

Åbo Akademi Process Chemistry Centre

Annual Report 2010 – 2011

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

Åbo Akademi Process Chemistry Centre (PCC)

The PCC is 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 (lead by Prof. Mikko Hupa)*
- *Wood and Paper Chemistry (Prof. Bjarne Holmbom)*
- *Catalysis and Reaction Engineering (Academy Prof. Tapio Salmi)*
- *Process Analytical Chemistry (Prof. Ari Ivaska)*

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 Industrial Advisory Board (2011): Örjan Andersson (Novia), Ilmo Aronen (Raisio), Stig-Erik Bruun (Chemigate), Håkan Gros (Danisco), Lars Gädda (Forestcluster), Heidi Fagerholm (Kemira), Markku Karlsson (UPM-Kymmene), Bertel Karlstedt (Nordkalk), Nina Kopola (Dynea), Eeva-Liisa Lakomaa (Vaisala), Heikki Laurila (Outotec), Timo Leppä (Chemical Industry Federation of Finland), Lars Peter Lindfors (Neste Oil), Leena Paavilainen (Metla), Ismo Reilama (Metsä-Botnia), Bengt-Johan Skrifvars (Top Analytica), Kenneth Sundberg (Tikkurila), Kari Toivonen (Elomatic) and Petri Vasara (Pöyry).

The PCC Scientific Advisory Board (2011): Professor Douglas Reeve (University of Toronto), Professor Jean-Claude Charpentier (CNRS/ENSIC/INPL, Nancy-Université) and Professor Jiri Janata (Georgia Institute of Science and Technology, Atlanta).

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PCC Annual Report 2010 – 2011

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I. Introduction to the Activities in 2010-2011

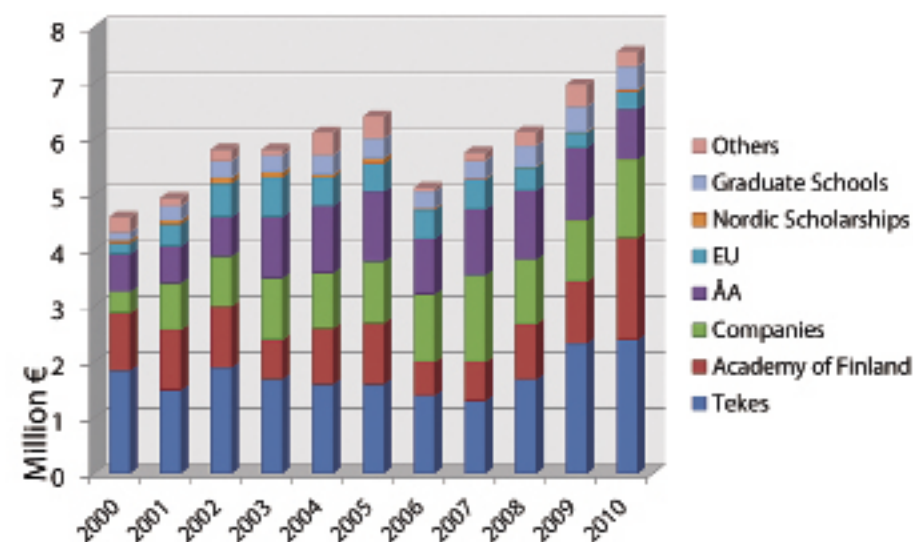
Background

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. The PCC has by the Academy of Finland been granted the status of a Centre of Excellence in research for two consecutive six-year periods: 2000-2005, and 2006-2011, respectively.

The PCC has successively grown in quantity and quality. Today we publish over 120 peer-reviewed journal articles per year in leading journals of chemical engineering and chemistry, the total number of PhD theses finished during the last five years (2006-2010) has been 40. We have been visible in the international scientific arena; taking part in conferences and symposia, organizing major international scientific events, holding positions of trust in scientific journals and organizations, taking part in the scientific discussion in society. We have worldwide scientific collaboration and extensive industrial contacts.

The Year 2010 in Numbers

The year 2010 was our last year as a National Centre of Excellence in research appointed by the Academy of Finland. In 2010 altogether 30 senior researchers and 45 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. Economically, the year 2010 was very good. The overall funding to the activities of the Centre was 7.5 Million €, which was higher than in any previous year since the founding of the Centre.



The funding of the Åbo Akademi Process Chemistry Centre 2000-2010

The table below gives some key numbers of our academic activities in 2010. Our research resulted in altogether 138 papers in scientific publication series with the full referee system, which is the all-time highest number of our Centre! Six doctoral theses and 15 masters' theses were finished.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
Doctoral Theses	5	7	8	2	11	8	8	8	9	7	6
Masters' Theses	21	23	27	26	17	15	20	23	19	17	15
Journal Articles	60	70	94	77	106	109	113	116	101	118	138
Other Publications	105	86	96	86	111	148	157	169	195	204	191

Theses and other publications by the Åbo Akademi Process Chemistry Centre 2000–2010

Besides the technical publications we again published two Newsletters. Our researchers also wrote popular texts in daily newspapers and journals and appeared on several radio and TV programs in the year 2010.

Organizing International Conferences

In the last ten months our Centre has been hosting three major international conferences.

In August 30 – September 3, 2010 we organized the conference *"Impacts of Fuel Quality on Power Production and Environment"*. The conference was held at the Hotel Riekonlinna in Saariselkä, Finland. This conference focuses on the research on fuel properties and their influence on their use in large scale industrial combustion power plants. Altogether 85 participants from 13 countries participated at the conference, which consisted of four keynote lectures and 46 oral presentations plus a number of posters. The conference coordinator was Maria Zevenhoven and conference chairman was Mikko Hupa.

The 9th Spring Meeting of the International Society of Electrochemistry was held at the Mauno Koivisto Centre in BioCity, Turku, Finland, from May 8 to May 11, 2011. The theme of the meeting was *"Electrochemical Sensors: From Nanoscale Engineering to Industrial Applications"*. The meeting attracted 223 participants from 35 countries. The program included four keynote lectures, 12 invited lectures, 58 oral presentations, more than 100 posters and an instrument exhibition. This conference was held in Finland for the first time. The conference chairman was Johan Bobacka.

The international joint conference *"Catalysis in Multiphase Reactors and International*



Conference participants gathering after the 9th ISE Spring Meeting Closing Session

Symposium on Multifunctional Reactors (CAMURE 8 & ISMR 7)" took place in Naantali, May 22-25, 2011 at the Naantali Spa Hotel, where over 160 leading experts from different parts of the world gathered to discuss the principles of multiphase operation and multifunctionality of chemical reactors.

The topics of the conference were very current. We are facing an enormous transition, a shift from fossil feedstocks to molecules from biomass in the production of chemicals and fuel components. To meet this challenge, chemical engineering and particularly chemical reaction engineering is urgently needed. The conference consisted of five plenary lectures, 52 oral presentations and 75 posters. The oral and poster presentations covered all aspects from catalyst preparation for multiphase system to CFD calculations of new reactor systems. The award for the best poster presentation was given to Sabine Schwidder (Brandenburg) for the development of an interactive simulation program for trickle bed reactors.

CAMURE 8 & ISMR 7 Conference, Naantali



Recent Awards and Recognitions

Again, our researchers have been granted a number of awards and prizes.

Anna Sundberg was awarded the Åbo Akademi Prize for outstanding teaching achievements, the Harry Elving Prize in 2010.

Pasi Virtanen received the Finnish Catalysis Society Prize for the best doctoral thesis in 2010. The title of Pasi's thesis is "Supported ionic liquid catalysts (SILCA) for preparation of fine chemicals".

Olatunde Jogunola received the Award for Best Annual Report and Presentation 2010, at the annual meeting of the national Graduate School in Chemical Engineering (GSCE) in November 12-13, 2010 in Lappeenranta. His presentation was entitled "Carbonylation of Methanol/Hydrolysis of Alkyl Formate".

Two of our papers presented at the 2010 International Chemical Recovery Conference in Williamsburg, Virginia (U.S.) were selected as best papers of their respective topic areas:

Brink, A., Laurén, T., Hupa, M., Koschack, R., Mueller, C., In-furnace temperature and heat flux mapping in a Kraft recovery boiler

DeMartini N., Monedero E., Yrjas P., Hupa M., Co-firing black liquor and biomass in a laboratory single droplet reactor – effects on emissions and combustion characteristics

Juho Lehmusto received the Prize of the Best Conference Paper at the international conference Impacts of Fuel Quality on Power Production and Environment, August 30 – September 3, 2010, in Saariselkä, Finland. Juho's paper was co-authored by Patrik Yrjas, Bengt-Johan Skrifvars, and Mikko Hupa. The title was "Effect of potassium chloride and potassium carbonate on the high temperature corrosion of pure Cr and 304L".

Juho Lehmusto receives the Prize for the Best Conference Paper from the chairman of the Prize Committee, Professor Terry Wall



Finally, The Finnish Society of Science and Letters gave the Magnus Ehrnrooth Prize to Academy Professor Tapio Salmi for his achievements in the research of reaction mechanisms and kinetics of several organic reaction systems. The work has led to numerous articles in top-level scientific journals, to several patents and industrial process improvements. The prize is given at three-year intervals to a researcher in chemistry. The Prize was given during the Finnish Annual Chemistry Days, March 22-24, 2011 in Helsinki.

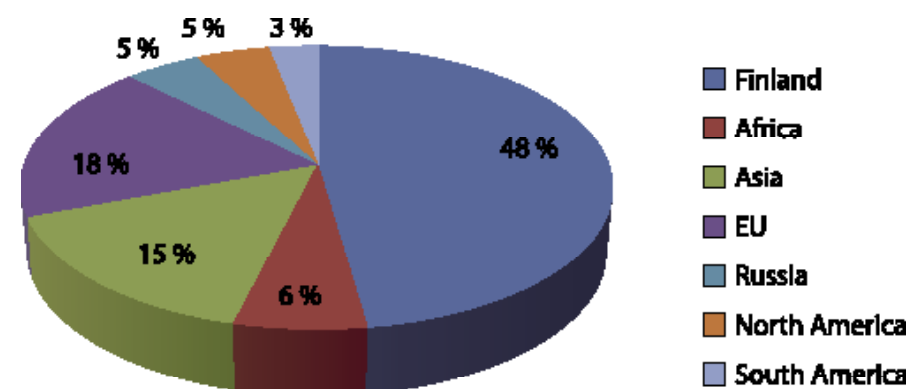
Doctoral Students

A central part of our research activities is done as doctoral theses works. Altogether about 50 PhD thesis projects are actively underway at the Centre. Our doctoral students are very international (see the graph below). More detailed information of the background of our PhD students is given in the Appendix 1 on page 168 of this Annual Report.

At the moment, 38 % of the PCC doctoral students are female.

Many of the PhD works are done with support from the national graduate schools. Currently the PCC is responsible for the coordination of the national Graduate School in Chemical Engineering (GSCE). The GSCE consists of altogether 26 participating laboratories at four universities: Aalto University School of Chemical Technology, Lappeenranta University of Technology, the University of Oulu and Åbo Akademi. In 2010 42 students were participating in the activities of the GSCE, 15 of them from our Centre. We recently received the delightful news from the Academy of Finland that the GSCE was granted continued funding for the next four-year period 2012-2015. Our Centre continues to be the host of the coordination office of this Graduate School.

In 2010 the PCC PhD students further participated in the graduate schools of Materials Research (GSMR), Pulp and Paper Science and Technology (PaPSaT), Chemical Sensors and Micro Analytical Systems (CHEMSEM), Environmental Science and Technology (EnSTe), Nanoscience (NGS-NANO), Biomaterial Graduate School (BGS), and the Graduate School for Biomass Refining (BIOREGS).



Nationality of the PhD students at PCC 2010-2011. For more detailed information see Appendix 1 on page 168

The Nordic Graduate School in Biofuel Science and Technology was part of the Nordic Energy Research activities funded by the Nordic Council of Ministers. This school was a collaborative effort by Chalmers University of Technology, the Technical University of Denmark, the Norwegian University of Science and Technology and Åbo Akademi University. The PCC acted as the coordinator for this collaborative School. The School had funding for the four-year period 2007-2010 and we are now looking for other funding opportunities to be able to continue with this kind of a very fruitful Nordic collaboration.

Bioraff

The overall title of our research program for the years 2006-2011 is “Sustainable Chemistry in Production of Pulp and Paper, Fuels and Energy, and Functional Materials”. This plan divides our research in nine research areas. In this Annual Report all our research activities are now divided into these nine research areas.

There is a great interest towards process concepts which make use of the biomass raw material in an optimum way in the production of pulp and paper, specialty chemicals of various kind, biomass derived fuels and energy. Research topics connected to these concepts, which nowadays are often referred to by the term biorefinery, have already long been in the focus of our Centre.

Our most important project in this area has the title Chemistry in Forest Biorefineries, “Bioraff”. In this project we address a number of aspects in such concepts using tree based feed stocks, forest biorefineries. This project in which we collaborate with several outside groups is the largest PCC project under way and funded by Tekes and ten industrial companies. The 2011 will be the last year of the Bioraff project. The project is co-ordinated by Professor Markku Auer and all four groups of the PCC actively participate in the project (see description on page 54).

Boards and Task Forces

The PCC is led by an executive board consisting of the four research group leaders, Professors Bjarne Holmbom, Mikko Hupa, Ari Ivaska and Academy Professor Tapio Salmi. Maria Ljung works with the coordination of the PCC and functions as secretary to the board. In 2010 the board met 15 times.

The board was supported by a Scientific Advisory Board (SAB) appointed by the Academy of Finland and an Industrial Advisory Board. In 2010 our Scientific Advisory Board consisted of the Professors Douglas Reeve from the University of Toronto, Jean-Claude Charpentier from CNRS/ENSIC/INPL in Nancy and Jiri Janata from the Georgia Institute of Science and Technology in Atlanta. In addition, Professor Heikki Tenhu from the University of Helsinki represented the Academy of Finland and Jukka Leppälähti represented Tekes, the Finnish Funding Agency for Technology and Innovation in this Board.

In 2010 the Scientific Advisory Board visited the Centre in August in connection with the Annual Seminar of the Centre (August 19–20, 2010).

Our Industrial Advisory Board (IAB) consists of representatives of the key industrial companies co-operating with the Centre. The members of the IAB are listed in Chapter 2 in this Annual Report.

In 2010 the PCC had 11 lectures in its Distinguished Lecturer Series:

- December 8, 2010: Assoc. Prof. Harry Brumer, Division of Glycoscience, School of Biotechnology, Royal Institute of Technology (KTH), Stockholm, Sweden: “Polysaccharide Functionalization: XG and Beyond”
- December 2, 2010: Prof. Dage Sundholm, Department of Chemistry, University of Helsinki, Helsinki, Finland: “Magnetically Induced Current Densities in Molecules”
- November 26, 2010: Prof. John Villadsen, Technical University of Denmark, Lyngby, Denmark: “Bio-reaction Engineering - A Multidisciplinary Research Field”
- October 6, 2010: Prof. Adam Pron, Laboratoire d'Electronique Moléculaire Organique et Hybride, CEA Grenoble, Grenoble, France: “Organic and Hybrid (Organic/Inorganic) Electronics - A Chemist Approach”
- September 10, 2010: Prof. Tadashi Kokubo, Chubu University, Japan: “Preparation of Novel Bioactive Ti-based Metals by Simple Chemical and Heat Treatment”
- August 18, 2010: Prof. Andrzej Stankiewicz, Delft Research Center for Sustainable Industrial Processes, Delft University of Technology, the Netherlands: “Perfect Chemical Reactors: Towards Full Control of Chemical Transformations at Molecular Level”
- June 17, 2010: Prof. James W. Frederick, Golden, CO, USA: “Integrated Biorefineries”
- June 3, 2010: Prof. Galip Akay, Newcastle University, Newcastle upon Tyne, UK: “Agro-, Bio-, Chemical- and Energy Conversion - Process Intensifications and their applications in Intensified Integrated Plants and Engineered Ecosystems”
- April 23, 2010: Prof. Miron Landau, Ben-Gurion University of the Negev, Beer-Sheva, Israel: “Grain Boundaries in Nanocrystals Assembled of Mesoporous Materials as an Available Source of Catalytic Active Sites”
- March 26, 2010: Prof. Rüdiger Lange, Technische Universität Dresden, Germany: “Process Intensification of Three-Phase Fixed Bed Reactors”
- March 18, 2010: Prof. Takashi Kakiuchi, Kyoto University, Japan: “Interfacial Chemistry of Ionic Liquids”

Annual Seminar 2011

This report will be published at the annual seminar of the PCC held in August 26-27, 2011 at the ICT House in Turku. This time the seminar will have the theme “Molecular Process Technology” and besides presentations by our own researchers we will also have our Scientific Advisory Board colleagues giving keynote presentations. The seminar will end with an opera evening at the Turku Castle. We will see the première of the new opera “Henrik och Häxhammaren” (Henrik and the Hammer of Witches) composed by Ulf Långbacka (libretto: Dan Henriksson).

Acknowledgements

This annual report gives an overview of the recent activities at the Centre. The report has a complete list of the journal articles, theses and other publications produced by the Centre in the calendar year 2010. 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 Maria Ljung, Anders Brink, Rose-Marie Latonen, Päivi Mäki-Arvela and Anna Sundberg. The layout was done by Paul Söderholm.

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

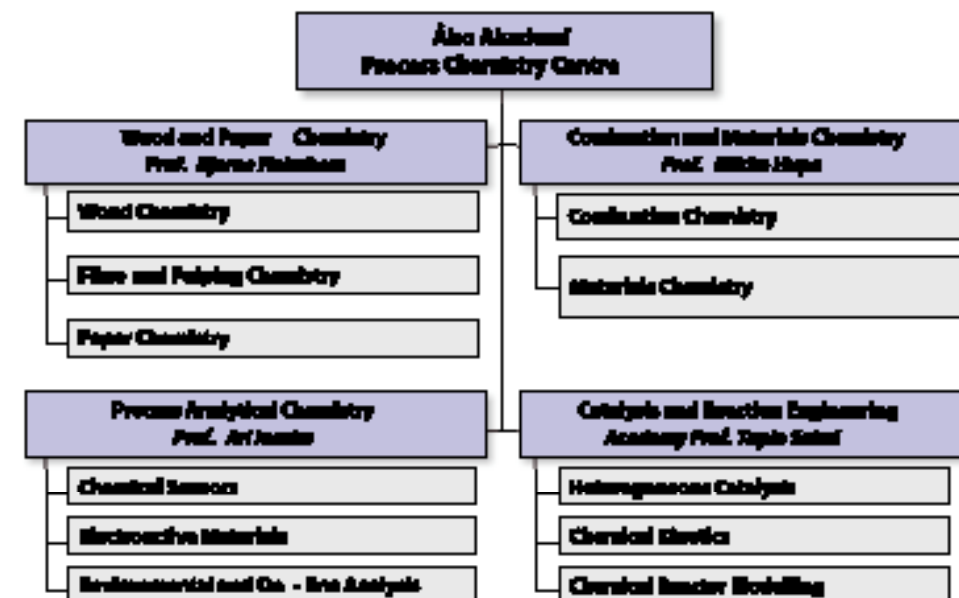
On behalf of the Board of the Åbo Akademi Process Chemistry Centre,

Mikko Hupa

Chairman

2. Organization and personnel

2.1 Organization



Åbo Akademi Process Chemistry Centre Organization

Executive Board

- Prof. Bjarne Holmbom
- Prof. Mikko Hupa (Chairman)
- Prof. Ari Ivaska
- Academy Prof. Tapio Salmi

- Coordination: Maria Ljung

Scientific Advisory Board

- Jean-Claude Charpentier, France
- Jiri Janata, USA
- Douglas Reeve, Canada

Industrial Advisory Board

- Örjan Andersson, Novia
- Ilmo Aronen, Raisio
- Stig-Erik Bruun, Chemigate
- Håkan Gros, Danisco
- Lars Gädda, Forestcluster
- Heidi Fagerholm, Kemira
- Markku Karlsson, UPM-Kymmene
- Bertel Karlstedt, Nordkalk
- Nina Kopola, Dynea
- Eeva-Liisa Lakomaa, Vaisala
- Heikki Laurila, Outotec
- Timo Leppä, Chemical Industry Federation of Finland
- Lars Peter Lindfors, Neste Oil
- Leena Paavilainen, Metla
- Ismo Reilama, Metsä-Botnia
- Bengt-Johan Skrifvars, Top Analytica
- Kenneth Sundberg, Tikkurila
- Kari Toivonen, Elomatic
- Petri Vasara, Pöyry



Åbo Akademi Process Chemistry Centre 2011

<http://www.abo.fi/institut/pcc/>

2.2 Wood and Paper Chemistry

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 biochemicals, novel biomaterials, 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 at the end. For example, selective extraction and recovery of hemicelluloses, lignin or polyphenols from wood, bark, or process waters is followed by functionalization and utilization in different end-uses. Remaining wood substances can then further be recovered or utilized as energy.

External research support during 2010 was obtained mainly from the Academy of Finland, Tekes, EU, and the industry.

The following new projects started during 2010:

- Refining lignocellulosics to advanced polymers and fibers (Nordforsk researcher network)
- Agro biomass by-products to multifunctional ingredients, chemicals and fillers (AgroBio)
- Design of hemicellulose block copolymers and their applications

In June 2011, the following projects were started:

- Future Biorefinery (FuBio) Joint Research 2

We have a close cooperation with Metla, the Finnish Forest Research Institute, 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 have chaired, coordinated, and acted as Grant Holders for the EU-supported COST Action FP0901, "Analytical methods for Biorefineries, 2009-2013". This Action currently has participants from 27 COST and 4 non-COST countries. We are active partners in the EPNOE network, "European Polysaccharide Network of Excellence" and are in the means of establishing more intensive cooperation with KTH in Sweden.

Personnel

<i>Professors</i>	Stefan Willför Bjarne Holmbom (Emeritus) Markku Auer (Visiting)
<i>Docents</i>	Patrik Eklund (Organic Chemistry)

	Andrey Pranovich Annika Smeds Anna Sundberg Robin Manelius Lari Vähäsalo
<i>Senior researchers</i>	Sylwia Bialczak Daniel Dax Jarl Hemming Matti Häärä Victor Kisonen Risto Korpinen Jens Krogell Ann-Sofie Leppänen Hanna Lindqvist Linda Nisula Sebastian von Schoultz Tao Song Anders Strand Ivan Sumerskiy Elena Tokareva
<i>Researchers</i>	Markku Reunanen Technician Leif Österholm
<i>Senior Technician</i>	Agneta Hermansson
<i>Secretary</i>	

<http://www.abo.fi/student/Content/Topic/topic/traochpapperskemi/?setlanguage=en>

2.3 Combustion and Materials Chemistry

Completely new techniques are being developed for cleaner and more efficient combustion. "Alternative" and "Non-Fossil" fuels, such as biomasses and various wastes or waste-derived fuels, are heavily entering the scene everywhere, especially in Europe. A large part of our Combustion and Materials Chemistry research activities is connected to the development of cleaner and more efficient combustion technologies using "difficult" fuels. Our recent work has dealt with the development and application of laboratory methods and modelling tools for prediction of the detailed behaviour of combustion processes for various biomasses and wastes.

The tools have been tested in a number of measurement and sampling campaigns in full-scale combustion processes in many locations in Europe. These tools were used to assist the equipment manufacturing companies in their work to design novel combustion devices. In 2010 a major sampling campaign was made in two power plants in India. These plants were using local brown-coal, lignite, which was shown to have several very characteristic properties.

In 2010 we were also interested in gasification of low grade biomasses or wastes. Several

chemical aspects of the gasification process have been of interest.

Our project consortium Chemistry in Biofuel Combustion (ChemCom), 2008-2010, combines most of our combustion research activities into one coordinated large project. It is supported by Tekes and a consortium of international industrial companies: Andritz, Foster Wheeler Energia, Metso Power, Metsä-Botnia, UPM, Clyde Bergemann and International Paper. This big project was successfully finished and reported at the end of the year 2010.

A completely new project has been planned together with the same companies and it was just about to start before the summer 2011. This three year project has been named Future Fuels for Sustainable Energy Conversion, FUSEC, and it will form the basis of our more long-term research in fuel conversion for the next three years 2011-2014.

A new three-year European Collaboration in the area of biomass fuels started 2010. We participate in this ERA-NET project together with the Technical Universities in Lyngby (Denmark), Graz (Austria) and Trondheim (Norway). This project focuses on advanced fuel characterization and its application in furnace modelling.

The year 2010 was the last one for the Nordic Graduate School in Biofuel Science and Technology. This graduate school was funded by the Nordic Energy Research Program and it became an important platform to our long-term collaboration in the area of bio-fuel research with Chalmers University of Technology in Sweden, with the Technical University of Denmark and the Norwegian University of Science and Technology. We are now looking for new funding opportunities to this very fruitful way of Nordic collaboration.

We are also responsible for the coordination of the national Graduate School in Chemical Engineering (GSCE). The GSCE consists of altogether 26 participating laboratories at four universities: Aalto University School of Chemical Technology and Lappeenranta University of Technology, the University of Oulu and Åbo Akademi University. The GSCE was recently granted a continuation for the years 2012-2015.

Another part of our on-going activities dealt with high-temperature inorganic materials of interest to various applications. In 2010 we continued our studies on bioactive glasses with optimized properties. We studied novel glazes which are easier to keep clean. We have several major projects on various aspects of the very essential problem of corrosion of steam tubes in boilers fired with biomass or waste derived fuels. We study corrosion mechanisms of various metal chlorides; we also study corrosion of alkali bromides and fluorides.

Recently these studies were expanded to include high temperature corrosion of ceramic materials as well. For the ceramic materials also erosion has become a recent new topic of research.

In 2010 we further worked with several projects connected to the development of fuel

cell electrodes. We are making tests of electrode catalysts as well as applicability tests for other fuel cell electrode materials using our in-house measurement techniques. We also participate in a national project activity to study so called supercapacitors. These, also called ultracapacitors or electrochemical double layer capacitors can be used as energy storage, and are from a performance or energy density viewpoint situated somewhere between traditional capacitors and batteries.

Personnel

Professor

Mikko Hupa

Docents

Rainer Backman

Edgardo Coda Zabetta

Kaj Fröberg

Leena Hupa

Christian Mueller

Bengt-Johan Skrifvars

Heimo Ylänen

Senior researchers

Mikael Bergelin

Anders Brink

Nikolai DeMartini

Markus Engblom

Daniel Lindberg

Jonathan Massera

Pia Sjöberg-Eerola

Johan Werkelin

Mizhang Xiao

Patrik Yrjas

Maria Zevenhoven

Di Zhang

Doctoral students

Dorota Bankiewicz

& researchers

Jan-Erik Eriksson

Susanne Fagerlund

Stig-Göran Huldén

Max Johansson

Oskar Karlström

Tooran Khazraie

Tor Laurén

Juho Lehmusto

Bingzhi Li

Na Li

Isak Lindén

Johan Lindholm

Sam Myllynen

Minna Piispanen

Patrycja Piotrowska

Linus Silvander

	Berndt Södergård
	Emil Vainio
	Xiaoju Wang
	Hao Wu
<i>Technicians</i>	Niklas Vähä-Savo
	Peter Backman
	Luis Bezerra
	Piia Leppäsalo
<i>Secretarial staff</i>	Jaana Paananen
	Eva Harjunoski
	Mia Mäkinen
<i>Coordination</i>	Maria Ljung
<i>Computer support</i>	Peter Ekholm

Links:

<https://www.abo.fi/student/en/ook>

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

2.4 Catalysis and Reaction Engineering

The main goal of the research is to develop green process technology based on molecular principles. In the shift to the use of renewable sources for the production of chemicals and fuel components, catalysis and chemical reaction engineering play a central role. Our know-how is continuously developed on catalyst preparation, characterization and screening. New catalytic systems have been taken in use, particularly micro- and mesoporous materials as well as supported nanogold catalysts, which are developed in collaboration with University of Helsinki (the group of Academy Professor M. Leskelä). A new concept for the production of biofuels through catalytic decarboxylation has been patented abroad and extensive work was performed on the leaching of hemicelluloses from wood. Supported Ionic Liquid Catalysts (SILCA) have been used for transformation of fine chemicals – the catalytic effect is based on immobilized metal nanoparticles. New molecules originating from biomass are under investigation. Research collaboration in the catalyst characterization is very intensive with University of Turku and University of Oulu.

Detailed kinetic studies were carried out in many applications, particularly in the hydrolysis and hydrolytic hydrogenation of hemicelluloses as well as hydrogenation and oxidation of mono- and disaccharides, preparation of percarboxylic acids, isomerisation and esterification reactions, enantioselective hydrogenation and cleaning of exhaust gas originating from biofuels. Reaction mechanisms based on first principles, i.e. quantum chemical calculations, have been revealed. Adsorption states and adsorption stoichiometry on solid metal surfaces has been studied extensively by quantum-chemical and conventional kinetic modelling. The complex interaction of reaction and diffusion in porous media was studied experimentally and with sophisticated simulations including

particle-size distributions. The concept was applied to catalytic two- and three-phase systems as well as reactions of solids with liquids. New computational tools were taken in use in the simulation of kinetics, diffusion and flow pattern.

A lot of effort is devoted to the development of continuous reactor technology: we have constructed several continuous reactors, the star among them being the parallel screening tube reactor system equipped with GC-MS analysis (financed by Academy of Finland). Microwave and ultrasound equipment were 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). A new 4-year research project on multiscale modelling of chemical processes was started. New kinds of structured catalysts were taken in use, such as solid foams, which are developed together with the group in Combustion and Materials Chemistry (PCC) foreign partners. The development of green process technology is advanced in many fields, particularly in the development of new continuous processes for biofuels and chemicals. Heterogeneous catalysts can replace homogeneous ones and a clean and continuous technology can replace the old concept,

we demonstrate in the synthesis of peracetic and perpropionic acid. One-pot synthesis, which combines heterogeneous catalyst and an enzyme in a single reactor unit, is an area for which intensive research work is going on and the expectations are high. Micro- and millireactors provide a technology jump; we use them for catalyst development, kinetic screening and continuous production of chemicals in gas and liquid phase. One of the breakthroughs of the year was the publication of an extensive book in reaction engineering: Chemical reaction engineering and reactor technology by T. Salmi, J. Wärnä and J-P. Mikkola.



Personnel

Professors

Tapio Salmi (Academy Professor)

Dmitry Murzin

Johan Wärnä

Jyri-Pekka Mikkola (together with Umeå University)

Docents

Kalle Arve

Narendra Kumar

Päivi Mäki-Arvela

Kari Eränen

Senior researchers

Atte Aho

Andreas Bernas

Heidi Bernas

Pierdomenico Biasi

Henrik Grénman

Jan Hájek

José Rafael Hernández Carucci

*Doctoral students
& researchers*

Olatunde Jogunola
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<http://www.abo.fi/student/tekniskkemi>

2.5 Process Analytical Chemistry

Process Analytical Chemistry is a scientific discipline in the crossroad of Chemistry and Chemical Engineering. In-line and on-line analysis with chemical sensors will play a crucial role in the near future in many areas of modern industry both in production and monitoring processes and monitoring the environment. Process Analytical Chemistry comprises analytical determinations in industrial and environmental processes and, as a scientific discipline; it develops and provides the tools for these determinations.

The main targets and challenges of analytical chemistry, and process analytical chemistry

in particular, is the development of robust and automatic analytical systems that can be used in process and environmental applications. Computer controlled instrumentation can collect a vast amount data even from simple measurements and sophisticated mathematical methods and algorithms are used to extract the relevant information from the acquired data and to group the analytical results in specific patterns. Determination of low concentrations is an everlasting challenge but the demand for accurate determinations at high concentration levels and in complex industrial sample matrices is as important in many processes. Speciation of elements in a particular sample is becoming more important as well as the spatial distribution of elements in solid samples. Modern instrumental methods also allow determination of isotope ratios of elements in samples and add a new dimension to the analytical information available today.

Research on new organic electroactive materials comprising carbon nanotubes, fullerenes and conducting polymers is continued. Organic electroactive thin films with specific redox behavior are of special interest. The charge transfer mechanism in these materials is particularly relevant for construction of electronic devices. Application of in situ spectroelectrochemical techniques such as UV-vis, Raman and FTIR spectroscopy in studying solid state properties of electroactive material (molecular and polymeric) is an important area of research for future use of electroactive materials in solar cell technology, transistors and sensors.

Chemical sensors can be applied to process and environmental analysis where they are used as in-line and on-line devices for monitoring purposes. They have also applications in many other areas of the human activity. The major problem in process control in chemical, pharmaceutical, biotechnological and pulp and paper industry is the total dependency of the control system on the information it receives from sensors. Control and process engineers have developed advanced data collection and control systems that mainly rely on measurement of physical parameters such as temperature, flow rate and pressure. The analytical methods used to receive continuous chemical information from industrial processes and of the state of the environment are still rather primitive or even non-existing. Another field where fast and reliable analysis is required is life sciences and clinical chemistry in particular.

Personnel

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Carita Kvarnström
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3. Research

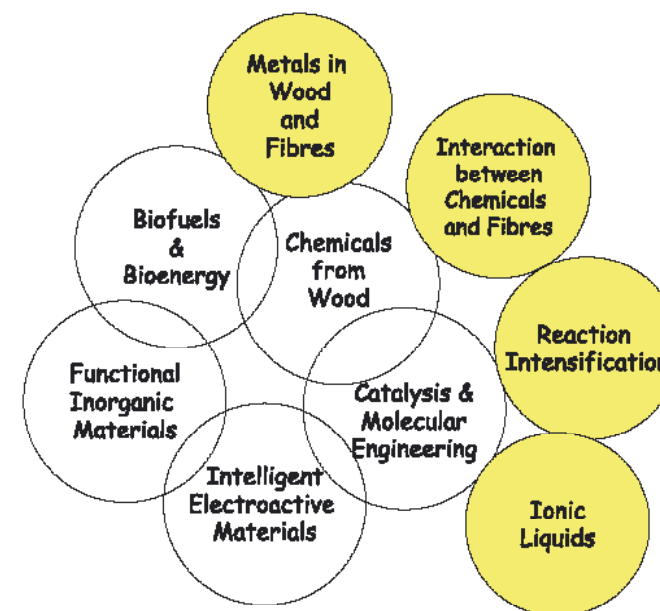
The starting points to the common research plan of the Centre for the period 2006–2011 are outlined below.

A general long-term trend in the industrial production is the move towards renewable and natural raw materials. Chemistry and chemical technology is going to change its direction towards long-term sustainability, implying:

- using renewable raw materials instead of fossil resources (mainly oil)
- producing natural, biocompatible materials and chemicals, thus replacing synthetic, artificial ones
- understanding “nature’s wisdom” in chemistry, thus recognizing and utilizing chemical solutions and mechanisms that have developed during millions of years of evolution

This approach can lead to “truly green” chemistry and chemical technology in harmony with nature, yet fulfilling urgent needs of mankind. In this development, deep understanding of the detailed chemistry – “Molecular Process Technology” – will be of crucial importance. A large part of our research will be connected to this trend.

There is an increased interest towards process concepts that make use of the biomass raw material in an optimum way in the production of pulp and paper, specialty chemicals of various kind, biomass derived fuels and energy. These concepts are today referred to by the term biorefinery. Our research will be associated with a variety of aspects in such concepts using tree based feed stocks, forest biorefineries.



ÅA-PCC Research Areas 2006–2011

The overall title of our research program for the years 2006–2011 is “Sustainable Chemistry in Production of Pulp and Paper, Fuels and Energy, and Functional Materials”.

It consists of nine research areas as shown in the figure below. The four research topics inside the yellow circles represent our new openings and new research areas. These areas bring in new questions, methodology or applications. They are also selected to take full benefit of the combined competence of our four research groups. In these activities, researchers from all groups are participating. The other five topics continue the most successful on-going long-term research activities in our Centre.

The basis of our work is naturally our special competence and our scientific tool-box, which we have developed during the course of many years. This tool-box consists of unique analytical capabilities, other experimental laboratory techniques, advanced chemical engineering models and a good understanding of the technical state and challenges of modern industrial processes. It also contains a long and successful experience in researcher training and fluent national and international networks.

In this Annual Report all our on-going research projects have been divided into these nine research areas. The four newer areas are presented first, followed by the already established research areas.

