Åbo Akademi
Process Chemistry Centre

Annual Report 2011 – 2012

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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. Stefan Willför)*
- *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 2010 – 2011

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1. Introduction to the Activities in 2011-2012

Background

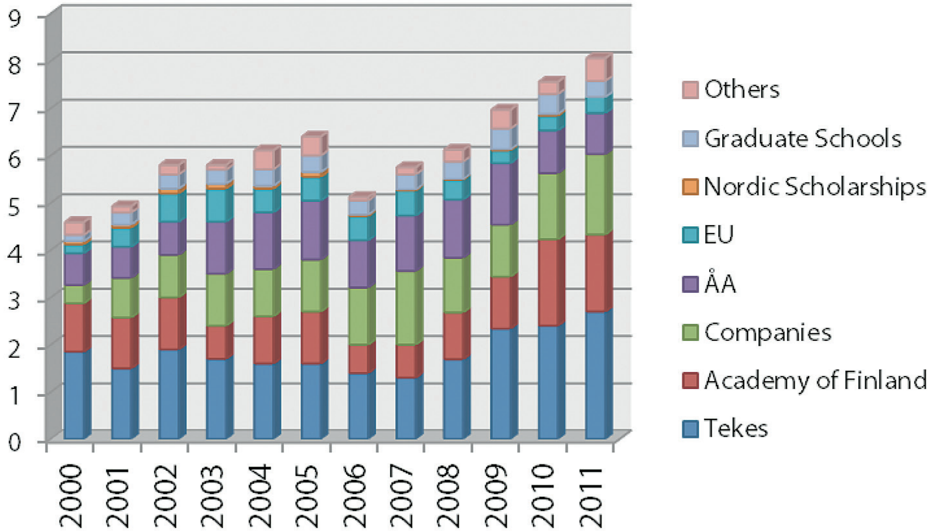
The Åbo Akademi Process Chemistry Centre (PCC) was formed in 1998 by joining four research groups at the Department of Chemical Engineering at Åbo Akademi into one research centre with common objectives and research strategy. PCC has won the status of a Centre of Excellence (CoE) in research granted by the Academy of Finland for two consecutive six-year periods: 2000-2005, and 2006-2011, respectively. Since 2012 the Centre continues its activities with a new research programme working in close collaboration with a number of industrial companies and research organizations around the world.

The PCC has successively grown in quantity and quality. Today we publish over 140 peer-reviewed journal articles per year in leading journals of chemical engineering and chemistry, the total number of PhD theses finished during the last five years (2007-2011) has been 40. We have been visible in the international scientific arena; taking part in conferences and symposia, organizing major international scientific events, holding positions of trust in scientific journals and organizations, taking part in the scientific discussion in society.

The Year 2011 in Numbers

In 2011 altogether 20 senior researchers and 50 full-time PhD candidates worked in the 60 major research projects of the Centre. In addition, a number of shorter term visitors, Master's students and support personnel participated in our activities.

Economically, the year 2011 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. However, the year 2011 was the last year when the Centre received the Academy of Finland CoE funding. Consequently, it will be an important challenge to the board of the Centre to find new ways to also in the future be able to work with more fundamental, longer term research topics heretofore covered by the CoE funding.



The funding of the Åbo Akademi Process Chemistry Centre 2000-2011

The table below gives some key numbers of our academic activities in 2011. Our research resulted in altogether 143 papers in scientific publication series with the full referee system. Ten doctoral theses and 11 masters' theses were finished.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Doctoral Theses	5	7	8	2	11	8	8	8	9	7	6	10
Masters' Theses	21	23	27	26	17	15	20	23	19	17	15	11
Journal Articles	60	70	94	77	106	109	113	116	101	118	138	143
Other Publications	105	86	96	86	111	148	157	169	195	204	191	168

Theses and other publications by the Åbo Akademi Process Chemistry Centre 2000-2011

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

Organizing International Conferences

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

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

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

Recent Awards and Recognitions

In 2011 the PCC members again have received several significant recognitions and below you may find a short list of the most important ones.

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

Henrik Grénman and Johan Werkelin won the two most important annual Åbo Akademi prizes, the Harry Elving Prizes. Henrik Grénman received the prize of the best doctoral thesis at Åbo Akademi. The title of his thesis is “Solid-liquid reaction kinetics, Experimental aspects and model development”. Johan Werkelin received the prize of “Teacher of the Year”.

The paper “Improving the wet strength and runnability” by Retulainen, E., Salminen, K., Lindqvist, H., Oksanen, A., and Sundberg, A. received the best paper award, or the Jasper Mardon Memorial Prize for significant contribution to the science and technology of papermaking at the 65th Annual Conference of Appita, the Australasian Pulp and Paper Industry Technical Association, in April, 2011, in Rotorua, New Zealand.

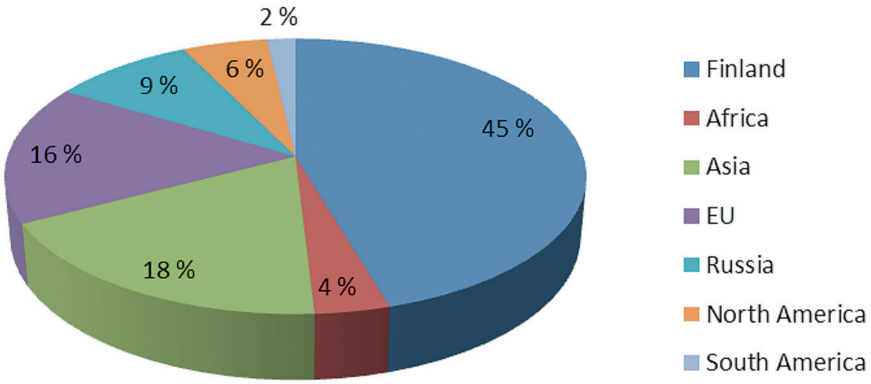
Doctoral Students

A central part of our research activities is done as doctoral theses works. Altogether about 50 PhD thesis projects are actively underway at the Centre. Our doctoral students are very international (see the graph below). More detailed information of the background of our PhD students is given in the Appendix 1 on page 177 of this Annual Report.

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

Many of the PhD works are done with support from the national graduate schools. Currently the PCC is responsible for the coordination of the national Graduate School in Chemical Engineering (GSCE). The GSCE consists of altogether 26 participating laboratories at four universities: Aalto University School of Chemical Technology, Lappeenranta University of Technology, the University of Oulu and Åbo Akademi. In 2011 41 students were participating in the activities of the GSCE, 12 of them from our Centre. The GSCE was granted continued funding for the next four-year period 2012-2015.

In 2011 the PCC PhD students further participated in the graduate schools of: Materials Research (GSMR), Pulp and Paper Science and Technology (PaPSaT), Chemical Sensors and Micro Analytical Systems (CHEMSEM), Environmental Science and Technology (EnSTe), Nanoscience (NGS-NANO), Biomaterial Graduate School (BGS), and the Graduate School for Biomass Refining (BIOREGS).



Nationality of the PhD students at PCC 2011-2012. For more detailed information see Appendix 1 on page 177

Research plans

The overall title of our research program for the years 2006-2011 has been "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 presented divided in these nine research areas.

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

Our most important project in this area has the title Chemistry in Forest Biorefineries, "Bioraff". In this project we have addressed a number of aspects in such concepts using tree based feed stocks, forest biorefineries. All four groups of the Centre have participated in this broad project in which we also collaborated with a number of other research groups. The Bioraff project has been funded by Tekes and ten industrial companies. 2011 was the last year of the Bioraff project and an extensive final report was produced in the spring of 2012.

Boards and Task Forces

The PCC is led by an executive board consisting of the four research group leaders, Professors Mikko Hupa, Stefan Willför, Ari Ivaska and Academy Professor Tapio Salmi. Maria Ljung works with the coordination of the PCC and functions as secretary to the board. In 2011 the board met nine times.

The board was supported by a Scientific Advisory Board (SAB) appointed by the Academy of Finland and an Industrial Advisory Board. In 2011 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 Heikki Tenhu from the University of Helsinki represented the Academy of Finland and Jukka Leppälahti represented Tekes, the Finnish Funding Agency for Technology and Innovation in this Board.

In 2011 the Scientific Advisory Board visited the Centre in August in connection with the Annual Seminar of the Centre (August 26-27, 2011). This being the last year of the mandate of the SAB we want to warmly thank our SAB members for the active and very useful support to our Centre. The many creative ideas and initiatives by the SAB have significantly helped us improve our Centre.

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 2011 the PCC had two lectures in its Distinguished Lecturer Series:

- December 8, 2011: Dr. Alan W. Rudie, US Forest Service, Forest Products Laboratory, Madison, WI, USA: “Value Prior to Pulping: Softwoods”

- May 5, 2011: Prof. Gordon G. Wallace, Australian Research Council Centre of Excellence for Electromaterials Science, Wollongong, Australia: “ACES - Novel Electromaterials for Energy and Medical Bionics: Materials Discovery, Fabrication and Characterisation”

Acknowledgements

This report will be published at the annual seminar of the PCC held on August 17, 2012 at the Åbo Akademi Arken Building in Turku. The report gives an overview of the recent activities at the Centre. It has a complete list of the journal articles, theses and other publications produced by the Centre in the calendar year 2011. 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 with the assistance of Lotta Österholm. The layout was done by Paul Söderholm.

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

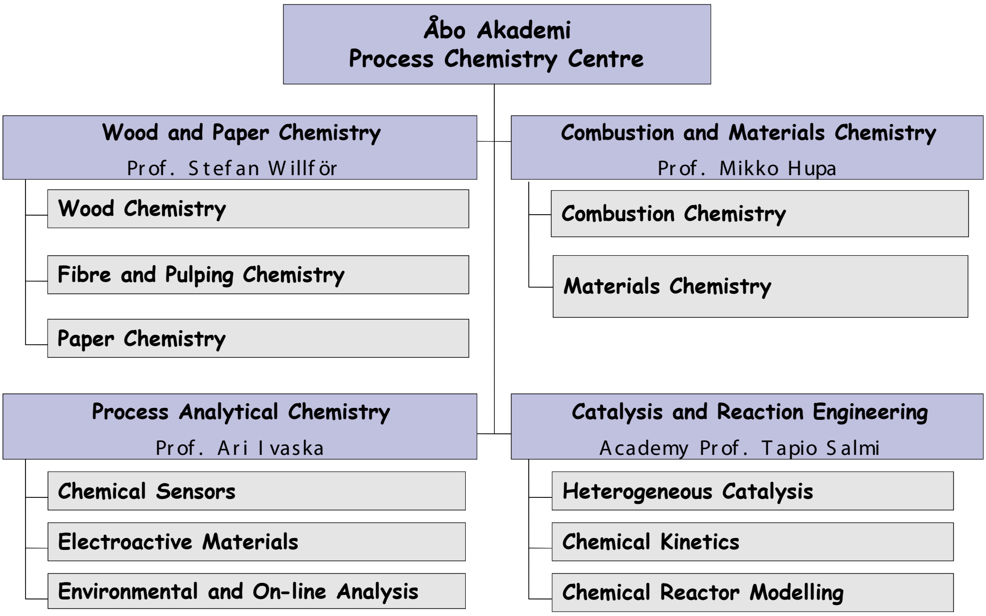
On behalf of the Board of the Åbo Akademi Process Chemistry Centre,

Mikko Hupa

Chairman

2. Organization and personnel

2.1 Organization



Åbo Akademi Process Chemistry Centre Organization

Executive Board

Prof. Mikko Hupa (Chairman)
Prof. Ari Ivaska
Academy Prof. Tapio Salmi
Prof. Stefan Willför

Coordination: Maria Ljung

Scientific Advisory Board

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

Industrial Advisory Board

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

2.2 Wood and Paper Chemistry

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

Our research is directed towards promoting sustainable, resource efficient, and multipurpose use of wood and other renewable raw materials in products including pulp, paper, fibre, and wood products but also for biochemicals, novel biomaterials, and bioenergy. Advanced analytical techniques are our tools to obtain knowledge at the molecular level on the various components of different natural raw materials and their reactions, interactions, and functions in different processes and products, including biorefining, pulping, and papermaking. Our biorefining approach aims at utilizing forest or other renewable resources as wide-ranging as possible, thus minimizing the amount of waste at the end. For example, selective extraction and recovery of hemicelluloses, lignin or polyphenols from wood, bark, or process waters is followed by functionalization and utilization in different end-uses. Remaining wood substances can then further be recovered or utilized as energy.

External research support during 2011 was obtained mainly from the Tekes and the Forest Cluster SHOK, EU, Academy of Finland, and the industry.

The following new projects started during 2011:

- Future Biorefinery (FuBio) Joint Research 2
- Pinosylvins as novel bioactive agents for food applications (PINOBIO, WoodWisdom ERA-NET)
- Wood lignins and tannins as renewable sources for novel adhesives, and biocomposites

We have a close cooperation with Metla, the Finnish Forest Research Institute, in the form of two joint senior research positions and a scientific advisor. Their field of research includes new products and biomaterials from the forest and other natural resources. In 2011 we also established cooperation with KTH and the Wallenberg Wood Science Centre in Sweden in the form of a joint senior researcher position.

We have chaired, coordinated, and acted as Grant Holders for the EU-supported COST Action FP0901, “Analytical methods for Biorefineries, 2009-2013”. This Action has participants from 27 COST and 4 non-COST countries. We are also active partners in the “European Polysaccharide Network of Excellence” (EPNOE) network.

Personnel

Professors	Stefan Willför
	Bjarne Holmbom (Emeritus)
Docents	Patrik Eklund (Organic Chemistry)
	Andrey Pranovich
	Annika Smeds
	Anna Sundberg
Senior researchers	Robin Manelius
	Lari Vähäsalo
	Protibha Nath Banjerjee
	Chunlin Xu
	Risto Korpinen
Researchers	Sylwia Bialczak
	Daniel Dax
	Jarl Hemming
	Matti Häärä
	Victor Kisonen
	Ekaterina Korotkova
	Jens Krogell
	Ann-Sofie Leppänen
	Hanna Lindqvist
	Linda Nisula
	Sebastian von Schoultz
	Tao Song
	Anders Strand

Senior Technician	Markku Reunanen
Technician	Leif Österholm
Secretary	Agneta Hermansson

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

2.3 Combustion and Materials Chemistry

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

The tools have been tested in a number of measurement and sampling campaigns in full-scale combustion processes in many locations in Europe. These tools were used to assist the equipment manufacturing companies in their work to design novel combustion devices. In 2011 a major sampling campaign was made in two large power plants in the UK and Poland. These plants were using a high share of biomass in their pulverized coal fired boilers.

In the latest years we have also had an interest in gasification of low-grade biomasses or wastes. Laboratory tests and chemical modelling have been applied to better understand the fate of the fuel impurities under the strongly reducing conditions of gasifiers. In particular the interaction between chlorine, alkalis and the metals lead and zinc have been in the focus of the research in 2011.

Our new consortium project Future Fuels for Sustainable Energy Conversion, FUSEC, was started in the spring of 2011. This major project is coordinated by Top Analytica Ltd and it forms the basis of our more long-term research in fuel conversion for the next three years 2012-2014. We work together with Aalto University, Lappeenranta University of Technology, Tampere University of Technology and the VTT. The project is supported by Tekes and a consortium of the following international industrial companies: Andritz, Foster Wheeler Energia, Metso Power, UPM, Clyde Bergemann and International Paper.

The three-year European Collaboration in the area of biomass fuels continued its second year in 2011. We work in this ERA-NET project together with the Technical Universities in Lyngby (Denmark), Graz (Austria) and Trondheim (Norway). This project focuses on advanced fuel characterization and its application in furnace modelling.

We have continued to have the responsibility of the coordination of the national Graduate School in Chemical Engineering (GSCE). The GSCE consists of altogether 26 participating laboratories at four universities: Aalto University School of Chemical Technology and Lappeenranta University of Technology, the University of Oulu and Åbo Akademi University. The GSCE was granted a continuation for a new four-year period, 2012-2015.

Another part of our on-going activities dealt with high-temperature inorganic materials of interest to various applications. In 2011 we continued our studies on bioactive glasses with optimized properties. Our on-line measurement system to establish the dissolution chemistry of bioactive glasses produced the first data on the rate of dissolution of the various ions from the glasses in simulated body fluid solutions. We have several major projects on various aspects of the very topical problem of corrosion of steam tubes in boilers fired with biomass or waste derived fuels. We study corrosion mechanisms of various metal chlorides; we also study corrosion of alkali bromides and fluorides. In 2011 these studies were expanded to include high temperature corrosion of ceramic materials as well. For the ceramic materials also erosion has become a recent new topic of research.

In 2011 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 participated 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. Our long-term Tekes-funded activity PEPSECOND - Printed Enzymatic Power Supply with Embedded Capacitor on Next generation Devices was successfully finished and reported in spring 2012. This activity was a joint effort with Aalto University, VTT and Tampere University of Technology and supported by a group of companies.

Personnel

Professor	Mikko Hupa
Docents	Rainer Backman
	Edgardo Coda Zabetta
	Kaj Fröberg

	Leena Hupa
	Christian Mueller
	Bengt-Johan Skrifvars
	Heimo Ylänen
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	Susanne Fagerlund
	Stig-Göran Huldén
	Max Johansson
	Oskar Karlström
	Tooran Khazraie
	Tor Laurén
	Juho Lehmusto
	Bingzhi Li
	Na Li
	Johan Lindholm
	Patrycja Piotrowska
	Christoffer Sevonius
	Linus Silvander
	Berndt Södergård
	Emil Vainio
	Leena Varila
	Hao Wu
	Niklas Vähä-Savo
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	Peter Backman
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Economy secretary	Eva Harjunkoski
Secretary	Mia Mäkinen
Computer support	Peter Ekholm

Links:

http://www.abo.fi/institution/en/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
	Valerie Eta
	Nicola Gemo
	Henrik Grénman
	Jan Hájek
	Olatunde Jogunola
	Bright Kusema
	Sébastien Leveneur
	Mats Rönnholm
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	Alexey Kirilin
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	Toni Riittonen
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Technician	Elena Murzina
Secretary	Lotta Alho

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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	Ari Ivaska
	Kalle Levon (adjunct)
	Andrzej Lewenstam (part-time)
Docents	Johan Bobacka
	Leo Harju
	Carita Kvarnström
	Tom Lindfors
	Li Niu
	Tomasz Sokalski
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	Kim Granholm
	Zekra Mousavi
	Anna Österholm
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Doctoral students & researchers	Jesús Arroyo
	Marceline Neg Akieh
	Maija Blomquist
	Cristina Dumitriu
	Henrik Gustafsson
	Marcin Guzinski
	Tingting Han
	Jerzy Jasielec
	Justyna Kupis
	Grzegorz Lisak
	Peter Lingenfelter
	Ulriika Vanamo
	He Ning

	Pingping Su
	Michał Wagner
	Zhe Yang
	Kai Yu
	Qi Zhang
Secretary & coordinator	Lotta Österholm
Technicians	Sten Lindholm
	Lassi Väinölä

Links

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3. Research

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

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

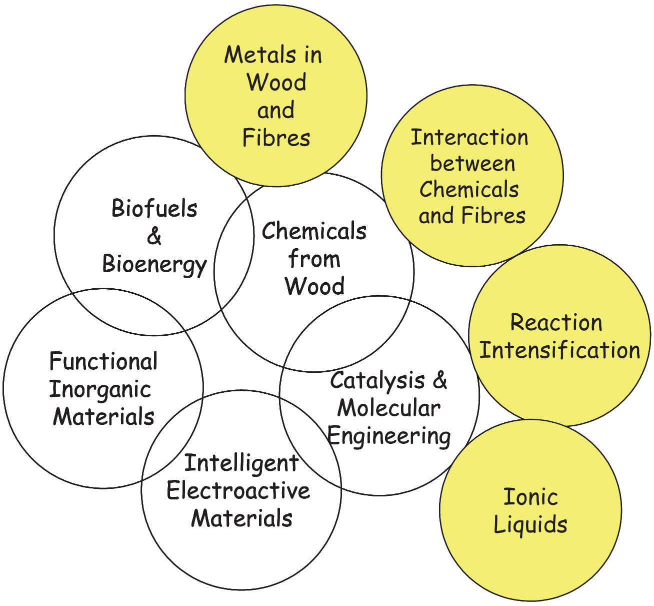
- using renewable raw materials instead of fossil resources (mainly oil)
- producing natural, biocompatible materials and chemicals, thus replacing synthetic, artificial ones
- understanding "nature's wisdom" in chemistry, thus recognizing and utilizing chemical solutions and mechanisms that have developed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

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

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

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

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



ÅA-PCC Research Areas 2006-2011

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

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

3.1 Ionic Liquids

Even though some ionic liquids were discovered in early 1900's, the area has made its real breakthrough in recent years, due to the discovery of room-temperature ionic liquids. Ionic liquids (ILs) have emerged as a novel class of materials and neoteric solvents that are applied in many fields such as solvents for electrochemistry and organic synthesis, as materials for recovery of metals from aqueous solution, synthesis of nano-structured materials and sequestration of carbon dioxide, to entrapment and activation of enzymatic and metal species for catalytic applications. The vast number of anticipated possibilities to form various ionic liquids, at least a million or even 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 frequently associated with very low vapour pressures and non-flammability and they have a large electrochemical potential window, although ILs can be designed to be distillable, explosive or combustible.

