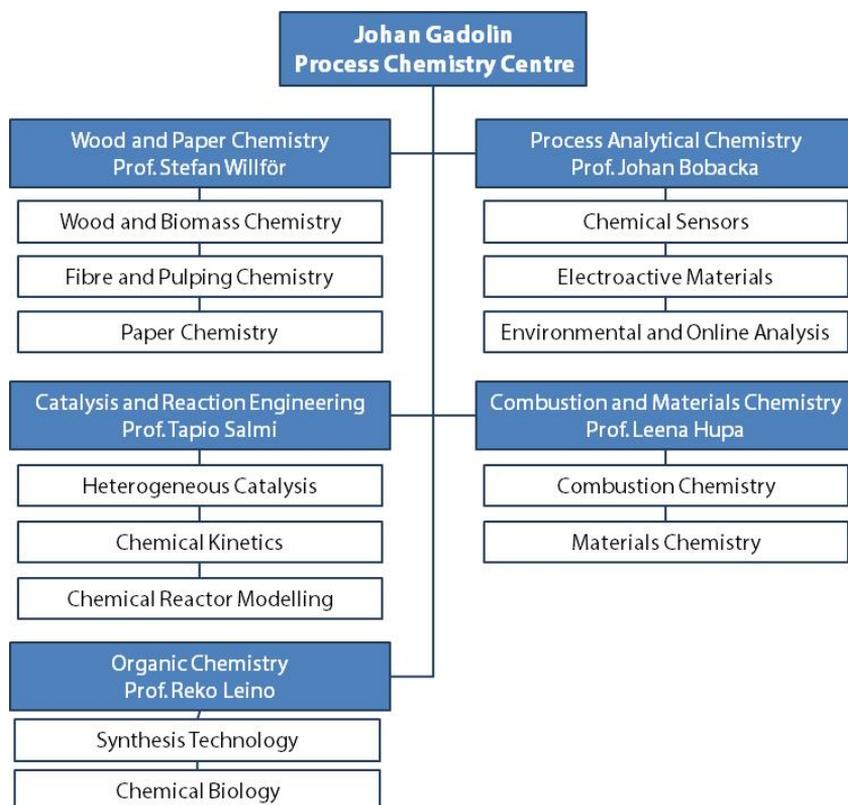
On behalf of the Board of the Johan Gadolin Process Chemistry Centre,

Stefan Willför

Chairman

2. Organization and personnel

2.1 Organization



Organization of the Johan Gadolin Process Chemistry Centre

Executive Board

- Prof. Stefan Willför (Chairman)
- Prof. Johan Bobacka (Vice)
- Prof. Tapio Salmi
- Prof. Reko Leino
- Prof. Leena Hupa
- Coordination:
Hanna Lindqvist (- 31.8.2015)
Otto Långvik (1.9.2015 -)

Scientific Advisory Board

- Prof. Raimo Alén, Finland
- Prof. Jan-Erling Bäckvall, Sweden
- Prof. Jiri Janata, USA
- Prof. Lars Pettersson, Sweden
- Prof. Andreas Seidel-Morgenstern, Germany

PCC Forum for Society

- Örjan Andersson, Novia
- Ilmo Aronen, Raisio
- Stig-Erik Bruun, Chemigate
- Kenneth Ekman, Crisolteq
- Heidi Fagerholm, Kemira
- Christine Hagström-Näsi, FIBIC
- Patrik Holm, Orion Pharma
- Jarkko Kaplin, Nordkalk
- Bertel Karlstedt, Valmet
- Kari Kovasin, Metsä Fibre
- Björn Lax, Chemec
- Timo Leppä, Chemical Industry Federation of Finland
- Lars Peter Lindfors, Neste
- Leena Paavilainen, Luke
- Jarkko Partinen, Outotec
- Leena Sarvaranta, VTT
- Bengt-Johan Skrifvars, Top Analytica
- Kenneth Sundberg, Tikkurila
- Kari Toivonen, Elomatic
- Petri Vasara, Pöyry
- Stefan Wallin, Member of Parliament

2.2 Wood and Paper Chemistry

The vision of our laboratory is to be an internationally recognized and leading team in wood, biorefining, and papermaking chemistry. 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.

External research support during 2014 was obtained mainly from Tekes and the Fibic SHOK, the industry, and Academy of Finland.

To the end of 2014 we had a close cooperation with the Finnish Forest Research Institute (today Luke or the Natural Resources Institute Finland), in the form of two joint senior research positions and a scientific advisor. Their field of research includes new products and biomaterials from the forest and other natural resources. We also have close cooperation with e.g. KTH and the Wallenberg Wood Science Centre in Sweden, as well as 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

Professors

Stefan Willför
Bjarne Holmbom (Emeritus)

Docents

Andrey Pranovich
Annika Smeds
Anna Sundberg
Chunlin Xu

Senior researchers

Ann-Sofie Leppänen
Hanna Lindqvist
Abhijit Sau

*Doctoral students &
Researchers*

Lari Vähäsalo
Jarl Hemming
Elena Ipatova
Victor Kisonen
Ekaterina Korotkova
Jens Krogell
Jun Liu
Linda Nisula
Sebastian von Schoultz
Klaus Söderback

*Technician
Secretary*

Wenyang Xu
Leif Österholm
Agneta Hermansson

Links

<http://www.abo.fi/fakultet/traochpapperskemi>

2.3 Combustion and Materials Chemistry

The research strategy of our laboratory is based on detailed knowledge on chemistry of high temperature processes and materials. Our main research efforts are in the fields of bioenergy, cleantech and medical technologies. Within the bioenergy and cleantech areas we characterize 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. In 2014 we had several major projects within these topics. Besides being published as scientific papers and academic theses, the research efforts were planned to assist the equipment manufacturing companies in their work to design novel combustion devices. Our newest research efforts dealt with recovering and recycling inorganic elements in industrial and municipal waste streams to novel high value products. Within the medical field, development of devices utilizing electrical stimulation for wound-healing and skin care, and tailoring of bioactive glasses for tissue engineering scaffolds and biosensors were the main research focuses.

Our consortium project Future Fuels for Sustainable Energy Conversion, FUSEC, 2011-2014 ended in spring 2014. Partly based on the research achievements within the FUSEC project, a new large consortium project Clustering Innovation Competence of Future Fuels in Power Production, CLIFF, was started in May 2014. ÅA-PCC is the scientific coordinator of this Tekes supported industry project. Several national and international industrial partners participate in this project. The research is done in collaboration with Tampere University of Technology, Lappeenranta University of Technology, Aalto University and VTT Technical Research Centre of Finland. The CLIFF project aims to support the partners’ development of innovations and new business in the area of future utilization of biomass and wastes as energy sources. In addition, the generic research topics in the common platform is selected to give the partners new strategic scientific information and tools for innovations, new products and business concepts to the global market.

We participated in the project BRISK - Biofuels Research Infrastructure for Sharing Knowledge. The four-year BRISK initiative funded under EC FP7 (Ref: 284498) runs to September 2015. BRISK is coordinated by the Royal Institute of Technology (KTH), Stockholm, and includes partners from Austria, Denmark, Finland, Germany, Greece, Italy, Netherlands, Norway, Poland, Spain, Sweden, Switzerland, Turkey and the UK. BRISK aims at developing a European Research

Infrastructure for Thermochemical Biomass Conversion, supporting R&D in innovative processes to convert sustainable feedstocks (agricultural/forestry wastes and energy crops) into liquid, gaseous or solid fuels.

We were also involved in the organization of the 2014 International Chemical Recovery Conference in Tampere, June 2014. In addition, the practical arrangements of the 22nd International Conference on Fluidized Bed Combustion in June, 2015 in Turku were initiated in 2014. The conference organizers are Amec Foster Wheeler, VTT Technical Research Centre of Finland, and Åbo Akademi. The conference chair is Professor Mikko Hupa.

In 2014 we worked with several projects connected to medical and well-being applications. Within our bioactive glass research we extended the composition ranges from the silicate -based systems to the phosphate and borate systems. One major goal was to develop novel compositions for glass fibres in biosensing applications. We also continued to develop our system for measuring the on-line ion release rates of bioactive glasses in dynamic solutions. As a new topic, we studied novel optical glass compositions with the special focus on biomedical applications.

The development of a printed self-powered cosmetics patch to allow for enhanced skin moisturization and rejuvenation was ended with good results. The project studied the possibility to utilize the “sugar battery” developed by ÅA/Aalto/TTY/VTT to power cosmetics patches and investigated the different electrode/skin interaction aspects. The approach was successful and resulted in a skin interaction innovation which is currently being patented (in National and PCT stages). The commercial potential of the invention is currently being investigated by VTT.

Also in 2014, the Tekes TUTLI supported project dealing with development of a multifunctional wound mapping and healing patch was successfully completed. A number of design and measurement technique-related innovations were found patentable, and the developed technology is currently being patented (in PCT-stage). A six-month clinical trial conducted at Tampere University Hospital clearly demonstrated the strengths and usefulness of the device, and the feedback from clinicians confirms that there is a clear market for the device. The device won the 2014 “Paras Businesspolku”-competition arranged by Turku Science Park and a team has been gathered to found a start-up company to commercialize the product.

The year 2014 included also other recognitions for the group. Based on our scientific and academic achievements the Chancellor of Åbo Akademi nominated Professor Mikko Hupa to the Research Leader of the Year. Said nomination was accompanied by the Chancellor’s prize to our research team. Later the same fall Professor Hupa received the Honorary Doctorate at the Aalto University. Aalto University motivated this in the following way: “In his research, Professor Hupa has specialized in high-temperature processes and materials, especially combustion processes and ceramic materials. In his capacity as an internationally respected researcher in his field, Professor Mikko Hupa has acted as an expert in several

organizations and institutions both in Finland and abroad, for instance he has been the President of the International Flame Research Foundation, IFRF. Professor Mikko Hupa's role as a developer of the doctoral education in technology programme is noteworthy, as he is a founder and the director of the Graduate School in Chemical Engineering, a nationwide research school."



Personnel

Professors

Mikko Hupa (Rector of ÅA since 1.1.2015)

Leena Hupa

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)

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*Economy Secretary
Secretary
Computer support*

Links:

<http://www.abo.fi/fakultet/ook>
<http://www.abo.fi/gsce>

2.4 Catalysis and Reaction Engineering

The core competence of the group is in catalysis, kinetics, modeling of chemical reactors 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 in 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 mining products. New theories 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 nanogold and bimetallic catalysts, which are developed in collaboration with domestic and foreign universities.

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 catalytic characterization is very intensive with University of Turku, University of Oulu and University of Umeå. Molecularly oriented kinetic studies are carried out in many 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.

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. 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 reactions of solids with liquids. New computational tools have been taken in use in the simulation of kinetics, diffusion and flow pattern, the most applications are in the fields of structured reactors and microreactors.

Continuous reactor technology is under intensive development: we have constructed several continuous reactors, the star among them being the parallel screening tube reactor system equipped with GC-MS. 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 development, such as solid foams, which are developed together with the group in Combustion and Materials Chemistry (PCC) and foreign partners.

The development of green process technology is advanced 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 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 phase. All the experimental efforts are coupled to advanced mathematical modelling of chemical phenomena in batch, semibatch and continuous reactors.

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.



Personnel

Professors

Tapio Salmi
Dmitry Murzin
Johan Wärnå
Jyri-Pekka Mikkola (part-time joint professor with
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Umeå

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Antonina Kupareva
Ewelina Leino
Karolina Maduna Valkaj
Gerson Martin Gurvelo
Toni Riittonen
Bartosz Rosmysłowicz
Doris Ruiz
Mats Rönnholm
Eero Salminen
Sabrina Schmidt
Juan Garcia Serna
Victor Sifontes Herrera
Martina Stekrova
Timo Petteri Suominen
Anton Tokarev
Pasi Tolvanen
Cesar de Araujo Filho
Steliana Aldea

Doctoral students

& researchers

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Marco Cingano
Lydia Godina
Imane Hachemi
Andrea Perez Nebreda
Ricardo Pezoa Conte
Maria Pinilla de Dios
Jussi Rissanen
Farhan Saleem
Valeri Shumilov
Stefano Sterchele
Alexandra Torozova
Nemanja Vucetic
Elena Murzina
Lotta Alho (part-time)

Technician
Secretary

Links

<http://www.abo.fi/fakultet/tekniskkemi>

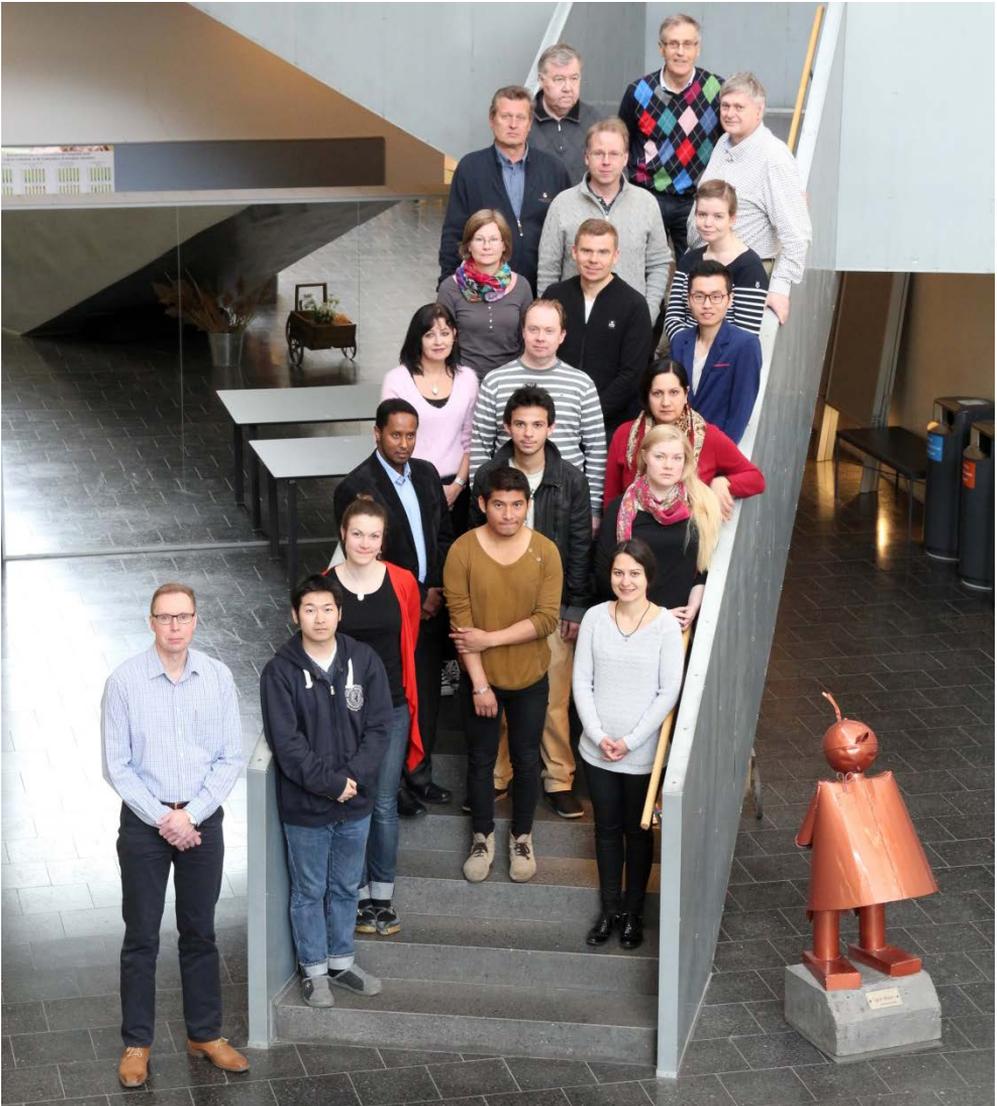
2.5 Process Analytical Chemistry

The availability of chemical information becomes increasingly important in today's modern world to ensure a safe and clean environment, sustainable industrial production, personal health and welfare for the growing population on Earth. New analytical methods, instruments and strategies are continuously developed and applied in important areas like environmental monitoring, process analysis and healthcare diagnostics. It has been estimated that more than 10 000 chemical analyses are done in the world every minute!

Process analytical chemistry is needed for efficient control of industrial processes, including (i) analysis of raw materials, (ii) determination of product quality, (iii) monitoring of effluents, and (iv) analysis of hazardous components for safety reasons. The main challenge of process analytical chemistry is the development of robust and automated analytical systems that can work continuously for a long time with a minimum of service needed. In addition to sophisticated analytical instrumentation, there is a growing need for inexpensive analytical tools such as chemical sensors that are easy to use on a large scale in various fields of applications.

An important research direction at the Process Analytical Chemistry group is the development of chemical sensors for applications in process analysis, environmental monitoring and healthcare diagnostics. Solid-contact ion-selective electrodes (SC-ISEs) have become a major research topic in our group over the last two decades. By combining SC-ISEs with our recently developed solid-state reference electrode we are able to provide powerful chemical sensors for various applications. Our current research includes also paper-based sampling and novel signal transduction methods for ion sensors. A unique feature of ion-selective electrodes is that they provide information about the free ion concentration (ion activity), while most other analytical methods give the total concentration.

Our research on chemical sensors is supported by electrochemical and spectro-electrochemical characterization of electroactive materials including conducting polymers, fullerenes, carbon nanotubes and graphene. Advanced nonequilibrium mathematical models are developed for accurate description of the potentiometric response of ion-selective electrodes. Electroactive materials are also studied as electrochemically controlled separation membranes, which is relevant for water purification. Our present research activities include also ion-exchange reactions and complexation of metal ions to biomass, which is relevant for the future refining of biomass. Our recently explored electrochemical oxidation of cellulose and hemicelluloses may open up entirely new pathways for utilization of biomass.



Personnel

Professors

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

Docents

Leo Harju
Carita Kvarnström
Rose-Marie Latonen
Tom Lindfors
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Organization and personnel

Senior researchers

Patrycja Bober
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Laboratory manager

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Doctoral students

Uliana Akhmetzyanova

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Jesús Arroyo
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Secretary & coordinator

Technicians

Links

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

2.6 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 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; and 4) Environmental organic chemistry including studies on the environmental fate of pharmaceuticals, antibiotics and endocrine disruptors.

External research support during 2014 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 including the COST Action CM1102 Multivalent Glycosystems for Nanoscience-MultiGlycoNano (Working Group 3: Vaccines and Modulators of the Immune System).



Personnel

<i>Professors</i>	Reko Leino Leif Kronberg Jorma Mattinen (Rector of Åbo Akademi until 31.12.2014)
<i>Docents</i>	Filip Ekholm Patrik Eklund Rainer Sjöholm Annika Smeds (Wood and Paper Chemistry)
<i>Senior researchers</i>	Jan-Erik Lönnqvist Denys Mavrynsky Tiina Saloranta
<i>Doctoral students & researchers</i>	Yury Brusentsev Andreas Gunell Ewelina Krzomyk Matilda Kråkström Lucas Lagerquist Otto Långvik Axel Meierjohann Jani Rahkila Sabine Rendon Patrik Runeberg Risto Savela Heidi Sundelin Andreas West Johnny Östman
<i>Laboratory technician</i>	Päivi Pennanen

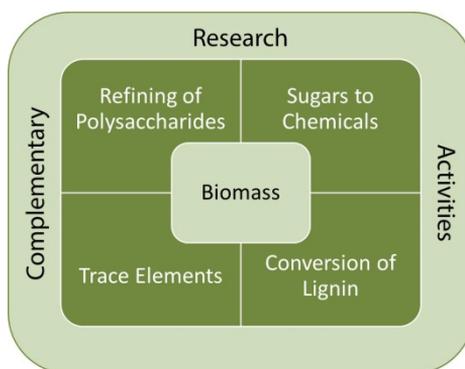
Links

<http://www.abo.fi/organiskkemi>

3. Research

PCC obtained the current CoE status with the research plan entitled: PCC – Future Refining of Forest Biomass. 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. New and clean processes and products will be developed, based on selective fractionation of lignocellulosic biomass using green solvents. The biomass fractions will be valorized through chemical transformations to achieve the desired molecules, which are necessary and useful in our everyday life. 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 will be 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). In addition, a great deal of research is done as a part of the Complementary Research Activities (CRA).



PCC research areas.

Research personnel

WP 1: Refining and Utilization of Polysaccharides

Doctoral students & researchers:

Laura Aalto-Setälä
Shuyana Hereda
Jun Liu
Aleksandra Makarova
Andrea Perez Nebreda
Ricardo Pezoa Conte
Jussi Rissanen
Patrik Runeberg (WP1, WP2, WP3)
Johan Sangder
Hasan Sherwani
Wenyang Xu
Muhammad Zubair

Patrik Eklund (WP1, WP2, WP3)
Kari Eränen (WP1, WP2)
Valerie Eta
Henrik Grénman
Jarl Hemming (WP1, WP3)
Olatunde Jogunola
Rose-Marie Latonen (WP1, CRA)
Tom Lindfors (WP1, CRA)
Päivi Mäki-Arvela (WP1, WP2)
Andrey Pranovich (WP1, WP3)
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Anna Sundberg (WP1, WP3)
Lari Vähäsalo (WP1, WP3)
Xiaoju Wang
Johan Wärnå (WP1, WP2)
Chunlin Xu

Senior researchers:

Ikenna Anugwom
Patrycja Bober
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WP 2: Conversion of Sugars to Chemicals

Doctoral students & researchers

Uliana Akhmetzyanova
Cesar de Araujo Filho
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Risto Savela
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WP 3: Refining Options of Lignin

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Patrik Runeberg (WP1, WP2, WP3)
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Klaus Söderback

Senior researchers

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Jarl Hemming (WP1, WP3)
Jan-Erik Lönnqvist
Andrey Pranovich (WP1, WP3)
Annika Smeds (WP1, WP3)
Anna Sundberg (WP1, WP3)
Lari Vähäsalo (WP1, WP3)

WP 4: Trace Elements in Refining of Biomass

Doctoral students & researchers

Jesus Arroyo (WP4, CRA)
Meheretu Dirbeba
Tooran Khazraie Shoulafar
Ekaterina Raguzina
Christoffer Sevonius
Maria Sundqvist
Kai Yu (WP4, CRA)

Niko DeMartini
Paul Ek
Kim Granholm (WP4, CRA)
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Pingping Su
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Senior researchers

Dorota Bankiewicz
Anders Brink

Complementary Research Activities (CRA)

Doctoral students & researchers

Abdifatah Mohamed Hussein
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Marco Cingano
Ning He
Alvaro Gongalez Vogel
Elisa Hupa
Ewelina Krzysmyk
Matilda Kråkström
Ewelina Leino
Jadielson Lucas da Silva Antonio
Otto Långvik
Axel Meierjohann
Jonne Niemi
Sabine Rendon
Paulo Santochi
Heidi Sundelin
Alexandra Torozova
Ulriika Vanamo
Andreas West

Hao Wu
Johnny Östman
Kai Yu (WP4, CRA)

Senior researchers

Dorota Bankiewicz
Zhanna Boeva
Nicola Gemo
Kim Granholm (WP4, CRA)
Rose-Marie Latonen (WP1, CRA)
Juho Lehmusto
Kalle Levon
Andrzej Lewenstam
Tom Lindfors (WP1, CRA)
Grzegorz Lisak
Karolina Maduna Valkaj
Zekra Mousavi
Tomasz Sokalski
Fiseha Tesfaye

3.1 Refining and Utilization of Polysaccharides

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 resulting cellulose, after removal of hemicelluloses and lignin, can be used to prepare nanocellulose. Our interest is currently mainly to utilize the hemicelluloses as polymers, e.g. in combination with conducting polymers and graphene, 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 in large amounts 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 hemicellulose-based structural composites. The other composite component can be conducting polymers or other carbon materials (e.g. graphene) aiming at applications in (bio)sensors and wound-healing promotion. Another option of the other composite component is bioactive glass aiming at the application as scaffolds in tissue engineering. The 3D printing technology will be applied by research visits to and cooperation with the Intelligent Polymer Research Institute at the University of Wollongong, Australia.

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 Riissanen, 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

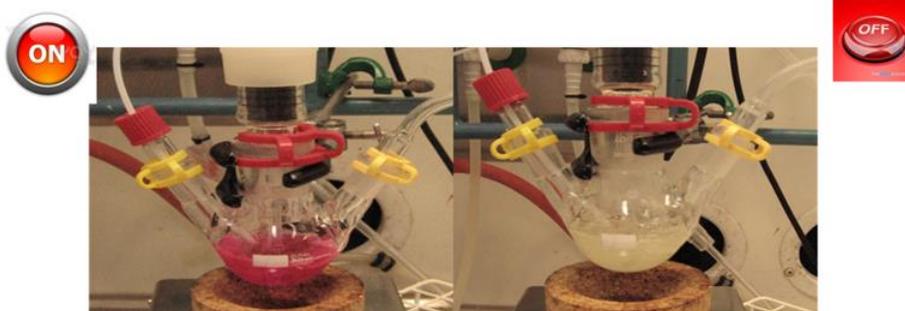
core of the program was to study and develop 1) new ways to fractionate wood into different material streams and 2) processing of these streams to generate material solutions for existing and new value chains. The first part of the project (FuBio Joint Research 1, 2009-2011) ended in 2011 and the continuation 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 superbases (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 solvent used in wood fractionation before and after switching changing colour from red to colourness.

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.

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

Publications:

- Anugwom, I., Eta, V., Virtanen, P., Mäki-Arvela, P., Hedenström, M., Yibo, M., Hummel, M., Sixta, H., Mikkola, J.-P., Towards optimal selective fractionation for Nordic woody biomass using novel amine-organic superbase derived switchable ionic liquids (SILs), *Biomass and Bioenergy* 70 (2014), 373-381
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- Eta, V., Anugwom, I., Virtanen, P., Eränen, K., Mäki-Arvela, P., Mikkola, J.-P., Loop vs. batch reactor setups in the fractionation of birch chips using switchable ionic liquids, *Chemical Engineering Journal* 238 (2014), 242-248
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- Korpinen, R., Kallioinen, M., Hemming, J., Pranovich, A., Mänttari, M., Willför, S., Comparative evaluation of various lignin determination methods on hemicellulose-rich fractions of spruce and birch obtained by pressurized hot-water extraction (PHWE) and subsequent ultrafiltration (UF), *Holzforschung* 68 (2014) 8, 971-979
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- Rissanen, J., Grénman, H., Willför, S., Murzin, D., Salmi, T., Spruce hemicellulose for chemicals using aqueous extraction: Kinetics, mass transfer, and modelling, *Industrial & Engineering Chemistry Research* 53 (2014) 15, 6341-6350
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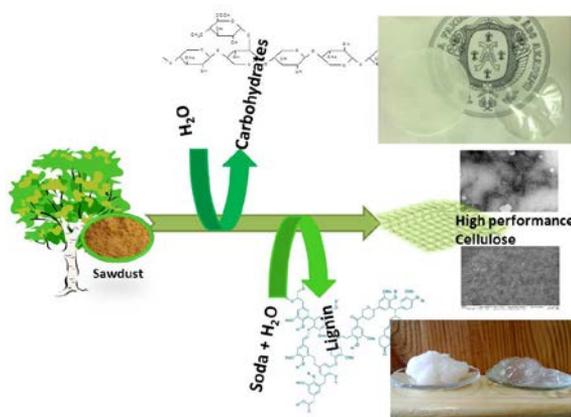
Nanocellulose Preparation

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

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

Nanocellulose represents a group of cellulosic nanomaterials. Cellulose nanofibrils (CNF), also termed 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 within the biorefinery concept. The residual cellulose of wood processing waste, sawdust, which was leftovers after sequential hot-water extraction processes to isolate hemicelluloses and lignin in a novel forest biorefinery concept, was explored as the starting material for 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 2,2,6,6-tetramethylpiperidine-1-oxyl radical (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 films from CNF 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.