3.1 Ionic Liquids

Even though some ionic liquids were discovered in early 1900's, the area has made its real breakthrough in recent years, due to the discovery of room-temperature ionic liquids. Ionic liquids (ILs) have emerged as a novel class of materials and neoteric solvents that are applied in many fields such as solvents for electrochemistry and organic synthesis, as materials for recovery of metals from aqueous solution, synthesis of nano-structured materials and sequestration of carbon dioxide, to entrapment and activation of enzymatic and metal species for catalytic applications. The vast number of anticipated possibilities to form various ionic liquids, at least a million or even 10¹⁸, gives the possibilities almost beyond our imagination, enabling task-specific configurations for different technology disciplines.

Room temperature ionic liquids have unique characteristics, such as an extremely wide liquidus range; they display unusual dissolution properties. Room temperature ILs are associated with very low vapour pressures and non-flammability and they have a large electrochemical potential window.

Our research at PCC involving ionic liquids concentrates on the following themes:

- Synthesis, development and characterization of novel, ionic liquid analogues
- Catalysis by supported ionic liquids (SILCA)
- Biorefining and fractionation of lignocellulose in ionic liquids
- CO₂-capture, activation and utilization for chemicals and fuels in ILs
- Biogas purification with ILs
- Cascade catalysis in terms of combined enzymatic and metal catalysis supported in ionic liquids
- Bio-transformations in ionic liquids
- Electrochemical studies and applications of ionic liquids

Several papers and conference presentations have emerged in various scientific journals and meetings. Active research collaboration is going on with a number of research communities, such as Moscow State University (the group of Prof. Leonid Kustov).

The main achievements have been obtained in two fields: preparation and use of supported ionic liquid catalysts (SILCA). The pores of the support material are filled with a thin ionic liquid layer, where e.g. an organometallic complex or an enzyme is solvated. Upon need, with further treatments, the organometallic species is decomposed and reduced, and we obtain, for instance, palladium nanoparticles. It turned out that this kind of novel heterogeneous catalyst is efficient in the reduction of carbonyl groups, as demonstrated by selective catalytic hydrogenation of citral and cinnamaldehyde. In our recent activities, we also found out that even an addition of a homogeneous modifier (e.g. Lewis/Brönsted acids or bases), the catalytic properties can be further fine-tuned. The potential of SILCAs is huge, since they open a way to heterogenize homogeneous catalysts thus providing the benefits of both homogeneous catalysis (high activity and high selectivity) and heterogeneous catalysis (easily separable catalysts).

The studies of cellulose derivatives have been focused on two reactions: carboxyalkylation and acetylation of cellulose. In addition, a lot of product characterization methods for the substituted products have been developed. The experiments with cellulose substitution were successful and they can in future lead to considerable process intensification, since the reactions of cellulose can be carried out as homogeneous reactions in the absence of volatile and poisonous solvents (see section Reaction intensification).

Fractionation and biorefining of lignocellulose is one of the areas where a lot of activities are on-going throughout the world. At the PCC we have recently developed an entire new family of 'switchable' ionic liquids capable of selective removal of hemicelluloses, lignin and extractives from wood. These techniques enable separation of pure cellulose to be used for other applications from industrial size chips.

For some time now, we have also been involved in the development of new technologies to replace classical alkanol-amine water solutions for CO₂ capture. Our focus in this area is two-fold: to develop techniques more suitable for small-scale installations (particularly biogas plants) by taking advantage of novel ionic liquid formulations.

SILCA and Ionic Liquids as Reaction Media

Main funding: Academy of Finland

Jyri-Pekka Mikkola, Pasi Virtanen, Hannu Karhu, Sari Hyvärinen, Elena Privalova, Ikenna Anugwom, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

The work is focused on supported ionic liquid catalysts (SILCA) and the use of ionic liquids as reaction media. Several new ionic liquids have been prepared and characterized. The project is focused on the use of ionic liquids in catalyst supports; we have successfully demonstrated that ionic liquids can be used to heterogenize homogeneous catalysts. Kinetic studies have been carried out for hydrogenation of fine chemicals, such as citral and cinnamaldehyde on SILCA. An extensive study of the physical properties of selected ionic liquids has been continued and kinetic modelling of hydrogenation processes on SILCA has been advanced. In 2009, Pasi Virtanen defended his doctoral thesis on SILCA. The thesis received the award of the Finnish Catalysis Society as the best doctoral thesis in catalysis in years 2007–2009.

Cooperation:

Zelinsky Institute of Organic Chemistry, Moscow, Russia; Moscow State University, Moscow, Russia; University of Jyväskylä, Jyväskylä, Finland

Publications:

- Hara, P., Mikkola, J.P., Murzin, D.Yu., Kanerva, L.T., Supported ionic liquids in Burkholderia ceracia lipase catalyzed asymmetric acylation, *Journal of Molecular Catalysis B: Enzymatic* 67 (2010), 129–134
- Pezoa, R., Cortinez, V., Hyvärinen, S., Reunanen, M., Hemming, J., Lienqueo, M.E., Salazar, O., Carmona, R., Garcia, A., Murzin, D.Yu., Mikkola, J.P., The use of ionic liquids in the pretreatment

of forest and agricultural residues for the production of bioethanol, *Cellulose Chemistry and Technology* 44 (2010) 4–6, 165–172

- Virtanen, P., Mikkola, J.P., Salmi, T., Miljövänliga katalysatorer av joniska vätskor, *Kemia-Kemi* 6 (2010), 32–34

Ionic Liquids as an 'Enabling' Media: SILCA

Supported Ionic Liquid Catalyst used in the transformation of unsaturated aldehydes and synthesis of furanic fuels and chemicals; Ionic liquid pre-treatment techniques for fermentable sugars; Biogas cleaning for vehicle grade fuel

Main funding: Academy of Finland, Tekes

Jyri-Pekka Mikkola, Eero Salminen, Pasi Virtanen, Hannu Karhu, Sari Hyvärinen, Elena Privalova, Ikenna Anugwom, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

The work is focused on supported ionic liquid catalysts (SILCA) and the use of ionic liquids as reaction media. Several new ionic liquids have been prepared and characterized. The project is focused on the use of ionic liquids in catalyst supports; we have successfully demonstrated that ionic liquids can be used to heterogenize homogeneous catalysts. Kinetic studies have been carried out for hydrogenation of fine chemicals, such as citral and cinnamaldehyde on SILCA. An extensive study of the physical properties of selected ionic liquids has been continued and kinetic modelling of hydrogenation processes on SILCA has been advanced. In 2009, Pasi Virtanen defended his doctoral thesis on SILCA. The thesis received the award of the Finnish Catalysis Society as the best doctoral thesis in catalysis in years 2007–2009.

The main goal in the work aiming for fermentable sugars is to pre-treat lignocellulose with selected ionic liquids after which, in combination with selected micro-organisms and enzymes suitable mother liquids for fermentation broths are obtained. The project deals both with Chilean and Nordic wood sources having different genotypes. The analysis is challenging since typical analytical columns do not tolerate high concentration of any salts (e.g. like ILs). Besides high precision liquid chromatography (HPLC), more unusual analysis techniques (such as capillary electrophoresis) are developed for analysing sugars retrieved from the lignocellulosic samples. The endeavour is to try different separation buffers and to work with different detectors to optimize the conditions for analysis of products obtained during the treatment procedure. Also, a long term goal is to develop a new type of detector in collaboration with the specialists in physics and optics from the University of Eastern Finland, that in future could be utilized in the routine analysis of molecules originated from the bio resources.

Biogas is one of the feasible, delocalized near-future solutions to the mobility needs of the society. Moreover, it does not contribute to the depletion of fossil fuel resources and is relatively easy to implement, both as production sites and to be used as a fuel in internal combustion engines. One of the biggest challenges has been the lack of economic and robust small-scale gas purification technologies needed to yield vehicle-grade fuel. Since biogas primarily consists of methane (just like natural gas), the established gas-cleaning

technologies based on aqueous alkanol amines in principle could be used. However, the volatility and corrosivity of amines and the large unit size of the existing techniques, new solutions are needed.

Cooperation:

University of Eastern Finland, Joensuu, Finland; Zelinsky Institute of Organic Chemistry, Moscow, Russia; Moscow State University, Moscow, Russia; University of Jyväskylä, Jyväskylä, Finland; Tezpur University, Tezpur, India; University of Chile, Santiago, Chile; Tallinn University of Technology, Tallinn, Estonia; University of Oulu, Oulu, Finland; Umeå University, Umeå, Sweden

Publications:

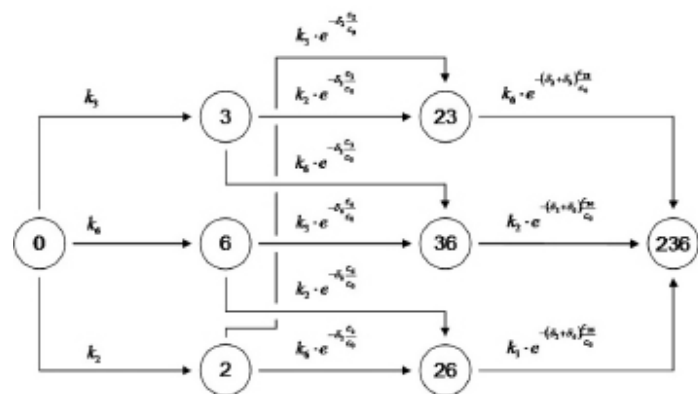
- Hyvärinen, S., Virtanen, P., Murzin, D.Yu., Mikkola, J.P., Towards ionic liquid fractionation of lignocellulosics for fermentable sugars, *Cellulose Chemistry and Technology* 44 (2010) 4, 187–195

Cellulose Derivatives in Ionic Liquids

Main funding: PCC, Åbo Akademi

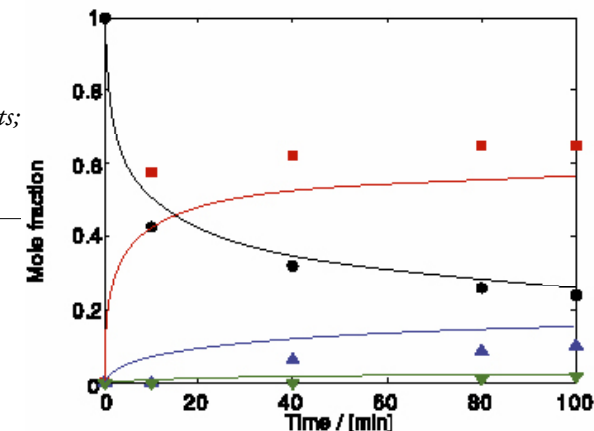
Jyri-Pekka Mikkola, Olatunde Jogunola, Pia Damlin, Matias Kangas, Tapio Salmi, Bjarne Holmbom

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. During 2009, a special attention was paid to the development of a detailed substitution kinetics of cellulose (see figure). Detailed kinetic modelling based on probabilistic theories and rate retardation was carried out.



Reaction scheme for the formation of substituted anhydroglucose units. Notation: 0, unsubstituted glucose unit; 2, 3, 6, monosubstituted glucose units (substituted at hydroxyl groups 2, 3 and 6); 23, 36, 26, disubstituted glucose units (substituted at hydroxyl groups 2 and 3, 3 and 6 and 2 and 6); 236, trisubstituted glucose units

Measured (symbols) and modelled (lines) mole fractions in the carboxymethylation of cellulose at 40°C: ●, unsubstituted glucose units; ■, mono-substituted; ▲, di-substituted; ▼, tri-substituted



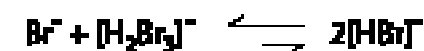
Brønsted Acidity: Fundamentals in Non-Aqueous Media and Solvation Behaviour

Main funding: Åbo Akademi University Foundation Research Institute

Gordon Driver

Ionic liquids (ILs) are a promising class of solvents with great potential to solve industrial/environmental problems related to the widespread use of volatile organic compounds (VOCs). As for molecular systems, there are two main sub-classes of ILs: aprotic and protic. In the latter sub-class the protons present often exhibit Brønsted acidities, and are therefore useful in common acid-base chemical processes. Unfortunately, it transpires in the literature, that there is a great tendency to assume that acidity in ILs (or any other non-aqueous medium) can be understood in terms of any given acid's behaviour in aqueous solution. That acid pKas are solvent dependent has in general been ignored in ILs literature, leading to detailed assumptions of acid speciation and relative potency.

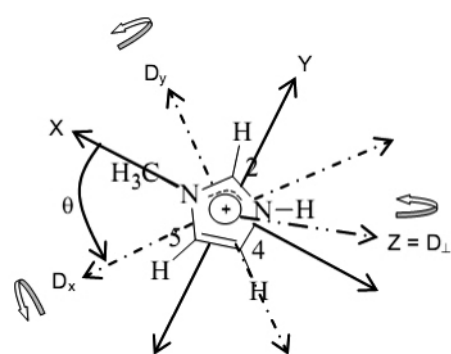
In water, hydrogen bromide (HBr) exists as $[H_3O]^+$ and solvated Br^- , as dictated by solvent levelling effects of H_2O molecules. In the IL $[Hmim]Br$ (3-methyl-1H-imidazolium bromide), however, HBr is present in the form of two distinct anionic complexes via formation of homo-conjugate halohydrogenate(I) type μ -2 hydrogen-bridged acidic anions, at the mercy of the following equilibrium:



We have also characterised native crystalline solids, formed in situ, which are found to be comprised of asymmetric unit cells containing $[(C_4H_7N_2)_3]^{2+} \cdot Br^- \cdot [H_2Br_3]^-$ clearly exemplifying the unique character of the proton, in stark contrast to its speciation in aqueous systems.

While acidity is in part due to an acid's propensity for proton transfer, it is also intimately dependent on its local environment, in terms of the thermodynamics of post proton transfer products. In order to gain insight into microscopic solvation effects, we have

employed NMR (T1) and DRS (Dielectric Relaxation Spectroscopy) to study the pure liquids. As the application of NMR rotational relaxation in ILs is a relatively new field, we found it necessary to verify, and in some cases improve upon, the current state of theoretical treatments, in order to avoid several approximations commonly employed, in terms of the rotational behaviour of non-spherical ion geometries and their frequency-independent behaviours. Here we developed a method to determine the eigenvalues of the diagonalised rotational diffusion tensor (i.e. the rotational diffusion constants) under conditions of “extreme narrowing” for planar asymmetric ions. The motivation for the NMR relaxation studies is linked to recent DRS studies where in the latter, reorientation of the ionic dipole is recorded but the ionic motions responsible remain unknown. Future research efforts will include NMR relaxation studies at various temperatures, in order to link discrete ion dynamics to these systems’ interesting temperature dependent dielectric behaviour.



Displacement of the rotational diffusion axes away from the principal symmetry axes for the planar asymmetric 3-methyl-1H-imidazolium cation, [Hmim]⁺. Numbers designate C2, C4 and C5. X, Y and Z \equiv principal internal axes. D_x , D_y and $D_z \equiv$ corresponding principal rotational diffusion axes. $\Theta \equiv$ the offset angle of the principal diffusion axes from the principle internal axes, in the X-Y plane

Cooperation:

Ruhr-Universität Bochum, Germany; Office of Energy and Environment, University of Regina, Canada; Department of Chemistry, Instrument Centre, University of Turku; Laboratory of Inorganic Chemistry, University of Helsinki

Publications:

- Johnson, K.E., Driver, G.W., Protons: Affinity and reduction in ionic liquids, *ECS Transactions* 25 (2010) 39, 33-40

Ionic Liquids in Electrosynthesis and in Characterization of Organic Electroactive Materials

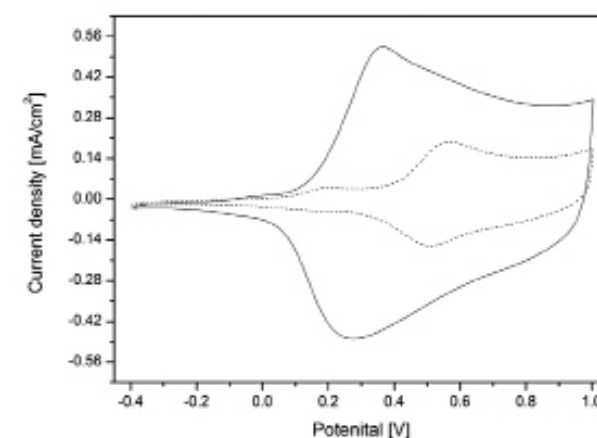
Main funding: Graduate School in Chemical Engineering (GSCE), Graduate School of Materials Research (GSMR)

Pia Damlin, Michał Wagner, Anna Österholm, Ari Ivaska

Room temperature ionic liquids have been studied as media for electrosynthesis of conducting polymers instead of using highly volatile and toxic solvents, such as acetonitrile and tetrahydrofuran. The resulting films often exhibit improved surface morphology, higher charging ability, and improved electrochemical activity, stability and reversibility.

Electrochemical polymerization as well as doping abilities in ionic liquid environment of poly(3,4-ethylenedioxythiophene) (PEDOT), poly(paraphenylene) (PPP) and polyazulene (PAz) have been studied. All of these materials have potential applications in organic electronic devices.

Comparison of both the electrochemical polymerization process and doping abilities of PPP has been made in acetonitrile and in [BMIM][PF₆] and [BMP][Tf₂N] ionic liquids. The results show that the PPP films made in [BMIM][PF₆] had the best film growth. This study indicates that ionic liquids are good solvents in electrochemical studies of conducting polymers. In situ FTIR-ATR experiments made on PAz films electrosynthesized in [BMP][Tf₂N] have shown that the films consist of chains with a longer effective conjugation length compared to films made in acetonitrile. This partly explains the three times higher charging ability obtained in PAz films made in [BMP][Tf₂N] compared to films made in acetonitrile.



PAz film synthesized in [BMP][Tf₂N] (solid line, polymerization charge: 6.8 mC, doping charge: 0.92 mC) and PAz synthesized in 0.1 M TBAPF₆-ACN (dashed line, polymerization charge: 6.5 mC, doping charge 0.28 mC)

Cooperation:

University of Turku

Publications:

- Wagner, M., Kvarnström, C., Ivaska, A., Room temperature ionic liquids in electrosynthesis and spectroelectrochemical characterization of poly(para-phenylene), *Electrochimica Acta* 55 (2010) 7, 2527-2535

3.2 Reaction Intensification

New reactor systems and new technologies which lead to an essential decrease of the size of a chemical plant are developed. Monolith reactors, fibrous catalyst structures as well as ultrasonic and microwave technologies are investigated. The 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 as well as hydrogenation of aldehydes and ketones, leaching of minerals and delignification of wood. Ultrasound technology was used in leaching studies (cellulose and minerals) as well as to enhance the rates of catalytic processes. A chemical method was developed to measure the exposed ultrasound effect in a precise way. This is very important in improving the understanding of the ultrasound effect on catalysis: on one hand, ultrasound can clean the catalyst surface and create new surface (Ni), but it can also contribute to the agglomeration metal nanoparticles in catalysts (Ru).

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. 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 applications have been in environmental catalysis, as well as in the production of chemicals.

Structured Reactors

Main funding: Academy of Finland

Jyri-Pekka Mikkola, Teuvo Kilpiö, Victor Sifontes, Kalle Arve, Johan Wärnå, Kari Eränen, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

Fibres, 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. Fibre catalysts and monoliths enable a continuous operation for processes, which traditionally have been carried out batchwise, particularly synthesis of fine chemicals. Three kinds of fibre catalysts have been investigated: polymer-based fibres as well as silica and carbon fibres. 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. First experiments with solid foams prepared in co-operation with the materials research experts at the PCC were carried out; in future, the research on structured reactors will be strongly focused on solid foams.

Cooperation:

Lappeenranta University of Technology

Micro- and Milliscale Reactor Technology

Main funding: PCC, Tekes, EU

Kari Eränen, Mats Rönholm, José Rafael Hernández Carucci, Mauricio Roche, Sabrina Schmidt, Narendra Kumar, Kalle Arve, Johan Wärnå, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

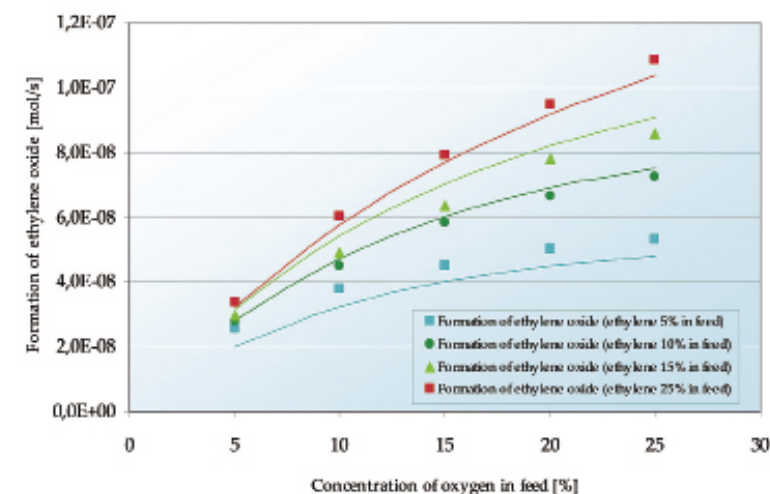
Micro- and millireactors enable an efficient performing of chemical processes because of enhanced mass and heat transfer. We have introduced the concept of microreactors to Finnish soil. Different kinds of microreactor systems have been constructed; e.g. for catalytic gas-phase systems and for liquid 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. Silver-based microreactor combined to micro-gas chromatography gave excellent results in the preparation ethylene oxide. A new research programme was started to prepare alkyl halogenides in gas-phase microreactors. 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. New liquid-phase microreactors were constructed and will be tested in the future.

Cooperation:

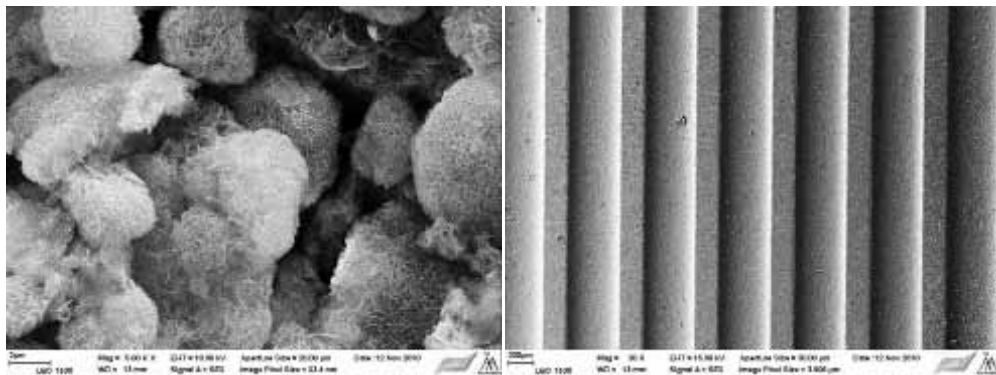
Lappeenranta University of Technology; University of Oulu; Aalto University, PCAS Finland; Kemira, several EU partners

Publications:

- Hernandez Carucci, J., Halonen, V., Eränen, K., Wärnå, J., Ojala, S., Huuhtanen, M., Keiski, R., Salmi, T., Ethylene oxide formation in a microreactor: from qualitative kinetics to detailed modeling, *Industrial & Engineering Chemistry Research* 49 (2010), 10897–10907



Ethylene oxidation formation kinetics in a gas-phase microreactor



Microreactor channels coated with MCM-22 mesoporous material

Multiphase Reactors

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

Johan Wärnå, Matias Kangas, Mats Rönnholm, Andreas Bernas, Henrik Grénman, Sigmund Fugleberg, Victor Sifontes, Mats Källdström, Heidi Bernas, Jyrki Kuusisto, Atte Aho, Sébastien Leveneur, Pierdomenico Biasi, Nicola Gemo, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

The project concerns advance modelling of multiphase reactors, 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, ring opening and reactions of solids with gases and liquids. A new model was published for the delignification of wood. The model can be used for process intensification as well as prediction of the behaviour of cellulose production. An advanced cascade reactor was used to determine the kinetics of hemicellulose leaching from wood by hot water extraction. The work was published in the doctoral thesis of Henrik Grénman. Direct synthesis of hydrogen peroxide was successfully carried out in batch reactors and three-phase trickle beds.

Cooperation:

Danisco; Forchem; Raisio; Lappeenranta University of Technology; Università di Padova, Padova, Italy, INSA Rouen, France

Publications:

- Bernas, A., Wärnå, J., Mäki-Arvela, P., Murzin, D.Yu., Salmi, T., Kinetics and mass transfer in hydroformylation – bulk or film reaction? *Canadian Journal of Chemical Engineering* 88 (2010), 618–624
- Biasi, P., Menegazzo, F., Pinna, F., Eränen, K., Canu, P., Salmi, T., Hydrogen peroxide direct synthesis: Selectivity enhancement in a trickle bed reactor, *Industrial & Engineering Chemistry Research* 49 (2010), 10627–10632

Batch and Semibatch Reactors for Reactive Solids

Main funding: Graduate School of Materials Research (GSMR), Raisio Foundation, Nordkalk

Henrik Grénman, Steliana Aldea, Pasi Tolvanen, Jussi Rissanen, Päivi Mäki-Arvela, Johan Wärnå, Dmitry Murzin, Tapio Salmi

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. Ultrasound enhanced the solid-state reactivity in the leaching of minerals and in the oxidation starch. Mathematical modelling advanced considerably in the description of non-ideal reactive solids; the doctoral thesis of Henrik Grénman was completed and the most important modelling results comprising non-ideal reactive solid particles with particle size distributions were published

Cooperation:

Perstorp; Danisco; Kemira; Raisio; Nordkalk; Outotec; INSA Rouen, France

Publications:

- Grénman, H., Salmi, T., Murzin, D.Yu., Addai-Mensah, J., Dissolution of boehmite in sodium hydroxide at ambient pressure: kinetics and modelling, *Hydrometallurgy* 102 (2010), 22–30
- Grénman, H., Salmi, T., Murzin, D.Yu., Addai-Mensah, J., The dissolution of gibbsite in sodium hydroxide at ambient pressure, *Industrial & Engineering Chemistry Research* 49 (2010), 2600–2607
- Grénman, H., Wärnå, J., Mikkola, J.P., Sifontes, V., Fardim, P., Murzin, D.Yu., Salmi, T., Modelling the influence of wood anisotropy and internal diffusion on delignification kinetics, *Industrial & Engineering Chemistry Research* 49 (2010,) 9703–9711
- Salmi, T., Grénman, H., Bernas, H., Wärnå, J., Murzin, D.Yu., Mechanistic modelling of kinetics and mass transfer for a solid-liquid system: leaching of zinc with ferric iron, *Chemical Engineering Science* 65 (2010), 4460–4471

Complex Reaction Kinetics and Thermodynamics

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

Johan Wärnå, Jyri-Pekka Mikkola, Matias Kangas, Pasi Tolvanen, Olatunde Jogunola, Valerie Eta, Ewelina Leino, Esko Tirronen, Andreas Bernas, Serap Şahin, José Rafael Hernandez Carucci, Sébastien Leveneur, 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. The doctoral thesis of Serap Şahin, which concerned combined heterogeneous catalysis and enzymatic catalysis, was finished. 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:

Perstorp; Raisio; Forchem; Kemira; Institute of Chemical Technology, Prague, Czech Republic; Université de Bourgogne, France; University of Oulu, INSA Rouen, France

Publications:

- Eta, V., Mäki-Arvela, P., Leino, A.R., Kordas, K., Salmi, T., Murzin, D.Yu., Mikkola, J.P., Sustainable synthesis of dimethyl carbonate from methanol and carbon dioxide under dehydration- the effect of magnesium enhanced reactions, *Industrial & Engineering Chemistry Research* 49 (2010), 9609–9611
- Leino, E., Mäki-Arvela, P., Eta, V., Murzin, D.Yu., Salmi, T., Mikkola, J.P., Conventional synthesis methods of short-chain dialkylcarbonates and novel production technology via direct route from alcohol and waste CO₂, *Applied Catalysis A: General* 383 (2010), 1–13
- Kangas, M., Kubička, D., Salmi, T., Murzin, D.Yu., Reaction routes in selective ring opening of naphthenes, *Topics in Catalysis* 53 (2010), 1172–1175
- Leveneur, S., Kumar, N., Salmi, T., Murzin, D.Yu., Stability of hydrogen peroxide during perhydrolysis of carboxylic acids on acidic heterogeneous catalysts, *Research on Chemical Intermediates* 36 (2010), 389–401
- Murzin, D.Yu., Kinetics of catalytic reactions on nanoclusters, *Langmuir* 26 (2010), 4854–4859
- Murzin, D.Yu., Size dependent heterogeneous catalytic kinetics, *Journal of Molecular Catalysis A: Chemical* 315 (2010), 226–230
- Murzin, D.Yu., Kinetic analysis of cluster size dependent activity and selectivity, *Journal of Catalysis* 276 (2010), 85–91
- Murzin, D.Yu., Parmon, V.N., Quantification of cluster size effect (structure sensitivity) in heterogeneous catalysis, *Catalysis-Special Periodical Reports RSC* 23 (2010), 179–203
- Murzin, D.Yu., Bernas, A., Salmi, T., Kinetic modeling of regioselectivity in alkenes hydroformylation over rhodium, *Journal of Molecular Catalysis, A: Chemical* 315 (2010), 148–154
- Murzin, D.Yu., Simakova, I.L., On quantitative description of metal particles size effect in catalytic kinetics, *Kinetics and Catalysis* 51 (2010), 828–831



Batch reactor system for direct synthesis of hydrogen peroxide

3.3 Metals in Wood and Fibres

Management of the metal flows and mass balances of metals in pulp and paper processes as well as in modern biorefineries is important in order to minimize the negative and maximize the positive effects the different metal ions have on the processes. The quality of the final products in today's pulp and paper mills but also in the future combined mills with additional chemicals and energy production, in the various biorefinery concepts, will strongly depend on the management of metals in the different stages of the process. Metals come in the processes principally from the following sources: with the raw material, with make-up water, with added chemicals and through corrosion of the process machinery. Alkaline, earth alkaline and transition metals are known to be important in the paper making process. Many transition metals are of significant environmental concern as well.

This project is to study the occurrence of metal ions in different part of the wood material used for pulp and paper making and energy production processes as well as in production of associated chemicals (in the “forest biorefinery” concept). The flows of metal ions and their balances in different parts of the process concepts as well as in the entire paper making process will be studied. The significant reactions of different metal ions and their effect on production processes will be clarified. In which chemical form the metals exist in wood, pulp and process liquors will also be studied because they strongly vary from metal to metal and the chemical speciation of the metals in the production process is of importance. Both production and environmental aspects will be considered in all the projects. Wood-based material is also used in energy production and therefore those fuels should also be characterized in respect of the type of metal ions and their content in different fuels. Study on metals gives important information in order to predict their reactions in different parts of paper making and in energy conversion processes so that the negative effects can be eliminated and the positive effects enhanced.

The ultimate goal is to understand the natural existence and distribution of metal ions in tree material and the reactions of the metal ions with wood fibres and other chemicals in different stages of the paper making process and in the energy conversion processes. The role and importance of individual metal ions in the different material cycles comprising the entire paper making process including the optional processes in a forest biorefinery is of crucial importance. Removal of metal ions from the process liquors is also an important operation and a sub-project in this direction has been started.

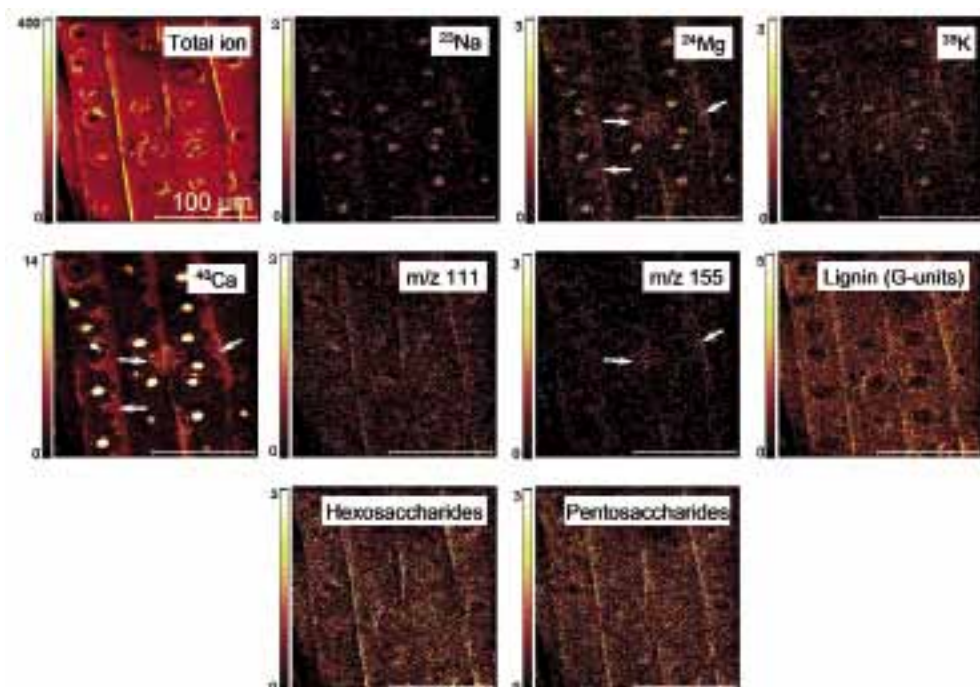
Chemical Microscopy and Chemical Microanalysis of Wood Tissues and Fibres: Anionic Groups in Wood and Fibres

Main funding: Academy of Finland, Tekes (Bioraff)

Andrey Pranovich, Elena Tokareva, Bjarne Holmbom, Paul Ek, Ari Ivaska

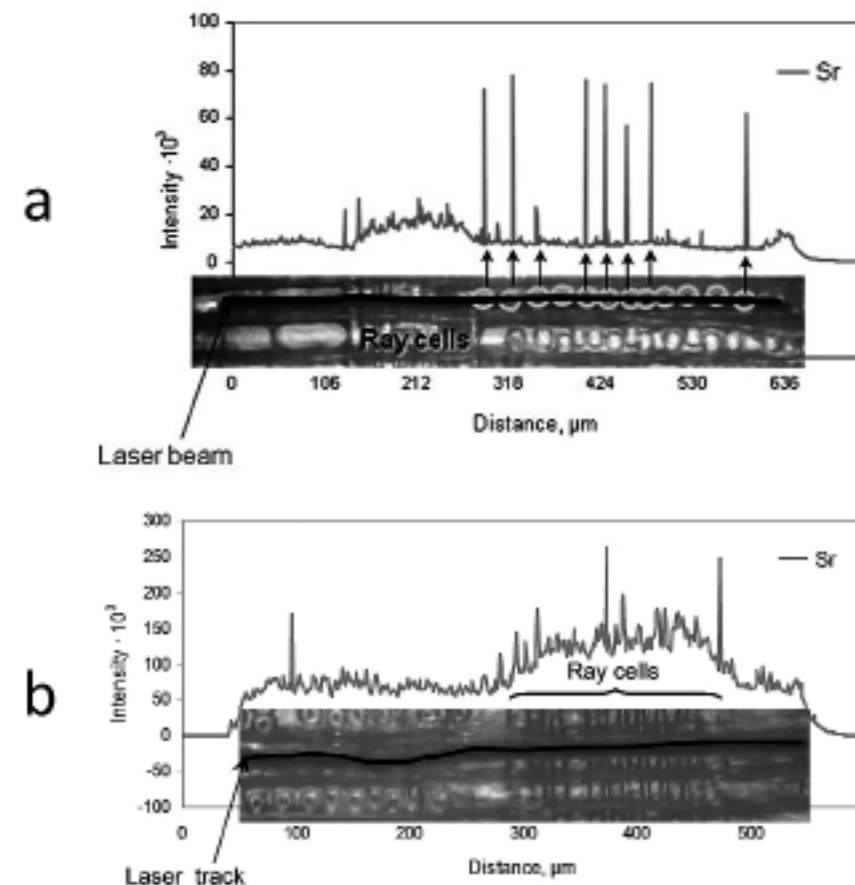
Spatial distribution of anionic groups – natively occurring in wood fibres, or formed during processing was assessed by applying time-of-flight secondary ion mass spectrometry (ToF-SIMS) to thin wood sections of Norway spruce and European aspen. Comparison

of sample preparation techniques for ToF-SIMS showed that extractive substances severely disturbed analysis of the main polymeric wood constituents, i.e., lignin, carbohydrates, and inorganic (metal) constituents as well. However, after pre-extraction of wood samples with acetone or/and ethanol, the metals Ca, Mg, Na and K were found to be preferably located in the bordered pit tori and the inner layer of ray parenchyma cell in spruce (see figure). No lignin was found in these morphological regions. In aspen, metal ions dominated in lumina of longitudinal parenchyma cells, ray cell wall layers, and pits between ray cells and vessels. Carbohydrates (cellulose and hemicelluloses) were fairly uniformly distributed both in spruce and aspen.