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

- Synthesis, development and characterization of novel, ionic liquids and their analogues
- Catalysis by supported ionic liquids (SILCA)
- Biorefining and fractionation of lignocellulose in ionic liquids
- CO_2 –capture, activation and utilization for chemicals and fuels in ILs
- Biogas purification with ILs
- Cascade catalysis in terms of combined enzymatic and metal catalysis supported in ionic liquids
- Bio-transformations in ionic liquids
- Electrochemical studies and applications of ionic liquids

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

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

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

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

For some time now, we have also been involved in the development of new technologies to replace classical alkanol-amine water solutions for CO_2 capture. Our focus in this area is two-fold: to develop techniques more suitable for small-scale installations (particularly biogas plants) by taking advantage of novel ionic liquid formulations.

Ionic Liquids as an 'Enabling' Media:

a) FUSILCA - Supported Ionic Liquid Catalyst used in the transformation of unsaturated aldehydes and synthesis of furanic fuels and chemicals;

b) OPTBIO, NoTre - Ionic liquid pre-treatment techniques for fermentable sugars; & Novel Treatment Processes of Lignocellulosics for Fermentable Building Blocks

c) BIOGASUP - Biogas cleaning for vehicle grade fuel

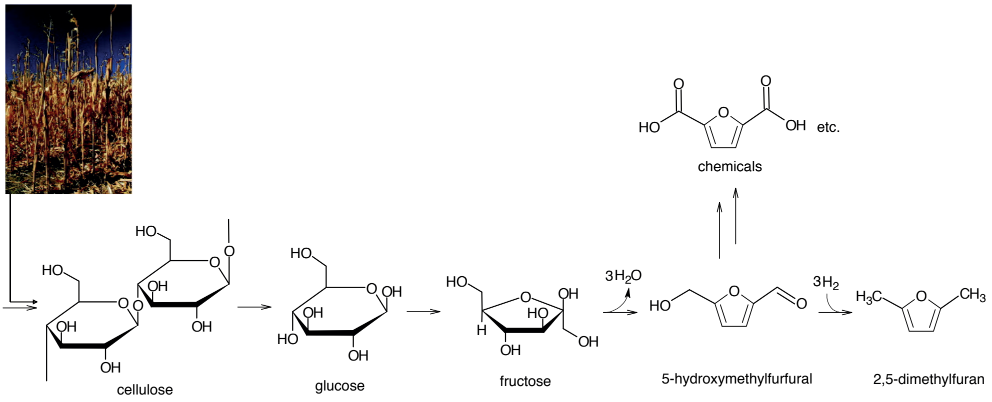
d) ILO – Metallien sähkökemiallinen pinnotus ja saostaminen ionisissa liuottimissa

Main funding: Academy of Finland, Tekes, Raisio Research Foundation

Jyri-Pekka Mikkola, Eero Salminen, Pasi Virtanen, 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 were 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.

Today, the focus of SILCA research is on developing new concepts for SILCA to be applied in the transformation of biomass to fuels and chemicals. In the FUSILCA project, under auspices of collaboration between Academy of Finland and DST India, the concept is applied to transform biomass to furanic fuels and chemicals.



A simplified reaction scheme for the synthesis of HMF and DMF from biomass

In yet another projects, OPTBIO and NoTre, the main goals are to obtain fermentable sugars and other compounds via lignocellulose pretreatments with selected ionic liquids. Thereafter, in combination with selected micro-organisms and enzymes suitable mother liquids for fermentation broths are obtained. The project deals both with Chilean and Nordic wood sources having different genotypes. The analysis is challenging since typical analytic columns do not tolerate high concentration of any salts (e.g. like ILs). Besides high precision liquid chromatography (HPLC), more unusual analysis techniques (such as capillary electrophoresis) are under development for analysing sugars retrieved from the lignocellulosic samples. The endeavour is to try different separation buffers and to work with different detectors to optimize the conditions for analysis of products obtained during the treatment procedure. In line with these efforts, collaboration was initiated with the Tallinn Technical University. Also, a long term goal is to develop a new type of detector in collaboration with the specialists in physics and optics from the Univ. of Eastern Finland that in future could be utilized in the routine analysis of molecules originated from the bio resources.

Biogas is one of the feasible, delocalized near-future solutions to the mobility needs of the society. Moreover, it does not contribute to the depletion of fossil fuel resources and is relatively easy to implement, both as production sites and to be used as a fuel in internal combustion engines. One of the biggest challenges has been the lack of economic and robust small-scale gas purification technologies needed to yield vehicle-grade fuel. Since biogas primarily consists of methane (just like natural gas), the established gas-cleaning technologies, based on aqueous alkanol amines, could in principle be used. However, the volatility and corrosivity of amines and the large unit size of the existing techniques, new solutions are needed. In BIOGASUP and ILO projects, various different ionic liquid -based strategies are being evaluated in CO_2 –capturing.

Cooperation:

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

Publications:

- Anugwom, I., Mäki-Arvela, P., Salmi, T., Mikkola, J-P., Ionic liquid assisted extraction of nitrogen and sulphur-containing air pollutants from model oil and regeneration of the spent ionic liquid, *Journal of Environmental Protection* 2 (2011) 6, 796-802 (Scientific Research Publishing, ISSN: 2152-2197)

- Hyvärinen, S., Damlin, P., Gräsvik, J., Murzin, D.Yu., Mikkola, J-P., Ionic liquid fractionation of woody biomass for fermentable monosaccharides, *Cellulose Chemistry and Technology* 45 (2011) 7-8 (Editura Academiei Romane, ISSN: 0576-9787)

- Hyvärinen, S., Leino, E., Eta, V., Privalova, E., Salminen E., Gräsvik, J., Virtanen, P., Mäki-Arvela, P., Mikkola, J-P., Ionic liquids as catalytic medium for biomass transformations, *Heterogeneous Catalysis in Biomass to Chemicals and Fuels* (eds. D. Kubička,, I. Kubičková), Research Signpost, Kerala, 2011, ISBN: 978-81-308-0462-0

Cellulose Derivatives in Ionic Liquids

Main funding: PCC, Åbo Akademi

Jyri-Pekka Mikkola, Olatunde Jogunola, Pia Damlin, Johan Wärnå, 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. A special attention was paid to the development of a detailed scheme for the substitution kinetics of cellulose. Detailed kinetic modelling based on probabilistic theories and rate retardation was carried out.

Publications:

- Salmi, T., Damlin, P., Mikkola, J-P., Kangas, M., A chemical engineering approach to cellulose substitution kinetics, *Chemical Engineering Transactions* 24 (2011), (AIDIC Servizi S.r.l., ISSN: 1974-9791, ISBN: 978-88-95608-15-0)
- Salmi, T., Damlin, P., Mikkola, J-P., Kangas, M., Modelling and experimental verification of cellulose substitution kinetics, *Chemical Engineering Science* 66 (2011) 2, 171-182 (Elsevier B.V., ISSN: 0009-2509)

3.2 Reaction Intensification

Reaction intensification implies new structures and methods, which lead to more efficient, energy saving and miniaturized processes. Monolith reactors, fibrous catalyst structures as well as ultrasonic and microwave technologies are investigated. PCC has unique experimental devices for in situ studies of reactions under the influence of ultrasound and microwaves. The chemical applications are several, such as esterification, catalytic oxidation as well as hydrogenation of aldehydes and ketones, leaching of minerals and hemicelluloses as well as delignification of wood. Ultrasound technology was used to enhance the rates of catalytic processes. A chemical method was developed to measure the exposed ultrasound effect in a precise way and a new device was constructed for carrying out in situ ultrasound experiments. Slurry reactors, fixed beds and structured reactors are exposed to ultrasound to reveal its effect on reaction rates.

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

Structured Reactors

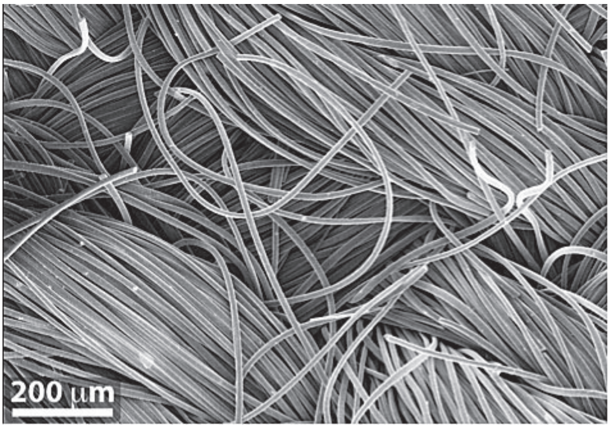
Main funding: Academy of Finland, EU

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

Fibres, solid foams and monoliths provide an attractive alternative for traditional catalyst technologies, since they combine the immobility of the catalyst to a short diffusion path, which guarantees a minimized mass transfer resistance. Fibre catalysts and monoliths enable a continuous operation for processes, which traditionally have been carried out batchwise, particularly synthesis of fine chemicals. Three kinds of fibre catalysts have been investigated: polymer-based fibres as well as silica and carbon fibres. The former ones have applications in esterification, etherification and aldolization reactions, while the latter ones are used after metal impregnation in oxidation and hydrogenation reactions. Hydrogenation of aldehydes and ketones has been used as model reactions. Compared to conventional catalysts, a clearly improved performance has been achieved, since the internal mass transfer limitation is suppressed. This was illustrated in the doctoral thesis of victor Sifontes (2012), where ruthenium-impregnated carbon cloths showed a high activity in the hydrogenation of various sugars, such as arabinose and galactose to corresponding sugar alcohols. Extensive mathematical modelling of structured reactors was continued.

Cooperation:
Università di Padova; TU Dresden, several EU partners

Carbon washcoated steel (CSS) support



SEM image of the active carbon cloth (ACC) support

Publications:

- Dalle Nogare, D., Salemi, S., Biasi, P., Canu, P., Taking advantage of hysteresis in methane partial oxidation over Pt on honeycomb monolith, *Chemical Engineering Science* 66 (2011) 24, 6341-6349 (Elsevier B.V., ISSN: 0009-2509)
- Sifontes Herrera, V.A., Oladele, O., Kordás, K., Eränen, K., Mikkola, J-P-. Murzin, D.Yu., Salmi, T., Sugar hydrogenation over a Ru/C catalyst, *Journal of Chemical Technology and Biotechnology* 86 (2011), 658-668 (Blackwell Publishing, ISSN: 0264-3413)

Micro- and Milliscale Reactor Technology

Main funding: PCC, Tekes, EU

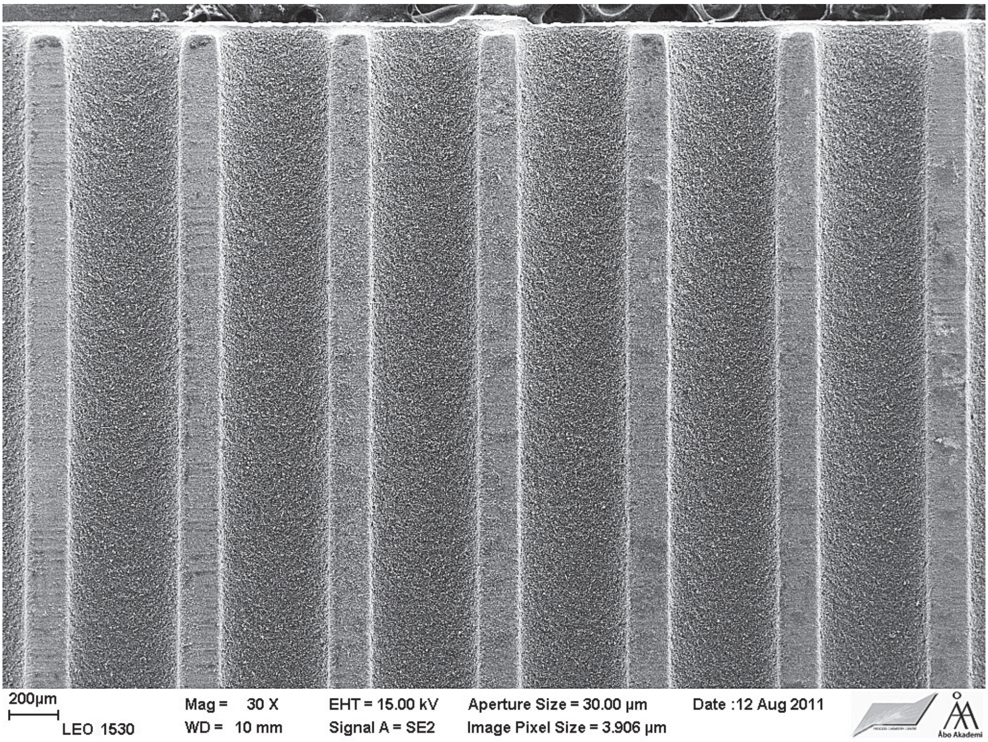
Kari Eränen, Mats Rönnholm, José Rafael Hernández Carucci, Sabrina Schmidt, Narendra Kumar, Kalle Arve, Johan Wärnå, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

Micro- and millireactors enable an efficient performing of chemical processes because of enhanced mass and heat transfer. We have introduced the concept of microreactors 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. Silver-based microreactor combined to micro-gas chromatography gave excellent results in the preparation ethylene oxide. The reaction kinetics of ethylene oxide formation was measured very precisely and a detailed mathematical model was developed for ethylene epoxidation. The research programme concerning the preparation of alkyl halogenides in gas-phase microreactors was continued. The microreactor coating technology by using aluminium oxide as well as micro- and mesoporous materials was successfully developed; we are able to prepare catalytically active and mechanically strong coatings. Micro and mesoporous material showed a high activity and selectivity in the halogenation process. Precise kinetic measurements of alkyl halogenide formation were carried out and modelled mathematically.

Cooperation:
Lappeenranta University of Technology; University of Oulu; Aalto University, PCAS Finland; Kemira, Università di Padova, several EU partners

Publications:

- Hernández Carucci, J.R., Arve, K., Bártová, Š., Eränen, K., Salmi, T., Murzin, D.Yu., Deposition of carbonaceous species over Ag(alumina catalysts for the HC-SCR of NO_x under lean conditions: a qualitative and quantitative study, *Catalysis Science & Technology* 1 (2011), 1456-1465 (RSC Publishing, ISSN: 2044-4753)
- Hernández Carucci, J.R., Eränen, K., Salmi, T., Murzin, D.Yu., Gas-phase microreactors as a powerful tool for kinetic investigations, *Rossijskij Khimicheskij Zhurnal* (Russian Chemical Journal) 55 (2011), 16-33 (Russian Chemical Society, ISSN: 0373-0247)



A SEM image of microreactor element

Multiphase Reactors

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

Johan Wärnå, Teuvo Kilpiö, Matias Kangas, Henrik Grénman, Victor Sifontes Herrera, Bright Kusema, Kalle Arve, Sébastien Leveneur, Pierdomenico Biasi, Nicola Gemo, Davide Durante, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

The project concerns advance modelling of multiphase reactors, involving various flow models in the bulk phases of the reactor as well as modelling of simultaneous reaction and diffusion in porous catalyst pellets: in process scale-up, the crucial step is the shift from small particles used in laboratory experiments to large particles characteristic for fixed bed reactors. The main applications are catalytic three-phase hydrogenation and oxidation, ring opening and reactions of solids with gases and liquids. The feasibility of hydrogen peroxide direct synthesis in a continuous fixed bed was successfully demonstrated and modelled mathematically. The work was combined to kinetic studies carried out in a tailored batch reactor for hydrogen peroxide synthesis. Production of percarboxylic acids over heterogeneous catalysts in a fixed bed reactor was carried out and a mathematical model was developed, which predicts the concentration profiles inside the reactor tube. Decarboxylation and sugar hydrogenation reactions which are of high importance for future biorefineries were modelled mathematically. The models include kinetics, catalyst deactivation, diffusion phenomena as well as residence time distributions.

Cooperation:

Università di Padova, Padova, Italy; INSA Rouen, France

Publications:

- Biasi, P., Canu, P., Pinna, F., Salmi, T., Hydrogen peroxide direct synthesis: from catalyst preparation to continuous reactors, *Chemical Engineering Transactions* 24 (2011), 49-54, (AIDIC Servizi S.r.l., ISSN: 1974-9791, ISBN: 978-88-95608-15-0)
- Biasi, P., Menegazzo, F., Pinna, F., Eränen, K., Salmi, T., Canu, P., Continuous H2O2 direct synthesis over Pd/Au catalysts, *Chemical Engineering Journal* 176-177 (2011), 172-177 (Elsevier B.V., ISSN: 1385-8947)
- Leveneur, S., Wärnå, J., Eränen, K., Salmi, T., Green process technology for peroxycarboxylic acids: Estimation of kinetic and dispersion parameters aided by RTD measurements: Green synthesis of peroxycarboxylic acids, *Chemical Engineering Science* 66 (2011) 6, 1038-1050 (Elsevier B.V., ISSN: 0009-2509)
- Salmi, T., Wärnå, J., Leveneur, S., Jogunola, O., Mikkola, J-P., Modelling of simultaneous reaction and diffusion in chemical reactors with particle size distributions: application of ion-exchange resins in heterogeneous catalysis, *Chemical Engineering Transactions* 24 (2011), (AIDIC Servizi S.r.l., ISSN: 1974-9791, ISBN: 978-88-95608-15-0)
- Leveneur, S., Wärnå, J., Salmi, T., Murzin, D., Catalytic synthesis and decomposition of peroxycarboxylic acids-Green catalytic synthesis of green compounds, *Trends in Chemical Engineering* 13 (2011), 17-52 (Research Trends, ISSN: 0972-4478)

Batch and Semibatch Reactors for Reactive Solids

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

Henrik Grénman, Pia Damlin, J-P. Mikkola, Matias Kangas, Steliana Aldea, Jussi Rissanen, Pasi Tolvanen, Päivi Mäki-Arvela, Johan Wärnå, Dmitry Murzin, Tapio Salmi

Kinetics and morphology of reactive solids is a fascinating area of chemical reaction engineering. In recent years, we have performed an extensive research programme concerning many liquid-solid reactions, from mineral leaching to selective extraction of hemicelluloses. Batch and semibatch reactors are frequently used in the production of fine and specialty chemicals through solid-liquid reactions. The aim of the project is to develop experimental equipment and procedures for obtaining very precise kinetic data and to carry out advanced modelling of chemical kinetics and mass transfer in (semi)batch reactors. Typical case studies are reactions of solid materials with organic compounds in liquid phase as well as decomposition of organic materials in liquid phase. A new theoretical approach was presented for cellulose substitution kinetics: the reactivity of cellulose declines as the substitution proceeds – we were the first in the world to describe this phenomenon mathematically. Solid particles change their morphology during the reaction; for instance, craters appear on the surface. Furthermore, the solid particle distribution changes as the reaction progresses. A new mathematical model was developed to describe these effects: morphology change, change of porous layer thickness change as well as change of the particle size distribution. The work was summarized in the doctoral thesis of Henrik

Grénman, who obtained the Elving Prize for best doctoral thesis at Åbo Akademi (2011).

Cooperation:

Raisio; Nordkalk; Outotec; INSA Rouen, France

Publications:

- Grénman, H., Eränen, K., Krogell, J., Willför, S., Salmi, T., Murzin, D.Yu., The kinetics of aqueous extraction of hemicelluloses from spruce in an intensified reactor system, *Industrial & Engineering Chemistry Research* 50 (2011) 7, 3818-3828 (ACS Publications, ISSN: 0888-5885)
- Grénman, H., Ingves, M., Wärnå, J., Corander, J., Murzin, D.Yu., Salmi, T., Common potholes in modeling solid-liquid reactions – methods for avoiding them, *Chemical Engineering Science* 66 (2011) 20, 4459-4467 (Elsevier B.V., ISSN: 0009-2509)
- Salmi, T., Damlin, P., Mikkola, J-P., Kangas, M., A chemical engineering approach to cellulose substitution kinetics, *Chemical Engineering Transactions* 24 (2011), (AIDIC Servizi S.r.l., ISSN: 1974-9791, ISBN: 978-88-95608-15-0)
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- Grénman, H., Salmi, T., Murzin, D.Yu., Solid-liquid reaction kinetics – Experimental aspects and model development, *Reviews in Chemical Engineering* 27 (2011) 1-2, 53-77 (Walter de Gruyter GmbH, ISSN: 0167-8299)

Complex Reaction Kinetics and Thermodynamics

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

Johan Wärnå, Jyri-Pekka Mikkola, Matias Kangas, Olatunde Jogunola, Valerie Eta, Ewelina Leino, Antonina Kupareva, Andreas Bernas, Serap Şahin, 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. New catalyst concepts and new kinetic models were used for the alkyl carbonate synthesis (CO_2 utilization). Detailed kinetic modelling was carried out for the industrial production process of formic acid.

