Åbo Akademi
Process Chemistry Centre

Annual Report 2009 – 2010

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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.

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PCC Annual Report 2009 – 2010

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1. Introduction to the Activities in 2009

Background

Our Åbo Akademi Process Chemistry Centre (PCC) was formed in 1998 by joining four research groups at the Faculty of Chemical Engineering at Åbo Akademi into one research centre with common objectives and research strategy. The PCC is a unique combination of chemistry, chemical technology and chemical engineering.

The PCC has successively grown in quantity and quality. Today we publish over 100 peer-review journal articles per year in leading journals of chemical engineering and chemistry, the total number of PhD theses finished during the last five years (2005-2009) has been 40. We have been visible in the international scientific arena; taking part in conferences and symposia, organizing 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.

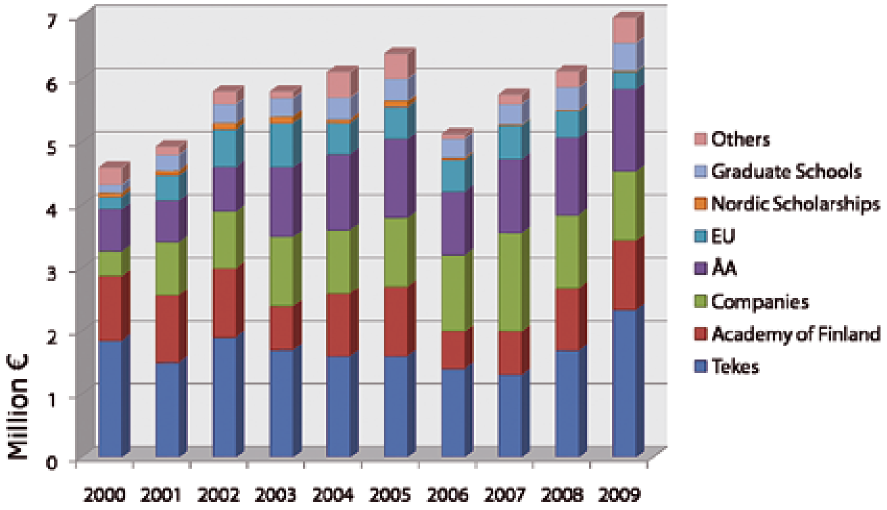
Several prestigious prizes and nominations have come to the members of the PCC. Bjarne Holmbom received the Finnish Science Prize 2005 and the Wallenberg prize 2008, Mikko Hupa received the Fortum Foundation Prize in 2005, Ari Ivaska has been Research Professor at the Åbo Akademi Foundation and Tapio Salmi was appointed Academy Professor by the Academy of Finland for the period 2009-2013.

During the years, a new generation of scientists has grown up at the PCC, achieving high positions in industry and academia. Carita Kvarnström became Professor at the University of Turku; Jyri-Pekka Mikkola received the Incentive Award 2006 by the Academy of Finland and became Professor at the University of Umeå. Johan Bobacka, Stefan Willför and Johan Wärnå are new young professors at the PCC. The PCC is the cradle of new science and new scientists and wants to progress towards future challenges.

A huge challenge for mankind is to shift the current technology, mainly based on fossil sources, to novel technologies based on renewable sources, such as the extensive and refined utilization of biomass. A real progress in this task requires close collaboration and interaction between researchers in chemistry and chemical engineering. The research teams forming the PCC at Åbo Akademi University have the competence in analytical chemistry, wood chemistry, combustion and materials chemistry, kinetics, catalysis and chemical reaction engineering. Our approach to understand the world and to solve the problems of the future we call *Molecular Process Technology*, which implies the development of new technological solutions based on a deep-going understanding of the chemical reactions and physical processes on the molecular level.

The Year 2009 in Numbers

The year 2009 was the fourth year of our second six-year period (2006-2011) as a National Centre of Excellence in research appointed by the Academy of Finland. In 2009 altogether 30 senior researchers and 50 PhD candidates worked in the 55 major research projects of the Centre. In addition, a number of shorter term visitors, Master's students and support personnel participated in our activities.



The funding of the Åbo Akademi Process Chemistry Centre 2000-2009

Economically, the year 2009 was very good. The overall funding to the activities of the Centre was higher than in any previous years since the founding of the Centre.

From an academic point of view the year 2009 was also very productive. The table below gives the key numbers. Our research resulted in altogether 118 papers in scientific publication series with the full referee system, and more than 200 other publications, reports and articles. Seven doctoral theses and 17 masters' theses were finished in 2009.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Doctoral Theses	5	7	8	2	11	8	8	8	9	7
Licentiate Thesis	4	4	5	5	3	2	4	1	5	0
Masters' Thesis	21	23	27	26	17	15	20	23	19	17
Journal Articles	60	70	94	77	106	109	113	116	101	118
Other Publications	105	86	96	86	111	148	157	169	195	204

Theses and other publications by the Åbo Akademi Process Chemistry Centre 2000-2009

Besides the technical publications the PCC again published two Newsletters. Our researchers also wrote popular texts in daily newspapers and journals and appeared on several radio and TV programs in the year 2009.

Awards and Recognitions

Niklas Vähä-Savo received the prize for the Best Masters' Theses in the field of Chemical Recovery in a Kraft Pulp Mill. The prize was granted by the Finnish Recovery Boiler Committee. The title of Niklas′ thesis was "Utveckling och användning av en korttidssond vid mätningar av överbäring i sodapannor" (*Development and application of a one-minute probe for measuring carry-over in a recovery boiler*, in Swedish), and his supervisors were Patrik Yrjas and Mikko Hupa.

Johan Bobacka and Ari Ivaska were granted a scholarship from the foundation Runar Bäckströms Stiftelse for their invention of a method for precipitation of noble metals from solutions.

Further, Ari Ivaska received the "FIA Honour Award for Science" for his "glorious contribution to advance of modern flow injection analytical method". The award was given by the Japanese Association for Flow Injection Analysis of the Japan Society for Analytical Chemistry.

Doctoral Students

As in previous years, a central part of our research activities is done as part of the doctoral theses works. Altogether 50 PhD thesis projects are actively underway at the Centre. Our doctoral students at the PCC are very international, and their diversity is presented in the graph below. More detailed information of the background of our PhD students is given in the Appendix 1 on page 162 of this Annual Report.

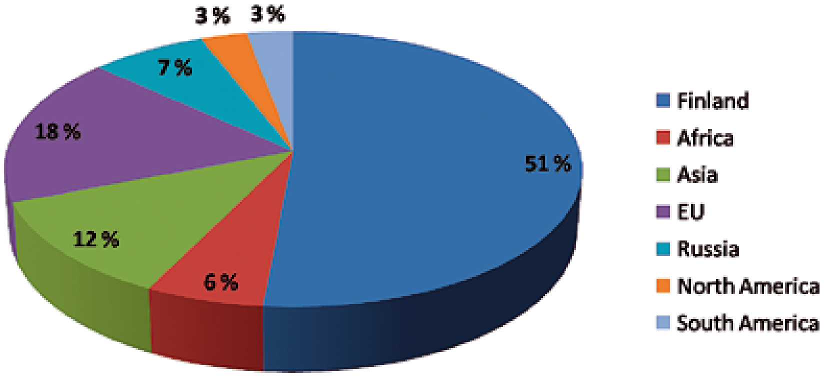
At the moment, 41% of the PCC doctoral students are female.

Many of the PhD works are done with support from the national graduate schools. At the moment 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 Science and Technology, Lappeenranta University of Technology, the University of Oulu and Åbo Akademi University. In 2009 44 students were participating in the activities of the GSCE, 12 of them from our Centre.

The PCC groups have 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).

The Nordic Graduate School in Biofuel Science and Technology is part of the Nordic Energy Research activities funded by the Nordic Council of Ministers. This school is a collaborative effort by Chalmers University of Technology, the Technical University of Denmark, the Norwegian University of Science and Technology and Åbo Akademi

University. This school has received funding for the four-year period 2007-2010. The PCC acts as the coordinator for this collaborative School.



Nationality of the PhD students at PCC 2009-2010. For more detailed information see Appendix 1 on page 162

Bioraff

For the period 2006-2011 as Centre of Excellence we made a completely new common overall research plan. The new 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.

Today 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 partners and Tekes confirmed their support to this project for the next three-year period 2009-2011. The Bioraff project is co-ordinated by Professor Markku Auer and all four groups of the PCC actively participate in the project.

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 2009 the board met 9 times.

The board was supported by a Scientific Advisory Board (SAB) appointed by the Academy of Finland and an Industrial Advisory Board. In 2009 our Scientific Advisory Board consisted of the Professors Douglas Reeve from the University of Toronto, Jean-Claude Charpentier from CNRS in Lyon and Jiri Janata from the Georgia Institute of Science and Technology in Atlanta. In addition, Professor Johanna Buchert from the VTT represented the Academy of Finland and Jukka Leppälahti represented Tekes, the Finnish Funding Agency for Technology and Innovation in this Board.

In 2009 the Scientific Advisory Board visited the Centre in August in connection with the Annual Seminar of the Centre (August 19-20, 2009).

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 2009 the PCC had three lectures in its Distinguished Lecturer Series:

March 6, 2009: Prof. Robert J. Davis, University of Virginia, Charlottesville, VA, USA: “Catalytic Conversion of Biorenewable Molecules to Fuels and Chemicals”

June 4, 2009: Prof. Marek Trojanowicz, Department of Chemistry, University of Warsaw, Warsaw, Poland: ”Exploiting Artificial Nanostructures in Modern Methods of Chemical Analysis”

November 19, 2009: Prof. Ernő Lindner, The University of Memphis, Memphis, TN, USA: ”Evaluating the Performance Characteristics of a New Device or Method: Method Comparison Studies and Their Pitfalls”

Acknowledgements

As previously, this annual report gives an overview of the activities in 2009-2010 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 2009. 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.

Again, we want to sincerely thank all our collaborating partners in Finland and all over the world for the inspiring work together.

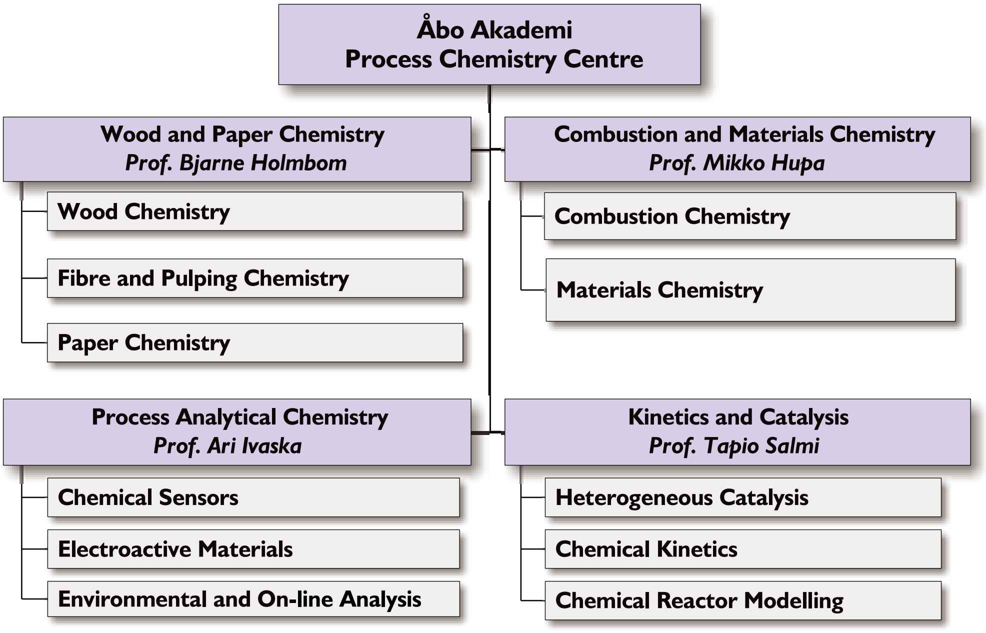
On behalf of the Board of the Åbo Akademi Process Chemistry Centre,

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
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
Håkan Gros, Danisco
Lars Gädda, Forestcluster
Johan Grön, Kemira
Markku Karlsson, UPM-Kymmene
Bertel Karlstedt, Nordkalk
Eeva-Liisa Lakomaa, Vaisala
Timo Leppä, Chemical Industry
Federation of Finland
Lars Peter Lindfors, Neste Oil
Leena Paavilainen, Metla
Jarkko Partinen, Outotec
Ismo Reilama, Metsä-Botnia
Bengt-Johan Skrifvars, Top Analytica
Kenneth Sundberg, Tikkurila
Kari Toivonen, Elomatic
Petri Vasara, Pöyry

Åbo Akademi Process Chemistry Centre 2010

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

2.2 Wood and Paper Chemistry

The vision of our laboratory is to be an internationally recognized and leading team in wood, biorefining, and papermaking chemistry. We strive towards creating and publishing novel and significant scientific findings and to educate students and scientists with excellent skills and creative problem-solving ability for the needs of industry and the society.

Our research is directed towards promoting sustainable and multipurpose use of wood and other renewable raw materials in products including pulp, paper, and fiber, but also for specialty biochemicals and biomaterials. 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 or polyphenols from wood, bark, or process waters is followed by functionalization and utilization in different end-uses. Remaining cellulose, lignin, and other wood substances can then further be recovered or utilized as energy.

External research support during 2009 was obtained mainly from the Academy of Finland, Tekes, EU, and the industry.

The following new projects started during 2009:

- Future Biorefinery (FuBio)
- Lignans as versatile chiral auxiliaries and chiral catalysts (Lignocats)
- Hemicelluloses as a feed source for ruminants

In the beginning of 2010, the following projects were started:

- Upgrading forest industry waste to bioactive chemicals for crop stimulation and bio control (BioCrop)
- Intelligent remote diagnostics
- “Hickeys” caused by calcium oxalate scale deposits – Formation and control
- Chemical modification of water-soluble spruce *O*-acetyl-galactoglucomannan
- Intensified and controlled water extraction of biopolymers from wood
- Environmentally sound extraction of biomasses

In the beginning of 2010 we also started 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 29 countries. Furthermore, we have also taken part in the COST

Action IE 0601, "Wood science for conservation of cultural heritage". We are active partners in the EPNOE network, "European Polysaccharide Network of Excellence" and have also established contacts to the Ili, "International Lignin Institute".

Personnel

Professors	Stefan Willför
	Bjarne Holmbom (Emeritus)
	Markku Auer (Visiting)
Docents	Andrey Pranovich
	Rainer Sjöholm (Organic Chemistry)
	Annika Smeds
	Anna Sundberg
Senior researchers	Patrik Eklund (Organic Chemistry)
	Robin Manelius
	Lari Vähäsalo
Researchers	Anna Boedeker
	Sylwia Bialczak
	Iveta Ceskova
	Christer Eckerman
	Jarl Hemming
	Matti Häärä
	Victor Kisonen
	Jens Krogell
	Ann-Sofie Leppänen
	Hanna Lindqvist
	Linda Nisula
	Sebastian von Schoultz
	Tao Song
	Anders Strand
	Elena Tokareva
Senior Technician	Markku Reunanen
Technician	Leif Österholm
Secretary	Agneta Hermansson

Links:

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

2.3 Combustion and Materials Chemistry

Combustion technologies are in state of new challenges. 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 were 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.

Another part of our ongoing activities dealt with inorganic materials of interest to various applications. In 2009 we continued our studies on bioactive glasses with optimized properties, we studied novel glazes which are easier to keep clean, and we applied our electrochemical measurement systems to support the development of better fuel cell electrode materials and more effective electric capacitors.

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.

We were partners in two EU projects in the year 2009. We continued coordinating the Nordic Graduate School in Biofuel Science and Technology. This graduate school is funded by the Nordic Energy Research Program and it has become an important platform to continue our long-term collaboration in the area of biofuel research with Chalmers University of Technology in Sweden, with the Technical University of Denmark and the Norwegian University of Science and Technology. 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 Science and Technology and Lappeenranta University of Technology, the University of Oulu and Åbo Akademi University.

Our work in high temperature corrosion was expanded in 2009. We have had several projects on various aspects of the corrosion of steam tubes in boilers fired with waste derived fuels. We have projects on the corrosion mechanisms of various metal chlorides; we study corrosion of alkali bromides and fluorides. Recently these studies were expanded to include high temperature corrosion of ceramic materials as well.

In 2009 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 Linda Fröberg Daniel Lindberg Jonathan Massera Pia Sjöberg-Eerola Johan Werkelin Patrik Yrjas Maria Zevenhoven Di Zhang
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	Xiaoju Wang
	Hao Wu
	Niklas Vähä-Savo
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	Luis Bezerra
	Jan-Erik Eriksson
	Piia Leppäsalo
	Jaana Paananen
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	Mia Mäkinen
Coordination	Maria Ljung
Computer support	Peter Ekholm

Links:

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

http://www.abo.fi/gsce

2.4 Catalysis and Reaction Engineering

The research is focused on heterogeneous catalysis, chemical kinetics, modeling of chemical reactors as well as exploring new reaction environments and development of green process technology. Our know-how is continuously developed on catalyst preparation, characterization and screening. New catalytic systems have been taken in use, particularly 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 catalytic pyrolysis of wood. Supported Ionic Liquid Catalysts (SILCA) were 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 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. Special attention was paid on the description of the reaction mechanisms based on first principles, i.e. quantum chemical calculations, which can elucidate the adsorption states and adsorption stoichiometry on solid metal surfaces. The complex interaction of reaction and diffusion in porous media 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.

Personnel

Professors	Tapio Salmi (Academy Professor)
	Dmitry Murzin
	Johan Wärnå
	Jyri-Pekka Mikkola (together with Umeå University)
Docents	Kalle Arve
	Narendra Kumar
	Päivi Mäki-Arvela
	Esa Toukoniitty
Laboratory manager	Kari Eränen
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	Andreas Bernas
	Heidi Bernas
	Pierdomenico Biasi
	Betiana Campo
	Pia Damlin
	Jan Hájek
	José Rafael Hernández Carucci
	Matias Kangas
	Sébastien Leveneur
	Mats Rönnholm
	Anton Tokarev
	Pasi Virtanen
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	Ikenna Anugwom

	Àngela Duque Huguet
	Valérie Eta
	Sigmund Fugleberg
	Henrik Grénman
	Sari Hyvärinen
	Olatunde Jogunola
	Teuvo Kilpiö
	Alexey Kirilin
	Bright Kusema
	Mats Käldström
	Ewelina Leino
	Gerson Martin
	Elena Privalova
	Toni Riittonen
	Bartosz Rozmysłowicz
	Serap Sahin
	Victor Sifontes Herrera
	Olga Simakova
	Timo Petteri Suominen
	Pasi Tolvanen
Technician	Elena Murzina
Secretary	Lotta Malminen

Links

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

Professors	Johan Bobacka
	Ari Ivaska
	Andrzej Lewenstam (part-time)
Docents	Leo Harju
	Carita Kvarnström
	Tom Lindfors
	Li Niu
	Tomasz Sokalski
Senior researchers	Pia Damlin
	Gordon Driver
	Dongxue Han
	Anna Kisiel
	Rose-Marie Latonen
	Beatriz Meana Esteban
	Konstantin Mikhelson
Doctoral students & researchers	Marceline Akieh
	Maija Blomquist
	Paul Ek
	Kim Granholm
	Henrik Gustafsson

	Tingting Han
	Jerzy Jasielec
	Marketa Kasparova
	Justyna Kupis
	Grzegorz Lisak
	Ulriika Mattinen
	Zekra Mousavi
	Maria Peshkova
	Kjell-Erik Saarela
	Pingping Su
	Fredrik Sundfors
	Julia Szűcs
	Agnieszka Teter
	Agnes Varga
	Kevin Vavra
	Michał Wagner
	Anna Österholm
Secretary & coordinator	Anne-Leena Gröning
Technicians	Sten Lindholm
	Lassi Väinölä

Links

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

3. Research

For the second period 2006–2011 as a Centre of Excellence a completely new common research plan was planned. The starting points of this planning 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 future research will be connected to this trend.

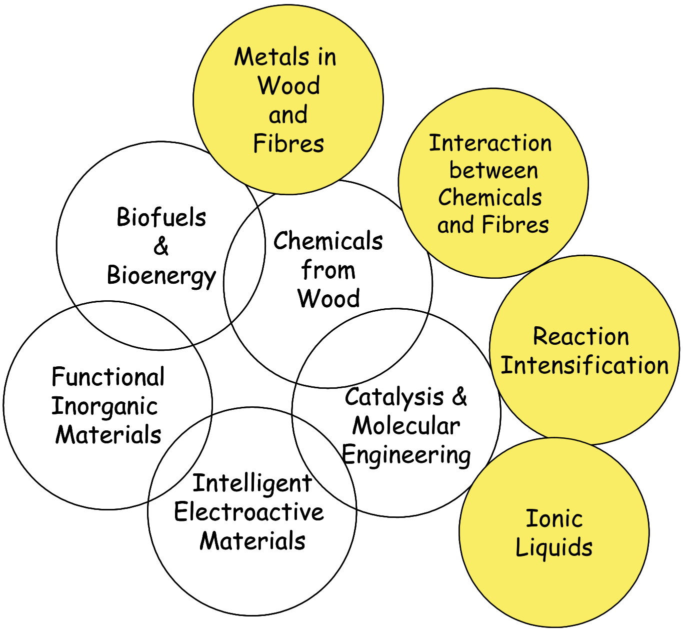
There is an increased interest towards process concepts that make use of the biomass raw material in an optimum way in the production of pulp and paper, specialty chemicals of various kind, biomass derived fuels and energy. These concepts are today referred to by the term *biorefinery*. Our future research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

The new 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 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 ongoing long-term research activities in our Centre.

The basis of our future work will naturally be 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 we have divided all our on-going research projects into these nine research areas. The four newer areas are presented first, followed by the already established research areas.



ÅA-PCC Research Areas 2006–2011

3.1 Ionic Liquids

Even though some ionic liquids were discovered in early 1900's – not to mention the early work on molten salts–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 10^{18}, 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 temperatures 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)
- Cascade catalysis in terms of combined enzymatic and metal catalysis supported in ionic liquids
- Bio-transformations in ionic liquids
- Carbon dioxide utilization

Industrial fractionations and processing of lignocellulosic materials
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 an ionic liquid, where an organometallic complex is dissolved. In the further treatment, the metal is reduced, and we obtain, for instance, palladium nanoparticles. It has 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. 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).

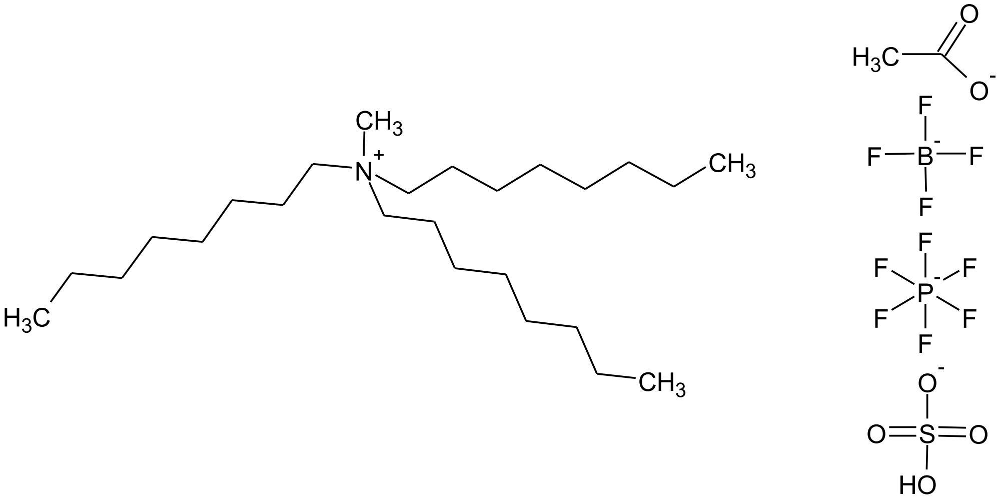
The studies of cellulose derivatives have been focused on two reactions: carboxyalkylation and acetylation of cellulose. In addition, a lot of product characterization methods for the substituted products have been developed. The experiments with cellulose substitution were successful and they can in 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).

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 obtained the award of Finnish Catalysis Society as a best doctoral thesis in catalysis in years 2007–2009.