ToF-SIMS images of tracheid region radial longitudinal section of spruce sapwood showing the spatial distribution of selected wood constituents. Specific location of Na, Mg, Na and K in bordered pit tori (rounded spots), but no lignin in this location were observed. Arrows indicates the presence of Ca, Mg and, probably, acidic pectin (as imaging of ion at m/z 155) in cell wall fragments.

In addition to the wood component distribution obtained for untreated wood samples, pectin distribution was assessed by applying labelling methods (i.e. for anionic groups, AGs). Methods for labelling of AGs with selected metals on wood surfaces were developed and applied to untreated, acid washed, alkali-treated and alkali-peroxide-treated wood sections. Sr²⁺ was found to be a very suitable marker for labelling of AGs. ToF-SIMS images of labelled wood after alkaline-peroxide treatment indicated the larger areas of AGs location in comparison with alkali-treated or untreated samples. Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) applied for semi-quantitative analysis of labelled AGs showed a 6-fold higher content of AGs in fibre walls of alkali-peroxide treated spruce sections than in untreated sample (see figure).



LA-ICP-MS analysis of the distribution of anionic groups along the fibre and across the ray cells in a radial spruce sections in acid washed untreated (a) and alkaline-peroxide treated (b) samples, as seen after labelling with Sr²⁺ ions.

Cooperation:
SLU/WUR, Sweden

Publications:

- Tokareva, E.N., Pranovich, A.V., Ek, P., Holmbom, B., Labelling of anionic groups in wood tissues for ToF-SIMS and LA-ICP-MS analysis, *Holzforschung* 64 (2010) 1, 35–43

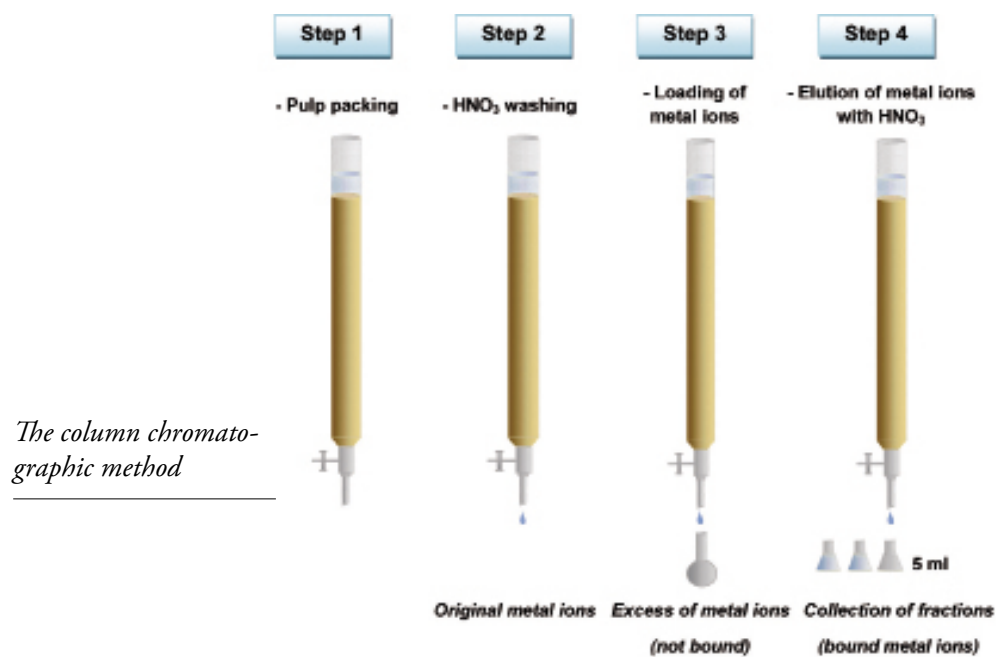
Distribution and Reactions of Metal Ions at Bulk and Fibre Level in Wood Materials, Pulp and Process Liquors

Main funding: Tekes (Bioraff), Åbo Akademi University Foundation Research Institute

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

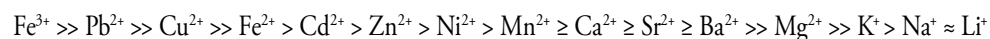
Affinity of metal ions to wood materials

The main objective of the study has been to study reactions of metal ions with functional groups in various cellulose materials. A column chromatographic method has been developed for the study of metal ion affinities to different types of pulps and wood materials.

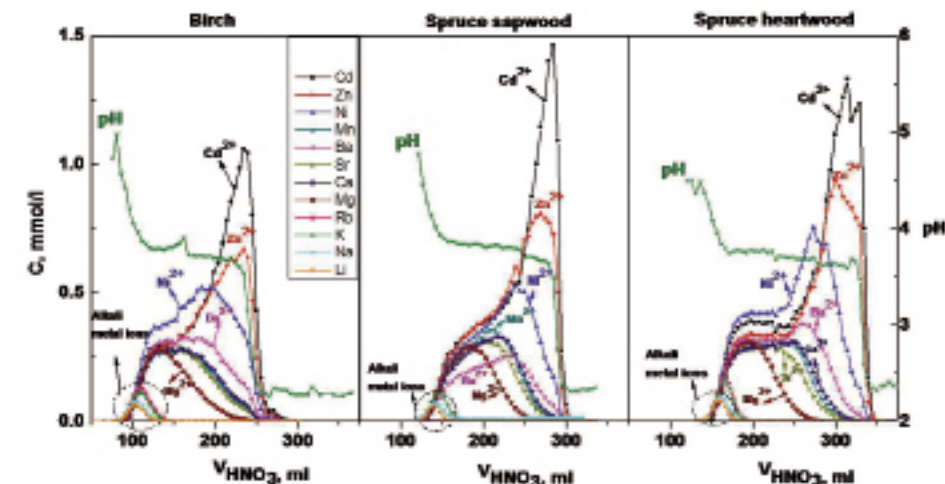


The column chromatographic method

The column chromatographic method was used to assess the differences in affinity of metal ion to different materials, e.g. wood particles and bark. The mechanism of this method is mainly ion exchange by complexation of metal ions to the functional groups, e.g. carboxyl groups and phenolic hydroxyl groups, in the materials. Different metal ions exhibited different sorption ability to wood particles and bark. The column method is very sensitive and even small affinity difference between metal ions can be detected. By combination of the sorption experiments with several different metal ion mixtures, the following affinity order was established, e.g. for spruce sapwood particles:



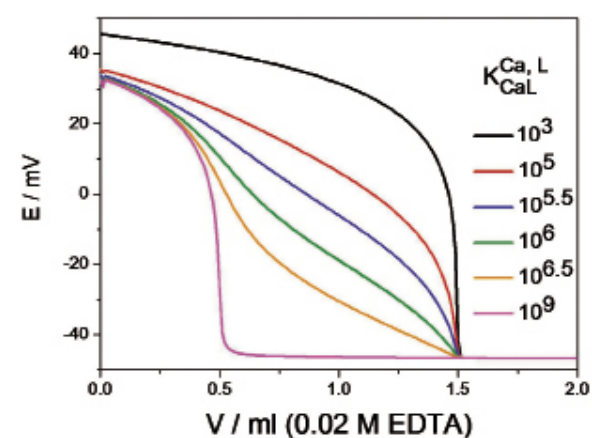
For the bark (spruce inner bark and outer bark) and the wood particles from birch, spruce sapwood and spruce heartwood, the affinity orders were almost the same. Trivalent iron was most strongly bound to the binding sites in wood. Precipitation of trivalent iron took place in the solid phase at the natural pH value. Lead and copper are also strongly adsorbed to the natural materials, whereas their sorption capacity is strongly decreased when the metal ions, having stronger affinity such as trivalent iron, are present in the solution. The alkali metal ions are most weakly bound to the natural materials. The metal sorption properties of natural materials imply that they could be potential materials for removal of heavy metal ions from aqueous solutions.



pH and concentrations of metal ions in the collected fractions as function of the elution volume (metal sorption to wood particles)

Determination of Ca in black liquor

A solid-contact Ca²⁺-selective electrode was used for speciation of calcium in black liquor. A new method for changing the potential to concentrations or activities in titration curves was proposed. The advantage with this method is that the electrode standard potential and the slope of the calibration curve do not have to be known. This is beneficial when the analyte has a complexed matrix or is a harsh environment which affects the properties of the electrode. The new method was implemented both in a method for linearization based on the Grans's plot and in determination of the stability constant of a complex and the concentration of the complexing ligand in the sample. The new method gave accurate results when using titrations data from experiments with samples of known composition. A complexometric titration model was also developed.



Simulated titrations of calcium with EDTA in presence of ligands (L) of different stability constants

Linearization of the complexometric titration curves were used to determine the concentrations of free, bound and total calcium in black liquor. With inductively coupled plasma optical emission spectrometry (ICP-OES), similar total calcium concentrations

were obtained as by the EDTA titration. By using a computer program (FITEQL), the stability constants and the concentrations of the calcium binding ligand in the black liquor, was obtained.

Publications:

- Granholm, K., Harju, L., Ivaska, A., Desorption of metal ions from kraft pulps, Part 1: Chelation of hardwood and softwood kraft pulp with EDTA, *BioResources* 5 (2010), 106–116
- Granholm, K., Harju, L., Ivaska, A., Desorption of metal ions from kraft pulps, Part 2: Chelation of kraft pulps with different complexing agents and with EDTA in a reducing environment, *BioResources* 5 (2010), 227–243
- Su, P., Granholm, K., Harju, L., Ivaska, A., Study on metal ion binding to unbleached softwood kraft pulp by column chromatography, *Appita Journal* 63 (2010) 2, 143–149
- Su, P., Granholm, K., Pranovich, A., Harju, L., Holmbom, B., Ivaska, A., Sorption of metal ions to untreated, alkali treated and peroxide-bleached TMP, *Cellulose* 17 (2010), 1033–1044

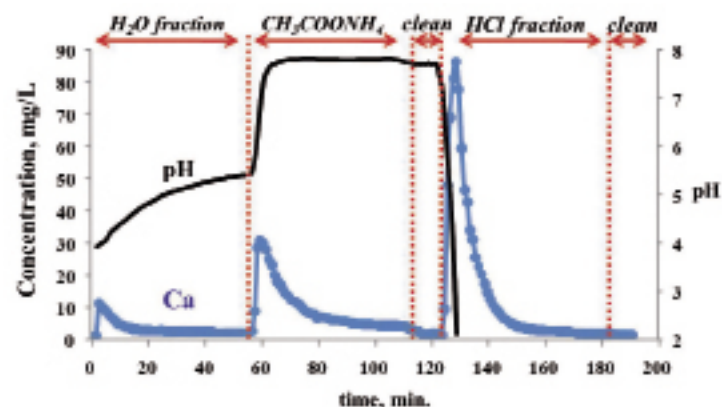
Dynamic Leaching of Biofuels for Determination of Ash-forming Matter

Main funding: Åbo Akademi Process Chemistry Centre

Warunya Boonjob, Manuel Miro-Llado, Maria Zevenhoven, Paul Ek, Mikko Hupa, Ari Ivaska

A standard method to characterize solid material for leachable substances is to extract the sample first with distilled water to determine the water soluble constituents. The ion-exchangeable cations are then extracted with ammonium acetate from this residue and finally hydrochloric acid is used in order to find the acid soluble constituents from the previous residue.

A dynamic extraction method based on sequential injection method by using the Lab-on-Valve concept was developed. The studied sample is placed in a flow-through extraction chamber. The extraction medium is automatically changed and the concentration of the elements under study is monitored on-line by ICP-OES technique. The extraction profile of calcium from bark and the pH of the extraction media are shown below.



On-line monitoring of leaching of calcium from bark. Concentration profile and pH at each extraction step are shown

Extraction profiles of Al, Ca, K, Mg, Na, P and Si were studied in bark, twigs and ash. With the developed method fuel characterization was done in three hours. To do the same characterization with the manual, static method requires several days.

Cooperation:

University of the Balearic Islands, Palma de Mallorca, Spain

3.4 Interaction between Chemicals and Fibres

Even if the consumption of certain types of paper, e.g. newsprint, have decreased in some of parts of the world, paper is still important. Paper is a renewable and environmentally friendly product. Besides the traditional paper products, such as printing and writing papers, packaging papers and sanitary products, new types of paper is being developed.

The runnability of the paper machine should be without disturbances such as web breaks and deposits to ensure an efficient production and a good quality product. The process waters at a paper machine are a complex mixture of substances released from the fibres and chemicals added to improve the process and the quality of the product. It is of outmost importance to understand the wet end chemistry and the interactions between the added chemical and the fibres. In order to control the wet end, good, reliable and, if possible, on-line methods are needed. Flow cytometry have been shown to be an excellent method to detect agglomeration in process waters and the amount of deposits in the press dryer section can be estimated by DepoSense. In order to further control the wet end, new analytical methods need to be developed, which give more detailed chemical information. New analytical methods for calcium oxalate, one of the most problematic scale salts occurring in pulping and papermaking, is also needed. The ultimate goal is to modify the processes or add novel chemicals to minimise the harmful forms of calcium oxalate.

The influence of additives and papermaking conditions in the initial wet web strength and the relaxation properties of the wet web have also been studied. The results might be used to decrease the numbers of web breaks at the beginning of the dryer section of a paper machine.

Depending on pH, the wood pitch components can be dissolved in the process water or dispersed as colloidal droplets. The phase distribution will affect pitch control and the washing efficiency. The wood pitch will also affect the surface properties of final paper. We have shown that the wood pitch is relocated, oxidised and polymerised during storage. These changes occur already at very low conditions, even at -18°C.

Controlling Strength and Runnability of Wet Paper by Tailored Wet End Chemistry (ChemRun)

Main funding: Tekes, Industry

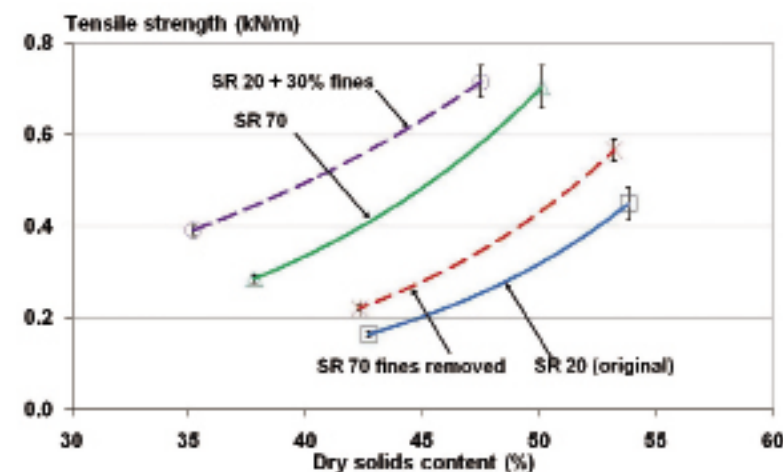
Hanna Lindqvist, Sylwia Bialczak, Anna Boedeker, Joakim Lind, Bjarne Holmbom, Lari Vähäsalo, Anna Sundberg

The wet web strength, tension at a certain strain and the rate of relaxation of the wet web are critical factors affecting the runnability in the beginning of the dryer section in paper machines. Poor strength and relaxation of the wet paper cause web breaks and can also impair the quality of the dry paper. Recent studies have indicated that, in addition to dry paper properties, also the wet web properties are affected by the wet end chemistry.

Strength properties, like tensile strength, strain at break, tensile stiffness and relaxation of the wet web, may also be controlled by the wet end chemistry, and this may bring new insight into the runnability of the paper machine. Previously we have studied the effects of pH, electrolytes, surfactants, wood components and polymers on the wet and dry strength properties of paper.

Dynamic tensile strength and relaxation properties of paper samples were determined with Impact, a fast tensile strength testing rig. The objectives of this part of the study were to determine the effects of refining on dry and wet web properties as well as on dewatering. Two types of refiners were used, the Valley beater and the Prolab refiner, in order to produce more fines and to introduce changes in the fibres, e.g. internal fibrillation and fibre cutting.

Refining of pulp resulted in increased wet tensile strength at constant dry content (see figure). When the Valley beater was used, the wet tensile strength increased and the dry content after wet pressing decreased with increased degree of refining. Removal of fines caused a decrease in the wet tensile strength compared to sheets containing fines. In the case of SR 70 where fines were removed, the tensile strength was higher than the tensile strength for sheets made from the original pulp (SR 20), indicating that the changes in the fibres, e.g. internal and external fibrillation, increased bonding. The dry content after wet pressing was similar to the dry content of the original pulp, which can be explained by the removal of the water-containing fines. When 30% fines were added to the original pulp, the wet tensile strength increased the most, indicating that the content of fines affected the wet strength more than the changes in the fibres caused by refining.



Wet tensile strength after refining, removal of fines or addition of fines. Pulp refined using the Valley beater. The sheets were pressed to two different dry contents (0.5 and 3.5 bar).

Cooperation:

VTI; Kemira; Metso Paper; Stora Enso; UPM-Kymmene

Publications:

- Lind, Joakim, Inverkan av finmaterial på avvattnings och initial våtstyrka (*Effects of fines on dewatering and initial wet web strength*, in Swedish), MSc Thesis
- Lindqvist, H., Salminen, K., Kataja-aho, J., Sundberg, A., Holmbom, B., Retulainen, E., Effect of electrolytes, pH, and surface tension on dry and wet web properties, *Journal of Pulp and Paper Science* 35 (2010), 148–154

Intelligent Remote Diagnostics (iReDi)

Main funding: Kemira

Lari Vähäsalo

The aim of the project is to develop new process water analysis instrumentation which can be used on-line. 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 analyse 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. The project will also use the on-line DepoSense technique in order to receive real time information of the amount of deposits in a paper machine press section.

During the project, we will characterize and clarify the properties and formation of kraft pulp pitch, which are often causing deposits on paper machines. New analytical procedures will also be developed. Process investigations and troubleshooting projects will also be undertaken. Possibilities for creating a new method for the detection and quantification of scales on process equipment, such as pulp towers, will be investigated during the project and possibly built.

Cooperation:

Kemira

Publications:

- MacNeil, D., Miranda, R., Monte, M.C., Blanco, A., Sundberg, A., Time variations of macrostickies and extractable stickies concentrations in deinking, *Industrial & Engineering Chemistry Research* 49 (2010) 10, 4933–4939

Influence of Pitch Composition and Wood Substances on the Phase Distribution of Resin and Fatty Acids at Different pH-Levels

Main funding: Åbo Akademi Process Chemistry Centre

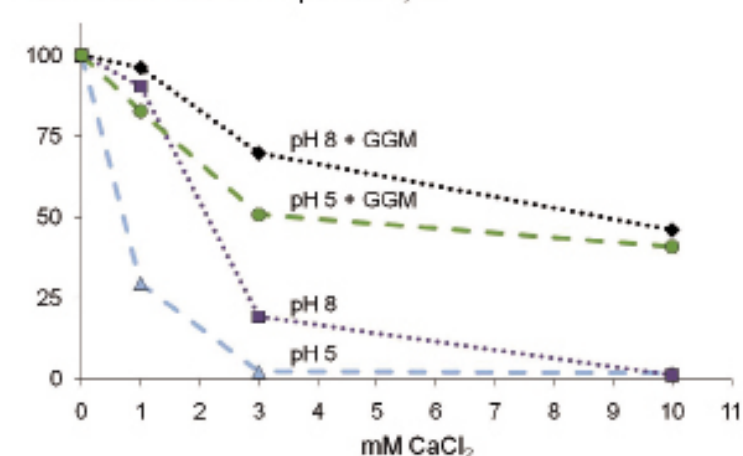
Anders Strand, Anna Sundberg, Lari Vähäsalo, Donald MacNeil, Bjarne Holmbom

Wood pitch, or lipophilic extractives, is released into the process water during the production of mechanical pulps. A large fraction of the pitch is dispersed as an oil-in-water emulsion in the process water, forming colloidal droplets with a two-layered structure. The core of these droplets consists of the most hydrophobic pitch components, i.e. steryl esters and triglycerides (neutral substances), while their surface consists of amphiphilic resin and fatty acids (RFAs). The colloidal pitch can be very detrimental for the papermaking process, leading to sticky deposits, extensive foaming or overall runnability problems. These problems are usually a result of uncontrolled aggregation of colloidal pitch; hence colloidal stability of pitch is of great interest.

The steric stabilisation of colloidal pitch by water-soluble galactoglucomannans (GGM) was assessed. The GGM was isolated from a side stream in a Finnish pulp mill producing thermomechanical pulp (TMP) from spruce. The colloidal stability of pitch emulsions against electrolyte-induced aggregation by CaCl_2 was determined in suspension of TMP with and without added GGM at pH 5 and pH 8. TMP and unstable pitch aggregates were removed by centrifugation, and the concentration of neutral substances in the supernatant was determined. The colloidal stability was much higher when GGM was added even in the presence of TMP fibres.

The results imply that problems related to uncontrolled aggregation of pitch in paper mills using mechanical pulp could be diminished by using GGM-rich side streams at the paper machine. GGM could also increase the colloidal stability of emulsions in other applications than papermaking even in the presence of fibres or other particles.

Neutral substances in supernatant, %



Relative amounts of neutral pitch components in the supernatant after CaCl_2 -additions to 1% suspensions of peroxide-bleached TMP at pH 5 and pH 8. The experiments were performed with and without added GGM

Publications:

- Holmbom, B., Sundberg, A., Strand, A., Surface-active compounds as forest-industry by-products, *Surfactants from Renewable Resources* (eds. M. Kjellin, I. Johansson), John Wiley & Sons, Ltd, New York, 2010, 45–62

Calcium Oxalate – from Hickey Problem to Sustainable Raw Material

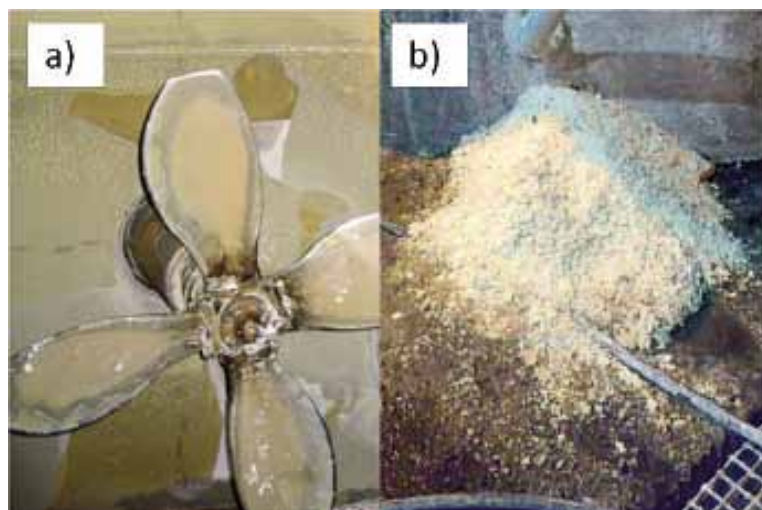
Main funding: Industry

Matti Häärä, Lari Vähäsalo, Anna Sundberg, Stefan Willför

Calcium oxalate is one of the most problematic scale salts occurring in pulping and papermaking, and particularly in the oxidative bleaching stages. It is a common problem in paper mills using peroxide-bleached mechanical pulps and calcium containing fillers and pigments. Hard scale with very low solubility causes severe operational and quality related problems. A special concern is the so-called hickies, a type of print defect caused by the calcium oxalate particles trapped in the paper sheet. In addition, calcium oxalate scaling is a well-known problem also in other industrial processes like kraft pulp bleaching, sulphite pulping, sugar plants, breweries and biorefineries, where extensive oxidation of organic material takes place. In humans, calcium oxalate precipitates occur in the form of kidney stones.

Calcium oxalate scale has a big economic impact on the mills in form of customer complaints, machine downtime due to cleaning and increased chemical costs. Scale inhibitors and dispersants are used to control deposition, but in most cases this is not enough to totally eliminate the problem.

The aim of this research project is to gain deeper understanding of the formation of oxalic acid and precipitation of calcium oxalate in mechanical pulp bleaching and papermaking processes. This requires suitable analysis methods and investigation of the formation kinetics both in a laboratory scale and in the process itself. Effects of different parameters in alkaline peroxide bleaching on oxalate formation are also studied. Based on the findings in this project, the target is to develop means for more effective control of calcium oxalate scale deposition as well as reliable tools for on-line monitoring. Different kinds of process modifications or novel additive chemistries in order to minimise the harmful forms of the precipitates are potential alternatives.



Calcium oxalate scale in a paper machine system. (a) Scale on machine chest wall; (b) Crumbled particles in the bottom of the chest

Cooperation:

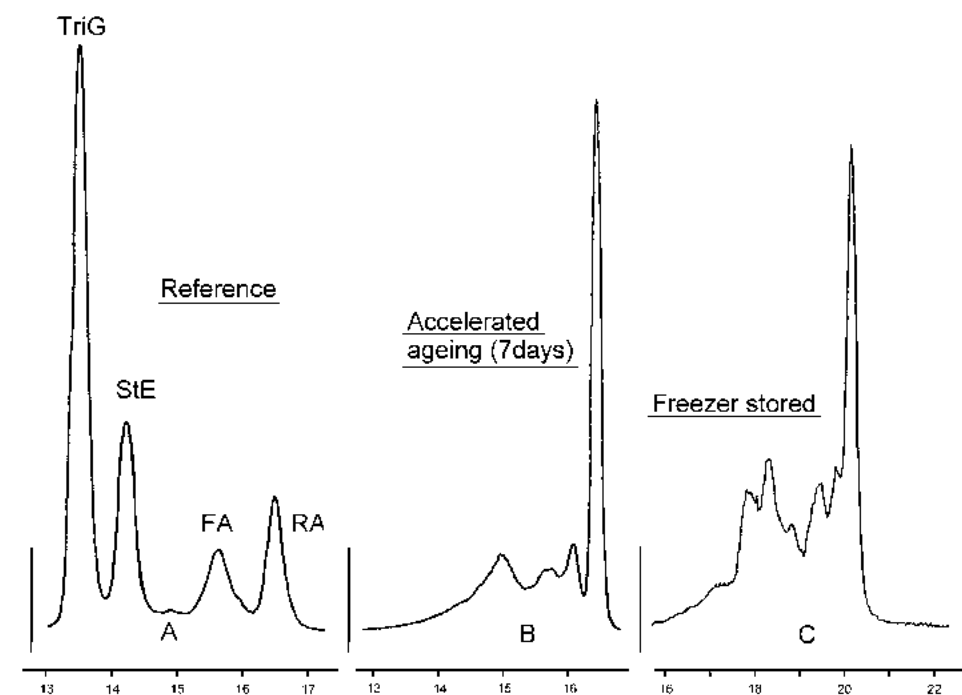
Sappi Fine Paper Europe, Kemira

Towards Chemical Understanding of Paper Properties – Role of Different Fibre Constituents on Sorption and Optical Properties

Main funding: PaPSaT Graduate School

Sylvia Bialczak, Jouko Peltonen, Bjarne Holmbom, Anna Sundberg

Paper produced from mechanical pulp, so-called wood-containing paper, contains almost all of the original wood components. Lipophilic extractives, also called wood resin or wood pitch, are causing many problems in papermaking. During production of mechanical pulp, part of the extractives is retained in the paper. The lipophilic extractives can influence the sorption of water and other solvents and consequently, affect the printability of the paper. The extractives can be oxidized, migrate to the paper surface or be polymerized during storage of the paper. The aim of the study was to analyse the changes occurring in extractives in TMP paper during ageing at different temperatures and times, and to monitor how ageing alters the surface properties of the paper.



HPLC-SEC chromatograms of extract from fresh TMP paper (A), paper submitted to accelerated ageing at 60°C for 7 days (B) and paper stored in the freezer at -18°C for 2 years (C). TriG: triglycerides, StE: steryl esters, FA: fatty acids, RA: resin acids. C was done with another column of the same type, hence the difference in the time scales

The extract of fresh TMP paper analysed by HPLC-SEC shows four distinct peaks, mainly consisting of triglycerides, steryl esters, fatty acids, and resin acids (Reference in figure). After accelerated ageing for 7 days, the extract exhibited a very different profile (Accelerated ageing). The triglycerides and steryl esters had disappeared, probably due to oxidation and further degradation, and polymerization (cross-linking) so they no longer could be extracted. The SEC profile of the extract of paper stored for 2 years in the freezer was similar to the accelerated aged paper, verifying that extensive changes in extractives can take place also at very low temperatures (Freezer stored). To manage and control the surface and printing properties of paper, appropriate attention should be paid to the amount and composition of extractives and to the storage conditions, especially for paper made from mechanical pulps.

Cooperation:

Laboratory of Paper Coating and Converting; Laboratory of Fibre and Cellulose Technology

3.5 Chemicals from Wood

The PCC aims at developing fundamental and applied knowledge and new processes and products especially for the forest industry. Resource efficiency and sustainable utilisation of renewable wood and bark raw materials in environmentally sound processes, as well as the use of existing pulping and papermaking process streams are important.

The PCC's intensive work on biomass fractionation chemistry and technology, with the aim to obtain pure fractions of wood chemicals, i.e. extractives, hemicelluloses, tannins, lignin, and cellulose for further utilisation, has given promising results. A fundamental understanding on a molecular level of hot water extractions and the use of novel ionic liquids gives the basis for future biorefineries. For the hemicellulose fraction we aim at obtaining large, intact molecules, but also the smaller oligomeric fractions can be used (see below) Wood and bark can thus be fractionated into pure components, which can be used as such or further modified to novel biomaterials and biochemicals.

Chemical and enzymatic modifications and controlled block polymerisation of hemicelluloses, especially galactoglucomannans from spruce, have been done to introduce new properties to the polysaccharides. The aim is to eventually have polymers with, for example, tailored hydrocolloid properties or barrier properties that can be utilised in specialty paper grades, food packaging or even in textiles. Hemicellulose oligomers and specialty sugars, either as a fraction of the hot water extract or produced through controlled chemical or enzymatic hydrolysis, have potential as bioactive substances or as starting material for polymerisation reactions. Such compounds have been tested as plant growth stimulator, for their effect of pathogenic bacteria, and for possible effects in certain cancer cell models to mention a few areas of interest.

Polyphenols, not only from wood but also from bark, continue to be in focus in several projects. The analysis and recovery of polyphenols are studied and now special emphasis has been laid on testing them as bioactive compounds and protective chemicals. Structural and structure-activity-relationship studies, development novel lignan-based chiral ligands and catalysts, and the use of lignans in radical polymerisation together with lignin have given both a fundamental understanding and a basis for new products. Stilbenes, both from wood and bark, have shown extraordinary potential as bioactive and protective agents.

The production of liquid, solid and gaseous fuels or fuel precursors through pyrolysis has also been done. Gasification processes are of major interest for the forest based biorefinery concepts we are working with. We are also working with developing cost-effective and sustainable technologies that could be utilised to produce tailor made filler particles from agricultural by-products. These degradable fillers could be utilised in e.g. food, paper, and cosmetic products.

Aiming at a molecular understanding of new biochemicals, biomaterials, and novel biorefinery processes producing these offers a huge challenge for developing novel, reliable analytical methods, which have either an academic or an industrial relevance. This is

continuously done in most projects and a special example of tremendous international cooperation is the COST Action FP0901, “Analytical Methods for Biorefineries”, where experts can exchange ideas, methods, and experiences.

Chemistry in Forest Biorefineries II (Bioraff II)

Main funding: Tekes, Industry, Åbo Akademi

Markku Auer, Atte Aho, Pia Damlin, Paul Ek, Kim Granholm, Henrik Grénman, Leo Harju, Bjarne Holmbom, Mikko Hupa, Ari Ivaska, Jens Krogell, Bright Kusema, Ann-Sofie Leppänen, Isak Lindén, Nikolai DeMartini, Jyri-Pekka Mikkola, Dmitry Murzin, Päivi Mäki-Arvela, Patrycja Piotrowska, Andrey Pranovich, Kjell Saarela, Tapio Salmi, Victor Sifontes, Tao Song, Pingping Su, Anna Sundberg, Elena Tokareva, Johan Werkelin, Stefan Willför, Maria Zevenhoven

“Replacing petroleum-based synthetic materials and energy with wood-derived materials”

The biorefinery concept may be compared to an oil refinery and petrochemical plant, where fuels and numerous intermediates are produced for further processing into high-value and speciality materials. In biorefineries, the raw material is bio-based materials instead of mineral oil. Biorefinery development at the US and European level mostly covers the use of annual crops and other bio-based materials. In this project the focus is on non-food materials primarily in industrial pulp and paper processes, and this project is limited to forest-based biorefineries. The aim of the project is also to preserve the molecular structures created by nature as much as possible, to explore new separation and purification methods and look at new applications in areas such as: functional food, nutritional additives, functional additives in paper making, antioxidants, new bio-based materials and bio-based energy.

Research work is carried out in three areas: specialty chemicals and materials, metals in trees and fibres, and biofuels and bioenergy. Earlier, a considerable amount of information has been generated and reported in publications and research reports in this and closely related areas.

The emphasis of the project is in the areas that still are mostly unexplored or where the options for the renewing of process chemistry or products are greatest.

Work packages

(R – research, I – information package):

WP 1 Bio-based materials – R&I

- Biomass fractionation chemistry and technology
- Derivatives of hemicelluloses
- Cellulose derivatives as replacement for petroleum-based plastic

WP 2 Bioactive compounds from tree biomass – R&I

- Hemicelluloses as bioactive compounds
- Polyphenols as protective chemicals
- Specialty sugars

WP 3 Metals in trees, fibres and fuels – R

- Metal ions and functional groups in trees and pulp
- Removal of metal ions from process liquors
- Presence of trace elements in biofuels
- Analysis of ash from combustion of biomass based fuels
- On-line methods to monitor the papermaking process

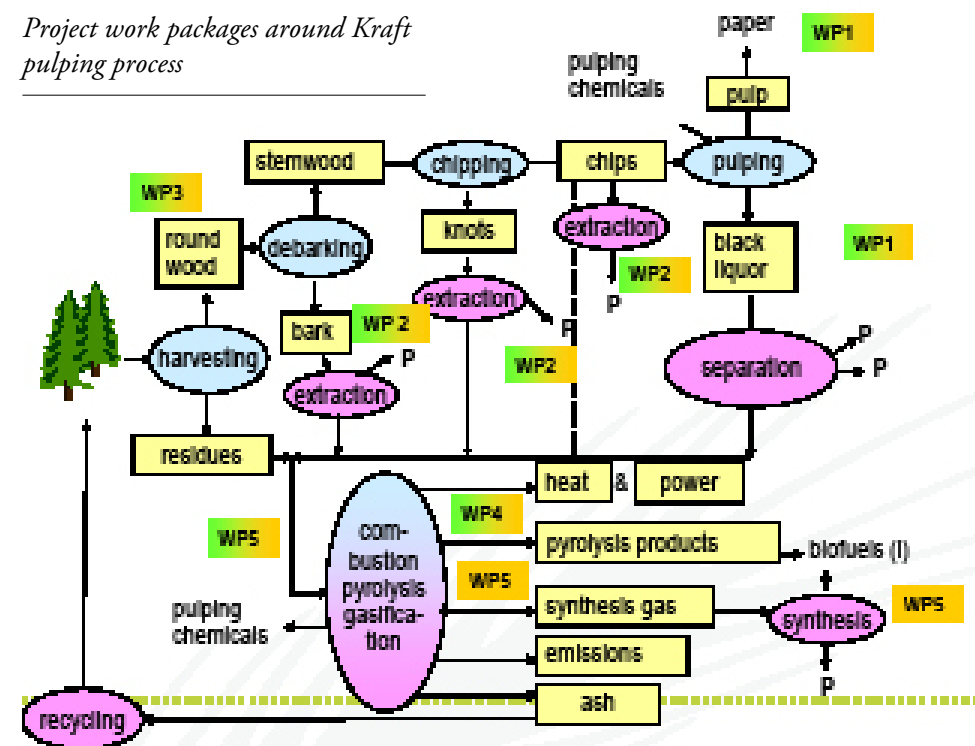
WP 4 Bio-based chemicals and fuels – R&I

- Influence of the impurities on the catalyst behaviour
- Options for catalysts for catalytic production of bio based liquid fuels

WP 5 Energy production options in the biorefinery – I (Information WP)

- Gasification based concepts to bark and forest residues and black liquor
- Advanced combustion and gasification characterization of various biomass fractions in a forest biorefinery

Project work packages around Kraft pulping process



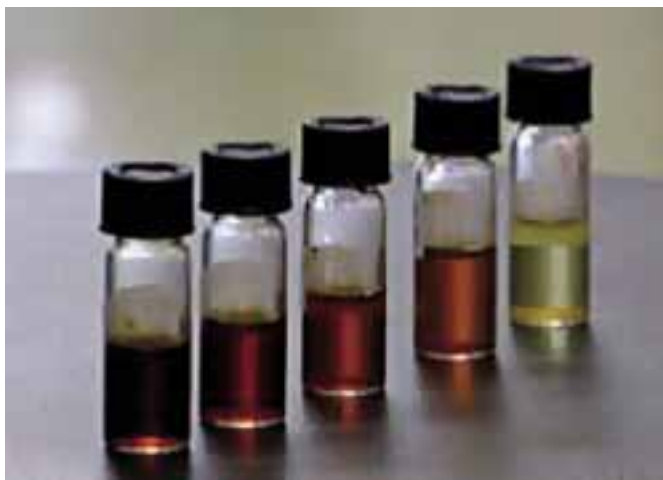
In biomass fractionation technologies one focus has been extractions of bark; the structure-preserving isolation has resulted in separation of stilbenes, betulinol, tannins and pycnogenol. The potential applications can be found in health food, dietary supplements, cosmetics and in technical antioxidants. The project focus is around the processes of existing chemical and mechanical pulping, as illustrated in the figure.