Upgrading of birch sawdust to value-added materials.

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

Publications:

- Liu, J., Korpinen, R., Mikkonen, K., Willför, S., Xu, C., Nanofibrillated cellulose originated from birch sawdust after sequential extractions: a promising polymeric material from waste to films, *Cellulose* 21 (2014) 4, 2587-2598

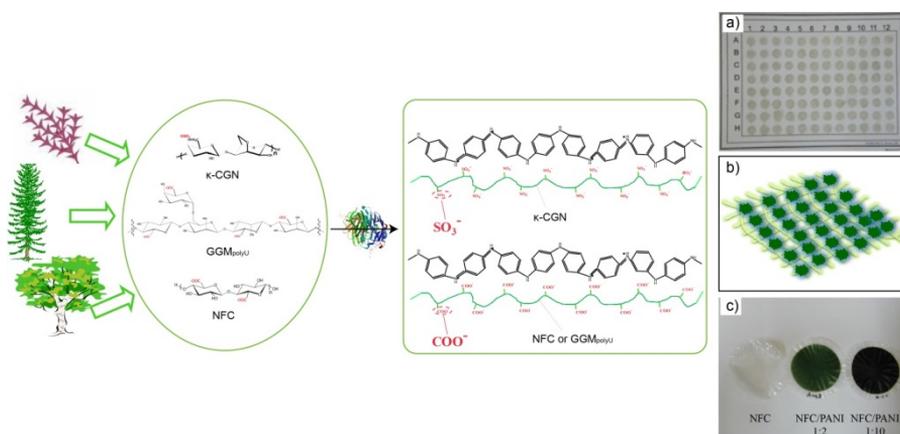
Development of Biocomposites

Main funding: Graduate School of Chemical Engineering (GSCE), Graduate School for Biomass Refining (BIOREGS), Chinese Council Scholarship, Johan Gadolin Scholarship Programme, 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 demanding 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 O-acetyl galactoglucomannan (GGM), TEMPO-oxidized cellulose derived nanofibrillated cellulose (NFC), 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, NFC can also be used as a template in the polymerization of pyrrole and thus the composites of NFC/polypyrrole and NFC/polypyrrole/silver nanoparticle can be prepared. The resulted conducting composite can be directly processed to flexible free-standing films with good mechanical strength and antimicrobial properties, which may find potential applications in biosensors and biomedical engineering.

NFC thin films, highly swollen hydrogels, and aerogels with super high porosity have also been developed for biomedical applications, e.g. wound healing and drug delivery. Biomolecules, such as protein, drugs, polysaccharides, or living cells, can be encapsulated into the NFC 3D network during the swelling of the NFC films. The NFC films- and aerogels-based extracellular matrix (ECM) mimicking matrices were found to promote the survival and proliferation of wound healing relevant cells. The tailored composites suggest promising and broad spectrum applications in different areas, such as in biomedical and pharmaceutical, food, and cosmetic areas.

Cooperation:

PCC and the Centre for Functional Materials (FUNMAT) at Åbo Akademi University; University of Helsinki, University of Eastern Finland; KTH, Wallenberg Wood Science Center, Sweden

Publications:

- Leppänen, A-S., Xu, C., Parikka, K., Eklund, P., Sjöholm, R., Brumer, H., Tenkanen, M., Willför, S., Targeted allylation and propargylation of galactose-containing polysaccharides in water, *Carbohydrate Polymers* 100 (2014) 1, 46-54
- Lindqvist, H., Bialczak, S., Willför, S., Sundberg, A., Functionalization of paper surfaces by modified galactoglucomannans in paper, *Journal of Science Technology for Forest Products and Processes (J-FOR)* 3 (2014) 4, 6-12

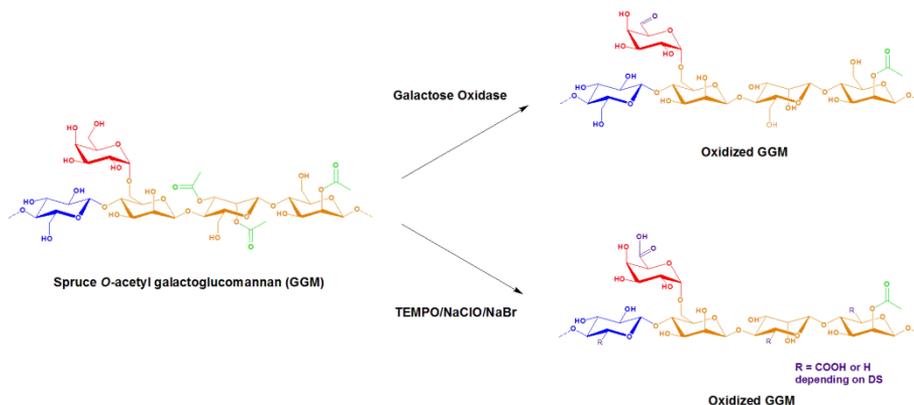
Chemical Modification of Water-Soluble Spruce O-Acetyl Galactoglucomannan

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

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

From a biomimetic perspective, the intrinsic affinity of cell wall heteropolysaccharides, 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.

O-acetyl galactoglucomannan (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 form of GGM was also applied in the synthesis of conducting polyaniline where the GGM derivative was used as synthesis template.

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 are studied for instance. The approach will be applied to GGM afterwards. The targeted applications are biodiagnostics and biosensing.

Cooperation:

University of Helsinki; PCC and the Centre for Functional Materials (FUNMAT) at Åbo Akademi University; KTH, Wallenberg Wood Science Center, Sweden

Publications:

- Leppänen, A-S., Xu, C., Parikka, K., Eklund, P., Sjöholm, R., Brumer, H., Tenkanen, M., Willför, S., Targeted allylation and propargylation of galactose-containing polysaccharides in water, *Carbohydrate Polymers* 100 (2014) 1, 46-54

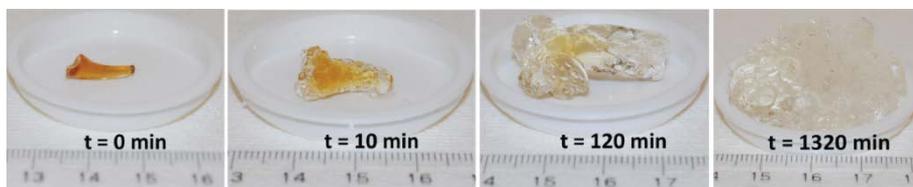
Design of Hemicellulose-Based Hydrogels for Wastewater Treatment

Main Funding: Aides à la Formation Recherche (AFR)

Daniel Dax, Chunlin Xu, Stefan Willför

O-acetyl galactoglucomanan (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 4-(dimethylamino)pyridine (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 cellulose nanofibrils 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

Publications:

- Dax, Daniel, Chemical derivatization of galactoglucomannan for functional materials
- Dax, D., Soledad Chávez Bastidas, M., Xu, C., Willför, S., Mendonça, R.T., Poblete, J.A.S., Cationic hemicellulose-based hydrogels for arsenic and chromium removal from aqueous solutions, *Carbohydrate Polymers* 111 (2014), 797-805

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 O-acetyl galactoglucomannan (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 GGM 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

Publications:

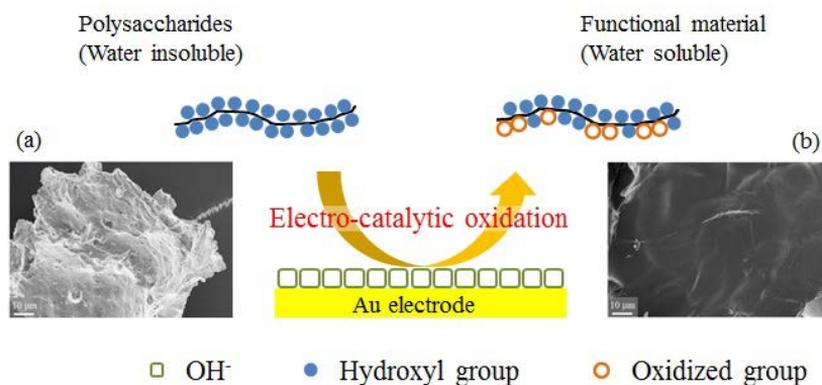
- Kisonen, V., Xu, C., Hemming, J., Nurmi, M., Bollström, R., Hartman, J., Rautkoski, H., Eklund, P., Willför, S., O-acetyl galactoglucomannan esters for barrier coatings, *Cellulose* 21 (2014) 6, 4497-4509
- Kisonen, V., Xu, C., Eklund, P., Lindqvist, H., Sundberg, A., Pranovich, A., Sinkkonen, J., Vilaplana, F., Willför, S., Cationised O-acetyl galactoglucomannan: synthesis and characterization, *Carbohydrate Polymers* 99 (2014) 1, 755-764

Electrochemistry of Polysaccharides Derived from Biomass

Main funding: PCC, Kone Foundation

Yasubito Sugano, Tiina Saloranta, Johan Bobacka, Ari Ivaska

Cellulosic biomass as an environmentally-friendly and an alternative resource that has been expected to play an important role for a sustainable society in the future. Particularly 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. The functional materials and their physical properties can be designed by modifying chemical groups of the macromolecules. Oxidation of cellulose, for example, is one of the major approaches for designing functional materials and their further modifications. 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, the results show that not only cellulose but also some hemicelluloses can be oxidized electrochemically at the electrode surface. This is the first systematic study about electrochemistry of polysaccharides. This research activity has offered a new unique approach for electrochemical modification, functionalization and innovative utilization of polysaccharides derived from cellulosic biomass.



Scheme of the electro-catalytic oxidation of polysaccharides: (a) SEM images of regenerated xylan, (b) SEM image of the electro-oxidized xylan.

Publications:

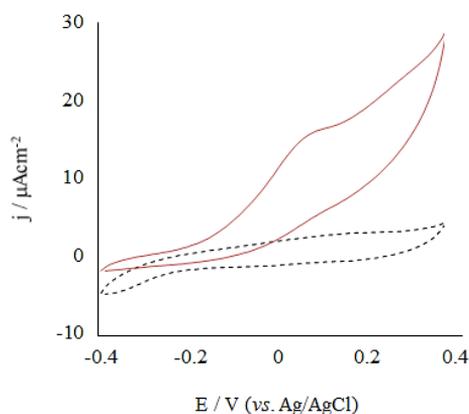
- Sugano, Y., Latonen, R.-M., Akiel-Pirkanniemi, M., Bobacka, J., Ivaska, A., Electrocatalytic oxidation of cellulose at a gold electrode, *ChemSusChem* 7 (2014) 8, 2240-2247

Electrochemical Characterization of Cellulose in Ionic Liquids

Main funding: PCC, Kone Foundation

Yasubito Sugano, Johan Bobacka, Ari Ivaska, Jyri-Pekka Mikkola

Design of an innovative utilization technology for cellulose - a promising, environmental-friendly and renewable resource for the production of valuable chemicals and raw materials for industry - offers a new platform for the material based sustainable society. Upon use of cellulose, solvent systems for the dissolution/distribution of the cellulose molecule have contributed to the development of the utilization technology and the scientific study of the material science of cellulose and its derivatives. In line with this research activity, we have synthesized special solvent systems based on ionic liquids - one of the most powerful and interesting solvent systems for cellulose dissolution - in order to construct an innovative reaction “platform” for the design of the series of functional materials and valuable chemicals from cellulose. In recent years, a new reaction pathway from cellulose, electro-oxidation of cellulose mediated by an Au electrocatalyst in alkaline media, was found and the key parameters of the process were investigated. Considering the mechanism of the reaction, it is expected that additional new functional materials can be obtained from cellulose by applying the special solvents that are designed for the electro-oxidation of cellulose. We have studied electrochemical reactivity of cellulose in tailor-made IL systems and found some novel IL systems which suit for the electro-oxidation of cellulose. This research activity provides not only a new research topic but also promising technology to produce different types of functional materials and chemicals for industry.



CVs of cellulose at an electrode in a special IL system. Black line: background, red line: with cellulose

Cooperation:

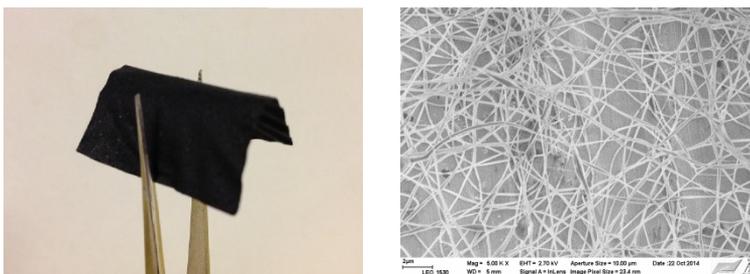
Umeå University, Chemical-Biological Centre, Umeå, Sweden

Composites Based on Conjugated Polymers, Graphene and Nanocellulose

Main funding: Johan Gadolin Scholarship, Academy of Finland

Patrycja Bober, Jun Liu, Aleksandra Makarova, Muhammad Zubair, Hasan Sherwani, Tom Lindfors, Rose-Marie Latonen, Chunlin Xu

Nanofibrillated cellulose (NFC) and nanocrystalline cellulose (NCC) originated from softwood cellulose fibers show high strength, stiffness, transparency and good film forming properties. By using NFC as template for chemical polymerization of polypyrrole (PPy) combined with Ag-nanoparticles, biocompatible, electroconductive, flexible and anti-bacterial free-standing composite papers have been prepared by a simple one-step procedure. The electrospinning method has also been used to prepare electroconductive nanofibers with a high surface area based on NFC and the water soluble conducting polymer PEDOT-PSS. Bead-free fibers were able to be formed by using polyethylene oxide as the supporting polymer. Moreover, composite materials of NFC and GO, rGO, exfoliated graphene or graphite have been studied in this project for different applications such as supercapacitors and substrate materials for sensors and for biodiagnostics.



Left: The free-standing conductive and anti-bacterial NFC/PPy/Ag-nanoparticle composite paper. Right: SEM image of conductive electrospun composite fibers based on NFC and PEDOT-PSS.

Aqueous ink formulations based on NCC and the conducting polymers PEDOT and PANI have been studied for use in printable and biodegradable electrochemical sensors. NCC is expected to have a dual role in the inks: first of all it will increase the adherence of the ink on the paper substrate and secondly, it may perform as the sensitive component after functionalization with a suitable probe molecule.

Cooperation:

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Czech Republic; Åbo Akademi University, Faculty of Science and Engineering, Centre for Functional Materials (FUNMAT), Laboratory of Physical Chemistry

Publications:

- Bober, P., Liu, J., Mikkonen, K., Ihalainen, P., Pesonen, M., Plumed-Ferrer, C., von Wright, A., Lindfors, T., Xu, C., Latonen, R-M., Biocomposites of nanofibrillated cellulose, polypyrrole, and silver nanoparticles with electroconductive and antimicrobial properties, *Biomacromolecules* 15 (2014) 10, 3655-3663

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

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

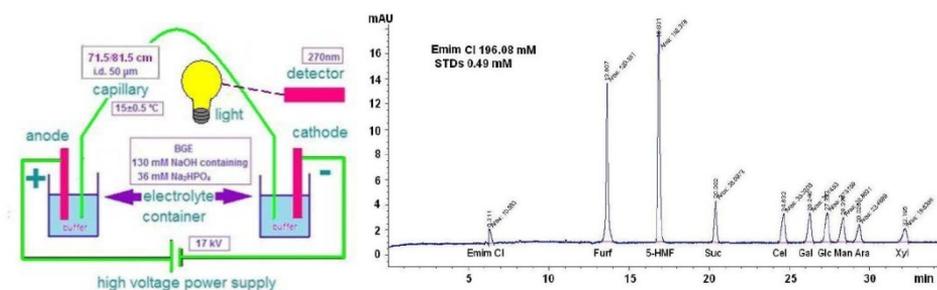
Ricardo Pezosa Conte, Allison Leyton, Cristina Ravanal, Áron Dombóvári, Melinda Mohl, Sari Hyvärinen, Päivi Mäki-Arvela, María Elena Lienqueo, Krisztián Kordás, Jyri-Pekka Mikkola

In the recent years, the use of different types of biomass has become more and more important for the production of biofuels. Still the old concept of biomass processing has been evolved to a biorefinery, where most of the biomass is utilized for the production of fuels, chemicals and materials by means of different processes. On this regard, 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 to render cellulose more accessible to hydrolysis. Further, lignin valorization is still an open field and it is generally considered a challenge in industry.

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

The main goal of this project is the production of bioethanol from algae, although the development of new processes designed under a biorefinery concept will be also assessed. In this regard, 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. The analysis of sugars contained in the ionic liquid fraction using capillary electrophoresis has also been assessed. Further, we also focus on the hydrolysis of algal carbohydrates using novel processes such as solid acid resins. Within the consortium, also photocatalytic hydrolysis of algae has been tried (University of Oulu). Ultimately, this project pursues also collaboration

with Chilean researchers, who are mostly focused on the finding of novel enzymes from marine microorganisms to hydrolyze alginate, and also in substituting metabolic routes on traditional fermentative microorganisms to be capable to produce bioethanol from uronic acids.



Schematic picture from capillary electrophoresis method (left) and separation of sugars and furfurals in the presence of ionic liquids in wood dissolution (right).

Cooperation:

University of Chile, Chile; University of Oulu

Publications:

- Ahlkvist, J., Mäki-Arvela, P., Mikkola, J-P., Macro-molecules as a source of levulinic acid, *International Review of Chemical Engineering* 6 (2014) 1, 44-58
- Hyvärinen, S., Mikkola, J-P., Murzin, D.Yu., Vaher, M., Kaljurand, M., Koel, M., Sugars and sugar derivatives in ionic liquid media obtained from lignocellulosic biomass: comparison of capillary electrophoresis and chromatographic analysis, *Catalysis Today* 223 (2014), 18-24
- Soudham, V.P., Brandberg, T., Mikkola, J-P., Larsson, C., Detoxification of acid pretreated spruce hydrolysates with ferrous sulfate and hydrogen peroxide improves enzymatic hydrolysis and fermentation, *Bioresource Technology* 166 (2014), 559-565

3.2 Conversion of Sugars to Chemicals

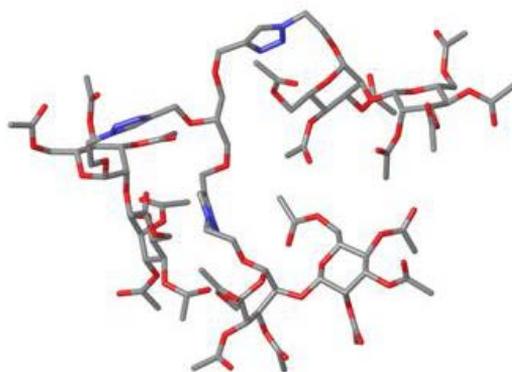
WP2 focuses on the chemistry and technology for making chemicals from monomeric sugars obtained by carefully controlled hydrolysis of hemicelluloses. Recent research by us and other groups has shown that rare monomer sugars can be obtained in high yields from hemicelluloses. Furthermore, platform, fine and specialty chemicals can be obtained from the monomers of hemicelluloses. WP2 combines 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 is at our disposal (batch autoclaves, parallel screening reactors, SEM, TEM, XRD, XPS, FT-IR).

Immunomodulation of Allergic Immune Response: Search of New Adjuvants for Allergen Immunotherapy Vaccines

Main funding: Academy of Finland, TEKES

Jani Rabkila, Denys Mavrynsky, Juba Forsblom, Tiina Saloranta, Reko Leino

The project aims at synthesis, discovery and development of immunostimulatory glycocluster adjuvants to be used in the treatment of infections, microbial, allergy and cancer vaccines. The mechanisms of action and conformational properties of the synthetic compounds are studied both *in vitro* and *in vivo* and by advanced MS and NMR spectroscopic methods. Commercialization potential of these glycocluster adjuvants for allergy therapy applications is currently investigated in a TEKES supported TutLi project (New Knowledge and Business from Research Ideas) involving up-scaling and optimization of the lead molecule synthesis and proof-of-concept *in vivo* studies in a chronic asthma murine model.



Cooperation:

University of Turku; Finnish Institute of Occupational Health, Helsinki; CIC bioGUNE, Spain; Ludwig-Maximilians-Universität München, Germany

Publications:

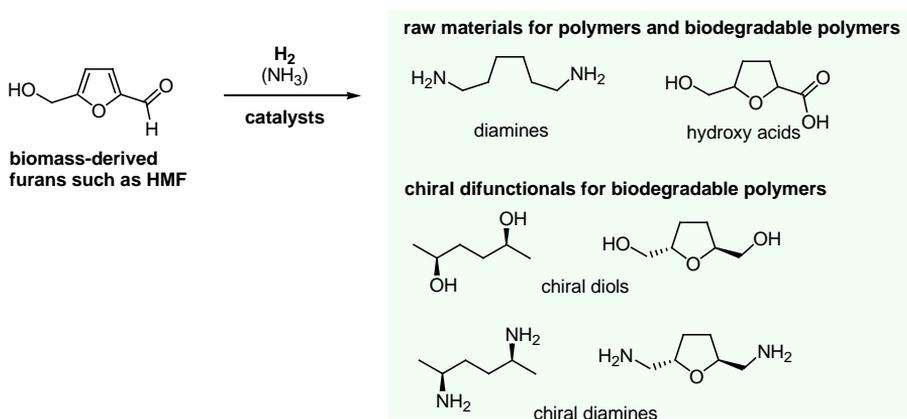
- Rahkila, J., Ekholm, F.S., Panchadhayee, R., Ardá, A., Cañada, F.J., Jiménez-Barbero, J., Leino, R., Synthesis and conformational analysis of phosphorylated β -(1 \rightarrow 2) linked mannosides, *Carbohydrate Research* 383 (2014), 58-68

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.



Cooperation:

University of Jyväskylä

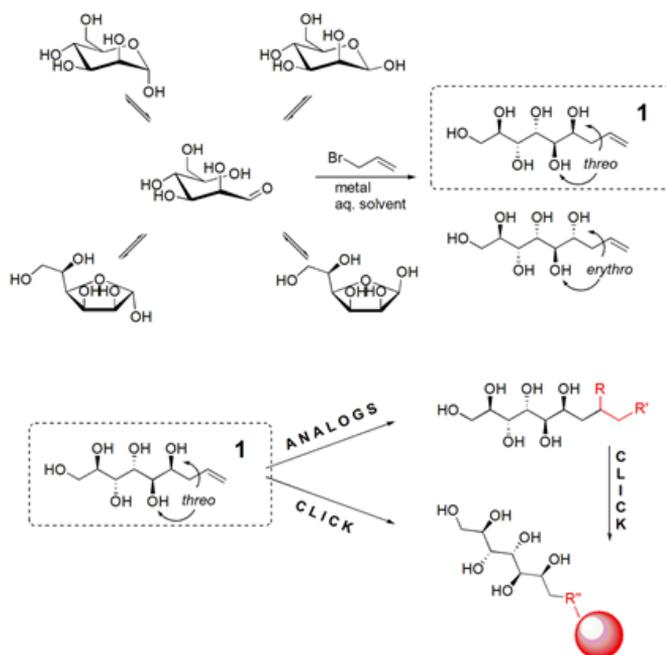
Targeted Functionalization of a Biomass Derived Polyol

Main funding: PCC

Andreas Gunell, Tiina Saloranta, Reko Leino

The metal-mediated allylation of unprotected monosaccharides leads generally to a mixture of homoallylic polyol diastereoisomers with either threo or erythro-type configuration (C-1/C-2), of which the threo form generally dominates. The major diastereomer derived from D-mannose (1, figure below) that can be isolated by simple precipitation from EtOH, has previously been shown to aggregate spontaneously in water solution. Our previous investigations suggested a low energy linear conformation for this particular substrate both in crystalline and aggregated states and in solution.

Currently, we are investigating the possibilities to modify compound (1, figure below) by applying some known catalytic procedures. Moreover, the possibilities to attach the polyol (1) on some core molecules via different “click” approaches are explored.



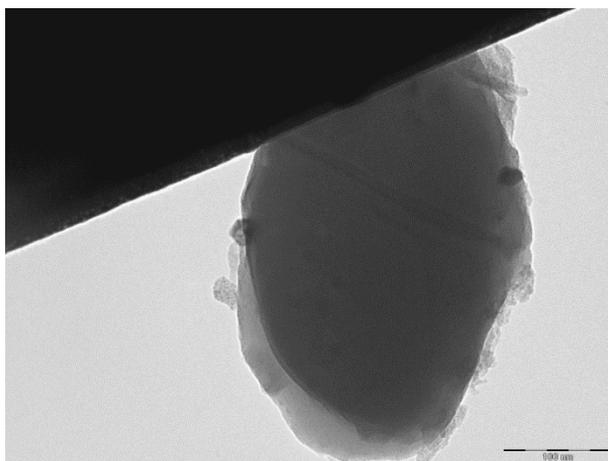
Preparation of Valuable Organic Chemicals – from Homogeneous Catalysis to SILCA and Batch to Continuous Technology

Main funding: Graduate School of Chemical Engineering (GSCE)

Nemanja Vucetic, Pasi Virtanen, 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). After this, a mixture of an ionic liquid and an organometallic palladium compound dissolved in a solvent is fed into the reactor tube using a recycle mode, allowing palladium and ionic liquid to absorb on silica. Different reaction conditions, reactants and ionic liquids will be tested.

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.



EFTEM images of palladium particles in ionic liquid active carbon cloth catalysts.