Cooperation:

Perstorp; Raisio; Forchem; Kemira; Université de Bourgogne, France; University of Oulu; INSA Rouen, France

Publications:

- Eta, V., Mäki-Arvela, P., Salminen, E., Salmi, T., Murzin, D.Yu., Mikkola, J-P., High yield synthesis of dimethyl carbonate from CO_2 and methanol using alkoxide ionic liquids as additives, *Catalysis Letters* 141 (2011) 9, 1254-1261 (Springer, ISSN: 1011-372X)
- Eta, V., Mäki-Arvela, P., Wärnå, J., Salmi, T., Mikkola, J-P., Murzin, D.Yu., Kinetics of dimethyl carbonate synthesis from methanol and carbon dioxide over ZrO_2-MgO catalyst using butylene oxide as a chemical trap for water, *Applied Catalysis A: General* 404 (2011) 1-2, 39-45 (Elsevier B.V., ISSN: 0926-860X)
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- Leveneur, S., Wärnå, J., Eränen, K., Salmi, T., Green process technology for peroxycarboxylic acids: Estimation of kinetic and dispersion parameters aided by RTD measurements: Green synthesis of peroxycarboxylic acids, *Chemical Engineering Science* 66 (2011) 6, 1038-1050 (Elsevier B.V., ISSN: 0009-2509)
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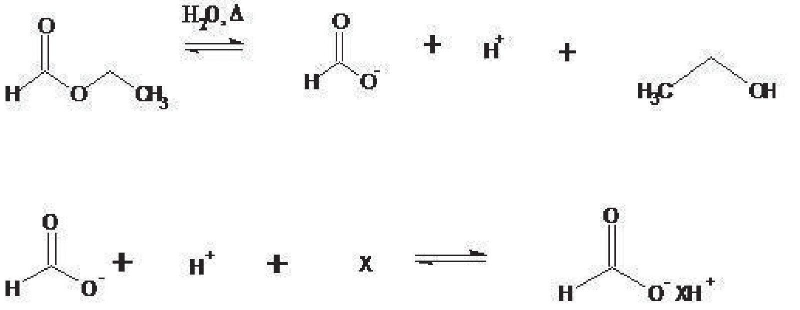
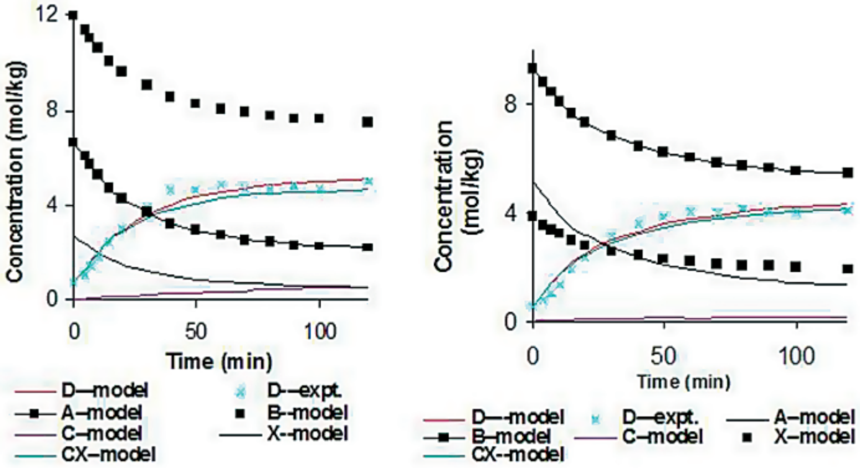
- Tolvanen, P., Sorokin, A., Mäki-Arvela, P., Leveneur, S., Murzin, D.Yu., Salmi, T., Batch and semi-batch partial oxidation of starch by hydrogen peroxide in the presence of iron tetrasulfophthalocyanine catalyst: The effect of ultrasound and catalyst addition policy, *Industrial & Engineering Chemistry Research* 50 (2011) 2, 749-757 (ACS Publications, ISSN: 0888-5885)
- Murzin, D.Yu., Parmon, V.N., Quantification of cluster size effect (structure sensitivity) in heterogeneous catalysis, *Catalysis - Special Periodical Reports* (eds. J.J. Spivey, K.M. Dooley), Royal Society of Chemistry, Cambridge, 2011, ISBN: 978-1-84973-142-3



Hydrolysis of ethyl formate followed by complexing

Concentration of components (mol/kg)	Rate equation (kg min/mol)
C_A	$\frac{dC_A}{dt} = -r_1$
$C_B = C_A - C_{OA} + C_{OB}$	$\frac{dC_B}{dt} = -r_1$
$C_C = \frac{\beta - C_A}{1+K_2 C_X^{\alpha}}$ where $\beta = C_{OA} + C_{OC} + C_{OCX}$	$\frac{dC_C}{dt} = \left(1 - \left[1 + \frac{\alpha^2 K_2(\beta - C_A)C_X^{\alpha-1}}{(1+K_2 C_X^{\alpha})^2}\right]^{-1}\left(\frac{K_2 C_X^{\alpha}}{1+K_2 C_X^{\alpha}}\right)\right) r_1$
$C_D = C_{OA} - C_A + C_{OD}$	$\frac{dC_D}{dt} = r_1$
C_X	$\frac{dC_X}{dt} = -\left[1 + \frac{\alpha^2 K_2(\beta - C_A)C_X^{\alpha-1}}{(1+K_2 C_X^{\alpha})^2}\right]^{-1}\left(\frac{\alpha K_2 C_X^{\alpha}}{1+K_2 C_X^{\alpha}}\right) r_1$
$C_{CX} = \frac{(\beta - C_A)K_2 C_X^{\alpha}}{1+K_2 C_X^{\alpha}}$	$\frac{dC_{CX}}{dt} = \left[1 + \frac{\alpha^2 K_2(\beta - C_A)C_X^{\alpha-1}}{(1+K_2 C_X^{\alpha})^2}\right]^{-1}\left(\frac{K_2 C_X^{\alpha}}{1+K_2 C_X^{\alpha}}\right) r_1$
Reaction rate	$r_1 = f\left(C_A C_B - \frac{1}{K_1} C_C C_D\right)$
	where $f = k_0 e^{\frac{-E_a z}{R}}\left[1 + \frac{k_0''}{k_0} e^{\frac{-E_a(\frac{E_a''}{E_a}-1)z}{R}} C_X\right]$

Summary of the mathematical modelling of ethyl formate hydrolysis



Comparison of simulated and experimental values in the hydrolysis of ethylformate

3.3 Metals in Wood and Fibres

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

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

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

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

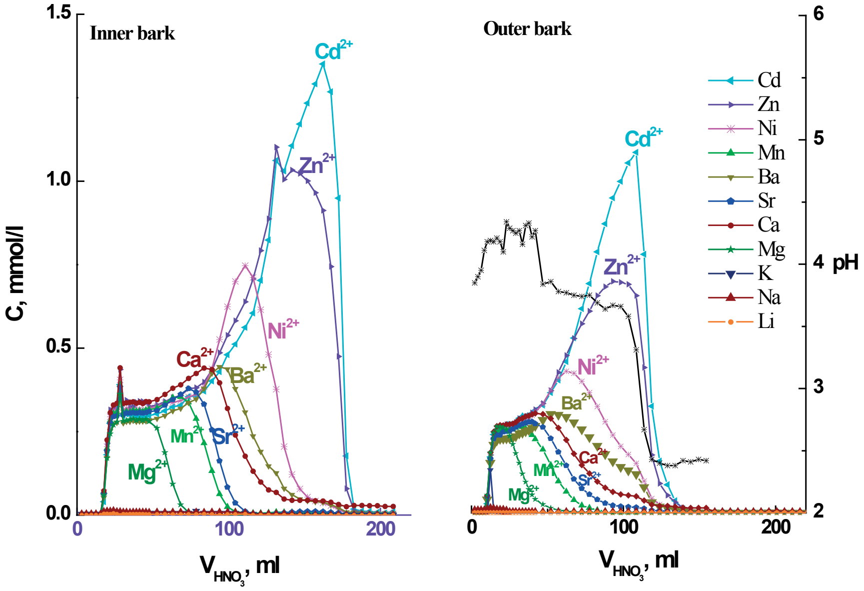
Main funding: Tekes (Bioraff), Research Institute of Åbo Akademi University Foundation

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

Affinity of metal ions to wood materials
The main objective of the study has been to study reactions of metal ions with functional groups in various wood based materials. A column-chromatographic method has been used for the study of metal ion affinities of different types of pulp, wood and bark materials. The mechanism of this method is mainly ion exchange by complexation of metal ions to the functional groups, e.g. carboxyl groups and phenolic hydroxyl groups, in the materials. Different metal ions exhibited different sorption ability to wood particles and bark. By combination of the sorption experiments with several different metal ion mixtures, the following affinity order was established, e.g. for spruce sapwood particles:

$Fe^{3+} >> Pb^{2+} >> Cu^{2+} >> Fe^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+} \geq Ca^{2+} \geq Sr^{2+} \geq Ba^{2+} >> Mg^{2+} >> K^{+} > Na^{+} \approx Li^{+}$

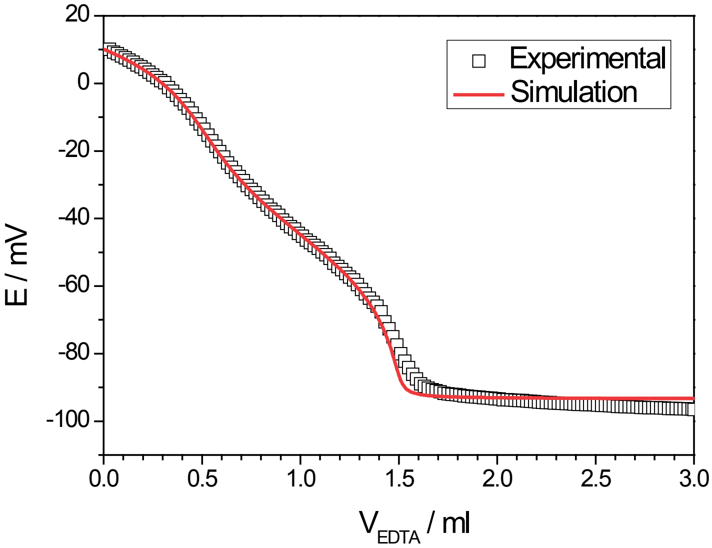
For the bark (spruce inner bark and outer bark) and the wood particles from birch, spruce sapwood and spruce heartwood, the affinity orders were almost the same.



Concentrations of metal ions and pH in collected fractions as function of the elution volume

Determination of Ca in black liquor

A solid-contact Ca^{2+}-selective electrode was used for speciation of calcium in black liquor. A new method for calculating the concentrations or activities from the titration curves was proposed. The advantage of this method is that the electrode standard potential and the slope of the calibration curve do not have to be known. This is beneficial when the analyte has a complexed matrix or is a harsh environment which affects the properties of the electrode. The new method was implemented both in a method for linearization based on the Grans´s plot and in determination of the stability constant of a complex and the concentration of the complexing ligand in the sample. The new method gave accurate results when using titrations data from experiments with samples of known composition. A complexometric titration model was also developed and used in titration simulations.



Experimental and simulated complexometric titration of calcium (3.0·10^{-5} M) with EDTA in presence of NTA (2.0·10^{-5} M). The following parameters were used: C_{Na} *= 0.027 M,* C_{EDTA}*=0.002 M,* $K_{CaNTA}^{Ca,\,NTA}=10^{6.9}$ *(at* μ*=0.027)*

Linearization of the complexometric titration curves were used to determine the concentrations of free, bound and total calcium in black liquor. With inductively coupled plasma optical emission spectrometry (ICP-OES), similar total calcium concentrations were obtained as by the EDTA titration. By using a computer program (FITEQL), the stability constants and the concentrations of the calcium binding ligand in the black liquor, was obtained.

Publications:

- Granholm, Kim, Sorption/desorption reactions of metal ions with pulp (doctoral thesis)
- Ovadova-Nejezchlebova, H., Vaculovic, T., Ek, P., Havlis, J., Kanicky, V., Cryogenic postseparation treatment of acrylamide gels for metaloproteomic analyses by combination of gel electrophoresis, laser ablation and inductively coupled plasma mass spectrometry, *Chemicke Listy* 105 (2011) 11, 896-902 (Association of Czech Chemical Societies, ISSN: 0009-2770)

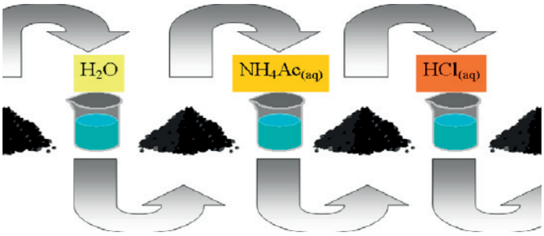
- Su, P., Granholm, K., Harju, L., Ivaska, A., Binding affinities of different metal ions to unbleached hardwood kraft pulp, *Holzforschung* 65 (2011) 4, 619-622 (Walter de Gruyter, ISSN: 0018-3830)

Dynamic Leaching of Biofuels for Determination of Ash-forming Matter

Main funding: Åbo Akademi University, PCC

Warunya Boonjob, Manuel Miró, Maria Zevenhoven, Paul Ek, Mikko Hupa, Ari Ivaska

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



Standard procedure for determination of leachable substances from solid material: extraction with water, ammonium acetate and hydrochloric acid

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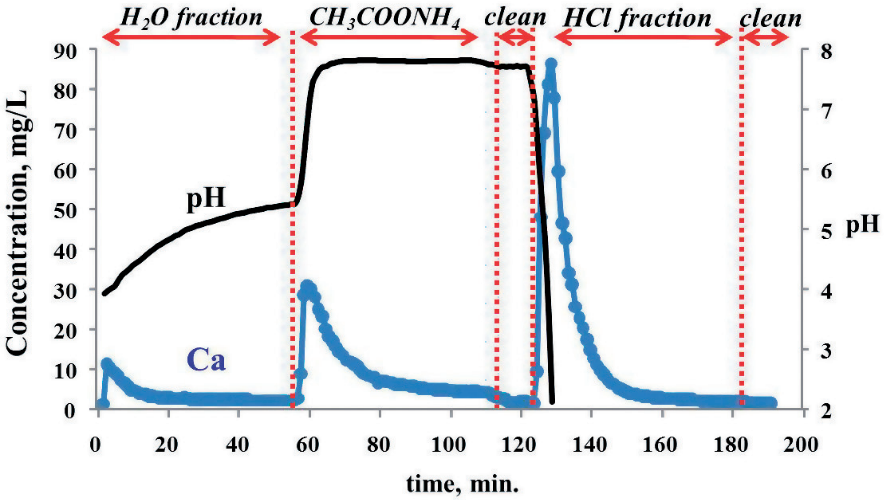
A dynamic extraction method based on sequential injection method by using the Lab-on-Valve concept was developed. The studied sample is placed in a flow-through extraction chamber. The extraction medium is automatically changed and the concentration of the elements under study is monitored on-line by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



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

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

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

3.4 Interaction between Chemicals and Fibres

Even in today's world of smart phones and tablets, Facebook and e-books, and the ever increasing amount of e-mails, paper is an inevitable part of our daily life. Important types of paper products are, for example, toilet paper, paper for our printers, liquid packages for milk and juice, cardboard boxes for things we buy through internet, and for some of us a real newspaper at the breakfast table. Paper is furthermore environmentally friendly; it is made from renewable resources and can easily be recycled, burned or composted.

A modern paper machine is about 10 m wide and can run up to 2000 m/min. The dewatering of the furnish should be fast and the wet web should have sufficient strength in order to maintain good runnability and to avoid web breaks. Substances are released from the fibres to the process water and chemicals are added to improve the process and the quality of the product. It is essential to understand how these interact with each other and with the fibres to ensure a smooth production and a high-quality product. For this we need reliable and fast analytical methods and to be able to reveal mechanisms by the use of model components. By using tailor-made additives, preferably made from natural polymers such as hemicelluloses, the wet end chemistry can be controlled.

Development of analytical techniques that can predict and give early warnings of problems is a key factor. Flow cytometry can detect and analyse agglomeration in process waters and it is furthermore a very rapid method. Flow cytometry can, for example, be used to detect formation of calcium oxalate precipitates, one of the most problematic scale salts in papermaking. These precipitates may form deposits later in the process that in turn will cause problems with runnability and also with the quality of the paper. The formation of calcium oxalate precipitates was found to be very dependent on the presence of certain components and on the process conditions, especially pH.

Adjusting the pH is also essential for the removal of wood pitch from process waters by froth flotation. More wood pitch can be removed at low pH than at neutral pH. This is due to the phase distribution of resin and fatty acids between the colloids and the water phase; more resin and fatty acids was associated with the colloids at low pH. However, the risk of overdosing the cationic foaming agent is much higher at low pH. The post-flotation water could be reintroduced to the papermaking process after removal of the detrimental wood pitch, thereby closing the water systems further.

The wood pitch that is retained in the paper will affect the surface and printing properties. It was shown that the wood pitch components will undergo changes during storage, especially in the presence of heat and oxygen. If the papers are stored in closed vials, preserving some of the humidity and limiting the availability of oxygen, significantly fewer changes occurred. This is important to know, not only for the printing industry, but to be able to correctly determine the content of extractives in pulp and paper.

Mechanisms during the Formation of the Fibre Network – Effect of Fibre Treatments and Tailor-made Additives

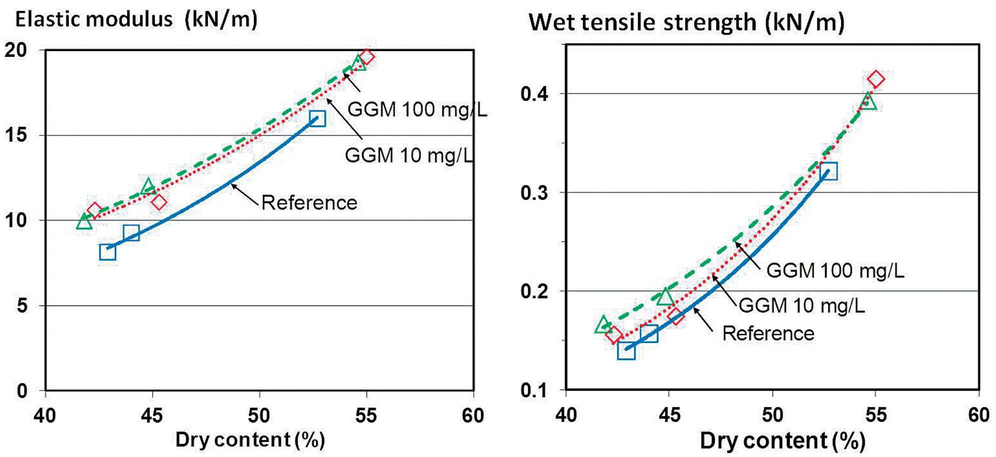
Main funding: Åbo Akademi

Hanna Lindqvist, Sylwia Bialczak, Bjarne Holmbom, Lari Vähäsalo, Pedro Fardim, Anna Sundberg

The runnability of the paper machine should be without disturbances such as web breaks and deposits to ensure an efficient production and a good quality product. The aim is to identify and develop new ideas and concepts for more efficient chemistry in papermaking, emphasizing the wet-end chemistry. The dewatering, retention, formation, flocculation as well as the pitch problems can be influenced and managed with appropriate chemistry in the wet-end. The long term goal is therefore to manage paper machine runnability and paper quality, through which the overall economy of paper production is improved

The tension and relaxation properties of the wet web are critical for the runnability in the beginning of the dryer section of paper machines. Poor strength and relaxation of the wet paper cause web breaks and can also impair the quality of the dry paper. Galacto-glucomannans (GGMs) have a strong affinity to fibers and are able to sterically stabilize colloidal wood pitch droplets and decrease the detrimental effects of wood resin on paper strength properties.

The wet web properties were measured on handsheets prepared from bleached kraft pulp. Addition of GGM increased the wet tensile strength at constant dry content (Figure). Recent research looking at the molecular and fibrillar level phenomena, suggest that the wet fibre surface could be considered as a gel-like layer consisting of cellulose and hemicelluloses. When polymeric additives are adsorbed onto the fibres, they are mixed with the fibrillar gel-like layer and will change the properties of this layer depending on the interactions between the fibrils and the polymers. Therefore, different polymers can have very different effects on the initial wet web strength. The effects depend mostly on the polymer and its ability to disperse fibrils on the fibre surface and/or to increase the hydration of the fibre surfaces. GGM is known to absorb onto wood fibres, and an increase in wet tensile strength properties can be expected. Addition of GGM also increased the elastic modulus of the wet web (Figure). The difference between the two addition levels was small. The increase was higher at lower dry contents. GGM could be used to increase wet web mechanical properties, since the tension of a running web in practise is controlled by the elastic modulus of the fibre network. The elastic modulus also controls the performance of the end-product through the tensile stiffness.



Wet web tensile strength (right) and elastic modulus of wet handsheets prepared from bleached kraft pulp after addition of GGMs. The sheets were pressed to three different dry contents (using 20, 50 and 350 kPa) and measured with the IMPACT test rig

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Cooperation:
VTT; Åbo Akademi University, Laboratory of Fibre and Cellulose Technology

Intelligent Remote Diagnostics (iReDi)

Main funding: Kemira

Lari Vähäsalo

The aim of the project is to develop new process analysis instrumentation which can be used on-line. For the past decade we used and developed flow cytometry (FCM) methods for the analysis of pulp and paper mill samples. The capability of FCM to detect and analyse agglomeration has turned out to have a great advantage compared to more traditional analytical techniques. In this project, we will develop and build a system that will produce the same type of valuable information as the FCM technique. The system will be installed on-line in order to get real time information of a paper process. The aim is also to develop a completely new analytical methods that will produce additional chemical information about the samples, traditionally only available after laboratory analysis. The project will also use the on-line DepoSense technique in order to receive real time information of the amount of deposits and scale in a paper machine.