Extraction experiments of GGM from wood continued. GGM can be extracted from spruce in high yields and deacetylation and hydrolytic cleavage can be partly avoided. Here the control of pH plays important role. In modification of GGM the physicochemical properties of GGM were studied with the aim of utilizing them as hydrocolloids in various applications and products. Chemical and enzymatic modification (e.g. cationisation) was done to obtain novel functionalities and properties that could be used also in specialty paper grades.

Derivatisations of hemicelluloses have been carried on for these applications. Additional functionalities to hemicelluloses have been achieved. The results have been especially promising in hydrophobicity modifications and in modification of charge characteristics. Hemicelluloses in many applications would benefit from the modification of the structure, especially to improve compatibility and solubility challenges in some applications.

In WP 3 – Metals in trees, fibres and fuels – it is recognized that metal ions are essential in the growing process of trees and are taken up through the roots from the soil and therefore metals will inevitably be carried to the pulping process. E.g. on-line dynamic chemical fractionation through leaching was proven suitable for quantitative analysis of elements in a fully automated mode. Also studies on speciation of Ca in black liquor produced additional information for understanding the chemistry of black liquor from kraft pulping.

We found that liquid, solid and gaseous fuels or fuel precursors can be produced through pyrolysis, which is the thermal degradation of an organic material. The quality of the highly oxygenated bio-oil can be improved by deoxygenation over different catalysts. Pine wood as well as cellulose and lignin have been studied in the pyrolysis. The catalysts used in the upgrading of the pyrolysis vapours include mesoporous MCM-41 and proton form and iron modified ferrierite, beta and Y zeolites. The oxygen content in the bio-oil produced from cellulose could be decreased over different MCM-41-



Bio-oils from pyrolysis research

type materials. Deoxygenation of pine wood pyrolysis vapours was also achieved with both the proton and iron modified zeolites. However, ferrierite was quite inactive due to the smaller pore size. Bio-oil was also produced from lignin, with the major product being the solid residue, i.e. char.

The work in BIORAFF II in the fuels area is to follow up the different gasification concepts under development and to test and develop laboratory methods for the characterization of the various biomass feedstocks with respect to their potential and behavior in the different processes. This follow-up is partially based on the results of a parallel project in the Process Chemistry Centre.

Gasification processes are of major interest for the forest based biorefinery concepts. The final products from these processes under development are the Fischer-Tropsch hydrocarbon “waxes”, which can further be refined into liquid fuels for cars. The solid biomasses of the greatest interest are bark and forest residues. The gasifier, especially in gas phase, is sensitive to a number of fuel characteristics such as ash forming matter, volatile matter, and the char oxidation reactivity.

In the studies on the nitrogen distribution in different parts of trees during different annual seasons increased the knowledge of plant physiology. Studies were conducted for aspen, birch, pine and spruce.

The project has international collaboration with around twenty research groups in Europe, USA, Canada and China. In addition, a close collaboration is established with partners in the European Polysaccharide Network of Excellence (EPNoE) and Analytical Methods in Biorefineries (COST), all working with the same topic, biorefinery.

Cooperation

Steering group: Danisco Sweeteners; Fortum; Neste Oil; Metsä-Botnia; Pöyry Forest Industry Consulting; Stora Enso; UPM-Kymmene; VTT; Top Analytica; Forestcluster; ÅA-PCC

Publications

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Future Biorefinery (FuBio)

Main funding: Tekes, Forestcluster

Ikenna Anugwom, Tea Tönno, Johan Bobacka, Tao Song, Jens Krogell, Petri Kilpeläinen, Joakim Jakobsson, Ekaterina Korotkova, Robin Manelius, Patrik Eklund, Rainer Sjöholm, Jarl Hemming, Nikolai DeMartini, Christer Eckerman, Patrik Eklund, Tingting Han, Paula Heikkilä, Bjarne Holmbom, Mikko Hupa, Ari Ivaska, Victor Kisonen, Outi Niittymäki, Ann-Sofie Leppänen, Jyri-Pekka Mikkola, Dmitry Murzin, Päivi Mäki-Arvela, Andrey Pranovich, Markku Auer, Markku Reunanen, Tapio Salmi, Rainer Sjöholm, Annika Smeds, Anna Sundberg, Pasi Virtanen, Lari Vähäsalo, Johan Werkelin, Maria Zevenhoven, Stefan Willför

The FuBio project is a top-down planned research program that will lay the foundation for a new knowledge-based forest biorefinery platform in Finland. The core of the program is 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 (2009–2011) consists of five research themes:

1. Fractionation technologies – Ionic liquids, hot water treatment and separation of hydroxy acids from black liquor
2. Cellulose for material applications – New cellulose and cellulose fibre based materials
3. Hemicelluloses for materials and hydroxy acids – New hemicellulose based polymers
4. Lignin for energy and materials – not active in the beginning
5. Biochemicals for protection of products and health – High-value biomolecules for protection of products and health

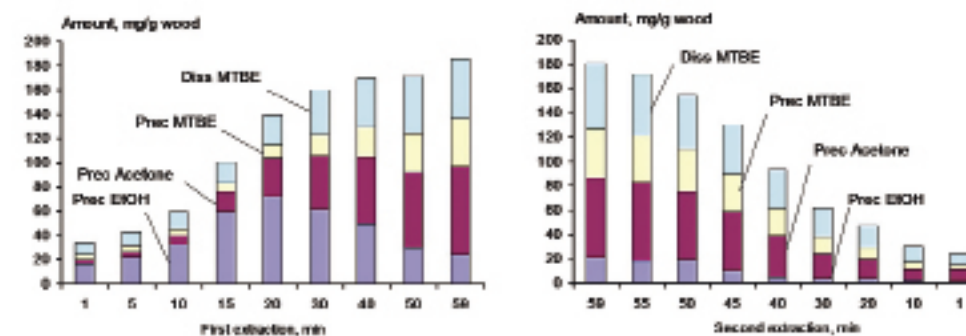
A sixth theme covers day-to-day management of the program and generates reports on specific topics. A literature review of both pyrolysis and gasification for black liquor and lignin was completed in the first year of this project. Both technologies were considered as possible means of upgrading these biomass streams to fuels and chemicals. In the second phase of this project we will be working in multiple concepts to evaluate the thermal treatment of waste streams.

Theme 1 focuses on two selected technologies, pressurized hot water treatment and ionic liquids, enabling novel fractionation of woody biomass into fractions with high potential for further refining. One aim is to obtain a new fundamental knowledge on structure preserving extraction and purification of major components from different parts of trees and create new ideas on chemical fractionation of wood to obtain high-value products.

One objective is 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. So far, finding optimal conditions for extraction of hemicelluloses from softwood with water in high yield and at the same time minimizing depolymerisation and deacetylation reactions has been in focus. Ground spruce sapwood was thus subjected to a series of sequential two-stage extractions with an Accelerated

Solvent Extraction (ASE) apparatus using plain water at 170°C, with 1 hour of total extraction time. The total yield of dissolved material after 1 h extraction was almost the same (about 25% of wood), irrespectively of the time ratios between the first and second extractions. The yield of hemicellulose polymers with an average molar mass of 8–10 kDa during the first stage extraction followed a Gaussian-type curve with a maximum at 20 min extraction time. The maximum yield of hemicellulose polymers was about 7%, on dry wood basis, which comprises about half of the total dissolved solids extracted at 20 min. A laboratory ultrafiltration technique was found useful to separate compounds according to molar mass in the hot-water extracts. Using a polyethersulfone UF-membrane with cut-off about 30 kDa, it was possible to isolate a fraction containing high-molar-mass compounds with an average Mw about 22 kDa.

Accelerated Solvent Extractor ASE 350



Mass-balance of fractions isolated by precipitation of water extracts from 1st and 2nd stages extraction in different solvents

Along with the progress of wood dissolution, the molar-mass of the hemicelluloses decreased and corresponding hemicellulose-derived oligomers dominated. The hemicelluloses and some pectin comprised 83–90% of the precipitated polymeric material; the content of galactoglucomannan in those precipitates was about 80%.

In terms of ionic liquid mediated fractionation, a breakthrough was reached and a patent application has been filed. The novel family of switchable ionic liquids used for this purpose are easy to generate; can be prepared from nature-derived species; are efficient even for never-dried industrial size wood chips; work for both soft- and hardwood (and other lignocellulosic species); do not require any stirring upon processing; work at relatively low temperatures (around 100°C); are reusable; and, lead to selective removal of hemicelluloses, lignin, and extractives from wood chips, leaving the three-dimensional cellulose network of the wood tissue untouched. Below a sample series of SEM images illustrate the power of this procedure.



Sample hardwood (*Birch, Betula pendula*) processing with SILs. 1) Native Birch; Birch after exposure to 2) CO₂-triggered and 3) SO₂-triggered carbonate vs. sulfonate salt, respectively

The target of Theme 2 is to develop technologies enabling modification of cellulose molecules and fibres from traditional, emerging, and future biorefineries. These up-graded cellulose products will be an essential part of novel materials, as well as find solutions in various relatively large scale applications within the wood products, packaging, graphical printing, tissue, and selected other value chains. Composite materials were produced from conducting polymer and cellulose. Polyaniline-cellulose composites were produced in the form of paper and the composite material was characterized by microscopy and electrical conductivity measurements. Composites consisting of cellulose beads and polyaniline were also successfully prepared and studied in this part of the project.

Theme 3 focuses on designing novel value chains, in which wood-derived hemicelluloses are converted into novel biopolymers, and to develop and test the technologies needed to enable such value chains in reality. Potential application areas of such biopolymers are e.g. in packaging, as coatings and films, and to improve the runnability of the paper machine. Different barrier properties are of special interest.

Different hydrophobic and cationic spruce galactoglucomannans (GGM) have been synthesized and evaluated in the project. Comprehensive data on controlled modification of GGM and resulting properties such as solubility and heat stability was obtained. Some hydrophobic GGM modifications showed promising results even as stand-alone films and later as coating of board regarding the barrier properties. These modified hemicelluloses have also called for the development of suitable analytical methods to follow the chemistry of the processes. Especially molar mass determinations and analysis of the degree of substitution called for improved methods.

Furthermore, some work has been done on purification of large-scale isolated hemicellulose fractions and analysis of the same. One important issue that has been addressed is the molecular structure and the possible presence of uronic acid units in GGM. Enzymatic depolymerisation and purification using ion exchange chromatography has been used to give a charged fraction that currently is being analysed further.

Theme 5 “Biochemicals for protection of products and health” focuses on biological and biomedical properties of wood and bark components, with the aim to create the knowledge base for development of bioactive products. Bioactive components could be used to protect biologically sensitive products, such as wood and paper products, or food and cosmetic products in packages, and as biomedically active components in dietary supplements, functional foods or pharmaceuticals.

In the work package “Hemicelluloses and specialty sugars”, we have studied the acid hydrolysis kinetics of galactoglucomannans in order to evaluate the possibility to produce monomeric and oligomeric sugars from GGM. We have also prepared and characterised GGM polymers and oligomers for further testing at the University of Turku on bifidobacteria and pathogenic bacteria present in the gastrointestinal tract. Specialty sugars have been tested at Pharmatest Services Ltd for their effect of pathogenic bacteria affecting the lower urinary tract, and for possible effects in certain cancer cell models.

In the work package “Polyphenols and tannins”, we have prepared different extracts rich in polyphenols, and pure polyphenols, from tree knots and bark of different tree species. The extracts and components have been tested at the Universities of Turku and Tampere for addressing the nature and extent of their bioactivity. The wide range of bioassays include, e.g., antimicrobial, biocidal, and anti-oxidative activity tests, as well as tests for the detection of anti-inflammatory, anti-allergenic, analgesic (pain-killing), anti-cancer, endocrine-, modulatory and immuno-modulatory properties. We have also prepared and characterised tannins extracted from barks and cones, which have been tested at the University of Eastern Finland, the University of Oulu and Metla for wood-protection properties.

Intensive planning has been conducted for a three-year continuation of the project. Based on the results obtained in FuBio 1, FuBio 2 will continue in three separate sub-programs and the PCC will be actively involved in all three of them.

Cooperation:

Forestcluster; VTT; Metla; Lappeenranta University of Technology; Aalto University; University of Jyväskylä; University of Helsinki; University of Turku; University of Tampere; University of Eastern Finland; Metsäliitto; Myllykoski; Metso; Kemira; BASF; Andritz; Pöyry; Stora Enso; UPM-Kymmene; Danisco; Orthotopix; Pharmatest Services; Separation Research

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Environmentally Sound Extraction of Biomass with Green Solvents

Main funding: Metla

Petri Kilpeläinen, Andrey Pranovich, Stefan Willför

The ultimate aim of this work is to develop and evaluate environmentally sound methods for extractions of biomass. Initially extractions will be done with pressurized hot water (PHWE) and supercritical carbon dioxide. Water-based extracts can also be further precipitated with supercritical carbon dioxide.

Birch sawdust was extracted using pressurized hot water at temperatures between 140 and 200°C. There was a constant flow of heated water through sawdust inside the extractions vessel. The aim of the extractions was to extract polymeric and water-soluble xylan. The extracts contained mostly polymeric, oligomeric and monomeric xylan. There was also some lignin derived compounds present in extracts. Most of lignin and almost all cellulose were, however, still present in the extracted sawdust. The extracted sawdust could be used in further processes for fractionation of lignin and cellulose.

The next phase of work is to study sequential carbon dioxide and water extraction. Supercritical carbon dioxide acts as a non-polar solvent like hexane. After extraction, carbon dioxide will evaporate from the extracts resulting pure substances. Water is a more polar solvent and pressurized hot water can be used to extract polyphenols and hemicelluloses from biomass. Compared to organic solvents, water and carbon dioxide are more environmentally friendly since they will not leave any harmful organic substances in extracted media.

Cooperation:

Metla; University of Helsinki

New Value-Added Natural Chemicals and Renewable Materials from Wood

Main funding: Academy of Finland, Tekes, Graduate School for Biomass Refining (BIOREGS)

Ann-Sofie Leppänen, Jens Krogell, Outi Niittymäki, Iveta Češková, Victor Kisonen, Petri Kilpeläinen, Jan-Erik Raitanen, Patrik Eklund, Rainer Sjöholm, Chunlin Xu, Markku Reunanen, Paula Ojala, Annika Smeds, Stefan Willför

This project aims at identifying natural tree compounds that can be upgraded to new value-added natural biochemicals or renewable materials. Chemical or enzymatic modifications in combination with state-of-the-art analytical methods are means used to produce potential bioactive or technically interesting biopolymers or biochemicals. These are then tested and evaluated for use in various applications.

Chemical or enzymatic functionalization of spruce galactoglucomannans (GGM) through, for example, acetylation, carboxymethylation, sulphonation, cationisation, enzymatic modification, and combinations thereof, have been carried out to introduce novel properties to the biopolymers. Native or functionalized GGM have also been tested in a wide range of different applications, for example in microencapsulation and in films, as emulsion stabilizers, as antibacterial substances, and as a possible substance in anticoagulant and antithrombotic drugs. Development of suitable analytical techniques for both native and functionalized biopolymers has also been in focus. Native hemicelluloses have also been tested in vitro as a feed source for ruminants and recently in vivo animal tests (sheep) were conducted in cooperation with MTT and Metla.

Phenolic compounds such as lignans, stilbenes, and flavonoids are potential antioxidants, radical scavengers, and bioactive substances that are of high interest to us. Structural studies and structure-activity-relationships for oxidized lignans may give new insights on how to utilise such compounds in e.g. medicine. An intensive analytical study on minor but still natively occurring softwood lignans have given valuable new data on the extractives in wood. Pinosylvin-type stilbenes and structurally similar norlignans synthesized from the abundant spruce knotwood lignan hydroxymatairesinol have been evaluated for their bioactive, antibacterial, and antifungal properties. Especially the pine heartwood substance pinosylvin showed potential for several applications and studies are ongoing to reveal the true potential of this compound.

Bark has been studied as a potential source of bioactive compounds and substrate for bioremediation. Furthermore, analyses of Soil Organic Matter (SOM) and the decomposition of different fractions thereof have been studied in cooperation with University of Oulu and Metla.

Cooperation:

UPM-Kymmene; Raisio Yhtymä; Metso Paper; M-real; Nordic Jam; Granula; Bio-Vita; Tampere University of Technology; University of Helsinki; University of Eastern Fin-

land (Kuopio); University of Oulu; Metla; University of Turku; University of Jyväskylä; VTT; MTT; Metla; KCL; Royal Institute of Technology (KTH), Sweden; University of Peshawar, Pakistan; Zonguldak Karaelmas University, Turkey; University of Maribor, Slovenia; University of Agricultural Sciences and Veterinary Medicine, Romania; Romanian Academy “P. Poni” Institute of Macromolecular Chemistry, Romania; “Al. I. Cuza” University, Romania; Universidad Miguel Hernández, Spain; Slovak Academy of Sciences, Slovakia; Health Sciences University of Hokkaido, Japan; Central Research Laboratories, Yomeishu Seizo, Japan; North Carolina State University, USA; United States Department of Agriculture, USA; Technical University of Luleå, Sweden; European Polysaccharide Network of Excellence (EPNOE)

Publications:

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Chemical Modification of Water-Soluble Spruce O-Acetyl-Galactoglucomannan

Main Funding: Graduate School for Biomass Refining (BIOREGS)

Ann-Sofie Leppänen, Haolin Lu, Patrik Eklund, Stefan Willför

The utilization of biomass as raw material and aqueous systems as solvents are steps towards more environmentally friendly synthetic procedures. Water is safe and cheap compared to many organic solvents, and when performing reactions in aqueous systems, water-soluble hydroxyl-containing compounds, such as polysaccharides, can be modified without the need of time-consuming protection-deprotection steps. O-acetyl-galactoglucomannans (GGM) is a potential raw material for natural biochemicals and biomaterials. GGM sorbes well to chemical pulps. By derivatizing only the galactose side groups, the high affinity to cellulose is preserved and modified GGM can be used for the functionalization of cellulose. The objective of this project is to develop modification procedures that are done in aqueous solutions, even with water as only solvent. Such procedures will lead to economically and environmentally more benign synthetic methods. The affinity of the modified GGM's to cellulose surfaces is also investigated.

One way of doing selective modification of galactose units in GGM is to combine enzymatic oxidation with chemical reactions. Examples on reactions where aldehyde groups formed during enzymatic oxidation are further chemically functionalized, are indium mediated allylation, and reductive amination. In addition to enzymatic oxidation, chemical oxidation has also been used for the activation of specific hydroxyls for further modification. The affinity of the modified polysaccharides to cellulose is also investigated.

Selective chemical modifications of GGM in water: Enzymatic oxidation followed by a) Indium mediated allylation and b) reductive amination. R = GGM backbone.

Cooperation:

University of Helsinki

Publications:

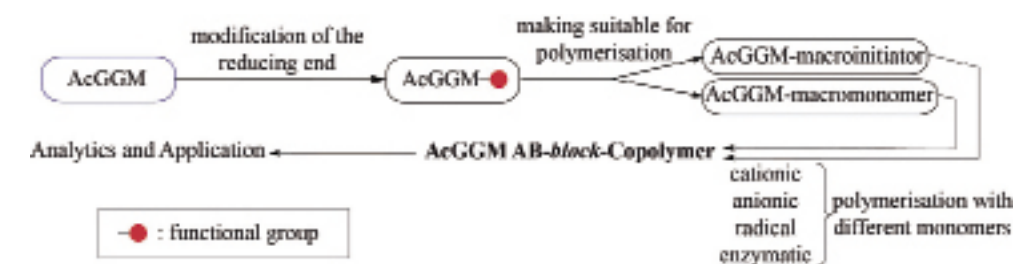
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Design of Hemicellulose Block Copolymers and Their Applications

Main Funding: Aides à la formation recherche (AFR)

Daniel Dax, Patrik Eklund, Filip Ekholm, Narendra Kumar, Markku Auer, Dmitry Murzin, Stefan Willför

Spruce O-acetyl-galactoglucomannans (AcGGM) can be isolated from wood or as a side product from process waters in paper production. The aim of this work is to modify AcGGM in order to produce AB-block-copolymers. In a first reaction, the reducing end of the polysaccharide chain has to be made suitable for a polymerisation. In subsequent reactions, polymerisation of a monomer can be performed. Depending on the physical properties of the monomers used, these reactions will result in AB-block-copolymers with different properties that can be used in different fields of application. Possible application might be modification of paper surfaces or as an additive in paints or cosmetics. In the illustration (see figure), the synthesis path is shown in a simplified way. In a first test, the oxidation of a monosaccharide (D-Galactose) was performed with H_2O_2 catalysed with tin modified Zeolites.



Aspired synthesis path for building up AcGGM-AB-block copolymers

A Sustainable Process for Production of Green Chemicals from Softwood Bark (PROBARK)

Main funding: Tekes, WoodWisdom Net

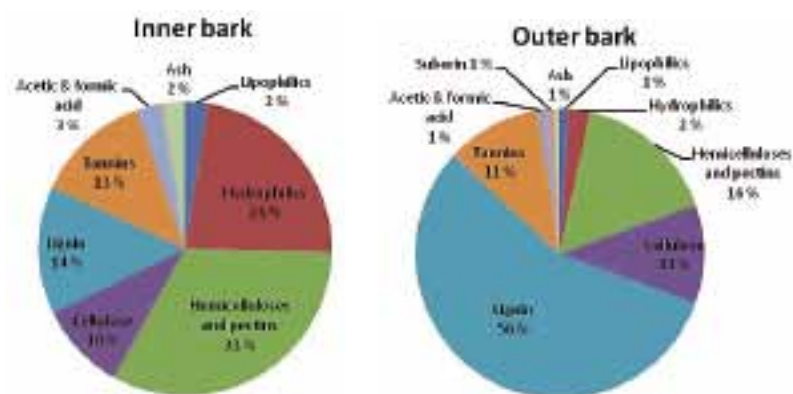
Jarl Hemming, Annika Smeds, Christer Eckerman, Jens Krogell, Sina Rasela, Bjarne Holmbom

The aim of this 3-year European project, which ended in March 2011, was to develop an “Integrated Bark Biorefinery”, in which softwood bark is efficiently used as a biomass feedstock for production of industrial and consumer products or suitable intermediates, and energy.

During the last year we have compiled our various extractions and chemical analyses on Scots pine (*Pinus sylvestris*) bark to a comprehensive overview of its composition pine bark, separately for inner bark and outer bark. The morphology and chemistry are very different for inner and outer bark and need to be studied separately, although it is not possible in industrial practice to separate inner and outer bark from each other.

Sequential extraction with 1. hexane, 2. ethanol and 3. pressurised hot water yielded fractions rich in 1. lipophilic extractives (fats and resins), 2. glucosides and sugars, as well as part of the tannins, and 3. hemicelluloses and pectins. The total extracted material amounts to more than half of the inner bark, but only to about 20% of the outer bark. The non-extractable residue consisted of cellulose and “Klason-lignin”, of which only a part is true lignin. The hemicelluloses and pectins have been further studied, and found to be composed mainly of arabinose, glucose and galacturonic acid units.

The pectic-type hemicelluloses have been isolated in larger scale from spruce inner bark for structural studies and testing of their bioactive properties. This work has been a cooperation with the research groups at the Royal Institute of Technology (KTH) in Sweden and the University of Oslo in Norway.



Group composition of pine inner and outer bark determined by sequential extractions and chemical analyses of the extracts and residues.

Cooperation:

VTI; Fraunhofer Institut, Germany; Royal Institute of Technology, Sweden; Technaro, Germany; University of Oslo, Norway

Publications:

- Xu, C., Qin, M., Fu, Y., Liu, N., Hemming, J., Holmbom, B., Willför, S., Lipophilic extractives in *Populus × euramericana* ‘Guariento’ stemwood and bark, *Journal of Wood Chemistry and Technology* 30 (2010) 2, 105–117

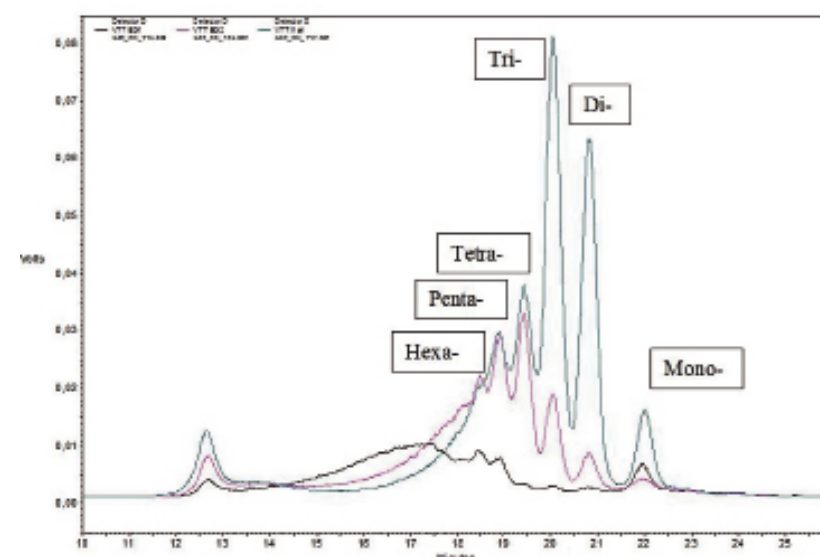
Upgrading Forest Industry Waste to Bioactive Chemicals for Crop Stimulation and BioControl (BioCrop)

Main Funding: Tekes, Industry

Stefan Willför, Robin Manelius

Today wood is primarily used as raw material for paper, building materials and furniture and for heating, while synthetic materials and chemicals have largely replaced the other, traditional, wood-based consumables. Wood could, however, have many other uses than being just a raw material for goods or fuel for heating. Trees have been shown to contain several bio-active compounds that can be used, for example in agriculture and in medicine.

Agrochemicals, such as fertilizers and pesticides, have to be used in order to make the agro-business profitable. A serious drawback in the usage of these mostly synthetic compounds is, however, that they pose a serious threat to human health and to the environment. The objective in this project is thus to combine ideas for forest side stream conversion to usable products with the need to pilot the agriculture towards environmentally friendlier farming techniques.



Isolated GGM is hydrolyzed using specific endo- and exo-acting enzymes: Endoglucanase I (black) and II (red) and Mannanase (green)

Wood raw materials were sampled, extracted and analysed. The main wood parts of interest are the bark, the wood knots (parts of the wood where the branches are attached to the tree trunk) and the hemicellulose galactoglucomannan (GGM). GGM can be hydrolysed with enzymes to obtain GGM oligomers (figure), which are tested as plant growth stimulators.

A feasibility study is essential to determine the usability. The availability of raw materials and the enrichment and extraction processes were studied in a literature survey. The survey outlined the most usable extraction methods and pinpointed several promising sources of raw materials. The efficacy tests determine, the usability of the extracts, e.g. for pest control and as plant growth enhancers (see the picture below).



The bark and knot extracts are tested for their efficacy on both pest control (left) properties and plant growth enhancers (right)

Cooperation:

VTT; MTT; UPM; Biolan, Hankkija Agrimarket/Aveve Group; Berner; Biokasvu; Neko; Agricultural University of Athens, Greece; Slovak Academy of Sciences, Slovakia

Upgrading Forest Industry Waste to Bioactive Chemicals for Crop Stimulation and BioControl (AgroBio)

Main Funding: Tekes, Industry

Stefan Willför, Robin Manelius, Magnus Gustavsson

The agriculture has to produce huge amounts of food to feed all people. The inevitable result of this is that an enormous amount of agro-waste is produced. The concept of converting organic agro-waste into valuable products is not a new one. Man has always converted all types of waste materials into products, especially at times when the supply of raw materials is scarce. In developed countries, however, economical and image factors and are often working against valorising of waste materials. Products, such as organic fillers, have therefore not been widely used even if the potential is great. Sustainability analyses are therefore almost as essential for the development of future successful applications, as the products themselves. Both materials and processes will be evaluated using tools developed for analysis of business operations (e.g. total life cycle analysis) so that the path is clear for a successful conversion of agro waste materials into products.

The project encompasses six work packages, where processing techniques and feasibility play a central role.

The main objective of the project is to develop cost-effective and sustainable technologies that could be utilised to produce tailor made filler particles from agricultural by-products (Figures A-C). More specific scientific and technological objectives of the project are to:

- Acquire raw materials and to study the demand of raw material pre-processing
- Develop the technology to convert agro side-streams, to tailoring of the material by chemical and enzymatic means, and to characterize the produced filler particles
- Evaluate the behaviour of the particles, in selected industrial uses, and their market potential
- Estimate the economic and business feasibility of the concept and compare it with the currently used filler materials



Figures A – C: Examples of side stream raw materials to be used in the project
A) From left: dried berry press cake fractions. The lighter materials on the right are untreated and ground bran
B) Low quality and un-matured berries to be discarded
C) Beet pulp cossettes

Cooperation:

Åbo Akademi University (Industrial Management); VTT; Sappi; Valio; Fazer; Hycail; Sokerijuurikkaan Tutkimuskeskus; University of Manitoba, Canada; Johan-Heinrich von Thunen Institut, Germany

COST Action FP0901, “Analytical Methods for Biorefineries”

Main funding: EU RTD 7th Framework Programme

Stefan Willför, Anna Sundberg, Anders Strand, Ari Ivaska, Sina Rasela

COST is an intergovernmental framework for European Cooperation in Science and Technology, allowing the coordination of nationally-funded research on a European level. FP0901 is chaired (Prof. Stefan Willför) and coordinated by Åbo Akademi University.

Trees, annual and perennial plants, recycled fibers, and lignocellulosic side streams from forest and agroindustry are renewable resources for the development of natural materials, biochemicals, and bioenergy. The chemical complexity of plant materials, the feed material of Biorefineries, renders the analyses of the feed constituents, processes, and valorized products challenging. The main objective of FP0901 is to develop new and evaluate existing analytical methods related to forest-based and agroindustrial Biorefineries. Especially analytical pretreatments are in focus. Critical steps are the representativeness of the sampling and samples, the extraction, fractionation, and sample storage methods applied. New methods are applied and evaluated for their relevance. Other emphasized areas are development of analytical on-line applications, hyphenated techniques, and applying statistical multicomponent analyses to sort out the relevant data from the main data stream.

Since start-up of the Action we have arranged workshops and seminars in Vienna, Hamburg, and Paris. Furthermore, several Short-Term Scientific Missions (STSMs) have taken place where Early Stage Researchers have visited other laboratories to learn new methods. One Training School on chemometrics for early stage researchers was arranged Rakvere in Latvia. A joint analysis project aims at comparing analytical methods used by different laboratories for a few well-defined samples. We also aim at involving relevant industrial partners to our Action. More information can be found at www.abo.fi/costfp0901.

Cooperation:

Universities, laboratories, research institutes, and companies from 27 EU COST and 4 affiliated countries.

Lignin Valorisation (LigniVal)

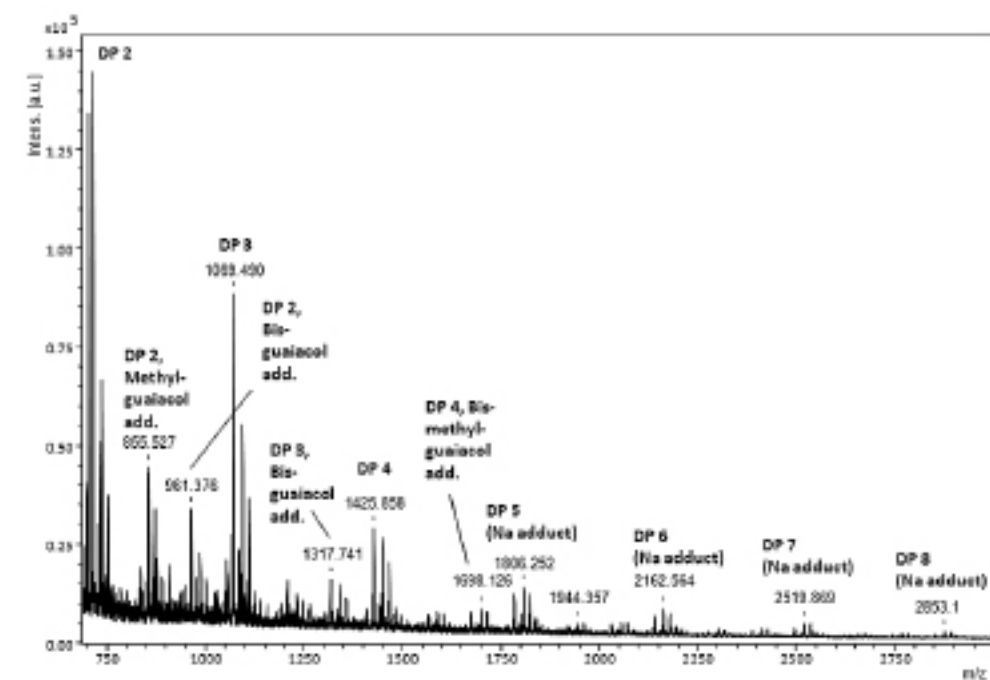
Main funding: Tekes

Annika Smeds, Patrik Eklund, Markku Reunanen, Andrey Pranovich, Stefan Willför

This project aims at finding new technologies for valorisation of lignin, that is, as a renewable wood and plant-based product replacement for oil-based polymers. The ultimate goal is to develop methods to modify lignin into materials applicable for composites, coating adhesives, and barriers.

Low-molecular aromatic compounds, such as lignans, are also an interesting source of phenolic materials, to be used as such, or in combination with lignins. In the LigniVal project, lignins and lignans are modified by chemical and enzymatic methods in order to produce lignins with a simplified structure and controllable reactivity. Co-polymerisation of lignin and lignans is applied in order to introduce more functionality to the materials.

Our task in the project has mainly been to study the reactions of the pure lignans matairesinol and pinoresinol with the stable radical DPPH. The results showed that both lignans reacted very rapidly with DPPH, and the reactions were almost quantitative. Pinoresinol formed polymers mainly in the MW range 2.5–21.4 kDa, whereas matairesinol formed polymers mainly in the MW range 1.8–5.3 kDa. The polymers contained mainly unmodified lignan units linked by 5–5' bonds.



MALDI-TOF MS spectrum of pinoresinol polymers. DP = degree of polymerization.