Structures of self-prepared ionic liquids based on Aliquat 336® cation (on the left) combined with different anions (on the right) e.g. from top to bottom: acetate, tetrafluoroborate, hexafluorophosphate and hydrogen sulphate, applied in SILCA's

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Cooperation:
Zelinsky Institute of Organic Chemistry, Moscow, Russia; Moscow State University, Moscow, Russia; University of Oulu, Finland

Publications:

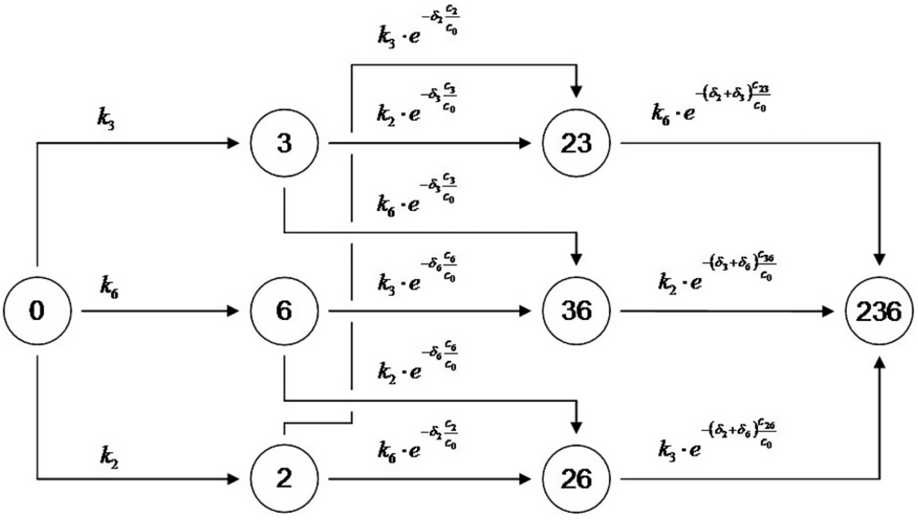
- Virtanen, P., Karhu, H., Toth, G., Kordás, K., Mikkola, J-P., Towards one-pot synthesis of menthols from citral: Modifying supported ionic liquid catalysts (SILCAs) with Lewis and Bronsted acids, *Journal of Catalysis* 263 (2009) 2, 209–219
- Virtanen, P., Mikkola, J-P., Toukoniitty, E., Karhu, H., Kordás, K., Eränen, K., Wärnå, J., Salmi, T., Supported ionic liquid catalysts–From batch to continuous operation in preparation of fine chemicals, *Catalysis Today* 147 (2009), S144–S148

Cellulose Derivatives in Ionic Liquids

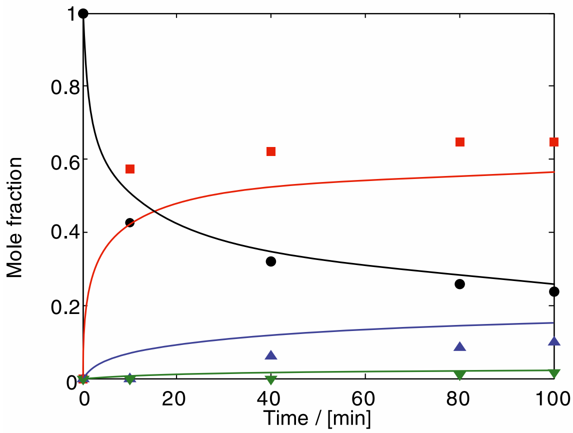
Main funding: ÅA-PCC

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

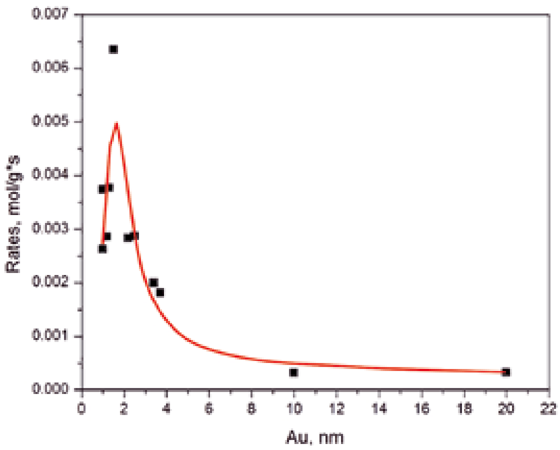
Ionic liquids are excellent reaction media for making cellulose derivatives, because cellulose can be dissolved in non-toxic, non-volatile ionic liquids. This implies that a big technology jump is taken: classical methods for preparing cellulose derivatives are based on the use of suspended cellulose 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 derivates 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*



Dependence of the catalytic activity in arabinose oxidation of Au cluster size

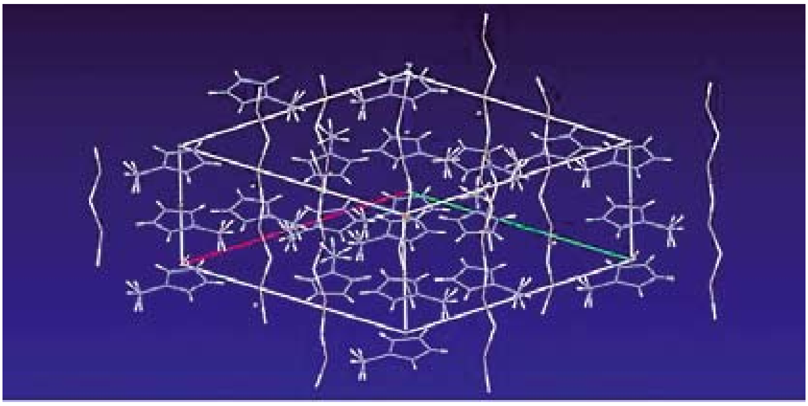
Ion Dynamics

Main funding: Johan Gadolin Post-Doctoral Fellowship (Åbo Akademi University Foundation)

Gordon Driver

Ionic liquids (*i.e.* liquid salts), studied at least as early as the 1830's, are extremely complex media that exhibit physical properties and solvation characteristics that are generally not well understood. While the past two decades have witnessed the development of a plethora of new liquid salts, this class of materials remains in the pioneering development stage. The purpose of this project is to investigate the microscopic physical behaviour of a variety of Brønsted neutral 3-methylimidazolium, $[Hmim]^+$, comprised Brønsted neutral (1:1) and acidic (2:1) ILs and to relate characteristics observed to macroscopic bulk liquid properties. Physical properties of particular interest are the variable-temperature (VT) static dielectric constant probed using GHz dielectric spectroscopy, VT translational and rotational non-Fickian self-diffusion and VT rotational ion dynamics probed using NMR spectroscopy at various magnetic field strengths.

Results obtained for the relative translational self-diffusion coefficients of cations and anions, D+ or D-, measured in the pure liquid using VT-DOSY-NMR, across 4 analogous systems comprised of either X-=Cl-, Br- or HX2- anions, reveal that addition of HX to sequester X- (forming HX2- anions) disrupts electrostatic H-bonding contacts of X- with [Hmim]+ leading to an ease of ion transport and a concomitant drop in resistance to flow. While the expected linear relationships for lnD+/- vs. 1000/T plots were observed for systems containing X=Br-, analogous treatment of the Cl- data revealed diffusion maxima (or the approach towards) for D+ of the 1:1 system, and for D- of the 2:1 system. These findings indicate temperature dependent activation energy barriers to self-diffusion are at play, and evidence the occurrence of bulk liquid structural reorganisations across various temperature regimes. In turn, the dynamic nature of directed inter-ionic interactions becomes apparent (also influenced by relative changes to anion speciation). Dielectric spectroscopy has revealed a rare if ever observed smooth increase of εs (static dielectric constant) with increases in temperature, for both [Hmim]X salts from the super-cooled state through the melting point and into the neat liquid. These materials therefore become more polar as temperatures rise, in stark contrast to more commonly observed behaviour of liquids (molecular or ionic) where εs values are observed to drop with rising temperatures, due to accompanying dipole orientation disruption, caused by increased thermal motion. Liquids exhibiting this type of behaviour are of interest in separations science, where a polarity gradient may result in high temperature miscibility gaps (phase splitting). Ongoing 13C-1H coupled and decoupled (with and without NOE) NMR T1 relaxation experiments are expected to facilitate elucidation of specific ionic motions giving rise to the observed physical behaviour. Several publications are forthcoming.



X-ray structure of crystals formed in co-existence with the pure [Hmim] [HBr$_2$] liquid indicating the presence of [H$_2$Br$_3$]$^-$ in the unit cell

Cooperation:

Physical Chemistry II, 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, Department of Chemistry, University of Helsinki

Publications:

- Driver, G.W., Johnson, K.E., From molecules to ions–Where do modern ionic liquids belong?, *ECS Transactions*16 (2009), 19-31
- Driver, G.W., Johnson, K.E., Experiments with ionic liquids in *Experiments in Green and Sustainable Chemistry* (Eds. H. Roesky, D. Kennepohl), Wiley-VCH, Göttingen, Germany, 2009, 118–127

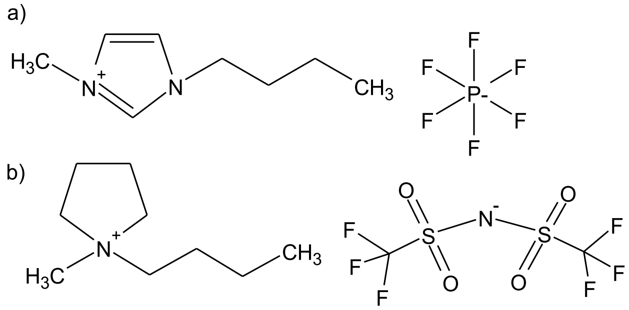
Ionic Liquids in Electrosynthesis and in Characterization of Organic Electroactive Materials

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

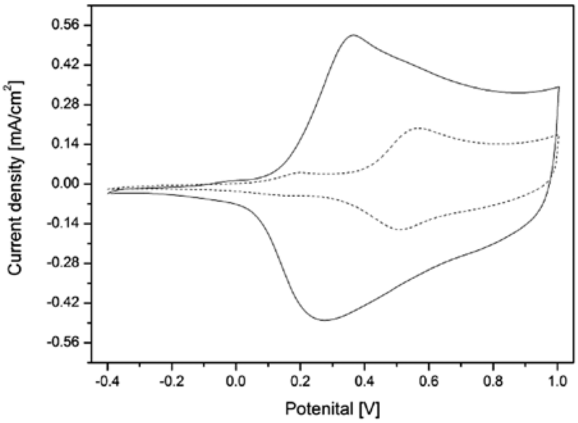
Pia Damlin, Michał Wagner, Anna Österholm, Ari Ivaska

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) and recently both 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][PF_6] and [BMP][Tf_2N] ionic liquids. The results show that the PPP films made in [BMIM][PF_6] 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][Tf_2N] 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][Tf_2N] compared to films made in acetonitrile.



Structure of: a) 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] and b) butylmethylpyrrolidinium bis (trifluoromethylsulfonyl) imide ([BMP][Tf_2N])



PAz film synthesized in [BMP][Tf$_2$N] (solid line, polymerization charge: 6.8 mC, doping charge: 0.92 mC) and PAz synthesized in 0.1 M TBAPF$_6$-ACN (dashed line, polymerization charge: 6.5 mC, doping charge 0.28 mC)

Cooperation:
University of Turku

Ionic Liquids in Industrial Fractionations and Processing of Lignocellulosic Materials

Main funding: Academy of Finland, Tekes, Forestcluster

Jyri-Pekka Mikkola, Pasi Virtanen, Päivi Mäki-Arvela, Ikenna Anugwom, Sari Hyvärinen

Trees, crop residues, agricultural by-products and forestry wastes, among others, are some examples of materials containing lignocelluloses, i.e. they are constituted for those close related substances present in plant cell walls. Traditionally, these resources have not been fully exploited for energy and chemical production. The world annual production of lignocellulosic biomass is up to 1011 to 1012 tons. This plant biomass is a crude, common and reproducible material that is present in every terrestrial environment. Its total caloric value is several times as high as that of the annual production of petroleum, gas and coal. Efficient and economical separation and fractionation processes are a critical part of a successful biorefinery.

Cooperation:
Metla; University of Helsinki; University of Oulu

Ionic Liquids in Carbon Dioxide Utilization

Main funding: Academy of Finland, Tekes

Elena Privalova, Ewelina Leino, Valérie Eta, Pasi Virtanen, Päivi Mäki-Arvela, Jyri-Pekka Mikkola

Increasing levels in environmental pollution and global warming effects are creating opportunities for the development of new catalytic systems for the optimization of chemical processes in order to avert existing rising trends with environmental benefits. The increasing interests in the use of CO_2 as a starting material in chemical syntheses can be ascribed to the widespread acknowledgement that rising atmospheric levels of CO_2 are responsible for the associated climatic changes and global warming. The CO_2 emitted by major fixed-site producers such as fossil fuel power stations, oil refineries, ammonia plants, cement factories, etc could be utilized as feedstock in the chemical industry thus providing new revenue stream and thereby boosting the global economy. The utilization of CO_2 as a cost-effective and highly functional carbon source in chemical manufacturing processes can mitigate the earth's growing blanket of CO_2, consequently reducing the global warming effect. Specific interest in CO_2 utilization is also magnified by its perceived 'green' properties – carbon dioxide is non-flammable, relatively non toxic and chemically stable.

The synthesis of alkyl carbonates from carbon dioxide and alcohol is restricted by reaction thermodynamics, catalyst deactivation and the low reactivity of CO_2. The thermodynamic limitations were relaxed when a dehydration additive was added, leading to an increased production of alkyl carbonates.

Another theme is the search of novel combinations possessing CO_2 capturing properties, such as mixtures of traditional room temperature ionic liquids and 'switchable' ionic liquids.

Cooperation:
University of Jyväskylä; University of Helsinki; Aalto University School of Science and Technology; Université de Bourgogne, Dijon, France; University of Oulu

3.2 Reaction Intensification

The aim of the project is to develop new reactor systems and new technologies which lead to an essential decrease of the size of a chemical plant. The following areas are of interest: monolith reactors, fibrous catalyst structures as well as ultrasonic and microwave technology. The group 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. A new breakthrough was obtained in the use of ultrasound technology in the chemistry of cellulose: it turned out that the dissolution of cellulose in ionic liquids can be considerably enhanced by the use of acoustic exposure. Thus the process intensification aspect was combined to the research tasks in ionic liquids (section 3.1) and chemicals from wood.

A special emphasis is 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, Johan Wärnå, Kari Eränen, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

Fibre catalysts 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.

Cooperation:
Lappeenranta University of Technology

Publications:

- Salmi, T., Intensifiering av kemiska processer, *Sphinx* (2009), 89–100

Micro- and milliscale reactor technology

Main funding: ÅA-PCC, Tekes, EU

Kari Eränen, Mats Rönnholm, José Rafael Hernández Carucci, Àngela Duque Huguet, Ville Halonen, Kalle Arve, Johan Wärnå, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

Micro- and millireactors enable the efficient performance of chemical processes because of enhanced mass and heat transfer. We have introduced the concept of microreactors on Finnish soil. Different kinds of microreactor systems have been constructed; e.g. for catalytic gas-phase systems and for liquid and liquid-liquid reactors. The catalyst coating technology was developed and we are now able to perform various reactions in gas-phase microreactors and conduct kinetic studies. Gas-phase microreactors were successfully used to make chemical intermediates, such as ethylene oxide. The doctoral thesis of José Rafael Hernandez Carucci was finished in 2009. It concerned the use of microreactors in the development of exhaust catalysts. Extensive modelling work of microreactors was continued.

Cooperation:

Lappeenranta University of Technology; University of Oulu; Aalto University School of Science and Technology; PCAS Finland; Kemira; several EU partners

Publications:

- Hernandez Carucci, J.R., Kurman, A., Karhu, H., Arve, K., Eränen, K.; Wärnå, J., Salmi, T., Murzin, D.Yu., Kinetics of the biofuels-assisted SCR of NO_x over Ag/alumina-coated microchannels, *Chemical Engineering Journal* 154 (2009) 1–3, 34–44
- Hernandez Carucci, J.R., Eränen, K., Murzin, D. Yu., Salmi, T.O., Experimental and modeling aspects on microstructured reactors applied to environmental catalysis, *Catalysis Today* 147S (2009), S149–S155

Multiphase Reactors

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

Johan Wärnå, Matias Kangas, Mats Rönnholm, Andreas Bernas, Henrik Grénman, Sigmund Fugleberg, Victor Sifontes Herrera, Mats Käldström, Heidi Bernas, Jyrki Kuusisto, Atte Aho, Sébastien Leveneur, Pierdomenico Biasi, Päivi Mäki-Arvela, Jyri-Pekka Mikkola, 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 developed for 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 constructed to study the kinetics of non-catalytic solid-liquid reactions, such as extraction of hemicelluloses and delignification of chips. Direct synthesis of hydrogen peroxide was successfully carried out in a three-phase trickle bed.

Cooperation:

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

Publications:

- Bernas, A., Myllyoja, J., Salmi, T., Murzin, D.Yu., Kinetics of linoleic acid hydrogenation on Pd/C catalyst, *Applied Catalysis A: General* 353 (2009), 166–180
- Salmi, T., Murzin, D., Eränen, K., Mäki-Arvela, P., Wärnå, J., Kumar, N., Villegas, J. Arve, K., A reasonable parallel screening system for catalytic multiphase processes, *Catalysis of Organic Reactions* 123 (2009), 419–424
- Leveneur, S., Salmi, T., Wärnå, J., Murzin, D.Yu., Estel, L., Interaction of intrinsic kinetics and internal mass transfer in porous ion-exchange catalysts: Green synthesis of peroxycarboxylic acids, *Chemical Engineering Science* 64 (2009), 4101–4114
- Lestari, S., Mäki-Arvela, P., Bernas, H., Simakova, O., Sjöholm, R., Beltramini, J., Max Lu, G.Q., Myllyoja, J., Simakova, I., Murzin, D.Yu., Catalytic deoxygenation of stearic acid in a continuous reactor over a mesoporous carbon-supported Pd catalyst, *Energy and Fuels* 23 (2009), 3842–3845
- Lestari, S., Mäki-Arvela, P., Simakova, I., Beltramini, J., Max Lu, G.Q., Murzin, D.Yu., Catalytic deoxygenation of stearic acid and palmitic acid in semibatch reactor, *Catalysis Letters* 130 (2009), 48–51

Batch and Semibatch Reactors for Reactive Solids

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

Henrik Grénman, Steliana Aldea, Pasi Tolvanen, Päivi Mäki-Arvela, Johan Wärnå, Dmitry Murzin, Jyri-Pekka Mikkola, Tapio Salmi

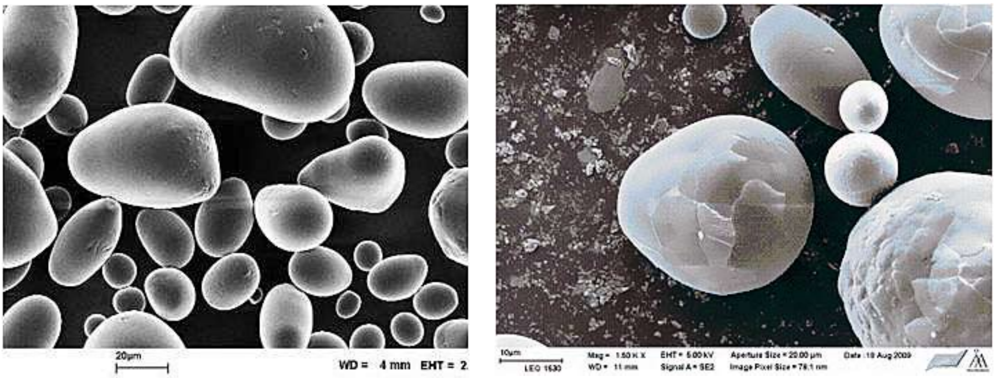
Batch and semibatch reactors are frequently used in the production of fine and specialty chemicals through solid-liquid reactions. The aim of the project is to develop experimental equipment and procedures for obtaining very precise kinetic data and to carry out advanced modelling of chemical kinetics 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 is used to enhance the solid-state reactivity. The project has contributed to essentially increased production capacities.

Cooperation:

Perstorp; Raisio; Nordkalk; Outotec

Publications:

- Tolvanen, P., Mäki-Arvela, P., Sorokin, A. B., Salmi, T., Murzin, D.Yu., Kinetics of starch oxidation using hydrogen peroxide as an environmentally friendly oxidant and an iron complex as a catalyst, *Chemical Engineering Journal* 154(2009) 1–3, 52–59



Starch particles before (left) and after (right) the ultrasound treatment

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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, Valérie Eta, Ewelina Leino, Esko Tirronen, Andreas Bernas, Serap Sahin, 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, CO_2 utilization and reactions between solids and liquids, production of pharmaceuticals and SCR. Both conventional and microreactors are used. The doctoral thesis of Sébastien Leveneur, which concerned the kinetics, thermodynamics and reactor technology for green chemicals (percarboxylic acids), was successfully finished.

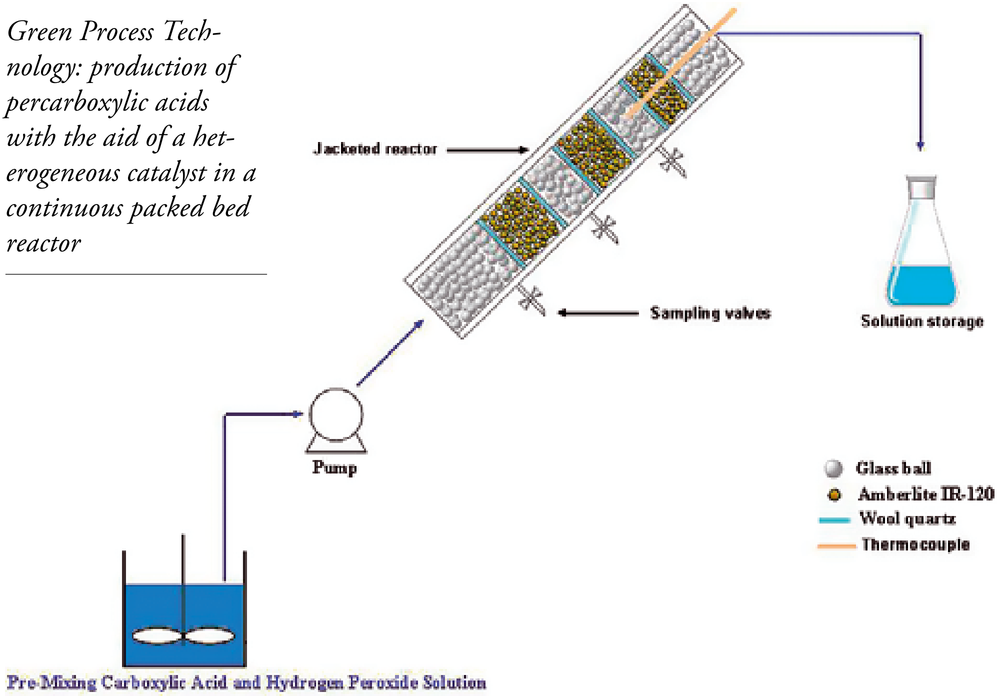
Cooperation:

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

Publications:

- Bernas, A., Ahlkvist, J., Wärnå, J., Mäki-Arvela, P., Lehtonen, J., Salmi, T., Murzin, D.Yu., Hydroformylation of 1-butene on Rh catalysts, *Catalysis of Organic Reactions* 123 (2009), 253–262

- Forsman, J.J., Wärnå, J., Murzin, D.Yu., Leino, R., Reaction kinetics and mechanism of acid catalyzed anomerization of 1-O-Acetyl-2,3,5-tri-O-benzoyl-L-ribofuranose, Carbohydrate Research 344 (2009), 1102–1109
- Forsman, J.J., Wärnå, J., Murzin, D. Yu., Leino, R., Reaction kinetics and mechanism of sulfuric acid catalyzed acetolysis of acetylated methyl L-ribofuranosides, European Journal of Organic Chemistry (2009), 5666–5676
- Leveneur, S., Murzin, D. Yu., Salmi, T., Application of linear-free energy relationships to perhydrolysis of different carboxylic acids over homogeneous and heterogeneous catalysts, Journal of Molecular Catalysis A: Chemical 303 (2009), 148–155
- Leveneur, S., Murzin, D. Yu., Salmi, T., Mikkola, J-P., Kumar, N., Estel, L., Eränen, K., Synthesis of peroxypropionic acid from propionic acid and hydrogen peroxide over heterogeneous catalysts, Chemical Engineering Journal 147 (2009) 2–3, 323–329
- Leveneur, S., Salmi, T., Wärnå, J., Murzin, D.Yu., Estel, L., Interaction of intrinsic kinetics and internal mass transfer in porous ion-exchange catalysts: Green synthesis of peroxycarboxylic acids, Chemical Engineering Science 64 (2009), 4101–4114
- Murzin, D.Yu., Size dependent interface energy and catalytic kinetics on non-ideal surfaces, Reaction Kinetics and Catalysis Letters 97 (2009), 165–171
- Murzin, D.Yu., Thermodynamic analysis of nanoparticle size effect on catalytic kinetics, Chemical Engineering Science 64 (2009), 1046–1052
- Salmi, T., Ahlkvist, J., Bernas, A., Wärnå, J., Mäki-Arvela, P., Still, C., Lehtonen, J., Murzin, D.Yu., Hydroformylation of 1-butene on Rh catalyst, Industrial & Engineering Chemistry Research 48 (2009),1325–1331
- Salmi, T., Kuusisto, J., Wärnå, J., Mikkola, J-P., Detailed kinetic analysis reveals the true reaction path: catalytic hydrogenation, hydrolysis and isomerization of lactose, Catalysis of Organic Reactions 123 (2009), 103–115


Green Process Technology: production of percarboxylic acids with the aid of a heterogeneous catalyst in a continuous packed bed reactor

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 makeup 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.

Application of Liquid Nitrogen in Chemical Analysis

Main funding: Industry

Paul Ek, Sten Lindholm, Ari Ivaska

The design of a cryo-cell for laser ablation system has been improved. The new design enables more effective analysis of soft tissue samples containing high concentration of water with the LA-ICP-MS technique.

A condensing flow through cell has been developed which enable hydride forming gases to be accumulated on a frozen tube surface. This technique enables the whole amount of hydride to be absorbed in a micro volume of reagent solution.

Cryo-cell developed for analysis of soft tissue samples with LA-ICP-MS

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

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

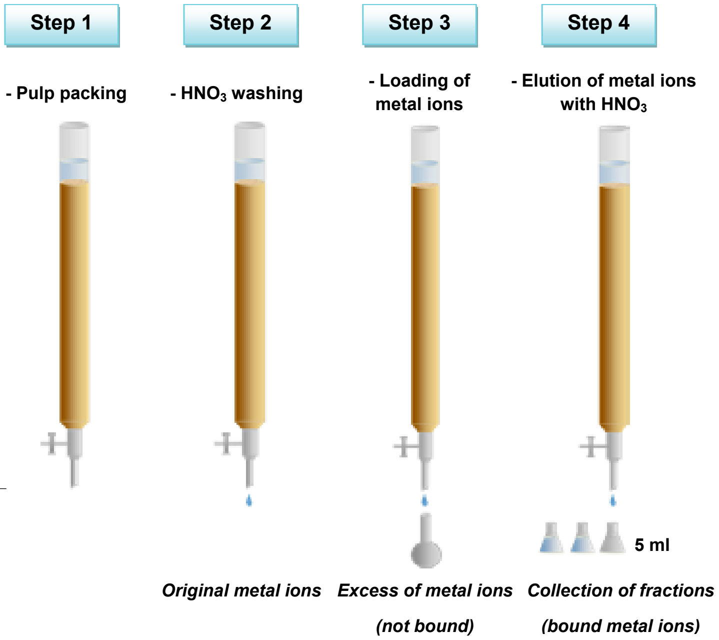
Kim Granholm, Leo Harju, Andrey Pranovich, Tomasz Sokalski, Pingping Su, Ari Ivaska, Bjarne Holmbom

Affinity of metal ions to TMP
The main objective of the study has been to study reactions of metal ions with functional groups in various chemical and mechanical pulps. A column chromatographic method has been developed for the study of metal ion affinities to different types of pulps and wood materials. Equilibrium constants for ion exchange reactions between metal ions and pulps have been determined by a batch technique.

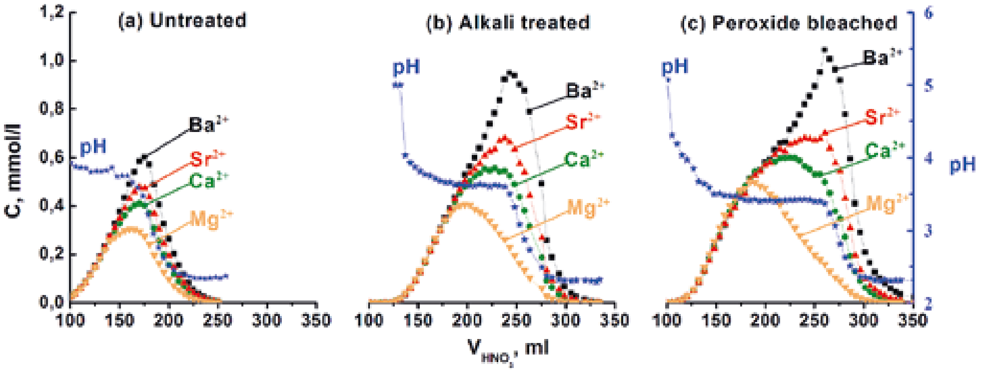
The column chromatographic method was used to assess the differences in affinity of 14 metal ions to untreated, alkali-treated and peroxide-bleached thermo-mechanical pulp (TMP). The method is very sensitive and even small differences in affinities can be detected.