Cooperation:
Kemira

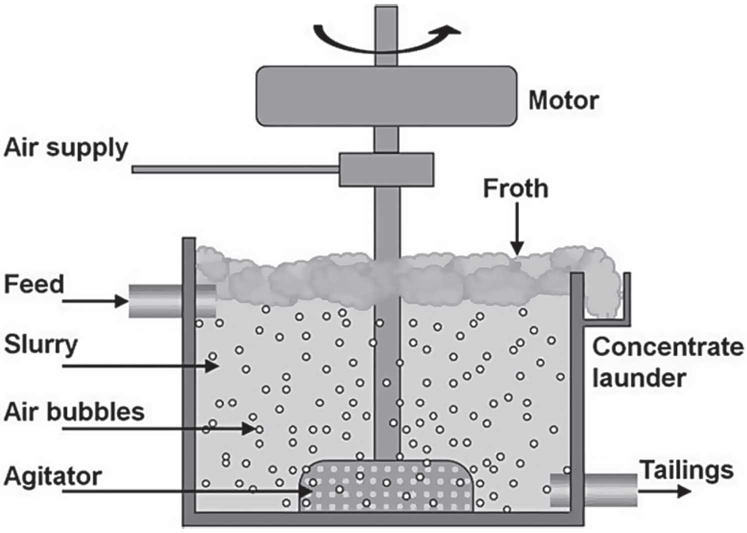
Influence of Pitch Composition and Wood Substances on the Phase Distribution of Resin and Fatty Acids at Different pH-Levels

Main funding: Åbo Akademi Process Chemistry Centre

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

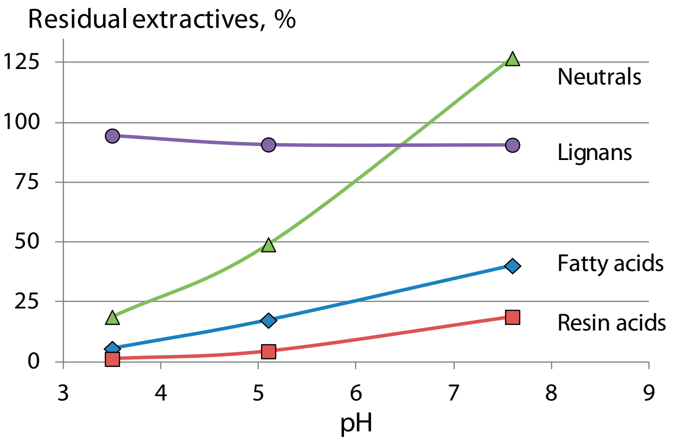
Wood pitch, or lipophilic extractives, is released into the process water during the production of mechanical pulps. A large fraction of the pitch is dispersed as an oil-in-water emulsion in the process water, forming colloidal droplets with a two-layered structure. The core of these droplets consists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

Selective removal of dissolved and colloidal pitch components from an unbleached thermomechanical pulp (TMP) pressate water by addition of a cationic foaming agent, dodecyltrimethylammonium chloride (DoTAC), and subsequent froth flotation was assessed (Figure). The experiments were conducted with varying pH, temperature, and concentrations of DoTAC and calcium. The concentrations of pitch components, lignans, and dissolved polysaccharides were determined before and after flotation.



Schematic illustration of the laboratory froth flotation cell

All pitch components were removed more efficiently by the flotation at pH 3.5 and 5 than by flotation at pH 7.6 (Figure). Resin and fatty acids were removed to a higher degree than neutral pitch substances at all the tested pH levels. Most of the water-soluble uronic acids and galactoglucomannans stayed in the TMP water after flotation. Froth flotation with DoTAC was an effective way of selectively removing colloidal pitch. Removal of pitch, especially of resin acids, at an early stage should be beneficial to the overall papermaking process.



Residual extractives after flotation of TMP water, with 80 ppm DoTAC at 20°C

Cooperation:
Åbo Akademi University PCC

Publications:

- MacNeil, D., Sundberg, A., Vähäsalo, L., Holmbom, B., Effect of calcium on the phase distribution of resin and fatty acids in pitch emulsions, *Journal of Dispersion Science and Technology* 32 (2011) 2, 269-276 (Taylor & Francis Inc., ISSN: 0193-2691)
- Strand, A., Sundberg, A., Vähäsalo, L., Holmbom, B., Influence of pitch composition and wood substances on the phase distribution of resin and fatty acids at different pH levels, *Journal of Dispersion Science and Technology* 32 (2011) 5, 702-709 (Taylor & Francis Inc., ISSN: 0193-2691)
- Strand, A., Sundberg, A., Vähäsalo, L., Holmbom, B., Aggregation and destabilisation of colloidal wood pitch by calcium ions in TMP suspensions, *Nordic Pulp & Paper Research Journal* 26 (2011) 4, 429-437 (SPCI, Swedish Association of Pulp and Paper Engineers, ISSN: 0283-2631)

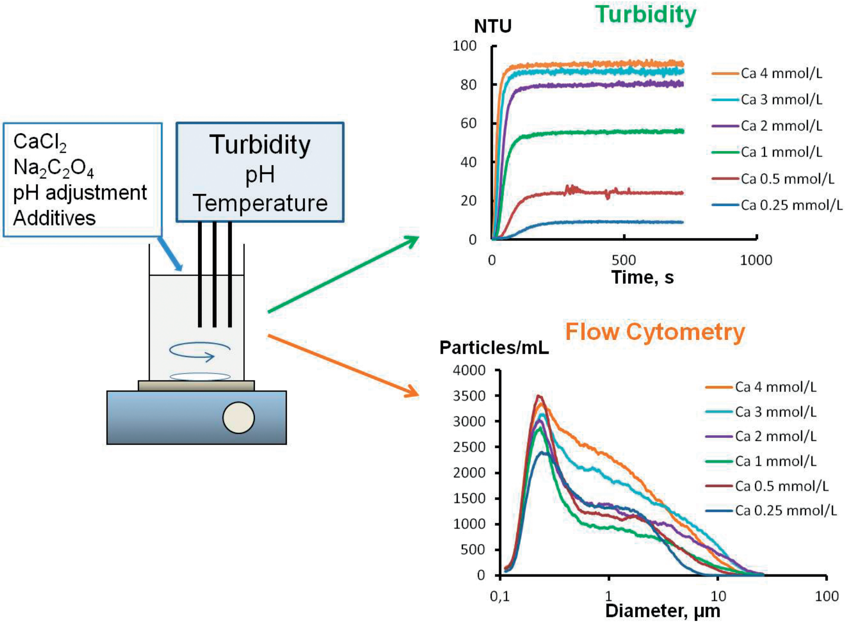
Calcium Oxalate – from Hickey Problem to Sustainable Raw Material

Main funding: Industry

Matti Häärä, Lari Vähäsalo, Wenwen Fang, Anna Sundberg, Stefan Willför

Calcium oxalate is one of the most problematic scale salts in the pulping and papermaking industry. The formed scale deposits often cause severe problems both in production and with paper quality. The aim of this research project has been to gain deeper understanding of the formation of oxalic acid and precipitation of calcium oxalate in mechanical pulp bleaching and papermaking processes. Calcium oxalate has a very low solubility in water, but in pulping process conditions the ions are often supersaturated above the solubility product without precipitation. This is because of the formation of other more soluble oxalate species, but also due to the inhibiting action of some organic acids present.

Previously within this project, we have looked at the parameters in alkaline peroxide bleaching that can affect the oxalic acid formation, as oxidative bleaching stages are major sources for oxalate ions in pulping processes. In order to study the precipitation of calcium oxalate, an experimental setup described in the figure below was used. Calcium and oxalate ions were mixed in different molar ratios under different conditions and in presence of different substances. Turbidity of the solution monitored and the formed precipitates were measured with flow cytometry (FCM), x-ray diffraction and scanning electron microscopy (SEM).



Experimental setup of the calcium oxalate precipitation studies. The precipitates were also collected and analysed by XRD and SEM for crystal structures

The combinations of analytical tools used were well suited for the precipitation studies. The results showed that by a careful process control, especially of pH, the calcium oxalate scaling can be decreased. It was also concluded that dissolved and colloidal substances in pulping and papermaking have an important role in the precipitation and crystallization of calcium oxalate.

Cooperation:

Sappi Fine Paper Europe, Kemira

Publications:

- Häärä, M., Sundberg, A., Willför, S., Calcium oxalate - A source of "hickey" problems – A literature review on oxalate formation, analysis and scale control, *Nordic Pulp & Paper Research Journal* 26 (2011) 3, 263-282 (SPCI, Swedish Association of Pulp and Paper Engineers, ISSN: 0283-2631)

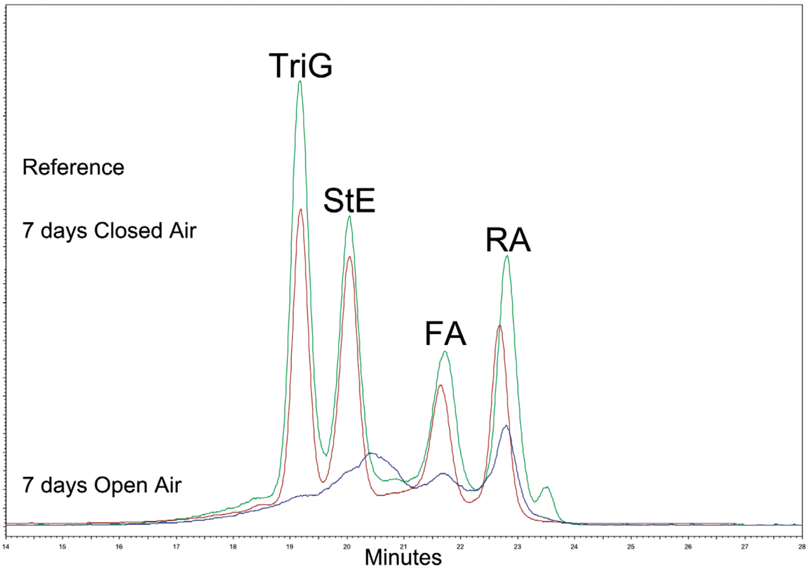
Towards Chemical Understanding of Paper Properties - Role of Different Fibre Constituents on Sorption and Optical Properties

Main funding: PaPSaT Graduate School

Sylwia Bialczak, Jouko Peltonen, Bjarne Holmbom, Anna Sundberg

Paper produced from mechanical pulp, so-called wood-containing paper, contains almost all of the original wood components. Lipophilic extractives, also called wood resin or wood pitch, are causing many problems in papermaking. During production of mechanical pulp, part of the extractives is retained in the paper. The lipophilic extractives can influence the sorption of water and other solvents and consequently, affect the printability of the paper. The extractives can be oxidized, migrate to the paper surface or be polymerized during storage of the paper. This will affect the results when determining the content of lipophilic extractives or when removing the extractives before surface analyses. The aim of the study was to analyse the changes occurring in extractives in TMP paper during ageing at different storing conditions.

The extract of fresh TMP paper analysed by HPLC-SEC shows four distinct peaks, mainly consisting of triglycerides, steryl esters, fatty acids, and resin acids (Reference in figure). After ageing for 7 days at 60°C in open air, the extract exhibited a very different profile (7 days Open Air). The triglycerides and steryl esters had disappeared, probably due to oxidation and further degradation, or polymerization (cross-linking) so they no longer could be extracted. The fatty acids did also decrease significantly. These changes did also occur at lower temperatures in open air. But if the papers were stored in closed vials in the oven at 60°C, only slight changes occur (7 days Closed Air). We suggest that not only the temperature but also the availability of oxygen and probably also water or humidity will affect the changes occurring in the extractives. To manage and control the surface and printing properties of paper, appropriate attention should be paid to the amount and composition of extractives and to the storage conditions, especially for paper made from mechanical pulps.



HPLC-SEC chromatograms of extract from fresh TMP paper (Reference), paper submitted to accelerated ageing at 60°C for 7 days in open air (7 days Open Air) and paper stored in closed vials at 60°C for 7 days (7 days Closed Air). TriG: triglycerides, StE: steryl esters, FA: fatty acids, RA: resin acids

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Cooperation:

Åbo Akademi University, Laboratory of Paper Coating and Converting; Laboratory of Fibre and Cellulose Technology

Publications:

- Bialczak, S., Sundberg, A., Holmbom, B., Changes in extractives and wetting properties of TMP paper during ageing, *Nordic Pulp & Paper Research Journal* 26 (2011) 4, 438-444, (SPCI, Swedish Association of Pulp and Paper Engineers, ISSN: 0283-2631)

Polymerized Extractives in Birch Kraft Pulp

Main funding: Industry

Sylwia Bialczak, Stefan Willför, Anna Sundberg

Not all extractives can be removed from the pulp during pulping and bleaching of especially birch pulp. Instead, some extractives probably polymerizes and some are even bound to the fibre surface. These polymerized extractives will strongly affect the properties of the pulp and decrease the quality of the pulp but are very difficult to analyse with conventional analytical methods. In this pre-investigation, the analytical procedures will be evaluated in order to find the right solvents and pretreatments needed to quantify the extractives in the pulp. These results will hopefully be used in a subsequent project to clarify which unit operations (such as individual bleaching steps) are the most critical for the polymerization process. The final aim, for the subsequent research project, is to understand the mechanisms behind the formation of polymeric extractives in kraft pulping and bleaching.

Cooperation:
Metsä Fibre; UPM; Kemira

3.5 Chemicals from Wood

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

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

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

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

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

Aiming at a molecular understanding of new biochemicals, biomaterials, and novel biorefinery processes producing these offers a huge challenge for developing novel, reliable analytical methods, which have either an academic or an industrial relevance. This is continuously done in most projects and a special example of tremendous international cooperation is the COST Action FP0901, "Analytical Methods for Biorefineries", where experts can exchange ideas, methods, and experiences.

Chemistry in Forest Biorefineries II (Bioraff II)

Main funding: Tekes, Industry, Åbo Akademi University

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

"Replacing petroleum-based synthetic materials and energy with wood-derived materials"

The biorefinery concept may be compared to an oil refinery and petrochemical plant, where fuels and numerous intermediates are produced for further processing into high-value and speciality materials. In biorefineries, the raw material is bio-based materials instead of mineral oil. Biorefinery development at the US and European level mostly covers the use of annual crops and other bio-based materials. In this project the focus was on non-food materials primarily in industrial pulp and paper processes, and this project is limited to forest-based biorefineries. The aim of the project was also to preserve the molecular structures created by nature as much as possible, to explore new separation and purification methods and look at new applications in areas such as: functional food, nutritional additives, functional additives in paper making, antioxidants, new bio-based materials and bio-based energy. Results obtained were related to chemical composition of wood, separation techniques, optimization of catalysts, purification and modification of products for different applications. Also various process parameters were studied for production of liquid fuels by pyrolysis or through synthesis gas route.

Research work was focused on following areas: bio-based materials, bioactive compounds from tree biomass, metals in trees, fibres and fuels and bio-based chemicals and fuels as well as on energy production options in biorefinery.

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

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

WP 1: Bio-based materials – R&I

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

WP 2: Bioactive compounds from tree biomass – R&I

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

WP 3: Metals in trees, fibres and fuels – R

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

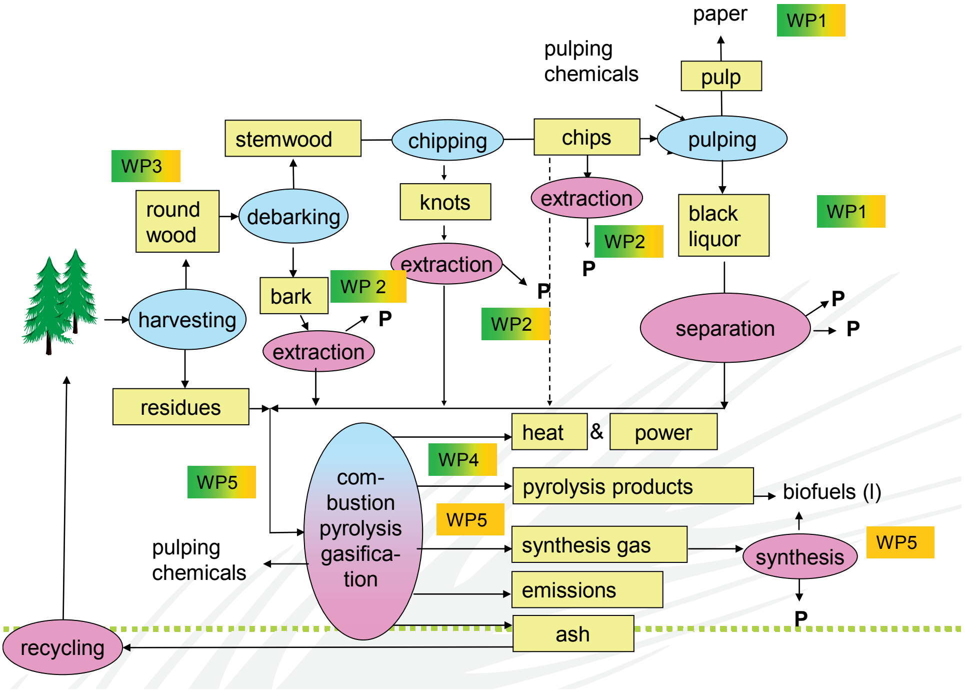
WP 4: Bio-based chemicals and fuels – R&I

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

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

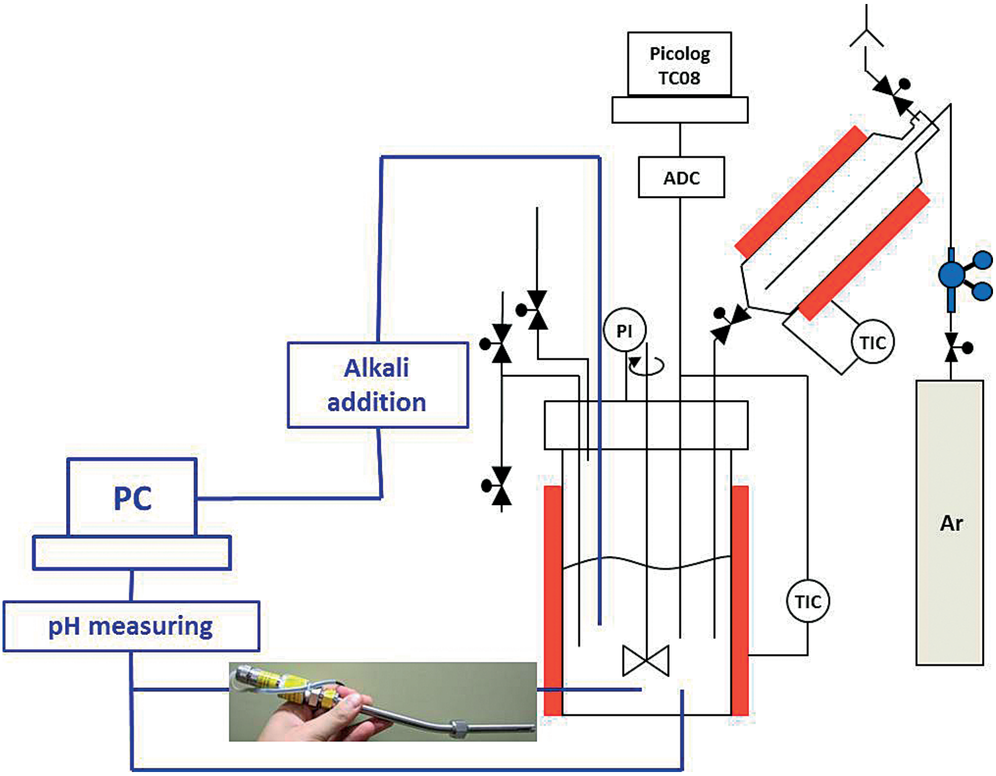
- Gasification based concepts to bark and forest residues and black liquor
- Advanced combustion and gasification characterization of various biomass fractions in a forest biorefinery

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



Project work packages around Kraft pulping process

Extraction experiments of GGM from spruce wood continued. GGM can be extracted in high yields and deacetylation and hydrolytic cleavage can be partly avoided. Our aim has been to obtain fundamental understanding of the hot water extraction process of wood hemicelluloses and furthermore to develop extraction parameters and reactor set-ups for intensified and controlled extraction of water-soluble and polymeric GGM. Here the control of pH plays important role. We have thus constructed a first reactor set-up with a unique possibility for inline pH measurement and later also the possibility for inline pH control. We have also designed new equipment for the extraction, based on cascade reactors, from which both liquid and solid samples can be taken. The new equipment will be a strong tool in further research of the extraction and leaching processes of wood and other solid materials.



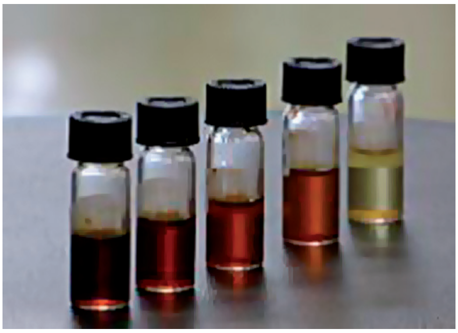
Setup for automated inline pH measurement and control

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, oxidation) was done to obtain novel functionalities and properties that could be used also in specialty paper grades. Hemicelluloses in many applications would benefit from the modification of the structure, especially to improve compatibility and solubility challenges in some applications.