Publications:

- Virtanen, P., Salminen, E., Mäki-Arvela, P., Mikkola, J-P., *Selective Hydrogenation for Fine Chemical Synthesis, Supported Ionic Liquids: Fundamentals and Applications* (eds. R. Fehrmann, A. Riisager M. Haumann), Wiley-V C H Verlag GmbH & Co, 2014, pp. 251-262
- Salminen, E., Mäki-Arvela, P., Virtanen, P., Salmi, T., Mikkola, J-P., Isomerization of α -pinene oxide to campholenic aldehyde over supported ionic liquid catalysts (SILCAs), *Topics in Catalysis* 57 (2014) 17-20, 1533-1538
- Salminen, E., Mäki-Arvela, P., Virtanen, P., Salmi, T., Mikkola, J-P., Kinetics upon isomerisation of α -, β -pinene oxides over supported ionic liquid catalysts (SILCAs) containing Lewis acids, *Industrial & Engineering Chemistry Research* 53 (2014), 20107-20115
- Salminen, E., Virtanen, P., Mikkola, J-P., Alkaline ionic liquids applied in supported ionic liquid catalyst for selective hydrogenation of citral to citronellal, *Frontiers in Chemistry* 2 (2014), 1-5

Chlorella Microalgae as Feedstock for the Production of Biofuels

Main funding: Academy of Finland

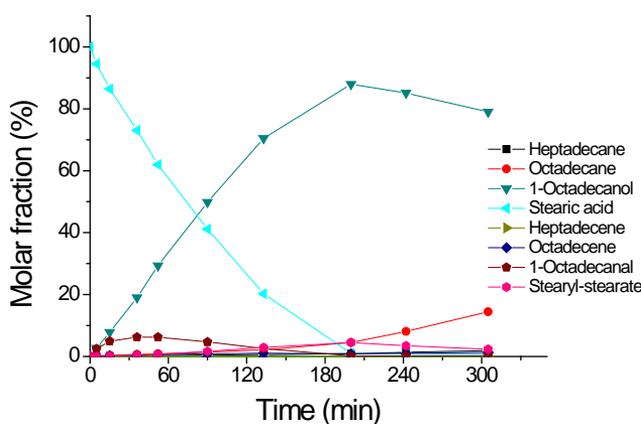
Imane Hachemi, Päivi Mäki-Arvela, Narendra Kumar, Donato Alexandre Gomes Aranda, Dmitry Yu. Murzin

In order to process microalgae to fuels, two processes with several steps were considered; *in situ*-transesterification, and saponification with extraction and

purification steps. The fractionation resulted in the production of mainly: proteins, carbohydrates, carotenoids, fatty acids methyl esters (FAME).

The catalytic HDO of FAME into green-diesel was performed in semi-batch reactor at mild conditions of temperature and hydrogen pressure. The conversion yielded aliphatic hydrocarbons (n-heptadecane and n-octadecane).

Nickel-supported catalysts were synthesized by wet-evaporation impregnation method and characterized by N₂-desorption, SEM, EDXA, TEM, TGA, NH₃-TPD, CO₂-TPD, ICP-OES, CO-chemisorption, and TPR. Ni/H-Y showed a high activity and therefore will be studied in further investigation in FAME HDO in a continuous reactor. Aqueous phase reforming will be studied. Thereafter a kinetic modeling of both reactors will be conducted.



Selective hydrogenation of stearic acid in dodecane over 4% Re/TiO₂ catalyst in hydrogen at 2 MPa of total pressure and temperature of 220°C.

Cooperation:

Federal University of Rio de Janeiro, Brazil

Publications:

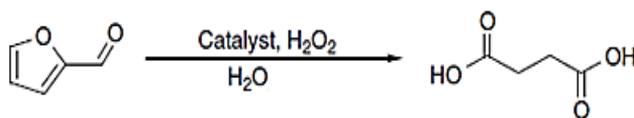
- Murzin, D.Yu., Mäki-Arvela, P., Aranda, D.G., Processing microalgae: beyond lipids, *Biofuels* 5 (2014), 29-32
- Mäki-Arvela, P., Hachemi, I., Murzin, D.Yu., Extraction of carotenoids from algae, *Journal of Chemical Technology and Biotechnology* 89 (2014), 1607–1626
- Mäki-Arvela, P., Mikkola, M., Hemming, J., Eränen, K., Willför, S., Murzin, D.Yu, Heat treatment and chemical composition of fatty acids and rosin acids mixtures: Effects on their thermal properties and morphology, *Journal of the American Oil Chemists' Society* 91 (2014) 6, 1035-1046

Valorization of Biomass

Main funding: TEKES

Farhan Saleem, Dmitry Yu. Murzin, Tapio Salmi

Lignocellulosic biomass originating from wood is an abundant non-food alternative as feedstock for chemical and petrochemical industry. However, the conversion processes of lignocellulose to fuels and chemicals are often up-to-date ineffective and unprofitable. Catalytic processes can provide the most selective routes from biomass to desired products. Furfural is an important compound which is obtained from acid-catalyzed dehydration of sugars. This furan derivative, which has been regarded as a key component to link between carbohydrates based chemistry and petrochemical industrial chemistry. A range of chemical intermediates and products can be produced from this compound. One such component is succinic acid. This acid can be used in a variety of commercial applications, which include food and beverage industry, as a precursor to pharmaceuticals ingredients, such as additives, solvents, as polymers and as an intermediate for the production of high value commodity chemicals. The non-renewable commercial technology of producing succinic acid is quite mature and is based on catalytic hydrogenation of maleic anhydride, followed by hydration of succinic anhydride. Although, some chemical manufactures utilize a varied route, which is through the hydration of maleic anhydride to maleic acid and then hydrogenate the subsequent acid to succinic acid. The drawback of this fossil based route is the use of expensive feedstock and the emission of greenhouse gases. The biotechnological route is also quite expensive due to the use of microorganisms and expensive recovery costs for these processes. Succinic acid can also be synthesized by oxidation of furfural using hydrogen peroxide in aqueous medium in presence of heterogeneous acid catalyst (figure 1). Besides the main product, side products [2(5H)-furanone, maleic acid, fumaric acid and formic acid] are also formed, but their yields are less than the succinic acid. This initial concept of producing succinic acid is performed in batch reactor. Further in future, the idea will also be tested in continuous reactor to make the process more efficient from commercial view point.



Oxidation of furfural to succinic acid using heterogeneous acid catalyst.

Development of Structured Reactors for Transformation of Biomass Components to High-Value Products – Green Process Intensification

Main funding: Graduate School of Chemical Engineering (GSCE)

Vladimir Shumilov, Pasi Virtanen, Rüdiger Lange, Dmitry Yu. Murzin, Tapio Salmi

Porous materials with different pore type and size made of ceramics, polymers or metals are widely applied in chemical industry. The unique properties of porous materials allow carrying out a spectrum of well-established and recent applications, such as molten metal filtration, catalysis, refractory and thermal insulation, hot gas filtration and bone replacement. Within the following work period the purpose is to give review on substances that are used for producing of porous materials, main processing ways that can be used for the fabrication of porous ceramics, applications in which such materials are used and physicochemical properties of foams. Emphasis is given to using porous materials as catalytic carriers. Different methods of producing porous materials, such as polyurethane replica technique, gel casting method, direct foaming technique and hollow beads method are described and compared in terms of gas and liquid transfer and mechanical properties of final foams. Finally, perspectives of the applying of porous materials in catalysis would be shifted.

Cooperation:

Technische Universität Dresden, Germany; Chemische Verfahrenstechnik, Germany

Publications:

- Shumilov, Vladimir, Manufacture of macroporous ceramic foams to be used as catalytic supports

Sustainable Fuel Production by Aqueous Phase Reforming – Understanding Catalysis and Hydrothermal Stability of Carbon Supported Noble Metals

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 (nano)materials. 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 macroscale 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, Germany; Boreskov Institute of Catalysis, Russia; Biomass Technology Group, the Netherlands; FutureCarbon GmbH, Germany; Universidad Autonoma de Madrid, Spain; University of Palermo, Italy; University of Twente, the Netherlands

Publications:

- Kirilin, A.V., Hasse, B., Tokarev, A.V., Kustov, L.M., Baeva, G.N., Bragina, G.O., Stakheev, A.Yu., Rautio, A-R., Salmi, T., Etzold, B.J.M., Mikkola, J-P., Murzin, D.Yu., Aqueous phase reforming of xylitol over Pt/C and Pt-CDC catalysts: catalyst characterization and catalytic performance, *Catalysis Science and Technology* 4 (2014), 387-401
- Kirilin, A.V., Tokarev, A.V., Manyar, H., Hardacre, C., Salmi, T., Mikkola, J-P., Murzin, D.Yu., Aqueous phase reforming of xylitol over Pt-Re bimetallic catalysts, *Catalysis Today* 223 (2014), 97-107

3.3 Refining Options of Lignin

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 ($< 150^{\circ}\text{C}$) than in traditional pulping, which seem to result in a scarce introduction of Lignin Carbohydrate Complexes (LCC) and also resulting in a lignin of low condensation degree.

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.

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, has 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. Oxidations can introduce chemical complexity by introduction of new functional groups, cyclizations etc. 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 polyols. 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-molybdenum 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. The isolation and purification of these substrates has been developed at our university, and the substrates are readily available to our group. The research will be focused on the development of methods for oxidation, but the oxidized substrates will be fully characterized and their properties and possible future applications will be evaluated. The research will be divided into four work programs performed at the Laboratory of Organic Chemistry (Åbo Akademi University, Finland) and at Laboratoire de Chimie de Coordination (Institut Universitaire de Technologie Paul Sabatier, France). The research team consists of five senior researchers with experience in wood chemistry, natural product chemistry, chemistry of transition metal complexes, chemical synthesis, and oxidations. The project will employ both post-doctoral researchers and PhD-students.

Cooperation:

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

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 Loubi-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 isolated novel lignin seems to have a low degree of LCC:s (Lignin Carbohydrate Complex) and a low degree of condensation. This lignin is also completely sulfurfree and it contains large amounts of reactive groups.

The aim of this project is to characterize this lignin 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. Quantification of specific functional groups will be achieved by suitable derivatizations. NMR analyses will be emphasized and the versatile methods using ³¹P NMR will be used for analysis of phosphites of different hydroxyl groups. 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 elucidated.

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

Wood Lignins and Tannins as Renewable Sources for Novel Adhesives and Biocomposites

Main funding: International Doctoral Programme in Bioproducts Technology (PaPSaT)

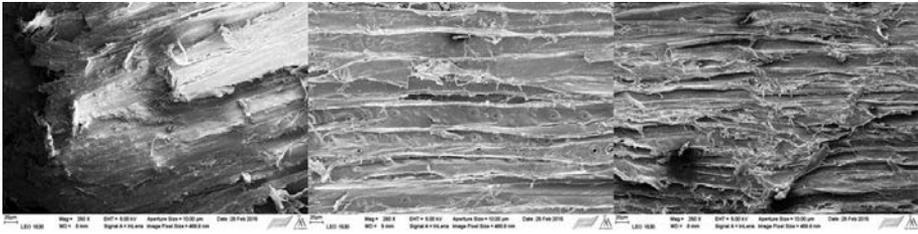
Ekaterina Korotkova, Andrey Pranovich, Annika Smeds, Stefan Willför

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.

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. Lignin is mainly separated from wood as lignosulfonates in sulfite pulping and as Kraft lignin in Kraft pulping. Lignosulfonates are produced in industrial scale at the remaining sulfite mills and are used as water-soluble polyelectrolytes in a variety of applications. Kraft lignin is mainly burned in the recovery boilers at pulp mills as concentrated black liquor. Only a small part of the Kraft lignin is purified for use in different chemical and material applications. A problem with Kraft lignin is the condensed structure and therefore low reactivity, as well as the high sulfur content.

New techniques are needed for more efficient extraction of lignin from wood. Milder extraction condition, compared to soda or Kraft pulping, can provide new, more reactive lignin with less condensed structure. The biorefinery concept includes a wide range of techniques to separate biomass, including wood, into its main components. Efficient fractionation of lignocellulosic biomass is a prerequisite for an economic lignocellulosic biorefinery. In particular, the use of lignocellulosic agricultural and forestry residues for biorefineries seems promising because of high availability, relatively low costs and no direct competition with food and feed production.

Lignin extraction from wood in an Accelerated Solvent Extractor (ASE) using hot water with small addition of alkali is promising way to obtain new, more reactive types of lignin for future applications. 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. Two concentration of alkali were studied, 1% and 2% aqueous NaOH. Extraction was performed for 4 hours total time, but different extraction sequences were studied: 1×240 min, 2×120 min, 4×60 min, 6×40 min, and 12×20 min. 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. Extraction with 2% alkali concentration results in more porous and fibrillated wood residue after extraction (Figure). Bordered pits are dissolved which makes mass-transfer easier. Xylose and galactose were the most abundant carbohydrate impurities in the isolated lignins. The average molar mass of lignin increased with the extraction time and concentration of alkali.



SEM images of wood before extraction (left), residue after 12×20 min extraction with 1% NaOH (middle) and residue after 12×20 min extraction with 2% NaOH (right)

Publications:

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3.4 Trace Elements in Refining of Biomass

The concentration and composition of inorganic elements in biomass depends on the type of biomass and the soil in which it is grown. Within a given type of biomass, different fractions can have very different concentrations of elements. For example in trees, the concentration of potassium is highest in the shoots which are the new growth of the tree, while the stem wood has the lowest concentration of K. Understanding the distribution and form of inorganics in biomass is important in understanding how those inorganics might be released during processing by different industries. The Johan Gadolin Process Chemistry Centre has a long history of studying the distribution of ash forming elements in biomass and how those elements behave during thermal conversion.

Work within the PCC focuses on understanding the form of inorganic elements all the way to their recovery and utilization after the biomass has been processed. The current work on inorganics in the current PCC project is more focused on understanding the distribution of inorganic elements in aqueous phase processing of biomass and understanding the distribution between the solid and liquid phases in particular. This will include both analysis and work to develop predictive thermodynamic models. This bridges current projects and builds new knowledge within the PCC.

In most biomass processes, there is a combustible part of the biomass that is currently burned but in the future may also be pyrolyzed or gasified. How the inorganics affect thermochemical conversion will continue to be an important topic in ever more efficient and cost-effective utilization of these streams. Additionally, the inorganic elements include elements important to plant growth such as K and P, so their recovery and re-use is important for both environmental and economic reasons.

Distribution and Reactions of Metal Ions at Bulk and Fiber Level in Wood Materials, Pulp and Process Liquors

Main funding: PCC

Pingping Su, Kim Granholm, Leo Harju, Andrey Pranovich, Ari Ivaska, Bjarne Holmbom

A method based on column chromatography was developed for determination of ion exchange constants for pairs of metal ions for different types of wood, pulp and bark samples. Bark samples were found to have the higher selectivity than wood and pulp samples for the metal ions studied. Of the 14 different metal ions selected for the sorption experiments, the toxic transition metal ions Pb, Cu and Cd were most strongly bound to all the materials used in this work. The validity of the column method was tested by using different mixtures of metal ions as loading solution in the experiments. The ion exchange constants obtained by the column method were compared with the corresponding constants obtained by the batch method reported earlier by our group. A good agreement was found between the

constants obtained by these two independent methods. The ion exchange constants were also determined for a synthetic weakly and a synthetic strongly acidic cation exchanger. It was found that the ion exchange constants of most pairs of metal ions are highest for the weakly acidic cation exchanger followed by bark, wood, and pulp samples as well as the strongly acidic cation exchanger.

Summary of ion exchange constants $\lg K_{Mg}^M$ for different tree-related materials. The loading solution contained Pb, Cu, Cd, Zn, Ni, Mn, Ba, Sr, Ca, Mg, K, Na and Li ions

	Pb/ Mg	Cu/ Mg	Cd/ Mg	Zn/ Mg	Ni/ Mg	Mn/ Mg	Ba/ Mg	Sr/ Mg	Ca/ Mg
Birch wood	1.56	1.29	0.52	0.43	0.30	0.18	0.26	0.12	0.12
Spruce sapwood	1.64	1.34	0.52	0.45	0.30	0.12	0.26	0.07	0.12
Spruce heartwood	1.68	1.41	0.52	0.48	0.34	0.12	0.26	0.12	0.12
Unbleached TMP	1.25	1.03	0.39	0.32	0.22	0.12	0.20	0.10	0.10
Alkali-treated TMP	1.34	1.15	0.43	0.38	0.25	0.14	0.24	0.10	0.12
Peroxide-bleached TMP	1.44	1.21	0.45	0.41	0.28	0.15	0.27	0.13	0.10
Unbleached softwood pulp	0.99	0.79	0.19	0.16	-	0.05	0.09	-	-
Unbleached hardwood pulp	1.10	0.87	0.31	0.25	0.21	0.14	0.11	0.15	0.16
Oxygen-delignified hardwood pulp	0.98	0.68	0.24	0.16	-	0.05	0.11	-	-
Inner bark of spruce	2.08	1.94	0.80	0.79	0.49	0.27	0.40	0.23	0.23
Outer bark of spruce	2.11	1.95	0.74	0.71	0.49	0.24	0.44	0.28	0.48

-: not determined

Publications:

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Clustering Innovation Competence of Future Fuels in Power Production - CLIFF

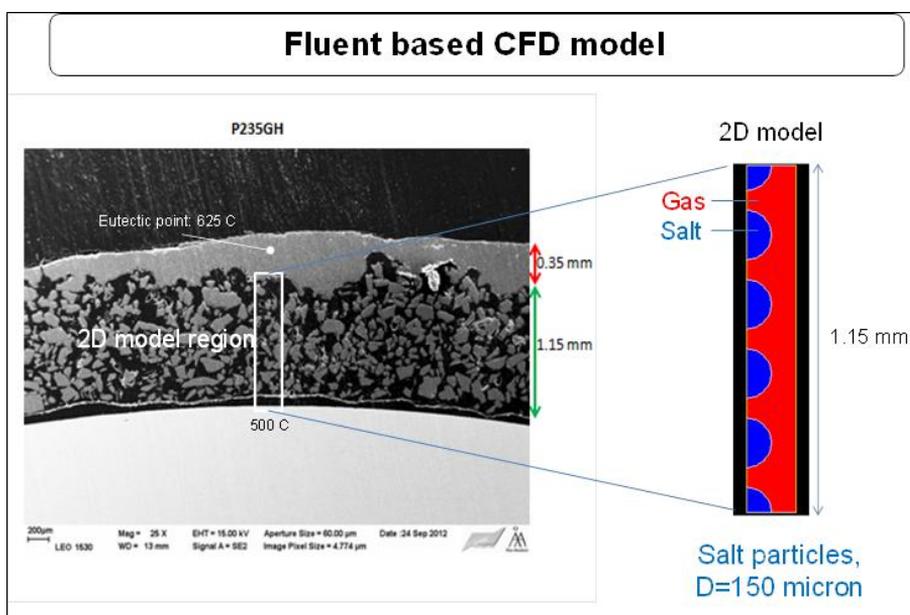
Funding (and partners): Tekes, Amec Foster Wheeler Energia Oy, Andritz Oy, Valmet Power Oy, UPM-Kymmene Oyj, International Paper Inc., Clyde Bergemann GmbH Research partners: Tampere University of Technology, Lappeenranta University of Technology, Aalto University and VTT Technical Research Centre of 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, Na Li, Hao Wu, Dirbeba Meberetu, Dorota Bankiewicz, Emil Väinö, Niklas Vähä-Savo, Christoffer Sevoni, Tooran Khazraie, Magnus Perander, Jonne Niemi, Paolo 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 University, 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 extent 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.



Publications:

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- Sorvajärvi, T., DeMartini, N., Rossi, J., Toivonen, J., In situ measurement technique for simultaneous detection of K, KCl, and KOH vapors released during combustion of solid biomass fuel in a single particle reactor, *Applied Spectroscopy* 68 (2014) 2, 179-84
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Systems Optimization of Manufacturing of Biofuels and Steel in an Integrated Site (SYMBIOSIS)

Main funding: Academy of Finland

Anders Brink, Oskar Karlström, Bingzhi Li, Mikko Hupa

The objective of this cross-disciplinary research project SYMBIOSIS (1.9 2011 to 31.8 2015) is to optimize a system with thermal conversion of biomass to biofuels and steel production. The task is tackled as a complex optimization problem, where different biomass feedstock can be allocated to a set of alternative biofuel manufacturing routes. The arising by-product streams are utilized in an integrated steel plant for reduction and as energy source. Conversely, the steel plant may supply the biofuel plant with heat and gases. This formulation leads to an optimization problem with a combinatorial part (e.g., choice of biomass feedstock(s), biomass conversion technique, alternative raw materials (pellets vs. sinter, coke vs. oil/coal, etc.) in the steel production) and a parametric part (material flows rates, operating temperatures and pressures, etc.). Process nonlinearities and constraints as well as different possible goals (e.g., minimize the energy, emissions or costs) further complicates the solution of the optimization problem. A challenge is thus to cast the problem into a solvable form and to develop specific numerical methods for tackling it. It is expected that the optimization will require hybrid techniques, such as memetic algorithms, to avoid the curse of dimensionality in the solutions. A systematic optimization approach of the integrated biofuel and steelmaking plants may give rise to completely new process alternatives, where the energy and raw materials are used much more efficiently than today.

Cooperation:

Thermal and Flow Engineering, Åbo Akademi University

Publication:

- Houshfar, E., Wang, L., Vähä-Savo, N., Brink, A., Lövås, T., Characterisation of CO/NO/SO₂ emission and ash-forming elements from the combustion and pyrolysis process, *Clean Technologies and Environmental Policy* 16 (2014) 7, 1339-1351

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

Main funding: Academy of Finland

Mikko Hupa, Daniel Lindberg, Fiseha Tesfaye

New technologies are being developed to increase the efficiency of thermal biomass conversion for electricity 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.

Material Value Chains – ARVI

Funding: Tekes and 18 Finnish companies

Patrik Yrjas, Emil Vainio, Daniel Lindberg, Mikko Hupa

The program, coordinated by CLEEN Ltd., consists of a consortium of 29 organizations out of which 18 are companies and 11 research organizations. 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 sophisticated overall analyses of material value chains. The program is divided into four work packages:

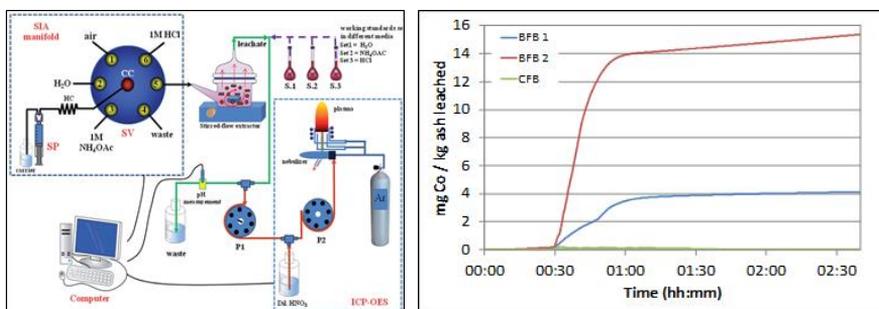
WP 1: Systemic evolution of business and its local environment

WP 2: Improved knowledge of material flows - analyses and foresight

WP 3: Systemic resource efficiency - concept building, modelling and optimization

WP 4: Case Studies for Plastics, WEEE, MSW and Ashes

Within the four work packages the work is divided into different themes: plastics, electronic waste, municipal waste and ashes. The work by Åbo Akademi University is focused on ashes and the elemental behavior and leachabilities. 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 HNO₃).

Sustainable Utilization of Ash, Slag and Pyrolysis Residuals – TUULI

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, 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 University was to test, analyze 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. ÅÅ also evaluated the behavior of ash minerals by thermodynamic equilibrium modeling. Also, a literature study on heavy metal separation from ashes has been done.

Cooperation:

University of Oulu; Ekolite Oy; University of Lapland; VTT Technical Research Centre of Finland; Oulu University for Applied Sciences

3.5 Complementary Research Activities

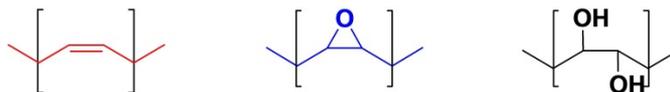
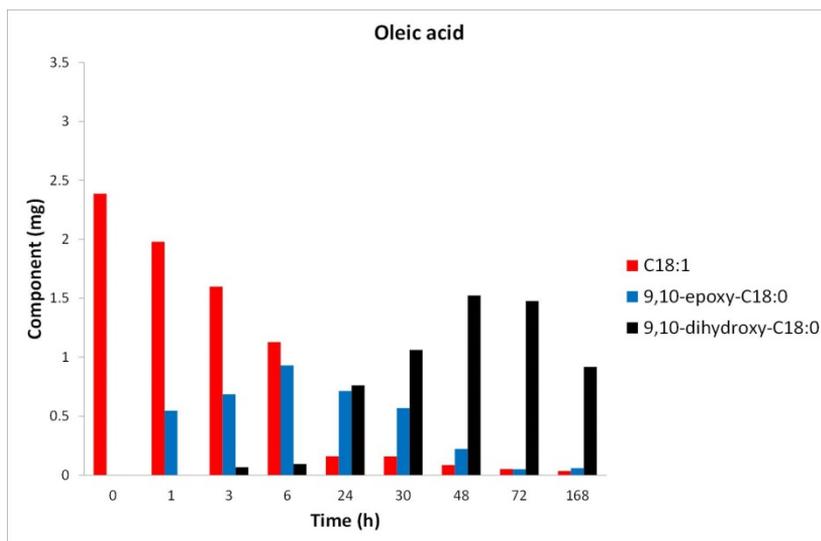
Effect of Peracetic Acid on Lipophilic Extractives in Chemical Pulp Bleaching – Paa-Ex

Main funding: Industry

Jan-Erik Raitanen, Anna Sundberg, Stefan Willför

Pulp mills constantly look for opportunities to increase their production capacity without major investments as well as saving in overall bleaching costs. The possibility to obtain cleaner pulps with a lower content of extractives while closing the water circulations is a major driver as well. Peracetic acid (PAA) is primarily used in post-bleaching of Kraft pulps in the Nordic countries and Central Europe to increase brightness, to prohibit brightness reversion due to long storage times and to prevent problems caused by extractives in the drying section and in the product.

Fatty acids and sterols with double bonds were shown to form epoxides and the corresponding diols upon treatment with PAA. Dehydroabietic acid (DeAb) was also shown to react with PAA by oxidation of the benzylic position. After longer reaction times, the reaction products of these extractives were degraded, but possibly also oligomerized. Furthermore, the epoxides and diols could be identified in samples from a pulp mill using PAA, suggesting that these can be used as markers for reactions between extractives and PAA.



The unsaturated fatty acid C18:1 will react with peracetic acid, forming first an epoxide and then the corresponding diol. These reaction markers can also be found in industrial pulp.