By combining the results from sorption experiments with four different metal ion mixtures the following order of affinity was obtained:

$Pb^{2+} >> Cu^{2+} >> Cd^{2+} > Zn^{2+} > Ni^{2+} > Ba^{2+} > Ca^{2+} > Mn^{2+} > Sr^{2+} > Mg^{2+} > > Rb^{+} \approx K^{+} > Na^{+} > Li^{+}$



The column chromatographic method

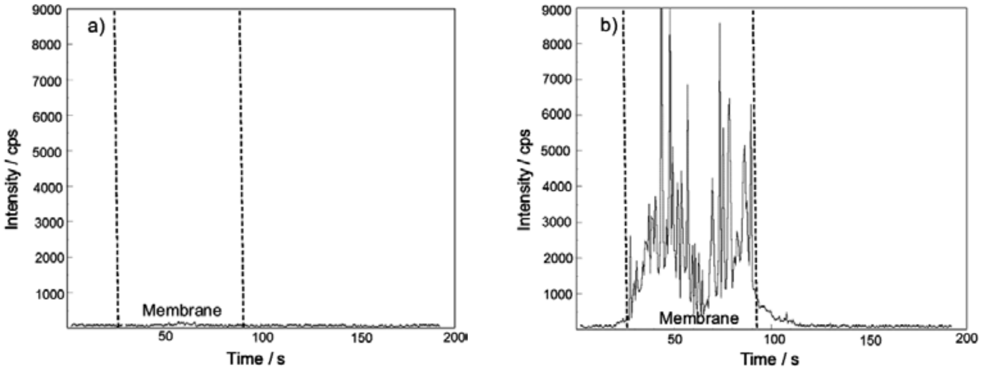


pH and concentrations of alkaline earth metal ions in the collected fractions as function of the elution volume

Of the studied metal ions, Pb^{2+} and Cu^{2+} are clearly the most strongly bound to the pulp fibres, whereas the alkali metal ions are only weakly bound. The different treatments did not change the order of affinity. However, the elution curves for the treated pulps, obtained by the column chromatographic method, were shifted and the shapes of the curves become more asymmetrical. This change is obviously due to the formation of new functional groups during the alkaline treatment and peroxide bleaching.

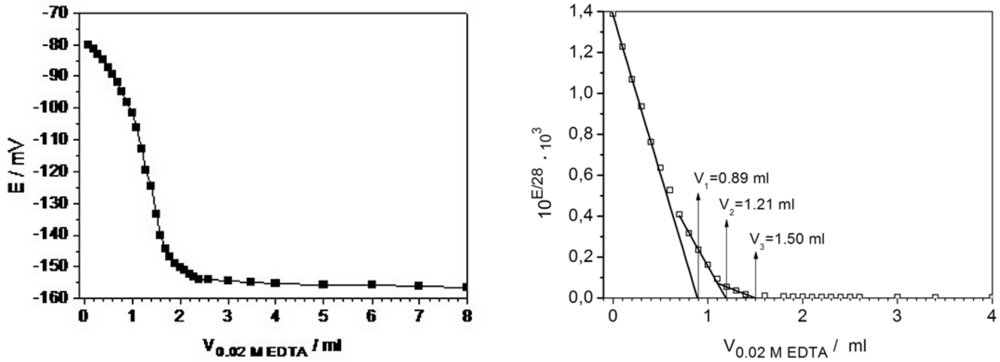
Determination of Ca in black liquor

A solid-contact Ca^{2+}-selective electrode was used for speciation of calcium in black liquor. During extended time of operation the standard potential was found to change, but the sensitivity of the electrode, and the selectivity coefficients remained unchanged. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) measurements showed sodium sorption to the electrode membrane during the measurement in black liquor.



Depth profiles of sodium inside the membranes after the following pretreatments: a) conditioned in 0.01 M $CaCl_2$ *and b) conditioned in 3.3% black liquor. Laser ablation was started at ca. 20 s and the laser penetrated the membrane (200 µm) at ca. 90 s.*

Linearization of the complexometric titration curves were used to determine the concentrations of Ca^{2+}, $CaOH^+$ as well as weak and strong calcium complexes. With inductively coupled plasma optical emission spectrometry (ICP-OES), similar total calcium concentrations were obtained as by the EDTA titration.



Left: Potentiometric titration of calcium with EDTA using Ca^{2+}*-ISE as the indicator electrode*
Right: Linearization of the potentiometric titration curve

Publications:

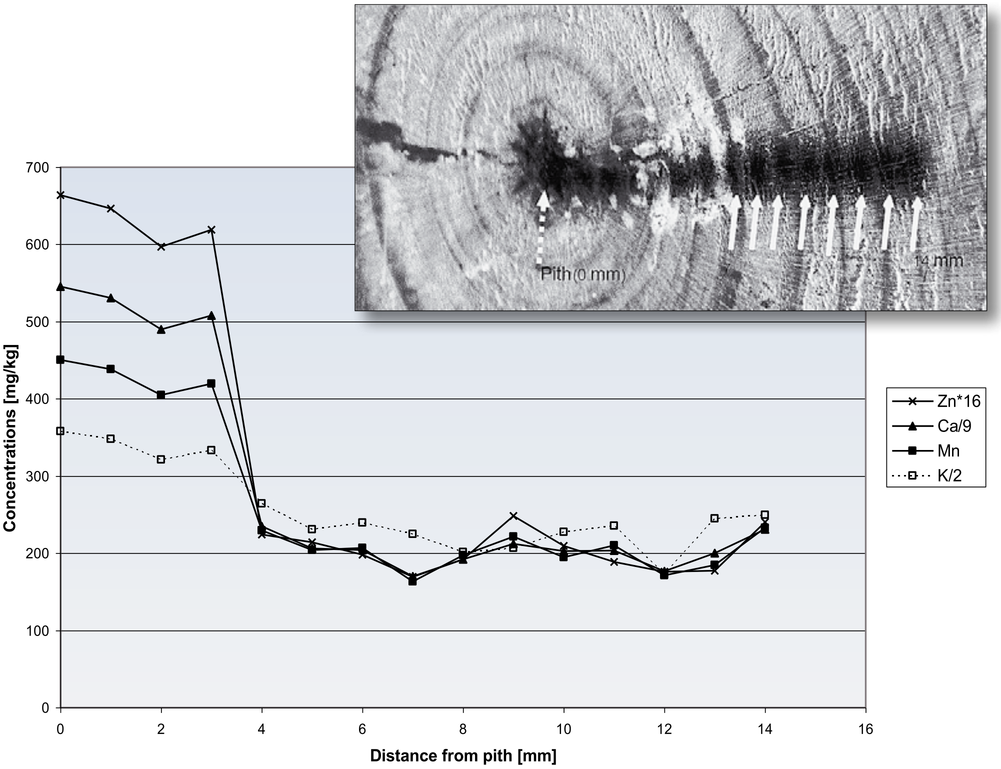
- Granholm, K., Su, P., Harju, L., Ivaska, A., Study on desorption of Mn, Fe and Mg from TMP and evaluation of the complexing strength of different chelation agents using side reaction coefficients, *Holzforschung* 63 (2009), 785–790
- Granholm, K., Ek, P., Sokalski, T., Harju, L., Bobacka, J., Ivaska, A., Determination of calcium with ion-selective electrode in black liquor from a Kraft pulping process, *Electroanalysis* 21 (2009) 2014–2021

Particle-induced X-ray Emission (PIXE) and Gamma Emission (PIGE) Analyses of Environmental Samples, Especially Wood-related Materials

Main funding: Åbo Akademi University, ÅA-PCC

Leo Harju, Kjell-Erik Saarela

The PIXE set-up at Åbo Akademi University has been developed for the determination of elemental concentration mainly in environmental, solid, biological samples. Thick target particle induced X-ray emission (PIXE) enables reliable and sensitive analysis of especially heavier metal ions. If emission of gamma radiation is detected during irradiation of the sample with the proton beam, (PIGE) light elements like C, N and O can be determined in a biological material. Sample preparation is relative easy; a flat surface of the solid material to face the proton beam is prepared. In bulk analyses of stem bark and wood, the materials are dry ashed at 550 °C, shaken and pressed to pellets. This target material is more homogeneous and enrichment of the ash forming elements is utilized. The ash contents obtained in the preparation procedure enables comparing elemental concentrations in the inorganic ash residues. In the case of e.g. pine bark the comparison of metal contents in ashed bark to that in the ashes of underlying stem wood (elemental



Above: Radial spot analyses of pine stem wood using PIXE, and the 1 mm proton beam. The first spot analysed represented pith. Below: Concentration profiles for the elements zinc, calcium, manganese and potassium over the 15 spots of pine wood (note the scaling factors for zinc, calcium and potassium shown in the insert) concentrations in the ashes are normally were similar, even in a case were the ash content of the bark is an order higher) was shown to be way of distinguishing between the air born uptake, and the uptake via root and stem into the bark.

The 1 mm proton beam enables quantification of metal concentration in areas down to less than 1 mm2, and by changing position of the sample in front of the beam; concentration profiles like the one below can be obtained for an element in e.g. wood materials.

Cooperation:

Åbo Akademi University (Accelerator Laboratory); Turku PET Centre

Publications:

- Saarela, Kjell-Erik, Elemental analysis of wood materials by external millibeam thick target PIXE (Doctoral Thesis)

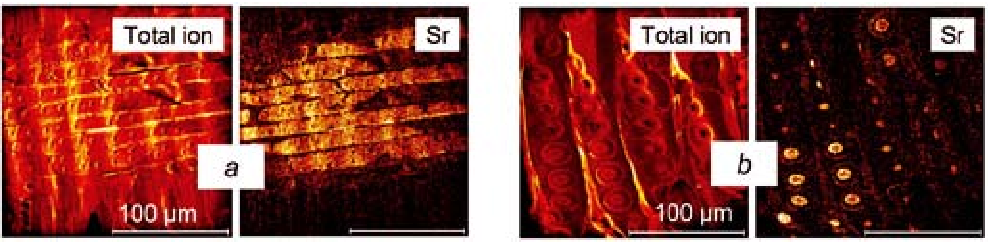
Chemical Microscopy and Chemical Microanalysis of Wood Tissues and Fibres: Anionic Groups in Wood and Fibres

Main funding: Academy of Finland, Tekes (Bioraff)

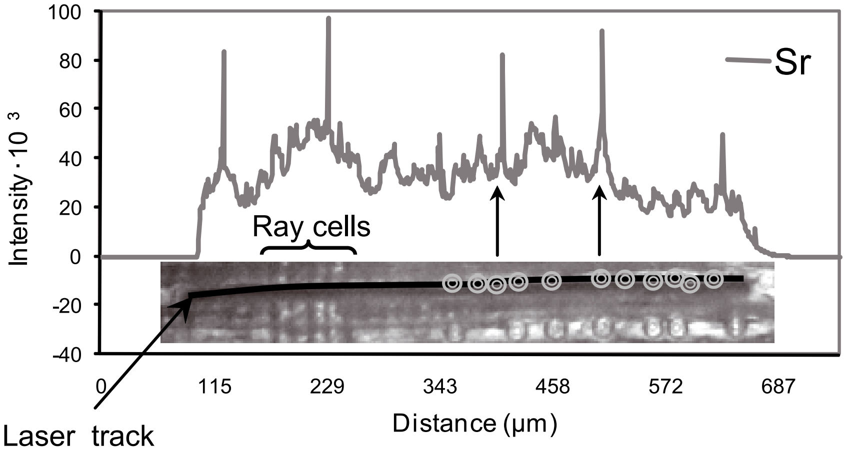
Andrey Pranovich, Elena Tokareva, Bjarne Holmbom, Paul Ek, Ari Ivaska

The amount and distribution of anionic groups – natively occurring in wood fibres, or formed during processing – is essential for certain wood and fibre properties. The ion-exchange interactions of anionic groups with metal ions lead to fibre swelling and softening and can thus significantly affect, e.g. the beatability of fibres and paper strength properties.

A novel method for labelling of anionic groups on wood surfaces and TMP fibres was developed and applied to spruce and aspen wood sections in native state as well as after acid washing, and alkaline and alkaline-peroxide treatments. The metal ions Mg^{2+}, Cu^{2+}, Sr^{2+}, and Zn^{2+} were applied as markers and their patterns of attachment to anionic groups were assessed by time-of-flight secondary ion mass spectrometry (ToF-SIMS). Sr^{2+} ions were found to be a very suitable marker for labelling of anionic groups (Fig. 1). In addition to ToF-SIMS, laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) was applied for semi-quantification of the labelled anionic groups on wood samples (Fig. 2). Labelling of anionic groups with Sr^{2+} ions followed by ToF-SIMS imaging of the Sr^{2+} ion peak showed abundant location of anionic groups in bordered pit membranes and ray parenchyma cell walls in spruce wood. LA-ICP-MS revealed that the relative concentration of Sr^{2+} ions in tori of bordered pits was about eight times higher than in fibre cell walls. After alkaline treatment, the concentration of anionic groups in the fibre cell wall was about three times higher than in the acid-washed spruce section.



ToF-SIMS images of alkali-treated spruce sections labelled with Sr^{2+} *ions showing the abundance of anionic groups in (a) ray cells and (b) pit membranes*



LA-ICP-MS analysis of the distribution of anionic groups in a radial spruce section after alkaline treatment with Sr^{2+} *ion as a marker*

Cooperation:

ÅA-PCC; SLU/WURC (Sweden)

Publications:

- Altaner, C.M., Tokareva, E.N., Wong, J.C.T., Hapca, A.I., McLean, J.P., Jarvis, M.C., Measuring compression wood severity in spruce, *Wood Science and Technology* 43 (2009), 279–290

3.4 Interaction between Chemicals and Fibres

Paper today is not only made of fibres! Process chemicals are needed e.g., to improve the retention of fines and fillers, for deposition and slime control, and as defoamers. Paper chemicals are added to change or improve some of the properties of the final paper, such as opacity, brightness, strength or hydrophobicity. An optimized recipe is needed for a smooth production of high quality paper.

One task of this area is to study the effects of wood components, fines and additives on initial wet strength. Although the initial strength is of great importance for the papermaking process, the chemistry is not fully understood. Our ultimate goal is to control the dewatering and initial wet strength by tailor-made chemistry in the wet-end. Valorisation of the residue from sugar production, the beet pulp, as organic filler in paper, has been studied in an EU project. Organic fillers have several advantages over the inorganic fillers used today. However, there are still some problems to be solved regarding the brightness and the release of substances from the beet pulp fillers but the results are promising.

Flow cytometry has already been shown to be a fast and reliable method for analysing process waters in paper mills. The interpretation of the data has, however, been time consuming and challenging. One goal is to design a system that would be able to detect problems on a paper machine in real time, or even before the problems cause runnability problems. The distribution of wood pitch between the lipophilic droplets and the water phase is very dependent on pH and type of extractive. This has been studied with flow cytometry, but also with other experimental methods.

The surface properties of paper will change during storage. This will affect e.g. the printing and deinking processes. Paper or wood samples used in laboratory experiments will also be affected by storage.

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

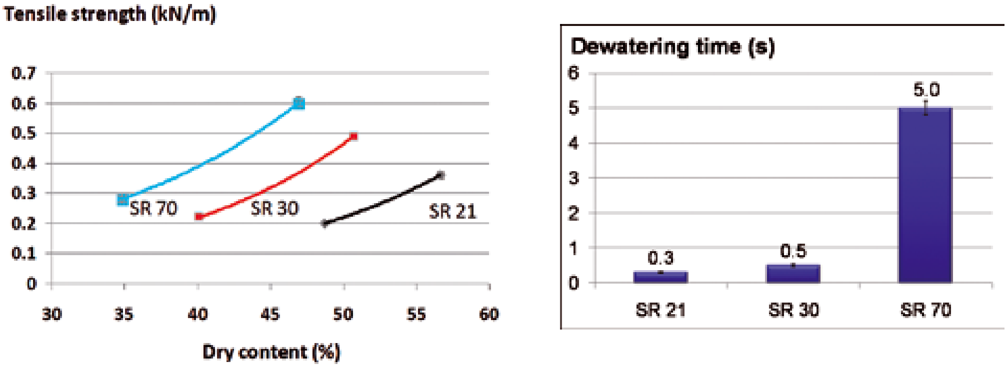
Main funding: Tekes, Industry

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

The tension and relaxation of the wet web are critical for the runnability of paper machines. Poor performance cause web breaks and may also impair the quality of the paper. Strength properties like tensile strength and stretch as well as runnability can be controlled by tailoring the wet-end chemistry.

At a low solids content two kinds of water are present in the assembly of fibres; water associated with the swollen fibres and free water outside fibres. The free water is believed to be partly responsible for keeping the fibres together through capillary forces. At this stage, the surface tension of the water becomes a critical parameter. When the free water is removed, the possibility of molecular bonding increases. As the solids content increases, the wet web strength also increases.

We have determined the effect of electrolytes, pH and surfactants for laboratory hand sheets. Tests showed that surfactant addition decreased the surface tension leading to faster drainage and higher solids content after sheet making and wet pressing. Refining or adding isolated fines to the pulp increased initial wet strength but also increased dewatering time significantly (see figure). Due to the slower dewatering, increased refining cannot be used to increase the initial wet strength on a papermachine.



Initial wet tensile strength (left) increased when pulp was refined to higher SR values. At the same time the dewatering times were longer (right)

Cooperation:
VTT Jyväskylä; Kemira; Metso Paper; Stora Enso; UPM-Kymmene

Publications:

- Boedeker, Anna, Inverkan av ett ytaktivt ämne och mannaner på våtstyrka och andra pappersegenskaper (Effects of a surface active agent and mannans on wet strength and other paper properties, Master's Thesis, in Swedish)
- Isaksson, Johan, Inverkan av ett ytaktivt ämne och vedsubstanser på avvattning av kemisk massa (*Effects of a surface active agent and wood substances on dewatering of a chemical pulp*, Master's Thesis, in Swedish)

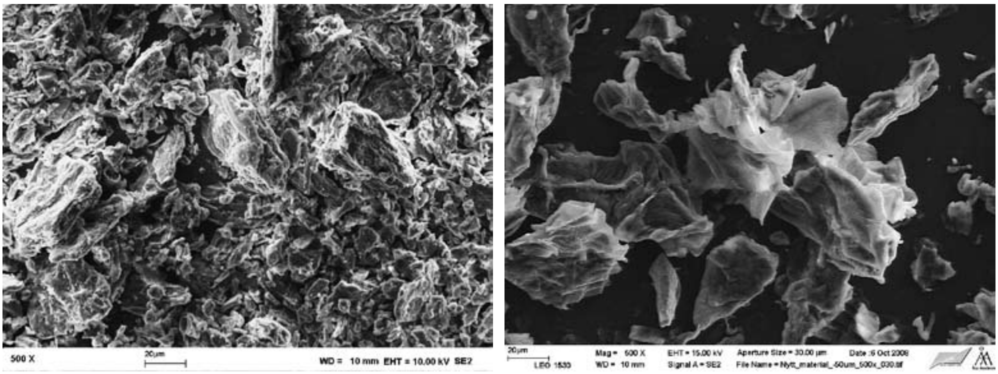
Beet Pulp

Main Funding: EU

Markku Auer, Robin Manelius, Sara Niemi, Bjarne Holmbom

The agriculture often generates large amounts of side streams of biomass, which are often costly to deal with. One such side stream is sugar beet pulp, which amounts up to about 6 million tons of dry matter per year only in the EU. The valorisation of beet pulp into a high added value product is therefore an important issue for the ~400 000 European sugar beet farmers. Efforts are made to transform the sugar beet pulp into organic fillers for paper and board production. Many paper grades contain inorganic fillers in order to improve, e.g. optical properties and to decrease production costs. The drawbacks of these fillers are that they decrease the strength of the produced paper and cause problems in the deinking processes. Additionally, inorganic fillers are abrasive to parts of the papermaking equipment. From the paper and board makers' perspective, organic fillers would promote several advantages, e.g. competitiveness and environmental friendliness, in comparison to the currently used inorganic fillers.

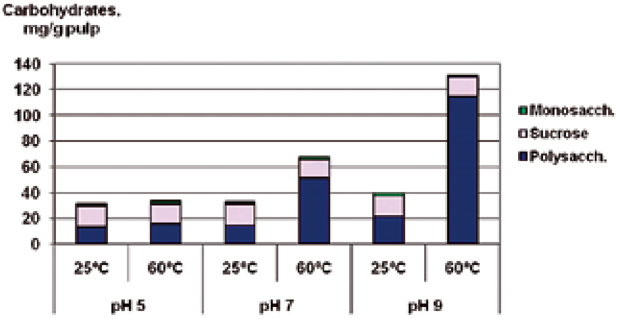
Beet pulp was treated with bleaching agents (H_2O_2 or $NaHSO_3$) and then dried and micronized into 1– ~500 µm particles (see figure). Papers were made and tested. The results showed that an addition of beet pulp fillers resulted in paper with better strength properties and a good opacity compared to kaolin. The whiteness was; however, lower for the paper containing beet pulp which, at this stage, limits the use of these filler to paper grades where the whiteness is not a critical property.



SEM pictures of micronized beet pulp bleached with peroxide (left) and sodium bisulfite (right). The particles are relatively large for being paper fillers but they are soft and therefore increase the paper thickness only slightly.

However, some components, such as pectins, sucrose and monosaccharides, are released from the beet pulp fillers into the process waters (see figure). Sucrose and monosaccharides should be removed from the beet pulp prior to micronization by a short washing stage. The release of pectins increased significantly at high pH and temperature. Beet pulp should therefore not be used at alkaline papermaking conditions. The results show that beet pulp has good potential in becoming a noteworthy paper filler, although there still are important refining issues to be solved.

Polysaccharides, sucrose and monosaccharides released from sodium bisulphite-bleached beet pulp fillers during water extraction at pH 5, 7 and 9, and 25°C and 60°C



Cooperation:

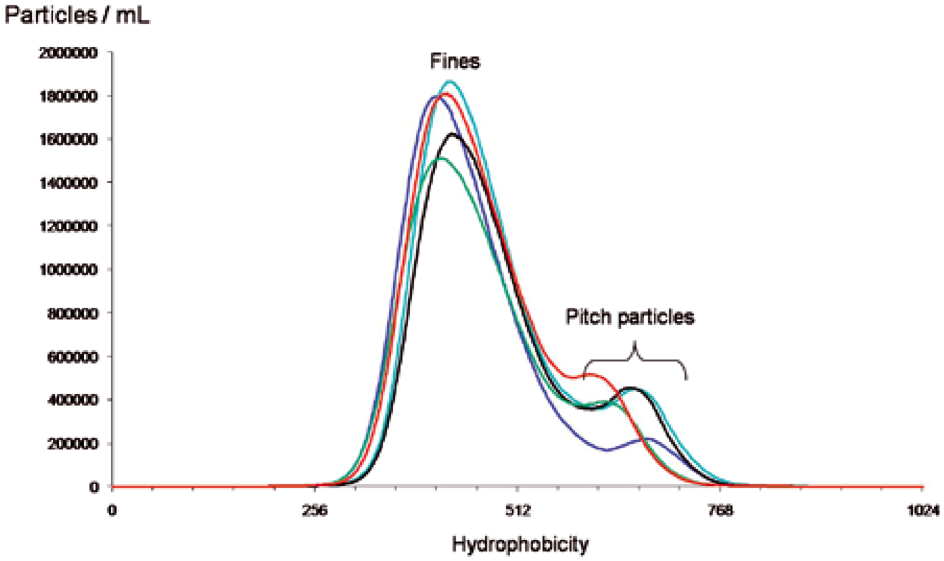
PAGORA, Grenoble-INP, France; Confédération Internationale des Betteraviers Européens, France; Krajowy Zwiazek Plantatorow Buraka Cukrowego, Poland; Association de Recherche Technique Betteravière, France; Union des Sica de Transformation de Pulpes de Betteraves, France; Fabrication et Ateliers L. Choquenet, France; W. Kunz Drytec, Switzerland; Sécopulpe de Bourgogne, France; Juan Romaní Esteve, Spain; Micronis, France; Daniel GOMEZ, France; Juresa, Spain

Intelligent Remote Diagnostics (iReDi)

Main funding: Kemira

Lari Vähäsalo

Paper machine wet-end chemistry is often very hard to control. Multiple chemical and physiochemical reactions and interactions occur simultaneously making the systems very complex. Paper machines can be monitored by on-line measurements and laboratory analysis. However, many of the on-line sensors only measure bulk properties and the more specific laboratory determinations are time consuming and costly. Through the years, we have developed Flow Cytometry methods for analyzing paper machine filtrates. The methods have turned out to be of great value. However, the data interpretation is often time consuming. There is also a need for specific on-line analysis, of the same type produced by flow cytometry.



Automated data interpretation of Flow cytometry data generates information about the hydrophobicity as a function of particle concentration in the samples. The different particle types can be quantified automatically using multivariate regression techniques.

The aim of this project is to develop, combine and utilize techniques that make it possible to detect deposition, runnability and product quality problems in paper mills in real time. This will include automated data analysis of flow cytometry data. New fast methods for DIP-pulp and microbe analysis will also be developed. A new on-line particle analyzer will be built and tested in the laboratory. We will also setup a data analysis system where laboratory and on-line data is easily accessible for the users.