Research in sugar derivatives was targeted to find means of producing high-value sugar-based fine chemicals. For hydrolysis of hemicelluloses the influence of different parameters was investigated, and reaction conditions and catalysts were suggested. The hydrolysis kinetics was described successfully with mathematical models. Parameters for continuous hydrogenation of different sugars such as L-arabinose and D-galactose mixtures over heterogeneous ruthenium catalyst were also studied. The hydrogenation kinetics was determined quantitatively and modelled mathematically. The effect of diffusion on the hydrogenation process was determined and continuous reactor technology based on structured catalysts was suggested. Very active and selective gold catalyst was developed for the oxidation of arabinose and galactose. The new catalyst is clearly better than the conventional palladium catalysts for this purpose. An advanced kinetic model was also proposed for sugar oxidation.

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

We found that liquid, solid and gaseous fuels or fuel precursors can be produced through pyrolysis, which is the thermal degradation of an organic material. The quality of the highly oxygenated bio-oil can be improved by deoxygenation over different catalysts. Pine wood as well as cellulose and lignin have been studied in the pyrolysis. The catalysts used in the upgrading of the pyrolysis vapours include mesoporous MCM-41 and proton form and iron modified ferrierite, beta and Y zeolites. The oxygen content in the bio-oil produced from cellulose could be decreased over different MCM-41-type materials. Deoxygenation of pine wood pyrolysis vapours was also achieved with both the proton and iron modified zeolites. However, ferrierite was quite inactive due to the smaller pore size. Bio-oil was also produced from lignin, with the major product being the solid residue, i.e. char.



Bio-oils from pyrolysis research

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

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

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

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

Cooperation

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

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Future Biorefinery I and II (FuBio)

Main funding: Tekes, Forestcluster Ltd

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

The FuBio project is a five-year top-down planned research program that will lay the foundation for a new knowledge-based forest biorefinery platform in Finland. The core of the program is to study and develop 1) new ways to fractionate wood into different material streams and 2) processing of these streams to generate material solutions for existing and new value chains. The first part of the project (FuBio Joint Research 1, 2009-2011) consisted of five research themes:

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

A sixth theme covered day-to-day management of the program and generated reports on specific topics. A literature review of both pyrolysis and gasification for black liquor and lignin was completed in the first year of this project. Both technologies were considered as possible means of upgrading these biomass streams to fuels and chemicals.

For the three-year-period occurring during 2011-2014, the project has been continued in two programs: FuBio Joint Research 2 (FuBio JR2) and Products from dissolved cellulose (FuBio cellulose). PCC is active in both new programs.

FuBio JR2 is divided into 7 research work packages, where PCC is involved in WP1 (Hot water extraction and separation), WP2 (Novel biomass fractionation), WP4 (Improving traditional fibre products), and WP5 (Health-related applications). FuBio cellulose is divided into 5 research work packages, where PCC is involved WP3 (New products). The main research areas considering PCC are hot water as well as ionic liquid fractionation of wood components, hemicelluloses and there especially spruce galactoglucomannans (GGM) as barriers in papermaking, extractives in health products, and cellulose bead application technology.

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

The main aims of our work during FuBio JR2 project have so far been

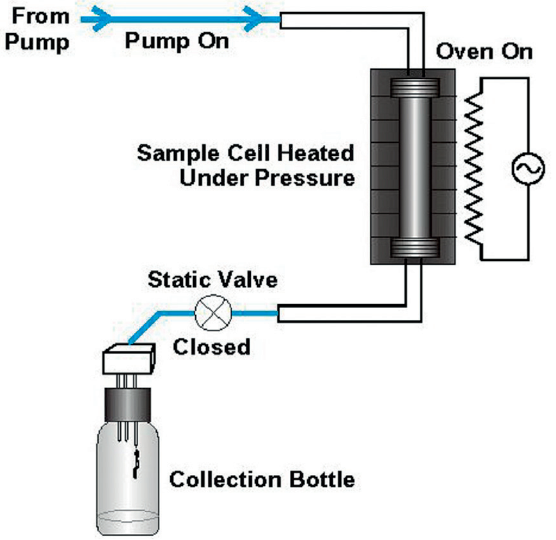
- high-yield extraction of high-molar-mass (polymeric) GGM
- from spruce wood
- with ONLY water and without buffer addition if possible
- providing as small as possible chemical altering of the residual material,
- which is important to a following extraction of lignin (lignin extraction

In the years 2011-12 the main aim was to study the influence on mass-transfer limitations:

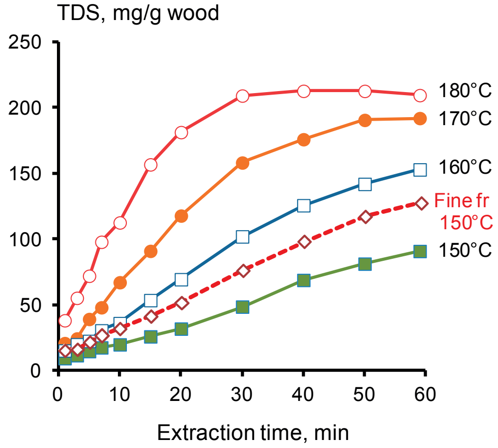
- internal cell wall diffusion
- surface

Experimental condition applied in this study:

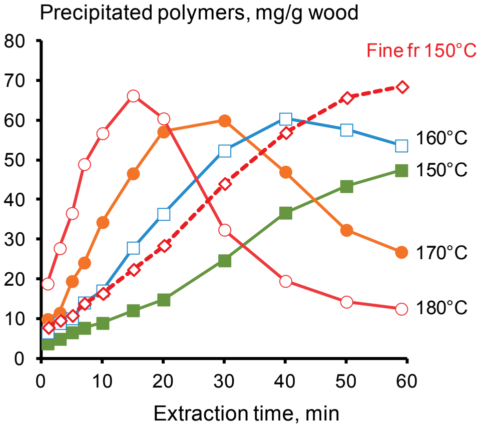
- ASE 350, Zr-type cell
- Temperature: 150°C
- Solvent: distilled water
- Fine fraction 0.05-0.1 mm of ground spruce sapwood



Principle of Accelerated Solvent Extraction



TDS of extracts obtained at different temperatures (particle size 0.25-1.0 vs fine fraction 0.05-0.1)



EtOH precipitated polymeric GGM from extracts obtained at different temperatures (particle size 0.25-1.0 vs fine fraction 0.05-0.1)

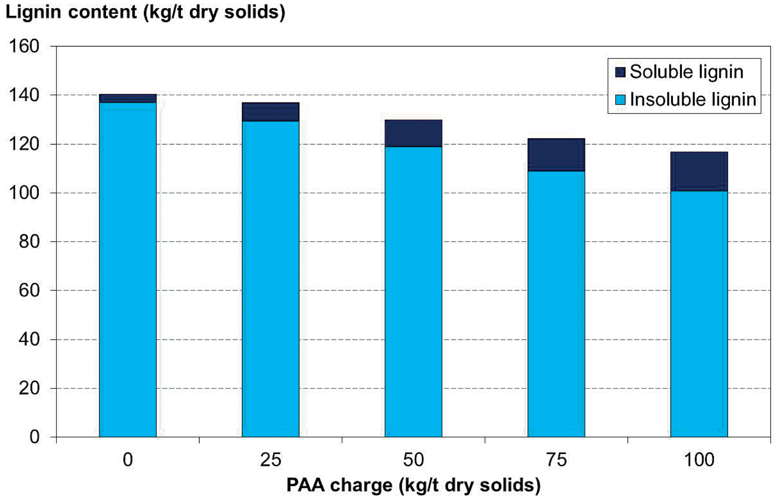
Experiments were done to improve the average molar mass and obtain high yield of extracted hemicelluloses , i.e., galactoglucomannan by reducing ASE extractions temperature (150°C) and size of particles (0.05-0.1 mm) from spruce sapwood.

It was established that after 60 min extraction, the yield of polymeric GGM, isolated by precipitation in EtOH:H_2O (85:15 v/v), was c. 70 mg/g of the dried wood. This is about half of TDS (ca 140 mg/g of dried wood) isolated from spruce sapwood by hot-water extraction at given conditions. The “quality of extract”, i.e., the max ratio of precipitated polymers to TDS of 58% was achieved after 40 min extraction at 150°C.

Additional work has also been done on the influence of particle size distribution and effect of stirring. Furthermore, the work with the reactor set-up with the unique possibility for inline pH measurement and control at temperatures up to 200°C, described above under Bioraff II, has been continued here and identified as one of the most important approaches to the hot water extraction.

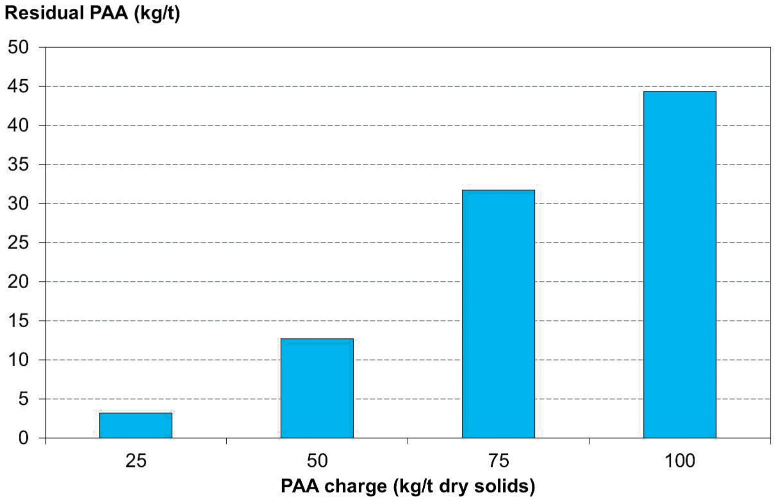
The purity of the extracted hemicellulose-rich fractions is an important factor and the major impurity is usually lignin. Lignin can be reactive when processing these hemicellulose fractions into new products. Also, lignin gives undesired colour and lignin-derived products even smell. In this study, conventional pulp bleaching chemicals which are already available in the forest industry will be applied in the purification experiments. They are relatively cheap, ready-to-use and easy to integrate to existing processes. Bleaching chemicals used in acidic conditions such as peracetic acid (PAA) and chlorine dioxide (ClO_2) will be applied because deacetylation of hemicelluloses occurs in alkaline conditions and will decrease the water solubility of the hemicelluloses.

Industrial Norway spruce *(Picea abies)* sawdust was extracted using a flow-through PHWE process. Thereafter the obtained hemicellulose-rich extract was ultrafiltered using 10 kDa cut-off membranes and a concentrate fraction containing high molecular weight hemicelluloses having relatively high dry solids content was obtained. The concentrate fraction was treated with PAA using the following conditions: 3 g. o.d. extract, treatment temperature 70°C, time 30 min, consistency 15%, pH 4.5 and PAA charge 25, 50, 75, and 100 kg/t dry solids. The initial lignin content (14% or kappa number ~93) of the concentrate was reduced considerably by PAA treatment. Additionally, the acid soluble lignin content was increased substantially.



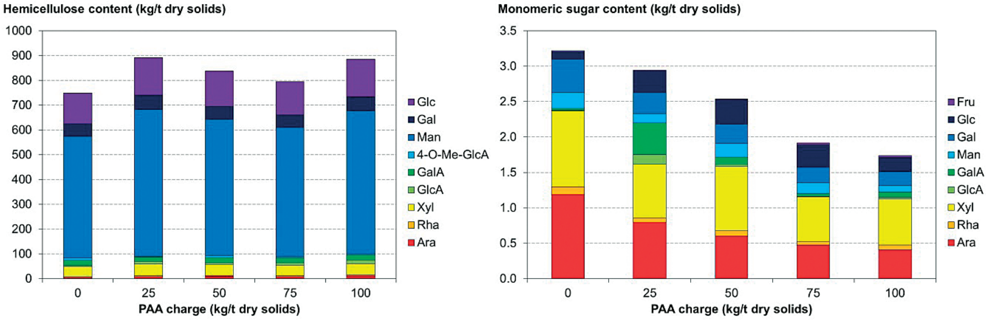
Lignin content of PAA treated concentrate

The PAA was almost entirely consumed when the charge was 25 kg/t. At higher PAA charge, there is still residual bleaching chemical left suggesting that the treatment time can be further increased and hence more lignin will be removed.



Residual PAA content after PAA treatment

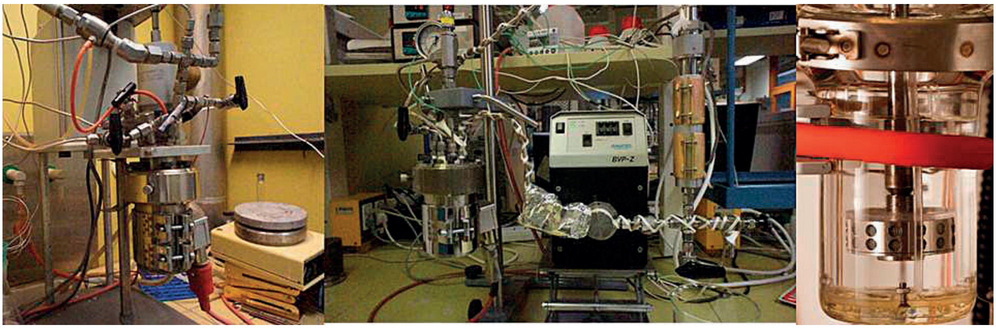
The hemicellulose content was not affected by PAA treatment which is an important issue. Additionally, the monomeric sugar content was not increased. This clearly suggests that PAA is a suitable bleaching chemical for PHW extract purification.



Hemicellulose (left) and monomeric sugar (right) content of PAA treated concentrate

In terms of ionic liquid mediated fractionation, a breakthrough was reached and a patent application has been filed. The novel family of switchable ionic liquids used for this purpose are easy prepare; can be prepared from nature-derived species; are efficient even for native (humid) industrial size wood chips; work for both soft- and hardwood (and other lignocellulosic species); do not require any stirring upon processing; work at relatively low temperatures (around 100°C); are reusable; and, lead to selective removal of hemicelluloses, lignin and extractives from wood chips, leaving the three-dimensional cellulose network of the wood tissue untouched.

In line with these efforts, various reactor technologies have been tried: in addition to the classical batch concept, also a loop reactor among others was compared.

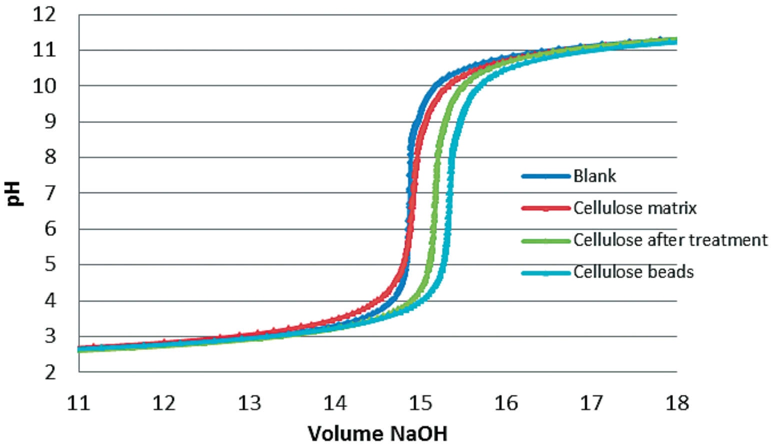


Sample wood processing with SILs. 1) Classical batch reactor to 2) loop reactor and 3) 'SpinChem' reactor

Hot-water extracted spruce galactoglucomannans (GGM) have been chemically modified to obtain hydrophobic barrier properties for coating of paper and board. Cross-linking has also been applied to increase the molar mass. The aim is to obtain GGM-derivatives that have either solution or dispersion properties usable in coating. Studies on the film properties of the derivatized GGM have shown that certain products are potential for coating applications.

Concerning the use of wood extractives for health-related applications, our work has continued mainly with chemical characterisation of the compounds and extracts selected for further biostesting and final proof-of-concept studies. Special emphasis has been laid on understanding the polymerisation process and products that certain compounds seem to undergo.

For the FuBio cellulose part, PCC is involved WP3 (New products) and especially the cellulose beads research. The protonation constants and concentration of acid groups of cellulose beads were determined by potentiometric acid-base titration. The cellulose matrix, obtained from Domsjö fabriker AB, was treated with HCl and ethanol to eliminate any lignin residue. Examples of titration curves for the cellulose matrix and cellulose beads are shown below.

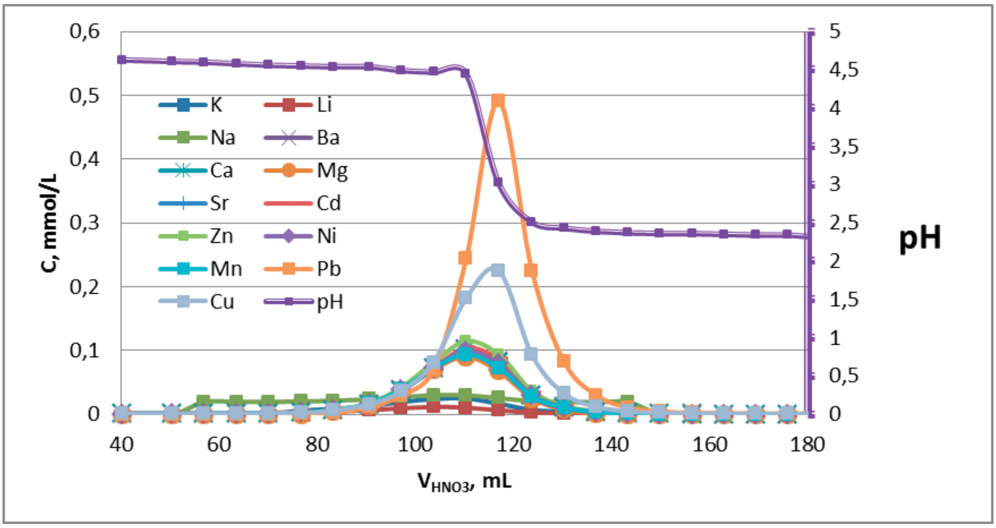


Potentiometric acid-base titration curve of cellulose beads

The potentiometric titration data was evaluated by the FITEQL software giving detailed information about the different acidic groups on the cellulose beads. The total amount of acid groups was around120 μeq/g.

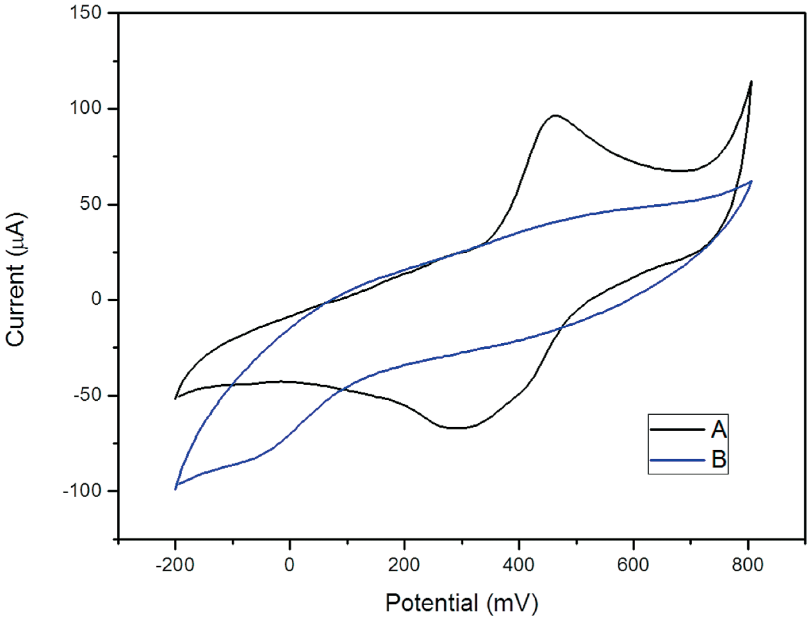
The cellulose beads were used further as stationary phase in column chromatography and the following affinity order for different metal cations to cellulose beads was established:

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



pH and concentration of metal ions in the collected fractions as function of the elution volume for a chromatographic column filled with cellulose beads

Cellulose beads were functionalized with the conducting polymer polyaniline (PANI) and the electrochemical response of the PANI–cellulose beads was studied with cyclic voltammetry as illustrated below.



Cyclic voltammogram of PANI–cellulose beads in 0.6M H_2SO_4*, (Scan rate 100mVs-1; the 5th scan is shown). A- Response of PANI-Beads; B- response of gold electrode without beads*

Cooperation:

Forestcluster; VTT; Metla; Lappeenranta University of Technology; Aalto University; University of Jyväskylä; University of Helsinki; University of Turku; University of Tampere; University of Eastern Finland; Metsä Fibre; Myllykoski/UPM; Metso; Kemira; BASF; Andritz; Pöyry; Stora Enso; UPM-Kymmene; Danisco; Orthotopix; Pharmatest Services; Separation Research; KTH, Wallenberg Wood Science Centre, Sweden; University of Maribor, Slovenia

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Environmentally Sound Extraction of Biomass with Green Solvents

Main funding: Metla

Petri Kilpeläinen, Andrey Pranovich, Stefan Willför

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

Birch sawdust was extracted using pressurized hot water at temperatures between 140 and 200°C. There was a constant flow of heated water through sawdust inside the extractions vessel. The aim of the extractions was to extract polymeric and water-soluble xylan, with a minimum of aromatic and other impurities.