Cooperation:
Kemira Oyj

Calcium Oxalate Scaling in Mechanical Pulping and Bleaching

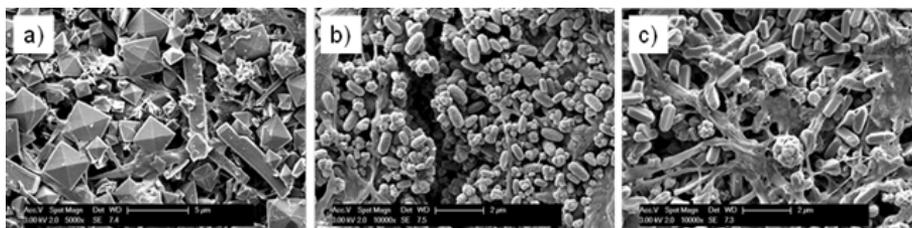
Main funding: Industry

Matti Häärä, Lari Vähäsalo, Anna Sundberg, Stefan Willför

Precipitation of the sparingly soluble calcium oxalate salt in pulping and papermaking processes can cause severe problems both in production and with paper quality in the form of hard scale deposits. Sources of oxalate are the wood raw material and especially the oxidative bleaching stages, where oxalic acid is formed mainly from lignin and hemicelluloses.

In this project, the factors affecting oxalic acid formation and calcium oxalate precipitation in production of wood-containing paper have been studied. In addition, methods for simple and convenient oxalate analysis as well as for studying calcium oxalate precipitation were established. These procedures were used, for example, to clarify the role of some dissolved and colloidal substances on crystallization phenomena and for screening of anti-scaling agents for calcium oxalate scale control.

In the latest part of this project, a mill-scale trial was conducted with an anti-scaling agent that was specifically formulated based on the findings in the laboratory screening work. The analytical scheme established for the screening, combining turbidity monitoring, FCM, x-ray diffraction (XRD), and scanning electron microscopy (SEM), was also used for evaluation of the product performance at process conditions. The figure below shows SEM-micrographs of calcium oxalate precipitates that were induced in peroxide-bleached groundwood pulp filtrate without additives (a), in the presence of the new product (b), and the old reference product (c). The precipitate without additives consisted mainly of different sized crystals of bipyramid shape, which are typical for calcium oxalate dihydrate. By addition of the anti-scaling agents, the crystal structure is clearly modified. Especially in the case of the new product, also the decreased particle size and aggregation can clearly be observed.



SEM-micrographs of calcium oxalate crystals precipitated in peroxide-bleached groundwood pulp filtrate by titration with sodium oxalate solution. a) Without additives; b) in the presence of the new product (50 ppm); c) in the presence of the reference product (50 ppm).

Cooperation:

Sappi Fine Paper Europe; Kemira Oyj

Publications:

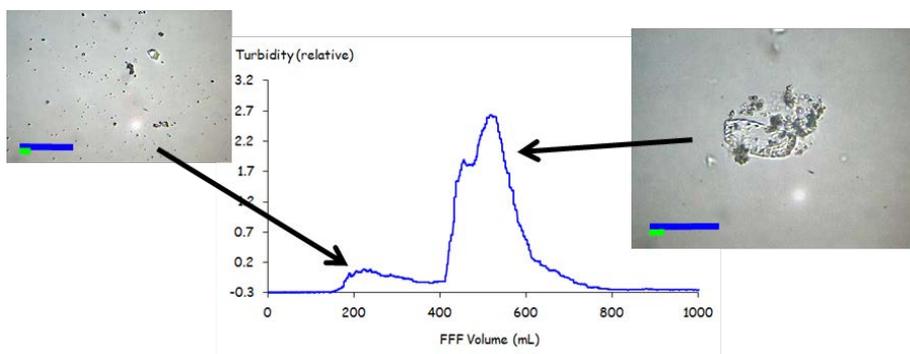
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Intelligent Remote Diagnostic

Funding: Kemira Oyj

Lari Vähäsalo

The aim of the project is to evaluate newly developed process analysis instrumentation. For the past decade we used and developed flow cytometry (FCM) methods for the analysis of pulp and paper mill samples. The capability of FCM to detect and analyze agglomeration has turned out to have a great advantage compared to more traditional analytical techniques. In this project, we will develop and build a system that will produce the same type of valuable information as the FCM technique. The system will be installed on-line in order to get real time information of a paper process. The aim is also to develop a completely new analytical methods that will produce additional chemical information about the samples, traditionally only available after laboratory analysis. During the project, data from on-line instrumentation will be analyzed and compared with available mill data. Advanced multivariate techniques will be used in an effort to find cause and effect relations between mill data and data from the on-line instrumentation.



Cooperation:

Kemira Oyj

Pinosylvins as Novel Bioactive Agents for Food (Pinobio)

Main funding: Academy of Finland (Woodwisdom Eranet+ program)

Patrik Eklund, Annika Smeds, Jan-Erik Raitanen, Wenwen Fang, Hanna Lindqvist, Anna Sundberg, Vaala Metso, Denys Mavrynsky, Viivi Luona, Stefan Willför

Wood, especially knotwood of *Pinus* species (at present a side stream of the forest industry) is an abundant source of stilbenes, such as pinosylvin and its derivatives. These compounds have demonstrated considerable antimicrobial activities and cytotoxicity against a murine hepatic carcinoma cell line. In further studies pinosylvin was shown to stimulate the SIRT1 expression as efficiently as resveratrol. The aim of the PINOBIO project (2011-2014) was to upscale the extraction of pinosylvin and its derivatives from wood and further characterize their biological activities with a clear focus on potential applications (antimicrobials in foods and industrial processes, functional ingredients).

Organic extraction was efficient in recovering pinosylvin and pinosylvin monomethyl ether from pine, while pressurized high-temperature water mainly extracted lignans. While significant amounts of pinosylvin monomethyl ether could be obtained with cyclohexane, ethanol-water or acetone-water was required for efficient pinosylvin extraction. Knotwood and heartwood were consistently superior sources for these compounds compared to sapwood. Certain variation in pinosylvin contents was observed in trees from different environmental conditions. For example, trees grown in wet forests in Latvia contained three times more pinosylvin compared to trees in dry forests. Since pinosylvins apparently are protective compounds, this might reflect a higher exposure to fungal infestations and pathogens in moist conditions. A wide range of different derivatives was also synthesized from pinosylvin for further testing and some potential industrial process streams were identified as potential sources for the pinosylvins.

Pinosylvin and pinosylvin monomethyl ether are potent antibacterial and antifungal compounds, and they can both be efficiently extracted from pinewood. Pinosylvin monomethyl ether efficiently induced the xenobiotic metabolism in exposed hepatic cells, while the influence of pinosylvin on the cellular energy metabolism pathways resembled that of resveratrol. Pinosylvin could be used to modulate energy sensing pathways to improve insulin sensitivity in patients with diabetes and prevent the development of metabolic syndrome. Provided that the safety aspects of pinosylvin and pinosylvin monomethyl ether can be satisfactorily addressed, these compounds could be used as novel biocides and even as nutraceuticals.

Cooperation:

University of Eastern Finland; University of Vigo, Spain; University of Ljubljana, Slovenia; Latvian State Institute of Wood Chemistry, Latvia; Metsä Fibre; Forchem; Arbonova

Publications:

- Conde, E., Fang, W., Hemming, J., Willför, S., Domínguez, H., Parajó, J.C., Recovery of bioactive compounds from *Pinus pinaster* wood by consecutive extraction stages, *Wood Science and Technology* 48 (2014) 2, 311-323

Characterization of High- and Middle-Molar Mass Fractions in a Norway Spruce Knotwood Hydrophilic Extract

Funding: Åbo Akademi University

Annika Smeds, Patrik Eklund, Stefan Willför

Only the low-molar mass fraction, i.e., the GC eluting compounds, which are lignans, has been characterized in Norway spruce knotwood hydrophilic extracts previously. Of this fraction, many lignans and sesquilignans and all peaks supposed to be dilignans remain unidentified. In this work, the GC non-eluting compounds (the middle- and high-molar mass fractions, MMM and HMM) were characterized in a 7-hydroxymatairesinol-reduced extract by using several fractionation and analytical techniques.

An MTBE insoluble fraction of the extract contained mainly MMM and HMM material, of which the main part was shown to consist of lignan oligomers and polymers. The lignan polymers (with a molar mass up to approximately 5300 Da) seemed to be linked by β -O-4 bonds, with the guaiacyl units partly modified by demethylation or methylation, i.e., the lignan polymer structure reminds of the lignin structure.

The MTBE soluble fraction, which accounted for the major part (81%) of the extract, contained mainly low-molar mass material (lignans, sesqui- and dilignans). The part of the HMM material that was easily isolable seemed to contain polymers of fatty and resin acids (dehydroabietic acid and cis-abienol) and sterols (sitostadiene-7-one and campestadiene-7-one).

Much work remains still to be done in this project, with more fractionations and characterizations, and hopefully, isolation of some pure compounds that can be characterized by NMR.

Electroactive Composites Based on Conjugated Polymers and Graphene for Chemical Sensors, Biodiagnostics, Printed Electronics, Supercapacitors and Batteries

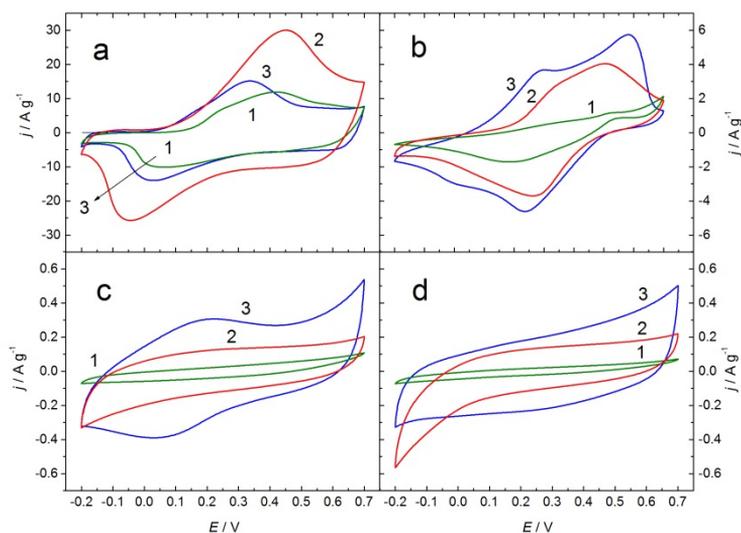
Main funding: Academy of Finland, Johan Gadolin Scholarship, Research Institute of Åbo Akademi University Foundation, ERASMUS

Zhanna Boeva, Cristina Dumitriu, Ning He, Rose-Marie Latonen, Tom Lindfors, Jadielson Lucas da Silva Antonio, Johan Bobacka, Ari Ivaska

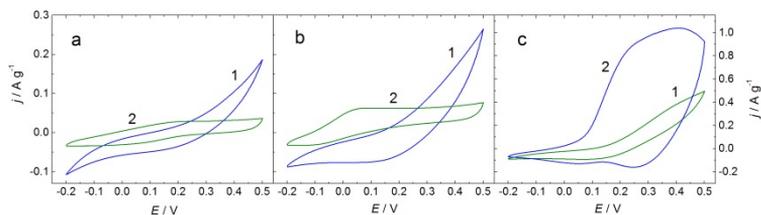
Composites of electrically conducting polymers and graphene oxide (GO), reduced graphene oxide (rGO), exfoliated few-layered graphene and graphite have been synthesized electrochemically and chemically. The composite materials developed

are aimed to be used in supercapacitors and batteries, electrochemical sensors and biodiagnostics.

We have studied the in situ polymerization of aniline in the presence of exfoliated graphite of two different grades (graphene and graphite) resulting in composite materials which are readily dispersible in *N*-methylpyrrolidone. Compared to polyaniline prepared without graphene/graphite which becomes electrically non-conducting at $\text{pH} > 3$, the PANI–graphene/graphite composites showed significantly improved pH stability and electrochemical behavior in aqueous electrolyte solutions at $\text{pH} \leq 8$. The improved electroactivity is ascribed to the synergistic effect of graphene/graphite and PANI, and the network formation of the electrically conducting exfoliated graphites in the PANI matrix. 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 ion-selective electrode applications operating at neutral pH. By using sodium ascorbate as a model substance, we have shown that its amperometric detection at $\text{pH}=7.3$ with the PANI–graphite films results in a current amplification of 1.3–10.2 times in the concentration range of 10^{-4} – 10^{-2} M, compared to conventional PANI.

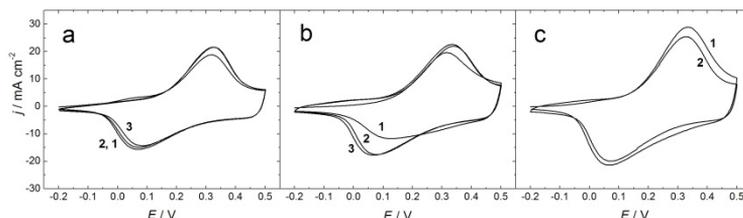


Cyclic voltammograms (1) neat PANI, (2) PANI–graphene and (3) PANI–graphite films measured at (a) $\text{pH}=0$, (b) $\text{pH}=3$, (c) $\text{pH}=6$ and (d) $\text{pH}=8$. Supporting electrolyte: 0.1 M NaCl at pH 3, 6 and 8. Reference electrode: Ag/AgCl/3 M KCl; $v=50 \text{ mV s}^{-1}$.

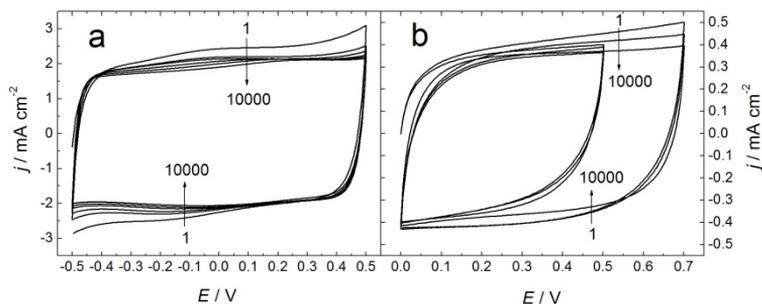


Cyclic voltammograms of (1) neat PANI and (2) PANI-graphite films measured in (a) 0.1 M KNO_3 (background electrolyte, $\text{pH}=6.5$) and (b) 10^{-3} M and (c) 10^{-2} M sodium ascorbate ($\text{pH}=7.3$) solutions containing 0.1 M KNO_3 as the supporting electrolyte. The y-axis of (a) and (b) has the same scale. Reference electrode: $\text{Ag}/\text{AgCl}/3\text{ M KCl}$; $\nu=50\text{ mV s}^{-1}$.

The supercapacitor properties of composite materials of electrically conducting polymers and GO/rGO were also studied within this project. The figures below demonstrate the outstanding cycling potential stability for 10,000 cycles of three composite materials of GO/rGO and polyaniline or poly(3,4-ethylenedioxythiophene) (PANI-GO, RANI-rGO and PEDOT-GO).



Cyclic voltammograms of the (a) PANI-Cl, (b) PANI-Cl-GO and the (c) PANI-Cl-rGO films measured during the potential cycling stability test carried out in 1.0 M HCl under nitrogen, $\nu = 100\text{ mV s}^{-1}$: (1) 1st, (2) 3,000th and (3) 10,000th cycle. The PANI-Cl-rGO film was measured for only 3000 cycles.



The potential cycling stability of PEDOT-GO in a (a) three-electrode cell and (b) two-electrode cell for 10,000 cycles in 0.1 M KCl as the electrolyte ($\nu=0.1\text{ V s}^{-1}$). The 1, 50, 200, 1,000, 3000, and 10,000th cycles are shown in (a) and the 1, 50 and 10,000th cycles in (b).

The work on conducting composites of a polypyrrole-hydro-sponge (PPy-HP) and GO have been continued in collaboration with Prof. Susana I. Córdoba de Torresi research group in Brazil. These composite materials have a 3D nanostructure and due to their large surface area they could be suitable materials in supercapacitor applications.

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, Russia; Turku University Centre for Materials and Surfaces (MATSURF), Laboratory of Materials Chemistry and Chemical Analysis, University of Turku; Åbo Akademi University, Center for Functional Materials (FUNMAT), Physics; Georgia Institute of Technology, School of Chemistry and Biochemistry, USA; AGH, University of Science and Technology, Kraków, Poland; St. Petersburg State University, St. Petersburg, Russia; University of São Paulo (USP), Chemistry Department, Laboratory of Electroactive Materials, São Paulo, Brazil

Publications:

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- Dumitriu, C., Stoian, A., Titorencu, I., Pruna, V., Jinga, V., Latonen, R-M., Bobacka, J., Demetrescu, I., Electrospun TiO₂ nanofibers decorated Ti substrate for biomedical application, *Materials Science and Engineering:C* 45 (2014), 56-63
- Lindfors, T., Boeva, Z., Latonen, R-M., Electrochemical synthesis of poly(3,4-ethylenedioxythiophene) in aqueous dispersion of high porosity reduced graphene oxide, *RSC Advances* 4 (2014) 48, 25279-25286
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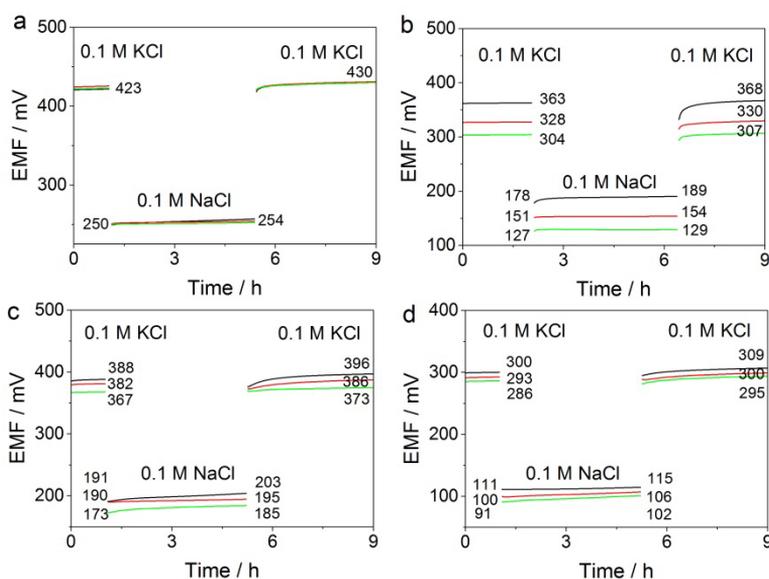
Study of Electrosynthesized Polypyrrole/H-ZSM-5 Zeolite Composites as Ion-to-Electron Transducer

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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 spectrometer (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 thicker compared to PPy/Cl⁻ which was synthesized in the same way. FTIR-ATR revealed the existence of H-ZSM-5 particles in PPy matrix with hexagonal structure. Similar cyclic voltammograms were observed for all PPy/H-ZSM-5 composites and PPy/Cl⁻. The hydrophobicity of the composites determined with 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.



Water layer test of solid-state K^+ -selective electrodes based on a PVC-DOS membrane with a) PPy/Cl⁻, b) PPy/H-ZSM-5-23, c) PPy/H-ZSM-5-80 and d) PPy/H-ZSM-5-280. Each composite was synthesized and tested on three electrodes and the measurements were switched between 0.1 M KCl and 0.1 M NaCl solutions.

Publications:

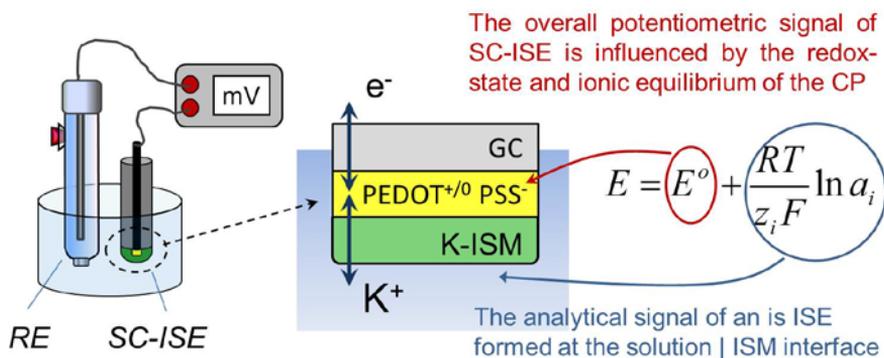
- Yu, K., Kumar, N., Roine, J., Pesonen, M., Ivaska, A., Synthesis and characterization of polypyrrole/H-Beta zeolite nanocomposites, *RSC Advances* 4 (2014) 62, 33120-33126

Electrochemical Adjustment of the Standard Potential (E°) and Novel Signal Transduction Principle of Ion-Selective Electrodes with Conducting Polymer as Solid Contact

Main funding: PCC, Valdemar Von Frenckell's Foundation, Stiftelsen för teknikens främjande, Graduate School in Chemical Engineering (GSCE)

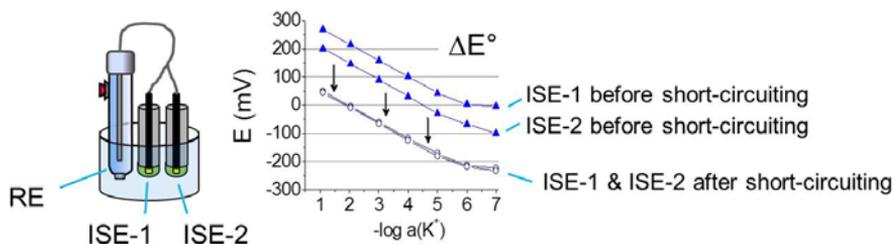
Ulriika Vanamo, Elisa Hupa, Johan Bobacka

The working principle of most existing ion sensors is based on potentiometry. In classical Nernstian potentiometry the zero-current potential between the working electrode (the ion sensor) and a reference electrode is measured. In solid-contact ion-selective electrodes (SC-ISE), where conducting polymers (CP) are used as ion-to-electron transducers between the ion-selective membrane (ISM) and electrical conductor, the redox state and ionic equilibrium of the CP-film influences the overall potentiometric signal of the SC-ISE. The standard potential (E°) of SC-ISEs can be manipulated by adjusting the redox state of the CP by applying a current or a potential to it.



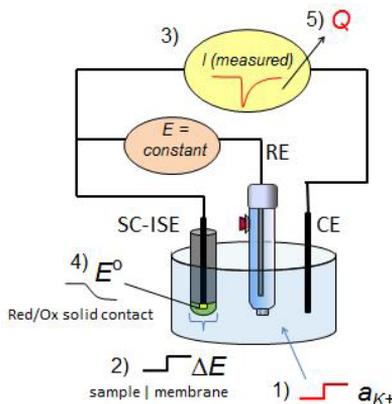
Potentiometric open-circuit measurement with a solid contact ion-selective electrode (SC-ISE), the ion-to-electron transduction via reduction/oxidation of the conducting polymer poly(3,4-ethylenedioxythiophene) covered with a potassium selective membrane and the Nernst equation describing the response of potentiometric ISE.

A corresponding instrument-free method to control (or “reset”) the E° of a SC-ISE is to short circuit it with a metallic wire to a conventional large capacitance Ag/AgCl/3MKCl reference electrode (RE) in a solution containing primary ions. The driving force of the oxidation/reduction reaction for CP-solid-contact is the potential difference between the RE and the SC-ISE. The piece-to-piece reproducibility of the adjusted potential was promising, and the day-to-day reproducibility for a specific sensor was excellent. The instrument-free approach to control E° is very attractive considering practical applications of calibration-free and disposable potentiometric sensors.



A schematic picture showing how calibration curves of two individual solid-contact ISEs can be shifted to be nearly identical by short-circuiting them with a conventional large capacitance reference electrode

The basic working principle of a new ion-to-electron transduction principle is depicted in the figure below. Here, instead of employing the sensor potentiometrically, the sensor is tested using a method called coulometry, more specifically controlled potential coulometry. The signal transduction mechanism utilizes the capacitance of the solid contact layer, in this case the CP poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate, PEDOT(PSS), to convert ion concentration (ion activity) into electrical current, which is then integrated to obtain the charge value. The charge is proportional to the redox capacitance of the PEDOT(PSS) layer in the ion-selective electrode. The experimental results obtained so far indicate that this new principle has good reversibility, reasonable resolution and is suitable for measuring minor changes in high concentration intervals.



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).

Publications:

- Vanamo, U., Bobacka, J., Electrochemical control of the standard potential of solid-contact ion-selective electrodes having a conducting polymer as ion-to-electron transducer, *Electrochimica Acta* 122 (Special Issue) (2014), 316-321
- Vanamo, U., Bobacka, J., Instrument-free control of the standard potential of potentiometric solid-contact ion-selective electrodes by short-circuiting with a conventional reference electrode, *Analytical Chemistry* 86 (2014) 21, 10540–10545

Water Uptake of Polymeric Materials

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

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

Fundamental aspects of the water uptake of both ion-selective membrane (ISM) materials and conventional polymers have been studied in this project. One of the main goals for the ISM materials is to develop useful experimental methods to identify membranes with low water uptake, which could prevent the detrimental water layer formation in solid-contact ion-selective electrodes (SCISEs) and thus be beneficial for ultra-trace analysis with these electrodes. It has recently been shown that low water content at the substrate/ISM interface correlates with superior potential stability of SCISEs. One of the main techniques to study the water is FTIR-ATR spectroscopy due to its ability to distinguish between different types of water in the ISM. The hyphenated technique for simultaneous measurement of the water uptake, impedance spectra and open circuit potential has been utilized for studying different polymeric materials. The project has also focused on quantifying the water uptake of plasticized poly(vinyl chloride) (PVC) and silicone rubber (SR) based ISMs with the oven based coulometric Karl Fischer technique. During 2014, the project has focused on studying the water uptake of hydrophobic conducting polymer ion-to-electron transducers, e.g. polyazulene and conventional thin free-standing polymeric films. Special attention was given to SCISEs with the ion-to-electron transducer consisting of few-layered graphene and polyaniline composites. The latter research has been carried out in collaboration with J. Prof. Christian Fischer and Prof. Stefan Wehner at the University of Koblenz-Landau in Germany.

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, Moscow, Russia; University of Koblenz-Landau, Department of Physics, Institute of Integrated Natural Sciences, Germany

In-situ Potentiometry and Ellipsometry

Main funding: Åbo Akademi Foundation

Grzegorz Lisak, Johan Bobacka

The aim of this project is to understand the fouling process and its influence on ion-selective membranes (ISM). Potentiometry allows continuous following of the kinetics of the fouling process at the ISM. However, a complementary analytical technique has to be used in order to quantify the fouling process. This can be offered by ellipsometry, which proved to be a useful technique in studying protein adsorption on various surfaces, including that of PVC.