Cooperation:

Kemira

Publications:

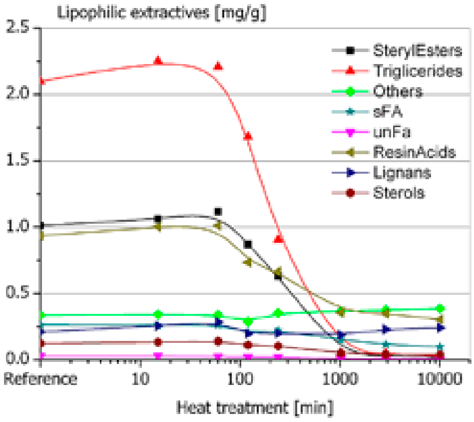
- Bergelin, E., Song, T., Holmbom, B., Co-deposition of wood resin components and betulinol in Kraft pulping and papermaking, *Nordic Pulp and Paper Research Journal* 24 (2009) 4, 428–432

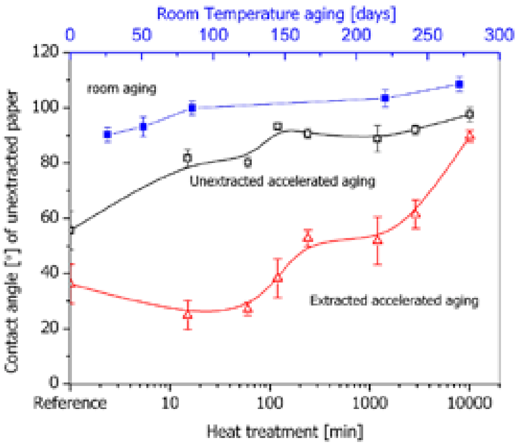
Towards Chemical Understanding of Paper Properties–Role of Different Fibre Constituents on Sorption and Optical Properties

Main funding: PaPSaT Graduate School

Sylwia Bialczak, Bjarne Holmbom, Anna Sundberg

The surface of paper will change during storage. In this study, TMP paper was submitted to accelerated ageing by treatment at 60°C or stored in darkness in room temperature. The content and composition of extractives was analyzed by gas chromatography after extraction with acetone:water (9:1). The surface properties of the paper were investigated by contact angle measurements, XPS/ESCA and ToF-SIMS. The content of acetone:water-soluble extractives decreased significantly during the accelerated ageing. Only 20% of the original extractives could be found in the GC analysis after 2 days of ageing. The contact angle increased with ageing, indicating a change in the surface coverage of extractives. These changes were also seen when storing the papers in room temperature.





Cooperation:
Åbo Akademi (Laboratory of Paper Coating and Converting, Laboratory of Fibre and Cellulose Technology)

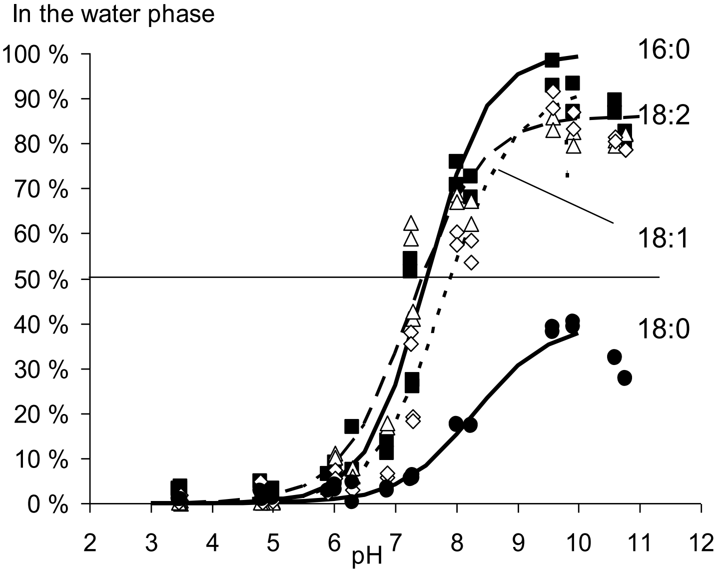
Influence of Pitch Composition and Wood Substances on the Phase Distribution of Resin and Fatty Acids at Different pH-Levels

Main funding: ÅA-PCC

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

Lipophilic extractives, commonly called wood pitch, are dispersed as colloidal droplets in process waters during production of wood-containing paper. The colloidal pitch can be very detrimental to the process, by causing sticky deposits, extensive foaming and overall problems with runnability. The stability of the colloidal system is dictated by the surface of the colloids, which consists mainly of resin and fatty acids (RFAs). The core of the droplets consists of neutral components, such as steryl esters and triglycerides.

Pitch emulsions were prepared from commercially available substances. The phase distribution of RFAs between the lipophilic pitch droplets (l) and the water phase (w) surrounding them was determined as a function of pH. The influence of triglyceride to RFA ratio, which fluctuates due to seasonal variations in real process waters, and the influence of water-soluble galactoglucomannans (GGM) on the phase distribution of RFAs was also determined. The results were expressed as phase-distribution curves and pK_{lw}-values for the individual resin- and fatty acids (see figure). The pK_{lw} of an acid is defined as the pH-value where 50% of that acid is associated with the lipophilic phase and 50% is found in the water phase.



Distribution of fatty acids between lipophilic pitch droplets and water phase in pitch emulsions with a high ratio of triglycerides to resin and fatty acids (RFAs), at 50°C. The weight ratio of triglycerides (TG): resin acids (RA): fatty acids (FA): was 5.1:1.5:1.0.

A low triglyceride to RFA ratio lowered the pK_{lw}-values of both resin and fatty acids by 0.4–1.8 pH-units. This implies that the phase distribution of RFAs in the same process water will differ depending on the time of year. Addition of GGM resulted in a decrease in the pK_{lw}-values of resin acids, and certain fatty acids, while the pK_{lw}-values of other fatty acids increased. Further increasing the concentration of GGM had no significant effect on the solubility of the RFAs.

These results predict the availability of soap anions in different types of colloidal pitch emulsions, which is of great importance for understanding pitch stability, foaming and pitch removal at industrial scale.

Cooperation:

ÅA-PCC

Publications:

- Blanco, A., Negro, C., Diaz, L., Saarimaa, V., Sundberg, A., Holmbom, B., Influence of thermostable lipase treatment of thermomechanical pulp (TMP) on extractives and paper properties, *Appita Journal* 62 (2009) 2, 113–117
- Sundberg, A., Strand, A., Vähäsalo, L., Holmbom, B., Phase distribution of resin and fatty acids in colloidal pitch emulsions at different pH-levels, *Journal of Dispersion Science and Technology* 30 (2009) 6), 912–919

3.5 Chemicals from Wood

One of the main interests in the PCC is to bring processes and products in the forest industry towards a sustainable utilisation of all resources. The use of renewable and natural wood and bark raw materials in environmentally sound processes will eventually bring mankind closer to a world with alternatives to synthetic products of oil or natural gas. The biorefinery concept is implemented both for totally new processes and products, as well as existing pulping and papermaking processes.

We are currently working with potential chemical substances and polymers obtained from waste material sources such as bark, knotwood from over-sized chips, and process waters going to biological treatment plants. Furthermore, whole-tree utilisation through selective extraction (e.g. pressurised hot water extraction) or total dissolution (ionic liquids) are promising methods investigated to obtain hemicelluloses, lignin, tannins, and cellulose in pure form.

The research on wood-derived hemicelluloses, especially O-acetyl galactoglucomannans (GGM) from spruce and arabinogalactans (AG) from larch, has been intensified within the PCC the last years. Both chemical and enzymatic modifications are used to functionalize GGM and introduce properties suitable for different applications. For example, appropriate film forming and different barrier properties are qualities desired in many food packaging applications. Generally, GGM can potentially be used for modification of cellulose surfaces in papermaking and textile applications. Specialty paper grades, abrasion-resistant clothing, antibacterial bandage, barriers against oxygen gas, water vapour, or fat barriers in food packages are high-value products of interest. Hemicellulose-based health promoting agents, such as prebiotic substances or anti-inflammatory agents, as well as emulsion stabilization in food and various technical applications are other potential areas of use. Recovered hemicelluloses can also be used as a renewable source for development of sugar-based fine chemicals or even bioenergy.

Concerning wood-derived polyphenols, we study the transformation of readily available knotwood lignans to other, value-added substances chemically, enzymatically, or by catalytic means. Some economical and technical evaluations of feasibility have been carried out for selected processes. Polyphenols, such as knotwood lignans and spruce bark stilbenes, have been identified as potential antioxidants and bioactive substances. Pine wood and spruce bark stilbenes exhibit antibacterial and decay resistance potential.

These new biochemicals, biomaterials, and the novel processes for producing those calls for a new approach in the analytical methodology as well. Hence a lot of effort is directed towards developing new methods and evaluating these and existing methods to eventually understand the detailed chemistry behind the raw materials, processes, and products. The COST Action FP0901, “Analytical Methods for Biorefineries”, is here an excellent international network that helps us in this effort.

Chemistry in Forest Biorefineries II (Bioraff II)

Main Funding: Tekes

Markku Auer, Atte Aho, Pia Damlin, Paul Ek, Kim Granholm, Leo Harju, Bjarne Holmbom, Mikko Hupa, Ari Ivaska, Jens Krogell, Nikolai DeMartini, Jyri Pekka Mikkola, Dmitry Murzin, Päivi Mäki-Arvela, Andrey Pranovich, Kjell Saarela, Tapio Salmi, Tao Song, Pingping Su, 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 specialty 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, focus is on non-food materials, primarily in industrial pulp and paper processes. The aim of the project is also to preserve the molecular structures created by the nature as much as possible, to explore new separation and purification methods and look at new applications in the areas such as: functional food, nutritional additives, and functional additives in paper making, antioxidants, new bio-based materials and bio-based energy.

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.

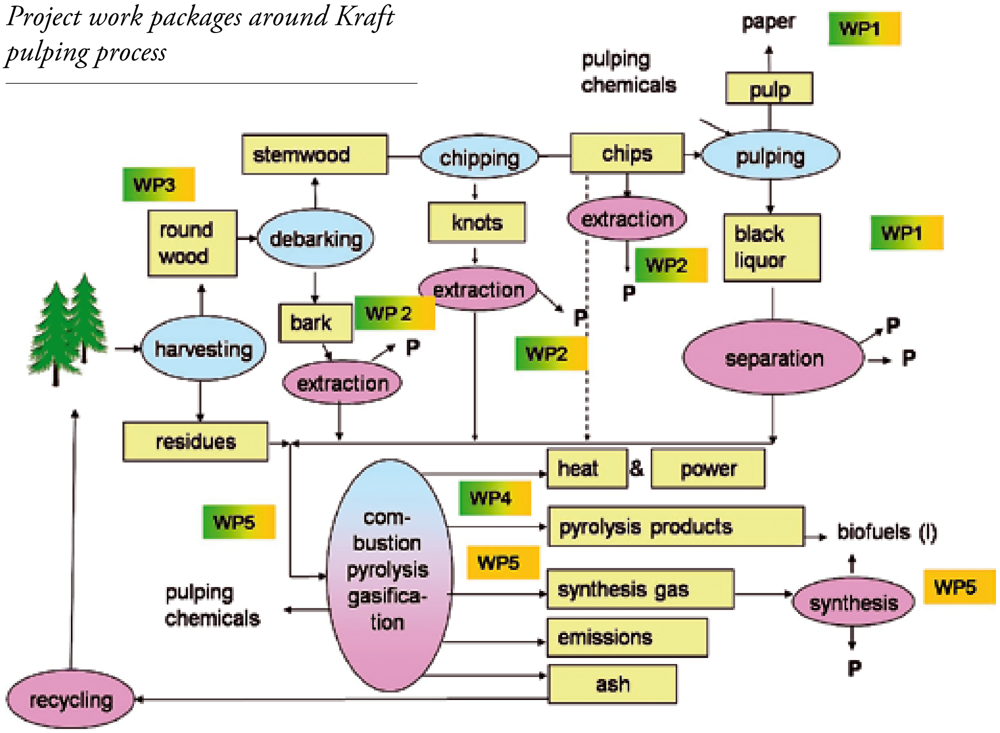
Work packages include (R – research, I – information package):

- Bio-based materials – R&I
- Bioactive compounds from tree biomass – R&I
- Metals in trees, fibres and fuels – R
- Bio-based chemicals and fuels – R&I
- Energy production options in the biorefinery – I (Information WP)

Two promising areas to highlight are derivatisations of both hemicelluloses and cellulosic materials. The goals here are twofold; we are looking for additional functionalities from polyphenols and hemicelluloses and search for new applications. Hemicelluloses would in many applications benefit from the modification of the structure, especially to improve compatibility and solubility challenges in some applications.

In biomass fractionation technologies, the idea is that the structure–preserving isolation would be beneficial for applications such as food products, functional chemicals in paper and for hemicelluloses as a source for specialty sugars. The project focus is around the processes of existing chemical and mechanical pulping, as illustrated in the figure.

Project work packages around Kraft pulping process



In the WP 1 for bio-based material, it was found that GGM can be extracted from spruce in high yields and deacetylation and hydrolytic cleavage can be 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.

In studies on bark, it was found that there are more hemicelluloses in inner bark than in outer bark. The composition of hemicelluloses is different than in wood. 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. Inorganic compounds are minor constituents, less than 1%, of the wood material, but are still of importance for the entire papermaking process. Metals enter the process also with make up water, with added chemicals and through corrosion of the process machinery.

In the studies of metals in wood, we found 17 natively occurring metals in wood. Differences in morphological parts of spruce were found to contain 2–3 times more Mn compared to same parts in aspen. In spruce, early wood from both sapwood and heartwood as well as juvenile wood contains the highest concentrations of Mn. Spruce also contains more Ca than aspen, especially the early wood in the heartwood and juvenile wood. A method for labelling of anionic groups in wood has also been developed.

In the study of pyrolysis, different zeolite catalysts were studied to produce bio-oils. It was found that it is possible to produce bio-oils from different raw materials. Important parameters were the structure of the catalyst, temperature and the type of raw material.

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 behaviour in the different processes. This follow-up is partially based on the results of a parallel project at the Process Chemistry Centre, "ChemCom", which focuses on chemical details of the thermal conversion of biomass based feedstocks.

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 to 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 connection with the BIORAFF project, effective laboratory techniques are under development to evaluate these characteristics. Forest residues with high share of green parts of the wood appear challenging in their gasification behavior due to their high content of some elements – for example potassium, phosphorus and chlorine–which may be harmful to the gasifier operation.

The project serves the aims of the Biorefine programme in developing innovative technologies in relation to biorefineries and in processing of woody biomass. It is also a valuable additional resource for increasing knowledge in chemistry in biorefinery processes, products and applications for chemicals, materials, and fuels. The ultimate goal is to replace petroleum-based synthetic materials and energy with wood-derived materials.

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:

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

Victor Kisonen, Andrey Pranovich, Christer Eckerman, Lari Vähäsalo, Ann-Sofie Leppänen, Tao Song, Jens Krogell, Petri Kilpeläinen, Joakim Jakobsson, Ekaterina Korotkova, Robin Manelius, Annika Smeds, Patrik Eklund, Rainer Sjöholm, Jarl Hemming, Markku Reunanen, Tea Tönnov, Pasi Virtanen, Ikenna Anugwom, Paul Ek, Päivi Mäki-Arvela, J-P Mikkola, Dmitry Murzin, Tapio Salmi, Bjarne Holmbom, Anna Sundberg, Markku Auer, Stefan Willför

The FuBio project is a top-down planned research program that will lay the foundation for a new knowledge platform for the forest cluster 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. Thus the focus is on future forest biorefineries. The project 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 – Currently not active
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. One report deals with "assessing the potential of wood lignin-based value chains for the Forestcluster Ltd. owners and writing a research plan for any potential topics". The objective of this work was to provide a literature and intellectual property review on Black Liquor Gasification. The final report "Black Liquor Gasification – State of the Art" was submitted to Forestcluster Ltd in April 2010. Based on the literature and intellectual property reviews suggestions were made for a path forward for research in Finland in the area of black liquor gasification. The findings of this report will be utilized by the board when they plan the research program for the wood lignin value chains.

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. The maximum yield of polymeric (about 10 kDa) polysaccharide (GGM) was about 7%, on dry wood basis, which comprises about half of the TDS extracted for 20 min at 170°C.

The target of Theme 2 is to develop technologies enabling modification of cellulose molecules 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.

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. Selected approaches towards producing hydrophobic or cationic spruce galactoglucomannans have been tested and are currently being evaluated in the project. These modified hemicelluloses have also called for the development of suitable analytical methods to follow the chemistry of the processes.

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 (GGM) 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 are tested at Pharmatest Services Ltd for their effect on 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 University of Turku and the University of 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-allergic, 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.

Cooperation:

Forestcluster; VTT; Metla; Lappeenranta University of Technology; Aalto University School of Science and Technology; University of Jyväskylä; University of Helsinki; University of Turku; University of Tampere; University of Eastern Finland; Metsäliitto;

Myllykoski; Metso; Kemira; Ciba Finland/BASF; Andritz; Pöyry; Stora Enso; UPM-Kymmene; Danisco; Orthotopix; Pharmatest Services; Separation Research

Publications:

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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, 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.

Through chemical and physico-chemical characterization of spruce galactoglucomannans (GGM) we have reached a better understanding of potential application areas for these biopolymers. Chemical or enzymatic functionalization of the GGM through, for example, acetylation, carboxymethylation, sulphonation, and combinations thereof, have been carried out to introduce novel properties to the biopolymers. In the FunMan project (Academy of Finland), we have worked with targeted enzymatic oxidation followed by metal-mediated allylation reactions in aqueous environment. Native or functionalized GGM have also been tested in a wide range of different applications, for example in microencapsulation and in films or as emulsion stabilizers. 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 the tests will be followed up by *in vivo* animal tests in cooperation with MTT and Metla.

Extractives and especially phenolic compounds such as lignans, stilbenes, and flavonoids are potential antioxidants, radical scavengers, and bioactive substances that still are in focus in our research at PCC. Structural studies and structure-activity-relationships for oxidized lignans are studies we lately have concluded. Stilbenes of the pinosylvin-type and structurally similar norlignans synthesized from the abundant spruce knotwood lignan hydroxymatairesinol have been evaluated for their bioactive, antibacterial, and antifungal properties within the Tekes (EU structural funds) project “Bioactive and wood-associated stilbenes as multifunctional antimicrobial and health-promoting agents (BIOSTIMUL)”. Especially the pine heartwood substance pinosylvin showed potential for several applications. Bark has also been studied as a potential source of bioactive compounds and substrate for bioremediation.

Cooperation:

UPM-Kymmene; Raisio; Metso Paper; M-real; Nordic Jam; Granula; Bio-Vita; University of Helsinki; University of Kuopio; Metla; University of Turku; University of Jyväskylä; VTT; MTT; Metla; KCL; 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; Tampere University of Technology; North Carolina State University, Raleigh, NC, USA; United States Department of Agriculture, USA; Technical University of Luleå, Sweden; European Polysaccharide Network of Excellence (EPNOE)

Publications:

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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 for 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. Carbon dioxide is produced in large amounts in processes like ethanol fermentation, so the future availability is ensured.

Sequential extraction with carbon dioxide and water extracts different kind of substances. Supercritical carbon dioxide acts as a non-polar solvent like hexane. After extraction, carbon dioxide will evaporate from the extracts resulting in 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.

Extraction unit at Metla

Cooperation:
Metla; University of Helsinki

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

Main Funding: Tekes, Industry

Stefan Willför, Robin Manelius

The forest has traditionally provided energy, construction materials, tools and sometimes even food to both industries and for common people in Finland. 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 wood based consumables. Trees, however, contain several bioactive compounds that can be of use, e.g. in agriculture and in medicine. Wood could thus have many other uses than being just a simple raw material.

The BioCrop project aims at creating surplus value for wood materials. The most interesting parts of the wood, for this project, are bark and wood knots. These materials are usually considered as waste but they contain varying amounts of biologically active molecules. These compounds are good candidates for being developed into growth regulation compounds and/or pest repellents for agricultural uses, instead of current synthetic ones used today that pose a serious threat to human health and the environment. Another interesting compound in wood is galactoglucomannan (GGM). Preliminary tests have shown that GGM oligomers, together with polyphenols, possess plant growth regulating properties.

The amounts of different wood wastes are vast in the Finnish forest industry. The most widely used tree species (spruce, pine, aspen, and birch), are therefore used as raw materials for the tests.

Cooperation:

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

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

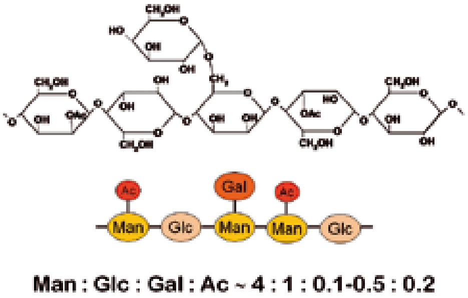
Main Funding: Graduate School for Biomass Refining (BIOREGS)

Ann-Sofie Leppänen, Patrik Eklund, Stefan Willför

Spruce galactoglucomannans (GGM) is a potential raw material for different biochemicals. By introducing functional groups to the molecule, physicochemical properties of GGM can be improved. Since already a small change in the degree of substitution of 0.01 might change the properties of a polysaccharide, a controlled substitution of only specific hydroxyl groups, e.g. the C-6 of the galactose unit, can be enough to lead to the desired improvement. Selective modifications decrease the chemical demand, thus leading to economically and environmentally more benign synthetic methods. The objective of this project is to develop procedures for selective chemical modification of GGM and to investigate how these structural changes affect the physicochemical properties of GGM. One way of doing a selective modification is to combine enzymatic oxidation with chemical reactions. An example on such a reaction is the indium mediated allylation of enzymatically oxidized GGM (see figure). Besides enzymatic oxidation also chemical oxidation will be tested for the activation of specific hydroxyls for further reactions. The

Raw materials

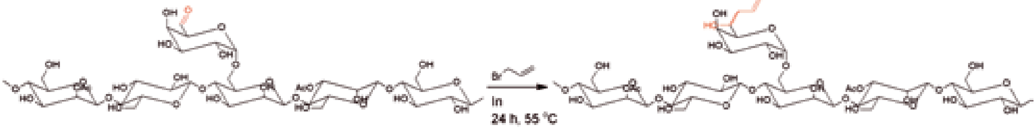
Bark and branch knot wood.
The bark and knot wood samples are extracted using ethanol.



GGM.
The isolated GGM is hydrolyzed using specific endo- and exo- acting enzymes.

Efficacy tests.
The bark and knot wood extracts are tested in simple laboratory tests for their efficacy on plant growth.

effect of modified GGM on paper properties, such as tensile strength, will be investigated. Initial tests show, that the addition of GGM, either modified or unmodified, increases the strength of paper. In order to better understand the reactivity of GGM, the fine structure of the molecule will further be characterized.



Example of selective chemical modification: Indium mediated allylation of oxidized GGM

Cooperation:
University of Helsinki

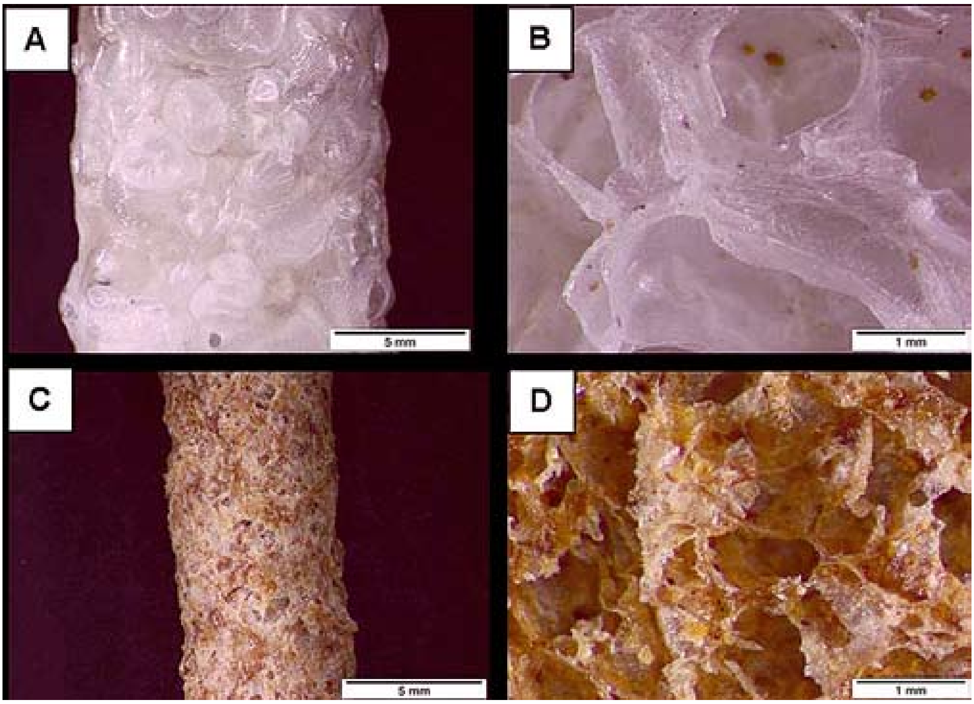
Biomass-Derived Novel Functional Foamy Materials (BIO-FOAM)

Main funding: Tekes

Annika Smeds, Markku Reunanen, Jarl Hemming, Stefan Willför

This project aims at developing novel functional solid foamy materials from renewable sources, i.e., natural polymers from biomass, by combining advanced polymer modification and analytical techniques with processing operations such as extrusion and injection and rotational moulding. The final aim is to replace synthetic and expensive material currently used in porous composite foams with renewable materials. The raw materials used are carbohydrate-based (spruce galactoglucomannan (GGM), polydextrose, starch, and several different cereal fractions), protein-based (whey protein, caseinate), or wood-based (lignin and different types of nanocellulose). These are converted to suitable constituents in different solid foam applications by chemical or enzymatic modifications. The applications studied are as construction and insulation materials, coating, packaging, and composite materials, explosives, and food (e.g., healthier snacks).

Our task in the project is to distribute the raw materials used, to chemically characterise the raw materials, and to chemically modify the carbohydrate-based raw materials GGM and polydextrose. The content of ash and lignin, as well as the content and composition of carbohydrates and extractives was determined. GGM and polydextrose were acetylated to different degrees of substitution.



Outlook and cross section of extrudates, visualised by stereomicroscopy. A and B: 100% barley starch; C and D: 100% rye bran.