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

Cooperation:

Metla; University of Helsinki

New Value-Added Natural Chemicals and Renewable Materials from Wood

Main funding: Academy of Finland, Tekes, BIOREGS Graduate School, Johan Gadolin Scholarship

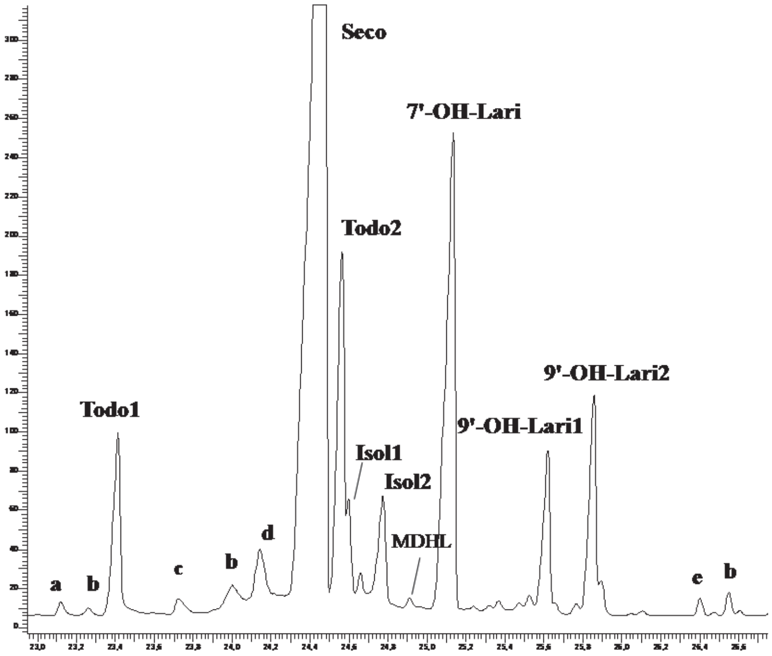
Ann-Sofie Leppänen, Jens Krogell, Outi Niittymäki, Iveta Češková, Victor Kisonen, Petri Kilpeläinen, Jan-Erik Raitanen, Patrik Eklund, Rainer Sjöholm, Chunlin Xu, Markku Reunanen, Paula Ojala, Vaula Metso, Wenwen Fang, Jarl Hemming, Annika Smeds, Ivan Sumiersky, Stefan Willför

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.

Water-soluble lignin, which is co-extracted from spruce wood in hot water extraction of hemicelluloses, was isolated, purified and thoroughly characterised. This kind of analytical work is tedious but crucial for building a deep, molecular understanding of water-based extraction processes. Furthermore, this kind of water-soluble and quite reactive lignin has been tested for some applications as valuable biochemicals.

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

Phenolic compounds such as lignans, stilbenes, and flavonoids are potential antioxidants, radical scavengers, and bioactive substances that are of high interest to us. Structural studies and structure-activity-relationships for oxidized lignans may give new insights on how to utilise such compounds in e.g. medicine. An intensive analytical study on minor but still natively occurring softwood lignans have given valuable new data on the extractives in wood. We identified a number of new lignans of the hydroxylated divanillyl 7,9’- or 9,9’-epoxy type in Norway spruce knotwood extracts: 7R- and 7S-todolactol A, 7R- and 7S-isoliovil, 7S- and 7R-9’R-9’-hydroxylariciresinol, 7’-hydroxylariciresinol, and monodemethoxylated 7’-OH-Lar (Fig. 1). 7-Hydroxylariciresinol, todolactol B, 7-hydroxydivanillyl tetrahydrofuran, and 9-hydroxypinoresinol were tentatively identified, and 10 other similar lignans were probably different stereoisomers of these lignans and/or of liovils. In addition, the mass spectra of 16 other unknown minor lignans indicated the presence of at least 35 previously unidentified lignans, accounting altogether for ca. 7% of the dry ethanol extract weight.



GC-FID chromatogram of a silylated flash chromatography fraction of a Norway spruce knotwood extract. Seco = secoisolariciresinol, Todo1 and 2 = 7R- and 7S-Todolactol A; MDHL = monodemethoxylated 7'-OH-Lar, Isol1 and 2 = 7R- and 7S-isoliovil; 7'-OH-Lari = 7'-hydroxylariciresinol; 9'-OH-Lari1 and 2 = 7S- and 7R-9'R-9'-hydroxylariciresinol; a = liovil-type lignan; b = unknown lignan; c = 7-hydroxy-divanillyl tetrahydrofuran (tentatively); d = isoliovil-type lignan; e = 7-OH-Lar (tentatively)

Pinosylvin-type stilbenes and structurally similar norlignans synthesized from the abundant spruce knotwood lignan hydroxymatairesinol have been evaluated for their bioactive, antibacterial, and antifungal properties. Especially the pine heartwood substance pinosylvin showed potential for several applications and studies are on-going how to reveal the true potential of this compound. This work has continued in the WoodWisdom ERA-NET project "Pinosyvins as novel bioactive agents for food applications (PINOBIO)".

Drying of industrial oversized chips for later recovery of pinosylvins in the PINOBIO project

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

Cooperation:

UPM-Kymmene; Raisio Yhtymä; Metso Paper; Metsä Fibre; Forchem; Arbonova; SCA; M-real; Nordic Jam; Granula; Bio-Vita; Tampere University of Technology; University of Helsinki; University of Eastern Finland (Kuopio); University of Oulu; Metla; University of Turku; University of Jyväskylä; VTT; MTT; Metla; KCL; Royal Institute of Technology (KTH), Wallenberg Wood Science Centre, Sweden; University of Peshawar, Pakistan; Zonguldak Karaelmas University, Turkey; University of Maribor, University of Ljubljana, 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, University of Vigo, Spain; Slovak Academy of Sciences, Slovakia; Health Sciences University of Hokkaido, Japan; Central Research Laboratories, Yomeishu Seizo, Japan; North Carolina State University, USA; United States Department of Agriculture, USA; Technical University of Luleå, Sweden; European Polysaccharide Network of Excellence (EPNOE); Latvian State Institute of Wood Chemistry, Latvia

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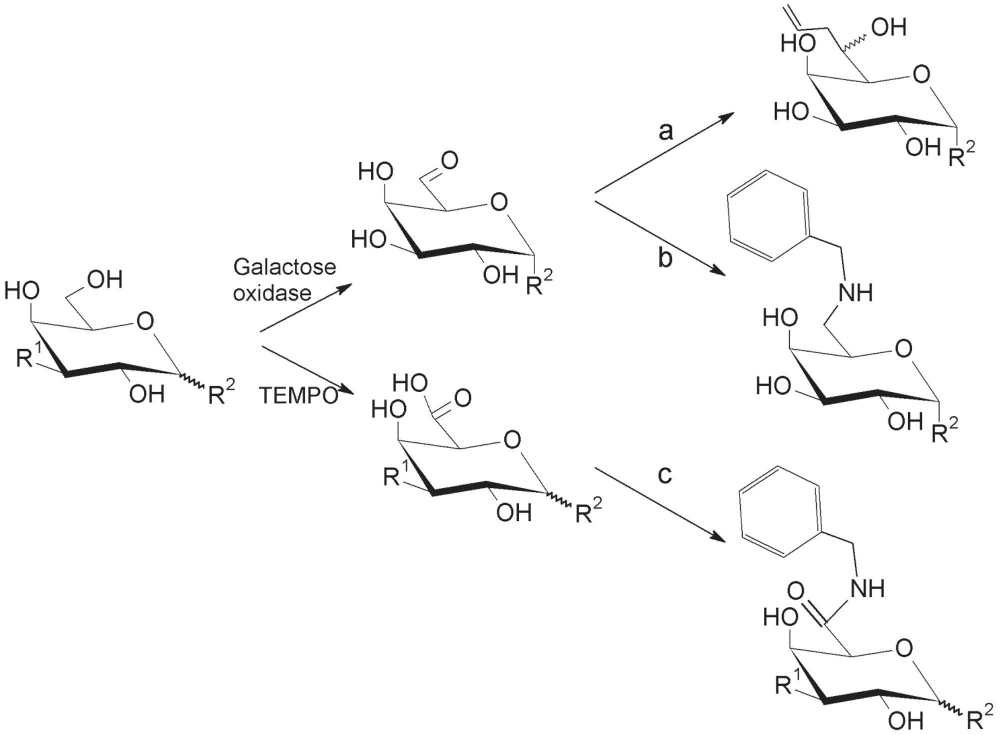
Chemical Modification of Water-Soluble Spruce O-Acetyl-Galacto-glucomannan

Main funding: Graduate School for Biomass Refining (BIOREGS)

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

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

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



Selective chemical modifications of GGM in water: Enzymatic oxidation followed by a) indium mediated allylation and b) reductive amination, and chemical oxidation followed by c) amidation. R1 = - OH or GGM backbone; R2 = GGM backbone

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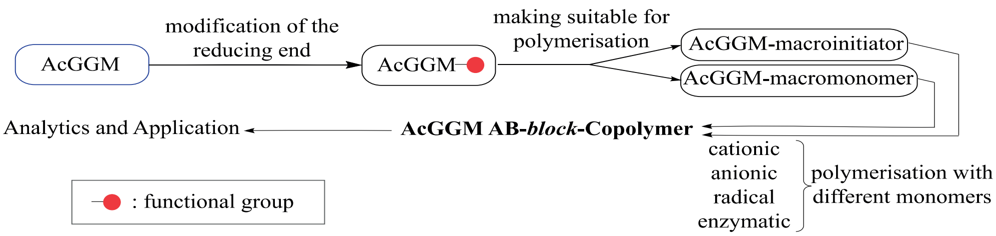
Cooperation:
University of Helsinki, KTH, Wallenberg Wood Science Centre

Design of Hemicellulose Block Copolymers and Their Applications

Main funding: Aides à la formation recherche (AFR)

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

Spruce O-acetylgalactoglucomannans (AcGGM) have been isolated from wood and purified. The aim of this work is to modify AcGGM in order to get AB-*block*-copolymers. In a first reaction, the reducing end of the polysaccharide chain has to be made suitable for a polymerization. Subsequently, a polymerization of a monomer can be performed; depending on the physical properties of the monomers used, these reactions will result in AB-*block*-copolymers with different properties and different fields of application. Possible application might be the modification of paper surfaces or the use as an additive in paints or cosmetics. In the following illustration the synthesis path is shown in a simplified way:



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

Also other reactions were tested, so for example AcGGM was converted with different saturated fatty acids in order to synthesis AB-*block*- and *grafted*-copolymers. Also, new routes for the preparation of AcGGM-PDMS copolymers are developed.

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

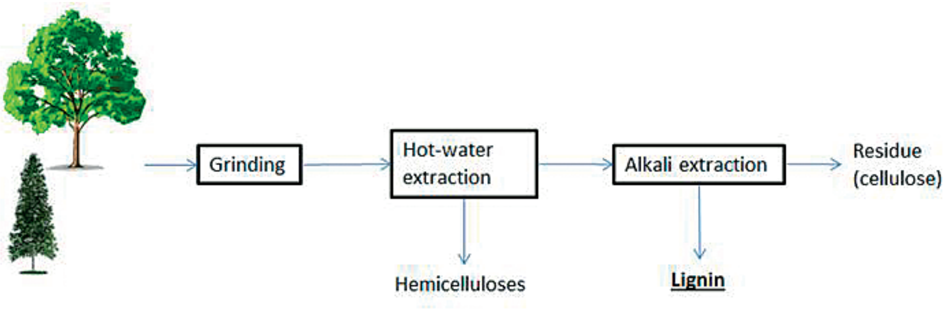
Main funding: International Doctoral Programme in Bioproducts Technology (PaPSaT)

Ekaterina Korotkova, Andrey Pranovich, Stefan Willför

Nowadays lignin can be isolated mainly as a by-product in paper and bioethanol production industries. The composition of lignins varies a lot depending on the tree species, as well as way of isolation and purification. Lignin is mainly separated from wood as lignosulfonates in sulphite pulping and as kraft lignin in kraft pulping. Lignosulfonates are produced in industrial scale at a few of the remaining sulphite mills and are used as water-soluble polyelectrolytes in a variety of applications. Kraft lignin is mainly burned in the recovery boilers at pulp mills as concentrated black liquor. Only a small part of the kraft lignin is extracted as a by-product in an industrial unit in USA and is further purified for use in different chemical and material applications. Major problems with kraft lignin are the condensed structure and therefore low reactivity, as well as the high sulfur content.

New techniques are needed for more efficient extraction of lignin from wood. Milder extraction condition, compared to soda or kraft pulping, can provide new, more reactive lignins with less condensed structure. Biorefinery concept includes the wide range of techniques to separate biomass, including wood, into its building blocks. Those blocks can be later converted to value added products and chemicals. Lignin has great potential in different areas such as producing of fertilizers, adhesives, composites, biodegradable films, resins, polymer additives etc.

Lignin can be extracted from wood as a second stage, after hemicelluloses removal, in a scheme with the goal to fractionate wood into its three main components, i.e., hemicelluloses, lignin, and cellulose as residue.



Wood fractionation, according to our biorefinery concept

Methods and techniques used in developing chemistry for future biorefineries should have minimal impact on the environment. Water is an ecologically friendly solvent. Lignin extraction from wood using plane hot water with and without addition of alkali is a promising way to obtain new, more reactive lignin for future applications.

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

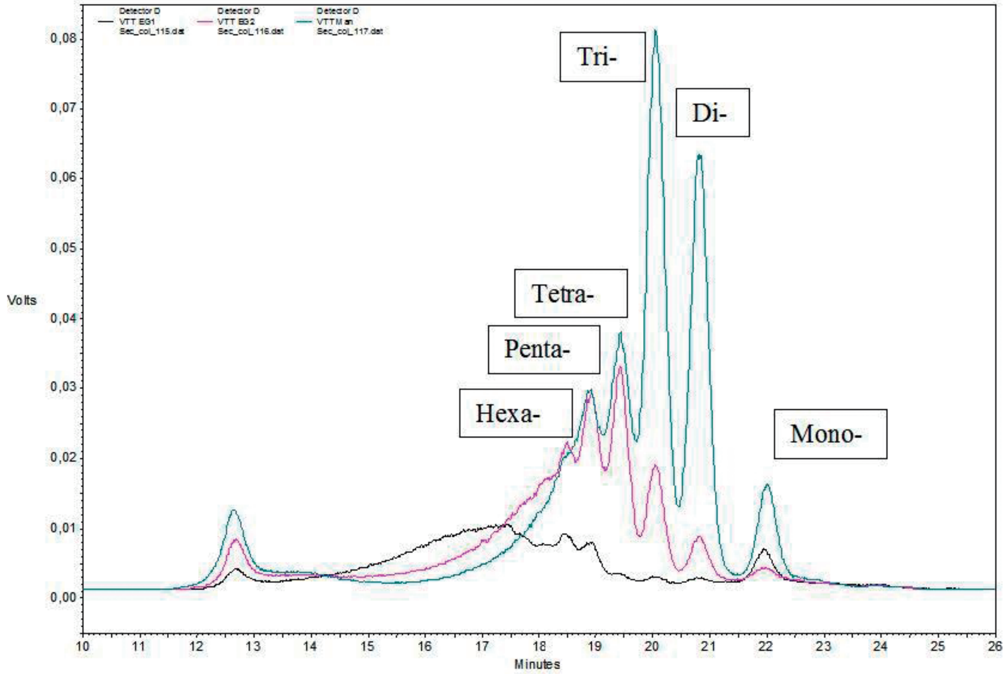
Main funding: Tekes, Industry

Stefan Willför, Robin Manelius

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

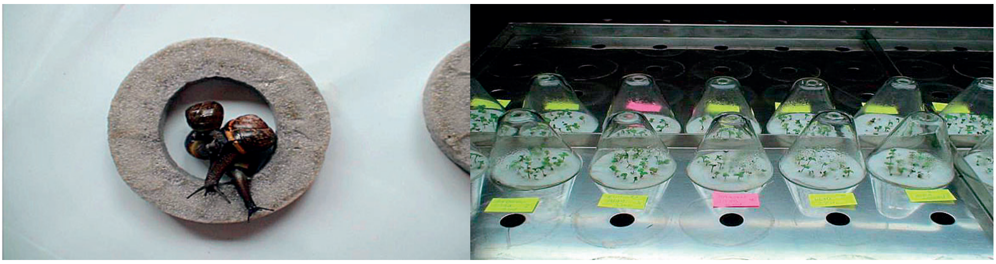
Agrochemicals, such as fertilizers and pesticides, have to be used in order to make the agro-business profitable. A serious drawback in the usage of these mostly synthetic compounds is, however, that they pose a serious threat to human health and to the environment. The objective in this project is thus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

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



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

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



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

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

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

Main funding: Tekes, Industry

Stefan Willför, Robin Manelius

The agriculture has to produce huge amounts of food to feed all people. The inevitable result of this is that an enormous amount of agro waste is produced. However, economical- and image factors and are often working against valorising waste materials and therefore products, such as organic fillers and, do not become successful products although the potential is obvious. Therefore, sustainability analyses are almost as essential, for the development of future successful applications, as are the products themselves. Both materials and processes are therefore evaluated using tools developed for analysis of business operations (ex. total life cycle analysis). The main objective of the project is to develop cost-effective and sustainable technologies that could be utilised to produce tailor made filler particles from various agricultural by-products (Figures A-C below).

A – C: Typical side stream raw materials to be used in the project
A) From left: Low quality and raw berries to be discarded. B) Beet pulp cossettes and C) Oat husk

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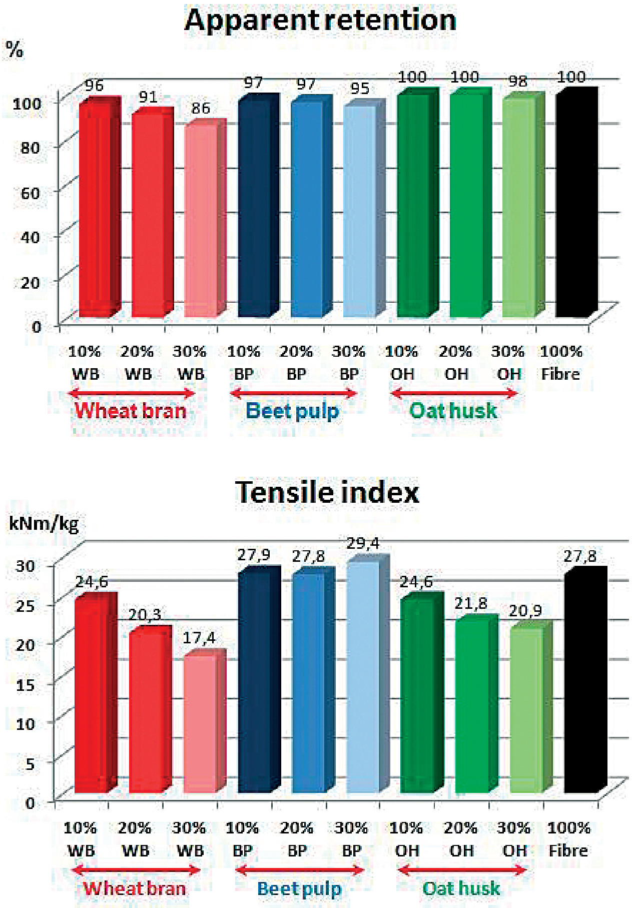
The agro side streams can be used, for example, as filler materials for paper. The paper making properties for the organic fillers are, generally, good but there are differences between the raw materials (Figures A and B below).



Important paper making properties Particles (20 – 200 µm) made by grinding wheat bran, beet pulp and oat husk, were used as fillers in paper making at 10wt.%-, 20wt.%-, and 30wt.% of the pulp. A) Apparent retention of pulp onto the paper B) Tensile strength (index) of the produced paper

One obvious problem with the raw materials is their colour, especially if they are meant to be used in applications requiring a high level of brightness, like paper. One aim of the project is, thus, to test different means of tailoring them to suit the planned applications.