Cooperation:

VTT; University of Helsinki; Tampere University of Technology; North Carolina State University, USA; SCION, New Zealand; Mie University, Japan; Metso Power; Roal; Metsäliitto; Metsä-Botnia; Stora-Enso

Lignans as Versatile Chiral Auxiliaries and Chiral Catalysts (LIGNOCATS)

Main funding: Academy of Finland

Patrik Eklund, Yury Brutsentsev, Stefan Willför

The objective of this research project is to develop and evaluate lignan-based chiral catalysts for applications in modern organic synthesis. Recent progress and development of Finnish biorefinery processes has shown that enantiopure natural products belonging to the class of lignans can be isolated from spruce knotwood in large quantities. Although several natural products such as tartaric acids and carbohydrates have successfully been derivatized to well-working chiral ligands, this is the first research project to develop natural lignans into chiral ligands and catalysts.

The development of novel lignan-based chiral ligands and catalysts is divided in 3 separate lines. 1) Synthesis and evaluation of TADDOL like ligands (chiral 1,4-diols). 2) Synthesis and evaluation of phosphorous containing ligands 3) Synthesis and evaluation of chiral Brønsted acid catalysts. The chemical structure of hydroxymatairesinol allows us to prepare numerous different derivatives by suitable synthetic modifications. The synthetic modifications will include reductions, oxidations, metathesis, aryl-aryl couplings, Grignard reactions etc. The lignan skeleton is thus transformed into chiral ligands with different degree of flexibility or with fixed “biting angels” or with atropisomeric properties or with a combination of these. The synthesis and the properties of the novel catalysts is supported by molecular modeling. Also, some of the testing and evaluation of the catalysts will be performed by international collaborating researchers, making research visits between laboratories possible. The final applications of the catalysts will be focused of stereoselective carbon-carbon bond formations and enantioselective hydrogenations/reductions.

3.6 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 nanofibres 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 palladium species and testing the catalyst in liquid phase hydrogenation of citral demonstrated the big potential of this novel catalytic system (see chapter 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 done 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.

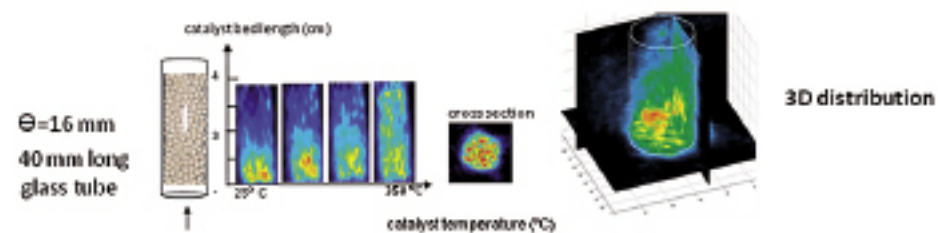
Modelling and simulation of catalytic reactors including catalyst deactivation and regeneration studies was a central topic of research. Advanced simulation techniques were applied in catalytic reactions in microreactors, gas-liquid reactors and various three-phase reactors, such as slurry and fixed bed reactors. The chemical applications were abatement of harmful emissions, synthesis of fine chemicals (e.g. derivatives of citral), and 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.

Micro and Mesoporous Materials

Main funding: Åbo Akademi

Narendra Kumar, Sabrina Schmidt, Matias Kangas, Eva Sárkadi-Pribóczki, Irina Simakova, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

Synthesis of new catalysts with different micro- and mesoporous materials has been carried out. The effect of ultrasonic treatment on zeolite crystallization has been studied. In situ metal modification has been applied in preparation of metal modified zeolites and molecular sieve catalysts. The prepared catalysts are characterized with modern techniques, such as XRD, SEM, TEM, AFM and TPD. The catalysts are applied in several 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.



Imaging of methanol on molecular sieve 4A

Cooperation:

Neste Oil; Ecocat; 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

Publications:

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Environmental Catalysis

Main funding: Academy of Finland

Kari Eränen, Hannu Karhu, Kalle Arve, José Rafael Hernández Carucci, Dmitry Murzin, Tapio Salmi

The project addresses fuel consumption and emissions from vehicles. The objectives are to show the potential for a continuous catalyst system to comply with the EU standard of year 2005 for diesel and lean-burn cars. An Ag/alumina catalyst converter, developed by our laboratory, has been installed in a prototype common rail diesel vehicle. This converter has shown high potential in NO_x reduction during stationary and transient vehicle tests. Detailed NO_x reaction mechanisms are investigated by transient techniques, combined with isotopic jumping, and the surface-induced gas-phase reactions are studied using modified reactor systems. New catalyst materials were prepared and characterized. Microreactors were successfully used in the development of HC-SCR catalysts.

Cooperation:

Several European universities and research institutes (Jyväskylä, Leuven, Mulhouse, Oulu, Prague, Beer Sheva, Lund, Sofia, Institute of Chemical Technology, Prague), European car manufacturers and catalyst manufacturers

Valorization of Components Derived from Biomass

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

Jyrki Kuusisto, Jyri-Pekka Mikkola, Mats Källdström, Anton Tokarev, Narendra Kumar, Bright Kusema, Victor Sifontes, Andreas Bernas, Heidi Bernas, Olga Simakova, Betiana Campo, Alexey Kirilin, Toni Riittonen, Bartosz Rozmysłowicz, Irina Simakova, Jan Hajek, Päivi Mäki-Arvela, Hannu Karhu, Dmitry Murzin, Tapio Salmi

Wood is one of the most versatile materials, being at the same time a renewable resource, for chemical derivatives of wood, which serve as raw materials for a large number of other chemical and reprocessing industries.

Chemical wood pulping processes extract many chemicals from wood – depending on the chemistry of the wood being pulped and the chemical process used. The liquors produced during kraft pulping cooking contain significant quantities of resin acids, tall oil, complex sugars and other organic compounds. Today, the most important chemical products originating from wood are various tall oil and turpentine products, but the markets are growing fast for several functional foods, like xylitol and sitosterol, e.g. products, which in addition to their nutritional function, have proven to promote health.

The project concerns valorization of components derived from biomass and focuses on catalytic hydrogenation of several types of sugars over supported metal catalysts, heterogeneous catalytic isomerization of linoleic acid and hydrogenolysis of hydroxymatairesinol. Within the framework of this project hydrogenation and oxidation of a disaccharide (lactose) is studied. The work of catalytic hydrogenolysis of hemicelluloses was started. Arabinogalactan from Siberian larch was the starting molecule. It turned out that the hydrogenolysis runs smoothly. Besides development of new active and selective catalysts, various aspects of reaction engineering, e.g. catalyst deactivation and reaction kinetics are considered.

Cooperation:

Université Louis Pasteur, Strasbourg, France; Prague Institute of Chemical Technology, Prague, Czech Republic; Forchem; Danisco; University of Helsinki; University of Turku; Technical University of Delft, Delft, the Netherlands; University of Cantabria, Cantabria, Spain; Boreskov Institute of Catalysis, Novosibirsk, Russia; Universidad Nacional del Sur, Bahía Blanca, Argentina

Publications:

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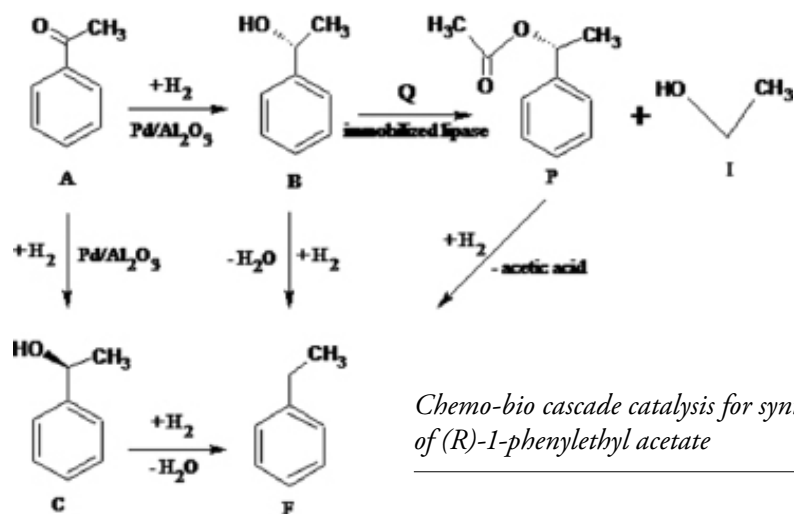
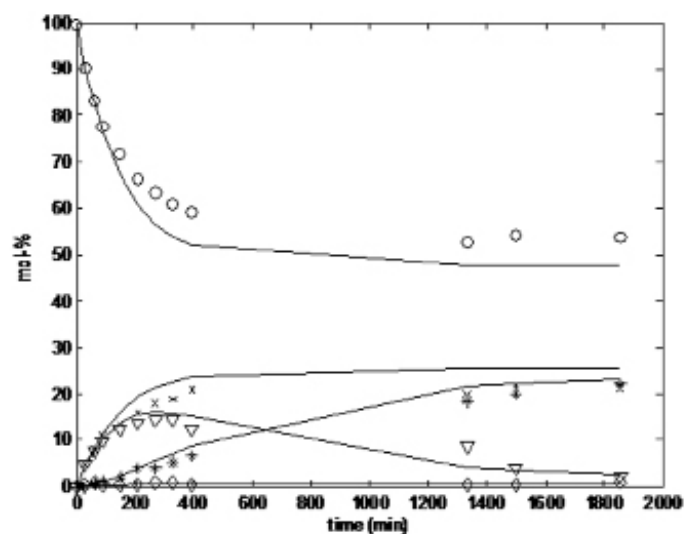
Asymmetric Catalysis

Main funding: Academy of Finland

Esa Toukoniitty, Igor Busygin, Päivi Mäki-Arvela, Ville Nieminen, Serap Şahin, Alexey Kirilin, Gerson Martin, Rainer Sjöholm, Reko Leino, 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. A particular emphasis is put on the development of better catalyst modifiers in collaboration with the research group at the laboratory of Organic Chemistry, Åbo Akademi University (Professor Reko Leino). 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 reactors and the transient behaviour of the system has been modelled quantitatively. Chemo-bio synthesis work in one pot was initiated and it was demonstrated that the concept works. Future work will be directed to a combination of enantioselective hydrogenation and chromatographic separation.

One-pot synthesis of (R)-1-phenyl ethyl acetate over Pd/Al₂O₃ and lipase catalysts at 70°C



Chemo-bio cascade catalysis for synthesis of (R)-1-phenylethyl acetate

Cooperation:
University of Turku

Publications:

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3.7 Biofuels and Bioenergy

The importance of biofuels has continuously increased. Today many thermal power plants are using or planning to use biofuels and waste derived fuels of various kinds instead of coal or other fossil fuels. The new biorefinery concepts all include conversion of parts of the feedstock biomass into energy via some novel processes based on pyrolysis, gasification or combustion. The PCC aims at developing improved understanding of chemical aspects in biofuel conversion processes – this way paving the road for development of future fuel conversion technologies.

To be able to use the many new biofuels, waste derived fuels or fuel mixtures with no increased flue gas emission or plant availability (corrosion, fouling) problems is a major challenge and requires deep understanding of the properties of the fuels. Conventional fuel analysis is not sufficient to evaluate the practical feasibility of these fuels.

The PCC has a wide fuel data base and we have developed several unique laboratory techniques to characterize the fuels for their combustion behaviour and emission formation tendency. The focus is on biofuels and wastes including wood and forest residues, black liquor, side streams from biorefinery processes and various waste derived fuels (RDF, PDF). Our laboratory tests and analysis techniques are further developed and applied. Combustion rates (devolatilization, char oxidation) are determined for single particles. Release rates and yields of the key elements as function of the combustion process are determined. The fate of the 12 heavy metals referred to in the recent EU Waste Incineration Directive will be of special interest.

The PCC also develops and applies modelling capabilities to make it possible to predict the combustion process for non-conventional fuels and, in particular, mixtures of two or more different fuels. Computational Fluid Dynamics, CFD, has opened excellent opportunities to study biofuel conversion in realistic furnace environments. To be useful in biofuel conversion processes these advanced CFD models however require tailored submodels to describe the many important aspects of the practical biofuel processes. We develop submodels for fuel particle oxidation, the chemistry of the unwanted pollutants, the fuel and ash particle behaviour, and fouling and corrosion phenomena in furnaces.

To be able to understand and predict the behaviour and interaction of fuels in a furnace when several fuels are used simultaneously is a major challenge. The emission formation tendency (NO_x , SO_x , trace metals) and the behaviour of the ash forming matter of fuel mixtures is studied using a variety of experimental and modelling techniques, including validations by full scale boiler measurements. These research projects are done in close collaboration with the major boiler manufacturing and energy companies.

In 2010 two major measuring campaigns were done in large scale combustion furnaces to get in-furnace information such as main gas composition, concentration of nitrogen and sulphur oxides and their precursors such as hydrogen sulphide and ammonia or hydrogen cyanide. These very tedious measurements have now given strong support to the furnace

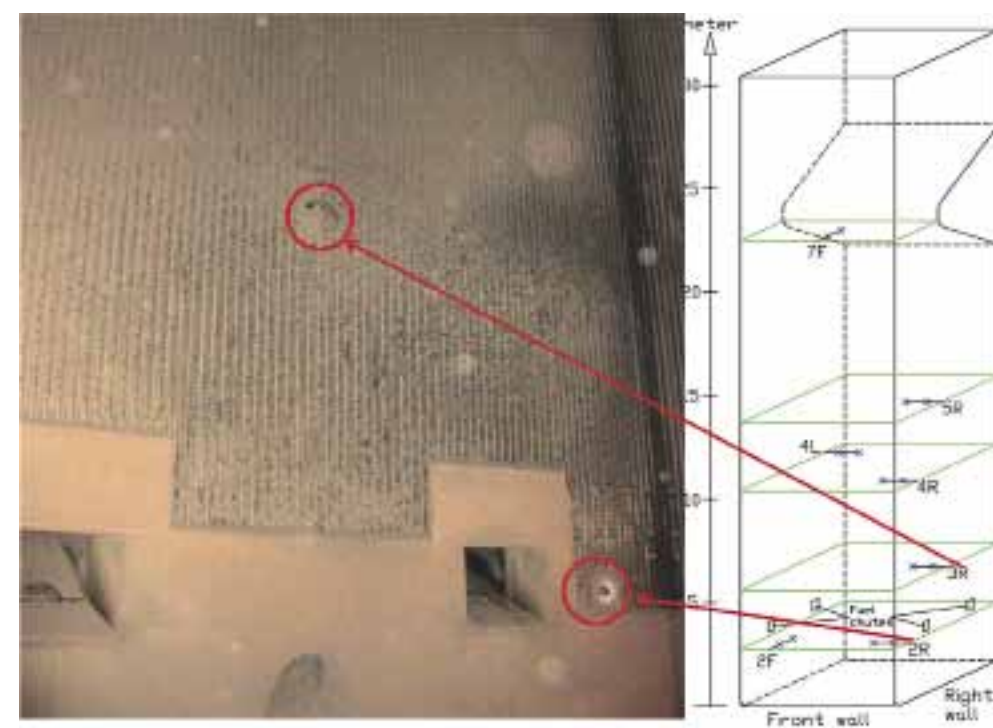
modelling activities. In the present year and near term future the data obtained are used to test and validate several of the furnace model components.

The biorefinery concepts imply the option of production of bio-based liquid fuels for use in vehicles by processes based on pyrolysis or gasification. All of the interesting process concepts require fundamental understanding of the conversion chemistry itself, but also of the behaviour of the many impurities in the biomass materials being used as feedstock. The laboratory scale fluidized bed pyrolysis work in the last two years at our Centre has been very fruitful. We have been able to carefully characterize the pyrolysis product composition as function of the feedstock properties. We have also demonstrated the potential of upgrading of the pyrolysis gas by *in-situ* catalytic conversion using a separate catalyst bed immediately behind the pyrolysis reactor.

Chemistry in Biomass Combustion (ChemCom 2.0)

Main funding: Tekes

Patrik Yrjas, Mikko Hupa, Rainer Backman, Anders Brink, Maria Zevenhoven, Nikolai DeMartini, Esperanza Monedero, Mikael Forssén, Johan Werkelin, Daniel Lindberg, Markus Engblom, Tarja Talonen, Micaela Westén-Karlsson, Tor Laurén, Johan Lindholm, Oskar Karlström, Juho Lehmusto, Patrycja Piotrowska, Na Li, Hao Wu, Dorota Bankiewicz, Bingzhi Li, Heddy Koyya, Emil Vainio, Niklas Vähä-Savo, Pasi Vainikka, Anders Bäckman, Christoffer Sevoni, Mia Mäkinen

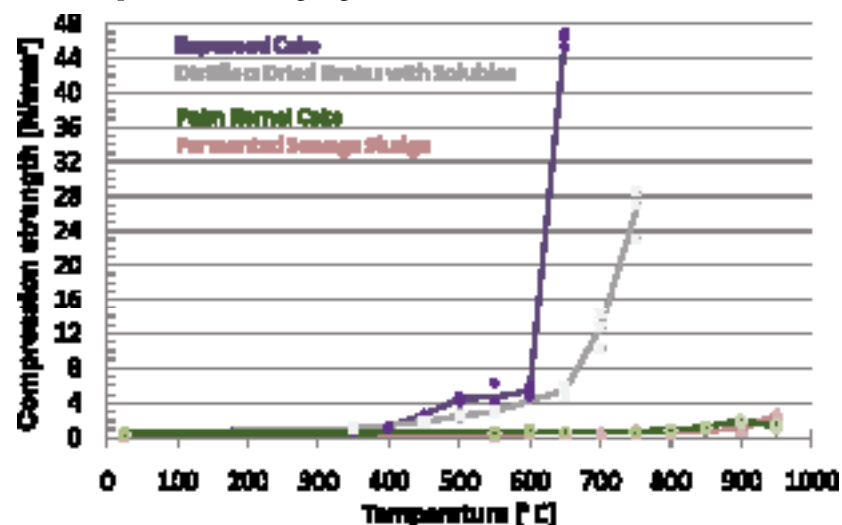


Some of the gas measurement points in an industrial bubbling fluidized bed

ChemCom 2.0 started in January 2008 and ended in February 2011. The project focused on fundamental chemical questions and solutions in combustion and gasification of solid biofuels and black liquor. However, although biofuels and black liquor were in focus, also waste fuel combustion was investigated. A heavy input on modelling of both bubbling fluidized beds and recovery boilers have been done and several different submodels have been produced. As a consequence, one of the main needs and also objectives of ChemCom 2.0 was the validation of these models, in combination with identifying shortcomings of the models and improving them. This is of highest importance since CFD modelling is nowadays utilized in the analysis of the reasons of practical furnace problems, and as a design tool in retrofit applications and in designing new furnaces.

Data for the validation has been gathered by measuring critical parameters during measurement campaigns in one recovery boiler in Pietarsaari (February 2009) and in one bubbling fluidized bed in Rauma (October 2009), in combination with laboratory testing and fuel analyses.

Although, modelling and model validation have had large roles in this project, also other issues will be emphasized to clarify fundamental chemical phenomena in combustion and gasification processes (see e.g. figure below).



Effect of temperature on ash sintering; an example of characterization results of ash from residual fuels – a rest from the production of liquid biofuels

Other issues studied in the project were the behaviour and release of ash forming matter and trace metals, corrosion issues, gaseous emissions, thermodynamic data development and calculations, combustion and gasification rate studies of biofuel and black liquors, etc. These subjects, among others, were in ChemCom 2.0 organized by using four overall topics:

- Full-scale measurements (F)
- Experiments (E)
- Modelling and validation (M)
- Information (I)

Based on the results obtained from the measurements in the recovery boiler several papers have been published e.g. four papers were orally presented at the International Chemical Recovery Conference, March–April 2010 in Virginia, USA and based on other project results a number of papers were presented in the Conference on Impacts of Fuel Quality on Power Production in Aug.–Sept. 2010 in Saariselkä, Finland. In total, 22 papers (journal and conference), two doctoral theses, three licentiate theses, one diploma thesis as well as a number of workshop and seminar papers have been published by ÅA within this project.

Cooperation:

Aalto University School of Chemical Technology; Tampere University of Technology; VTT; Andritz; Foster Wheeler Energia; International Paper; Metso Power; Metsä-Botnia; Clyde Bergemann; UPM-Kymmene

Publications:

- Engblom, M., Modeling and Field Observations of Char Bed Processes in Black Liquor Recovery Boilers, *Report 10-1, Åbo Akademi Process Chemistry Centre, Laboratory of Inorganic Chemistry*, ISBN 978-952-12-2440-9, Painsalama, Turku, Finland 2010 (doctoral thesis)
- Bäckman, Anders, Konstruktion och drift av ett laboratoriereaktorsystem för studier av reaktionerna mellan kaliumkloridångor och aluminiumsilikater (*Construction and running of a laboratory reactor system for studies of the reactions between evaporated potassium chloride and alumina silicates*, in Swedish), MSc Thesis
- Bergroth, N., Engblom, M., Mueller, C., Hupa, M., CFD-based modeling of kraft char beds – Part 1: Char bed burning model, *Tappi Journal* 9 (2010) 2, 6–13
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- DeMartini, N., Monedero, E., Yrjas, P., Hupa, M., Co-firing black liquor and biomass in a laboratory single droplet reactor – effects on emissions and combustion characteristics, *Tappi Journal* 9 (2010) 9, 29–34
- Engblom M., Bergroth, N., Mueller, C., Jones, A., Brink, A., Hupa, M., CFD-based modeling of kraft char beds – Part 2: A study on the effects of droplet size and bed shape on bed processes, *Tappi Journal* 9 (2010) 2, 15–20
- Giuntoli J., de Jong W., Verkooijen A.H.M., Piotrowska P., Zevenhoven M., Hupa M., Combustion characteristics of biomass residues and biowastes: Fate of fuel nitrogen, *Energy & Fuels* 24 (2010) 10, 5309–5319
- Link, S., Arvelakis, S., Hupa, M., Yrjas, P., Külaots, I., Paist, A., Reactivity of the biomass chars originating from reed, Douglas fir, and pine, *Energy & Fuels* 24 (2010) 12, 6533–6539
- Lundmark, D., Mueller, C., Backman, R., Zevenhoven, M., Skrifvars, B-J., Hupa, M., CFD based ash deposition prediction in a BFBC firing mixtures of peat and forest residue, *Journal of Energy Resources Technology* 132 (2010) 3, 031003/1–031003/8
- Piotrowska, P., Zevenhoven, M., Davidsson, K., Hupa, M., Åmand, L.-E., Barišić, V., Coda Zabetta, E., Fate of alkali metals and phosphorus of rapeseed cake in circulating fluidized bed boiler, Part 1: Co-combustion with wood, *Energy & Fuels* 24 (2010) 1, 333–345
- Piotrowska P., Zevenhoven M., Davidsson K., Hupa M., Åmand Lars-E., Barišić V., Coda Zabetta E., Fate of alkali metals and phosphorus of rapeseed cake in circulating fluidized bed boiler, Part 2: Co-combustion with coal, *Energy & Fuels* 24 (2010), 4193–4205

- Saw, W.L., Hupa, M., Nathan, G.J., Ashman, P.J., Influence of stoichiometry on the release of atomic sodium from a burning black liquor droplet in a flat flame with and without boron, *Fuel* 89 (2010) 9, 2608–2616
- Saw, W.L., Nathan, G., Ashman, P., Alwahabi, Z., Hupa, M., Simultaneous measurement of the surface temperature and the release of atomic sodium from a burning black liquor droplet, *Combustion and Flame* 157 (2010) 4, 769–777
- Saw, W.L., Nathan, G.J., Ashman, P. J., Hupa, M., Influence of droplet size on the release of atomic sodium from a burning black liquor droplet in a flat flame, *Fuel* 89 (2010) 8, 1840–1848
- Werkelin, J., Skrifvars, B.-J., Zevenhoven, M., Holmbom, B., Hupa, M., Chemical forms of ash-forming elements in woody biomass fuels, *Fuel* 89 (2010) 2, 481–493

Science to Biomass Combustion

Main funding: ERANET Bioenergy (Tekes)

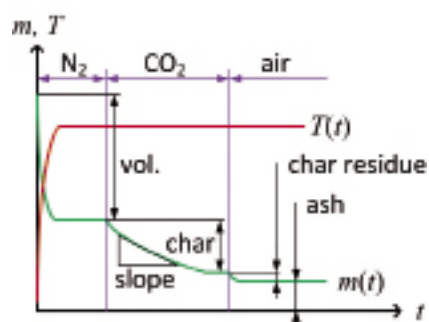
Maria Zevenhoven, Anders Brink, Oskar Karlström, Johan Werkelin, Daniel Lindberg, Bingzhi Li, Piia Leppäsalo, Luis Bezerra, Peter Backman, Mikko Hupa

It is essential to gain knowledge about the combustion and volatile release behavior of different fuels and fuels mixtures. This is of special relevance for “new” and “difficult-to-use” fuels (e.g. short rotation crops, energy grasses and residues from agricultural industries), which usually show considerably higher ash contents and lower first ash melting temperatures in comparison to conventional wood fuels (wood pellets, wood chips, bark) leading to increased problems concerning slagging, ash deposit formation and fine particulate emissions (heavy metals such as Cd, Pb Zn). Moreover, these fuels usually show elevated N, S and Cl contents leading to increasing SO_x, NO_x and HCl emissions.

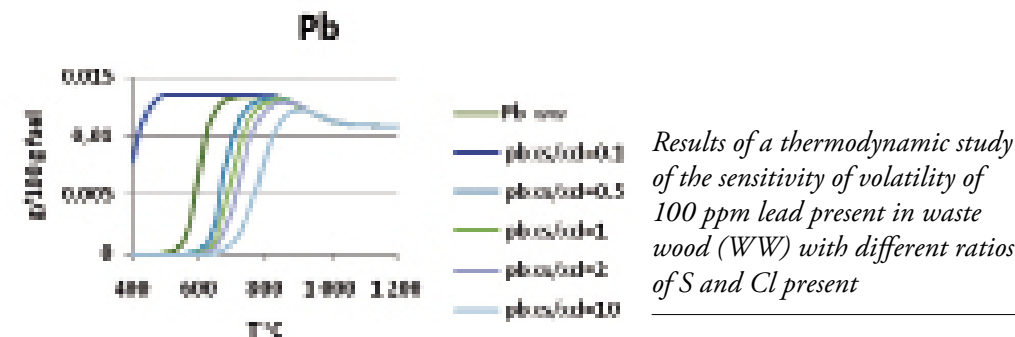
Modern simulation tools are needed to efficiently analyse the underlying processes during biomass combustion. For biomass combustion plants, CFD modeling may be a highly efficient tool for process analyses as a basis to optimize plant design concerning flue gas burnout, CO emissions, plant efficiency and availability.

The project is aiming at the development of advanced fuel analysis and characterization methods concerning the combustion of different biomass fuels in various plant technologies of different size ranges. The goal is to provide the basis for an improved understanding of the combustion behaviour and to collect the data in an advanced fuel database.

For example experiments in a ThermoGravimetric Analyser (TGA) provide basic input data for the kinetic modeling of pyrolysis of the above mentioned fuels.



TGA curve obtained when pyrolysing biomass fuels in N₂



Results of a thermodynamic study of the sensitivity of volatility of 100 ppm lead present in waste wood (WW) with different ratios of S and Cl present

The advanced fuel characterization methods, together with thermodynamic studies and CFD based models will contribute to a more efficient and reliable design of future biomass furnaces and boilers and will contribute to a better understanding of the differences regarding combustion behavior between various fuels or fuel mixtures.

Cooperation:

Technical University of Denmark, Lyngby, Denmark; Norwegian University of Science and Technology, Trondheim, Norway; BIOENERGY 2020+, Graz Austria

Publications:

- Karlström, O., Brink, A., Hercog, J., Hupa, M., Tognotti, L., Oxidation model for 24 bituminous coal chars: variable or constant activation energy?, Proceedings: 33rd International Symposium on Combustion, August 1–6, 2010, Beijing, China

Design of Novel Non-halogenated Flame Retardants – Combustion and Polymer Scientists Join Forces (PyroAzo)

Main funding: Academy of Finland/Ketju

Johan Lindholm, Anders Brink, Mikko Hupa

In the project new flame retardants in the family of novel azoalkane flame retardants are developed. The approach is based on synthesis of novel model flame retardant compounds; new fire test methodologies; and new techniques for evaluating results, including mathematical modelling and simulation that will further increase the knowledge in fire retardancy theory and applications. During 2010 scaling effects in the Cone Calorimeter technique has investigated. Down scaling of the technique may be of interest when working laboratory synthesized chemical. In addition various types of mainly inorganic flame retardants for use with polyurethane glues have been investigated.

Cooperation:

Åbo Akademi University (Polymer Technology)

Future Combustion Technology for Synthetic and Renewable Fuels in Compression Ignition Engines (ReFuel)

Main funding: Tekes

Anders Brink, Mikko Hupa

“Future Combustion Technology for Synthetic and Renewable Fuels in Compression Ignition Engines, Project ReFuel” is a research project towards emission-free engine combustion with future fuels and future combustion technology. The project is carried out in the years 2009 – 2011.

The objective of the project is to develop new extremely low emission combustion technologies for renewable fuels in compression ignition engines. The target is to cut down emissions at least by 70%. The scope is to utilize the physical and chemical properties of the renewable fuels that differ from properties of the traditional crude oil based fuels and to develop optimum combustion technologies for them. The project is also a part of a Collaborative Task “ReFuel” of the International Energy Agency (IEA) Combustion Agreement coordinated by Finland. Countries Participating the Combustion Agreement are: Belgium, Canada, Germany, Finland, Italy, Japan, Korea, Norway, Sweden, Switzerland and USA. Moreover, the international program “ReFuel” will be a collaboration framework between IEA Combustion Agreement and IEA AMF (Advance Motor Fuels) Agreement.

In this project, the ÅA-PCC is responsible for combustion chemistry and emission chemistry. During 2010 soot precursors and NO_x formation have been modelled using conditions typical for Diesel engines with exhaust gas recirculation. Especially recycled NO showed an interesting behaviour. At low temperatures the NO was oxidized to NO₂. Two distinct temperature regimes, where reburning occurred, could also be identified.

Cooperation:

Aalto University School of Science and Technology; Tampere University of Technology; VTT

Feasibility of Finnish and Brazilian Biomasses in Advanced Biorefineries (FEASEBIO)

Main funding: Academy of Finland, CNPq, Brazil

Johan Werkelin, Mikko Hupa, Konstantin Gabov, Pedro Fardim

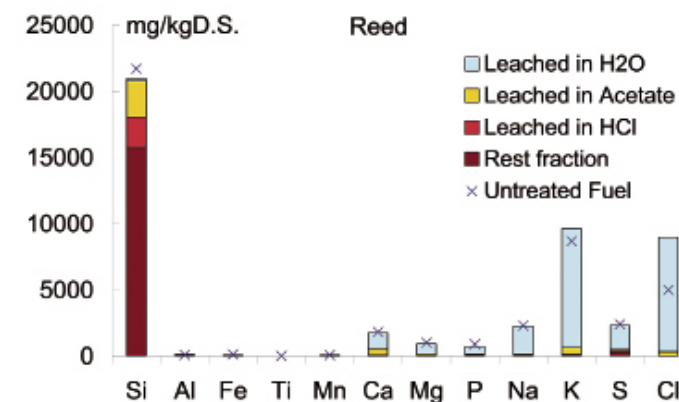
The feasibility of Finnish and Brazilian biomasses to thermal and bioconversion is a key question to advance the utilization of biomass for production of fuels, chemical and materials. This three year project started in 2010 and aims to take a unique research approach combining advanced pretreatment of the biomass with excellent expertise in thermal and bioconversion.

In case of Brazil, the use of sugar cane to produce bioethanol contributes to reduce the country’s petroleum dependence. Nowadays 7 million hectares of field is used in Sugar cane farming in Brazil and it is estimated that the area will grow 12% a year over the next five years. In the production of bioethanol, large amount of bagasse is formed from the sugar cane. Bagasse is a promising feedstock material to thermo- and bioconversion, but research and development is needed to make a feasible conversion processes from bagasse to fuels, energy and chemicals.

In southern Finland there are 30 000 hectares of common reed from which 12 000 hectares are suitable for bioenergy consumption. Reed is a fast growing biomaterial which is underused and is a potential raw material of thermal conversion. One of the goals of this project is to produce much needed information into burning technology and also new ideas on feasibility of reed as feedstock to thermal conversion and bioconversion. Birch, Eucalyptus and Pine on the other hand, are commonly used raw materials in the Finnish pulp and paper industry. Residues from pulp and paper industry are mostly used for their fuel value to produce steam and energy but could also be used as a stock material in bioconversion processes.

The research concerning energy conversion focuses on fuel characterization, ash behaviour (agglomeration, formation of deposits, heavy metals), corrosion, and CFD-modelling of different biomass boiler applications. The Laboratory of Inorganic Chemistry have a broad set of test techniques to characterize the technical feasibility of different kinds of biomasses (including bi-products and e.g. black liquor) for thermal conversion. These methods have proven to give highly relevant and useful information about the properties of the feed stocks with respect to thermal conversion.

Finnish reed, Brazilian bagasse and birch wood lignin from hydrothermal extraction was analysed by thermal gravimetry (TG) for proximate analysis, chemical fractionation analysis (CFA) for quantification of its ash-forming matter. The samples were further combusted in a single particle reactor (SPR) for quantification of fuel-NO_x and SO₂ formation, and pyrolysed in a wire-mesh reactor (WMR) to quantify the release of some ash-forming elements to the gas phase.



Chemical fractionation analysis of the minor elements in Finnish reed

The tests showed that reed and bagasse have lower energy density and more problematic ash-forming matter like water-soluble potassium and chlorine (see figure above) compared to coal – the conventional solid fuel for heat and power production in the two countries. However, large-scale utilization of these biomasses is still possible, i.e. in co-combustion with coal.

The sulphur-free lignin produced by hydrotropic extraction is a promising raw material in the production of important platform chemicals or bio-oil. It is practically ash-free and the char yield in rapid pyrolysis is only 20% of the dry weight.

Cooperation:

Centre of Sugarcane Technology; University of São Paulo, São Paulo, Brazil; Åbo Akademi University (Fibre and Cellulose Technology)

Publications:

- Werkelin, J., Skrifvars, B.-J., Zevenhoven, M., Holmbom, B., Hupa, M., Chemical forms of ash-forming elements in woody biomass fuels, *Fuel* 89 (2010) 2, 481–493

Shipping-induced NO_x and SO_x Emissions – Operational Monitoring Network (SNOOP)

Main funding: EU/Central Baltic INTERREG IVA; Centre for Economic Development, Transport and the Environment (ELY) of Southwest Finland

Anders Brink, Kalle Arve, Kari Eränen

Maritime born traffic is international by its nature which makes also its emissions internationally important issue. After MARPOL 73/78 Annex IV is entered into force, shipping-induced SO_x and NO_x emissions are regulated stricter. Based on an existing framework of ship exhaust emission, SNOOP aims to take the strategic evaluation of ship emission effects to a new level by enlargement the scope from nitrogen oxides to SO_x, PM, CO and CO₂ emissions. The cause-effect chains are studied by monitoring ambient air quality and estimating its human health effects in harbour areas, by modelling the nitrogen input from ship exhaust emissions to marine environment and the impact of nitrogen emissions on marine environment. SNOOP also pursues to establish a long-term follow-up network on ship exhaust emissions in the Central Baltic area, to study the effects of emissions on marine ecosystem and to tie the information from the network to an effect estimation framework for large cities. The results are tied to policymaking through liaison with the policy process as well as through the organisation of thematic policy forums addressing shipping emissions.

In this project the ÅA-PCC focuses on two different topics. One is emission modelling based on AIS data combined with a vessel data base, the second is laboratory measurements of NO adsorption into water.

Cooperation:

City of Turku (Environmental and City Planning Department); Finnish Meteorological Institute; HSY Helsinki Region Environmental Services Authority; University of Turku (Centre for Maritime Studies); Åbo Akademi University; Metropolia University of Applied Sciences; Kymenlaakso University of Applied Sciences; Estonian Environmental Research Centre; Tallinn University of Technology (Marine Systems Institute)

Future Combustion Engine Power Plant (FCEP)

Main funding: Tekes, Consortium partners

Anders Brink, Mikko Hupa

The objective of the FCEP research program is to ensure that Finnish combustion engine industry can maintain its leading position on global markets. The objective of the program is to support Finnish companies and research institutes through close cooperation to further develop their research facilities, know-how, technologies and products to meet the future market requirements, which are closely connected to the emissions legislations including greenhouse gas emissions. The ÅA-PCC is participating in three out of a total of six work packages. These work packages are WP1: Advanced Combustion, WP3: Emission Control and WP5: Intelligent Automation and Control.