Cooperation:
VTT; University of Helsinki; Åbo Akademi (Laboratory of Physical Chemistry); UPM-Kymmene; Danisco Sugar; Finnfoam; Forcit; Termex Eriste; Laihian Mallas; West Mills; Weekend Snacks; Consolis Technology

Extraction of Hemicelluloses from Wood with Pressurised Water (HemU)

Main funding:, Tekes, European Polysaccharide Network of Excellence (EPNOE)

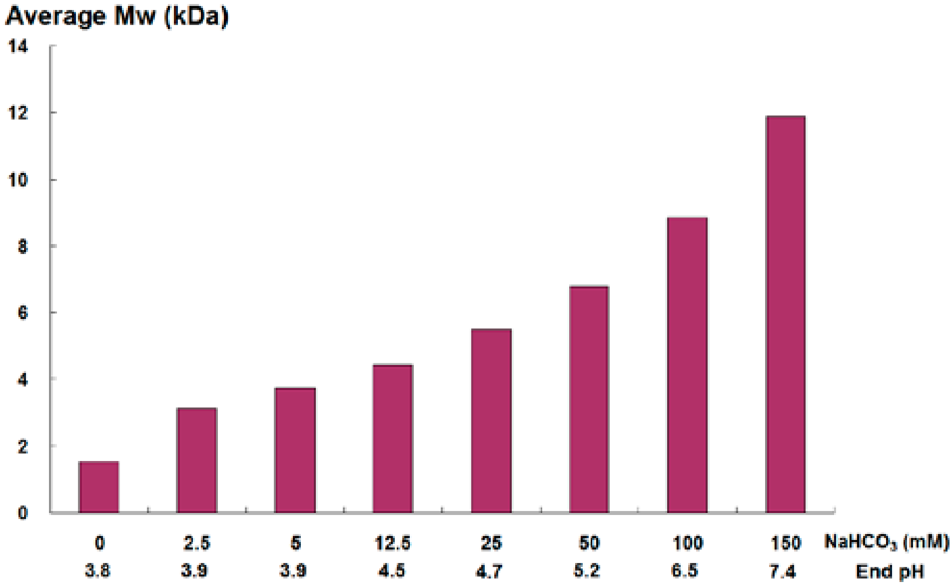
Tao Song, Andrey Pranovich, Bjarne Holmbom

Our aim is to develop new industrially feasible techniques for extraction of the main wood components, while preserving their structure as well as possible, with selective extraction of hemicelluloses as the first target. Spruce chips and ground wood, both sapwood and heartwood, have been extracted for different time and at different conditions using an Accelerated Solvent Extraction (ASE) apparatus:

- With plain water in the temperature range of 160–180°C
- With addition of sodium bicarbonate ($NaHCO_3$) at 170°C
- With addition of phthalate buffers at different pH-levels at 170°C

We have proved the possibilities to selectively extract GGM with plain water in the temperature range 160–180°C. However, at elevated temperatures, hydrolytic de-polymerisation and de-esterification (de-acetylation) of polymeric carbohydrates will occur, leading to a higher portion of monosaccharides and free acetic acid in extracts. It has also be found, that hot-water extraction kinetic of spruce wood with different particle size is different.

Addition of $NaHCO_3$ in small amounts enhanced the hot-water extraction of wood compared to extraction with plain water. At low $NaHCO_3$ concentrations, hydrolytic depolymerisation of hemicelluloses was inhibited. An end-pH value of 4 seems to be optimal for obtaining a high yield of high-molar-mass GGM, under which conditions hydrolysis of acetyl groups and hydrolytic cleavage of GGM are minimised (see figure).



Average molar mass of hemicelluloses extracted at 170°C and 60 min.

Addition of phthalate buffers with pH values of 3.8; 4.0; 4.2 and 4.4 also enhanced the extraction of wood compared to the extraction with plain hot water. Compared to plain water, extraction with phthalate solution (pH level around 4) gives as high yield of GGM extraction and efficiently inhibits the hydrolysis of hemicelluloses and deacetylation of GGM, i.e., preserving polymeric chain.

Cooperation:
Metla; Lappeenranta University of Technology; European Polysaccharide Network of Excellence (EPNOE)

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

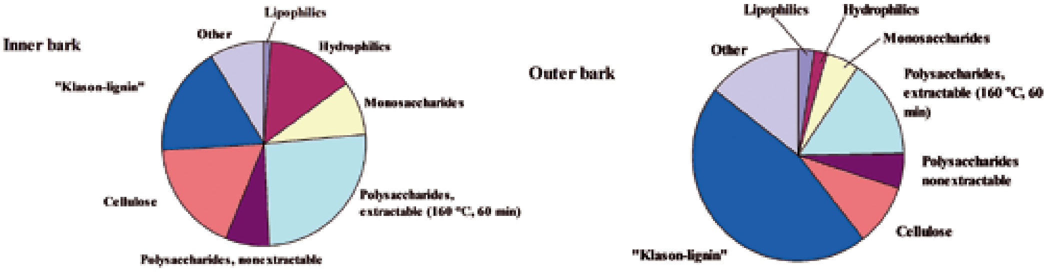
Main funding: Tekes, WoodWisdom Net

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

The aim of this large 3-year European project, now in its last year, is 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 this year we have compiled our various extractions and chemical analyses to a comprehensive overview of spruce bark, separately for inner bark and outer bark. The chemical composition of inner and outer bark is quite different (see figure). However in industrial practice, separation of inner and outer bark is not possible, at least not for now.

Sequential extraction with 1) hexane, 2) ethanol (or acetone) and pressurised hot water yields fractions rich in 1) lipophilic extractives (fats and resins), 2) stilbene glucosides and stilbenes, as well as sugars and 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 one fourth of the outer bark. The non-extractable residue consists of cellulose



Group composition of spruce inner (left) and outer bark (right) determined by sequential extractions and chemical analyses of the fractions and “Klason-lignin”, of which only a part is true lignin. Klason lignin also includes non-extractable tannins and suberin. The hemicelluloses and pectins have been further studied, and found to be composed mainly of arabinose, xylose and glucose sugar units. These pectic-type hemicelluloses have been isolated in larger scale for structural studies and testing of their bioctive properties.

Sequential extraction with water only, at increasing temperatures, has been studied and the obtained fractions have been analysed.

Cooperation:

VTT; Fraunhofer Institut, Germany; Royal Institute of Technology, Stockholm, Sweden; Technaro, Germany

Publications:

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COST Action FP0901, “Analytical Methods for Biorefineries”

Main funding: EU RTD 7th Framework Programme

Stefan Willför, Anna Sundberg, Anders Strand, Sina Rasela

Trees, annual and perennial plants, recycled fibres, and lignocellulosic side streams from forest and agro industry 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 valorised products challenging. The main objective of this Action is to develop new and evaluate existing analytical methods related to forest-based and agro-industrial Biorefineries. Thus, the Action covers the analytical methods for the Biorefinery feed material and for processed biochemicals, biomaterials, and process residues. Especially analytical pretreatments are evaluated. Critical steps are the representativeness of the sampling and samples, the extraction, fractionation, and sample storage methods applied. New methods will be applied and evaluated for their relevance. Other emphasized areas will be development of analytical on-line applications, hyphenated techniques, and applying statistical multicomponent analyses to sort out the relevant data from the main data stream. FP0901 is chaired (Prof. Stefan Willför) and coordinated by Åbo Akademi University.

COST is an intergovernmental framework for European Cooperation in Science and Technology, allowing the coordination of nationally-funded research on a European level. The objectives of FP0901 will be achieved through the organization of state-of-the-art conferences, workshops, and seminars, exchange of reports, publications, and experimental procedures, and involvement of the industry. Furthermore, the arrangement of

Short-Term Scientific Missions (STSMs) and Training Schools for early stage researchers are also important means of reaching the goals. More information can be found at www.abo.fi/costfp0901.

Cooperation:

Universities, laboratories, research institutes, and companies from more than 30 EU COST and affiliated countries

Publications:

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Lignin Valorisation (Lignival)

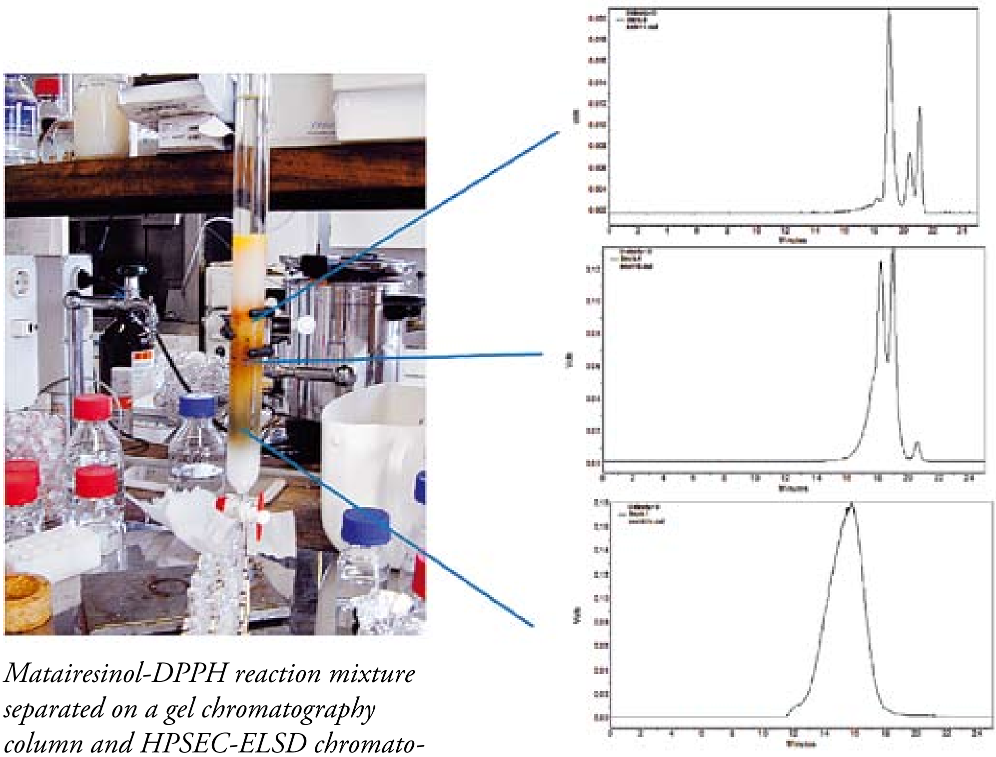
Main funding: Tekes

Annika Smeds, Patrik Eklund, Rainer Sjöholm, Jakob Lövdahl, Markku Reunanen, Andrey Pranovich, Stefan Willför

In the past, several promising technologies have been developed for valorisation of lignin, e.g., in the field of glues and plastic-like materials. Novel innovations are urgently needed in, e.g., packaging, in order to improve the competitiveness of fiber-based packaging materials. Applications based on lignin and other natural polymers are the most interesting in this respect, providing a source of sustainable raw materials. Especially lignin-based fiber-reinforced composite structures are among the most potential application areas as wood- and plant-based product replacements for oil-based polymers. In addition, low-molecular aromatic compounds, such as lignans, are an interesting source of phenolic materials to be used as such or in combination with lignins.

The structure of the lignin macromolecule is highly heterogeneous. In order to facilitate industrial use, lignins with a simplified structure and controllable reactivity are needed. In this project, lignins and lignans are modified by chemical and enzymatic methods in order to produce such lignins. The chemistry behind the reactions occurring during the modifications are investigated by using lignans as model substances. Co-polymerisation of lignin and lignans is applied in order to introduce more functionalities to the materials. The ultimate goal of this project is to develop methods to modify lignin into materials applicable for composites, coating adhesives, and barriers.

Our task in the project is mainly to study the reactions of the pure lignans matairesinol and pinoresinol with the stable radical DPPH. The kinetics of the reaction and the molecular weight distribution of the reaction mixtures are studied, and the oligomeric reaction products are chemically characterised.



Matairesinol-DPPH reaction mixture separated on a gel chromatography column and HPSEC-ELSD chromatograms of three different fractions

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

Publications:

- Mattinen, M-L., Struijs, K., Suortti, T., Mattila, I., Kruus, K., Willför, S., Tamminen, T., Vincken, J-P., Modification of lignans by *Trametes hirsuta* laccase, *BioResources* 4 (2009) 2, 482–496
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Lignans as Versatile Chiral Auxiliaries and Chiral Catalysts (LIGNOCATS)

Main funding: Academy of Finland

Patrik Eklund, Yury Brutsentsev, Rainer Sjöholm, Stefan Willför, Annika Smeds

This project is focused on semisynthetic approaches for the preparation of functional chiral molecules from the natural lignan hydroxymatairesinol. Recent progress and development of Finnish biorefinery processes has shown that hydroxymatairesinol can be isolated from spruce knotwood in large quantities (up to tons). 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 four 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 Brönsted acid catalysts
4. Synthesis and evaluation of lignan-based stoichiometric reagents for enantioselective reactions and for resolution of racemates

The chemical structure of hydroxymatairesinol is transformed into chiral ligands with different degree of flexibility or with fixed "biting angels" or with atropoisomeric properties or with a combination of these. The properties of the different types of the chiral ligands and the catalysts are then evaluated, and/or submitted to further derivatisation.

The synthesis of several different structures is ongoing. Also, some preliminary result from testing of the catalytic activity shows that the synthesized hydroxymatairesinol-based chiral catalysts can induce enantioselectivity in the well-known test reaction, addition of diethyl zinc to benzaldehyde. The synthesis and the properties of the novel catalysts is supported by molecular modeling and advanced structural characterization by NMR.

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 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, carbon nanofibres to name a few, were used in heterogeneous catalytic reactions, including hydrogenation, ring opening, skeletal isomerization, dimerization, oxidation, pyrolysis of biomass.

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

A special way in molecular engineering of catalysts is to have metals in non-zero valence state dissolved in a liquid layer, attached to the solid surface. Immobilization of ionic liquids onto solid materials with subsequent introduction of catalytically active species palladium species and testing the catalyst in liquid phase hydrogenation of citral demonstrated the big potential of this novel catalytic systems (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 the 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 (see chapter 3.2).

Micro and Mesoporous Materials

Main funding: Åbo Akademi University

Narendra Kumar, Matias Kangas, José Villegas Perdomo, Éva Sarkadi-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 have been synthesized and successfully applied. Quantum chemical calculations, FTIR and solid state NMR have been used to characterize the active sites on zeolites. The doctoral thesis of Éva Sarkadi-Pribóczki was finished.

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, Russia

Publications:

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Environmental Catalysis

Main funding: Academy of Finland, EU/Central Baltic INTERREG IVA Programme (SNOOP)

Kalle Arve, Kari Eränen, Dmitry Murzin, Tapio Salmi

Academy of Finland

The project addresses fuel consumption and emissions from vehicles. The main objective of the study is to generate new catalytic and their up scaling for industrial use for HC-SCR of NO_x from diesel vehicles. The developed materials and the knowledge about the reaction mechanism generated by the project are essential for catalytic redox technologies and particularly for the breakthrough in development of $deNO_x$ catalysts for catalytic reduction of nitrogen oxides to dinitrogen by hydrocarbons in the oxidizing atmosphere. Other main focus in the project is in the use of biofuels. The challenge set by the use of renewable fuels will bring the aftertreatment catalysis to a totally new era of their life cycle. To overcome this problem caused by the great variety of different renewables commonly called as biofuels, catalytic materials are developed and tested. In the final phase of the project focus is put on the catalyst scale up.

European Union–SNOOP

The Laboratory of Industrial Chemistry and Reaction Engineering is involved in the European Union-funded project *Shipping-induced* NO_x *and* SO_x *emissions – Operational monitoring network*, project acronym SNOOP. The aim of the project is to find out how the exhaust emissions form ships affect the Baltic Sea area. The role this ÅA-PCC project is to create an experimental method to measure the NO_x dissolution and transformation rate in the water phase and thereafter create a model able to predict this phenomenon at different conditions.

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)

Publications:

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Valorisation of Chemicals Derived from Biomass

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

Jyrki Kuusisto, Jyri-Pekka Mikkola, 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 Hájek, Päivi Mäki-Arvela, Hannu Karhu, Stefan Willför, 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 valorisation of chemicals 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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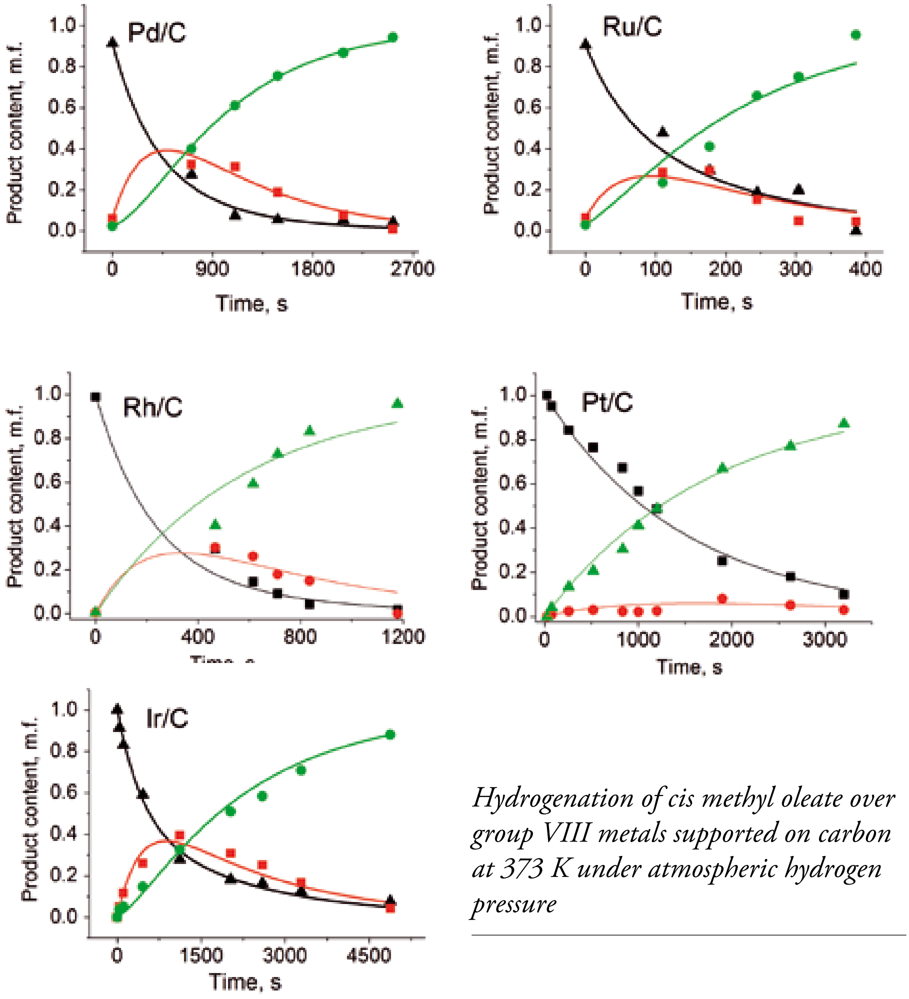
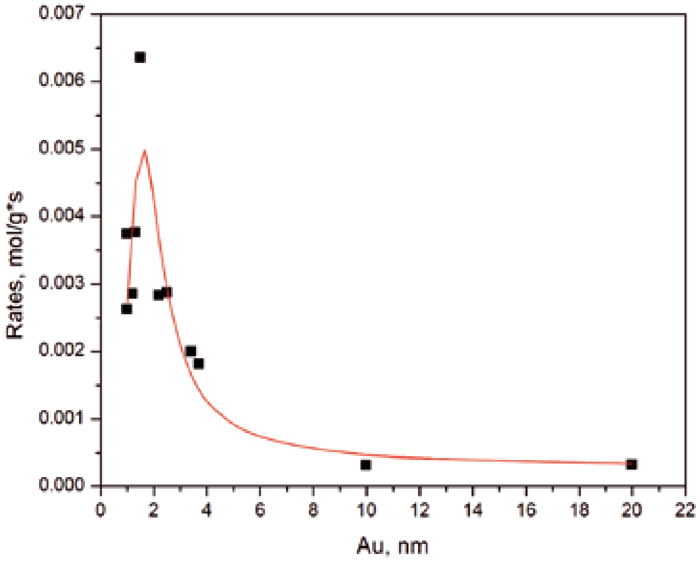


Hydrogenation of cis methyl oleate over group VIII metals supported on carbon at 373 K under atmospheric hydrogen pressure



Dependence of the catalytic activity in arabinose oxidation of Au cluster size

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Asymmetric Catalysis

Main funding: Academy of Finland

Esa Toukoniitty, Igor Busygin, Päivi Mäki-Arvela, Ville Nieminen, Serap Sahin, Alexey Kirilin, Gerson Martin Curvelo, 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.

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. Releases 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 modeling 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.

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 PCC wants to contribute to the development of process concepts of liquid biofuel production.

Since many of the components in biofuels are markedly different from the components present in traditional fuels, a new catalytic technology has to be developed for liquid biofuel production. Catalyst preparation, characterization and screening effort will take place, to develop a generation of catalysts for future biofuel refineries.

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, Tor Laurén, Johan Lindholm, Oskar Karlström, Juho Lehmusto, Patrycja Piotrowska, Hao Wu, Bingzhi Li, Emil Vainio, Pasi Vainikka, Anders Bäckman, Mia Mäkinen

ChemCom 2.0 started in January 2008 and will continue until the end of 2010. The project focuses on fundamental chemical questions and solutions in combustion and gasification of solid biofuels and black liquor. However, although biofuels and black liquor are in focus, also waste fuel combustion and oxyfuel combustion will be investigated. In ChemCom 2.0 we will take advantage of the results that have been achieved in ChemCom 2005–2007, and turn them to the best possible account. Especially, 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 is 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.

Left: Gas measurements at the recovery boiler (Pietarsaari), right: video recording at the fluidized bed boiler (Rauma)

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. Based on the results obtained from the measurements in the recovery boiler there were four papers presented orally at the International Chemical Recovery Conference, March–April 2010 in Williamsburg, VA, USA.

Although modelling and model validation have large roles in this project, other issues will also be emphasized to clarify fundamental chemical phenomena in combustion and gasification processes. Such issues are 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, are in ChemCom 2.0 organized by using four overall topics:

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

Cooperation:

Aalto University School of Science and Technology; Tampere University of Technology; VTT; Andritz; Foster Wheeler Energia; International Paper, USA; Metso Power; Metsä-Botnia; Clyde Bergemann, Germany; UPM-Kymmene

Publications:

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Science to Biomass Combustion

Main funding: ERA-NET Bioenergy (Tekes)

Maria Zevenhoven, Anders Brink, Oskar Karlström, Bingzhi Li, Johan Werkelin, Tiina Alanko, Piia Leppäsalo, Luis Bezerra, Mikko Hupa

It is essential to gain knowledge about the combustion and volatiles release behaviour of different fuels and fuel mixtures. This is of special relevance for "new" and "difficult-to-use" fuels (e.g. short rotation crops, energy grasses, residues from agricultural industries), which usually show considerably higher ash contents and lower first ash melting points in comparison to conventional wood fuels (wood pellets, wood chips, bark) leading to increased problems concerning slagging, ash deposit formation and fine particulate emissions. Moreover, these fuels usually also show elevated N S and Cl contents leading to increasing NO_x, SO_x and HCl emissions. Modern simulation tools are needed to efficiently analyse the underlying processes during biomass combustion. For biomass combustion plants, CFD modelling may be a highly efficient tool for process analyses as a basis to optimise plant design concerning flue gas burnout, CO emissions, plant efficiencies and availabilities.

The project is aiming at the development of advanced fuel analysis and characterisation 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.

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

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

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

Main funding: Academy of Finland, CNPq, Brazil

Tiina Alanko, Johan Werkelin, Mikko Hupa

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 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. The tests include:

1. Thermal gravimetric test for proximate fuel analyses
   - moisture content, volatile yield, char amount and ash content

2. Chemical fractionation of the fuel's ash forming matter by step-wise leaching
   - concentrations of ash forming elements (Si, Al, Fe, Ca, Mg, Mn, Na, K, P, S, Cl,)
   - determining the water soluble, ion exchangeable, acid soluble and insoluble fractions

3. Laboratory combustion of single particles including visual study with video camera
   - combustion characteristics at different stages and conditions (atmosphere and temperature)
   - measurement of CO, CO_2, NO and SO_2 concentrations from single particle combustion

4. Rapid pyrolysis (1000 K/s) of fuel samples in a wire mesh reactor purged with N_2
   - quantitative release of K, Na, Zn and Pb at different temperatures and residence times

5. Modelling of ash properties in large scale applications
   - chemical characteristics of the ash formed in full scale combustion (slagging and fouling)

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

Modelling Interfacial Partitioning in Multi-phase Systems (Inter)

Main funding: Tekes/Masi

Anders Brink, Bingzhi Li, Mikko Hupa

New models for monomolecular surface and interface layers are developed and coupled with multi-phase thermodynamic simulation. Modelling include: consistent models for complex interface phenomena in reactive flows; common modelling base for bubbles, droplets and particulates and their transport; formation of segregating and depositing layers; sorption and surface layer models in multi-phase flows; models for interfacial partitioning in both wet and high-temperature systems; coupling of interfacial potentials with multi-phase chemistry; control of surface effects with external force fields. The research at Åbo Akademi University focus on the interface between flowing molten layers with the surrounding, including interaction with the gas phase and with impacting solid material. A model has been implemented in to CFD that computes the thickness of the resulting deposit, separating between the solid part and the outer viscous part.

Cooperation:
VTT (Coordinator); Helsinki University of Technology; University of Oulu; Andritz; Fortum; Outotec; Outokumpu Stainless; Process Flow; UPM-Kymmene

Publications:

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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 2009, two types of flame retardants have been investigated: 1) flame retardants producing a physical mass transfer barrier and 2) flame retardants producing additional mass transfer resistance by giving off gases as during their thermal decomposition. The former group mainly consist of inorganic salts and inorganic salt mixtures with a low first melting point. The second group mainly consists of compounds giving of water as they decompose.

Cooperation:
Åbo Akademi University (Polymer Technology)

Biomass Waste as an Energy Source in Large Shares without Risk (Biosafe)

Main funding: Tekes/Climbus

Patrik Yrjas, Tor Laurén, Mikko Hupa

The Biosafe project started in August 2006 continued until the end of April 2009. The objective is to increase the shares of demanding biomass waste fuels in power plants with high electrical efficiency. This will be done by mixing problematic waste flows into one less problematic flow, in which some of the characteristics of one fuel will neutralize the negative qualities of the other, e.g. by using the positive effect of kaolinite type minerals which are present in sludges of different kinds. These minerals can bind alkali, thus decreasing the risk of corrosive alkali chloride formation. Accordingly, the project not only helps in solving the problems with waste disposal but also make it possible to increase the production of CO_2-neutral electricity and heat.

The optimization of the fuel mixture and combustion conditions is done by detailed fuel analyses together with pilot-scale fluidized bed testing and thermodynamic modelling.

Cooperation:
VTT; University of Kuopio; Metso Power; Kemira; Lassila & Tikanoja; Helsingin Vesi

Publications:

- Yrjas, P., Aho, M., Zevenhoven, M., Taipale, R., Silvennoinen, J., Hupa, M., Co-firing of sewage sludge with bark in a bench-scale bubbling fluidized bed – a study of deposits and emissions, Proceedings: *20th International Conference on Fluidized Bed Combustion (20th FBC)*, May 18–20, 2009, Xi'an, China

Development and Demonstration of Advanced SRF Co-firing for High Efficiency Fluidised Bed CHP Boilers (AdCof)

Main funding: Tekes/Climbus

Patrik Yrjas, Pasi Vainikka, Tor Laurén, Mikko Hupa

The project started in spring 2007 and ended in spring 2009. The objective is to develop and demonstrate an advanced co-firing concept for fluidised bed combustion enabling of increasing the electric efficiency of SRF fired CHP boiler plants from current 23% to about 35% with simultaneously maximizing the share of SRF in the fuel mix to above 50% on energy basis.