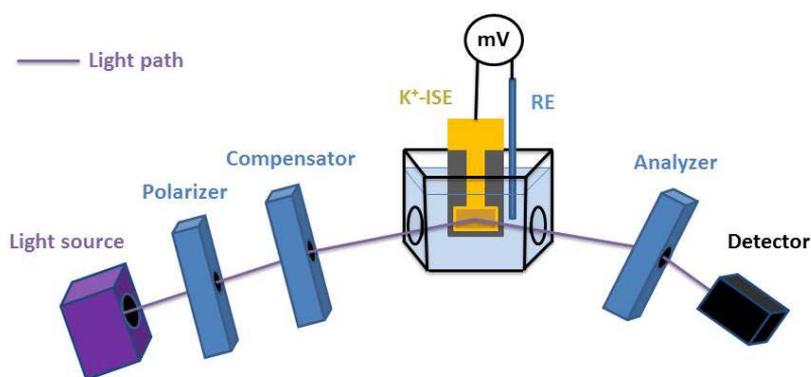


Illustration of the general view of setup for in-situ potentiometry and null ellipsometry.

In this work, in-situ potentiometry and null ellipsometry are applied to follow the kinetics and to quantify the adsorbed amount of proteins on ion-selective electrodes (e.g. K⁺-ISEs) under clinical conditions. The newly developed technique was used by us for the very first time in order to continuously follow biofouling of ISEs under clinically relevant conditions.

Cooperation:

Department of Biomedical Science, Faculty of Health and Society, Malmö University, Malmö, Sweden; Biofilms – Research Center for Biointerfaces, Malmö University, Malmö, Sweden

Health Diagnostics with Chemical Sensors

Main funding: Tekes (FiDiPro), Industry

Zhanna Boeva, Ulriika Vanamo, Kalle Levon, Andrzej Lewenstam, Johan Bobacka, Ari Ivaska

Fast and easy-to-use DNA hybridization sensors are needed to shorten the analysis time, and for the point-of-care devices. Conducting polymers as sensor substrate are promising and very fast signal transducers. The aim of this project is to study

conducting polymer substrates as signal transducer and immobilization platform for potentiometric ion-sensitive electrodes for DNA hybridization.

For this purpose a potentiometric biosensor has been fabricated with the use of chemically prepared polyaniline (PANI) on Nylon template. The resulting PANI-Nylon films were used as prepared for non-covalent immobilization of single stranded oligonucleotides (probe) with different length (20, 30, 40 and 50 nucleobases in a strand). The non-covalent immobilization is the first and essential step for fabrication of DNA sensor and is necessary for the successful implementation of the technique as a whole. The immobilization of the probe was monitored potentiometrically and the drop of the potential upon the probe immobilization was detected due to electrostatic interactions between positively charged PANI surface and negatively charged phosphate groups of oligonucleotide strands. The next step is the use of this probe immobilized PANI-Nylon surface for the detection of single stranded oligonucleotide (target) with a sequence complementary to the sequence in the immobilized probe. Addition of the target to the solution containing the indicator electrode leads to an increase of the potential of the electrode due to formation of a double helix of target and probe (hybridization) followed by its release to the solution. This can additionally be confirmed with fluorescent spectroscopy. It was found that the fluorescent response on hybridization of the DNA onto PANI surface is proportional to the length of the oligonucleotides used in the experiments and increases upon the increase of DNA length. The potentiometric response was also 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 amount of DNA released from the electrode detected with fluorescent spectroscopy and the potentiometric response of the PANI indicator electrode upon the DNA hybridization

Number of bases	20	30	40	50
Amount of ssODN adsorbed on PANI surface, μM	84	116	162	270
Potentiometric response, mV	-	-	31	62

Covalent immobilization of the probe with the use of thiol chemistry causes a similar drop of the potential of the indicator electrode. Addition of the target gives a similar positive response however it is not accompanied with a release of the double helix from the electrode surface due to the covalent attachment. The response amplitude of the biosensor depends on the length of the target and probe in a similar way as it was observed for non-covalently immobilized probe. Furthermore, the response of the DNA sensor depends on the presence of 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 found phenomenon is very important and has a strong potential in future development of electrochemical biosensors for the detection of mutations in genomic DNA.

Cooperation:

Polytechnic Institute of New York University, USA; Perkin Elmer; ThermoFisher Scientific; Labmaster Ltd; TYKSLAB; Radiometer

Paper- and Textile-Based Sampling

Main funding: Åbo Akademi Foundation, PCC

Grzegorz Lisak, Jingwen Cui, Sylvia Strzałkowska, Johan Bobacka

In modern analysis of ions it is recommended to minimize any pre-treatment and manipulation of the sample. Operations, such as dilution, pre-concentration, standard additions and even a time delay may influence the speciation of ions in the sample. Potentiometric sensing utilizing paper- and textile-based microvolume sampling is a rather new approach of ion determination in samples containing very little moisture. It is a part of a new initiative to explore the possibilities using ion-selective electrodes in samples containing high amount of solids compared to liquids or micro volumes of liquids containing fouling biological matter, e.g. red blood cells. The potentiometric measurement utilizing paper- and textile-based sampling is illustrated in the figure below. In this technological design, calibration solutions and samples are absorbed into textiles while the potentiometric cell (ion-selective electrodes and reference electrode) are pressed against the textile. Once the liquid, by wicking action, reach the place where potentiometric cell is pressed onto the textile, hence closing the electric circuit, the potentiometric response is obtained. The paper substrates and the textiles act both as a sampling unit and as a sample container during potentiometric sensing. To summarize, paper- and textile-based sampling offers great possibilities in clinical and environmental analysis of ions in very specific sample types. Finally, the paper- and textile-based micro volume sampling coupled with ISEs can be applied as a simple and cheap method to screen various materials for their effects on samples, e.g. to identify which material is the most suitable for on-body sensing.

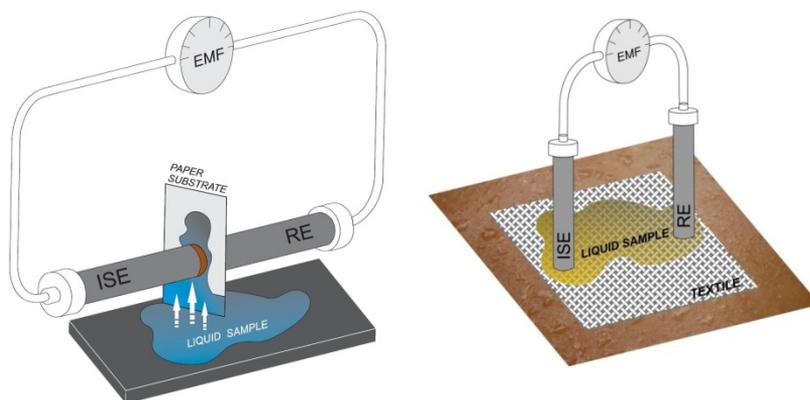


Illustration of the general view of potentiometric setup utilizing paper-based (left) and textile-based (right) sampling.

Collaboration:

Department of Chemistry, University of Warsaw, Warsaw, Poland;
Department of Biomedical Science, Faculty of Health and Society, Malmö
University, Malmö, Sweden; Biofilms – Research Center for Biointerfaces,
Malmö University, Malmö, Sweden

Publications:

- Cui, J., Lisak, G., Strzalkowska, S., Bobacka, J., Potentiometric sensing utilizing paper-based microfluidic sampling, *Analyst* 139 (2014) 9, 2133-2136

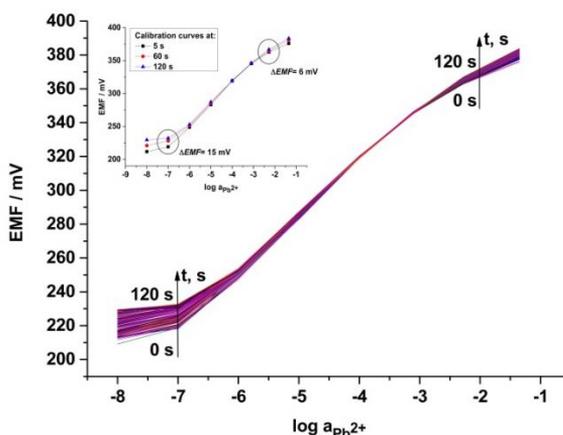
Ion Sensors with Low Detection Limit for Trace Analysis of Heavy Metals in Environmental Samples

Main funding: Åbo Akademi Foundation

Grzegorz Lisak, Ari Ivaska, Andrzej Lewenstam, Johan Bobacka

Monitoring natural waters for toxic components (such as heavy metals) is essential for human well-being. In Finland shallow lakes are easily contaminated by pollution. At present approx. 48% of Finland's rivers are considered as moderate, poor or bad quality. As a result of the concern of the European Union as well as of the U.S. Environmental Protection Agency, rigorous limits have been set for the maximum allowed concentration for each pollutant in the environment. The main objective of these regulations is to prevent and control the pollution of the environment through constant monitoring of natural waters, soil and the atmosphere.

Owing to several advantages such as portability, low energy consumption, and relatively low cost, ion-selective electrodes may be considered useful in measurements of ionic pollutants. Such measurements are mainly possible when extending the sensitivity range of the ISEs by lowering the detection limit.



Ground water sampling in the Finnish Archipelago for measurements of low and ultra-low concentrations of lead(II) in untreated environmental samples.

A multicalibrational approach was demonstrated using Pb^{2+} -ISEs. This scientific approach gives comprehensive information about the non-equilibrium (time-dependent) response of a potentiometric sensor. The developed method allows better handling of non-equilibrium conditions in quantitative determinations of analytes. The multicalibrational approach with time optimization showed to be superior when compared to the “fixed measurement time approach” using Pb^{2+} -ISEs at non-equilibrium in the determination of lead(II) in environmental samples.

Publications:

- Lisak, G., Ivaska, A., Lewenstam, A., Bobacka, J., Multicalibrational procedure for more reliable analyses of ions at low analyte concentrations, *Electrochimica Acta* 140 (Special issue) (2014), 27-32

Universal Solid Electrochemical Platform (UNISEP)

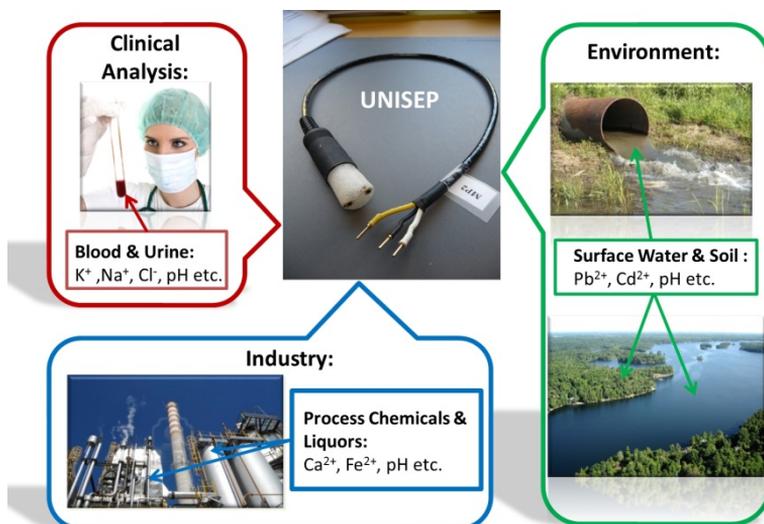
Main funding: Tekes (TUTLI)

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.

The UNISEP can be used in different electrochemical techniques using various combinations of indicator electrodes, such as ion-selective electrodes for potentiometric measurements, or glassy carbon, gold, and platinum electrodes for other electrochemical measurements.



The UNISEP concept is novel because:

- The solid-state reference electrode is based on a polymeric matrix containing an inorganic salt which eliminates the need for an internal solution.
- The UNISEP body exhibits a double role. It acts both as a reference electrode and a physical body/encasing for the whole electrode system.
- It can be used as a reference electrode with any external indicator electrode.
- It can be used as complete stand-alone electrochemical system including both a reference and indicator electrodes.

Cooperation:

Orion Diagnostica Oy; Nokeval Oy; Peilituote Oy; LS Link Ab; Patiq Oy; Kolster Oy; AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Krakow, Poland

Publications:

- Granholm, K., Mousavi, Z., Sokalski, T., Lewenstam, A., Analytical quality solid-state composite reference electrode manufactured by injection moulding, *Journal of Solid State Electrochemistry* 18 (2014) 3, 607-612
- Lewenstam, A., Routines and challenges in clinical application of electrochemical ion-sensors, *Electroanalysis* 26 (2014) 26, 1171-1181
- Sokalski, T., Granholm, K., Mousavi, Z., Lewenstam, A., Analytical quality solid-state composite reference electrode and electrochemical platform, 225th ECS Meeting, May 11-15, 2014, Orlando, USA, *ECS Transactions* 61 (2014) 15, 1-10, ISSN 1938-5862
- Szyszkiewicz, K., Danielewski, M., Fausek, J., Jasielc, J., Kuczka, W., Lewenstam, A., Sokalski, T., Filipek, R., Breakthrough in modeling of electrodiffusion processes, continuation and extensions of the classical work of Richard Buck, 225th ECS Meeting, May 11-15, 2014, Orlando, USA, *ECS Transactions*, 61 (2014) 15, 21-30, ISSN 1938-5862

Electroactive Membrane Separation of Ions

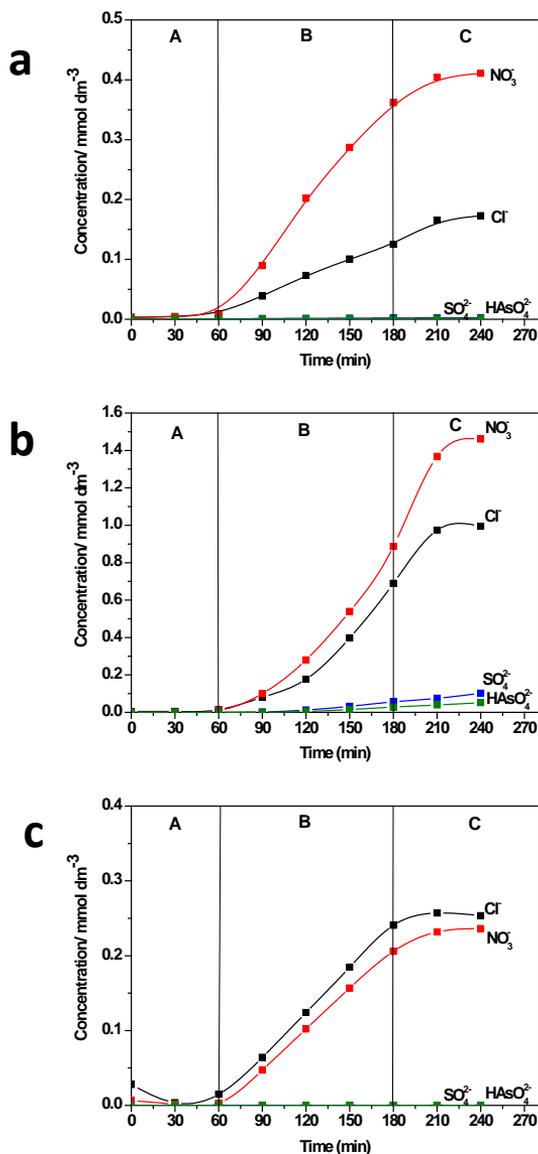
Main funding: Åbo Akademi Foundation, PCC

Jesus Arroyo, Rose-Marie Latonen, Ari Ivaska, Johan Bobacka

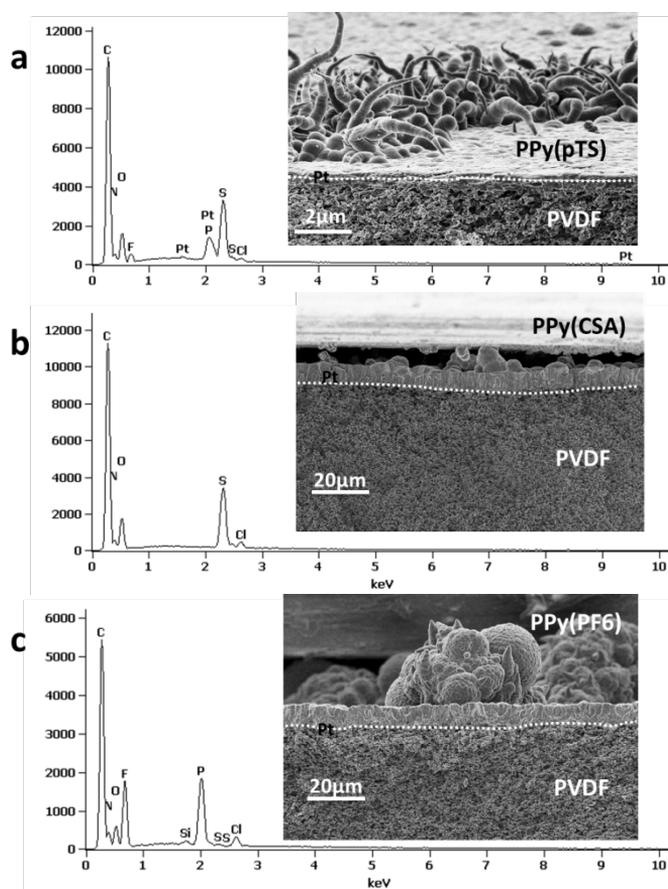
In this project the use of electroactive membranes based on conducting polymers has been studied for separation of both anions and cations from aqueous solutions. For this purpose a membrane based on the conducting polymer polypyrrole (PPy) was synthesized in presence of different dopant ions such as para-toluene sulfonate (pTS), camphor sulfonic acid (CSA) and hexafluorophosphate (PF6).

Concentrations of ions were determined by using an electrochemically controllable transport cell in which the membrane separates the source from the receiving solution. The source cell was filled with an aqueous mixture of different anions and samples were taken from the receiving cell every half an hour. The content of anions in the samples was thereafter analyzed by ion chromatography and inductively coupled plasma optical emission spectroscopy. The total measurement time was four hours, during the first hour no electrical stimulus was applied, during the following two hours a pulsed potential was applied and during the last hour of the experiment no pulsed potential was applied.

During the first hour of the experiment no separation of anions was observed, but when the pulsed potential was applied, as it is shown in the graphs, a separation of the different anions could be observed. According to the experiments, a better separation of monovalent anions than divalent anions was achieved. The dopant ions (pTS, CSA and PF6) gave also different properties to the conducting polymer membrane. SEM micrographs of the cross-sections of the PPy based membranes and elemental analysis of the membranes are further shown in the figures below.



(a) Transport profile of a mixture of Cl⁻, NO₃⁻, SO₄²⁻ and HAsO₄²⁻ across PPy(pTS) composite membrane. (b) Transport profile of a mixture of Cl⁻, NO₃⁻, SO₄²⁻ and HAsO₄²⁻ across PPy(-)CSA composite membrane. (c) Transport profile of a mixture of Cl⁻, NO₃⁻, SO₄²⁻ and HAsO₄²⁻ across PPy(PF6) composite membrane. For all experiments the source cell contained an equimolar concentration of Cl⁻, NO₃⁻, SO₄²⁻ and HAsO₄²⁻. Region (A): no potential is applied, (B) pulsed potential waveform is applied (-0.8V to +0.5V, 50s) and (C) no potential is applied.



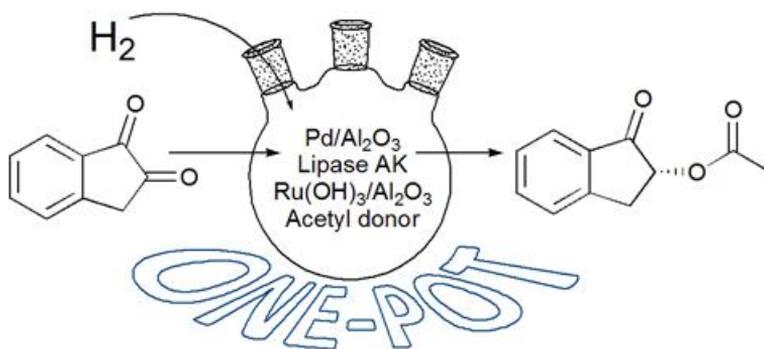
(a) SEM micrograph and elemental analysis of the surface of a PVDF/Pt-PPy(pTS) membrane. (b) SEM micrograph and elemental analysis of the surface of a PVDF/Pt-PPy(CSA). (c) SEM micrograph and elemental analysis of the surface of a PVDF/Pt-PPy(PF6).

Transition Metal and Enzyme Catalysis for Fine Chemical and Building Block Synthesis

Main funding: Stiftelsen för Åbo Akademi and other foundations

Otto Långvik, Risto Savela, Denys Mavrynsky, Tiina Saloranta, Reko Leino

The development of cost efficient and sustainable synthetic methods for preparation of (chiral) building blocks is of paramount importance in contemporary synthetic and industrial organic chemistry. In ongoing work, selective one-pot reaction sequences combining both homogeneous and heterogeneous transition metal catalysts with enzymes, as well as new reaction methodologies for transformations of small organic molecules utilizing iron catalysis are developed, including arylation, etherification and silane chlorinations.



Publications:

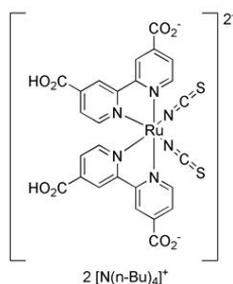
- Mavrynsky, D., Leino, R., An approach to chemoenzymatic DKR of amines in Soxhlet apparatus, *Journal of Organometallic Chemistry* 760 (2014), 161-166
- Savela, R., Majewski, M., Leino, R., Iron-catalyzed arylation of aromatic ketones and aldehydes mediated by organosilanes, *European Journal of Organic Chemistry* (2014), 4137-4147

Analysis and Influence of Dye Degradation and Purity on the Performance and Stability of Dye Sensitized Solar Cells

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

Sabine Rendon, Denys Mavrynsky, Leif Kronberg, Reko Leino

Dye-sensitized solar cells (DSSC) are molecular level electrochemical devices where light absorption and current generation occurs in dye molecules attached to a nanostructured TiO₂ electrode. While with DSSC technology, promising energy conversion efficiencies can be achieved using relatively simple manufacturing methods, stabilities of the cells depend on specific degradation mechanisms and is a key issue for their commercialization. Stability issues may occur, for example, at high temperatures, under UV-exposure or due to water in the electrolyte. Another critical component in DSSCs is the often ruthenium based photosensitizer, which absorbs photons from sunlight. In this project, together with the New Energy Technologies Research Group at Aalto University, the influence of photo-induced dye degradation and component purity on the performance of DSSCs is investigated by combinations of different analytical techniques including UV, LC-MS and NMR spectroscopy



Cooperation:
Aalto University

Assessment of Fate of Diphenols, Diphenyls and Antibiotics in the Environment and of Degradation Pathways

Main funding: Kone foundation, The Graduate School of Environmental Science and Technology (EnSTe), Maa- ja vesitekniikan tuki ry.

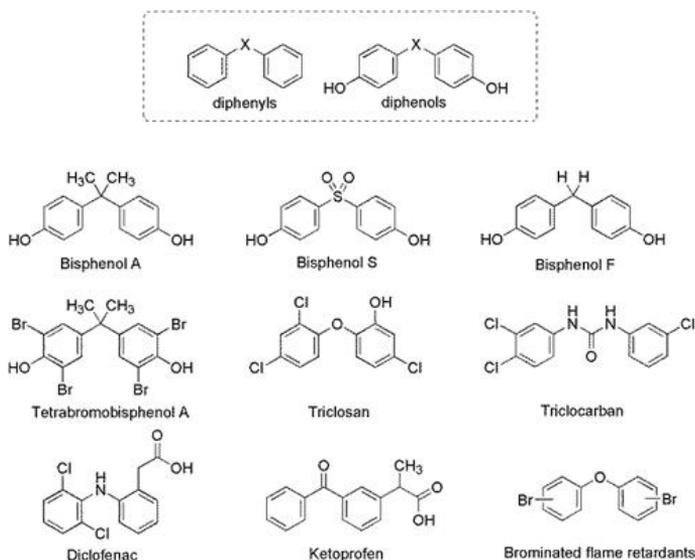
Axel Meierjohann, Ewelina Krzomyk, Leif Kronberg,

An ever increasing amount of chemicals and pharmaceuticals are used in the modern society. Most of the compounds eventually end up in waste water and enter the aquatic environment through discharges from the waste water treatment plants. Although approved for use in consumables, often very little is known about the environmental fate of the compounds and the risk they possess on the aquatic organisms and possibly to humans.

Very common structural features in a large number of our chemicals and pharmaceuticals are the diphenyl and the diphenol units (Figure). Contrary to the diphenols, the diphenyls are not soluble in water. However, the diphenyls may through metabolic pathways and photo reactions be transformed to diphenols (eg. ketoprofen). Many of the “diphenols” are known to possess hormonal activity and are considered to be endocrine disruptors. In this respect, most interest has been attributed to bisphenol A, while the substitutes bisphenol S and F have not yet been evaluated. Due to the structural similarities of the diphenols and the un-specificity of the “hormone receptor”, we may assume that many of the compounds or their phenol-analogues act as endocrine disruptors.

Antibiotics (Ab) are designed to hinder to growth of bacteria and human pathogens. However, the extensive use of Abs by humans and in connection with diary and fish farming has resulted in a harmful spread of Abs in the environment. As a consequence, bacteria in soil and water have developed resistance to most of our Abs. This new hazard for the environment and in extension for humans needs to be acted on. We need to get an understanding of the fate of Abs in the environment and at the same time develop method for their efficient degradation in especially waste water treatment plants.

The objective of our work is to determine the fate of especially diphenyls and diphenols and of antibiotics in aquatic environments receiving discharges from municipal waste water treatment plants. More specifically we aim to a) study the stability of the compounds in the environment, i.e. determination of the photo transformation rates and structural characterization of the main products, b) determine the concentrations of parent compounds and transformation products in the environmental compartments, i.e. water, sediment and biota and c) study degradation pathways for especially antibiotics.



Structure of some chemicals and pharmaceuticals bearing diphenyl and diphenol units.

Behavior and Properties of Molten Ash in Biomass and Waste Combustion

Main funding: Academy of Finland (Academy of Finland Research Fellow)

Daniel Lindberg, Fiseba Tesfaye, 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.

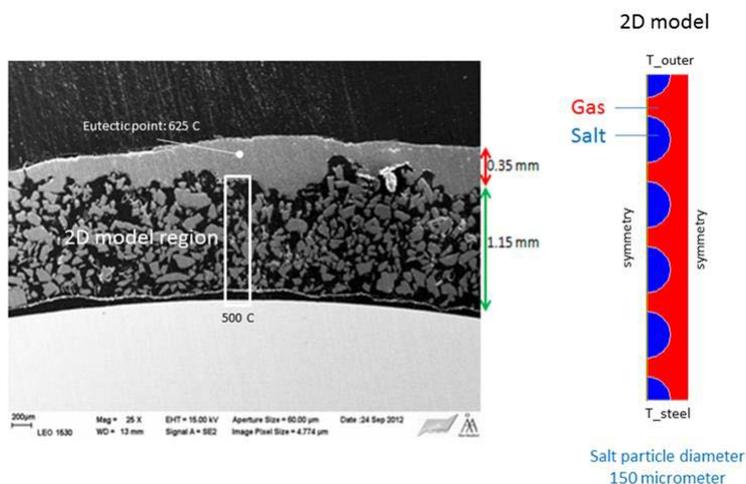
The present project sheds more light to the chemical phenomena of industrial significance related to the presence of a molten phase, especially connected to the role of the melt in ash deposits in biomass and waste combustion. The chemical and physical changes of partly molten ash deposits in thermal gradients are studied simulating the condition in boilers. The mobility of components in the melt phase in temperature gradients is 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-Na₂SO₄ 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.