Bleaching experiments with wheat bran

More specific scientific and technological objectives of the project are to:

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

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

Cooperation:
Åbo Akademi University (Coordinator); VTT (Technical Research Centre of Finland); Sappi Finland; Valio; Fazer; Hycail Finland; Sokerijuurikkaan Tutkimuskeskus; University of Manitoba, Canada; Johann-Heinrich-von-Thünen-Institut, Germany

COST Action FP0901, "Analytical Methods for Biorefineries"

Main funding: EU RTD 7th Framework Programme

Stefan Willför, Anna Sundberg, Anders Strand, Ari Ivaska

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

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

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

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

Lignin Valorisation (LigniVal)

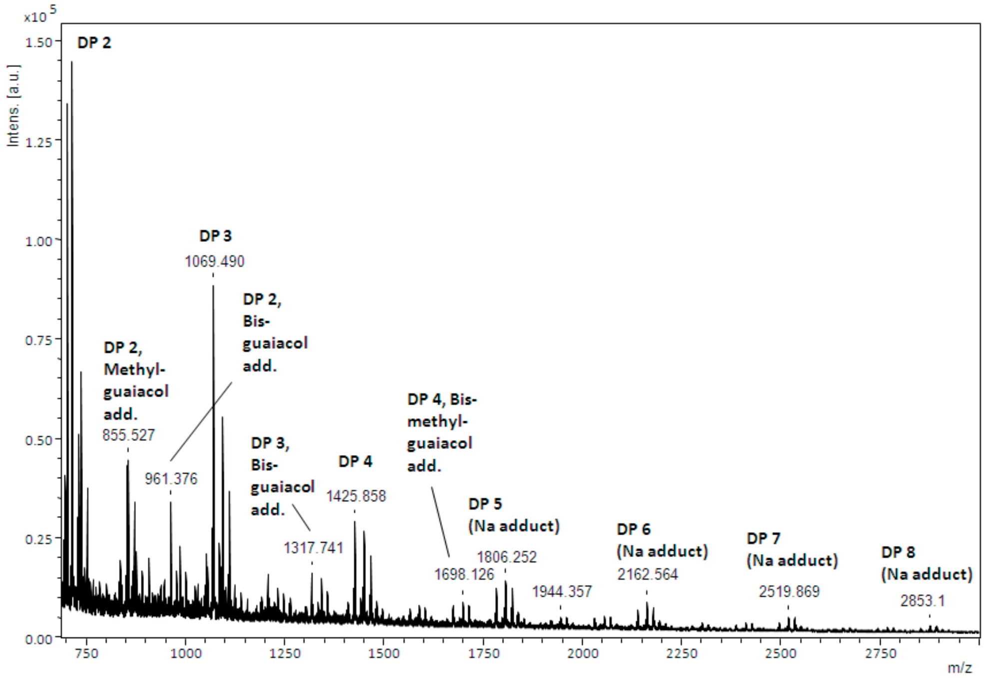
Main funding: Tekes

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

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

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

Our task in the project was to study the reactions of the pure lignans matairesinol and pinoresinol with the stable radical DPPH, as well as coordinate part of the analytical determinations especially for the enzyme treated polyphenols. The results showed that both lignans reacted very rapidly with DPPH, and the reactions were almost quantitative. Pinoresinol formed polymers mainly in the MW range 2.5-21.4 kDa, whereas matairesinol formed polymers mainly in the MW range 1.8-5.3 kDa. The polymers contained mainly unmodified lignan units linked by 5–5′ bonds.



MALDI-TOF MS spectrum of pinoresinolpolymers. DP = degree of polymerization.

Cooperation:

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

Publications:

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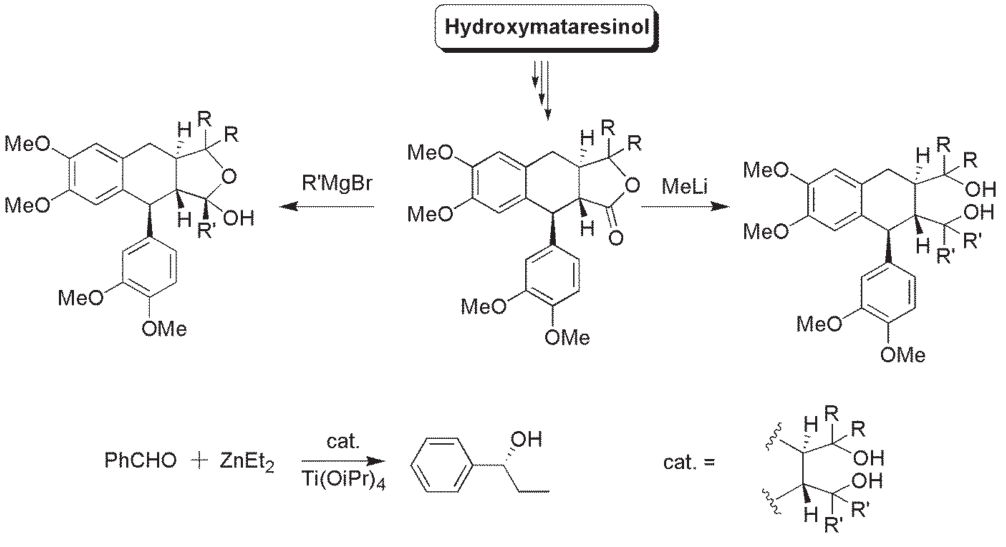
Lignans as Versatile Chiral Auxiliaries and Chiral Catalysts (LIGNOCATS)

Main funding: Academy of Finland

Patrik Eklund, Yury Brutsentsev, Stefan Willför

The objective of this research project is to develop and evaluate lignan-based chiral catalysts for applications in modern organic synthesis. Recent progress and development of Finnish biorefinery processes has shown that enantiopure natural products belonging to the class of lignans can be isolated from spruce knotwood in large quantities.



R, R' = Ph, 2-naphthyl, Me, H

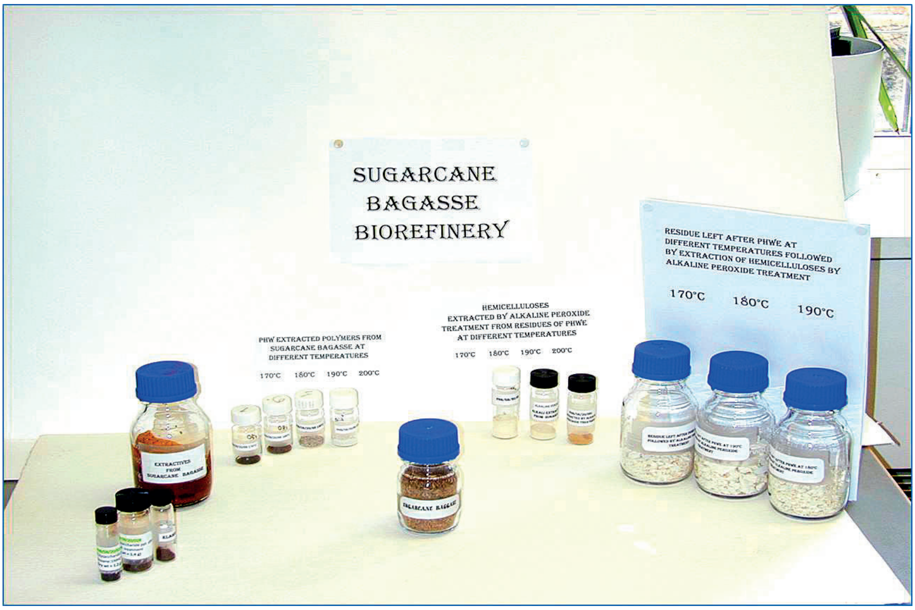
The development of novel lignan-based chiral ligands and catalysts is divided in 3 separate lines. 1) Synthesis and evaluation of TADDOL like ligands (chiral 1,4-diols, shown above). 2) Synthesis and evaluation of phosphorous containing ligands 3) Synthesis and evaluation of chiral Brönsted acid catalysts. The synthetic modifications will include reductions, oxidations, metathesis, aryl-aryl couplings, Grignard reactions etc. The synthesis and the properties of the novel catalysts are supported by molecular modelling. The final applications of the catalysts will be focused of stereoselective carbon-carbon bond formations and enantioselective hydrogenations/reductions.

Sugarcane Bagasse Biorefinery

Main funding: PCC/Johan Gadolin Scholarship

Protibha Nath Banerjee, Andrey Pranovich, Stefan Willför

Sugarcane bagasse is a waste material of the sugar industry that has been underutilized for several decades by industries to generate electricity under waste management policy. In view of the constantly increasing demand for renewable natural materials and biofuels, together with the environmental concern over the use of fossil fuel and uncertainty in long term availability of crude oil, lignocellulosic biomass like sugarcane bagasse has found considerable attention of current international research groups and industries for their potential in producing chemicals and biofuels. Hence the development of a feasible process is indeed needed to develop a sustainable sugarcane bagasse based biorefinery, which will not only reduce the dependence on crude oil based products, but will also increase local rural economy and employment. With this in mind this research project was initiated to develop a sugarcane bagasse biorefinery.



Sugarcane bagasse biorefinery

Sequential extraction of sugarcane bagasse with 1) toluene: ethanol (2:1), 2) hot water at temperatures between 170 and 200°C, and 3) alkaline peroxide yielded fractions rich in extractives, water-soluble hemicelluloses together with lignin, and alkali-soluble hemicelluloses. The total extractable material was slightly more than half of the dry sugarcane bagasse weight. The non-extractable residue mostly consists of cellulose together with lignin. The chemical characterization of the materials and the structural elucidation of the hemicelluloses (total 8 hemicelluloses) by permethylation followed by GC-MS analysis, NMR and other spectroscopic studies are in progress. An analytical methodology suitable for sugarcane bagasse has been developed.

Later, the cellulosic residue will be converted to bioethanol by 1) Simultaneous saccharification and fermentation process and 2) saccharification followed by fermentation process (2 steps) and the optimum condition will be evaluated. The hemicelluloses can also be tested for their anti-ulcerative property in the gastrointestinal tract. Film barriers properties of these hemicelluloses could also be one of the potential areas.

3.6 Catalysis and Molecular Engineering

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

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

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

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

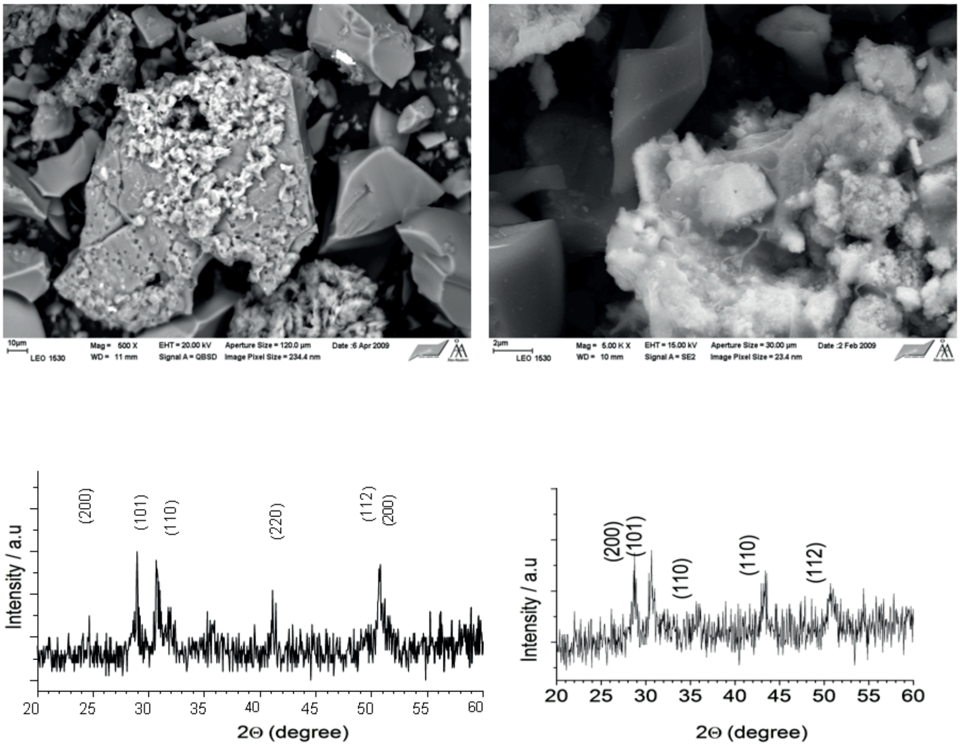
A particular challenging was development of catalysts, containing gold, which was considered for centuries as catalytically inactive. Various types of supported gold catalysts, including structured ones, were synthesized and tested in reactions, involving carbohydrates, e.g. oxidation, hydrogenation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

A special way in molecular engineering of catalysts is to have metals in non-zero valence state dissolved in a liquid layer, attached to the solid surface. Immobilization of ionic liquids onto solid materials with subsequent introduction of catalytically active species palladium species and testing the catalyst in liquid phase hydrogenation of citral demonstrated the big potential of this novel catalytic system (see Section 3.1: Ionic liquids).

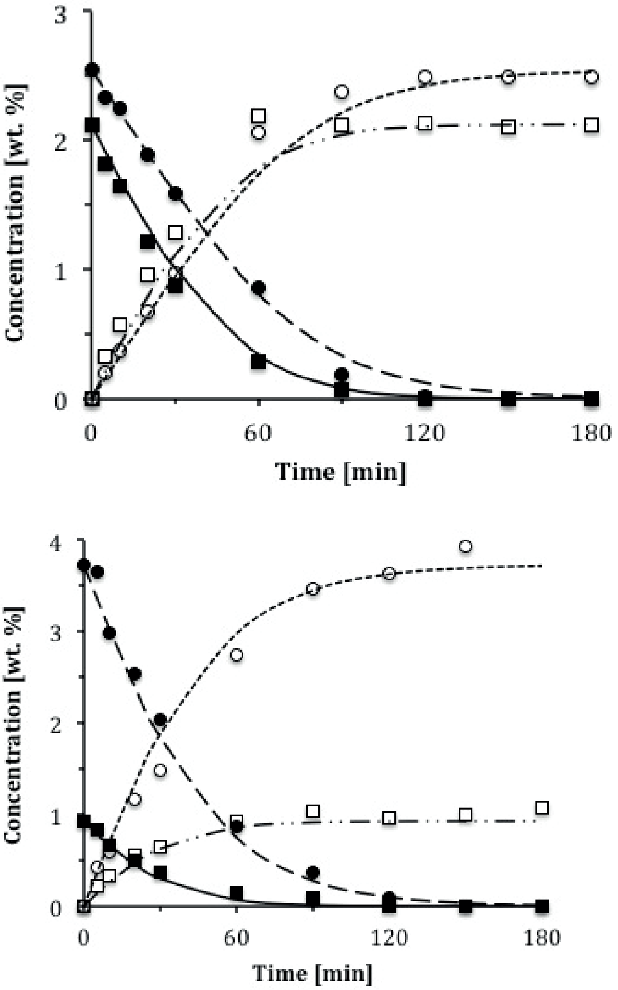
The materials were characterized with modern techniques, such as SEM, TEM, XRD, AFM, TPD, and FTIR. An electrochemical method, cyclic voltamperometry, which is mainly used for bulk metals, was developed to characterize supported metals with low metal loading.

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

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



SEM images from the recycled catalyst surface showing crystallites of MgO and KCl deposited on zirconia surface (above) and XRD patterns from ZrO_2*-KCl (left) and* ZrO_2*, KCl and MgO (right) catalysts below*



Modelling results from hydrogenation of mixture of arabinose and galactose 1:1 (left) and 3.6:1 at 120°C and 40 bar (right)

Micro and Mesoporous Materials

Main funding: Åbo Akademi

Narendra Kumar, Sabrina Schmidt, Biao Zhang, 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. Thee catalysts are applied in many projects, for instance in hydrocarbon transformations as well as in preparation of fine chemicals. Thee deactivation and regeneration of zeolite materials is investigated. Sensor materials and microreactor coatings have been synthesized and successfully applied. Quantum chemical calculations, FTIR and solid state NMR have been used to characterize the active sites on zeolites.

Cooperation:

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

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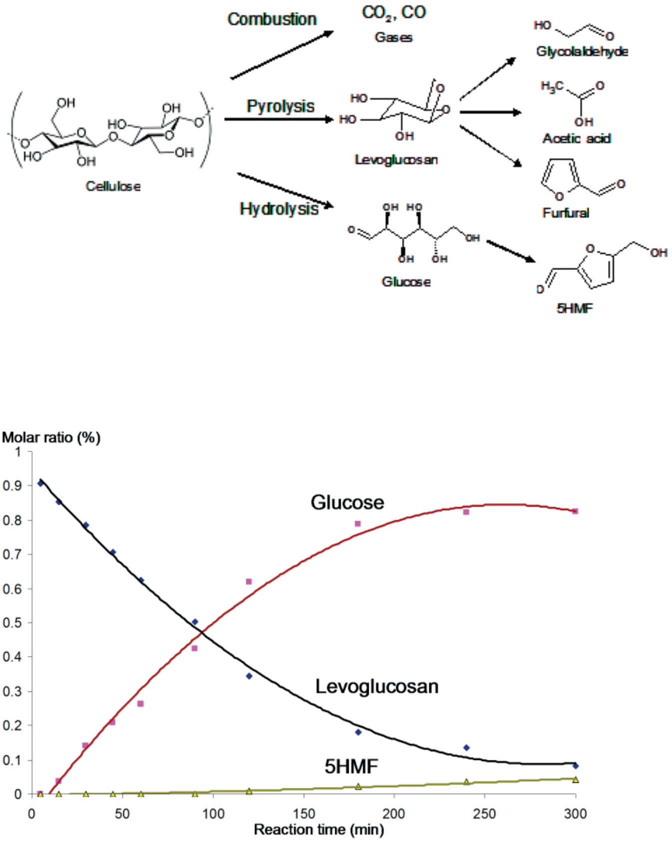

Common ways for biomass processing and catalytic transformation of levoglucosan into glucose

Valorization of Components Derived from Biomass

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

Jyri-Pekka Mikkola, Mats Käldström, Anton Tokarev, Narendra Kumar, Bright Kusema, Victor Sifontes Herrera, Andreas Bernas, Heidi Bernas, Olga Simakova, Alexey Kirilin, Antonina Kupareva, Toni Riittonen, Bartosz Rozmysłowicz, Cesar Araujo Filho, Irina Simakova, Jan Hájek, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

Wood is one of the most versatile materials, being at the same time a renewable resource, for chemical derivatives of wood, which serve as raw materials for a large number of other chemical and reprocessing industries. Chemical wood pulping processes extract many chemicals from wood - depending on the chemistry of the wood being pulped and the chemical process used. The liquors produced during kraft pulping cooking contain significant quantities of resin acids, tall oil, complex sugars and other organic compounds. Today, the most important chemical products originating from wood are various tall oil and turpentine products, but the markets are growing fast for several functional foods, like xylitol and sitosterol, e.g. products, which in addition to their nutritional function, have proven to promote health.

The project concerns valorization of components derived from biomass and focuses on catalytic hydrogenation of several types of sugars over supported metal catalysts, heterogeneous catalytic isomerization of linoleic acid and hydrogenolysis of hydroxymatairesinol. Within the framework of this project hydrogenation and oxidation of mono and disaccharides is studied. The work of catalytic hydrogenolysis of hemicelluloses is going on 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; DuPont; 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

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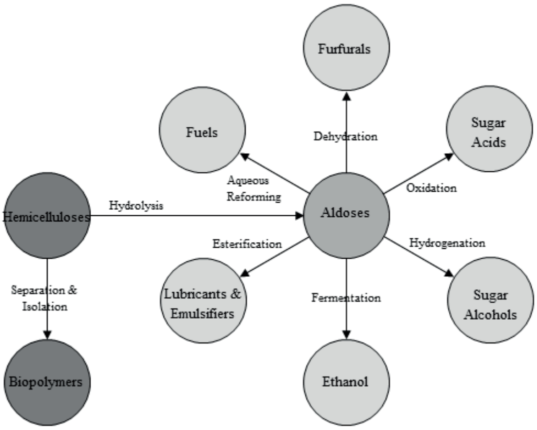

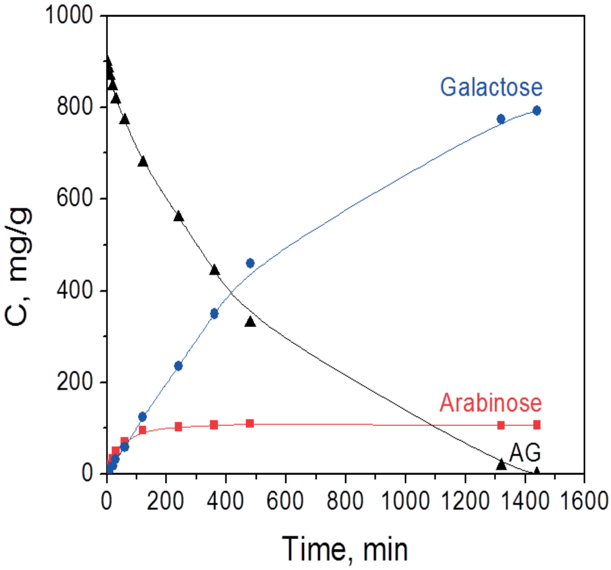

Different catalytic routes for the transformaiton of hemicelluloses to chemicals (above) and kinetics for acid hydrolysis of arabinogalactan to arabinose and galactose (below)

Asymmetric Catalysis and Chromatographic Separation

Main funding: Academy of Finland

Gerson Martin, Esa Toukoniitty, Päivi Mäki-Arvela, Serap Şahin, Alexey Kirilin, Rainer Sjöholm, Reko Leino, Henrik Saxén, Frank Pettersson, 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 reactor 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. In 20111, the work was directed to the combination of enantioselective hydrogenation and chromatographic separation in order to elaborate a green process concept, which minimizes waste production and maximizes the production of desired enantiomers.