Major operational challenges are faced with slagging, fouling and corrosion in SRF fired boilers when higher electric output and steam values are reached for. With proper selection of the co-fired fuels combined with pre-treatment and quality control of SRF these operational problems and risks can be avoided. The project aims to demonstrate these effects in practice, and further, estimate how much potential this concept could provide in terms of additional TWhe/a in selected EU member states.

The project is in alignment with the European Community objectives of securing and diversifying the energy supply, increasing the utilisation of biomass fuels–including waste–reducing CO_2 emissions and improving the quality of air.

The main innovation of the project is to reduce ash melting problems, chlorine induced corrosion and formation of fine particles by taking advantage of coal minerals as fuel bound additives.

Cooperation:

VTT; Metso Power; UPM-Kymmene; Lassila & Tikanoja; Network of Excellence in Bioenergy

Publications:

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

Main funding: CLEEN, Tekes

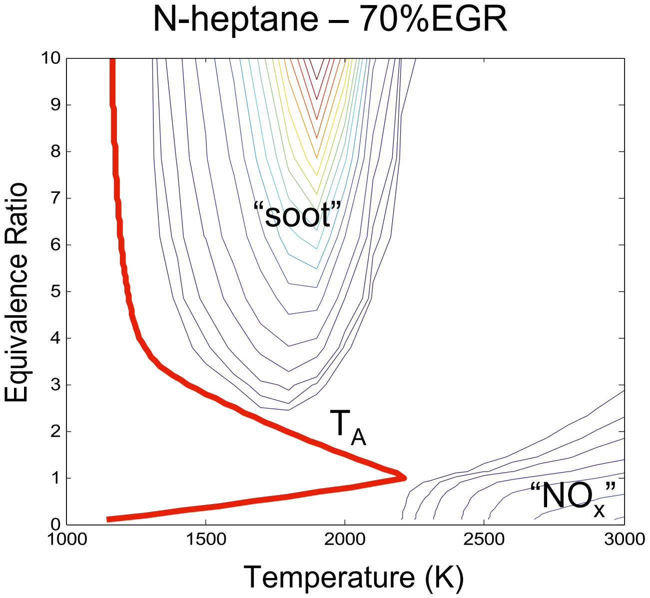
Anders Brink, Mikko Hupa

"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. In this project, ÅAU is responsible for combustion chemistry and emission chemistry. ÅAU will study combustion and emission reaction schemes and simulate combustion and emission kinetics for emission mapping and combustion optimization.

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.

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



A Phi-T map showing the adiabatic combustion temperature using 70 % exhaust gas recycling. In the figure also the regions with conditions prone to soot formation and NO_x formation are shown. These have been calculated with a detailed reaction mechanism for PAH and NO_x

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 CO_2 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.

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)

Publications:

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Chemical Thermodynamics of Ash-forming Elements in Biomass Fuels

Main funding: Academy of Finland

Daniel Lindberg

In the present project a thermodynamic database will be developed for the ash-forming elements in biomass fuels. The project will focus on modeling the thermodynamic properties of the molten ash, which has a critical role for the ash-related problems in boilers. The database and model development will mainly cover alkali and alkaline earth salts, with additions of heavy metals such as zinc and lead, and also phosphorus. In particular, the role and chemistry of phosphorus in combustion processes are still to a large degree unknown, and the present project will shed new light on both the possible negative and positive effects of phosphorus in biomass combustion. The developed and optimized thermodynamic models and databases will accurately predict chemical phenomena, such as phase stabilities, melting processes and thermodynamic properties. This will allow the study of chemical processes in biomass combustion, such as corrosion, fouling and deposition in biomass and waste-fired boilers

Cooperation:

École Polytechnique de Montréal, Canada; GTT-Technologies, Aachen, Germany; SINTEF Energy Research, Trondheim, Norway

3.8 Intelligent Electroactive Materials

An **intelligent material** can be defined as a material that can (i) recognize environmental stimuli, (ii) process the information arising from the stimuli and (iii) respond to the stimuli in an appropriate and timely manner. An **electroactive material** is a material that can be electrochemically oxidized or reduced, so when we combine all these properties we obtain an **intelligent electroactive material**. Electroactivity is a key parameter in many devices and applications, including electrochemical sensors and actuators, organic electrochemical transistors, electroactive membranes, charge storage devices (batteries, supercapacitors), fuel-cells and electrochromic devices (displays). Our current research on electroactive materials includes conjugated polymers, fullerenes, carbon nanotubes and graphene.

New conjugated oligomers and polymers are synthesized electrochemically in order to obtain multi-functional conducting polymers that can function as intelligent electroactive materials. Different parameters are controlled during electrochemical polymerization and functionalization so that a desired structure and film thickness is obtained. The 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. On the other hand, when used in photovoltaic devices (solar cells), covalent bonding 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 are characterized by cyclic voltammetry, *in situ* FTIR, Raman and UV-Vis spectroscopy, *in situ* electron spin resonance spectroscopy and *in situ* conductivity measurements. Impedance spectroscopy, electrochemical quartz crystal microbalance, scanning electron microscopy and atomic force microscopy are also used.

New electroactive materials are essential building blocks in chemical sensors. Conducting polymers and carbon nanotubes are used in combination with polymeric ion-selective membranes to obtain solid-contact ion-selective electrodes (SC-ISEs) with improved analytical performance, such as high potential stability and low detection limit. The water uptake of polymeric ion-selective membranes is an important parameter that has been studied in detail. Theoretical modelling of membrane potentials by the Nernst-Planck-Poisson system of differential equations helps us to optimize the sensor materials for different applications. Recent efforts have resulted in a fully integrated electrochemical sensor system including a solid-contact reference electrode and solid-contact ion-selective electrodes that were applied for determination of lead in natural waters. In addition to applications in chemical sensors and solar cells, electroactive materials were also used as immobilization matrix for enzymes in the development of biofuel cells showing direct electron transfer between the enzyme and the electrode matrix.

The 9th Spring Meeting of the International Society of Electrochemistry will be held in Åbo-Turku, May 8–11, 2011. This meeting will be focused on Electrochemical Sensors: from nanoscale engineering to industrial applications.

Chemical Sensors and Biosensors Based on Conjugated Polymers, Carbon Nanotubes, C_{60} and Graphene

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

Dongxue Han, Tingting Han, Zekra Mousavi, Li Niu, Agnieszka Teter, Andrzej Lewenstam, Johan Bobacka, Ari Ivaska

The conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) doped with multi-walled carbon nanotubes and fullerene (C_{60}) were used as ion-to-electron transducing layers in solid-contact potassium-selective electrodes based on plasticized PVC containing valinomycin as ionophore. Carbon nanotubes were also integrated into the ion-selective membrane, resulting in a new type of single-piece ion-selective electrode that were compared to those 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.

Cooperation:

University of Pécs, Pécs, Hungary; University of Warsaw, Warsaw, Poland; State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China

Publications:

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Health Diagnostics with Chemical Sensors

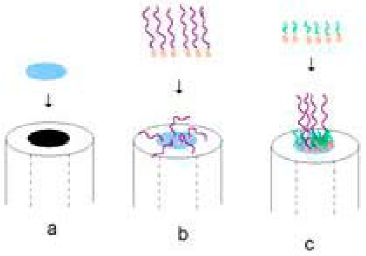
Main funding: Tekes (FiDiPro), Industry, Åbo Akademi University Foundation Research Institute, Graduate School in Nanosciences (NGS-NANO)

Maija Blomquist, Alok Prabhu, 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 glass or glassy carbon 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 fibres 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.

Cooperation:

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

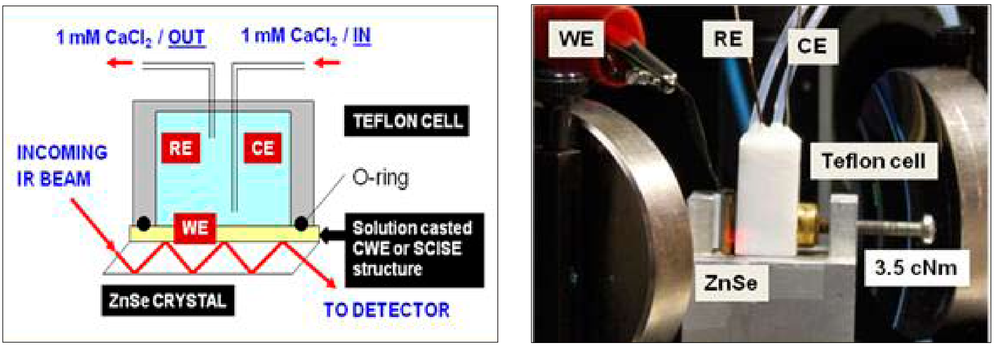
Water Uptake of Membrane Materials Used in Ion-selective Electrodes

Main funding: Academy of Finland

Tom Lindfors, Fredrik Sundfors

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. In 2009, the project has focused strongly on developing a method for simultaneous measurement of the water uptake, impedance spectra and open circuit potential of ion-selective



Left: Schematic view of the FTIR-ATR setup used in the water uptake measurements in 1 mM CaCl$_2$; 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.

electrodes. This is the first time these three parameters have been successfully measured simultaneously and the results were presented at the Pittcon 2010 conference in Orlando (USA) in March 2010. It is now studied if there is a correlation between the water uptake and low detection limit of electrically conducting SCISEs.

Cooperation:

Budapest University of Technology and Economics, Budapest, Hungary (Prof. Róbert E. Gyurcsányi)

Publications:

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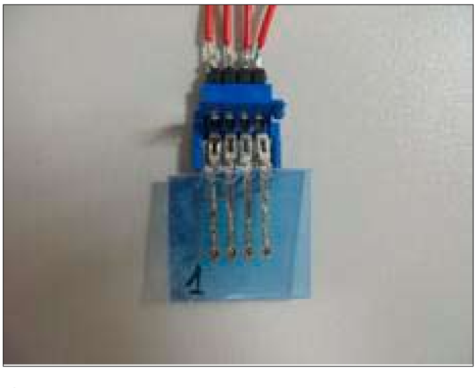
Miniaturized All-Solid-State Sensors for Trace Analysis of Substances Relevant to Health and Welfare (MASTRA)

Main funding: EU (MATERA ERA-NET), Tekes, Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM), Graduate School in Chemical Engineering (GSCE)

Jerzy Jasielec, Anna Kisiel, Grzegorz Lisak, Ulriika Mattinen, Tomasz Sokalski, Andrzej Lewenstam, Johan Bobacka

Prototypes of miniaturized all-solid-state sensor systems were developed and tested in real applications in collaboration with our project partner at Dublin City University, Dublin, Ireland. An example of the developed sensor system containing three solid-contact ion sensors and one solid-contact reference electrode is illustrated in the figure below. The



Sensor prototype

Environmental analysis

developed sensor systems were used to measure lead at very low concentrations (0.5–10 ppb) in natural waters. Simultaneous measurements of pH and lead (Pb^{2+}) allowed speciation of lead in natural waters.

The experimental studies were supported by mathematical modeling of the signal formation mechanism together with our project partner at AGH University of Science and Technology, Kraków, Poland.

It can be concluded that all major goals of this 3-year project (2007–2009) have now been achieved.

Cooperation:

AGH University of Science and Technology, Kraków, Poland; Dublin City University, Dublin, Ireland; Thermo Fisher Scientific, Finland; DHN, Poland; Environmental Protection Agency, Ireland

Publications:

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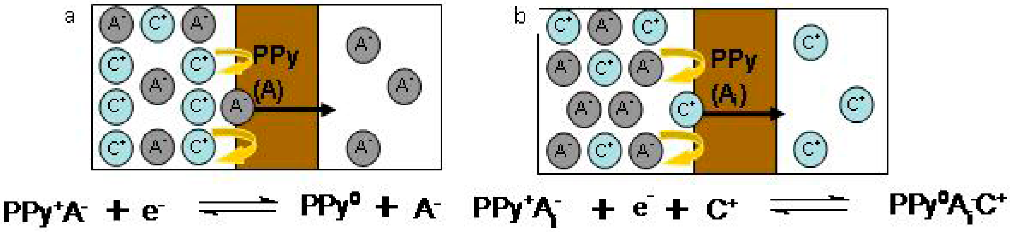
Electroactive Ion-Exchange Membranes Based on Conducting Polymers for Monitoring of Anions and Cations

Main funding: Magnus Ehrnrooth Foundation

Marceline Akieh, Rose-Marie Latonen, Ágnes Varga, Kevin Vavra, 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 so far has focused on the transport of either only metal ions or in some cases 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 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 polypyrrole 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 membranes known to have cation, anion and mixed ion-exchange properties have been performed. 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.



Polypyrrole membranes demonstrating permselectvity, where only one type of ion is transferred across the membrane. (a) Anion exchange membrane, where only anions are transferred across. (b) Cation exchange membrane, where only cations are transferred across the membrane. A_i^- *is an immobile doping anion,* A^- *is a mobile doping anion and* C^+ *is a cation.*

Cooperation:

University of Wollongong, Australia; University of Pécs, Hungary; Georgia Tech, Atlanta, GA, USA

Publications:

- Akieh, M.N., Price, W.E., Bobacka J., Ivaska, A., Ralph, S., Ion exchange behaviour and charge compensation mechanism of polypyrrole in electrolytes containing mono-, di-, and trivalent metal ions, *Synthetic Metals* 159 (2009), 2590–2598

Integrating Enzymes, Mediators and Nanostructures to Provide Bio-powered Bio-electrochemical Sensing Systems (BIO-MEDNANO)

Main funding: EU 6th Framework Programme

Mikael Bergelin, Pia Sjöberg-Eerola, Tomasz Sokalski, Rose-Marie Latonen, Xiaoju Wang, Jennie Sirén, Johan Bobacka, Mikko Hupa, Ari Ivaska

EU BioMedNano is a joint targeted research project in cooperation with 8 European research groups and companies. The project focuses in particular on improving enzymatic electron transfer reactions to enable the use of these devices in for instance integrated bio-powered biosensing systems for diagnosis and healthcare. The project aims to improve such systems by: (i) screening for novel enzymes, (ii) development of appropriate mediators and immobilisation methods, (iii) modification of enzymes, and (iv) design of novel nano-structured scaffolds for enzyme immobilisation, to provide devices with improved stability and electron transfer efficiency (sensitivity and/or power output).

Within the project, novel ways of manufacturing these enzyme scaffolds have been explored, and three alternatives have been identified. These have been tested, and one of them has been found to enable a sufficient activity and stability of the enzyme electrode. At present this method is being explored further, and the first test cells have been built. The target for the demonstration systems is set on development of a biofuel cell functioning on in-vivo available biofuels.

Cooperation:
National University of Ireland, Galway, Ireland; VTT Technical Research Centre of Finland, Finland; The Hebrew University of Jerusalem, Israel; University of Southampton, UK; University of Rome "La Sapienza", Italy; BVT Technologies, Czech Republic

Printed Enzymatic Power Supplies with Integrated Capacitor Structures (PEPSic)

Main funding: Tekes

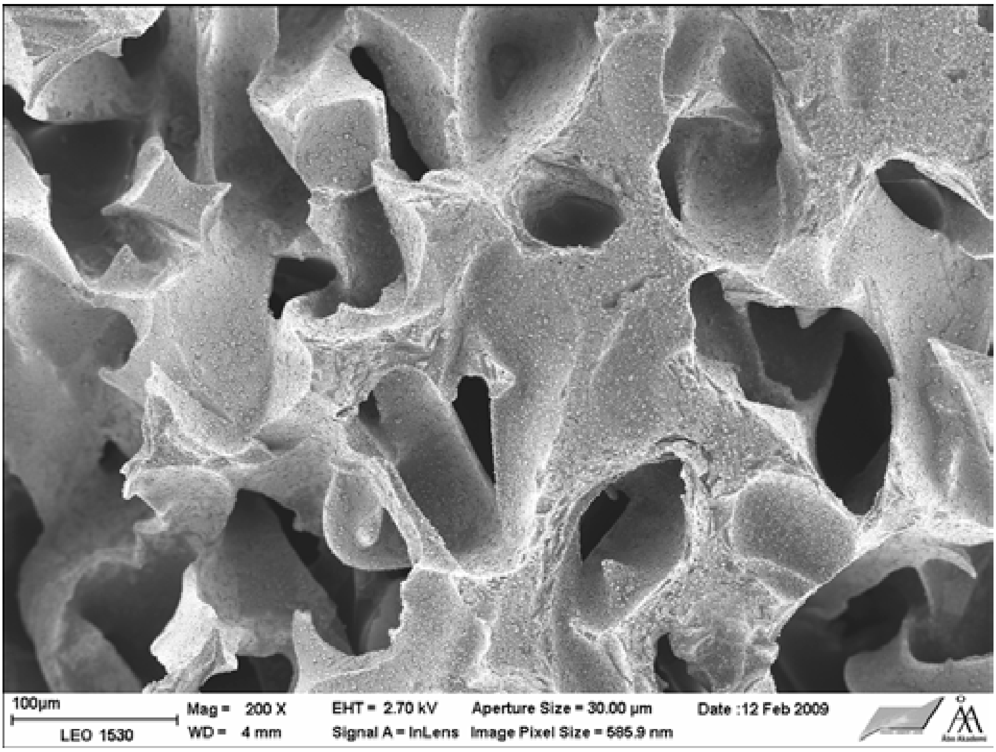
Mikael Bergelin, Jan-Erik Eriksson, Max Johansson, Pia Sjöberg-Eerola, Xiaoju Wang, Mikko Hupa

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.

Common targets to be reached are; 1) a fully enzymatic printable power supply, 2) a printable supercapacitor, 3) a biofuel cell based power supply with an integrated supercapacitor, 4) a cell voltage exceeding 1.2 V, 5) a peak current of at least 50 mA for 0.3 seconds, 6) the size (area) less than 10 cm^2, thickness no more than 0.5 mm.

A number of critical components have been identified, and the main challenges have been solved. Regarding the substrate (outer shell) material, the required oxygen diffusion and moisture retention properties have been solved by the use of a suitable commercial cardboard based material, although it is acknowledged that at least part of the material selection of the power supply body will be dictated by the "point-of-use"-application, into which the battery is integrated. Regarding the electrochemical components, at present 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 display the required properties.

The performance of the developed power supply in combination with a number of low power-demanding applications have also been demonstrated



Cross section of a Reticulated Vitreous Carbon electrode coated with a Laccase/PEDOT layer for use in a Bio Fuel Cell

Cooperation:

VTT; Aalto University School of Science and Technology; Ciba Speciality Chemicals; Joutsenpaino; Tervakoski; Stora Enso; Evox-Rifa Group

Publications:

- Wang, Nianxing, Promoting direct electron transfer in bio fuel-cell enzyme electrodes by using carbon nano-tubes as electron carrier (Master's Thesis)

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.

An activation system for the power supply will be developed, that also takes into account the point-of-use requirements. Optimization of cell components and manufacturing methods will also be conducted to allow for R2R manufacturing with a minimum of separate steps required.

Interfacing of the BioBattery with potential applications will be investigated, and suitably simple electronic interfaces will be developed and tested. The complexity of the interface is strongly dependent on the point of use, and hence two alternatives of different nature will be realized.

The disposability of the BioBattery will be assessed by verification of its combustability 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 Technical Research Centre of Finland;, Aalto University School of Science and Technology; Tampere University of Technology; ABEnzymes; Confidex; Enfucell; Evox-Rifa Group; Joutsenpaino; Panipol; Stora Enso; Tervakoski

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 the high activity of the nanomaterial with the 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. Further, the performance decrease due to ageing will be tested.

Cooperation:
VTT Technical Research Centre of Finland; University of Eastern Finland; Nokia; SAFT; OMG Kokkola Chemicals

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 and optimize novel material for PEM-FC stack components in the 1–50 kW power range, suitable for use as auxiliary power units in e.g. electric/hybrid working machines. Novel materials solutions have been developed, tested and benchmarked in combination with commercial stack components.

The Pt catalyst, normally carbon black supported and applied with spray coating techniques onto the proton conducting membrane, has been applied directly onto nanostructured carbon non-wovens, manufactured from electrospun poly(acrylonitride) precursors, with different physical surface coating techniques, aiming at achieving high-performing membrane electrode assemblies with ultra-low Pt content.

Development and optimization of low-resistance gas diffusion layers (GDL), manufactured by a wet-laid process, have also been done in order to get rid of the energy consuming high-temperature treatment that is common in commercial state-of-the-art GDLs.

In order to replace the expensive graphite-based bipolar plates (BPP), the chemical and electrochemical resistance towards corrosion of differently coated stainless steel BPP:s have been investigated using SEM-EDXA.

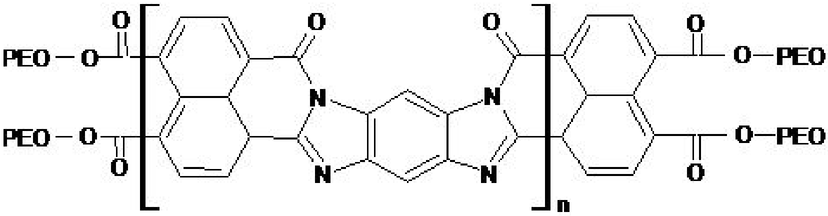
Cooperation:
VTT Technical Research Centre of Finland; Aalto University School of Science and Technology; Tampere University of Technology; Ahlstrom; Beneq; Premix; Outokumpu

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

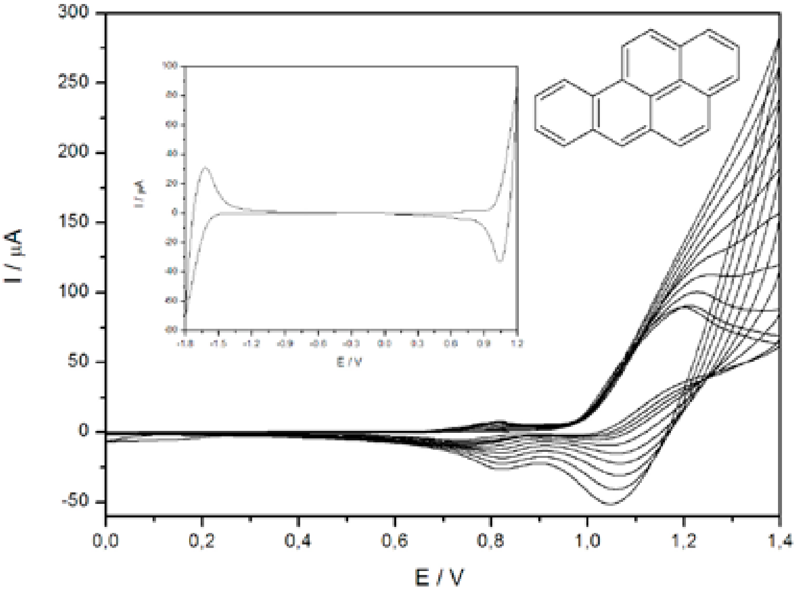
Main funding: Tekes, Industry, Academy of Finland, Graduate School in Chemical Engineering (GSCE), Graduate School of Materials Research (GSMR), Fortum Foundation

Henrik Gustafsson, Rose-Marie Latonen, Beatriz Meana Esteban, 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 the electron transfer layers and the connection to the electrodes in the solar cell is 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

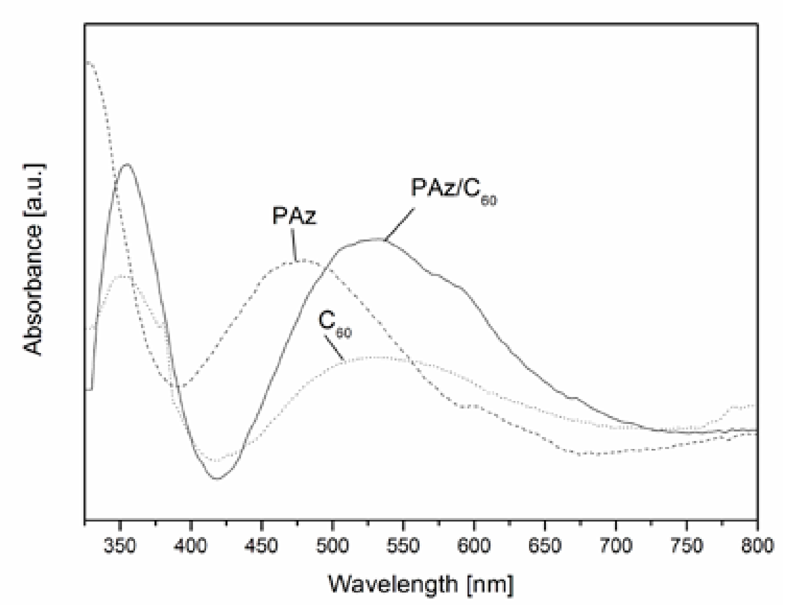


The structure of BBL-PEO



Electrosynthesis of PBP in propylenecarbonate+TBAPF$_6$ (10 mV/s). Insert: Cyclic voltammo-grams recorded during p- and n-doping of PBP film in propylenecarbonate+TBAPF$_6$ (5 mV/s) and the structure of benzo(a)pyrene

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. In the future other graphite-like molecules will also be studied.



UV-vis-NIR spectra of PAz, C$_{60}$ and PAz/C$_{60}$

As one step further different type of donor-acceptor material combinations for solar cell applications has been developed. Composite films consisting of PAz and C_{60} have been studied by comparing the photoinduced and the electrochemically induced changes in thin polymer and fullerene films. Also hybrid electron donor-acceptor materials consisting of inorganic wide band gap nanostructured TiO_2 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.

Cooperation:

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

Publications:

- Latonen R-M., Meana Esteban, B., Kvarnström, C., Ivaska, A., Electrochemical polymerization and characterization of a poly(azulene)-TiO_2 nanoparticle composite film, *Journal of Applied Electrochemistry* 39 (2009) 653–661

Pressurized PEM Electrolyzer Stack (PrimoLyzer)

Main funding: EU 7th Framework Programme, Tekes

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

Stationary micro combined heat and power units (µCHPs) based on fuel cells are in demonstration all over the world. Almost all these systems are fed with reformed fossil fuel like natural gas. The fuel cell based (FC-based) µCHPs are more efficient than the technologies they replace, resulting in substantial reduction in the CO_2 emission, calculated to be about 1 tons CO_2/year/'single family house' when fuelled with natural gas. However, the emission reduction is even five times higher when the µCHPs are fuelled with hydrogen produced with excess renewable energy e.g. wind power or photovoltaics-generated power. Hydrogen production by electrolysis of water is presently associated with substantial energy losses. Furthermore, small electrolyzers are prohibitively expensive while larger electrolyzers with a relatively smaller plant investment cost require additional hydrogen distribution grids. The PrimoLyzer project addresses these challenges. The primary objective of the PrimoLyzer project is to develop, construct, and test a cost-minimized highly efficient and durable electrolyzer stack, based on proton exchange membranes (PEM) and aimed for integration with domestic µCHPs. This will be achieved through a combination of the following activities:

1. Specification done by the end-user(s).
2. To increase electrode stability and efficiency, development of new catalyst and materials for lowering costs and improving performance.