Consortium:

ABB; AGCO SISU POWER; Ecocat; Gasum; Metso Power; Metso Automation; Wapice; Wärtsilä Finland; Centre for Metrology and Accreditation; Lappeenranta University of Technology; Tampere University of Technology; Aalto University; Turku University of Applied Sciences; University of Oulu; University of Vaasa; VTT; Åbo Akademi University

COST Action CM901: Detailed Chemical Kinetic Models for Cleaner Combustion

Main funding: EU RTD 7th Framework Programme

Anders Brink, Mikko Hupa

The key objective of this Action is to promote at the European level the development of cleaner and more efficient combustion technologies through the implementation of theoretically grounded and more accurate chemical models. This is motivated by the fact that the current models which have been developed for the combustion of hydrocarbons and oxygenated compounds present in natural gas, kerosene, gasoline, diesel and bio-fuels do a reasonable job in predicting auto-ignition and flame propagation parameters, and the formation of the main regulated pollutants. However their success rate deteriorates sharply in the prediction of the formation of minor products (alkenes, dienes, aromatics, aldehydes) and soot nano-particles, which have a deleterious impact on both the environment and on human health. The work in this action is organized into six working groups. The ÅA-PCC is active in WG3.

- WG1: Enlargement of the range of families of initial reactants for which well-validated detailed combustion models are available
- WG2: Writing of models of the formation and consumption of oxygenated pollutants
- WG3: Improvement of the models for formation of polyaromatic compounds and soot
- WG4: Improvement of the methods for mechanism reduction and uncertainty analysis
- WG5: Experimental and theoretical determination of thermochemical parameters and rate coefficients for elementary steps crucial for successful simulation, but for which important uncertainties remain

Cooperation:

Universities, laboratories, research institutes and companies from 19 EU COST and affiliated countries

3.8 Intelligent Electroactive Materials

Electroactive materials are essential components in many devices and applications, including electrochemical sensors and actuators, organic electrochemical transistors, electroactive membranes, charge storage devices (batteries, supercapacitors), fuel-cells, electrochromic devices (displays) and solar cells. Our current research projects on intelligent electroactive materials are related to most of these application areas.

Conjugated polymers are synthesized electrochemically in order to obtain multi-functional and intelligent electroactive materials. Different parameters are controlled during electrochemical polymerization so that a desired structure and film thickness is obtained. Functionalization of the polymer material is tailored to meet the demands of a certain application. Functional groups showing specific interactions with certain molecules or ions are particularly important for chemical sensors. Changes in electronic and ionic conductivity upon electrochemical switching between oxidized (p-doped) and neutral forms of conjugated polymers are important for organic electrochemical transistors and electroactive membranes. When used in photovoltaic devices (solar cells), covalent binding of functional groups is made to control the size of the band gap of the polymer or to obtain solubility of the polymer material. Electroactive materials for charge storage applications are optimized to provide highly reversible charging and discharging properties combined with engineering of these devices for mass production.

Electroactive materials are characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), electrochemical quartz crystal microbalance (EQCM), potentiometry, in situ FTIR, Raman and UV-Vis spectroscopy, in situ electron spin resonance spectroscopy and in situ conductivity measurements. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to obtain information about the morphology of the materials.

Our research activities in the area of intelligent electroactive materials continued on a broad basis in year 2010. Solid-contact ion-selective electrodes (SC-ISEs) and solid-contact reference electrodes (SC-REs) were developed further. The study of the water uptake of polymeric ion-selective membranes was continued in 2010 and so was the theoretical modelling of membrane potentials by the Nernst-Planck-Poisson system of differential equations. Recently developed solid-contact ion sensors were used to follow the dissolution kinetics of some pharmaceutical compounds including lidocaine and propranolol. Conducting polymers were prepared both by electropolymerization and by electrospinning for future applications in potentiometric DNA biosensors. Our research on electroactive ion-exchange membranes was extended towards separation of chiral compounds. Furthermore, electroactive materials for optical and photovoltaic devices were extensively studied in year 2010.

The 9th Spring Meeting of the International Society of Electrochemistry was held in Åbo-Turku, May 8–11, 2011. The meeting was focused on “Electrochemical sensors: from nanoscale engineering to industrial applications” and attracted 223 participants from 35 countries.

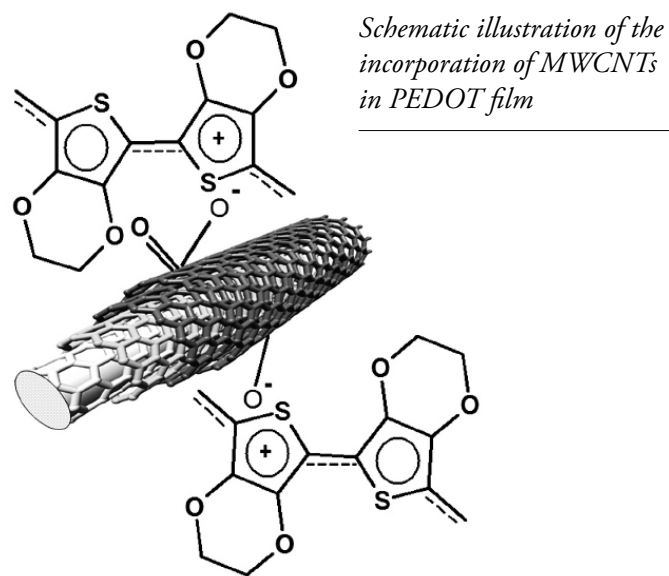
Chemical Sensors and Biosensors Based on Conjugated Polymers, Carbon Nanotubes, C₆₀ and Graphene

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

Dongxue Han, Tingting Han, Ulriika Mattinen, Zekra Mousavi, Li Niu, Hossein Vakili, Andrzej Lewenstam, Johan Bobacka, Ari Ivaska

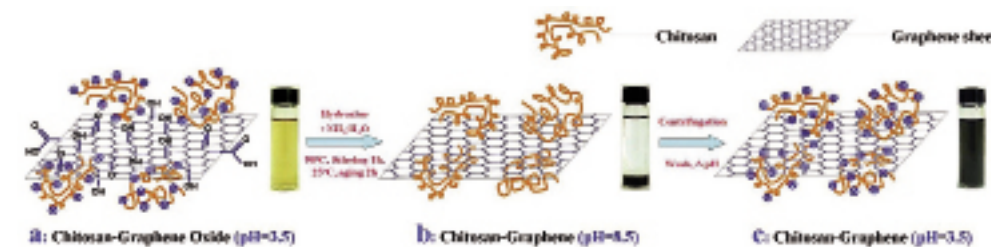
The conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) doped with multi-walled carbon nanotubes (MWCNTs) and fullerene (C₆₀) were used as ion-to-electron transducing layers in solid-contact potassium-selective electrodes based on plasticized PVC containing valinomycin as ionophore.

The negatively charged MWCNTs used as dopants in the electrochemical synthesis of PEDOT were incorporated as charge compensators for the positively charged polymer backbone.



Carbon nanotubes were also integrated into the ion-selective membrane, resulting in a new type of single-piece ion-selective electrodes that were compared to those based on poly(3-octylthiophene). The overall impedance of the electrodes based on carbon nanotubes showed to be notably lower than that of the electrodes based on poly(3-octylthiophene). PEDOT was also used to prepare solid-contact micropipette ion-selective electrodes for SECM and in-vivo applications. Glucose biosensors showing direct electron transfer to the glucose oxidase enzyme were developed based on carbon nanotubes and graphene.

The biopolymer chitosan was used to modify graphene for electroanalytical determination of ascorbic acid, dopamine and uric acid. The modification process is shown in the figure below. The modified surface showed different catalytic activity to oxidation of the compounds allowing simultaneous determination of them.



The procedure to modify graphene with chitosan

Cooperation:

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China

Publications:

- Anastasova, S., Mattinen, U., Radu, A., Bobacka, J., Lewenstam, A., Migdalski, J., Danielewski, M., Diamond, D., Development of miniature all-solid contact potentiometric sensing system, *Sensors and Actuators B: Chemical* 146 (2010) 1, 199–205
- Han, D., Han, T., Shan, C., Ivaska, A., Niu, L., Simultaneous determination of ascorbic acid, dopamine and uric acid with chitosan-graphene modified electrode, *Electroanalysis* (2010) 22, 2001–2008
- Lisak, G., Wagner, M., Kvarnström, C., Bobacka, J., Ivaska, A., Lewenstam, A., Electrochemical behaviour of poly(benzopyrene) films doped with eriochrome black T as a Pb²⁺-sensitive sensors, *Electroanalysis* 22 (2010) 23, 2794–2800
- Wang, Z., Latonen, R.-M., Kvarnström, C., Ivaska, A., Niu, L., Preparation of multi-walled carbon nanotube/amino-terminated ionic liquid arrays and their electrocatalysis toward reduction of oxygen, *Materials* (2010) 3, 672–681
- Bobacka, J., Ivaska, A., Chemical sensors based on conducting polymers, *Electropolymerization: Concepts, Materials and Applications* (eds. S. Cosnier, A. Kariakin), Wiley-VCH, Weinheim, 2010, Chapter 9, 173–187, ISBN 978-3-527-32414-9

Health Diagnostics with Chemical Sensors

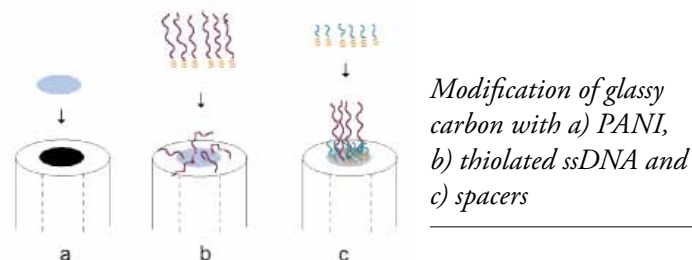
Main funding: Tekes (FiDiPro), Industry, Research Institute of Åbo Akademi University Foundation, Graduate School in Nanosciences (NGS-NANO)

Maija Blomquist, Ulriika Mattinen, Hari Malireddy, Kalle Levon, Andrzej Lewenstam, Johan Bobacka, Ari Ivaska

The aim of the project is to develop fast and easy-to-use potentiometric ion-sensitive electrodes for DNA hybridization, which give information on presence of a specific DNA sequence, and can therefore indicate a disease. Potentiometry offers a unique method for monitoring DNA hybridization without additional labelling.

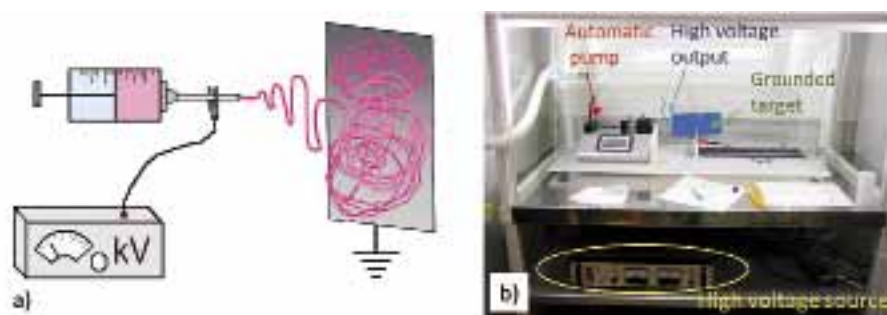
The substrate for probe DNA is a conducting polymer layer on glassy carbon or glass substrate prepared by electrochemical polymerization or by electrospinning. The immobilization of the probe DNA to conducting polymer substrate is done by using thiolation.

Shorter thiol compounds are used as spacers to hinder non-specific binding. The first part of the project focuses on the impact of thiolation on conducting polymer, quantitative determination of thiolation on the surface and optimizing of the electrode design. The electrodes are prepared by methods described earlier and are characterized with spectroscopic and electrochemical methods.



Modification of glassy carbon with a) PANI, b) thiolated ssDNA and c) spacers

The polyaniline layer (PANI-layer), to which the probe DNA is attached, can also be prepared by electrospinning PANI fibres on a substrate. Electrodes with PANI fibrers give larger surface area and are therefore considered to possibly improve response intensity of DNA hybridization. Comparison of these two PANI-substrate preparation methods will be carried through, since it is very important to find optimized electrode preparation method and design.



Electrospinning: a) schematic presentation b) experimental set-up

Cooperation:

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

Intelligent Monitoring for Health and Well-being

Main funding: Tekes (Salwe, IMO), Åbo Akademi University Foundation Research Institute (Johan Gadolin Post-doctoral Fellowships), Academy of Finland

Marcin Guzinski, Peter Lingenfelter, Magdalena Zmudzka, Tomasz Sokalski, Johan Bobacka, Andrzej Lewenstam

The goal of this project is to develop novel sensors, and multi-electrode platforms, that allow individuals or healthcare professionals to promote well-being or health. The project is

supported by Tekes (70%) and other sources (30%). This is a three-year project that started in autumn 2010. The project is part of the Strategic Centres for Science, Technology and Innovation via the centre "Health and Well-being" in the call for "Intelligent Monitoring for Health and Well-being (IMO)". All data concerning this programme which is a public domain information is available at the following address <http://www.salwe.org/>

Cooperation:

AGH University of Science and Technology, Krakow, Poland

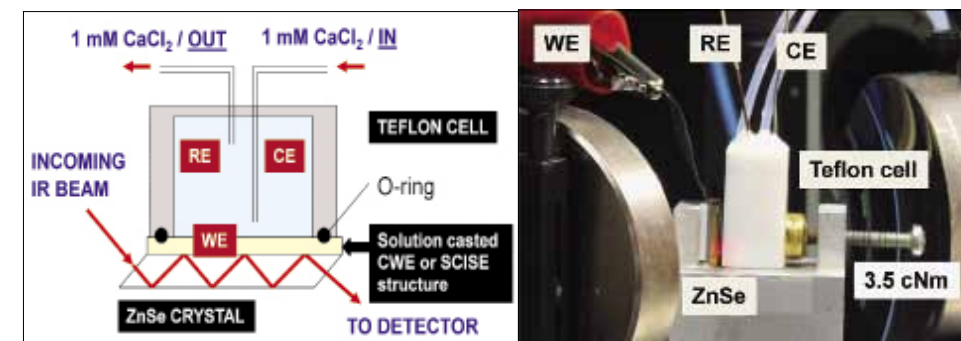
Water Uptake and Transport Properties of Membrane Materials Used in Ion-selective Electrodes

Main funding: Academy of Finland, Graduate School in Chemical Engineering (GSCE), Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM)

Ning He, Jerzy Jasiolec, Grzegorz Lisak, Tom Lindfors, Fredrik Sundfors, Tomasz Sokalski, Andrzej Lewenstam

Fundamental aspects of the water uptake of both commonly used and new ion-selective membrane (ISM) materials are studied in this project. Its main goal is to develop useful experimental methods to identify membranes with low water uptake, which could be beneficial for ultra-trace analysis with solid-contact ion-selective electrodes (SCISEs). The low water uptake of ISMs will prevent the formation of detrimental water layers (or scattered clusters of water) at the interfaces of the 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 project has received funding from the Academy of Finland since 1.8.2009 in the form of a 5-year Academy Research Fellowship granted to the research leader of this project. The project has focused strongly on developing a method for simultaneous measurement of

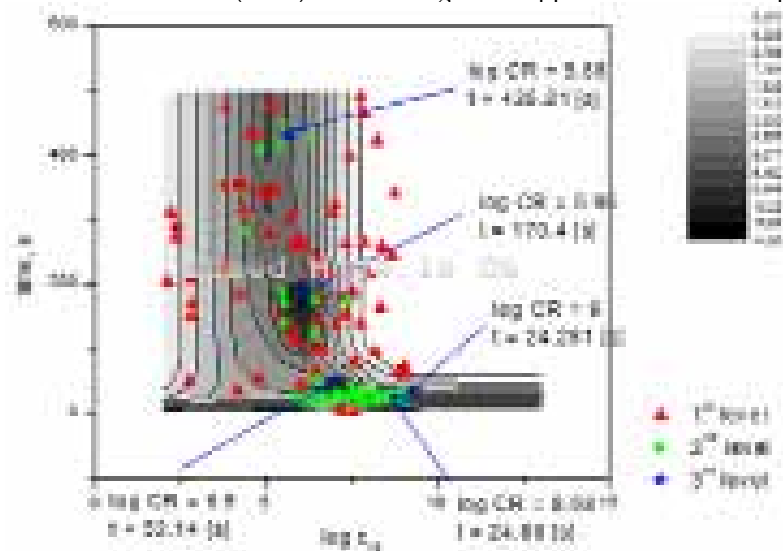


Left: Schematic view of the FTIR-ATR setup used in the water uptake measurements in 1 mM CaCl₂. Right: Experimental setup of the simultaneous measurement of the water uptake, impedance spectra and open circuit potential of ion-selective electrodes. WE: Working electrode; RE: Reference electrode; CE: Counter electrode. The Teflon cell and the ZnSe crystal are pressed against the cell holder with a constant torque of 3.5 cNm.

the water uptake, impedance spectra and open circuit potential of ion-selective electrodes. This is the first time these three parameters have been successfully measured simultaneously. It is currently studied if there is a correlation between the water uptake and the low detection limit of SCISEs. Furthermore, the water uptake of plasticized PVC and SR based ISMs is quantified by the oven based coulometric Karl Fischer titration method.

The detection limit (DL) of an analytical method determines the range of its applicability. For ion selective electrodes (ISE) used in potentiometric measurements, this parameter can vary by several orders of magnitude depending on the inner solution concentrations or the time of measurement. The detection limit of ISE can be predicted using the Nernst-Planck-Poisson model (NPP), as a general approach to the description of the time-dependent electro-diffusion processes. To find the optimal parameters, we need to formulate the inverse electro-diffusion problem. In this project the Nernst-Planck-Poisson model has been combined with the Hierarchical Genetic Strategy with real number encoding (HGS-FP). The HGS-FP method has been used to approximate inner solution concentrations as well as the measuring time that provide a linear dependence of the membrane potential over the widest concentration range. It has been shown that the HGS-FP method allows us to find the solution of the inverse problem. The presented calculations show a great future potential of the NPP method combined with the HGS-FP strategy. The NPP-HGS algorithm was able to find all the minima on the map. Only 214 calibration curves needed to be calculated in order to achieve this task. The computational effort was around 6 times smaller compared with the “brute force” approach.

The Nernst-Planck-Poisson (NPP) model is a general approach to the description of the



Time concentration map with all the individuals (points) of HGS. The red, green and blue colours denote the individuals of the first, second and third populations, respectively.

electro-diffusion processes which lead to the formation of the membrane potential. It takes into consideration several parameters of ion-selective electrodes (ISEs) which are ignored in simpler models. In this project we have made a critical comparison between the NPP model and simpler models. The influence of different parameters on the detection limit of ISEs has been discussed. This has been achieved by comparing direct predictions of the models and, in contrast to any earlier treatment, by inverse modelling. This made it possible to simultaneously find out which set of physical parameters of the system will produce the desired detection limit.

Lead(II) is a major pollutant in the environment and requirements for reliable determination of lead(II) in industrial wastes and environmental samples is crucial. A lowering of the detection limit of ion-selective electrodes (ISEs) has become a significant part of electroanalysis and has created the possibility of measurements at extremely low concentrations of analyte. The detection limit has been an issue of interest since early stages of the history of ISEs and initially solid-state membranes were in focus. The possibility of lowering the detection limit for ISEs with plastic membranes was reported later. In this project we have studied solid-state lead (II) ion-selective electrodes and their performance at low concentrations of Pb^{2+} ions was inspected by different methods. The electrodes were applied in direct measurements of ultra-low concentrations of Pb^{2+} . The lowering of the detection limit of Pb^{2+} -ISE has been achieved by a procedure based on concentration-time dependent adsorption of the analyte to the surface of the membrane as well as tuned galvanostatic polarization of the solid-state membrane. By this research the area of solid-state membranes used for lowering of the detection limit has been revitalized.

Cooperation:

Budapest University of Technology and Economics, Budapest, Hungary

Publications:

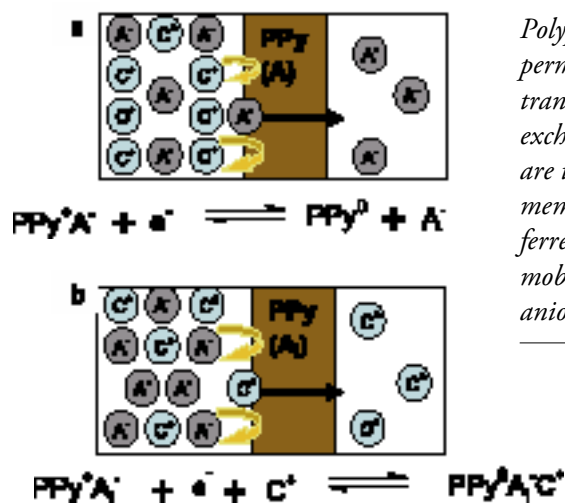
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Electroactive Ion-Exchange Membranes Based on Conducting Polymers for Monitoring of Anions and Cations

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

Marceline Akieh, Jesus Arroyo, Jiayi Huang, Rose-Marie Latonen, Ari Ivaska, Johan Bobacka

The use of conducting polymeric membranes has extensively been studied to separate either anions or cations from aqueous solutions. The research has focused on the transport of either only metal ions or anions. In order to fully utilise conducting polymer based materials for membrane separation purposes, or other applications that take advantage of the electroactivity of conducting polymers, it is essential to have a complete understanding of the processes involved in maintaining charge balance in the receiving solution. If permselectivity is achieved, membranes based on polypyrrole (PPy) doped with mobile anions will be permeable only towards anions, and cations will be retained in the source solution. In a similar way, membranes based on PPy doped with immobile anions will be permeable only towards cations, and anions will be retained in the source side. The question to be addressed is how the macroscopic charge balance in such systems is maintained. In order to solve this problem, transport experiments with selected PPy and PEDOT membranes known to have cation, anion and mixed ion-exchange properties have been performed. To increase the knowledge of PPy membrane properties affecting the ion transport, PPy films doped with acid-treated multi-walled carbon nanotubes have also been studied. Concentrations of both cations and anions were determined in the receiving solutions of an electrochemically controllable transport cell, and source solutions containing either monovalent or divalent metal nitrate solutions or monovalent anions as sodium salts. Also some attempts to prepare chiral conducting polymer films to separate molecules according to their chirality have been made.



Cooperation:
University of Wollongong, Australia

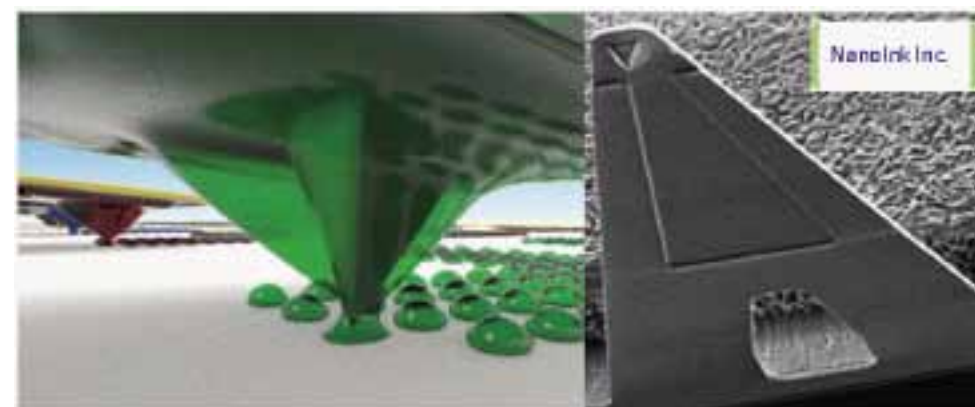
Publications:

- Akieh, M.N., Ralph, S.F., Bobacka, J., Ivaska, A., Transport of metal ions across an electrically switchable cation exchange membrane based on polypyrrole doped with a sulfonated calix[6]arene, *Journal of Membrane Science* 354 (2010) 1–2, 162–170

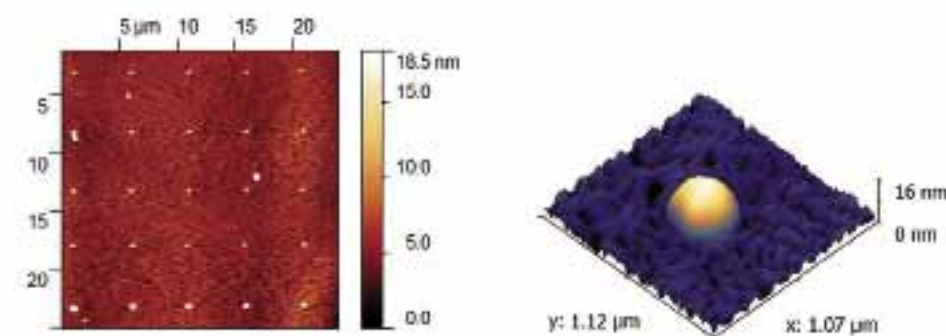
Fabrication of Micro-size Arrays for Sensor Applications by Dip Pen Nanolithography

Main funding: Australian National Fabrication Facility (ANFF), Graduate School of Materials Research (GSMR)

Michał Wagner, Cathal O'Connell, Michael Higgins, Ari Ivaska, Gordon Wallace



Schematic representation of DPN patterning and SEM micrograph of working tip used in the process



AFM images of PEDOT:PSS pattern on silicon substrate. Each dot is approx. 500 nm wide in diameter and 16 nm high

Dip Pen Nanolithography (DPN) is a fabrication method in which materials are deposited on various surfaces at ambient conditions by a nanoscale sharp tip. In DPN process it is possible to print features at micro and nano level. We utilize this method to print arrays of conducting polymer which can be used for sensor and biological applications. We successfully developed the ink based on poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) which can be printed by DPN providing good reproducibility of both shape of the array and the size of single dot. Our main goal is to fabricate a platform composed of micro-arrays of conducting polymer electrodes for ion selective sensing as well as living cell stimulation.

Cooperation:

University of Wollongong, Australia

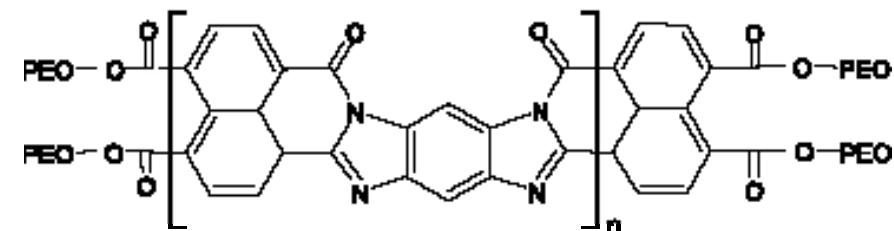
Electroactive Materials for Optical and Photovoltaic Devices – Ordered Structures of Organic Electronic Materials

Main funding: Tekes, Industry, Academy of Finland, Graduate School in Chemical Engineering (GSCE), Graduate School of Materials Research (GSMR), Fortum Foundation

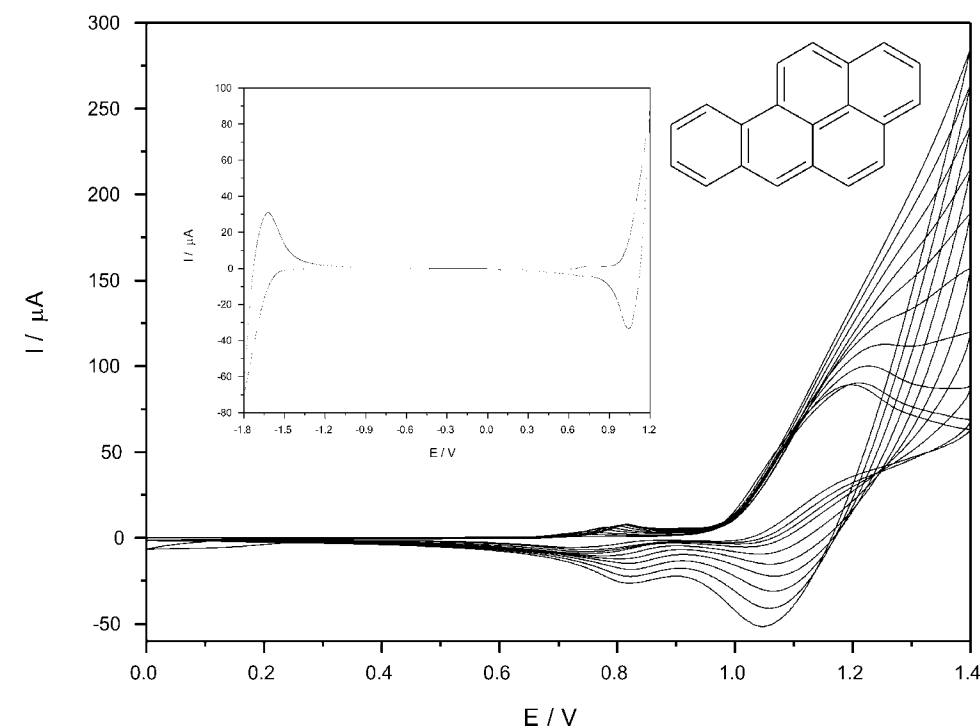
Pia Damlin, Henrik Gustafsson, Rose-Marie Latonen, Michał Wagner, Kai Yu, Anna Österholm, Ari Ivaska

New electrosynthetic routes have been established for the production of n- and p-dopable conducting polymers. The charge transfer in the resulting electronically conducting films has mainly been studied in situ by UV-vis, Raman and FTIR spectroelectrochemical techniques. The development of electron transfer layers and their connection to the electrodes in the solar cell has been a central issue in this project. The focus has been on synthesis of n-type semiconducting polymers. Poly(3,4-ethylenedioxythiophene) (PEDOT) has been studied as an electron transfer layer on alumina by impedance spectroscopy, in situ FTIR spectroscopy and Electron Spectroscopy for Chemical Analysis (ESCA). A new n-type water dispersible poly(benzimidazobenzophenanthroline) (BBL) functionalized with poly(ethyleneoxide) (PEO) side-chains have been studied. The effect of side-chain length has been investigated by comparing the electrochemical behavior of four BBL-PEO films with varying PEO length. From the *in situ* UV-vis-NIR experiments the optical band gap was estimated to be approximately 1.7 eV. Electrosynthesis conditions to obtain thick and electrochemically stable films of another acceptor-like material, poly(benzopyrene) (PBP), from benzo(a)pyrene using cyclic voltammetry has also been established. Electrochemical and optical band gaps of approximately 2.6 eV and 2.5 eV, respectively, was obtained. The important finding was that PBP films made in propylene carbonate exhibited high electrochemical stability. The results imply that novel electroactive films based on benzopyrenes are interesting candidates for the active layer in organic electronic devices.

As one step further different type of donor-acceptor material combinations for solar cell applications has been developed. Composite films consisting of PAz and C₆₀ have been studied by comparing the photoinduced and the electrochemically induced changes in

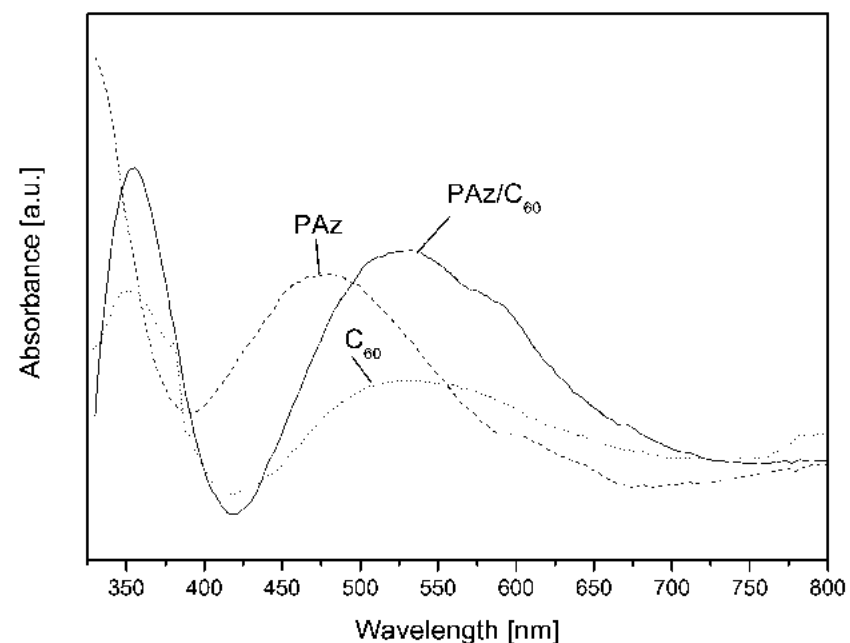


The structure of BBL-PEO



Electrosynthesis of PBP in propylenecarbonate+TBAPF₆ (10 mV/s). Insert: Cyclic voltammograms recorded during p- and n-doping of PBP film in propylenecarbonate+TBAPF₆ (5 mV/s) and the structure of benzo(a)pyrene

thin polymer and fullerene films. Also hybrid electron donor-acceptor materials consisting of inorganic wide band gap nanostructured TiO₂ as the electron acceptor and organic low band gap conducting polymer PAz, as the electron donor have been studied. As the third donor-acceptor material PEDOT functioning as an electron donor has been combined with the electron accepting BBL-PEO in a bilayer structure. These donor-acceptor materials have been characterized by cyclic voltammetry, in situ UV-vis spectroelectrochemistry, both ex situ and in situ FTIR spectroscopy, Raman and XRD spectroscopy techniques and by Scanning Electron Microscopy. In the future BBL-PEO will be studied in combination with PAz having graphene oxide as the transparent electrode.



UV-vis-NIR spectra of PAz, C₆₀ and PAz/C₆₀

Cooperation:

University of Turku (Analytical Chemistry); Johannes Kepler University of Linz, Austria; Tampere University of Technology; University of Helsinki; Rautaruukki; KSV Instruments, Systems Biology Worldwide

Publications:

- Yu, Kai, Electrosynthesis of electroactive films made of benzo(a)pyrene, MSc Thesis
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Printed Enzymatic Power Supplies with Integrated Capacitor Structures (PEPSic)

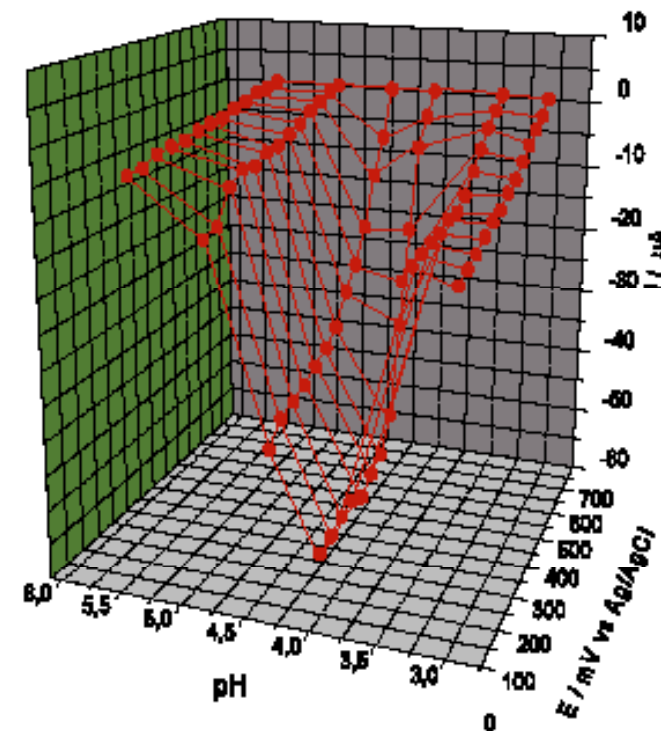
Main funding: Tekes

Mikael Bergelin, Jan-Erik Eriksson, Max Johansson, Pia Sjöberg-Eerola, Xiaoju Wang, Mikko Hupa

This project is aimed at developing a printable fully enzymatic biofuel cell, based on the use of enzymes as catalyst on both electrodes, a so called BioBattery. The power supply is developed to meet the demand of cheap disposable electronics applications for logging, tracking, displaying or various medical uses. The challenge in this development effort is the selection of suitable materials and manufacturing methods, to meet the “point-of-use”-requirements, the disposability requirements as well as the required low unit price demands. The base materials chosen are mainly cellulose and carbon based materials, in combination with suitable electrolyte and organic constituents, and the manufacturing methods are mainly based on printing techniques.