Publications:

- Lindberg, D., Engblom, M., Yrjas, P., Laurén, T., Lindholm, J., Hupa, M., Influence of deposit aging on superheater corrosion, *Proceedings: 2014 International Chemical Recovery Conference*, June, 9-12, 2014, Tampere, Finland, Vol. 2, 101-113, ISBN: 978-952-68166-0-9

Fuel additives to Reduce Corrosion at Elevated Steam Data in Biomass Boilers

Funding: Swedish Energy Agency

Patrik Yrjas, Daniel Lindberg, Mikko Hupa

The project started in late 2011 and ended in spring 2014. The project identified and evaluated the use of additives and fuel blends to reduce furnace wall, and possibly also superheater, corrosion for biomass fuel mixes including waste wood. The expected effect of the additives on the rest of the boiler (uncooled components in the furnace, heat exchangers in the flue gas pass, flue gas cleaning equipment, emissions) will also be investigated.

Åbo Akademi University participated with extensive fuel and additive analyses in combination with thermodynamic equilibrium calculations. The research was done in close contact with the industrial partners together with SP Technical Research Institute of Sweden, which was the other research organization in the project.

Cooperation:

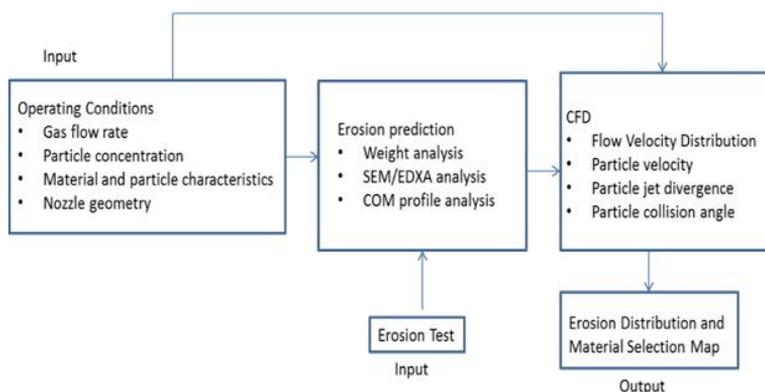
Vattenfall; Valmet Power; E.ON; Sandvik Heating Technology; Outokumpu; SP Technical Research Institute of Sweden, Sweden

Corrosion and Erosion of Metals and Refractories

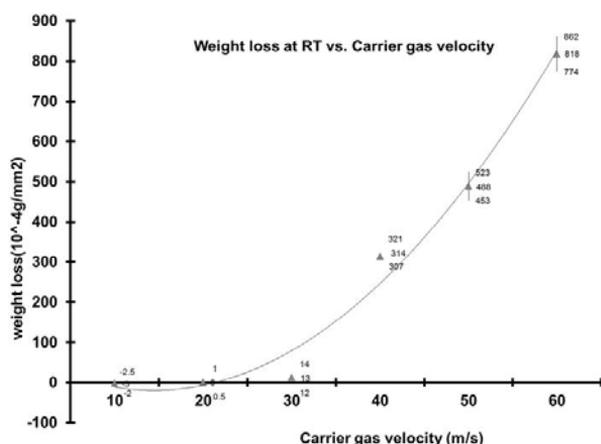
Main funding: PCC, FUSEC and CLIFF project partners

Leena Hupa, Emil Vainio, Na Li, Ismoil Bello, Varun Rai, Mikko Hupa

The objective of this research is to evaluate and compare the chemical and mechanical durability of refractory metals and ceramics in biomass combustion devices. We have developed a laboratory scale procedure in which the performance of the materials is measured after short term experiments at demanding environments imitating the conditions in combustion devices. We have characterized the chemical durability of the refractories by exposing the materials for synthetic ashes at various temperatures for one week. In addition, the influence of the abrasive effect of the bed particles in fluidized bed combustion has been measured as weight loss and abrasion rate.



Schematic procedure for erosion testing.



Short term erosion of stainless steel by olivine sand given as weight loss per surface area as a function of carrier gas velocity at room temperature. Eroderent amount 900 g, impact angle 45°.

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

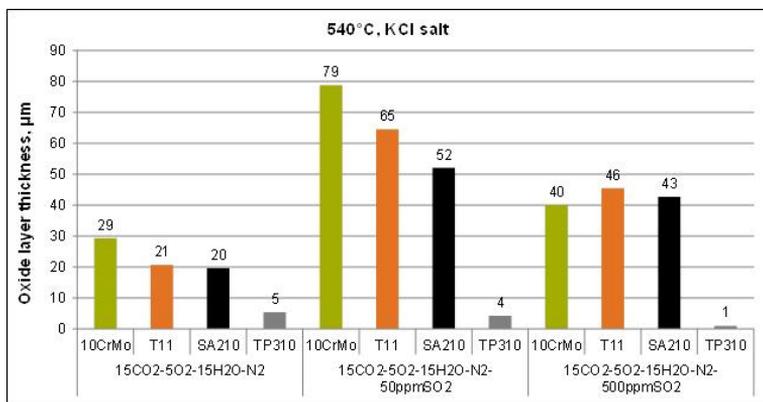
Funding: Research Fund for Coal and Steel (EU-RFCS)

Patrik Yrjas, Dorota Bankiewicz, Mikko Hupa

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 sulfur 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 pulverized fuel and fluidized 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 University focuses on advanced fuel characterization, fuel mix calculations, alkali absorption laboratory tests, ash behavior 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.

Cooperation:

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

Publications:

- Sui, J., Lehmusto, J., Bergelin, M., Hupa, M., The onset of potassium chloride induced high temperature corrosion: A novel experimental approach, *Oxidation of Metals* 82 (2014) 5-6, 437-456

High-Temperature Corrosion in Flash-Smelting and Other Outotec Application

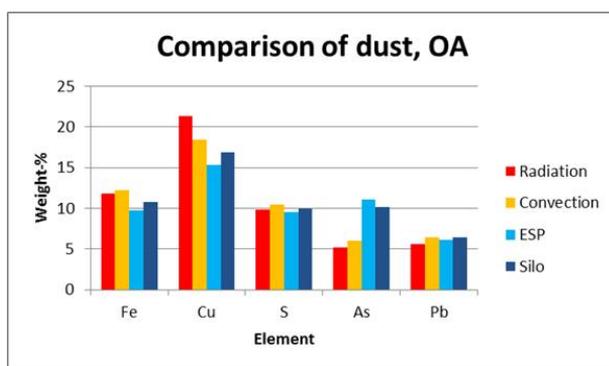
Funding: Boliden Harjavalta Oy and Outotec

Patrik Yrjas, Juho Lehmusto, Daniel Stenlund, Tor Laurén, Emil Vainio, Mikko Hupa

The project was carried out between May 2014 and February 2015. It was divided in two independent tasks, described in greater detail below.

1. In-furnace measurements of deposit build-up and corrosion in a copper flash smelting waste heat boiler

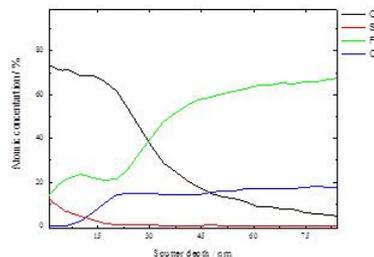
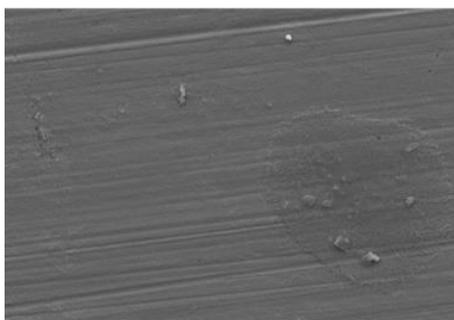
This task was carried out as a diploma work for a master's thesis. The aim of the work was to increase the understanding of deposit formation and corrosion chemistry in a copper flash smelting plant, focusing on the effect of different compounds in the feedstock on the deposit formation and corrosion rate. The primary goals were to examine, what adheres first to the waste heat boiler surfaces, and how do deposits transform, both chemically and physically, as a function of time. In addition, the behavior of sulfur in terms of acid dew point corrosion was addressed. The results support the development of the heat recovery process in a flash smelter and improving the productivity of the smelter process, since broader understanding about the build-up chemistry and corrosion behavior will surely provide improved tools for the plant operators.



Chemical compositions of dust samples taken from different parts of the process line.

2. Corrosion under deposits

In copper and nickel smelters, compounds containing arsenic (As) are often found closest to the corroded heat transfer surfaces under deposits. However, the role of arsenic trioxide in heat transfer surface corrosion has not been addressed previously. Therefore, the corrosivity of arsenic trioxide was studied in laboratory-scale with genuine steel materials. On a more general level, the goal of the study was to obtain more information on the possible material degradation under conditions relevant to the flash smelting process.



The surface of a heat-transfer material exposed to a SO₂-rich atmosphere (left) at 275°C; the depth profile of the formed oxide (right).

Cooperation:
Boliden Harjavalta Oy; Outotec

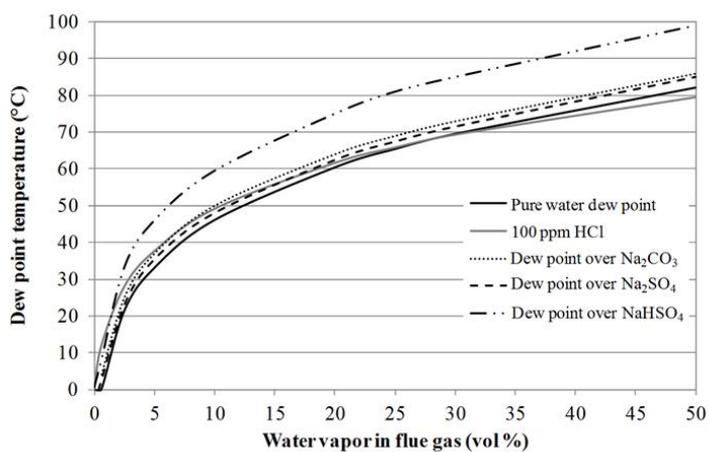
Understanding Low Temperature Corrosion in Black Liquor Combustion

Funding: Finnish Recovery Boiler Committee

Nikolai DeMartini, Emil Vainio, Patrik Yrjas, Mikko Hupa

Historically, some low temperature corrosion has been observed in recovery boilers. However, the underlying cause has not been clearly documented. One previously held hypothesis was the presence of a sulfuric acid dew point in Kraft recovery boilers. This was the driving force for maintaining a flue gas temperature of about 140 °C. This elevated flue gas temperature results in additional heat losses from the boiler. A part of this energy can be captured if the flue gas temperature can be reduced further without having significant corrosion. Thus, if there is no sulfuric acid in recovery boilers, how low can the flue gas temperature be dropped and what is the controlling mechanism for corrosion? These are the questions this study is designed to answer.

In probe studies, we have found that the condensation of water has to be reached in order for low temperature corrosion to occur. The water dew point can be elevated in the presence of hygroscopic salts. Thus, if hygroscopic salts are on the tube surface, water may condense at higher temperatures than if the tube surface is clean. The hygroscopic nature of salts is different for different salts (see figure below) and mixtures can behave differently than their individual components. In this work, we are mapping the conditions in which corrosion occurs, by measuring corrosion at different temperature and humidity combinations for carbon steel in the presence of different salts and salt mixtures relevant to Kraft recovery boilers.



Pure water dew point, HCl dew point, and dew point over hygroscopic salts (Na₂CO₃, Na₂SO₄ and NaHSO₄) as a function of water vapor concentration.

Publications:

- Vainio, E., Laurén, T., DeMartini, N., Brink, A., Hupa, M., Sulfuric acid induced low temperature corrosion in recovery boilers, *Proceedings: 2014 International Chemical Recovery Conference*, June, 9-12, 2014, Tampere, Finland, Vol. 2, 189-203, ISBN: 978-952-68166-0-9

Reduced Lignin Black Liquor –Pyrolysis Tests and CFD Modeling Study

Funding: Finnish Recovery Boiler Committee

Nikolai DeMartini, Markus Engblom, Anders Brink

Lignin extraction will change the chemical composition of black liquor (see table below) which will affect the operation of Kraft recovery boilers. Lignin removal is being implemented at some mills and as markets for lignin are developed, more mills are likely to implement lignin removal technology. In removing lignin, the heating value of the black liquor is reduced. Another possible impact is a change in the amount of carbon that reaches the lower furnace. Combustion of carbon in the lower furnace is critical for reduction of sulfate to sulfide, which is the first step in the efficient recovery of chemicals in the Kraft recovery cycle. Lignin is the primary source of char carbon. Other organic components in black liquor form less char than lignin. Thus, lower lignin black liquors may form less char carbon at a given temperature. This would require that the spraying conditions are changed so that fewer droplets are burned in flight and more are burned on the char bed.

Additionally, because the heating value is lower, the air distribution needs to be changed to maintain the lower furnace temperature. In practice this means more air needs to be directed to the lower furnace and more, not less char needs to be burned in the lower furnace. The pyrolysis experiments will help clarify the distribution between volatile and char carbon and the CFD calculations will help the industry estimate how much spraying and air distribution should be changed in order to maintain the lower furnace temperature which is so important to recovery boiler operation.

Composition of black liquor and 10% and 20% lower lignin.

	Original Black Liquor (wt% d.s.)	10% lower lignin (wt%	20% lower lignin (wt%
C	32.2	30.9	28.9
H	3.3	3.2	3.03
N	0.09	0.09	0.09
Na	21.4	22.8	23.9
K	2.4	2.6	2.7
Cl	0.3	0.32	0.34
Tot. S	6.4	7.0	7.5
SO ₄	5.4	6.7	7.87
SO ₄	5.4	6.7	7.87
OH	1.74	1.4	1.1
HHV (MJ/kg d.s.)	13.2	12.4	11.6

Publications:

- Vähä-Savo N., DeMartini, N., Ziesig, R., Tomani, P., Theliander, H., Välimäki, E., Hupa, M., Combustion properties of reduced-lignin black liquors, *Tappi Journal* 13 (2014) 8, 81-90
- Engblom, M., Vainio, E., Brink, A., Hupa, M., Välimäki, E., Heikkilä, V-P., Understanding the formation of NO_x in pulp mill boilers, *Proceedings: 2014 International Chemical Recovery Conference*, June, 9-12, 2014, Tampere, Finland, Vol. 2, 155-170, ISBN: 978-952-68166-0-9
- Vähä-Savo, N., DeMartini, N., Ziesig, R., Tomani, P., Theliander, H., Välimäki, E., Hupa, M., Combustion properties of reduced lignin black liquors, *Proceedings: 2014 International Chemical Recovery Conference*, June, 9-12, 2014, Tampere, Finland, Vol. 1, 334-354, ISBN: 978-952-68166-0-9
- Vähä-Savo, N., DeMartini, N., Engblom, M., Brink, A., Hupa, M., The fate of char N in black liquor combustion – cyanate formation and decomposition, *Proceedings: 2014 International Chemical Recovery Conference*, June 9-12, 2014, Tampere, Finland, Vol. 2, 131-141, ISBN: 978-952-68166-0-9

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 characterization; 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 utilizing the fundamental data and modelling tools developed within the project.
- Dissemination and technology transfer of findings to project stakeholders.

The main activities at Åbo Akademi University in this project are related to underpinning technology investigation. Three different tasks are undertaken: “Task 1.1 Fuel and Combustion Characterization”, “Task 1.4 Investigation of High Temperature Gas-Side Corrosion”, “Task 2.1 CFD Sub-models”.

Cooperation:

University of Glamorgan – Coordinator, UK; Åbo Akademi University; 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, Italy; Fundación Ciudad de la Energía, Spain; International Flame Research Foundation, Italy

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 divided 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 feedstock, 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 framework 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 characterization of feedstock, 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

Publication:

- Houshfar, E., Wang, L., Vähä-Savo, N., Brink, A., Lövås, T., Characterisation of CO/NO/SO₂ emission and ash-forming elements from the combustion and pyrolysis process, *Clean Technologies and Environmental Policy* 16 (2014) 7, 1339-1351

Development of Drug Delivery Systems for Nonsteroidal Anti-Inflammatory Drugs in Chronic Wound Healing

Main funding: Academy of Finland

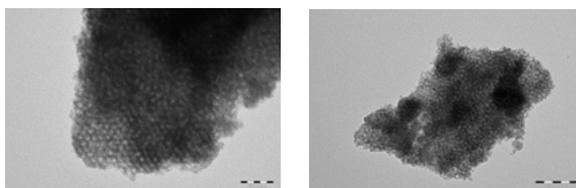
Xiaoju Wang

Chronic wounds cause patients severe emotional and physical stress and create a significant financial burden on patients and the whole healthcare system. Electrostimulation therapy, which employs electrical stimulations in chronic wounds repair and care, mimics the endogenous electrical fields as a directional signal for cell migration in wound repair processes. Inflammation control is an aspect of great importance in chronic wound management. Topical application of nonsteroidal anti-inflammatory drugs (NSAIDs) in low dosages on the surface of chronic wounds, e.g., ibuprofen, can accelerate wound healing, reduce pain and exudate, and suppress hypergranulation tissue formation. In clinics of chronic wounds healing and care, a dressing product with multi-functionality and more precise controllability is desired for point of-use of medical care to the chronic wounds.

This 3-year project funded by Academy of Finland in a postdoctoral researcher call aims to develop a wound dressing surface with both the delivery of electric stimulation for accelerated wound healing and the anti-inflammatory functionality integrated. The delivery of direct micro-current to the wound is realized via a novel electrode array design, which is fabricated via printing technology on polyethylene (PE) films. This type of wound-dressing product has been earlier developed in Tekes-TUTLI project MC-Patch.

We are currently working with two strategies to integrate the anti-inflammatory functionality onto this type wound healing dressing surface.

- Sol-gel derived mesoporous bioactive glass (MBG) particles as drug delivery system (DDS) of NSAIDs to be integrated into the wound healing dressing surface; controlled release of the adsorbed NSAIDs through the bioactivity of MBG with physiological fluids.
- Modification the partitioned electrodes in the array with conducting polymers to create such a DDS; electrically-controlled release of the doped NSAIDs.



TEM images of MBG particles with well-ordered, few nm mesopore in bulk structure.

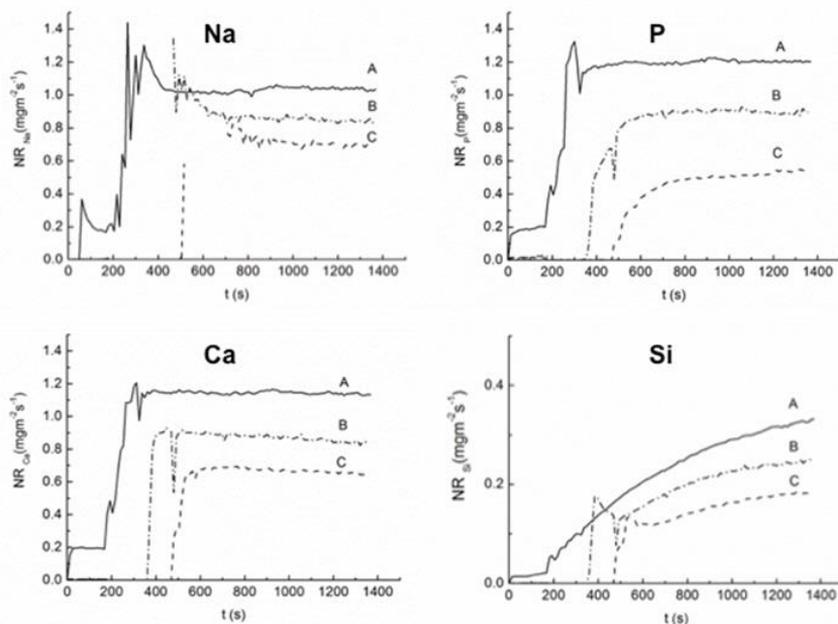
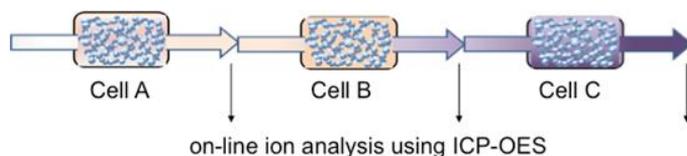
Cooperation:
PCC

Bioactive Glasses and Their Properties

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

Leena Huja, Jonathan Massera, Di Zhang, Leena Björkvik, Chao Gao, Johan Sangder, Anna Lisa, Paul Ek, Mikko Huja

The focus of our bioactive glass research was to measure and define the influence of glass oxide composition on the dissolution kinetics in vitro. We measured the dissolution in static and dynamic solutions simulating the composition of the body fluids. The results are of importance for the behavior of the glass at the moment of the implantation but give also information on the anticipated long-term dissolution behavior and capability to support and stimulate the regeneration of damaged or diseased living tissue. We also studied the influence of the oxide composition on the high temperature properties of the glasses. Detailed understanding of the thermal properties is the key for tailoring glasses for desired product types such as porous implants and scaffolds. In addition, we have studied the interactions of the bioactive glasses in composites together with biostable and biodegradable polymers.



Normalized initial ion release from particles (300-500 μ m) of the bioactive glass S53P4 into TRIS buffered solution in a cascade reactor consisting of three sample cells A, B, and C.

Cooperation:

University of Turku; University of Tampere; Tampere University of Technology; University of Helsinki; Friedrich-Schiller University Jena, Germany; University of Erlangen-Nuremberg, Germany

Publications:

- Abdulmajeed, A.A., Walboomers, X.F., Massera, J., Kokkari, A.K., Vallittu, P.K., Närhi, T.O., Blood and fibroblast responses to thermoset BisGMA-TEGDMA/glass fiber-reinforced composite implants in vitro, *Clinical Oral Implants Research* 25 (2014) 7, 843-851
- Abdulmajeed, A.A., Kokkari, A.K., Kämpylä, J., Massera, J., Hupa, L., Vallittu, P.K., Närhi, T.O., In vitro blood and fibroblast responses to BisGMA-TEGDMA/bioactive glass composite implants, *Journal of Materials Science: Materials in Medicine* 25 (2014) 1, 151-162

Optical Fibers with Bioactive Surface

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

Jonathan Massera, Laeticia Petit, Leena Hupa

This project studied core-clad glass/glass-ceramic fibers in which an optical quality glass core was combined with a bioactive glass clad giving rapid tissue bonding. The goal was to design novel fibers for medical and sensing applications. For this, several new silicate, borosilicate, and phosphate based glass compositions were developed. The influence of Ce and Er doping on the thermal, structural and optical properties were measured. In addition, changes in the optical properties and in vitro reactions as a function of the immersion in simulated body fluid were studied. The results showed that the dissolution reactions and layer formation at the glass fiber could be followed by the changes in the optical properties.

Cooperation:

University of Turku; nLight corp., Finland; University of Nottingham, UK; University of Rennes, France; University of Bordeaux, France; Politecnico di Torino, Italy

Publications:

- Bourhis, K., Shpotyuk, Y., Massera, J., Aallos, V., Jouan, T., Boussard-Plédel, C., Bureau, B., Petit, L., Koponen, J., Hupa, L., Hupa, M., Ferraris, M., Thermal and structural characterization of erbium-doped borosilicate fibers with low silica content containing various amounts of P₂O₅ and Al₂O₃, *Optical Materials* 37 (2014), 87–92
- Massera, J.M., Vassallo-Breillot, M., Törngren, B., Glorieux, B., Hupa, L., Effect of CeO₂ doping on thermal, optical, structural and in vitro properties of a phosphate based bioactive glass, *Journal of Non-Crystalline Solids* 402 (2014), 28–35
- Massera, J., Sevette, B., Petit, L., Koponen, J., Törngren, B., Glorieux, B., Hupa, L., Hupa, M., Effect of partial crystallization on the thermal, optical, structural and Er³⁺ luminescence properties of silicate glasses, *Materials Chemistry and Physics* 147 (2014) 3, 1099–1109
- Massera, J., Hupa, L., Influence of SrO substitution for CaO on the properties of bioactive glass S53P4, *Journal of Materials Science: Materials in Medicine* 25 (2014) 3, 657–668
- Massera, J., Ahmed, I., Petit, L.V., Aallos, V., Hupa, L., Phosphate-based glass fiber vs. bulk glass: Change in fiber optical response to probe in vitro glass reactivity, *Materials Science and Engineering: C* 37 (2014), 251–257

Structure of Gradient Nanocomposites: Interaction of Bioactive Glasses with Nanoparticles and Polymers (MoreBAGS)

Main funding: Academy of Finland, PCC

Leena Hupa, Leena Björkvik, Sara Kiran, Mikko Hupa

MoreBAGS project aims to gain a thorough understanding of the mutual interactions of biodegradable and bioactive materials in aqueous solutions, such as simulated body fluid. The research has been done with binary and ternary composites of polymers and melt-derived bioactive glasses or sol-gel derived nanoparticles. In addition, bioactive glasses have been applied to the surface of load-bearing fiber-reinforced composite (FRC) implant. The goal is to utilize these materials to tailor implants with a gradient structure giving controlled resorption and controlled guidance of tissue regeneration. The results will be utilized to develop implants with a FRC core giving long-term stability and with bioactive surface layers providing good bonding to tissue.

Cooperation:

University of Turku, Institute of Dentistry; Central Glass & Ceramic Research Institute, Kolkata India

Process Intensification

Reaction intensification is a sub-field of process intensification. The approach implies new structures and methods, which lead to more efficient, energy saving and miniaturized processes. With reaction intensification an essential reduction of the equipment size or energy consumption can be achieved. Monolith reactors, solid foams and fibrous catalyst structures as well as ultrasonic and microwave technologies are investigated. PCC has unique experimental devices for in situ studies of reactions under the influence of ultrasound and microwaves. The chemical applications are several, such as esterification, catalytic oxidation, vegetable oil epoxidation as well as hydrogenation of aldehydes and ketones, leaching of minerals and hemicelluloses as well as delignification of wood. Ultrasound and microwave technologies are used to enhance the rates of catalytic processes. A chemical method was developed to measure the exposed ultrasound effect in a precise way and a new device was constructed for carrying out in situ ultrasound experiments. Slurry reactors, fixed beds and structured reactors are exposed to ultrasound to reveal its effect on reaction rates.