3. To develop an efficient, low cost and durable membrane with sufficiently low gas cross-over to allow high pressure operation.
4. Process development to fabricate high performance membrane electrode assemblies (MEAs).
5. Engineering of a durable, reliable, and robust high pressure PEM stack through computational fluid dynamics (CFD) modelling and design optimization.
6. Continuous test for 2,000 hours together with a 1.5 kW µCHP.
7. An evaluation headed by the end-user(s).

The PrimoLyzer project is focused on the electrolyzer stack. The concluding tests will be done in a spread-out setup together with a 1.5 kW µCHP-system. The key-targets for the stack are as follows:

a. Hydrogen production capacity: 1 Nm^3/h.
b. Pressure: 10 MPa (100 bar).
c. 1.68 V at 1.2 A/cm^2, also after 2,000 hours of continuous operation.
d. Cost: <5,000 € per Nm^3 H_2 production capacity per hour in series production.
e. Durability: >20,000 hours at constant load.
f. Operation of the PEM electrolyzer stack together with a µCHP (1.5 kWAC) for at least 2,000 hours.

Furthermore, the stack will be liquid cooled to enhance durability and enable easy heat utilization. This is important as a PEM electrolyzer operated with renewable energy sources will run when the electricity is cheap and therefore not simultaneous with the µCHP. The combination of the electrolyzer with the µCHP unit and its performance optimization will be extremely important in the future energy production as it enables the use of renewable energy sources (wind and solar power) in an effective and creative way.

Cooperation:
IRD Fuel Cells, Denmark; Stichting Enerieonderzoek Centrum Nederland, the Netherlands; VTT Technical Research Centre of Finland, Finland; Fuma-Tech Gesellschaft Für Funktionelle Membranen und Anlagentechnologie, Germany; Hynergreen, Spain

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.

The bioactive glass compositions used in clinical applications show high bioactivity, i.e. the glasses start to react and bond to living tissues within a few days after implantation. So far, the clinical applications of glasses deal with non-load bearing applications only. However, during the past years bioactive glasses have been studied intensively as components of composites together with polymers. Using thin fibres or thin-walled highly porous structures increases the surface area of the glasses. Accordingly, the glasses are likely to react rapidly *in vitro* and *in vivo* and thus might lose their mechanical strength more rapidly than new bone forms. For these applications the glasses should have a slower bioactivity and higher chemical durability. The need of tailoring glass compositions with desired *in vivo* reactivity has encouraged us to further develop our understanding of glasses for medical applications. The results will be applied for finding compositions of bioactive glasses with a desired product form and a desired *in vitro* bioactivity ranging from very bioactive to almost inert compositions.

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. Main focus has been on estimating the influence of the new compositions and/or coatings containing nanoparticles on chemical and mechanical durability of the glazed ware. 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 an 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.

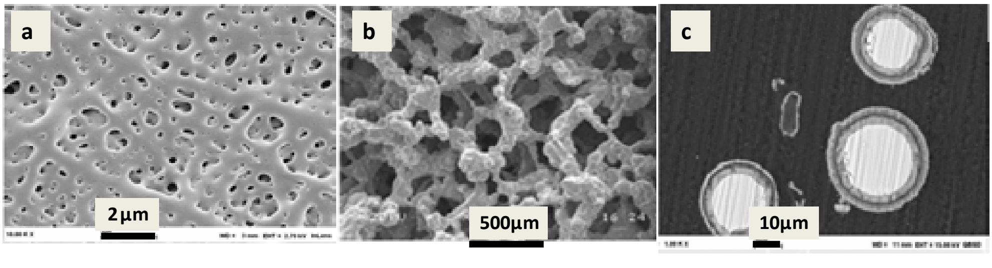
As a new area we have studied corrosion of stainless steel with the focus of understanding the detailed mechanism of chromium oxide protective film formation and corrosion in the high temperature environments.

Bioactive Glass Structures and Their Reactivity

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

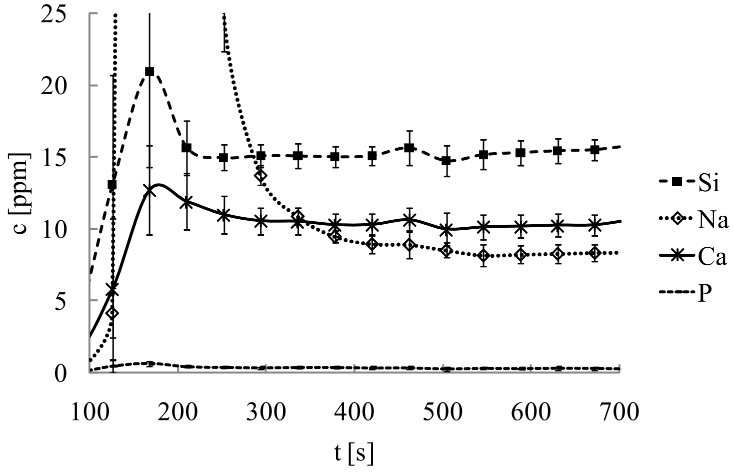
Leena Hupa, Zhang Di, Susanne Fagerlund, Lukas Brázda, Paul Ek, Mikko Hupa

One of the main tasks has been to manufacture and characterize novel structures of bioactive glass compositions calculated by using the property models developed during the past years within our group. Thin continuous fibres have been manufactured through conventional fibre drawing techniques from molten glass and preforms. Nanoscaled fibres have been manufactured by electrophoretic spinning from sol-gels. Porous scaffold structures were obtained by sintering glass particulates. Further, template sintering technique was used to obtain thin highly porous scaffolds from fine glass powder. The goal is to tailor the glass composition to allow the manufacture of special products with desired reactivity.



SEM images of various products of bioactive glasses manufactured from ÅA property-optimized bioactive glasses: a) nanoporous thin sheet sintered from nanofibres manufactured by electrophoretic spinning; b) porous sintered scaffold (Mantsos, T. et al, Biomed. Mater. 4, 2009); c) cross-section of continuous bioactive glass fibres at two weeks in SBF showing reaction layers

The early stage ion release from bioactive glasses has been measured with a continuous flow-through-cell connected directly to an inductively coupled plasma optical emission spectrometry, ICP-OES. The aim is to use this method to measure and model dissolution degree of bioactive and biodegradable glasses in a constant flow of buffered solutions imitating the conditions in body fluids. The method enables a simultaneous on-line analysis of the ions dissolving from the glasses.



Concentration of ions dissolved from bioactive glass 45S5 in water at 40°C as a function of time measured by ICP-OES in a continuous flow-through cell

Cooperation:

University of Turku (Orthopaedics and Traumatology, Dentistry); Imperial College London, UK; Institute of Chemical Technology, Prague, Czech Republic; Vivoxid

Publications:

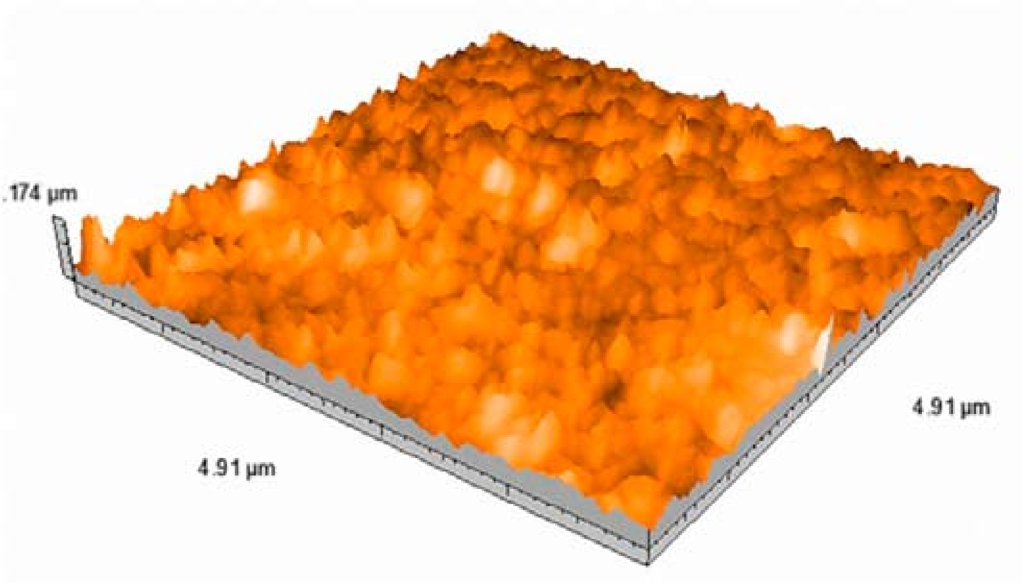
- Madanat, R., Moritz, N., Vedel, E., Svedström, E., Aro, H.T., Radio-opaque bioactive glass markers for radiostereometric analysis, *Acta Biomaterialia* 5 (2009) 9, 3497–3505
- Mantsos, T., Chatzistavrou, X., Roether, J.A., Hupa, L., Arstila, H., Boccaccini, A.R., Non-crystalline composite tissue engineering scaffolds using boron-containing bioactive glass and poly($_{D,L}$-lactic acid) coatings, *Biomedical Materials* 4 (2009) 5
- Vedel, E., Zhang, D., Arstila, H., Hupa, L., Hupa, M., Predicting physical and chemical properties of bioactive glasses from chemical composition, Part IV: Tailoring compositions with desired properties, *Glass Technology: European Journal of Glass Science and Technology A* 50 (2009) 1, 9–16
- Zhang, D., Vedel, E., Hupa, L., Aro, H.T., Hupa, M., Predicting physical and chemical properties of bioactive glasses from chemical composition, Part III: *In vitro* reactivity, *Glass Technology: European Journal of Glass Science and Technology A* 50 (2009) 1, 1–8
- Zhang, D., Ylänen, H., Hupa, M., Hupa, L., Factors affecting *in vitro* bioactivity of glasses, *Key Engineering Materials* 396–398 (2009), 115–118

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 manufactures 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 indentify the composition, thickness and structure of different nanostructured coatings on glasses and glazed ceramics.



AFM image of a fluorine doped tin oxide (FTO) coating on float glass made using nAERO technology (Beneq). The TCO films made of fluorine doped tin oxide (FTO) are used as transparent electrodes for thin film photovoltaic applications

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Cooperation:

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

Publications:

- Fröberg, L., Hupa, L., Hupa, M., Corrosion of the crystalline phases of matte glazes in aqueous solutions, *Journal of the European Ceramic Society* 29 (2009) 1, 7–14
- Fröberg, L., Kronberg, T., Hupa, L. Effect of soaking time on phase composition and topography and surface microstructure in vitrocrystalline whiteware glazes, *Journal of the European Ceramic Society* 29 (2009) 11, 2153–2161
- Piispanen, M., Määttä, J., Areva, S., Sjöberg, A-M., Hupa, M., Hupa, L., Chemical resistance and cleaning properties of coated glazed surfaces, *Journal of the European Ceramic Society* 29 (2009) 10, 1855–1860

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. The aim is to use this method to study corrosion of refractories in biomass combustion devices.

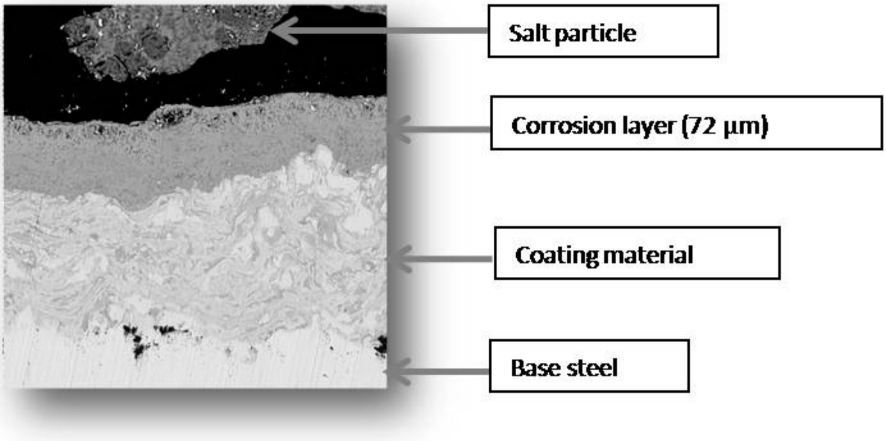
Cooperation:
Foster Wheeler

Durable Boiler – Advanced Solutions for Boiler Materials and Surfaces (Dublo)

Main funding: Tekes

Patrik Yrjas, Dorota Bankiewicz, Mikko Hupa

The Dublo project started in February 2007 and ended in February 2010. The aim was to optimize coating material solutions to withstand corrosion and erosion phenomena in power plant boilers. The formation of the oxide layers was determined together with their mechanical characteristics both in the laboratory tests and in full scale. The purpose was to improve the materials within two temperature intervals i.e. 400–600˚C (high



A cross-section SEM image of a severely corroded coating exposed to a KCl-K_2SO_4 *salt mixture in the presence of* H_2O*. Temp. = 600°C, time = 168 h* temperature corrosion) and below 160°C (dewpoint corrosion). The focus has been on finding economical and durable material solutions and also to develop methods to repair eventual material damages that may occur by time.

Some of the results were very promising and further additional tests on certain coatings will be done, although the project has already ended. Results from the project have been published at the 8th Baltica Conference 2010 – "International Conference on Life Management and maintenance for Power Plants" and also one article has been accepted for oral presentation at the 9th Liège Conference on Materials for Advanced Power Engineering in Belgium in the fall of 2010.

Cooperation:
VTT; Aalto University School of Science and Technology; Turku Energia – Åbo Energi; Oitin Valu; Ekokem; Ingmar Westerlund Consulting; Foster Wheeler Energia; Kuopion Konepaja; Fortum

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 will continue until the end of 2010. 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 coal oxy-fuel, biomass, and waste combustion. Also the intent is to develop and demonstrate advanced online corrosion monitoring probes and to combine the results from computational materials modelling, online corrosion 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- ÅA will support these objectives by making laboratory corrosion tests under different process conditions, by changing the gas atmosphere, synthetic ash compositions, etc. The materials meant for testing will be provided by the project partners.

Cooperation:
VTT; Aalto University School of Science and Technology; Fortum; Foster Wheeler Energia

4. Publications 2009

4.1 Theses

4.1.1 Doctoral Theses (7)

Aho, Atte, Catalytic pyrolysis of biomass in a fluidized bed reactor

Hernández Carucci, José Rafael, Experimental and modelling aspects of nitrogen oxides reduction in mini- and microreactors

Leveneur, Sébastien, Catalytic synthesis and decomposition of peroxycarboxylic acids

Mousavi, Zekra, Ion sensing based on the conducting polymer poly(3,4-ethylenedioxythiophene)

Saarela, Kjell-Erik, Elemental analysis of wood materials by external millibeam thick target PIXE

Sarkadi-Pribóczki, Éva, Novel 11C-radioisotope method for studying methanol transformations over H- and metal-modified zeolites and MCM-41

Virtanen, Pasi, Supported ionic liquid catalysts (SILCA) for preparation of fine chemicals

4.1.2 Licentiate Theses (0)

4.1.3 Masters Theses (17)

Anugwom, Ikenna, Extraction of nitrogen and sulphur compounds from heavy fuel oil using ionic liquids

Boedeker, Anna, Inverkan av ett ytaktivt ämne och mannaner på våtstyrka och andra pappersegenskaper (*Effects of a surface active agent and mannans on wet strength and other paper properties*, in Swedish)

Ciepela, Filip, Signal processing in electrochemical trace analysis

Halonen, Ville, Preparation of ethylene oxide in a microreactor (in collaboration with the University of Oulu)

Isaksson, Johan, Inverkan av ett ytaktivt ämne och vedsubstanser på avvattning av kemisk massa (*Effects of a surface active agent and wood substances on dewatering of a chemical pulp*, in Swedish)

Kirilin, Alexey, One-pot cascade transformation of acetophenone to R-1-phenylethyl acetate using heterogeneous and enzymatic catalysis (in collaboration with Moscow State University)

Krogell, Jens, Kemisk karakterisering av granbark samt extraktion av hemicellulosor och pektiner (*Chemical characterization of spruce bark and extraction of hemicelluloses and pectins*, in Swedish)

Lindén, Isak, Deposit formation and heat transfer in a recovery lime kiln cooler

Oladele, Oluwamuyiwa, Catalytic hydrogenation of carbohydrates – Modelling and kinetics

Penttinen, Matias, Metodutveckling för kemisk analys av mikroorganismer (*Development of methods for chemical analysis of microorganisms*, in Swedish)

Rivero, Daniel, Physical properties of sugar solutions and hydrogenation reactions of sugar into sugar alcohols over Ru/C monolithic catalysts

Rozmysłowicz, Bartosz, Catalytic deoxygenation of tall oil fatty acids over palladium, mesoporous carbon catalyst

Smeds, Felix, Utveckling av en mätmetod för elektrokemisk detektering av korrosion i realtid i högtemperaturomgivning (*Development of a method for electrochemical detection of corrosion in real time in high temperature ambient*, in Swedish)

Stepien, Milena, Conducting polymers as model to study propagation of biological membrane potential with time

Vainio, Emil, Mätning av gassammansättning i eldstaden i en stor sodapanna (*In-furnace gas composition measurement in a large Kraft recovery boiler*, in Swedish)

Wang, Nianxing, Promoting direct electron transfer in bio fuel-cell enzyme electrodes by using carbon nano-tubes as electron carrier

Vähä-Savo, Niklas, Utveckling och användning av en korttidssond vid mätningar av överbäring i sodapannor (*Development and application of a one-minute probe for measuring carry-over in a recovery boiler*, in Swedish)

4.2 Articles in Refereed International Scientific Journals and Series (118)

Akieh, M.N., Price, W.E., Bobacka J., Ivaska, A., Ralph, S., Ion exchange behaviour and charge compensation mechanism of polypyrrole in electrolytes containing mono-, di-, and trivalent metal ions, *Synthetic Metals* 159 (2009), 2590–2598

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4.4 Åbo Akademi Reports (9)

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4.5 General Articles (in newspapers etc.) (8)

Bioöljyn happipitoisuus pienenee pyrolyysihöyryjen jalostuksessa, *Keskipohjanmaa*, 25.9.2009, *Atte Aho*

Endast forskaren skapar ny vetenskap, *Acatiimi*, 3/2009, *Tapio Salmi*

Finland behöver ett ministerium för vetenskap och kultur, *Åbo Underrättelser*, 10.12.2009, *Tapio Salmi*

Internationell vetenskaplig konferens till Finland, *Meddelanden från Åbo Akademi*, 11.12.2009, *Tapio Salmi*

Jäte – Polttoaine siinä missä muutkin*, Sitaatti,* May 2009, No. 1, *Pasi Vainikka*

Kemisk reaktionsteknik i går, i dag och i morgon, *Redox 2009*, Kemistklubben vid Åbo Akademi, *Tapio Salmi*

Unilagen – rondo, presto, agitato, *Åbo Underrättelser*, 18.2.2009, *Tapio Salmi*

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4.6 Patents (4)

Holmbom, B., Eckerman, C., Hemming, J., Reunanen, M., Sundberg, K. Willför, S., A method for isolating phenolic substances or juvabiones form wood comprising knotwood, *EP 1 395 539 B1 (2009)*

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Murzin, D. Yu., Kubičkova, I., Snåre, M., Mäki-Arvela, P., Myllyoja, J., Method for the manufacture of hydrocarbons, *US Patent* 7, 491,858, 17 Feb 2009

Pranovich, A., Holmbom, B., Konn, J., Method for treating lignocellulosic materials, *PCT Int. Appl. (2009)*, CODEN: PIXXD2 WO 2009050336 A1 20090423 CAN 150:450193 AN 2009:487294 CAPLUS

4.7 Awards (3)

Vähä-Savo, Niklas, Best Masters' Theses in the field of chemical recovery in a kraft pulp mill, Finnish Recovery Boiler Committee, 2009

Bobacka, Johan; Ivaska, Ari, Scholarship from the foundation Runar Bäckströms Stiftelse for the invention of a method for precipitation of noble metals from solutions

Ivaska, Ari, FIA Honor Award for Science "For his glorious contribution to advance of modern flow injection analytical method", Japanese Association for Flow Injection Analysis, Japan Society for Analytical Chemistry

5. Courses 2009

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

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
Gregory Yablonsky, St. Louis University, MO, USA
Johan Wärnå
Tapio Salmi

Summer School: Materials – Catalytic or Not?

Time: June
Place: Kristinestad
Lecturers: Narendra Kumar
Olga Simakova
Mats Käldström
Teemu Heikkilä, University of Turku
Krisztián Kordás, University of Oulu
Hannu Karhu, University of Turku
J-P. Mikkola
Kalle Arve
Heidi Bernas
Päivi Mäki-Arvela
Dmitry Murzin
Kari Eränen

Lecturers (cont.): Matias Kangas
Henrik Grénman
Pia Damlin
Jan Hájek
José Rafael Hernández Carucci
Steliana Aldea

Application of IR Spectroscopy to the Problems of Catalysis

Time: September
Place: Åbo Akademi University
Lecturer: Jerzy Datka, Jagiellonian University, Cracow, Poland

Analytical Techniques in Combustion, Part 4

Course Supervisors: Mikko Hupa, Maria Zevenhoven
Time: September
Place: Åbo Akademi University
Cooperation: Nordic Graduate School in Biofuels Science and Technology (biofuels GS-2)
Lecturers: Maria Zevenhoven
Mikko Hupa
Tor Laurén
Nikolai DeMartini
Linda Fröberg

Modern Analytical Tools for Pulp and Paper

Course Supervisor: Stefan Willför, Anna Sundberg
Course Coordinator: Anna Boedeker
Time: November
Place: Åbo Akademi University
Cooperation: International Doctoral Programme in Pulp and Paper Science and Technology (PaPSaT)
Lecturers: Stefan Willför
Anna Sundberg
Bjarne Holmbom
Antje Potthast, BOKU University, Vienna
Anna-Stina Jääskeläinen, TKK
Chunlin Xu, BASF
Andrey Pranovich
Lari Vähäsalo
Elena Tokareva
Ari Ivaska
Patrik Eklund

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)
Nordic Graduate School in Biofuels Science and Technology (biofuelsGS-2)
Lecturers: Mikko Hupa
Markus Engblom
Bengt-Johan Skrifvars, Top Analytica
Johan Werkelin
Maria Zevenhoven

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)
Lecturer: Dmitry Murzin
Demonstrators and assistants: Johan Wärnå
Matias Kangas

Åbo Akademi Process Chemistry Centre Internal Workshops and Courses

Workshop VII: Instrumental Methods – Part I, October 14, 2005

- Docent Leif Kronberg: HPLC-MS
- Dr. David Kubička: Chemometrics
- Mr. Jyrki Kuusisto: HPLC
- Mr. Markku Reunanen: GC-MS
- Mr. Johan Werkelin: Ion chromatography

Workshop II: Instrumental Methods – Part II, November 18, 2005

- Dr. Mikael Bergelin: Non-optical microscopy
- Docent Carita Kvarnström: FTIR & Raman spectroscopy
- Docent Rainer Sjöholm: NMR spectroscopy
- Dr. Lari Vähäsalo: Flow cytometry

Workshop III: Metals from Wood – Biorefinery Aspects, February 3, 2006

- Docent Stefan Willför: Biorefinery – an existing proposal
- Dr. Andrey Pranovich: Metals in wood
- Dr. Maria Zevenhoven: Metals from wood to ash
- Mr. Kim Granholm: Removal of metal ions from pulps by chelation

Workshop IV: Introduction to Modelling at PCC, April 25, 2006

- Docent Johan Wärnå: Kinetics and reactor modelling
- Docent Christian Mueller: Computational Fluid Dynamics
- Dr. Ville Nieminen: Molecular models
- Docent Tomasz Sokalski: Does Analytical Chemistry need mathematical modelling?
- Ms. Eija Bergelin: Extractive flows

Workshop V: Functional Materials – Part I, October 6, 2006

- Docent Leena Hupa: Tailoring of surfaces for everyday life environment
- Docent Narendra Kumar: Engineering crystal morphology and metal modification of porous materials
- Prof. Ronald Österbacka: Organic electronics
- Prof. Johan Bobacka: Chemical sensors based on functionalized materials

Workshop VI: Functional Materials – Part II, November 10, 2006

- Lic. Tapio Mäkelä, co-ordinator of the Åbo Akademi Center for Functional Materials: Patterning methods for inherently conducting polyaniline
- Docent Heimo Ylänen, director of the Turku Biomaterials Centre (TBC): Bioactive glasses
- Prof. Markku Auer, New functions for paper – A challenge

Workshop VII: Biochemistry in Åbo – An opportunity for the PCC, May 16, 2007

- Doc. Eric Bertoft, ÅA, Dept. of Biochemistry and Pharmacy: Advances in understanding of the structure of amylopectin, the major starch component
- Prof. Pia Vuorela, ÅA, Dept. of Biochemistry and Pharmacy: Microfractionation and bioassays in natural product drug discovery
- Prof. Bjarne Holmbom: Bioraff

Workshop VIII: Young Scientists – Session I, January 25, 2008

- Matias Kangas: Structure-performance effects in zeolite catalyzed skeletal isomerization
- Michal Wagner: Electropolymerization of poly(para-phenylene) in ionic liquids

- Di Zhang: Glass-based biomaterials
- Chunlin Xu: Spruce galactoglucomannan: A potential raw material for hydrocolloids and novel advanced natural materials

Workshop IX: Young Scientists – Session II, May 8, 2008

- Hanna Lindqvist: Derivatization of mannans
- Minna Piispanen: Glazes with functional coatings
- Henrik Gustafsson: "Abandon all hope, ye who enter here" – Mankind's future energy supply
- Pasi Virtanen: Applications of ionic liquids

Course: Effective Presentation Skills in English, January–February 2009

- Theory Day: January 23, 2009
- Conference Days:
    - Group 1: January 31
    - Group 2: January 31
    - Group 3: February 2
    - Group 4: February 2
    - Group 5: February 3
- Lecturer: Patrick Gallagher, Kielikanava

6. Other Activities 2009

6.1 Organization of Conferences, Courses and Seminars

Location, Meeting, Date, Number of Participants

Espoo, Finland, Graduate School in Chemical Engineering (GSCE) Annual Seminar, November 26–27 (50)