Performance targets; a) a biofuel cell based power supply with an integrated supercapacitor, b) a power supply voltage exceeding 1.2 V, capable of producing a peak current of at least 50 mA for 0.3 seconds, with the size (area) less than 10 cm², thickness no more than 0.5 mm.

A number of critical components have been identified, and the main challenges have been solved. Regarding the electrochemical components, the cathode enzyme electrode displays a sufficient power output, but some challenges still remain in the optimization of the anodic enzyme electrode structure in order to ensure sufficient fuel diffusion and a maximal active surface area. The separation of the anode and cathode side has been solved, and two developed alternatives were found to fulfil the required properties.



The current output of the enzyme cathode as a function of potential and pH

The performance of the developed power supply in combination with a number of low power demanding applications have also been demonstrated, and the development work is continuing in the project PEPSecond.

Cooperation:

VTT; Aalto University; Ciba Speciality Chemicals; Joutsenpaino; Tervakoski; Stora Enso; Evox-Rifa

Printed Enzymatic Power Supplies with embedded capacitor on next generation devices (PEPSecond)

Main funding: Tekes

Mikael Bergelin, Jan-Erik Eriksson, Max Johansson, Pia Sjöberg-Eerola, Xiaoju Wang, Mikko Hupa

This project is linked with the PEPSIC project, and aims at the development of the BioBattery towards an advanced prototype that displays the commercialization potential of the power supply. The anode electrode power output will be increased by the development of a tailored ink allowing for a suitable microporous print quality, in combination with an increased enzyme loading and enlarged active surface area. Alternative approaches to increase power output of the cell will also be investigated. As a highlight can be mentioned that the anode current output has now been increased tenfold from the “state of the art” performance during the PEPSIC project ($30 \mu\text{Acm}^{-2}$) to more than $280 \mu\text{Acm}^{-2}$ by tailoring substrate properties to better accommodate the enzyme with minimal deactivation.

Activation systems for the power supply have been developed, that accommodates the requirements of two “case study” applications. Optimization of cell components and manufacturing methods will further be conducted to allow for R2R manufacturing with a minimum of separate steps required.

Interfacing of the BioBattery with potential applications is currently being investigated, and suitable simple electronic interfaces are being tested. The complexity of the interface is strongly dependent on the point of use, and hence two alternatives of different nature are realized.



BioBattery prototype consisting of two serially connected cells

The disposability of the BioBattery will be assessed by verification of its combustibility and other means of disposal in accordance with national and international directives.

A final demonstrator, featuring a BioBattery integrated into an accelerated wound healing patch will be constructed using only mass-production mimicking techniques, and its performance will be assessed.

Cooperation:

VTT; Aalto University; Tampere University of Technology; ABEnzymes; Confidex; Enfucell; Evox-Rifa Group; Joutsenpaino; Panipol; Stora Enso; Tervakoski

Publication:

- Wang, X., Sjöberg-Eerola, P., Eriksson, J.-E., Bobacka, J., Bergelin, M., The effect of counter-ions and substrate material on the growth and morphology of poly(3,4-ethylenedioxythiophene) films: Towards the application of enzyme electrode construction in biofuel cells, *Synthetic Metals* 160 (2010), 1373–1381

Active Nanocomposite Materials (ActCom)

Main funding: Tekes

Mikael Bergelin, Jan-Erik Eriksson, Max Johansson, Pia Sjöberg-Eerola, Mikko Hupa

This research project aimed at developing novel functional nanocomposite materials with tailored properties to be used as anode material in next generation lithium-ion batteries. The novelty of this work lays in the combination of high tech nanocomposite synthesis methods with a novel surface functionalization of the active material. These manufactured composites combine a high activity of the nanomaterial with a high surface area and cohesion of the agglomerate, while the added polymer matrix provides protection towards ageing and excessive volume changes.

The target has been set on a volumetric capacity of the nanocomposite of at least 3 times that of the standard graphite anode, and on a life time comparable with the present anode materials, as the main drawback of the current substitutes is a significant volume changes during battery cycling which causes rapid fading and poor cycle life especially at elevated temperatures.

Within the project novel composites have been synthesized by induction nucleation, spray pyrolysis and CVS. The physical structure and electrochemical properties of these composites have been characterised in their native form and during electrochemical cycling, and their performance regarding charging, loadability and potential stability have been assessed. The performance decrease due to ageing has also been tested using various EC and EIS techniques.

Cooperation:

VTT; University of Kuopio; University of Joensuu; NOKIA; SAFT; OMG Kokkola Chemicals

Pressurized PEM Electrolyzer (Primolyzer)

Main funding: EU

Mikael Bergelin, Max Johansson, Mikko Hupa

The primary objective of the PrimoLyzer project is to develop, construct, and test a cost-minimised highly efficient and durable PEM-Electrolyzer stack aimed for integration with μCHP technology. The research tasks within the project have concentrated around developing mixed metal oxide (MMO) anode catalyst and CNT supported PtPd cathode

catalyst facilitating MEA performance of 1.2 A/cm² at 1.64 VDC and extrapolated durability of 20,000 h. The performance target for the anode catalyst is 1.2 A/cm² at 1.45 V (RHE) with a loading of 1,0 mg/cm² and for the cathode catalyst 1.2 A/cm² at -40 mV (RHE) with a noble metal loading of 0,5 mg/cm². At ÅA/PCC nanostructured IrO₂ and different binary Ir_xRu_yO_z MMO catalysts manufactured by VTT have been characterized by TGA, SEM and cyclic voltammetry in 0,5 M H₂SO₄. The oxygen evolution reaction (OER) onset potential and the limiting current have been studied in a potential window of 1,0–2,5 V (RHE). The OER onset data showed that the activity of IrO₂ prepared by Adams fusion are close to the commercial reference and the activity increases with increasing amount of Ru in the mixed oxides. The catalysts prepared by FSP are less active but show similar trend in Ru content. The limiting current measurements show an opposite trend in Ru content: the more Ru the lower the limiting current. Once more, the FSP catalysts are less active than those prepared by the Adams method. The superior performance of IrRu₃O₈ catalyst has been verified at MEA level.

The IrRu alloy stability has been tested using accelerated ageing to assess Ru oxidation and dissolution rate in the operation ambient.

Cooperation:

IRD, Denmark; ECN, the Netherlands; VTT; Fumatech, Germany; Hynergreen, Spain

Advanced Material Solutions for PEM Fuel Cells (MARAPOKE)

Main funding: Tekes

Mikael Bergelin, Max Johansson, Mikko Hupa

The objective of the project is to develop materials for PEM-FC and DMFC stack components. The main emphasis is in the development of components to PEMFC stacks in 1 to 50 kW power range needed for industrial vehicles and working machines. The project will concentrate in the development and testing of the components where the industrial competence and commitment is highest. The other components needed to test the components in fuel cell single cells and stacks will be purchased from the world market.

Commercial LT and HT electrolyte membranes will be used to verify the compatibility of the components developed within the project. Unsupported or carbon black (CB) supported Pt or Pt alloy catalysts are state-of-the-art catalyst for PEMFC. Recently, use of carbon nanotubes (CNT) and nanofibres (CNF) as catalyst support has been studied extensively. However, as CNTs and CNFs grown by CVD remain rather expensive, a more cost effective production of CNF will be attempted. This process includes electrospinning of polyacrylonitrile (PAN) precursor nano nonwovens followed by partial oxidation and carbonization of the precursor fabric. This fabric will then be catalyzed by addition of Pt catalyst in various ways

The main setback of carbon paper and cloth production processes is the high cost of the

heat treatment processes needed for the carbonization of the PAN precursor fibre and the carbonization and graphitization of the binders needed for the paper or cloth. An attempt will be made to use conductive polymers, e.g. polyaniline (PANI), polypyrrole (PPy) or polythiophene (PEDOT) as binders. The membrane electrode assembly is typically produced by printing or coating an ink consisting of the catalyst material, dissolved proton conducting membrane and solvent on the membrane or the MPL of the GDL. Typical application techniques are screen printing and spray coating. An alternative method to produce high performance MEAs with ultralow Pt content of less than 0,1 mg/cm² will be attempted. The Pt catalyzed GNF fabrics developed in the project will be laminated with commercial or experimental GDLs and LT or HT electrolyte membranes. The use of GNF fabrics as the catalyst support facilitates the location of the Pt catalyst exactly at the GDL membrane interface. Within the project bipolar-plate related development will also be made.

Cooperation:

VTT; Aalto University; Tampere University of Technology; Ahlstrom; Beneq; Finetex; Premix; Outokumpu

3.9 Functional Inorganic Materials

The main topics of our recent materials research have been characterization and improving the understanding of the surface properties of inorganic materials glasses, glazed ceramics, refractory ceramics and steel qualities used at high temperatures. Additionally, several different types of coatings rendering the surfaces special properties were studied. Common to all these materials is their interaction with high temperatures either during the material manufacture or final application. When studying the surface properties the bulk composition and bulk properties of the materials were important parameters giving solid background for understanding the development of surface structures and their interaction with the surrounding environment.

The glass research was concentrated on bioactive glasses used as implants to guide tissue growth and tissue regeneration in medical applications. In bodily fluids the bioactive glasses form a dual surface layer of silica and hydroxyapatite that bonds to bone. The influence of the oxide composition on the layer formation, and thus bioactivity was reported by our group recently. We have continued to study the mechanisms of glass dissolution and layer formation to get a more comprehensive knowledge of all parameters affecting bioactivity and biodegradability of glasses. Similarly, the detailed knowledge of thermal properties is essential in the manufacture of products in different shapes of bioactive glasses. As the forming takes place at high temperatures at viscosities which partly overlap with the temperature range at which the glasses crystallize, the measurement of crystallization characteristics has been one of our main focuses.

The chemical and mechanical durability of easy-to-clean coatings on glasses and glazed ceramics has been one of the focuses for surfaces used in everyday environments. Additionally, we have studied how nanoparticles in the glazes or nanoparticle thin films on the surfaces affect the properties of glazed tableware ceramics. Effort has been put to find out suitable procedures and methods to measure the thin surface films accurately. Some effort has also been put to develop reliable characterization methods of nanoparticles deposited on surfaces via different aerosol-based coating techniques. This method development serves not only our research activities within self-cleaning and easy-to-clean surfaces but paves road to some new areas such as characterization of transparent conductive oxides (TCO) on float glasses.

Increasing the power production efficiency in combustion devices and boilers by allowing higher material temperatures in e.g. superheaters has called for development of better high temperature materials for steam power plants. The presence of various alkali salts such as potassium and sodium chlorides, sulphates or carbonates is the main reason to severe high temperature corrosion of the hottest surfaces of combustion devices burning biofuels. Our laboratory corrosion exposure technique, together with microscopic and analytical techniques, has been used to establish the corrosion tendency of various steel qualities. For detailed understanding of the corrosion mechanisms we have especially focused on the role of partial melting of the salt deposit on its corrosion properties. Recently, similar approach has been used to develop a method for characterization of high temperature

deterioration of ceramic refractories used in grid bottom plates in circulated fluidized bed boilers for waste firing.

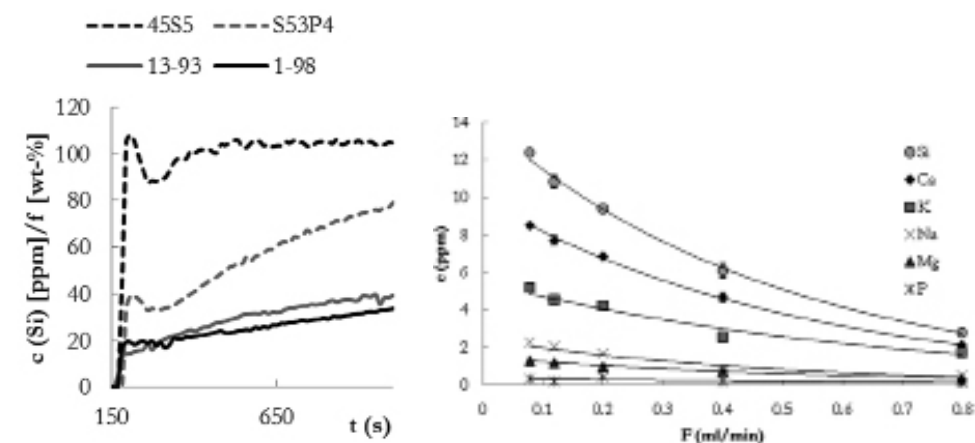
As a new area we have studied corrosion of stainless steel with the focus of understanding the detailed mechanism of chromium oxide protective film formation and corrosion in the high temperature environments.

Bioactive Glass Structures and Their Reactivity

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

Leena Hupa, Jonathan Massera, Linda Fröberg, Zhang Di, Susanne Fagerlund, Leena Varila, Corinne Claireaux, Jeanette Lönnberg, Paul Ek, Mikko Hupa

Our bioactive glass research continued with the characterization of the influence of glass composition on the dissolution kinetics in aqueous solutions. The dissolution kinetics measured in different solutions measured using different flow rates gives information on the behaviour of the glass at the moment of implantation and the dissolution rate in the body fluids. The results can be used to design novel bioactive glass implants with desired dissolution rate. Ideally, the glass should dissolve gradually with a rate that matches the growth rate of new tissue. The figure below shows the averaged values (600–1300 s) of silicon (silicate ion) dissolution from four bioactive glasses in Tris buffer at 40°C and the flow rate of 0.2 ml/min. The normalized values given as element concentration in the solution (ppm) to oxide content in the glasses (weight-%) show clear differences in the dissolution behaviour of the glasses. The influence of the flow rate on the dissolution rate of different ions from glass 1-98 in water is also given. At low flow rates, the ion exchange reaction of alkalis increases the pH of the solution to values enhancing the silicate network breakup. Accordingly, the dissolution rate of silicate ions is high at low flow rates.



A) Dissolution of silicate ions (c [ppm]/weight-% in glass) in Tris (0.2 ml/min, 40°C) measured by ICP-OES in a continuous flow-through cell. B) Concentration of ions dissolved from bioactive glass 1-98 in water: at steady state conditions (900–1400 s) as a function of flow rate (40°C)

The SEM images of the cross-sections of the bioactive glass S53P4 (BonAlive®) at one week immersion in three in vitro solutions at static conditions (37°C) show clear differences in the reaction layer development at the surfaces. Similar reaction layers form also in vivo; these layers are taken as an indication of the bioactivity of the glass. Our results clearly show that the composition of the glass, the flow rate of the solution and the composition of the solution all affect the observations of the bioactivity of glasses in vitro. Thus, several variables have to be taken into account when studying the bioactivity of glasses.



SEM images of cross-sections of bioactive glass S53P4 at 168 immersion in Simulated Body Fluid (left), Tris buffer (middle), and Sodium Phosphate Buffered Saline (right)

We also continued to measure the thermal properties of the glasses. Our goal was to get detailed information on the crystallization tendency of the glasses in manufacturing porous implants by sintering of crushed glass. We also measured the crystallization at the liquidus temperature. For bioactive glasses the liquidus is close to temperatures for optimal fibre drawing viscosity values. It should be noted that the crystallization can be utilized when making glass-ceramics from the parent glasses. Glass-ceramics have a better mechanical strength than glasses, thus being good candidate materials in applications where the fracture sensitivity of glasses due to their inherent brittleness has to be avoided.

As a conclusion, detailed understanding of the crystallization kinetics within whole the temperature range of interest of glass forming processes is needed when tailoring compositions for complex shapes of products based on bioactive glasses.

Cooperation:

University of Turku (Orthopaedics and Traumatology, Dentistry); University of Erlangen-Nuremberg, Germany; Institute of Chemical Technology, Prague, Czech Republic; École Nationale Supérieure de Chimie de Rennes, Rennes, France; Vivoxid

Publications:

- Fagerlund, S., Ek, P., Hupa, M., Hupa, L., On determining chemical durability of glasses, *Glass Technology: European Journal of Glass Science and Technology, Part A* 51 (2010) 6, 235–240
- Fagerlund, S., Hupa, L., Crystallization of 45S5 during isothermal heat treatment, *Materiały Ceramiczne/Ceramic Materials* 62 (2010) 3, 349–354
- Fagerlund, S., Hupa, L., Hupa, M., Comparison of reactions of bioactive glasses in different aqueous solutions, *Ceramic Transactions (Advances in Bioceramics and Biotechnologies)* 218 (2010), 101–113
- Hupa, L., Hupa, M., Recent research on composition dependence of the properties of bioactive glasses, *Ceramic Transactions (Advances in Bioceramics and Biotechnologies)* 218 (2010), 145–156

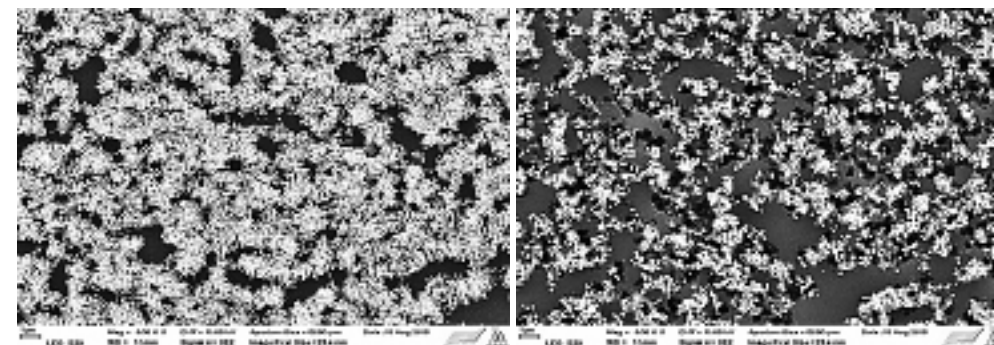
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Surface Coatings on Ceramics and Glasses

Main funding: Graduate School of Materials Research (GSMR), Industry, ÅA-PCC

Leena Hupa, Minna Piispanen, Linda Fröberg

Coatings and nanoparticles which give glazed ceramics and glasses special surface properties have been tested. The coatings have been manufactured through sol-gel synthesis or different aerosol based nanoparticle processes. On glass and glazed tiles the long-term easy-to-clean and self-cleaning properties have been the main focus. The nanoparticle coatings on glazed tableware ceramics have been tested for their chemical and mechanical durabilities. On further goal has been to develop reliable characterization methods to identify the composition, thickness and structure of different nanostructured coatings on glasses and glazed ceramics.



SEM image of glazed tiles with ZrO₂ nanoparticles applied using Liquid Flame Spray method (left). The figure on the right shows that the interfaces of the nanoparticles have partly corroded after exposure to alkaline detergent solution (1000 x washing cycles)

Cooperation:

Tampere University of Technology (Department of Physics); Fiskars Home Arabia; Beneq

Publications:

- Piispanen, M., Aromaa, M., Mäkelä, J.M., Hupa, L., Effect of functional coatings on topographical properties of glass, *Ceramic Transactions (Ceramics for Environmental and Energy Applications)* 217 (2010), 131–139
- Piispanen, M., Hupa, L., *In situ* analysis of corrosion of glazed surfaces using confocal optical microscopy, *Materiały Ceramiczne/Ceramic Materials* 62 (2010) 4, 560–564

Ceramic Refractories in Boilers

Main funding: ÅA-PCC

Leena Hupa, Na Li, Patrik Yrjas, Mikko Hupa

In recent years, the environment in combustion devices has changed when biomass, wood and waste derived fuels have been used as renewable energy sources. In combustion of biomass alkali metals, chlorine and sulphur are released into the fuel gas and reversed to alkali carbonates or sulphates. Alkaline ash deposits might lead to chemical deterioration of the refractories and thus be a big challenge for their service life. We have developed a laboratory method test the chemical resistance of refractory materials to typical ashes formed in biomass combustion. This method will be used to examine corrosion of refractories in biomass combustion devices.

Cooperation:

Foster Wheeler

Publication:

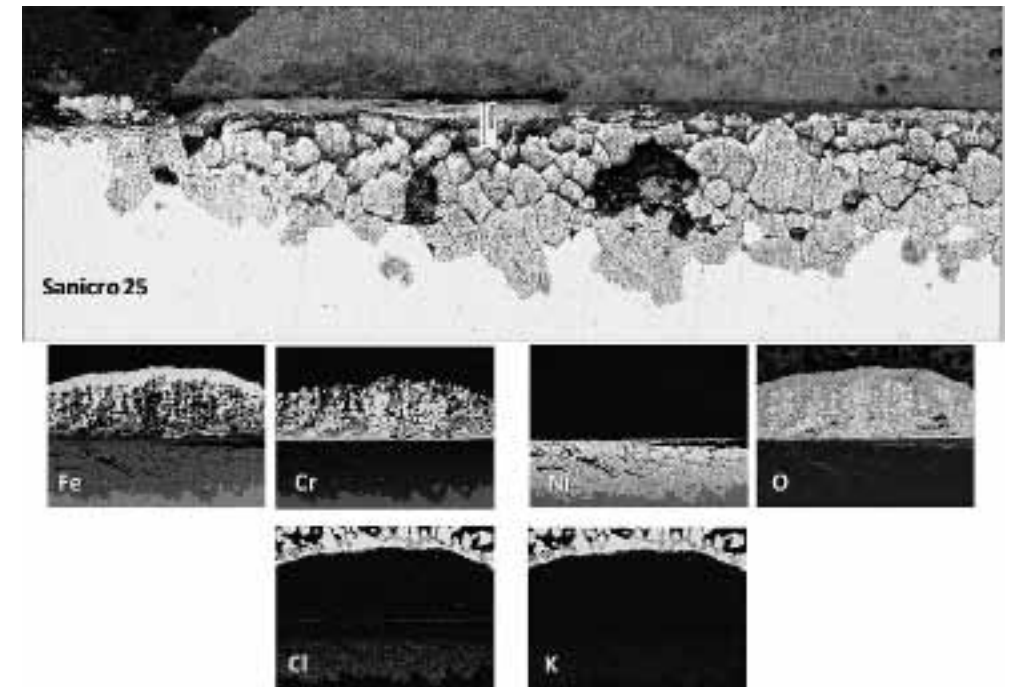
- Li, N., Hupa, L., Yrjas, P., Hupa, M., Laboratory study of corrosion of an alumina refractory by molten potassium salts, *Advances in Science and Technology* (2010) 70, 65–71

High Performance Materials and Corrosion Control for Efficient and Low Emission Biomass and Waste Combustion (Hi-Cor)

Main funding: Tekes

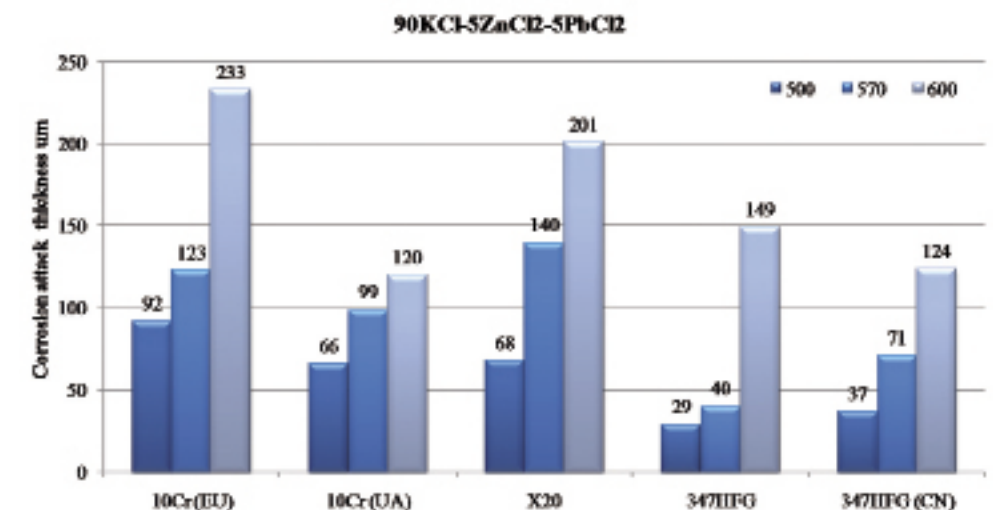
Patrik Yrjas, Dorota Bankiewicz, Mikko Hupa

The project started in May 2008 and ended in March 2011. The principal scientific objectives are to develop and validate improved high performance alloys to withstand the impact of hot corrosion and other high temperature damage in under three different combustion conditions: coal oxy-fuel, co-firing biomass, and biomass/waste combustion. The tests at ÅA-PCC were performed using a laboratory method for studying high temperature corrosion. The method is based on the estimation of the oxide layer thickness or/and depth of the material degradation. The recognition of the oxide layer composition is also included. Below is a figure showing severe corrosion of a high alloy steel in contact with KCl at high temperature.



A SEM image together with elemental analyses of Sanicro 25 after 168 h with KCl at 650°C

The corrosion results are commonly presented as bar diagrams, and this is also illustrated in the figure below showing the corrosion of five different steels at three different temperatures.



The mean oxide layer thickness after 168 h with a 90 w-% KCl + 5 w-% ZnCl₂ + 5 w-% PbCl₂ salt mixture in ambient air at 500, 570, and 600°C

Also the intent was to develop and demonstrate advanced online corrosion monitoring probes and to combine the results from computational materials modelling, online cor-

rosion monitoring and laboratory testing for life prediction of new advanced alloys, and to validate the results by comparison to field testing. Further, one part of the project is to clarify material challenges and alternatives for oxyfuel combustion. The PCC supported these objectives by making laboratory corrosion tests under different process conditions, by changing the gas atmosphere, synthetic ash compositions, etc. Although the project has now ended, the purpose is to continue the cooperation in one way or other, since there are still open questions, especially concerning the behaviour of metals in oxyfuel conditions.

Cooperation:

VTT; Aalto University; Fortum; Foster Wheeler Energia

4. Publications 2010

4.1 Theses

4.1.1 Doctoral theses (6)

Engblom, Markus, Modeling and field observations of char bed processes in black liquor recovery boilers

Grénman, Henrik, Solid-liquid reaction kinetics, Experimental aspects and model development

Sahin, Serap, Engineering bio-chemo catalytic reactions

Simakova, Irina, Catalytic transformations of fatty acid derivatives, for food, oleochemicals and fuels over carbon supported platinum group metals

Sundfors, Fredrik, Solid-contact ion sensors: Materials and properties

Taskinen, Antti, Molecular modelling of asymmetric induction in heterogeneously catalyzed hydrogenation of the C=O bond (in co-operation with Physical Chemistry, Åbo Akademi University)

4.1.2 Licentiate theses

4.1.3 Masters' theses (15)

de Araujo Filho, César, Catalytic synthesis of peroxyfatty acids (in co-operation with INSA Rouen, France)

Björkvik, Thomas, Measurement of sulfur release from black liquor droplets in a single particle reactor

Bäckman, Anders, Konstruktion och drift av ett laboratoriereaktorsystem för studier av reaktionerna mellan kaliumkloridångor och aluminiumsilikater (*Construction and running of a laboratory reactor system for studies of the reactions between evaporated potassium chloride and alumina silicates*, in Swedish)

Durante, Davide, Modelling of a trickle-bed reactor for sugar hydrogenation (in co-operation with Università di Padova, Italy)

Hilpmann, Gert, Reaction studies on the cleavage of arabinogalactan in a stirred batch reactor (in co-operation with TU Dresden, Germany)

Lind, Joakim, Inverkan av finmaterial på avvattnings och initial våtstyrka (*Effects of fines on dewatering and initial wet web strength*, in Swedish)

Niemi, Sara, Bleaching of sugar beet and its environmental load

Niittymäki, Outi, Metallförmedlad allylering av oxiderad metyl- α -D-galaktopyranosid (*Metal mediated allylation of oxidized methyl- α -D-galactopyranoside*, in Swedish)

Poleo Vargas, Eduardo Enrique, Kinetic analysis and modeling of the ring opening reaction of decalin over a Pt-modified beta-zeolite catalyst

Riittonen, Toni, Bioethanol valorization to biobutanol (in co-operation with the University of Turku)

Roche, Mauricio, Ethylene oxide synthesis in microreactors

Salminen, Eero, Supported ionic liquid catalysts in the selective hydrogenation of citral (in co-operation with the University of Turku)

Tourvieille, Jean-Noel, Ultrasound effect on hydrogenation of sugars – catalyst deactivation and modelling (in co-operation with CPE Lyon, France)

Yu, Kai, Electrosynthesis of electroactive films made of benzo(a)pyrene

Zhu, Weizhen, Decomposition kinetics of sodium cyanate in smelt from kraft recovery boilers

4.2 Publications

4.2.1 Articles in refereed international scientific journals and series (138)

- Aho, A., Kumar, N., Eränen, K., Salmi, T., Holmbom, B., Backman, P., Hupa, M., Murzin, D.Yu., Catalytic pyrolysis of woody biomass, *Biofuels* 1 (2010) 2, 261–273
- Aho, A., Kumar, N., Lashkul, A.V., Eränen, K., Ziolk, M., Decyk, P., Salmi, T., Holmbom, B., Hupa, M., Murzin, D.Yu., Catalytic upgrading of woody biomass derived pyrolysis vapours over iron modified zeolites in a dual-fluidized bed reactor, *Fuel* 89 (2010) 8, 1992–2000
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- Bernas, A., Simakova, I., Eränen, K., Myllyoja, J., Salmi, T., Murzin, D.Yu., Continuous mode linoleic acid hydrogenation on Pd/sibunit, *Kataliz v Promyshlennosti* 2 (2010), 7–13 (Russian); *Catalysis in Industry* 2 (2010), 95–100 (English)
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4.4 Åbo Akademi reports (7)

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Bernas, A., Hajek, J., Leino, A.-R., Sifontes, V., Eränen, K., Murzin, D., Kordas, K., Mikkola, J.P., Salmi, T., *URAKAMU – Final report 2008–2010*, 60 p

Engblom, M., Modeling and Field Observations of Char Bed Processes in Black Liquor Recovery Boilers, *Report 10–1, Åbo Akademi Process Chemistry Centre, Laboratory of Inorganic Chemistry*, ISBN 978-952-12-2440-9, Painosalama, Turku, Finland 2010 (doctoral thesis)

Hilpmann, G., Experimental investigations on acid hydrolysis of arabinogalactan, *Åbo Akademi University & Technische Universität Dresden*, 2010

Jula, O., Catalytic synthesis of peroxyformic acid in a fixed bed reactor, *Åbo Akademi University, Laboratory of Industrial Chemistry and Reaction Engineering*, 2010, 17 p

Ljung, M. (ed.), *Graduate School in Chemical Engineering Yearbook 2010*, Åbo Akademi University 2010, ISSN 1238–2647, Uniprint, Åbo, Finland, 2010

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4.5 General articles (in newspapers etc.) (4)

Bioenergi på frammarsch, *Forum för ekonomi och teknik* 10(2010), Mikko Hupa

Katalysiseura palkitsee Pasi Virtasen, *Kemia-Kemi* 4 (2010), 52 ISSN: 0355–1628

Molekylär processteknologi utvecklas i flera dimensioner, *Meddelanden från Åbo Akademi* 3 (2010), 18–19, Tapio Salmi

Syvällistä tietoa teollisuuden prosesseista, *A propos* (Academy of Finland web publication), November 23, 2010

4.6 Radio/TV programs (4)

Regional News (YLE Turku): Mustalipeällä eväät biopolttonesteeksi, *Mikko Hupa*, on the web http://yle.fi/alueet/turku/2010/05/mustalipealla_evaata_biopolttonesteeksi_1710783.html

Regional News (YLE Turku): Huonosti poltettu puu pilaa ilmaa, *Mikko Hupa*, on the web http://yle.fi/alueet/turku/2010/01/huonosti_poltettu_puu_pilaa_ilmaa_1394665.html

Regional News (God morgon Åboland), November 24, 2010, *Henrik Grénman*

Regional TV (TurkuTV Åktur), October 21, 2010, *Ann-Sofie Leppänen*

4.7 Patents (4)

Bergelin, M., Bobacka, J., Latonen, R.M., Sjöberg-Eerola, P., Wang, X., Eriksson, J.E., An enzyme electrode, 20105700 (2010)

Lewenstam, A., Blaz, T., Migdalski, J., Duda, L., Reference electrode for the electro-gravimetric measurements, particularly for potentiometric measurements, PL 206043 B1 (2010)

Mikkola, J-P., Virtanen, P., Anugwom, I., Mäki-Arvela, P., Dissolution and fractionation and processing of lignocellulosic materials and polymers with bicarbonate ionic solvents formed from amides, alcohols and carbon dioxide, Finnish Patent application No. 20106142, Åbo Akademi University/ForestCluster Oyj

Murzin, D.Yu., Kubičková, I., Snåre, M., Mäki-Arvela, P., Myllyoja, J., Method for the manufacture of hydrocarbons, WO 2006075057, 2006, pp. 21. US Patent 7, 491,858

4.8 Awards granted in 2010 (5)

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DeMartini N., Monedero E., Yrjas P., Hupa M., Co-firing black liquor and biomass in a laboratory single droplet reactor – effects on emissions and combustion characteristics, Best Session Paper, *2010 International Chemical Recovery Conference*, March 29–April 1, 2010, Williamsburg, VA, USA

Jogunola, Olatunde, Award for Best Annual Report and Presentation 2010, *Graduate School in Chemical Engineering (GSCE)*, November 12–13, 2010, Lappeenranta, Finland

Lehmusto J., Yrjas P., Skrifvars B-J., Hupa, M., Effect of potassium chloride and potassium carbonate on the high temperature corrosion of pure Cr and 304L, Best Conference Paper: *Impacts of Fuel Quality on Power Production and Environment*, August 30 – September 3, 2010, Saariselkä, Finland (Fraser Wigley, CD-ROM)

Sundberg, Anna, Harry Elving Prize, teacher's prize, Åbo Akademi University 2010

Virtanen, Pasi, Finnish Catalysis Society Prize for the best doctoral thesis 2010

5. Courses 2010

Concentrated postgraduate courses organised by the Åbo Akademi Process Chemistry Centre members

Chemistry in Combustion Processes I

Course Supervisor: Mikko Hupa
Course Coordinator: Markus Engblom
Time: March
Place: Åbo Akademi University
Cooperation: Graduate School in Chemical Engineering (GSCE)
Lecturers: Mikko Hupa
Edgardo Coda Zabetta, Foster Wheeler
Markus Engblom
Bengt-Johan Skrifvars, Top Analytica
Johan Werkelin
Maria Zevenhoven

The Forest-based Biorefinery: Chemical and Engineering Challenges and Opportunities

Course Supervisor: Mikko Hupa
Course Coordinator: Nikolai DeMartini
Time: May
Place: Åbo Akademi University
Cooperation: Graduate School in Chemical Engineering (GSCE)
Lecturers: Nikolai DeMartini
Markku Karlsson, UPM-Kymmene
Anna Sundberg
Bjarne Holmbom
Dmitry Murzin
Johan Bobacka
Jan Gustafsson
Jyri-Pekka Mikkola
Mikko Hupa
Pedro Fardim
Stefan Willför
Tapio Salmi

Computer-aided Chemical Reaction Engineering

Course Supervisor: Tapio Salmi
Time: May
Place: Åbo Akademi University
Cooperation: Graduate School in Chemical Engineering (GSCE)

Lecturers: Heikki Haario, Lappeenranta University of Technology
Johan Wärnä
Tapio Salmi

Towards New Reactors

Lecturer: Tapio Salmi
Time: September
Place: Università di Padova, Padova, Italy
Assistants: Daniela Dalle Nogare
Nicola Gemo
Pierdomenico Biasi

Non-Cellulosic Plant Polysaccharides

Course supervisors: Stefan Willför and Anna Sundberg
Time: November
Place: Åbo Akademi University
Cooperation: Graduate School for Biomass Refining (BIOREGS)
Lecturers: Hanna Lindqvist
Ann-Sofie Leppänen
Victor Kisonen
Tea Hannuksela, Kemira
Maja Tenkanen, University of Helsinki
Chunlin Xu, Royal Institute of Technology (KTH), Sweden
Robin Manelius
Andrey Pranovich
Fons Voragen, Wageningen University, the Netherlands
Kaisu Leppänen, Metla
Pasi Virtanen