The research was strongly focused on multiphase reactors, where a gas phase, a liquid phase and a solid catalyst are present. Modern computational techniques and reactor structures, such as CFD and microreactors are applied. The modelling tool gProms was taken into active use by our research group. We have constructed several new millireactor and microreactor systems, for catalytic gas-phase reactions and for liquid-phase reactions. Detailed mathematical modelling has been applied. The main application has been safe production of chemical intermediates.

Structured Reactors

Main funding: PCC, Academy of Finland, EU

Jyri-Pekka Mikkola, Teuvo Kilpiö, Vladimir Shumilov, Erfan Behravesb, Leena Hupa, Mikko Hupa, Johan Wärnå, Kari Eränen, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

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.

Cooperation:

Helmholtz-Institut Dresden-Rossendorf, TU Dresden, Germany; University of Tver, Russia

Publications:

- Behravesb, Erfan, Preparation and optimization of alumina foams via replica technique

Modern Polymer-Based Catalysts and Microflow Conditions as Key Elements of Innovations in Fine Chemical Syntheses

Main funding: EU FP7

Atte Aho, Heid Bernas, Reko Leino, Dmitry Murzin

The major objective of the project is to develop efficient and stable heterogeneous polymer and carbon nanotubes based nanoparticulate catalysts for the efficient implementation of catalytic processes. Nanostructured polymers of several types: rigid nanoporous hypercrosslinked polystyrene (HPS) with various functionalities; spherical polyelectrolyte brushes (SPB); polyelectrolytes deposited on inert inorganic supports; thermosensitive core-shell microgel particles and shape-persistent poly(phenylene pyridyl) dendrons were used. Varying the structure of the

metal compounds as well as the composition and the structure of the polymeric systems, nanoparticulate catalysts containing monodisperse mono- (Au, Pt, Pd, and Ru) and bimetallic (Pt-Zn, Ru-Zn Pd-Sn, Pd-Zn, Pd-Bi, Au-Pt, etc.) nanoparticles were synthesized. Catalytic properties of the developed catalysts were investigated in hydrogenation of sugars and amination of alcohols.

Cooperation:

Institut für Mikrotechnik Mainz, Sanofi-Aventis, Bayer Technology Services, Evonik-Degussa, Ehrfeld Mikrotechnik BTS GmbH, ThalesNano Inc, Alvigo, Picosun, Newcastle University, CNRS/CPE Lyon, France; FORTH; EPFL Lausanne, Switzerland; University of Palermo, Italy; University of Jena, Germany; Eindhoven University of Technology, the Netherlands; Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Science, Russia; Tver Technical University Russia

Publications:

- Bernas, H., Kumar, N., Aho, A., Leino, R., Murzin, D.Y., Hydrogenation of 2-methylindole using supported metal catalysts, *Catalysis Communications* 56 (2014), 41-44

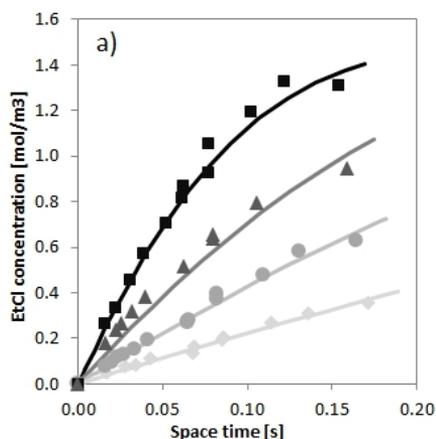
Micro- and Milliscale Reactor Technology

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

Kari Eränen, José Rafael Hernández Carucci, Sabrina Schmidt, Zsuzsana Vajglova, Quentin Balme, Erfan Behravesb, Narendra Kumar, Teuvo Kilpiö, Vincenzo Russo, Johan Wärnå, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

Micro- and millireactors enable an efficient performing of chemical processes because of enhanced mass and heat transfer. We have introduced the concept of microreactors on Finnish soil. Different kinds of microreactor systems have been constructed; e.g. for catalytic gas-phase systems and for liquid and liquid-liquid reactors. The catalyst coating technology was developed and we are now able to perform various reactions in gas-phase microreactors and conduct kinetic studies. Gas-phase microreactors were successfully used to make 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 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. Separation technology based on selective condensation was developed for the product mixture in the synthesis of methyl chloride. A detailed mathematical model was developed for catalyst layers in the microreactor structures. The model describes the reaction-diffusion phenomena in

the porous structure very well. Separation technology was developed for the product mixture in the synthesis of methyl chloride. A new millireactor system was constructed 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. The MICATOX project was successfully continue in a close collaboration with Lappeenranta University of Technology and Aalto University.



Model and experimental data for formation of ethylene chloride at four different temperatures.

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

Publications:

- Schmidt, S.A., Vajglova, Z., Eränen, K., Murzin, D.Yu., Salmi, T., Microreactor technology for on-site production of methyl chloride, *Green Processing and Synthesis* 3 (2014), 345–352

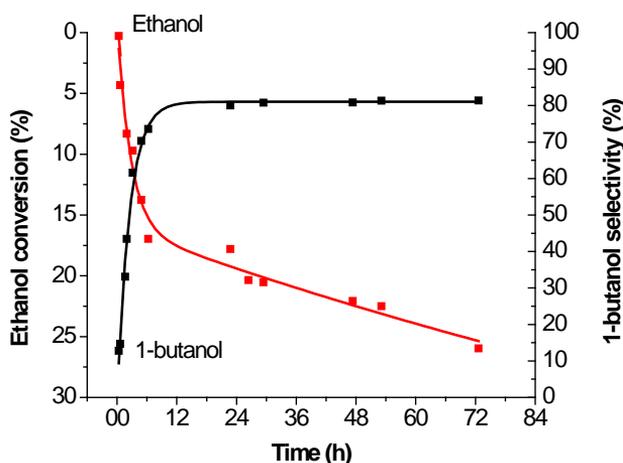
Multiphase Reactors

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

Johan Wärnä, Teuvo Kilpiö, Pasi Tolvanen, Adriana Freitas, Sébastien Leveneur, Pierdomenico Biasi, Nicola Gemo, Gianluca Gallina, Cesar De Araujo Filbo, Toni Riittonen, Stefano Sterchele, Juan Garcia Serna, Irene Huerta, Paolo Canu, Lionel Estel, Tapio Salmi

Advanced modelling of multiphase reactors is the topic of the subproject, 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, transformation of ethanol to 1-butanol, ring opening and reactions of solids with gases and liquids. 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. Advanced mathematical models were developed; the models include kinetics, catalyst deactivation, transport phenomena as well as residence time distributions. The modelling work was summarized in the extensive thesis of Teuvo Kilpiö which obtained a national award.



Production of butanol from ethanol over Ni/Al₂O₃ catalyst.

Cooperation:

Università di Napoli, Naples, Italy; Università di Padova, Padova, Italy; INSA Rouen, France; Universidade de Valladolid, Spain

Publications:

- de Araujo Filho, C., Eränen, K., Mikkola, J-P., Salmi T., A comprehensive study on the kinetics, mass transfer and reaction engineering aspects of solvent-free glycerol hydrochlorination, *Chemical Engineering Science* 120 (2014), 88-104
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- Leveneur, S., Zheng, J., Taouk, B., Burel, F., Wärnä, J., Salmi, T., Interaction of thermal and kinetic parameters for a liquid-liquid reaction system: Application to vegetable oils epoxidation by peroxycarboxylic acid, *Journal of the Taiwan Institute of Chemical Engineers* 45 (2014) 4, 1449-1458
- Leveneur, S., Ledoux, A., Estel, L., Taouk, B., Salmi, T., Epoxidation of vegetable oils under microwave irradiation, *Chemical Engineering Research and Design* 92 (2014) 8, 1495-1502
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- Tolvanen, P., Kilpiö, T., Mäki-Arvela, P., Murzin, D., Salmi, T., Esterification of fatty acids and short-chain carboxylic acids with stearyl alcohol and sterols, *ACS Sustainable Chemistry & Engineering* 2 (2014), 537-545

Batch and Semibatch Reactors for Reactive Solids

Main funding: PCC, FIBIC

Henrik Grénman, J-P. Mikkola, Steliana Aldea, Jussi Rissanen, Andrea Perez Nebreda, Pasi Tolvanen, Päivi Mäki-Arvela, Johan Wärnä, 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.

Cooperation:

Raisio; Nordkalk

Publications:

- Rissanen, J., Grénman, H., Willför, S., Murzin, D., Salmi, T., Spruce hemicellulose for chemicals using aqueous extraction: Kinetics, mass transfer, and modelling, *Industrial & Engineering Chemistry Research* 53 (2014) 15, 6341-6350
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Complex Reaction Kinetics and Thermodynamics

Main funding: Academy of Finland, Graduate School of Materials Research (GSMR)

Johan Wärnä, Jyri-Pekka Mikkola, Matias Kangas, Olatunde Jogunola, Valerie Eta, Ewelina Leino, Antonina Kupareva, Andreas Bernas, Heidi Bernas, Timo Petteri Suominen, 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 hydroformylation, esterification, oxidation of aldols, various catalytic hydrogenations, CO₂ utilization and reactions between solids and liquids, production of pharmaceuticals and SCR. Both conventional and microreactors are used. New catalyst concepts and new kinetic models were used for the alkyl carbonate synthesis (CO₂ utilization). Detailed kinetic modelling was carried out for the industrial production process of formic acid.

Cooperation:

VTI; Recoil; Forchem; Universite de Bourgogne, France; University of Oulu; INSA Rouen, France

Publications:

- Kirilin, A.V., Wärnä, J., Tokarev, A.V., Murzin, D.Yu., Kinetic modelling of sorbitol aqueous phase reforming over Pt/Al₂O₃, *Industrial and Engineering Chemistry Research* 53 (2014), 4580-4588
- Murzin, D.Yu., Evolution of heterogeneous catalytic reactions kinetics with time, *Comptes Rendus Chimie* 17 (2014), 612-614
- Murzin, D.Yu., Catalyst deactivation and structure sensitivity, *Catalysis Science and Technology* 4 (2014), 3340-3350

- Reinik, J., Heinmaa, I., Ritamäki, J., Boström, D., Pongracz, E., Huuhtanen, M., Larsson, W., Keiski, R., Kordas, K., Mikkola, J.-P., Direct CO₂ sequestration onto alkaline modified oil shale fly ash, *Oil Shale* 31 (2014) 1, 79-90
- Suominen, P., Kilpiö, T., Salmi, T., Mass transfer in a porous particle – MCMC assisted parameter estimation of dynamic model under uncertainties, *Computer Aided Chemical Engineering* 33 (2014), 277- 282

Catalysis and Molecular Engineering

The development of new products and processes nowadays is indispensable from the application of the principles of green and sustainable chemistry. One of the cornerstones of sustainable technology is application of catalysis, since catalytic reagents are superior to stoichiometric reagents. Our activities cover mainly heterogeneous catalysis, but homogeneous and enzymatic catalysis is incorporated in some projects.

Molecular approach to heterogeneous catalysis requires understanding of physical chemistry of surfaces, ability to tailor materials with desired properties and employ their specific features to obtain required molecules. Such approaches improve the predictability and application of catalytic science, and strengthen the relationship between materials science and chemical process engineering.

Furthermore, the activities are focused on the design, synthesis, and possible applications not only of materials with special functionalities, but also of complex mixtures with specific properties, which could be used in a variety of areas, ranging from fuels to fine chemicals and pharmaceuticals.

Among the new materials which are actively researched at the PCC are various micro- and mesoporous materials, which are synthesized by different methods and then subjected to modification, e.g. by introduction of metals. The intimate interactions between the metal and sites are sensitive to the applied treatment and could be fine-tuned in a way that the molecularly engineering materials have, for instance, a specific acidity. Besides metal-supported zeolites and mesoporous materials, also materials with hierarchical micro-mesoporous structure, as well as metals on other supports, like alumina, silica, active carbon and carbon nanofibers were used in heterogeneous catalytic reactions, including hydrogenation, ring opening, skeletal isomerization, dimerization, oxidation, pyrolysis of biomass.

A particular challenging was development of catalysts, containing gold, which was considered for centuries as catalytically inactive. Various types of supported gold catalysts, including structured ones, were synthesized and tested in reactions, involving carbohydrates, e.g. oxidation, hydrogenation and isomerization of mono- and disaccharides. For example, in the oxidation of lactose to lactobionic acid, gold catalysts turned out to be superior to classical Pd catalysts.

A special way in molecular engineering of catalysts is to have metals in non-zero valence state dissolved in a liquid layer, attached to the solid surface. Immobilization of ionic liquids onto solid materials with subsequent introduction of catalytically active species palladium species and testing the catalyst in liquid

phase hydrogenation of citral demonstrated the big potential of this novel catalytic system (see Section 3.1: Ionic liquids).

The materials were characterized with modern techniques, such as SEM, TEM, XRD, AFM, TPD, and FTIR. An electrochemical method, cyclic voltamperometry, which is mainly used for bulk metals, was developed to characterize supported metals with low metal loading.

Substantial efforts were made to reveal the mechanism of catalytic reactions through state-of-the-art theoretical methods, e.g. quantum chemical calculations were performed in order to elucidate adsorption modes of complex organic molecules on solid surfaces, explain catalytic activity, regio- and enantioselectivity in asymmetric catalysis and uncover the cluster size effect in heterogeneous catalysis.

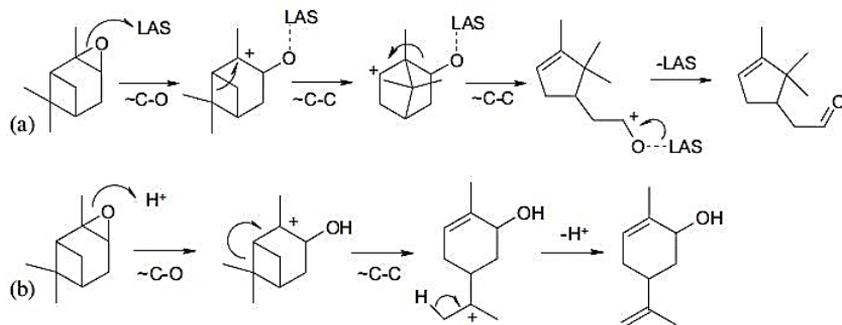
Modelling and simulation of catalytic reactors including catalyst deactivation and regeneration studies was a central topic of research. Advanced simulation techniques were applied in catalytic reactions in microreactors, gas-liquid reactors and various three-phase reactors, such as slurry and fixed bed reactors. The chemical applications were abatement of harmful emissions, synthesis of fine chemicals (e.g. derivatives of citral), manufacture of alimentary products (e.g. mannitol, sorbitol, lactitol and xylitol) as well as bulk chemicals (e.g. hydroformylation products). Advanced dynamic models including complex kinetics, catalyst deactivation and regeneration as well as flow modeling (classical and CFD) were applied. The effect of ultrasound and microwave irradiation on catalytic processes was studied intensively and gave encouraging results.

Novel Functional Materials

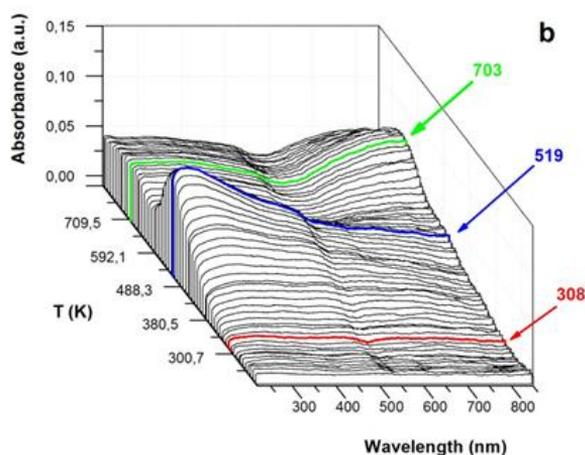
Main funding: Åbo Akademi University

Narendra Kumar, Sabrina Schmidt, Kai Yu, Alexandra Torozova, Karolina Maduna Valkaj, 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. These 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.



Formation of campholenic aldehyde over Lewis acidic sites and trans-carveol over Brønsted acidic sites.



Profiles of oxygen consumption and product formation (a) and UV-Vis spectra in-situ (b) under temperature programmed oxidation of the spent Au/Al₂O₃ catalyst.

Cooperation:

Estonian National Institute of Chemical Physics and Biophysics, Tallinn, Estonia; University of Turku; Åbo Akademi University (Quantum Chemistry and Molecular Spectroscopy); Hungarian Academy of Sciences, Budapest, Hungary; Jagiellonian University, Kraków, Poland; Alexander von Humboldt-Universität, Berlin, Germany; Boreskov Institute of Catalysis, Novosibirsk

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- Baeza, J.A., Calvo, L., Murzin, D.Yu., Rodriguez, J.J., Gillaranz, M.A., Kinetic analysis of 4-chlorophenol hydrodechlorination by Rh nanoparticles based on the two-step reaction and Langmuir-Hinshelwood mechanisms, *Catalysis Letters* 144 (2014) 12, 2080-2085
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Cellulose and Hemicellulose Derivatives in Ionic Liquids

Main funding: PCC, Åbo Akademi University

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

Ionic liquids are excellent reaction media for making cellulose derivatives, because cellulose can be dissolved in non-toxic, non-volatile ionic liquids. This implies that a big technology jump is taken: classical methods for preparing cellulose derivatives are based on the use of suspended cellulose in a solvent, which implies that the reaction is heterogeneous with all cumbersome mass transfer limitations involved. In dissolved state, cellulose reacts eagerly, and a new world of derivatives is opened. The existing processes can be considerably intensified by shifting to the ionic liquid technology and new derivatives can be prepared. The focus of the research project is in the etherification and esterification of cellulose. Breakthroughs have been made in the selection of suitable ionic liquids for cellulose acetylation and carboxymethylation. A 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.

Publications:

- Jogunola, O., Salmi, T., Mikkola, J-P., Screening of potential complexing agents in methyl formate hydrolysis, *Journal of Molecular Liquids* 196 (2014), 334-339
- Teerikoski, Sakari, Nya modeller för substitution av cellulosa och depolymerisation av polysackarider

Asymmetric Catalysis and Chromatographic Separation

Main funding: Academy of Finland

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.

Cooperation:

University of Porto, Portugal

Publications:

- Martin, G., Mäki-Arvela, P., Murzin, D.Yu., Salmi, T., Kinetics and catalyst deactivation in the enantioselective hydrogenation of ethyl benzoylformate over Pt/Al₂O₃, *Catalysis Science & Technology* 4 (2014) 1, 170-178
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4. Publications 2014

4.1 Theses

4.1.1 Doctoral theses (16)

Anugwom, Ikenna, Towards optimal fractionation of lignocellulosic biomass using switchable ionic liquids

Dax, Daniel, Chemical derivatization of galactoglucomannan for functional materials

Demidova, Yuliya, Terpenoid transformations over gold catalysts

Fugleberg, Sigmund, Improving the competitiveness of the electrolytic zinc process by chemical reaction engineering approach

Grönqvist, Stina, Action of laccase on mechanical softwood pulps

Hyvärinen, Sari, Ionic liquid mediated biomass deconstruction: from analysis to fermentable sugars

Hääriä, Matti, Oxalic acid and calcium oxalate in production of wood-containing paper: formation, analysis, and control

Martin Curvelo, Gerson, Novel technology for preparation of optically active agents

Rüttonen, Toni, Bio-ethanol valorization towards C4s including 1-butanol over metal modified alumina and zeolite catalysts

Rozmysłowicz, Bartoż, Deoxygenation of fatty acids for production of fuels and chemicals

Salminen, Eero, Catalytic upgrading of biomass extractives to fine chemicals over supported ionic liquid catalysts (SILICAs)

Schmidt, Sabrina, Methyl and ethyl chloride synthesis in microreactors

Stekrova, Martina, α -pinene oxide and verbenol oxide isomerizations over heterogeneous catalysts

Suominen, Petteri, Thermal reactions of the major hydrocarbon components of biomass gasification gas

Vainio, Emil, Fate of fuel-bound nitrogen and sulfur in biomass-fired industrial boilers

Vähä-Savo, Niklas, Behavior of black liquor nitrogen in combustion – formation of cyanate

4.1.2 Master's theses (16)

Behravesb, Erfan, Preparation and optimization of alumina foams via replica technique

Bilyavichyus, Roman, Homogeneous and heterogeneous catalytic hydrolysis of inulin from chicory root

Bizzotto, Francesco, Application of the catalyst wet pre-treatment method (CWPM) for catalytic direct synthesis of H₂O₂

Freites Aguilera, Adriana Samantha, Epoxidation of fatty acids assisted by microwaves for development of biolubricants

Gonzalez Vogel, Alvaro, Amperometric Sensor for quantification of condensed lignin structures in chemical pulping

Hupa, Elisa, Novel signal transduction principle for ion sensors

Matamala, Verónica, Furfural production from prehydrolysis Kraft liquor of Eucalyptus wood

Mattsson, Ida, Synthesis of a water soluble cellulose derivative by butyl glycidyl etherification of cellulose

Niemi, Jonne, Effect of temperature gradient on synthetic ash deposit chemistry, deposit morphology and superheater corrosion

Nuñez, Tomás, Valorisation of hemicelluloses from *Pinus radiata* sawdust through hot water extraction towards production of valuable chemicals and materials

Raitanen, Jan-Erik, Syntes av imperanenderivat utgående från hydroximatairesinol

Rujana, Luis, Isomerization of α - and β -pinene oxide over supported ionic liquids catalysts (SILCA)

Shumilov, Vladimir, Manufacture of macroporous ceramic foams to be used as catalytic supports,

Sundqvist, Maria, Rening av aluminiumhaltigt slam

Toivari, Maunu, Mechanical and chemical characterization of BLN pulp

Torožova, Alexandra, Reactions of verbenol oxide for synthesis of fine chemicals over acidic and Fe-modified zeolite catalysts

4.2 Publications

4.2.1 Articles in refereed international scientific journals and series (126)

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4.2.4 Articles in refereed international edited volumes and conference proceedings (9)

137. Boguslaw B., Lewenstam, A., Tkacz-Smiech, K., Danielewski, M., Electrochemistry of symmetrical ion channel: A three-dimensional Nernst-Planck-Poisson model, 225th ECS Meeting, May 11-15, 2014, Orlando, USA, *ECS Transactions* 61 (2014) 15, 11-20, ISSN 1938-5862
138. Engblom, M., Vainio, E., Brink, A., Hupa, M., Välimäki, E., Heikkilä, V-P., Understanding the formation of NO_x in pulp mill boilers, *Proceedings: 2014 International Chemical Recovery Conference*, June, 9-12, 2014, Tampere, Finland, Vol. 2, 155-170, ISBN: 978-952-68166-0-9
139. Kinnunen, K., Bankiewicz, D., Lindberg, D., Enestam, S., Haaga, K., Hupa, M., Influence of the deposit CO₃/SO₄ ratio on superheater corrosion, *Proceedings: 2014 International Chemical Recovery Conference*, June, 9-12, 2014, Tampere, Finland, Vol. 2, 90-100, ISBN: 978-952-68166-0-9
140. Lindberg, D., Engblom, M., Yrjas, P., Laurén, T., Lindholm, J., Hupa, M., Influence of deposit aging on superheater corrosion, *Proceedings: 2014 International Chemical Recovery Conference*, June, 9-12, 2014, Tampere, Finland, Vol. 2, 101-113, ISBN: 978-952-68166-0-9
141. Sokalski, T., Granholm, K., Mousavi, Z., Lewenstam, A., Analytical quality solid-state composite reference electrode and electrochemical platform, 225th ECS Meeting, May 11-15, 2014, Orlando, USA, *ECS Transactions* 61 (2014) 15, 1-10, ISSN 1938-5862
142. Szyszkievicz, K., Danielewski, M., Fausek, J., Jasielec, J., Kucza, W., Lewenstam, A., Sokalski, T., Filipek, R., Breakthrough in modeling of electrodiffusion processes, continuation and extensions of the classical work of Richard Buck, 225th ECS Meeting, May 11-15, 2014, Orlando, USA, *ECS Transactions*, 61 (2014) 15, 21-30, ISSN 1938-5862

143. Vainio, E., Laurén, T., DeMartini, N., Brink, A., Hupa, M., Sulfuric acid induced low temperature corrosion in recovery boilers, Proceedings: *2014 International Chemical Recovery Conference*, June, 9-12, 2014, Tampere, Finland, Vol. 2, 189-203, ISBN: 978-952-68166-0-9
144. Vähä-Savo, N., DeMartini, N., Ziesig, R., Tomani, P., Theliander, H., Välimäki, E., Hupa, M., Combustion properties of reduced lignin black liquors, Proceedings: *2014 International Chemical Recovery Conference*, June, 9-12, 2014, Tampere, Finland, Vol. 1, 334-354, ISBN: 978-952-68166-0-9
145. Vähä-Savo, N., DeMartini, N., Engblom, M., Brink, A., Hupa, M., The fate of char N in black liquor combustion – cyanate formation and decomposition, Proceedings: *2014 International Chemical Recovery Conference*, June 9-12, 2014, Tampere, Finland, Vol. 2, 131-141, ISBN: 978-952-68166-0-9

4.3 Edited conference proceedings and reports (2)

Lindqvist, H., Brink, A., Latonen, R-M., Mäki-Arvela, P., Sundberg, A. (eds.) *Åbo Akademi Process Chemistry Centre Annual Report 2013-2014*, Åbo Akademi University, 2014, ISSN: 1459-8213, Newprint, Loimaa, Finland, 2014

Vanysek, P., Lewenstam, A., (eds.) *Symposium in Honor of Richard Buck, 225th ECS Meeting*, May 11-15, 2014, Orlando, USA, ECS Transactions, 61 (2014) 15, ISSN 1938-5862, The Electrochemical Society, 2014

4.4 General articles (1)

Reactor technology in catalytic transformation of biomass, *60 Jahre Chemische Verfahrenstechnik an TU Dresden - Festschrift 2014*, Tapio Salmi

4.5 Patents and invention disclosures (5)

Aldea, S., Eränen, K., Grenman, H., Mikkola, J-P., Murzin, D., Salmi, T., Wärnä, J., Fagerholm, M., Snåre, M., Preparation of salt particles from precipitated calcium carbonate, PCT Int. Appl. WO 2014131950 A1

Bergelin, M., Eriksson, J.-E., Hyttinen, J., Johansson, M., Kekonen, A., Köppä, S., Leppänen, A-S., Viik, J., Willför, S., Xu, C., Ylänen, H.O., An arrangement for facilitating wound healing, a method for measuring wound healing and a wound dressing. PCT Int. Appl. WO 2014188070 A1

Kleen, M., Korpinen, R., Raitanen, J-E., Willför, S., Cold-refining and pressurized hot water extraction of biomass (CoRefEx) II, U/03/2014

Konkol, Y., Bernoulli, J., Holmbom, B., Vuorikoski, H., Pranovich, A., Halleen, J., Ligneous plant-derived heteropolysaccharides for use in treatment of urologic symptoms and diseases. PCT Int. Appl. WO 2014072585 A1

Sugano Y., Ivaska A., Electro-catalytic degradation of cellulose at Au electrode, U/05/2014

4.6 Awards granted (6)

Bergelin, Mikael, 1st prize in "Best Business Path Competition", awarded by Turku Science Park

Hupa, Mikko, Kanslerspriset (The Chancellor's Prize), research leader of the year, awarded by the Chancellor of Åbo Akademi Jarl-Thure Eriksson

Häärä, Matti, Metso Mechanical pulping award, awarded by Paper Engineers' Association

Kilpiö, Teuvo, Best doctoral thesis in the field of chemical engineering, awarded by The Finnish Society of Chemical Engineers

Privalova, Elena, Annual BUP prize, awarded by the Baltic University Programme 'BUP' international board

Salmi, Tapio, Honorary membership, awarded by Czech Society of Chemical Engineering

5. Other activities 2014

5.1 Organisation of conferences, courses and seminars

March

Helsinki, Finland, AEL INSKO National Seminar “Continuous process analysis” practical applications and possibilities?