Iaşi, Romania, 12th International Magnesium Symposium, September 22–25, 2009 (110)

Naantali, Finland, Finnish-Swedish Flame Days, January 28–29 (90)

Snekkersten, Denmark, Joint Meeting of the Scandinavian-Nordic and French Sections of the Combustion Institute, November 9–10 (80)

Trondheim, Norway, Nordic Graduate School in Biofuels Science and Technology (biofuels GS-2) Annual Meeting, June 14–16 (24)

Turku, Finland, CO_2-SUSE-seminar (Academy of Finland Sustainable Energy (SusEn) and Sustainable Production and Products (KETJU) research programmes), October 8–9 (40)

Turku, Finland, Lappeenranta, Finland, Graduate School in Chemical Engineering (GSCE) Spring Seminar, April 23–24 (50)

6.2. Participation in Major Conferences, Meetings and Courses

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

January

Naantali, Finland, Swedish-Finnish Flame Days, 8

Raisio, Finland, Ciba Chemicals/BASF, invited lecturer, *J-P. Mikkola*

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

Salt Lake City, UT, USA, University of Utah Chemical Engineering 2008–2009 Distinguished Lecturer Series, *Mikko Hupa*

Stockholm, Sweden, Värmeforskdagarna 2009: "Miljöriktig användning av askor", 1

Turku, Finland, Intensification of chemical processes, *Societas Scientiarum Fennica*, invited lecture, *Tapio Salmi*

February

Copenhagen, Denmark, BiofuelsGS-2 course: Analytical Techniques in Combustion, part 2, 3

Espoo, Finland, Skogsbrukets vinterdagar (Forest Owners' Association winter meeting), invited lecturer, *Bjarne Holmbom*

Graz, Austria, European Winter Conference on Plasma Spectrochemistry, 1

Helsinki, Finland, DIAS-gillet, invited lecturer, *Mikko Hupa*

Helsinki, Finland, KETJU annual seminar, invited lecturer, *J-P. Mikkola*

Huittinen, Finland, Metsäammattilaisten talvikoulutuspäivät (Winter School for Forest Professionals), invited lecturer, *Bjarne Holmbom*

Pisa, Italy, EU-INECSE Half-Yearly Meeting, 1

Pisa, Italy, International Flame Research Foundation (IFRF) TOTeM 33, 2, conference chairman, *Mikko Hupa*

Pori, Finland, Outotec research centre, "Modelling of solid-liquid reactions – leaching of zinc", invited lecture, *Tapio Salmi*

Stockholm, Sweden, FPIRC Graduate School Course on Biorefinery, invited lecturer, *Bjarne Holmbom*

Sundsvall, Sweden, Fibre Science and Communication Network (FSCN), Mid-Sweden University, Guest Seminar, invited lecturer, *Bjarne Holmbom*

Turku, Finland, Seminar on Microfabrication Technology, Turun koneteknologiakeskus, 20

March

Helsinki, Finland, AIR 25 Years Seminar, invited lecturer, *Mikko Hupa*

Johannesburg, South Africa, 14th Southern African Coal Science and Technology Conference, 1

Santiago de Chile, Chile, Workshop "Optimal Treatment Processes of Lignocelluloses for Bioethanol Production", 1

April

Brussels, Belgium, 8th International Congress on Catalysis and Automotive Pollution Control (CAPoC 8), 1

Espoo, Finland, Biorefinery Lecture Series, Helsinki University of Technology, invited lecturer, *Bjarne Holmbom*

Espoo, Finland, Microreactors in catalysis, Finnish Catalysis Society, invited lecture, *Tapio Salmi*

Joensuu, Finland, Science Café, Chemistry is green, too, invited lecture, *Tapio Salmi*

Lappeenranta, Finland, Graduate School in Chemical Engineering (GSCE) Spring Seminar, 10

Ljubljana, Slovenia, University of Ljubljana, Recent advances in microreactor technology, distinguished lecture, *Tapio Salmi*

Oulu, Finland, Graduate School for Energy Science and Technology, Waste minimization and resources use optimization course, invited lecturer, *J-P. Mikkola*

Turku, Finland, CHEMBIO-Turku Seminar, invited lecturer *Päivi Mäki-Arvela*

Turku, Finland, Poiju (Meeting place for senior citizens in Turku), Research – an important part of life, invited lecturer, *Bjarne Holmbom*

May

Budapest, Hungary, Hungarian Academy of Sciences, Analytical Chemistry Session, Annual Seminar, keynote lecture, *Ari Ivaska*

Cairns, Australia, 3rd Congress on Ionic Liquids (CoIL-3), 1, 1

Espoo, Finland, MIKES Course of Quality of Measurements, 2

Helsinki, Finland, Academy Professors' Annual Meeting, invited lecture, *Tapio Salmi*

Helsinki, Finland, ChemBio Conference, Biochemicals for protection of goods and health, invited lecturer, *Bjarne Holmbom*

Helsinki, Finland, ChemBio Conference, Health and business from spruce trees, invited lecturer, *Bjarne Holmbom*

Helsinki, Finland, ChemBio Conference, invited lecture, *Tapio Salmi*

Lyngby, Denmark, Technical University of Denmark Workshop "Combustion Carbon Capture and Storage", invited lecturer, *Mikko Hupa*

Montpellier, France, European Forum on New Glass Applications (EFONGA) Workshop for New Researchers in Glass Science and Technology, 1

Montpellier, France, European Forum on New Glass Applications (EFONGA) Expert Workshop, 1

Oulu, Finland, Course: "Environmental Applications of TiO_2 Photocatalysis", 1

San Francisco, USA, 215th ECS Meeting, keynote lecture, *Ari Ivaska,* invited lecture, *Andrzej Lewenstam*

Seoul, Korea, Energy from Biomass and Waste Workshop, University of Seoul, CWEG EcoStar Consortium and Korean Society of Waste Management, invited plenary lecture, *Mikko Hupa*

Trondheim, Norway, BiofuelsGS-2 course on Analytical Techniques in Combustion, part 3, 3

Turku, Finland, EU COST-D40 Action in Innovative Catalysis: New Processes and Selectivities, 1 invited lecturer, *Bjarne Holmbom*

Umeå, Sweden, Wood in NextGen Biorefineries: Beyond pulping, invited lecturer, *J-P. Mikkola*

Vancouver, BC, Canada, 8th Pacific Rim Conference on Ceramic and Glass Technology, 3

Xian, China, 20th International Conference on Fluidized Bed Combustion, 5, member of organizing committee, *Mikko Hupa*, session chairmen, *Mikko Hupa, Patrik Yrjas*

June

Boston, MA, USA, 16th IFRF Members' Conference "Combustion and Sustainability: New Technologies, New Fuels, New Challenges", 3, *Mikko Hupa*

Cracow, Poland, 11th Conference of the European Ceramic Society, 2

Cracow, Poland, 2nd International Symposium on Surface Imaging Spectroscopy (ISIS 2009), keynote lecture, *Andrzej Lewenstam*

Hamburg, Germany, 17th European Biomass Conference & Exhibition – From Research to Industry and Markets, 1

Hamilton, Canada, 7th Paper and Coating Chemistry Symposium, 2

Lahti, Finland, Finnish Recovery Boiler Committee 45th Anniversary International Recovery Boiler Conference, 2, conference chairman and plenary lecturer, *Mikko Hupa*

Novosibirsk, Russia, VIII International Conference “Mechanisms of Catalytic Reactions” (MCR-2009), invited lecture, session chairman, *Dmitry Murzin, 5, 3*

Oslo, Norway, 15th International Symposium on Wood, Fibre and Pulping Chemistry (ISWFPC 2009), 2, 3

Oulu, Finland, EnePro Conference: New, innovative and sustainable transportation fuels, *J-P. Mikkola*

Rome, Italy, 5th International Conference on Diffusion in Solids and Liquids, 1

St. Petersburg, Russia, International Academy of Wood Science, plenary lecture, *Bjarne Holmbom*

Strasbourg, France**,** European Material Research Society (E-MRS) Conference, 1

Trondheim, Norway, Nordic Graduate School in Biofuels Science and Technology (biofuelsGS-2) Annual Seminar, 4

Venice, Italy, 2nd International Green Process Engineering Congress and European Process Intensification Conference (GPE-EPIC), 4, 4

July

Heidelberg, Germany, 5th International Conference on Gold Science, Technology and Its Applications, 1

Kazimierz Dolny, Poland, 7th International Symposium Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids (ISSHAC-7), member of the scientific committee, *Dmitry Murzin*

Kazimierz Dolny, Poland, 11th International Symposium on Catalyst Deactivation, member of the scientific committee, *Dmitry Murzin*

Nürnberg, Germany, Universität Nürnberg-Erlangen, invited lecturer, *Dmitry Murzin*

Strasbourg, France, Université Louis Pasteur, invited lecturer, *Dmitry Murzin*

Szczyrk, Poland, International Workshop on Electrochemistry of Electroactive Materials (WEEM 2009), invited lecture, *Andrzej Lewenstam*

August

Beijing, China, 60th Annual Meeting of the International Society of Electrochemistry, 4, keynote lecture, *Ari Ivaska*

Kokkola, Finland, New Products from Forest Biomass Seminar, invited lecturer, *Bjarne Holmbom*

Montréal, Quebec, Canada, 8th World Congress on Chemical Engineering, 11, 11, session chairmen, *J-P. Mikkola, Tapio Salmi, Johan Wärnå*

Salamanca, Spain, EuropaCat IX conference, 15, 6, keynote lecture, *Dmitry Murzin*

September

Brussels, Belgium, EU-BioMedNano Final Meeting, 1

Davos, Switzerland/Nagoya, Japan, R'09 Twin World Congress and World Resources Forum, 1

Frankfurt am Main, Germany, European Federation of Corrosion Workshop: Solutions for High Temperature Corrosion Protection in Energy Conversion Systems, 2

Hamburg, Germany, Japanese-European Workshop on Cellulose and Functional Polysaccharides, 1

Helsinki, Finland, 2nd Nordic Wood Biorefinery Conference (NWBC 2009), 10, invited lecture, *Bjarne Holmbom*

Iaşi, Romania, 12th International Magnesium Symposium, keynote lecture, *Andrzej Lewenstam*

Ischia, Italy, 3rd International Conference on Structured Catalysts and Reactors, 2

Kotka, Finland, Danisco Sweeteners, Sugar hydrogenation kinetics, invited lecture, *Tapio Salmi*

Pollensa, Mallorca, Spain, Flow Analysis Conference, 2

Rio de Janeiro, Brazil, 11th International Conference on Advanced Materials (ICAM 2009), 1

Stockholm, Sweden, XIV International Symposium on Relations between Homogeneous and Heterogeneous Catalysis (ISHHC XIV), 4

Turku, Finland, BiofuelsGS-2 course on Analytical Techniques in Combustion, part 4, 4

Turku, Finland, European Polysaccharide Network of Excellence (EPNOE) Conference "Polysaccharides as a Source of Advances Materials" Conference, plenary lecturers, *Bjarne Holmbom*, *Stefan Willför*, 20

Varenna, Italy, Italic 5 – Science & Technology of Biomasses: Advances and Challenges, 1, 2

Örnsköldsvik, Sweden, Processum, invited lecturer, J-P. *Mikkola*

October

Cape Town, South Africa, International Conference on Coal Science & Technology (ICCS&T), 1

Czestochowa, Poland, 59th International Energy Agency-Fluidized Bed Conversion Implementing Agreement (59th IEA-FBC), 2, lecturer, *Mikko Hupa*

Delft, the Netherlands, 11th International Symposium on Catalyst Deactivation, session chairman *Dmitry Murzin*, 2

Eindhoven, the Netherlands, Some experiences on microreactor technology, Eindhoven University of Technology, guest lecture, *Tapio Salmi*

Espoo, Finland, Microreactor technology – an overview, Finnish Chemical Engineering Society, invited lecture, *Tapio Salmi*

Fray Bentos, Uruguay, Botnia pulp mill visit and combustion course, lecturer, *Mikko Hupa*

Helsinki, Finland, Academy of Finland Science Gala, 5

Jyväskylä, Finland, Nanoscience Days 2009, 1

Kalmar, Sweden, 8th ScanBalt Forum and Biomaterials Days, 2

Naantali, Finland, Annual Meeting of Teachers in Mathematics and Sciences in Finland (MAOL), What are chemists doing – and what should they do, invited lecturer, *Bjarne Holmbom*

Santiago de Chile, Chile, Chilean Chemical Engineering Congress, invited lecture *Sari Hyvärinen*

Sao Paulo, Brazil, ABTCP-PI 2009 Pulp and Paper International Congress and Exhibition, invited plenary lecturer, *Mikko Hupa*

Tampere, Finland, Wood-based Materials Seminar, invited lecturer, *Bjarne Holmbom*

Turku, Finland, CO_2-SUSE-seminar, chairman *J-P. Mikkola*

Turku, Finland, The chemist's reply to the challenges of today, Frukostklubben, invited lecture, *Tapio Salmi*

Turku, Finland, 50th Anniversary Seminar of Food Scientists in Turku, Edible products also from trees, invited lecturer, *Bjarne Holmbom*

Umeå, Sweden, Umeå Plant Science Center, invited lecturer, *J-P. Mikkola*

Uppsala, Sweden, Forest Values Conference, The relevance of science for innovations, Invited lecturer, *Bjarne Holmbom*

Vienna, Austria, 216th Fall Meeting of the Electrochemical Society, 6

Viňa del Mar (Valparaíso), Chile, XVII Congreso de Ingeniería Química, 2

November

Brussels, Belgium, EU Bioenergy Network of Excellence Final Seminar, 1

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

Helsinki, Finland, University of Helsinki, invited lecturer, *J-P. Mikkola*

Okinawa, Japan, Okinawa Institute for Science and Technology, invited lecture, *Andrzej Lewenstam*

Paris, France, EDF-IFRF Coal Characterization Workshop, 1

Santiago de Chile, Chile, Workshop "Biofuels and Their Future in the Energy Matrix", 1

Snekkersten, Denmark, Joint Meeting of the Scandinavian-Nordic and French Sections of the Combustion Institute, 3

Stockholm, Sweden, EU Forest Technology Platform, invited lecture, *Bjarne Holmbom*

Stockholm, Sweden, MISTRA Black Liquor Gasification Program

Turku, Finland, Konsistoriesällskapet vid ÅA, Chemical engineering towards a bright future, invited lecturer, *Bjarne Holmbom*

Turku, Finland, Samhällspolitiska föreningen i Åbo, invited lecturer, *Bjarne Holmbom*

Washington DC, USA, TAPPI Research Managers' Annual Meeting

Örnsköldsvik, Sweden, BSR Baltic Sea Innonet Meeting, invited speaker, *J-P. Mikkola*

December

Dakar, Sénégal, Centre Sunuker, Possibilités de chimie verte, invited lecture, *Tapio Salmi*

Jakobstad, Finland, UPM-Kymmene – ÅA Recovery Boiler Seminar Day, invited lecturers *Mikko Hupa*, *Atte Aho*

Porto, Portugal, Green process technology, University of Porto, guest lecture, *Tapio Salmi*

Prague, Czech Republic, Modern Electroanalytical Methods 2009, keynote lecture, *Ari Ivaska*

Santiago de Chile, Chile, Workshop "Biofuels and Chemical Products from Woody Biomass", invited lecturer, *Sari Hyvärinen*

Turku, Finland, Finnish Society for Industrial Ecology Annual Conference, Finnish Platform on Life Cycle Assessment (FINLCA), invited speaker, *J-P. Mikkola*

6.3. Visitors and Visits

Visitors to PCC

Ali Ak-Kandari, Halena, Kuwait University, Kuwait (August)

Biasi, Pierdomenico, Università di Padova, Padova, Italy (March–May, August–November)

Campo, Betiana, PLAPIQUI, Bahia Blanca, Argentina (January–December)

Cortinez Villalobos, Victoria Andrea, University of Chile, Santiago, Chile (March–May)

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

Han, Dongxue, State Key Laboratory of Electroanalytical Chemistry, Changchun, China (April–December)

Hilpmann, Gerd, Technische Universität Dresden, Dresden, Germany (October–December)

Jakobitz, Christopher, Technische Universität Dresden, Dresden, Germany (January–February)

Kannisto, Hannes, Chalmers University of Technology, Gothenburg, Sweden (September–December)

Kasparova, Marketa, Charles University, Hradec Králové, Czech Republic (April–June)

Khakalo, Alexey, St. Petersburg State Forest Technical Academy, St. Petersburg, Russia (September–November)

Kisiel, Anna, University of Warsaw, Warsaw, Poland (January–June, September–December)

Korotkova, Ekaterina, Tver State Technical University, Tver, Russia (October–December)

Kupis, Justyna, AGH University of Science and Technology, Cracow, Poland (April–June)

Li, Niu, State Key Laboratory of Electroanalytical Chemistry, Changchun, China (May)

Marton, Aurel, University of Veszprem, Veszprem, Hungary (November)

Mikhelson, Konstantin, St. Petersburg University, St. Petersburg Russia (January–April)

Monedero, Esperanza, UCLM, Instituto de Investigación en Energías Renovables, Spain (January–April)

Patil, Narendra, Eindhoven University of Technology, Eindhoven, the Netherlands (May)

Peshkova, Maria, St. Petersburg University, St. Petersburg, Russia (January–February, April)

Pezoa Conte, Ricardo, University of Chile, Santiago, Chile (March–May)

Plaza, Piotr, Cardiff University, Cardiff, UK (November–December)

Prabhu, Alok, Polytechnic Institute of New York, New York, USA (November–December)

Sárkadi-Pribóczki, Eva, Hungarian Academy of Sciences, Budapest, Hungary (December)

Spetz, Peter, Finnish Forest Research Institute *Metla* (August, October)

Szűcs, Julia, Budapest University of Technology and Economics, Budapest, Hungary (August–October)

Teter, Agnieszka, University of Warsaw, Warsaw, Poland (January–May)

Varga, Agnes, University of Pécs, Pécs, Hungary (April–June)

Zieba, Mariusz, University of Stuttgart, Stuttgart, Germany (April–May)

Visits by PCC members

Eta, Valérie, CNRS, Université de Bourgogne, Dijon, France (July–August)

Ivaska Ari, Poland, University of Warsaw, Department of Chemistry (March)

Ivaska, Ari, France, University of Bordeaux, Faculty of Science and Technology (October)

Mattinen, Ulriika, Dublin City University, Ireland (November)

Meana Esteban, Beatriz, University of Milan CNR–ISMAC, Milan, Italy (February)

Meana Esteban, Beatriz, Johannes Kepler University of Linz, Austria (January–November)

Murzin, Dmitry, University of Otago, Dunedin, New Zealand, MacDiarmid Institute, Christchurch, New Zealand, University of Canterbury, Christchurch, New Zealand (October)

Wang, Xiaoju, Sapienza University of Rome, Italy (March–May)

6.4. External PhD Examinations and Reviews

Bio4Energy research programme (Swedish Energy Agency), member of steering group, *J-P. Mikkola*

Biorefinery of the Future, Member of the scientific board, *J-P. Mikkola*

COST action 543 Bioethanol for Fuel Cells, Member *J-P. Mikkola*

COST action CM0903 Utilisation of Biomass for Sustainable Fuels & Chemicals (UBIOCHEM), Member of Management Committee, *J-P. Mikkola*

Editorial Board Member for *Holzforschung*, *Bjarne Holmbom*

Editorial Board Member for *Wood Science and Technology*, *Bjarne Holmbom*

Editorial Board Member for *Cellulose Chemistry and Technology*, *Bjarne Holmbom*

Editorial Board Member for *O Papel*, *Bjarne Holmbom*

Editorial Board Member for *Analytical Letters*, *Ari Ivaska*

Editorial Board Member for *Bulletin on Chemical Reaction Engineering Catalysis*, *Dmitry Murzin*

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

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

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

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

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

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

Editorial Board Member for *Open Catalysis Journal*, *Dmitry Murzin*

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

Editorial Board Member for *Progress in Industrial Ecology, An International Journal*, *J-P. Mikkola*

European Federation of Catalysis Societies, Vice President, *Dmitry Murzin*

Evaluation of Docentship competence, (*Mehrdad Arshadi*), SLU, Umeå, Sweden, *Bjarne Holmbom*

Evaluation of Docentship competence, (*Arto Laari*), Lappeenranta University of Technology, *Tapio Salmi*

Evaluation of Docentship competence (*Sustainable Chemical Technology*), University of Oulu, Oulu, Finland, *J-P. Mikkola*

Evaluation of Professorship competence (*Marcin Palys*), University of Warsaw, Warsaw, Poland, *Andrzej Lewenstam*

Evaluation of research projects, Fundacao para a Ciencia e a Tecnologia, Lisbon, Portugal, *Tapio Salmi*

Evaluation of the Swedish Energy Agency Research Programme "Consortium of material technology for thermal energy processes 2006–2009", *Mikko Hupa*

Evaluator of Fondecyt, Santiago de Chile, Chile, *J-P. Mikkola*

Evaluator of the candidates and referee for the research professorship, Modelling of complex chemical systems, VTT, Espoo, *Tapio Salmi*

Expert for project evaluation at NWO, the Netherlands, *Tapio Salmi*

Expert for the Czech Research Council, *Dmitry Murzin*

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

Mosca, Alessandra, Luleå Technical University, Member of thesis review committee, *J-P. Mikkola*

Muraza, Oki, Eindhoven University of Technology, faculty opponent, *Dmitry Murzin*

Pereira, Carla, University of Porto, Portugal, faculty opponent, *Tapio Salmi*

Rasi, Saija, University of Jyväskylä, evaluator of PhD thesis, *J-P. Mikkola*

Referee for the professorship at Helsinki University of Technology, *Dmitry Murzin*

Regional representative for Finland in the International Society of Electrochemistry (ISE), 2004–2009, *Johan Bobacka*

Sundman, Ola, University of Umeå, Member of thesis review committee, *J-P. Mikkola*

Invited lecturers

Davis, Robert J., University of Virginia, Charlottesville, VA, USA, March

Estel, Lionel, INSA Rouen, France, October

Lanza, Roberto, Royal Institute of Technology, Stockholm, Sweden, November

Lindner, Ernő, The University of Memphis, Memphis, TN, USA, November

Trojanowicz, Marek, Department of Chemistry, University of Warsaw, Warsaw, Poland, June

6.5 Publicity

Television and Radio

Interview on national TV news, February, *Tapio Salmi*

Newspapers and General Journals

"Efficient Production of Fuels from Biomass"-projektille rahoitusta, *Turun Sanomat*, September, 2009

Biobränsleprojekt vid ÅA fick finansiering, *Åbo Underrättelser*, September, 2009

En kommunikation som behövs, *Meddelande för Åbo Akademi*, February 20, 2009, interview with Johan Werkelin

Hälsopreparat av granens kvistar, *Skogsbruket* nr 4 2009, interview with Bjarne Holmbom

I framtiden äter vi kanske ved, interview at the EPNOE Polysaccharide Conference, *Åbo Underrättelser*, September 2009

Kemikalier från naturen, Tapio Salmi arbetar som akademiprofessor i fem år, *Meddelanden från Åbo Akademi*, January 23, 2009

Kemiska föreningar för miljövänliga produkter, Sebastién Leveneur disputerade, *Meddelanden från Åbo Akademi*, October 30, 2009

Med exakt koll på elementen, *Meddelanden från Åbo Akademi,* October 30, 2009, interview with Kjell-Erik Saarela

Metsien visionäärit, *Satakunnan Kansa*, June 14, 2009, interview with Bjarne Holmbom and others

Metsä on mahdollisuuksia täynnä, *Metsä.fi* nr 3 May 2009

Mycket mera värde ur skogen, *Meddelanden från Åbo Akademi*, May 11, 2009

Ny internationell utbildning i kemiteknik, *Meddelanden från Åbo Akademi,* December 11, 2009

Vesien kemian tekniikkaa, *Kemia-Kemi* 36 (2009) 1, interview with Tapio Salmi

Appendix I

Åbo Akademi Process Chemistry Centre Doctoral Theses in Progress 2010

Students from Outside Finland

- Steliana Aldea (Romania, *F*), MSc University of Bucharest, Bucharest, Romania 2006, BSc University of Bucharest, Bucharest, Romania 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
- Iveta Ceskova (Czech Republic, *F*), MSc Brno University of Technology, Czech Republic, 2007
- Àngela Duque Huguet (Spain, *F*), MSc Universitat de Barcelona, Spain 2007
- 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, Krákow, Poland 2008 (double degree)
- Olatunde Jogunola (Nigeria, *M*), MSc ÅA 2007, BSc University of Lagos, Nigeria 1995
- Alexey Kirilin (Russia, *M*), MSc D.I. Mendeleyev University of Chemical Technology of Russia, Moscow, Russia 2009
- Bright Kusema (Zimbabwe, *M*), MSc D.I. Mendeleyev 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
- 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 Bolivar, Caracas, Venezuela 2008
- Elena Murzina (Russia, *F*), MSc D.I. Mendeleev University of Chemical Technology of Russia, Moscow, Russia 1987
- 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)
- Serap Sahin (Turkey, *F*), MSc ÅA 2007, BSc Ege University 2006, Izmir, Turkey
- Victor Sifontes Herrera (Venezuela, *M*), MSc Universidad Simón Bolivar, 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 ÅA2004, BSc Shandong Institute of Light Industry, China 2002
- Elena Tokareva (Russia, *F*), MSc Moscow State University, Russia 1999
- Michał Wagner (Poland, *M*), MSc AGH University of Science and Technology, Krákow, 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

Doctoral Students from Finland

- Maija Blomquist (Nousis, *F*), MSc ÅA 1998
- Markus Engblom (Åbo, *M*), MSc ÅA 2005
- Sonja Enestam (Åbo, *F*), LicTech ÅA 2000
- Susanne Fagerlund (Åbo, *F*), MSc ÅA 2007
- Henrik Grénman (Åbo, *M*), MSc ÅA 2005
- Henrik Gustafsson (Ekenäs, *M*), MSc ÅA 1999
- Kim Granholm (Pargas, *M*), LicTech ÅA 2006
- Sari Hyvärinen (Viitasaari, *F*), MSc ÅA 2007
- 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
- Mats Käldström (Larsmo, *M*), MSc ÅA 2007
- Tor Laurén (Pargas, *M*), LicTech 2008 ÅA
- Juho Lehmusto (Åbo, *M*), MSc University of Turku 2007
- Ann-Sofie Leppänen (Nådendal, *F*), MSc ÅA 2004
- Isak Lindén (Jakobstad, *M*), MSc ÅA 2009
- Johan Lindholm (Ekenäs, *M*), MSc ÅA 2004
- 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
- Anders Strand (Nykarleby, *M*), MSc ÅA 2008
- Fredrik Sundfors (Jakobstad, *M*), MSc ÅA 2000
- 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