Chemistry in Combustion Processes II

Course Supervisor: Mikko Hupa
Course Coordinator: Maria Zevenhoven
Time: November
Place: Åbo Akademi University
Cooperation: Graduate School in Chemical Engineering (GSCE)
Lecturers: Mikko Hupa
Markus Engblom
Christian Mueller, Clyde Bergemann
Bengt-Johan Skrifvars, Top Analytica
Johan Werkelin
Maria Zevenhoven

Wood Extractives in Pulping and Papermaking

Course supervisors: Stefan Willför and Anna Sundberg
Time: December
Place: Åbo Akademi University
Cooperation: The International Ph.D. Program in Pulp and Paper Science and Technology (PaPSaT)
Lecturers: Jens Krogell
Sylwia Bialczak
Anders Strand
Bjarne Holmbom
Lari Vähäsalo
Mari Zabihian, Kemira

Chemical Kinetics

Course supervisor: Dmitry Murzin
Time: December
Place: Åbo Akademi University
Cooperation: Graduate School in Chemical Engineering (GSCE)
Graduate School of Materials Research (GSMR)
Lecturers: Dmitry Murzin
Tapio Salmi
Johan Wärnä

REACH and CLP

Lecturer: Anders Lassus
Time: December
Place: Åbo Akademi University

Structured Materials

Time: December
Place: Åbo Akademi University
Cooperation: Graduate School of Materials Research (GSMR)
Lecturers: Petra de Jongh, University of Utrecht, the Netherlands
Freek Kaptejn, Technical University of Delft, the Netherlands
Narendra Kumar
Kalle Arve
Dmitry Murzin

6. Other Activities 2010

6.1 Organization of Conferences, Courses and Seminars

February

Turku, Finland, Åbo Akademi Process Chemistry Centre Winter Colloquium, 90

April

Turku, Finland, Graduate School in Chemical Engineering (GSCE) Spring Meeting, 45

September

Saarisekä, Finland, Impacts of Fuel Quality on Power Production and the Environment, 85

November

Lappeenranta, Finland, Graduate School in Chemical Engineering (GSCE) Annual Meeting, 50

6.2 Participation in Conferences, Major Meetings and Courses

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

January

Cardiff, Wales, UK, INECSE Final Meeting, 1

Espoo, Finland, IFRF V Liekkipäivä, 2

Espoo, Finland, Professor Installation at VTT, *Tapio Salmi*

Gothenburg, Sweden, Interdisciplinary Course in Biomaterials (BIOSUM), Gothenburg University, 1

Helsinki, Finland, Technology Academy Finland (TAF) Tekniikan Päivät, invited lecturer, *Mikko Hupa*

Paris, France, Beet Pulp Final Meeting (COLL-CT-2006-030340), 1

St. Petersburg, FL, USA, TAPPI Kraft Recovery Short Course, invited lecturer, *Mikko Hupa*

Stockholm, Ekman-dagarna, invited lecturer, *J.-P. Mikkola*

Stockholm, Sweden, Värmeforskdagar, 1

Turku, Finland, Functional Materials for Healthcare - Current Developments in Biomaterials and Drug Formulations Research, 1

February

Orlando, FL, USA, 61st Annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, invited lecturer, *Johan Bobacka*, 2

Stockholm, Sweden, Royal Institute of Technology, guest lecture, *Tapio Salmi*

March

Akron, OH, USA, University of Akron, invited lecturer, *Dmitry Murzin*

Bamberg, Germany, EUCHEM 2010 Conference on Molten Salts and Ionic Liquids, 1, 1

Berkeley, CA, USA, University of Berkeley, invited lecturer, *Dmitry Murzin*

Kyoto, Japan, 11th International Conference on Microreaction Technology, 1, 1

Longyearbyen, Svalbard, Norway, Nordic Environmental Chemistry Conference (NECC 2010), invited lecturer, *Ari Ivaska*

Monterey, CA, USA, 23rd Organic Reactions Catalysis Society Conference, 4, 4

Padova, Italy, Università di Padova, guest lecturer, *Tapio Salmi*

Roscoff, France, ERA Chemistry Meeting, invited lecturer, *Tapio Salmi*

San Francisco, CA, USA, 239th American Chemical Society National Meeting, 2

Turku, Finland, 2nd FABTECH Seminar, lecturers, *Tapio Salmi, José Rafael Hernández Carucci, Mats Rönnholm*

Turku, Finland, Tekniska Föreningen i Finland (TFiF) Seminar, invited lecturer, *Mikko Hupa*

Umeå, Sweden, Umeå Renewable Energy Workshop, invited lecturer, *Päivi Mäki-Arvela*

April

Calabria, Italy, COST Action 543 Second Training School, 2

Helsinki, Finland, INSKO-AEL Course “Polttotekniikka”, invited lecturer, *Mikko Hupa*

Helsinki, Finland, LASTU Research Programme Annual Seminar, invited lecturer, *Johan Wärnä*

Newcastle, UK, 2nd General Assembly of CoPIRIDE (Combining Process Intensification-driven Manufacture of Microstructured Reactors and Process Design regarding to Industrial Dimensions and Environment), 2,1

Turku, Finland, 1st Annual Meeting of Finnish Society of Zeolites and Mesoporous Materials

Turku, Finland, Graduate School in Chemical Engineering (GSCE) Spring Meeting, 10, chairman, *Mikko Hupa*

Turku, Finland, KTF-65, invited lecturer, *Tapio Salmi*

Williamsburg, VA, USA, 2010 TAPPI/PAPTAC International Chemical Recovery Conference, 5, members of the technical programme committee, *Patrik Yrjas, Mikko Hupa*

Zonguldak, Turkey, 3rd National Catalysis Congress, plenary lecturer, *Dmitry Murzin*

May

Córdoba, Spain, COST Action CM0903, Utilisation of Biomass for Sustainable Fuels & Chemicals (UBIOCHEM I), 4

Gothenburg, Sweden, International Energy Agency-Fluidized Bed Conversion (IEA-FBC) Meeting, invited lecturer, *Mikko Hupa*

Helsinki, Finland, 47th Nordic Polymer Days 2010, 2

Helsinki, Finland, SusEn Annual Seminar (Research Programme for Sustainable Energy), 7

Mariehamn, Åland, Joint Seminar in Industrial Chemistry: Åbo Akademi University - Royal Institute of Technology, Stockholm, Sweden, 15

Novosibirsk, Russia, Boreskov Institute of Catalysis, invited lecturer, *Dmitry Murzin*

Vail, CO, USA, Surface Stability of Materials in High-Temperature Aggressive Environments, 1

Vysoké Tatry, Slovakia, Slovakian Congress in Chemical Engineering, plenary lecturer, *Tapio Salmi*

June

Braunschweig, Germany, 8th International Conference on Coatings on Glass and Plastics, 2

Clearwater, FL, USA, 35th International Technical Conference on Clean Coal & Fuel Systems, 1

Gijón, Spain, 13th International Conference on Electroanalysis (ESEAC 2010), invited lecturer, *Ari Ivaska*, 2

Helsinki, Finland, FuBio Seminar, 2, 1

Helsinki, Finland: French-Finnish Seminar “How does REACH Impact Research on Green Chemistry and Engineering”, invited lecturer, *J-P. Mikkola*

Iasi, Romania, 9th International Symposium of the Romanian Catalysis Society (RomCat), plenary lecturer, chairperson, *Dmitry Murzin*

Jyväskylä, Finland, Nanoscience Graduate School (NGS-NANO) Annual Meeting, 1

Kiel, Germany, 10th European Workshop on Laser Ablation, 1

Magdeburg, Germany, 10th Conference of the European Society of Glass Technology, 2

Montecatini Terme, Italy, 12th International Ceramic Congress, 2

Oulu, Finland, Energy Research at the University of Oulu, keynote lecturer, *Tapio Salmi*

Pargas, Finland, FuBio Seminar

Pargas, Finland, Joint Seminar of Organic Chemistry and Industrial Chemistry and Reaction Engineering at Åbo Akademi University: Liaisons for the Future, 7, 40

Paris, France, Mid-term SuSe Meeting, 2, 1

Philadelphia, PA, USA, 21st International Symposium on Chemical Reaction Engineering (ISCRE-21), 3, 2

St. Petersburg, Russia, Catalysis for Renewable Sources: Fuel, Energy, Chemicals, 8, plenary lecturer, chairperson, *Dmitry Murzin*, keynote speaker, *J-P. Mikkola*

St. Petersburg, Russia, Chemistry and Full Conversion of Forest Biomass, 2

Turku, Finland, 5th Japan–Finland Biotechnology Symposium, 1

Turku, Finland, Industrial Chemistry and Reaction Engineering at Åbo Akademi 90 years, Special Symposium, 11, 50

Wiesbaden, Germany, 105th ZELLCHEMING General Meeting, 2

July

Concepción, Chile, 1st Chilean International Seminar on Biogenic Gases as Fuel for the Future, 1, invited lecturer, *Atte Aho*

Cracow, Poland, Analytics for Society of XXI Century, VIII Polish Conference on Analytical Chemistry, plenary lecture, *Andrzej Lewenstam*

Glasgow, Scotland, 43rd IUPAC World Polymer Congress (MACRO 2010), keynote lecturer, *Johan Bobacka*

Karlsruhe, Germany, 1st International Conference on Materials for Energy, 1, 2

Kyoto, Japan, 20th International Conference on Science and Technology of Synthetic Metals (ICSM), 5

Louvain-la-Neuve, Belgium, 10th International Symposium on Scientific Bases for the Preparation of Heterogeneous Catalysts (PREPA-10), 3, 1

Sapporo, Japan, 6th Tokyo Conference on Advanced Catalytic Science and Technology & 5th Asia Pacific Congress on Catalysis, 1, 1

August

Beijing, China, 33rd International Symposium on Combustion, 2

Graz, Austria, Summer School, 1

Hamburg, Germany, 11th European Workshop on Lignocellulosics and Pulp, 11

Helsingør, Denmark, 14th Nordic Symposium on Catalysis, 3, 3

Kloster Seeon, Germany, Summer School in Biorefinery, plenary lecturer, *Dmitry Murzin*, 2

Ottawa, ONT, Canada, 3rd International IUPAC Conference on Green Chemistry, 1, 1

Paris, France, International Commission on Glass Roadmap Workshop, 1

Prague, Czech Republic, 7th European Congress of Chemical Engineering (ECCE-7-CHISA 2010), chairpersons *Tapio Salmi*, *Dmitry Murzin*, *J-P. Mikkola*, *Johan Wärnå*,

Mats Rönnholm, keynote speakers *Tapio Salmi*, *Dmitry Murzin*, 18, 10

Prague, Czech Republic, EFCE Working Party in Chemical Reaction Engineering, 1

Turku, Finland, Åbo Akademi Process Chemistry Centre Annual Meeting, 130

September

Copenhagen, Denmark, Nordic Graduate School in Biofuels Science and Technology (biofuelsGS-2) Final Seminar, 5, member of organizing committee, *Mikko Hupa*

Espoo, Finland, Future Solutions for Energy, Forest Cluster Graduate School Seminar, invited lecturer, *Mikko Hupa*

Helsinki, Finland, Academy of Finland KETJU Final Seminar, 1

Madrid, Spain, Institute of Catalysis and Petrochemistry, invited lecturer, *Dmitry Murzin*

Nancy, France, COST Action CM0901 Detailed Chemical Kinetic Models for Cleaner Combustion General Meeting, 1

Nice, France, 61st Annual Meeting of the International Society of Electrochemistry (61st ISE), invited lecturers, *Johan Bobacka*, *Ari Ivaska*, 7

Pisa, Italy, International Flame Research Foundation (IFRF) ToTeM 35 Meeting: Co-firing Secondary Fuels in Power Generation, 1

Poznan, Poland, 12th International Congress of the Polish Magnesiological Society, plenary lecture, *Andrzej Lewenstam*

Saariselkä, Finland, Impacts of Fuel Quality on Power Production and the Environment, 15, members of local organizing committee, *Anders Brink*, *Patrik Yrjas*, *Maria Zevenhoven*, keynote lecture, *Daniel Lindberg*, conference chairman, *Mikko Hupa*

Salvador, Bahia, Brazil, 22nd International Congress on Glass, 2

Salvador, Bahia, Brazil, Fundamentals of Glass Science & Technology Course, 1

Tampere, Finland, 23rd Annual Conference of the European Society for Biomaterials, 2, session chairperson, *Leena Hupa*

Turku, Finland, Åbo Akademi Alumnidag - Kemiteknik i 90 år vid Åbo Akademi, organizing committee chairman, *Mikko Hupa*, invited presentation, *Stefan Willför*

Turku, Finland, Special symposium in honour of the book "Chemical Reaction Engineering and Reactor Technology", *Tapio Salmi*, *Johan Wärnå*, *J-P. Mikkola*

Vienna, Austria, XIX International Conference on Chemical Reactors (Chemreactor-19), chairperson, *Dmitry Murzin*, 11, 9

Zaragoza, Spain, 9th Congress on Catalysis Applied to Fine Chemicals, chairperson, *Dmitry Murzin*, 3, 4

October

Berchtesgaden, Germany, Green Solvents for Synthesis Conference, 3, 4

Copenhagen, Denmark, Nordic Energy Research 25 Years Seminar, 1

Ischia, Italy, Combining Process Intensification-driven Manufacture of Microstructured Reactors and Process Design regarding to Industrial Dimensions and Environment (CoPIRIDE) General Assembly Meeting, 2, 2

Moscow, Russia, 9th International Frumkin Symposium, invited lecturer, *Ari Ivaska*

Nice, France, 61st Annual Meeting of International Electrochemistry Society (ISE), 1

Salerno, Italy, 61st International Energy Agency – Fluidized Bed Conversion (IEA-FBC) Meeting, 1

November

Boston, MA, USA, 2010 Materials Research Society Fall Meeting, 1

Cambridge, UK, NOKIA Research Centre, invited lecturer, *Ari Ivaska*

Dalian, China, 4th International Symposium on Carbon for Catalysis (CarboCat IV), 1, 2

Gothenburg, Sweden, HTC/KME/Värmeforsk Research Symposium and Workshop, keynote speaker, *Mikko Hupa*

Lappeenranta, Finland, Graduate School in Chemical Engineering (GSCE) Annual Seminar, 12

Lappeenranta, Finland, Lappeenranta University of Technology, Dept. of Mathematics and Physics, invited lecturer, *Tapio Salmi*

Madison, WI, USA, TAPPI Research Management Committee Meeting, 1

Moscow, Russia, 3rd Nanotechnology International Forum (Rusnanotech), 1, 1

Munich, Germany, 8th Euro Fed Lipid Congress: Fats, Oils, and Lipids: Health & Nutrition, Chemistry & Energy and Oils, 1, 1

Paris, France, International Flame Research Foundation (IFRF) Coal Characterization Seminar, 1

Piteå, Sweden, Solander Symposium, invited lecturer, *Johan Wärnå, J-P. Mikkola*

Prague, Czech Republic, 42nd Symposium on Catalysis, invited lecturer, *J-P. Mikkola*

Santiago de Chile, Chile, International Conference and Fair on Education, Research & Employment in the Renewable Energy Sector (ICERE2 2010), invited lecturer, *J-P. Mikkola*

Toronto, Canada, 2010 Annual Research Review Meeting, University of Toronto Pulp & Paper Centre, invited lecturer, *Mikko Hupa*

Zushi, Japan, International Symposium on High-Temperature Oxidation and Corrosion 2010, 1

December

Stockholm, Sweden, Swedish Forest Industries Federation, NRA Sweden meeting, invited lecturer, *J-P. Mikkola*

Turku, Finland, Graduate School of Materials Research (GSMR) Annual Seminar, 4

Turku, Finland, Åbo Akademi University, Professor Rainer “Pancho” Sjöholm Farewell Symposium, invited lecturer, *Tapio Salmi*

6.3 Visitors and Visits

Visitors to the PCC

Biasi, Pierdomenico, Università degli studi di Padova, Italy (May-December)

Bikovens, Oskars, Latvian State Institute of Wood Chemistry, Riga, Latvia (November)

Boonjob, Warunya, University of Balearic Islands, Palma de Mallorca, Spain (August-October)

Campo, Betiana, Universidad Nacional del Sur, Bahia Blanca, Argentina (January)

Češková, Iveta, University of South Bohemia, Czech Republic (April-July)

Claireaux, Corinne, ENSC-Rennes, France (June-August)

Cortese, Remedios, Università degli studi di Palermo, Palermo, Italy (May-November)

De Araujo Filho, César, INSA, Rouen, France (March-August)

Driver, Gordon, Queen's University of Belfast, Northern Ireland, UK (January)

Durante, Davide, Università degli studi di Padova, Italy (March- August)

Gema, Nicola, Università degli studi di Padova, Italy (September-December)

Gudarzi, Davood, Lappeenranta University of Technology, Finland (March-June)

Guzinski, Marcin, Gdansk University of Technology, Gdansk, Poland (October-December)

Hernandez Malo, Rafael, Universitat Rovira i Virgili, Tarragona, Spain (September-December)

Hilpmann, Gert, Technische Universität Dresden, Germany (January-March)

Hrobar, Vlastimil, Institute of Chemical Technology, Prague, Czech Republic (June-December)

Jain, Shilpi, India (June-July)

Kadlickova, Marcela, Institute of Chemical Technology, Prague, Czech Republic (June-August)

Kasparova, Marketa, Charles University, Hradec Kralove, Czech Republic (March)

Korotkova, Ekaterina, Tver State Technical University, Tver, Russia (January-December)

Kupis, Justyna, AGH University of Science and Technology, Cracow, Poland (May-June; October-December)

Le Normand, Myriam, Royal Institute of Technology, Stockholm, Sweden (May-June)

Levon, Kalle, Polytechnic Institute of New York University, New York City, NY, USA (August-December)

Madsen, Anders Theilgaard, Technical University of Denmark, Lyngby, Denmark (January-April)

Malireddy, Hari Prasad, Polytechnic Institute of New York University, New York City, NY, USA (October-November)

Massera, Jonatan, Clemson University, Clemson, SC, USA (January-December)

Miro-Llado, Manuel, University of Balearic Islands, Palma de Mallorca, Spain (August)

Mishra, Ayush, India (June-July)

Plaza, Piotr, Cardiff University, Cardiff, Wales, UK (January-February)

Qiu, Ping, Nanchang University, Nanchang, China (January-September)

Rabiej, Sylwia, AGH University of Science and Technology, Cracow, Poland (March-August)

Roche, Mauricio, Universidad Simón Bolívar, Caracas, Venezuela (January-May)

Rose, Liga, Latvian State Institute of Wood Chemistry, Riga, Latvia (November)

Shkute, Marite, Latvian State Institute of Wood Chemistry, Riga, Latvia (January)

Simakova, Irina, Boreskov Institute of Catalysis, Novosibirsk, Russia (March-April)

Solana Maranon, Marta, Universidad de Cantabria, Santander, Spain (January-November)

Tourvieille, Jean-Noel, CPE Lyon, France (February-July)

Vikele, Laura, Latvian State Institute of Wood Chemistry, Riga, Latvia (January)

Xiao, Mizhang, Chinese Academy of Sciences, Wushan, China (November-December)

Zmudzka, Magdalena, AGH University of Science and Technology, Cracow, Poland (September-December)

Visits by PCC Members

Blomquist, Maija, Polytechnic Institute of New York University, New York City, NY, USA (April)

DeMartini, Nikolai, USA (March-April)

Fagerlund, Susanne, Gothenburg University, Gothenburg, Sweden (January)

Han, Tingting, State Key Laboratory of Electroanalytical Chemistry, Changchun, China (January-March)

Hupa, Leena, San Salvador, Brazil (September)

Hupa, Mikko, Chennai, India (January)

Hupa, Mikko, Madison, WI, USA & Toronto, Canada (November)

Hupa, Mikko, St. Petersburg, FL, USA (January)

Hupa, Mikko, Tirichirappalli, India (July)

Ivaska, Ari, Gdansk University of Technology, Gdansk, Poland (April)

Ivaska, Ari, NOKIA Research Centre, Cambridge, UK (April)

Kirilin, Alexey, Haldor Topsoe, Lyngby, Denmark (November-December)

Laurén, Tor, Poland (October-November)

Laurén, Tor, Tirichirappalli, India (March)

Lehmusto, Juho, Vail, CO, USA (May)

Lehmusto, Juho, Zushi, Japan (November)

Lindberg, Daniel, École Polytechnique de Montréal, Montréal, Canada (April)

Lindfors, Tom, Hungarian Academy of Science, Technical University of Budapest, Budapest, Hungary (May-June)

Lindholm, Johan, Tirichirappalli, India (March)

Mattinen, Ulriika, Polytechnic Institute of New York University, New York City, NY, USA (April)

Piotrowska, Patrycja, University of Umeå, Sweden (December)

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

Simakova, Olga, University of Virginia, Charlottesville, VA, USA (November-December)

Song, Tao, Shandong Institute of Light Industry, Jinan, China (November)

Sundfors, Fredrik, Hungarian Academy of Science, Technical University of Budapest, Budapest, Hungary (May-June)

Wang, Xiaojun, University of Lund, Sweden (July-December)

Zevenhoven, Maria, Clearwater, FL, USA (June)

Zhang, Di, Lehigh University, Bethlehem, PA, USA (September-December)

6.4 External PhD Examinations and Reviews

Chairman of Organising Committee, 9th Spring Meeting of the International Society of Electrochemistry, May 8–11, 2011 Turku, Finland, *Johan Bobacka*

Conference Chairman, Impacts of Fuel Quality on Power Production and the Environment, Saariselkä, Finland, *Mikko Hupa*

Editorial Board Member for *Clean Air: International Journal on Environmental Combustion Technologies*, *Mikko Hupa*

Editorial Board Member for *Electroanalysis*, *Andrzej Lewenstam*

Editorial Board Member for *Foundations of Science*, *Andrzej Lewenstam*

Editorial Board Member for *Fuel*, *Mikko Hupa*

Editorial Board Member for *IFRF Combustion Journal*, *Mikko Hupa*

Editorial Board Member for *Journal of Elementology*, *Andrzej Lewenstam*

Editorial Board Member for *Kinetics and Catalysis*, *Dmitry Murzin*

Editorial Board Member for *Magnesium Research*, *Andrzej Lewenstam*

Editorial Board Member for *Open Analytical Chemistry Journal*, *Andrzej Lewenstam*

Editorial Board Member for *Philosophy of Science*, *Andrzej Lewenstam*

Evaluation of research proposals: Agency for Science, Technology and Research, Singapore, *Ari Ivaska*

Evaluation of Associate Professor competence (*Zhiqiang Gao*), National University of Singapore, *Johan Bobacka*

Evaluation of Professorship competence (*Zhiqiang Gao*), National University of Singapore, Singapore, *Ari Ivaska*

Evaluation of Professorship competence (*Marian Jaskula*), Jagiellonian University, Cracow, Poland, *Andrzej Lewenstam*

Evaluation of Professorship competence (*Marta Radecka*), AGH University of Science and Technology, Cracow, Poland, *Andrzej Lewenstam*

Evaluation of Professorship in Chemical Engineering, Royal Institute of Technology (KTH), Stockholm, Sweden, *Tapio Salmi*

Guest Editor for *Journal of Molecular Catalysis A.*, *Dmitry Murzin*

Member of EFCE Prize Committee, Ph.D. works in Process Intensification, Prague, Czech Republic, *Tapio Salmi*

Member of Local Organizing Committee, Impacts of Fuel Quality on Power Production and the Environment, Saariselkä, Finland, *Anders Brink*

Member of Local Organizing Committee, Impacts of Fuel Quality on Power Production and the Environment, Saariselkä, Finland, *Patrik Yrjas*

Member of Local Organizing Committee, Impacts of Fuel Quality on Power Production and the Environment, Saariselkä, Finland, *Maria Zevenhoven*

Member of Organizing Committee, Nordic Graduate School in Biofuels Science and Technology (biofuelsGS-2) Final Seminar, Copenhagen, Denmark, *Mikko Hupa*

Member of Organizing Committee, 9th Congress on Catalysis Applied to Fine Chemicals (CAFC9), Zaragoza, Spain, *Dmitry Murzin*

Member of Prize Committee, Graduate School in Chemical Engineering (GSCE) Annual Seminar, Lappeenranta, Finland, *Tapio Salmi*

Member of Scientific Advisory Board, 1st Annual World Congress of Catalytic Asymmetric Synthesis, Beijing, China, *Tapio Salmi*

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

Member of Scientific Committee, 11th International Symposium on Catalyst Deactivation, Kazimierz Dolny, Poland, *Dmitry Murzin*

Member of Scientific Committee, 5th International Symposium on the Molecular Aspects of Catalysis by Sulphides, Copenhagen, Denmark, *Dmitry Murzin*

Member of Scientific Committee, 7th European Congress of Chemical Engineering (ECCE-7), Prague, Czech Republic, *Tapio Salmi*

Member of Scientific Committee, 9th International Symposium of the Romanian Catalysis Society (RomCat), Iasi, Romania, *Dmitry Murzin*

Member of Society Council, International Society for the Development of Research on Magnesium (SDRM), Paris, France, *Andrzej Lewenstam*

Member of Technical Programme Committee, 2010 TAPPI/PAPTAC International Chemical Recovery Conference, Williamsburg, VA, USA, *Patrik Yrjas*

Member of Technical Programme Committee, 2010 TAPPI/PAPTAC International Chemical Recovery Conference, Williamsburg, VA, USA, *Mikko Hupa*

Scientific Advisory Board Member for *Catalysis Letters*, *Dmitry Murzin*

Scientific Advisory Board Member for *Topics in Catalysis*, *Dmitry Murzin*

Vice President of Scientific Committee, Catalysis for Renewable Sources: Fuel, Energy, Chemicals, St. Petersburg, Russia, *Dmitry Murzin*

Vice President of Scientific Committee, XIX International Conference on Chemical Reactors (Chemreactor-19), Vienna, Austria, *Dmitry Murzin*

External Examinations

Claesson, Frida, University of Borås, Sweden, reviewer of licentiate thesis, *Patrik Yrjas*

CPE Lyon, Evaluation Jury Member, *Tapio Salmi*

Crespo, Gastón A., Universitat Rovira i Virgili, Tarragona, Spain, opponent, *Johan Bobacka*

Giuntoli, Jacopo, Delft University of Technology, the Netherlands, opponent, *Mikko Hupa*

Gourdon, Mathias, Chalmers University of Technology, Member of Evaluation Committee, *Nikolai DeMartini*

Ounnunkad, Suriya, University of Wollongong, Wollongong, Australia, Examiner of PhD thesis, *Ari Ivaska*

Rasilainen, Tiina, University of Eastern Finland, Joensuu, Finland, opponent, *Leena Hupa*

Repo, Eveliina, Aalto University, Espoo, Finland, Examiner of licentiate thesis, *Johan Bobacka*

Rutanen, Henrikki, Åbo Akademi University, member of thesis review committee, *Johan Werkelin*

Simakova, Irina, Åbo Akademi University, member of thesis review committee, *Mikko Hupa*

Invited Lecturers at ÅA-PCC

Abiev, Rufat, St. Petersburg State Institute of Technology, St. Petersburg, Russia, June

Akay, Galip, Newcastle University, Newcastle upon Tyne, UK, June

Brumer, Harry, Royal Institute of Technology (KTH), Stockholm, Sweden, December

Frederick, James W., Golden, CO, USA, June

Holmen, Anders, Norwegian University of Science and Technology, Trondheim, Norway, June

Jokinen, Mika, Turku University of Applied Sciences, Turku, Finland, December

Kakiuchi, Takashi, Kyoto University, Japan, March

Kalantar Neyestanaki, Ahmad, Shell Global Solutions, Amsterdam, the Netherlands, June

Klingstedt, Fredrik, City of Turku, Turku, Finland, June

Kokubo, Tadashi, Chubu University, Japan, September

Landau, Miron, Ben-Gurion University of the Negev, Beer-Sheva, Israel, April

Lange, Rüdiger, Technische Universität Dresden, Dresden, Germany, March

Lehtonen, Juha, Neste Oil, Borgå, Finland, June

Pesonen, Janne, Department of Chemistry, Laboratory for Instruction in Swedish, University of Helsinki, May

Pron, Adam, Laboratoire d'Electronique Moléculaire Organique et Hybride, CEA Grenoble, Grenoble, France, October

Sandelin, Fredrik, Shell Global Solutions, Amsterdam, the Netherlands, June

Stankiewicz, Andrzej, Delft Research Center for Sustainable Industrial Processes, Delft University of Technology, the Netherlands, August

Sundholm, Dage, University of Helsinki, Helsinki, Finland, December

Tirronen, Esko, Kemira, Helsinki, Finland, June

Villadsen, John, Technical University of Denmark, Lyngby, Denmark, November

6.5 Publicity

Television and Radio

Interview on local radio, God morgon Åboland, November, *Henrik Grénman*

Newspapers and General Journals

Biomassa är en framtida möjlighet, *Meddelanden från Åbo Akademi* 4 (2010), 8-9

Engagerad lektor får lärarpris, *Meddelanden från Åbo Akademi* 11 (2010), 4-5

Han gillar nya problem att lösa, *Österbottens Tidning*, September 3, 2010

Heta bränslediskussioner i norr, *Meddelanden från Åbo Akademi* 13 (2010), 19

Medicinsk framtid utvecklas vid Åbo Akademi, *Meddelanden från Åbo Akademi* 13 (2010), 8-9

Ny typ av jonsensorer, *Forum för ekonomi och teknik*, September 30, 2010

Omfattande lärobok i kemisk reaktionsteknik, *Meddelanden från Åbo Akademi* 14 (2010), 16-17

Samarbete kring nya metoder för bioraffinering, *Meddelanden från Åbo Akademi* 5 (2010), 14-15

Stipendieprogram lockar fler forskare, *Meddelanden från Åbo Akademi* 3 (2010), 3

Åbo Akademi Process Chemistry Centre Doctoral Theses in Progress 2011

Students from Outside Finland

Part-time and external students included

- Steliana Aldea (Romania, *F*), MSc University of Bucharest, Bucharest, Romania 2006, BSc *ibid.* 2002
- Marceline Akieh (Cameroon, *F*), MSc Martin-Luther-Universität Halle-Wittenberg, Germany 2005, BSc University of Buea, Cameroon 1999
- Ikenna Anugwom (Nigeria, *M*), MSc ÅA 2009, BSc Satakunta University of Applied Sciences, Pori, Finland
- Dorota Bankiewicz (Poland, *F*), MSc Czestochowa University of Technology, Poland 2005
- Sylwia Bialczak (Poland, *F*), MSc Poznan University of Technology, Poland 2007
- Pierdomenico Biasi (Italy, *M*), PhD Università di Padova, Italy 2009
- Daniel Dax (Luxembourg, *M*), MSc RWTH Aachen University, Aachen, Germany, BSc *ibid.*
- Valérie Eta (Cameroon, *M*), MSc ÅA 2007, BSc University of Buea, Cameroon 2000
- Tingting Han (China, *F*), MSc ÅA 2008, BSc Shandong Institute of Light Industry, China 2006
- Jerzy Jasielec (Poland, *M*), MSc ÅA and AGH University of Science and Technology, Krakow, Poland 2008 (double degree)
- Alexey Kirilin (Russia, *M*), MSc D.I. Mendeleev University of Chemical Technology of Russia, Moscow, Russia 2009
- Bright Kusema (Zimbabwe, *M*), MSc D.I. Mendeleev University of Chemical Technology of Russia, Moscow, Russia 2007, BSc *ibid.* 2005
- Ron Lai (Canada, *M*), MSc University of British Columbia, Vancouver, Canada 1994
- Ewelina Leino (Poland, *F*), MSc Silesian University of Technology, Gliwice, Poland 2006
- Bingzhi Li (China, *M*), MSc ÅA 2006, BSc Shandong Institute of Light Industry, China 2004
- Na Li (China, *F*), MSc ÅA 2007, BSc Shandong Institute of Light Industry, China 2005
- Peter Lingenfelter (USA, *M*), MSc ÅA 2000, BSc Oberlin College, Oberlin, OH, USA 1995
- Grzegorz Lisak (Poland, *M*), MSc ÅA and Poznan University of Technology, Poland 2007 (double degree)
- Donald MacNeil (Canada, *M*), MSc ÅA 2002, BEng Dalhousie University, Halifax, Canada 1994
- Gerson Martin Curvelo (Venezuela, *M*), MSc Universidad Simón Bolívar, Caracas, Venezuela 2008
- He Ning (China, *M*), MSc ÅA 2009, BSc Shandong Polytechnic University, China 2007
- Patrycja Piotrowska (Poland, *F*), MSc Czestochowa University of Technology, Poland 2005
- Elena Privalova (Russia, *F*), MSc D.I. Mendeleev University of Chemical Technology of Russia, Moscow, Russia 2008
- Bartosz Rozmysłowicz (Poland, *M*), MSc ÅA and Poznan University of Technology, Poland 2009 (double degree)
- Sabrina Schmidt (Germany, *F*), Diplom Chemiker RWTH Aachen University, Aachen, Germany 2010
- Victor Sifontes Herrera (Venezuela, *M*), MSc Universidad Simón Bolívar, Caracas, Venezuela 2006
- Olga Simakova (Russia, *F*), MSc Novosibirsk State University, Russia 2008
- Tao Song (China, *M*), MSc ÅA 2006, BSc Shandong Institute of Light Industry, China 2003
- Pingping Su (China, *F*), MSc ÅA 2004, BSc Shandong Institute of Light Industry, China 2002
- Michał Wagner (Poland, *M*), MSc AGH University of Science and Technology, Krakow, Poland 2007
- Xiaoju Wang (China, *F*), MSc ÅA 2007, MSc Shandong University, China 2005, BSc Shandong University, China 2002
- Hao Wu (China, *F*), MSc ÅA 2007, BSc Shandong Institute of Light Industry, China 2005
- Zhe Yang (China, *M*), MSc Jilin University, China 2010
- Kai Yu (China, *M*), MSc ÅA 2010, BSc Shandong Polytechnic University, China 2008

Doctoral Students from Finland

Part-time and external students included

- Maija Blomquist (Nousis, *F*), MSc ÅA 1998
- Sonja Enestam (Åbo, *F*), LicTech ÅA 2000
- Susanne Fagerlund (Åbo, *F*), MSc ÅA 2007
- Henrik Gustafsson (Ekenäs, *M*), MSc ÅA 1999
- Kim Granholm (Pargas, *M*), LicTech ÅA 2006

- Sari Hyvärinen (Viitasaari, *F*), MSc ÅA 2007
- Matti Häärä (Åbo, *M*), MSc ÅA 1994
- Oskar Karlström (Jomala, *M*), MSc ÅA 2008
- Petri Kilpeläinen (St. Michel, *M*), MSc University of Helsinki 2002
- Teuvo Kilpiö (Riihimäki, *M*), LicTech Helsinki University of Technology 1993
- Victor Kisonen (Masku, *M*), MSc University of Turku 2005
- Jens Krogell (Mariehamn, *M*), MSc ÅA 2009
- Juho Lehmusto (Åbo, *M*), MSc University of Turku 2007
- Ann-Sofie Leppänen (Nådendal, *F*), MSc ÅA 2004
- Isak Lindén (Jakobstad, *M*), MSc ÅA 2009
- Christian Lindfors (Helsingfors, *M*), MSc Helsinki University of Technology 2008
- Hanna Lindqvist (Nagu, *F*), MSc ÅA 2004
- Ulriika Mattinen (Åbo, *F*), MSc ÅA 2008
- Sam Myllynen (Borgå, *M*), LicTech ÅA 2002
- Linda Nisula (Vasa, *F*), MSc ÅA 2003
- Minna Piispanen (Malax, *F*), MSc ÅA 2005
- Toni Riittonen (Åbo, *M*), MSc University of Turku 2009
- Jussi Rissanen (Åbo, *M*), MSc University of Turku 2010
- Eero Salminen (Nystad, *M*), MSc University of Turku 2010
- Anders Strand (Nykarleby, *M*), MSc ÅA 2008
- Timo Petteri Suominen (Tammerfors, *M*), MSc ÅA 2007
- Pasi Tolvanen (Hangö, *M*), MSc ÅA 2006
- Pasi Vainikka (Villmanstrand, *M*), MSc Lappeenranta University of Technology 2002, MSc Cranfield University, UK 2001
- Emil Vainio (Pargas, *M*), MSc ÅA 2009
- Niklas Vähä-Savo (Björneborg, *M*), MSc ÅA 2009
- Anna Österholm (Borgå, *F*), MSc ÅA 2006