April

Helsinki, Finland, National FTIR Symposium

Åbo/Turku, Finland, 23. Keraaminen päivä

May

Orlando, USA, Symposium in Honor of Richard Buck, 225th Meeting of the Electrochemical Society

July

Åbo/Turku, Finland, International Conference on Science and Technology of Synthetic Metals

August

Åbo/Turku, Finland, PCC Annual Meeting

October

Åbo/Turku, Finland, Chemical Engineering at Åbo Akademi University Alumni Day

November

Åbo/Turku, Finland, Wood extractives - friend or foe in industry?

5.2 Participation in conferences, major meetings and courses

Location, Meeting/Organizer, Contribution, Number of PCC participants

January

Amalia Island, FL, USA, Winter Conference on Plasma Spectrochemistry, 1

Copenhagen, Denmark, Visions in Chemistry, The Torkil Holm Symposium, 3

Toulouse, France, Workshop on Food Waste Valorisation, ENCIASET, invited lecturer, *Bjarne Holmbom*

February

Erlangen, Germany, Committee for Glassy and Crystalline Multi-Functional Materials, invited lecturer, *Leena Hupa*

Kirchberg, Austria, International Winterschool on Bioelectronics: Bio-compatible, Bio-integrated, Bio-inspired Materials and Devices, 1

Oulu, Finland, Sustainable Chemistry and Process Technology for the Northern Baltic Region (POKE) workshop, 7

March

Cambridge, UK, Joint meeting of the British and Scandinavian-Nordic Sections of the Combustion Institute, 2

Dallas, TX, United States, 247th ACS National Meeting & Exposition, 3

Espoo, Finland, Finnish Flame Research Committee annual meeting, 1

La Serena, Chile, International Workshop on Ionic Liquids: Melting Temperatures, Other Properties and Applications, 4

Mainz, Polycat EU project meeting, 3

Oslo, Norway, 2nd Nordic Meeting on Organometallic Chemistry, 2

Santiago de Chile, Chile, International Workshop in Algal Biorefinery, 4

Stockholm, Sweden, The 5th Nordic Wood Biorefinery Conference (NWBC), 2

Tucson, USA, 25th biennial meeting Organic Reactions Catalysis Society (ORCS), 5

April

Helsinki, Finland, Kansallinen FTIR symposiumi, 2

Munich, Germany, EU-OnCord kick-off meeting, 1

Ories, Portugal, UCL Vaccine Bioprocess Development and Commercialisation Course, 1

Åbo/Turku, Finland, 23. Keraaminen päivä, 4

Åbo/Turku, Finland, IX Valtakunnallisen kemian opetuksen päivä, invited lecturer, *Leena Hupa*

May

Beijing, China, 68th International Energy Agency - Fluidized Bed Conversion (IEA-FBC) meeting, 1

Beijing, China, 11th International Conference on Fluidized Bed Technology, 1

Espoo, Finland, VTT workshop, Power plant testing and modeling, 3

Orlando, USA, 225th Meeting of the Electrochemical Society, 2

Palermo, Italy, 6th COST ORCA Organocatalysis Meeting, 1

Stockholm, Sweden, Askdagen 2014, 1

St. Petersburg, Russia, Conference on Oil Refining Catalysts and Hydrogenation Processes, *Dmitry Murzin*

Toulouse, France, Graphene 2014, 2

Umeå, Sweden, Sustainable Chemistry and Process Technology for the Northern Baltic Region (POKE) Symposium, 7

June

Budapest, Hungary, 13th International Conference on Microreaction Technology, 2

Budapest, Hungary, 23rd European Symposium on Computer Aided Process Engineering, 2

Djurönäset, Sweden, Analysdagarna 2014, Invited keynote lecturer, *Andrzej Lewenstam*

Gnesta, Sweden, Wallenberg Wood Science Center Workshop, 5

Hakodate, Japan, The International Symposium on High Temperature Oxidation And Corrosion, 1

Helsinki, Finland, Seminar “Luonnontuotteista terveyttä?”, invited lecturer, *Bjarne Holmbom*

Helsinki, Finland, PulPaper 2014, invited lecturer, *Bjarne Holmbom*

IJmuiden, The Netherlands, IFRF Joint committee, 1

Kraków, Poland, Electroanalysis: Theory and Practice, XIII Conference, 1

Sevilla, GPE-4th International Congress on Green Process Engineering, 7

Sienna, Italy, Annual COST CM1102 MultiGlycoNano meeting, 2

Stockholm, Sweden, 22nd Analysdagarna 2014 (Analytical Days 2014), Analytical techniques for biorefineries – Did we solve all challenges in COST Action FP0901?, invited lecturer, *Stefan Willför*

Stavanger, Norway, Nordtek, 1

Seville, Spain, 13th European Workshop on Lignocellulosics and Pulp (EWLP-2014), 5

Tampere, Finland, 2014 International Chemical Recovery Conference, 8

Tampere, Finland, 2014, 50th Anniversary International Recovery Boiler, Conference, invited lecturer, *Mikko Hupa*, 7

Valladolid, Spain, The 10th International Conference on Renewable Resources and Biorefineries, 1

Visegrád, Hungary, Matrafüred 2014, International Conference on Electrochemical Sensors, invited lecturers, *Johan Bobacka*, *Tom Lindfors*, 5

Warsaw, Poland, International Flame Research Foundation Topic Oriented Technical Meeting IFRF TOTeM 41 “Optimisation of OXY/COAL/RFG systems”, 1

July

Louvain-la-Neuve, Belgium, Scientific Bases for the Preparation of Heterogeneous Catalysts (PREPA11), 3

Tallinn, Estonia, EUCHEM 2014 Molten Salts and Ionic Liquids, 1

Åbo/Turku, Finland, International Conference on Science and Technology of Synthetic Metals, 9

August

Larnaca, Cyprus, 6th Young Investigators Workshop of the Organic Division of EuCheMS, 1

Prague, Czech Republic, 21st International Congress of Chemical and Process Engineering (CHISA 2014), 8

Saarenmaa, Estonia, Sustainable Chemistry and Process Technology in the Northern Baltic Sea Region, Summerschool on Saarenmaa, 31

September

Aix-en-Provence, France, 69th International Energy Agency - Fluidized Bed Conversion (IEA-FBC) meeting, 1

Delft, The Netherlands, XXI International Conference on Chemical Reactors (CHEMREACTOR-21), 3

Helsinki, Finland, International Bioenergy Conference on BioEnergy from Forest, 1

Kokkola, Finland, Kokkola Material Week, plenary lecture, *Tapio Salmi*

Lausanne, Switzerland, 65th Annual Meeting of the International Society of Electrochemistry, invited lecturer, *Johan Bobacka*, 5

Montpellier, France, 12th Euro Fed Lipid Congress "Oils, Fats and Lipids: From Lipidomics to Industrial Innovation", 2

Parma, Italy, 12th European Society of Glass (ESG) Conference, 4

Prague, Czech Republic, 22nd Conference on Isoprenoids, 1

Stockholm, Sweden, TAPPI International Research Management Committee Fall 2014 Meeting, 1

St. Petersburg, Russia, Science of the Future, 2

Sydney, Australia, 4th Asia-Pacific Conference on Ionic Liquids and Green Processes / 6th Australasian Symposium on Ionic Liquids, 3

October

Campinas, Brazil, Sao Paulo Advanced School on the Present and Future of Bionenergy, 1

Concepción, Chile, Lignobiotech Conference, 1

Ifrane, Morocco, Nano Micro Biotechnology Conference (NaMiBiTech), invited lecturers, *Tapio Salmi, Jyri-Pekka Mikkola*

Malmö, Sweden, Nanomedicine Workshop, 1

Niagara Falls, Canada, 64th Canadian Chemical Engineering Conference, 1

Rio de Janeiro, Brazil, International Workshop – Brazil and Finland Dialogues on Technological Innovation, 1

Samara, Russia, 2nd Russian Congress on Catalysis, plenary lecture, *Dmitry Murzin*

Sardinia, Italy, 10th European Symposium on Electrochemical Engineering, 1

Snowbird, UT, USA, Impacts of Fuel Quality on Power Production, 3

Tampere, Finland, Soodakattilapäivä 2014, 1

Tianjin, China, 1st International Symposium on Catalytic Science and Technology in Sustainable Energy and Environment, *Dmitry Murzin*

Åbo/Turku, Alumni Day, Department of Chemical Engineering, Åbo Akademi University

November

Frankfurt, Germany, BIO-Europe, 1

Gliwice, Poland, Corrosion 2014, 2

Helsinki, Finland, The 8th CALSIF (Chinese Association of Life Scientists in Finland) annual meeting, 1

December

Brussels, Belgium, Informa Life Sciences: Development and Manufacturing of Vaccines

Gothenburg, Sweden, Wallenberg Wood Science Center Workshop, 7

Lyon, France, 9th International symposium on Catalysis in Multiphase Reactors & 8th International Symposium on Multifunctional Reactors, 4

Porto, Portugal, 12th International Chemical and Biological Engineering, 2

Varberg, Sweden, Chalmers University of Technology course on Hemicelluloses, invited lecturer, *Bjarne Holmbom*

5.3 Visitors and visits

Visitors to the PCC

- Anderez Fernandez, Maria, University of Valladolid, Spain (September-December)
- Balme, Quentin, CPE Lyon, Université de Lyon, France (March-August)
- Bernardini, Andrea, University of Padova, Italy (August-December)
- Berhard, Daniel, TU Dresden, Germany (October)
- Bizzotto, Francesco, University of Padova, Italy (January-August)

- Bober, Patrycja, Institute of Macromolecular Chemistry of the Academy Sciences of the Czech Republic, Czech Republic (January-March)
- Boeva, Zhanna, Lomonosov Moskow State University, Russia (February-June)
- Brückner, Raika, Friedrich-Schiller-University, Germany (October-November)
- Cingano, Marco, University of Padova, Italy (November-December)
- Costa, Mario, Instituto Superior Técnico, Portugal (August)
- Demidova, Yulia, Boreskov Institute of Catalysis, Russia (February)
- Diniz, Nicolas, Federal University of Amazonas, Brazil (September-December)
- Dorofeeva, Elizaveta, Saint-Petersburg Technological Institute, Russia (August)
- Freites, Adriana, Simon Bolivar University, Venezuela (January-August)
- Galetta Paz, Maria Alejandra, University of Republic of Uruguay, Uruguay (October)
- Garcia Serna, Juan, University of Valladolid, Spain (August)
- Gaussiran, Maude, Polytech' Montpellier, France (May-August)
- Gemo, Nicola, University of Padova, Italy (January-December)
- Gestruaud, Cecilia, Bordeaux University, France (May-June)
- Heredia, Shuyana, Universidad Complutense, Spain (November-December)
- Jarvis, Jennifer, University of Memphis, USA (September-December)
- Jenistová, Klára, University of Pardubice, Czech Republic (September-December)
- Kholkina, Ekaterina, Saint Petersburg Technological Institute, Russia (August)
- Kundu, Biswanat, Indian Institute of Glass and Ceramics, India (March)
- Leyton Pachero, Allison, University of Chile, Chile (April-June)
- Li, Bin, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, China (January – May)
- Maduna Valkaj, Karolina, University of Zagreb, Croatia (June-December)
- Malinovski, Alexander, Mendeleev University Chemical Technology, Russia (August)
- McDonagh, Anthony, NUI Galway, Ireland (September-October)
- Novell, Marta, University Rovira in Virgili, Spain (April-June)
- Paiva Mendes, Eduardo, Univ. Federal do Parana, Brazil (January-August)
- Pérez Martínez, Victor, University of Valladolid, Spain (September-December)
- Ravanal, Maria Cristina, University of Chile, Chile (September-October)
- Rujana, Luis, Simon Bolivar University, Venezuela (January-August)
- Sabatier, Fantine, Polytech' Montpellier, France (May-August)

- Sanches, Julio, University of Concepción, Brazil (January-February)
- Sau, Abhijit, Bose Institute, Division of Molecular Medicine, India (September-December)
- Shestopalova, Anna, St. Petersburg State Technological Institute, Russia (August)
- da Silva Antonio, Jadielson Lucas, University of Sao Paulo, Brazil (January-June)
- Sinitcyna, Polina, St. Petersburg State Institute of Technology, Russia (August)
- Sobkowiak, Marek, Poznan University of Technology, Poland (August)
- Stekrova, Martina, Institute of Chemical Technology, Czech Republic (September-December)
- Sterchele, Stefano, University of Padova, Italy (January-December)
- Sugano, Yasuhito, Osaka University, Japan (January-December)
- Suprun, Anastasia, St. Petersburg State Technological Institute, Russia (August)
- Turakova, Maria, Univ. of Bratislava, Slovakia (March-June)
- Yedro, Florencia Micaela, University of Valladolid, Spain (August-September)

Visits by PCC members

- Dax, Daniel, University of Concepción, Chile (June-October)
- Lisak, Grzegorz, Malmö University, Sweden (April-December)
- Liu, Jun, KTH Royal Institute of Technology, Sweden (October)
- Pranovich, Andrey, St. Petersburg Forest Technical University, Russia (April)
- Rahkila, Jani, CIB-CSIC, Madrid, Spain (February-March)
- Salmi, Tapio, University of Valladolid, Spain (June)

5.4 External PhD examinations and reviews

Board Member in evaluation of the candidates to the Chair in Physical Chemistry at Aalto University, Finland, *Ari Ivaska*

Board member of the Glyco Division of the Finnish BioBio Society, *Reko Leino*

Board member of the Graduate School of Environmental Science and Technology (EnSTe), *Leif Kronberg*

Chairman of the Scientific Meetings Committee (SMC) of the International Society of Electrochemistry (ISE), *Johan Bobacka*

Editorial Board Member for Nordic Pulp and Paper Research Journal, Mittuniversitetet, Sweden, *Anna Sundberg*

Editorial Board Member for “Khimiiia rastitel'nogo syr'ia” (Chemistry of plant raw material), *Andrey Pranovich*

Editorial Board Member for Analytical Letters, (Taylor & Francis), *Ari Ivaska*

Editorial Board Member for Journal of Electroanalytical Chemistry (ACS), *Ari Ivaska*

Editorial Board Member for Chemosensors (MDPI), *Johan Bobacka*

Editor of Environmental Science and Pollution Research, *Leif Kronberg*

Evaluator of Dr. Leonid Vradman application for Docentship at Ben Gurion University of the Negev, Israel, *Dmitry Murzin*

Evaluator of Dr. Toni Kinnunen for Docentship at University of Oulu, Finland, *Tapio Salmi*

Evaluator of Jonas Sjöblom for Docentship at Chalmers University of Technology, Sweden, *Päivi Mäki-Arvela*

Evaluator for M-Era-net, Turku, Finland, *Päivi Mäki-Arvela*

Evaluator for EU-Erasmus, Helsinki, Finland, *Päivi Mäki-Arvela*

Evaluator of lecturer track position in Biomass Refining, Aalto University, *Stefan Willför*

Evaluator of docentship of Martin Lawoko at KTH, Sweden, *Stefan Willför*

Evaluator of Academic Lecturer position of Martin Lawoko at KTH, Sweden, *Stefan Willför*

Evaluator of docentship in Polymer chemistry, University of Helsinki, *Reko Leino*

Evaluator of docentship in Organic chemistry, University of Helsinki, *Reko Leino*

Evaluator of docentship in Pharmacy, Åbo Akademi University, *Leif Kronberg*

Evaluator of tenure-track position, University of Groningen, *Tapio Salmi*

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

Evaluation of proposals in the EU 7th Framework Programme, Marie Curie Programme IEF-IIIF-IOF, *Päivi Mäki-Arvela*

- Evaluation of European doctoral degrees, University of Padova, Italy, *Tapio Salmi*
- Evaluation of proposals in the EU H2020 Marie-Sklodowska-Curie Actions-IF-ST-CHE, Brussels, *Päivi Mäki-Arvela*
- Evaluation of research proposals, Qatar National Science Foundation, Qatar, *Ari Ivaska*
- Evaluation of research proposals for the Qatar National Research Fund (QNRF), Qatar, *Johan Bobacka, Reko Leino,*
- Evaluation of research proposal for the Estonian Research Council, *Johan Bobacka*
- Evaluation of proposal for the Research Council of Norway, *Anders Brink*
- Evaluation of associate professorship, Aalborg University, Denmark, *Leena Hupa*
- Evaluation of Technical University of Denmark Chemical Engineering program, Denmark, *Mikko Hupa*
- Evaluation of post doc research funding, Technical University of Denmark, Denmark, *Mikko Hupa*
- Expert for the Portuguese Foundation of Science and Technology, *Tapio Salmi*
- Expert for the Estonian Agency of Science and Technology, *Tapio Salmi*
- Expert for the ACS Petroleum Research Fund, *Dmitry Murzin*
- Expert, Haldor Topsoe PhD scholarship program, Denmark, *Dmitry Murzin*
- Expert evaluator for The Netherlands Organisation for Scientific Research (NWO), *Reko Leino*
- Expert evaluator for the Belgian Fund for Scientific Research (FNRS), *Reko Leino*
- Expert evaluator for the Estonian Research Council, *Leif Kronberg*
- Expert for the Qatar Research Council, *Dmitry Murzin*
- Management Committee member of the EU COST Action CM1102 Multivalent Glycosystems for Nanoscience-MultiGlycoNano, *Reko Leino*
- Management Committee member of the EU COST Action CM0905 Organocatalysis-ORCA, *Reko Leino*

Member of the Expert Group “Vasa Preservation Council”, *Bjarne Holmbom*

Member of the Scientific Advisory Board, UNICRE, Czech Republic, *Dmitry Murzin*

Member of Scientific Committee, CHISA2014, Prague, Czech Republic, *Tapio Salmi*

Member of Scientific Committee, ISCRE2014, Bangkok, Thailand, *Tapio Salmi*

Member of International Program Committee, TU Delft Process Technology, *Tapio Salmi*

Member of Scientific Advisory Board, Czech Academy of Sciences, Institute of Chemical Process Fundamentals, *Tapio Salmi*

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

Member of the Scientific Committee, 15th International Conference on Electroanalysis, *Andrzej Levenstam*

Member of Advisory Committee, 2014 International Chemical Recovery Conference, Finland, *Mikko Hupa*

Mid-term expert evaluator of two FP7-PEOPLE-ITN projects for the EU Research Executive Agency, *Reko Leino*

Reviewer and Rapporteur, Romanian National Research Council, Romania, *Chunlin Xu*

Scientific advisory board member for Wood Sci. Technol, Holzforschung, Cellul Chem Technol, O’Papel, Chemistry of Plant Raw Materials, *Bjarne Holmbom*

Scientific advisory board member for Nordic pulp and Paper Research Journal, Holzforschung, Cellulose Chemistry and Technology, Journal of Wood Chemistry and Technology, *Stefan Willför*

Vice-chair of the H2020-MSCA-ITN panel for the EU Research Executive Agency, *Reko Leino*

External evaluations

Ariyaratne, Hiromi, Telemark University College, Porsgrunn, Norway, opponent, *Mikko Hupa*

Binti Saleh, Suriyati, Technical University of Denmark, Denmark, opponent, *Anders Brink*

Ciftci Aysegul, Eindhoven University of Technology, The Netherlands, opponent, *Dmitry Murzin*

Cuertero, Maria, University of Murcia, Spain, reviewer, *Tom Lindfors*

Del Mar Cortada Mut, Maria, Technical University of Denmark, Denmark, opponent, *Mikko Hupa*

Donoeva, Baira, University of Canterbury, UK, referee of doctoral thesis, *Dmitry Murzin*

Enberg, Sofia, Mid Sweden University, Sweden, examination committee for doctoral thesis, *Anna Sundberg*

Fagerlund-Edfeldt, Amelie, Mid Sweden University, Sweden, opponent, *Holmbom, Bjarne*

Farrell, Mark, The National University of Ireland, Galway, Ireland, external examiner of doctoral thesis (viva voce), *Reko Leino*

Feng, Davei, Aalto University, Finland, opponent, *Daniel Lindberg*

Gabrielson, Erik, Linköping University, Sweden, opponent, *Ari Ivaska*

Hernandez Malo, Rafael, Rovira i Virgili University, Spain, reviewer, *Tom Lindfors*

Huerta, Irene, Univ. Valladolid, Spain, opponent and president of the jury, *Tapio Salmi*

Huovinen, Eero, University of Eastern Finland, Finland, thesis reviewer, *Leena Hupa*

Hörhammer, Hanna, Aalto University, Finland, reviewer, *Andrey Pranovich*

Julcour-Lebique, Carine, ENSIACET, France, opponent and jury member in the habilitation *Tapio Salmi*

Kokko, Lauri, Technical University of Tampere, Finland, opponent, *Mikko Hupa*

Kuitunen, Susanna, Aalto University, Finland, opponent, *Tapio Salmi*

Labafzadeh, Sara Rahim, University of Helsinki, reviewer, *Stefan Willför*

Lambers, Heikki, University of Eastern Finland, Finland, reviewer, *Patrik Yrjas*

Langsch, Robert, Technische Universität Dresden, Germany, opponent, *Tapio Salmi*

Lehto, Joni, University of Jyväskylä, Finland, reviewer, *Andrey Pranovich*

Molegaard Mortensen, Peter, Technical University of Denmark, Denmark, opponent,
Dmitry Murzin

Obradovic, Ana, National Institute of Chemistry, Ljubljana, Slovenia, opponent,
Tapio Salmi

Olsson, Henrik, Uppsala Universitet, Sweden, opponent, *Johan Bobacka*

Shen, Gulou, Luleå University of Technology, Sweden, member of evaluation
committee, *Päivi Mäki-Arvela*

Sjöberg, Erik, Luleå University of Technology, Sweden, member of examination
committee, *Narendra Kumar*

Testova, Lidia, Aalto University, Finland, reviewer, *Stefan Willför*

Zasadowski, Dariusz, Mid Sweden University, Sweden, opponent, *Bjarne Holmbom*

Xie, Yujiao, Luleå University of Technology, Sweden, discussion leader for licentiate
thesis, *Päivi Mäki-Arvela*

Yarulin, Artur, École polytechnique fédérale de Lausanne, Switzerland,
examiner/opponent, *Dmitry Murzin*

Invited Lecturers at PCC

Parvulescu, Vasile, University of Bucharest, Romania

Schouten, Jaap, Technische Universiteit Eindhoven, Netherlands

Maggini, Michele, University of Padova, Italy

Doctoral Theses in Progress 2014 at the PCC

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

- David Agar (Canada, *M*), MSc University of Jyväskylä 2004
- Cesar de Araujo Filho (Brazil, *M*), MSc Federal University of Ceara, Fortaleza, Brazil 2010
- Steliana Aldea (Romania, *F*), MSc University of Bucharest, Bucharest, Romania 2006, BSc *ibid.* 2002
- Jesús Arroyo Condori (Peru, *M*), MSc ÅAU 2011, BSc Universidad Nacional Mayor de San Marcos (UNMSM), Peru 2010
- Erfan Behraveshteh (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
- 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
- Antonina Kupareva, (Russia, *F*) MSc Gubkin Russian State University of Oil and Gas, Moscow Russia 2008
- 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 Krzyszyk (Poland, *F*), MSc University of Gdansk, Poland 2013
- Ron Lai (Canada, *M*), MSc University of British Columbia, Vancouver, Canada 1994
- Ewelina Leino (Poland, *F*), MSc Silesian University of Technology, Gliwice, Poland 2006
- 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

- Konstantin Milakin (Russia, *M*), MSc M.V. Lomonosov Moscow State University, Moscow, Russia 2011
- 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
- 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
- Jadelson Lucas da Silva Antonio (Brazil, *M*), BSc Federal Rural University of Pernambuco, Recife, Brazil 2010
- Vladimir Shumilov (Russia, *M*), MSc ÅA 2014 & Tver State Technical University, Russia 2014 (double degree), BSc Tver State Technical University, Russia 2012
- Jingxin Sui (China, *M*), MSc ÅA 2011, BSc Shandong Institute of Light Industry, China 2009
- Alexandra Torozova (Russia, *F*), MSc Tver State Technical University, Russia 2014
- Nemanja Vucetic (Serbia, *F*), MSc Belgrade University, Serbia 2013
- Hao Wu (China, *F*), MSc ÅA 2007, BSc Shandong Institute of Light Industry, China 2005
- Wenyang Xu (China, *M*), MSc ÅA 2015, BSc Qilu University of Technology, China 2013
- Kai Yu (China, *M*), MSc ÅA 2010, BSc Shandong Polytechnic University, China 2008

Doctoral Students from Finland (incl. Part-time and external students)

- Laura Aalto-Setälä, (Kokemäki, *F*), MSc University of Helsinki 2014
- Leena Björkvik (Vasa, *F*), MSc ÅA 2011
- Elisa Hupa (Åbo, *F*), MSc ÅA 2014
- Petteri Kangas (Villmanstrand, *M*), LicTech Helsinki University of Technology 2009
- Victor Kisonen (Masku, *M*), MSc University of Turku 2005
- Jens Krogell (Mariehamn, *M*), MSc ÅA 2009
- Lucas Lagerquist (Vasa, *M*), MSc ÅA 2011

- Christian Lindfors (Helsingfors, *M*), MSc Helsinki University of Technology 2008
- Otto Långvik (Vanda, *M*), MSc ÅA 2004
- 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
- Jussi Rissanen (Åbo, *M*), MSc University of Turku 2010
- Patrik Runeberg (Borgå, *M*), MSc ÅA 2014
- Risto Savela (Åbo, *M*) MSc University of Turku 2009
- Christoffer Sevonius (Sibbo, *M*), MSc ÅA 2012
- Maria Sundqvist (Pargas, *F*), MSc ÅA 2015
- Ulriika Vanamo (Åbo, *F*), MSc ÅA 2008