Cooperation:

University of Turku

Publications:

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Characterization of the Acid-base Properties of Microporous Zeolite Materials by Potentiometric Titration

Main funding: PCC

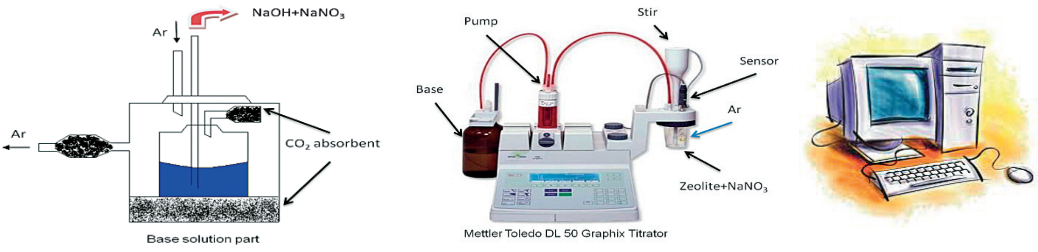
Kai Yu, Ari Ivaska, Narendra Kumar

Zeolites are a crystalline aluminosilicates and mainly composed by a three-dimensional network of SiO_4^{4-} tetrahedral. When a heteroatom with a lower valency than Si, such as Al, B, Ga, or Fe is introduced to the framework, the formal charge on that tetrahedron changes from neutral to negative charge. This negative charge is balanced by a hydroxyl proton or a metal cation forming a strong Brønsted acid site or a weak Lewis acid site. The aim of this work is to determine the properties of various acid sites in zeolites by using potentiometric titration method.

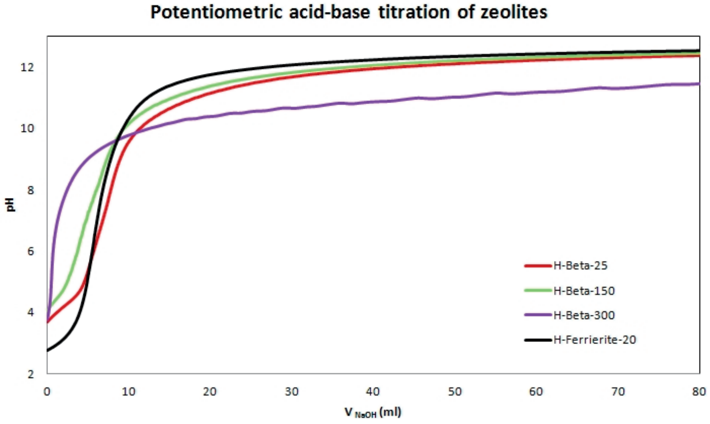
In this experimental work zeolite powder was dispersed in a sodium nitrate solution which was then titrated with standard solution of sodium hydroxide. Parallel experiments were done by adding nitric acid in the suspension prior the titration in order to protonate the acid sites inside the zeolite structure before performing the titration. The protonation constants of the acid sites and their concentrations in zeolites were obtained by evaluation of the raw titration data through the nonlinear, least-squares fitting computer program FITEQL and the total amount of acid sites in zeolites was also determined by the Gran method.

$$R_i^- H^+ + OH^- \longrightarrow R_i^- + H_2O$$

Titration of the acid sites in zeolite:



The instrumentation used for the titration



Potentiometric titration curves of different zeolites

3.7 Biofuels and Bioenergy

The importance of fuels originating from growing biomass has continuously increased. Today many thermal power plants are using or planning to use biomass 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 biomass conversion processes – this way paving the road for development of future fuel conversion technologies.

To be able to use the many new biomasses, 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 methods are not sufficient to evaluate the practical feasibility of these fuels.

The PCC has a wide fuel data base and we have developed several unique laboratory techniques to characterize the fuels for their combustion behaviour and emission formation tendency. The focus is on biofuels and wastes including wood and forest residues, black liquor, side streams from biorefinery processes and various waste derived fuels (RDF, PDF). Our laboratory tests and analysis techniques are further developed and applied. Combustion rates (devolatilization, char oxidation) are determined for single particles. Release rates and yields of the key ash forming 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 have lately been of special interest.

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

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

In 2010 two major measuring campaigns were done in large scale combustion furnaces to get in-furnace information such as main gas composition, concentration of nitrogen and sulphur oxides and their precursors such as hydrogen sulphide and ammonia or hydrogen cyanide. These very tedious measurements have now given strong support to the furnace modelling activities. In the present year and near term future the data obtained are used to test and validate several of the furnace model components.

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

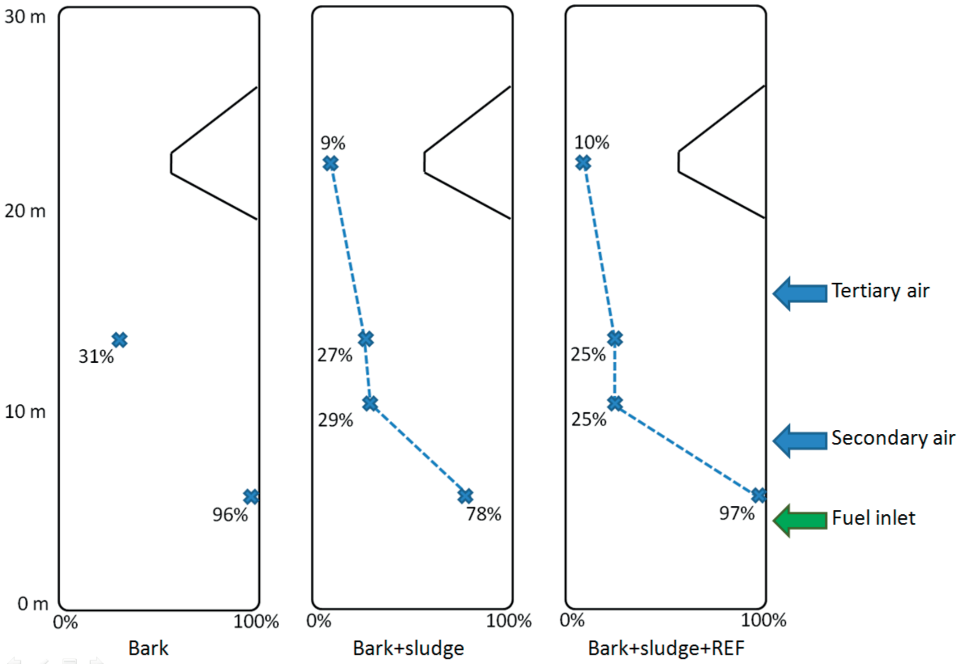
Chemistry in Biomass Combustion (ChemCom 2.0)

Main funding: Tekes

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

ChemCom 2.0 started in January 2008 and ended in February 2011. The project focused on fundamental chemical questions and solutions in combustion and gasification of solid biofuels, waste fuels and black liquor. A strong focus was put on CFD modelling of both bubbling fluidized beds and recovery boilers and several different submodels have been produced.

Data for the validation was 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.



Fuel-N conversion to NO, NH_3, and HCN at different levels in the boiler for the three cases. The crosses indicate the measurement level and the fuel-N conversion to NO, NH_3, and HCN

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

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

Based on the results obtained from the measurements in the recovery boiler several papers have been published e.g. four papers were orally presented at the International Chemical Recovery Conference, March-April 2010 in Virginia, USA and based on other project results a number of papers were presented in the Conference on Impacts of Fuel Quality on Power Production in Aug.-Sept. 2010 in Saariselkä, Finland. In total, 22 papers (journal and conference), two doctoral theses, three licentiate theses, one diploma thesis + a number of workshop and seminar papers have been published by ÅA within this project and the work continues within the FUSEC-project that started in April 2011.

Cooperation:

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

Publications:

- Järvinen, M., Mueller, C., Hupa, M., Fogelholm, C-J., A CFD-applicable discrete combustion model for thermally large particles, *Progress in Computational Fluid Dynamics* 11 (2011) 6, 373-383 (Inderscience Publishers, ISSN: 1468-4349)
- Vainio, E., Brink, A., DeMartini, N., Hupa, M., Vesala, H., Tormonen, K., Kajolinna, T., In-furnace measurement of sulphur and nitrogen species in a recovery boiler, *Journal of Pulp and Paper Science* 36 (2011) 3-4, 135-142 (TAPPI Press, ISSN: 0826-6220)
- Vähä-Savo, N., Yrjas, P., Laurén, T., Hupa, M., Development and application of a short-time probe for measuring carryover in a recovery boiler, *Journal of Pulp and Paper Science* 36 (2011) 3-4, 143-150 (TAPPI Press, ISSN: 0826-6220)
- Werkelin, J., Lindberg, D., Skrifvars, B-J., Hupa, M., Boström, D., Ash-forming elements in four Scandinavian wood species part 3: Combustion of five spruce samples, *Biomass & Bioenergy* 35 (2011) 1, 725–733 (Elsevier Ltd., ISSN: 0961-9534)

Future Fuels for Sustainable Energy Conversion (FUSEC)

Main funding: Tekes, Industry

Patrik Yrjas, Mikko Hupa, Leena Hupa, Anders Brink, Maria Zevenhoven, Nikolai DeMartini, Johan Werkelin, Daniel Lindberg, Markus Engblom, Tor Laurén, Johan Lindholm, Oskar Karlström, Juho Lehmusto, Patrycja Piotrowska, Na Li, Hao Wu, Dorota Bankiewicz, Bingzhi Li, Emil Vainio, Niklas Vähä-Savo, Christoffer Sevonius, Ismoil Bello, Mia Mäkinen

FUSEC is a three-year (April 2011–April 2014) joint research project between several industrial companies operating in the area of biomass and waste to energy. The project, which is coordinated by Top Analytica, consists of the research efforts of five Finnish companies with the additional support from two international companies (the companies are mentioned below). The research efforts include company-specific tasks and a major common research program – the FUSEC Core Program, which is coordinated by Åbo Akademi University. It additionally includes three Finnish universities and one national research laboratory (Tampere University of Technology, Lappeenranta University of Technology, Aalto University and VTT Technical Research Centre of Finland).

The FUSEC Core Program focuses both on practical and fundamental chemical questions and solutions in combustion and gasification of solid fuels, waste fuels (RDF, MSW, sludges, etc.) and black liquor. These questions concern among others the following themes:

A. Deposit cozntrol

B. Corrosion/material control
C. Bed management
D. Flue gas quality control (NOx, SO_2, $PM_{2.5}$, etc.)
E. Furnace process prediction
F. Recovery boiler control (incl. changing BL quality)

The above listed subject themes and the problems connected to these are tackled within five work packages in which the actual project plan is divided into:

WP 0: Scientific co-ordination

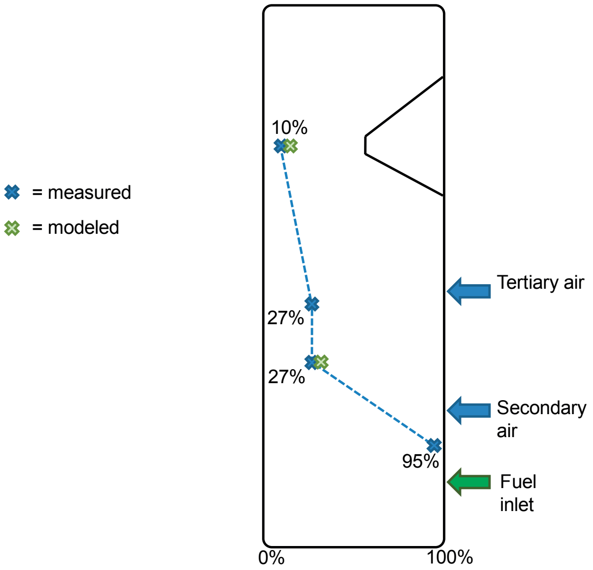
WP 1: Characterization of fuels and fuel mixes with novel and advanced methods

WP 2: Modelling

WP 3: High temperature corrosion

WP 4: Development of equipment and methods for high temperature research

WP 5: Information and international co-operation



Modelling of nitrogen compounds from measurements done within the ChemCom project

Cooperation:
Top Analytica; Foster Wheeler Energia; Andritz; Metso Power; UPM-Kymmene; International Paper; Clyde Bergemann; Tampere University of Technology; Lappeenranta University of Technology; Aalto University; VTT Technical Research Centre of Finland

Publications:

- Lehmusto, J., Skrifvars, B-J., Yrjas, P., Hupa, M., High temperature oxidation of metallic chromium exposed to eight different metal chlorides, *Corrosion Science* 53 (2011) 10, 3315-3323 (Elsevier Ltd, ISSN: 0010-938X)
- Lehmusto, J., Yrjas, P., Skrifvars, B-J., Hupa, M., Detailed studies on the high temperature corrosion reactions between potassium chloride and metallic chromium, *Materials Science Forum* 696 (2011), 218-223 (Trans Tech Publications, ISSN: 0255-5476)
- Vähä-Savo, N., DeMartini, N., Hupa, M., Combustion of black liquor-solid biomass mixtures in a single particle reactor - Characteristics and fate of nitrogen, *Energy & Fuels* 25 (2011) 11, 4944-4951 (ACS Publications, ISSN: 0887-0624)

Science to Biomass Combustion

Main funding: ERANET Bioenergy (TEKES)

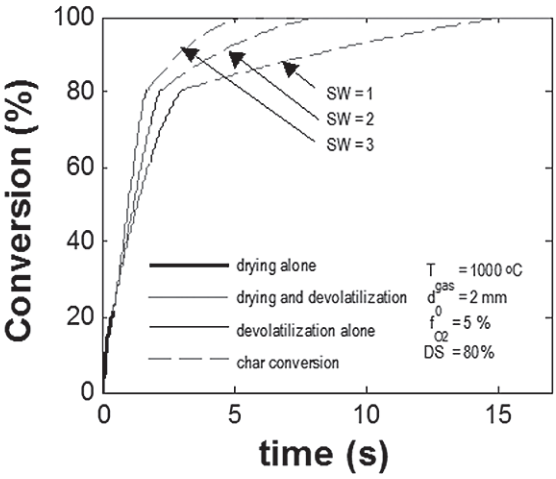
Maria Zevenhoven, Anders Brink, Oskar Karlström, Johan Werkelin, Daniel Lindberg, Luis Bezerra, Peter Backman, Mikko Hupa

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

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

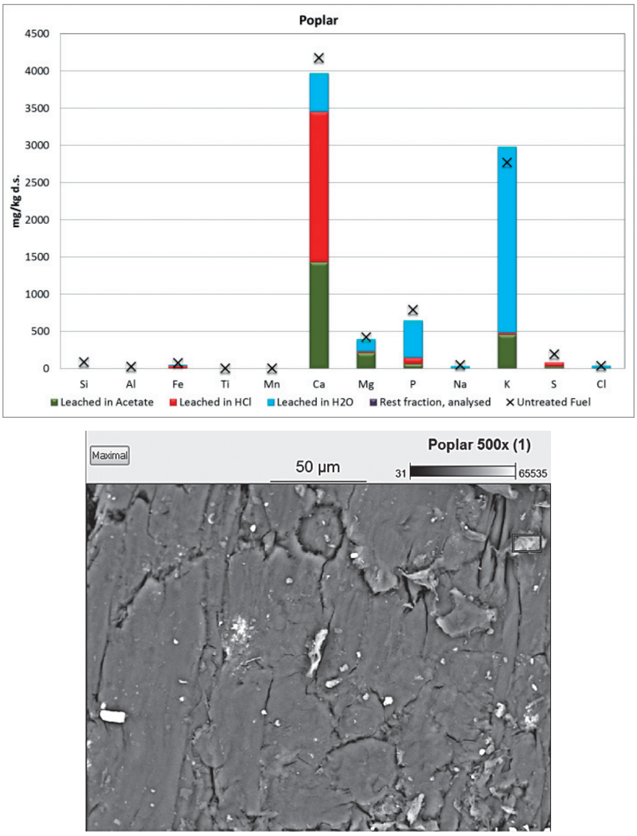
The project is aiming at the development of advanced fuel analysis and characterization methods concerning the combustion of different biomass fuels in various plan technologies of different size ranges. The goal is to provide the basis for an improved understanding of the combustion behaviour and to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

The Single Particle Furnace has been used extensively to obtain relevant input parameters for modeling of both N- and alkali release from biomass fuels



Single Particle Furnace measurements

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



An example of advanced fuel characterisation: Chemical Fractionation results and SEM analyses of poplar

Cooperation:

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

Publications:

- Karlström, O., Brink, A., Hupa, M., Tognotti, L., Multivariable optimization of reaction order and kinetic parameters for high temperature oxidation of 10 bituminous coal chars, *Combustion and Flame* 158 (2011) 10, 1950-1956 (Elsevier/The Combustion Institute, ISSN: 0010-2180)

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

Main funding: Academy of Finland, CNPq, Brazil

Johan Werkelin, Mikko Hupa, Konstantin Gabov, Pedro Fardim

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

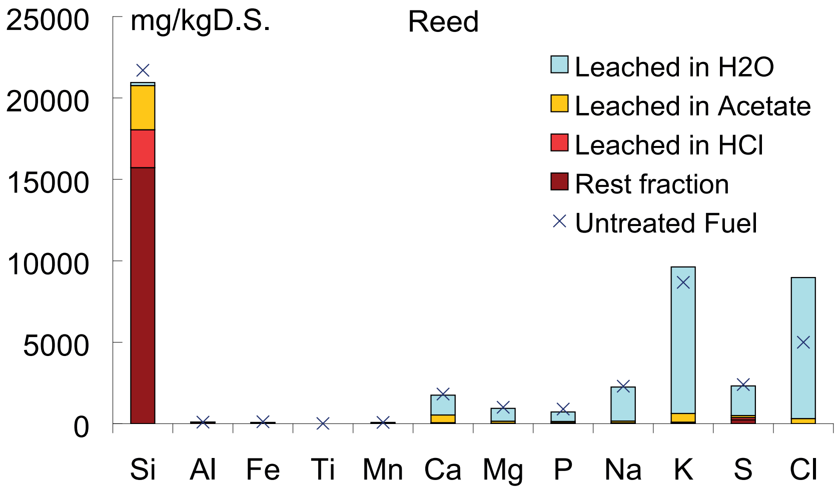
In case of Brazil, the use of sugar cane to produce bioethanol contributes to reduce the country's petroleum dependence. Nowadays 7 million hectares of field is used in Sugar cane farming in Brazil and it is estimated that the area will grow 12% a year over the next five years. In the production of bioethanol,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

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

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

Finnish reed, Brazilian bagasse and birch wood lignin from hydrotropic extraction was analysed by thermal gravimetry (TG) for proximate analysis, chemical fractionation analysis (CFA) for quantification of its ash-forming matter. The samples were further combusted in a single particle reactor (SPR) for quantification of fuel-NO_x and SO_2 formation, and pyrolysed in a wire-mesh reactor (WMR) to quantify the release of some ash-forming elements to the gas phase.

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



Chemical fractionation analysis of Finnish reed

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

Cooperation:

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

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

Main funding: Tekes

Anders Brink, Mikko Hupa

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

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

In this project, ÅAU is responsible for combustion chemistry and emission chemistry. During 2010 soot precursors and NO_x formation have been modelled using conditions typical for Diesel engines with exhaust gas recirculation. Especially recycled NO showed an interesting behaviour. At low temperatures the NO was oxidized to NO_2. Two distinct temperature regimes, where reburning occurred, could also be identified.

Cooperation:
Aalto University School of Chemical Technology; Tampere University of Technology; VTT

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.

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

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

Chemical Thermodynamics of Ash-forming Elements in Biomass Fuels

Main funding: Academy of Finland

Daniel Lindberg

In the present project a thermodynamic database is being developed for the ash-forming elements in biomass fuels. The project focuses 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 mainly cover alkali and alkaline earth salts, with additions of heavy metals such as zinc, lead, and chromium. In particular, the role and chemistry of phosphorus in combustion processes are of primary interest, and the present project sheds 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; Umeå University, Sweden; Aalto University, Finland; VTT, Finland

Future Combustion Engine Power Plant (FCEP)

Main funding: Tekes, Consortium partners

Anders Brink, Mikko Hupa

The objective of the FCEP research program is to ensure that Finnish combustion engine industry can maintain its leading position on global markets. The objective of the program is to support Finnish companies and research institutes through close cooperation to further develop their research facilities, know-how, technologies and products to meet the future market requirements, which are closely connected to the emissions legislations including greenhouse gas emissions. AAU is participating in three out of a total of six work packages. These work packages are WP 1: Advanced Combustion, WP 3: Emission Control and WP 5: Intelligent Automation and Control.

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

COST Action CM901: Detailed Chemical Kinetic Models for Cleaner Combustion

Main funding: EU RTD 7th Framework Programme

Anders Brink, Mikko Hupa

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

WG1: Enlargement of the range of families of initial reactants for which well-validated detailed combustion models are available

WG2: Writing of models of the formation and consumption of oxygenated pollutants

WG3: Improvement of the models for formation of polyaromatic compounds and soot

WG4: Improvement of the methods for mechanism reduction and uncertainty analysis

WG5: Experimental and theoretical determination of thermochemical parameters and rate coefficients for elementary steps crucial for successful simulation, but for which important uncertainties remain

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

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

Main funding: European Commission 7th Framework Programme

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

The RELCOM project (1.12.2011 to 30.11.2015) is designed to undertake a systematic and focused series of applied research, development and demonstration activities involving both experimental studies and combustion modelling work to enable full-scale early demonstration oxyfuel plant to be designed and specified with greater confidence as well as providing improved assessment of the commercial risks and opportunities.

The key tasks within the project are:

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

Cooperation:
University of Glamorgan – Coordinator (UK); Åbo Akademi (Finland); E.ON. New Build & Technology (UK); Technische Universität München (Germany); Electricité de France (France); University of Leeds (UK); Instytut Energetyki (Poland); Universität Stuttgart (Germany); Katholieke Universiteit Leuven (Belgium); Doosan Power Systems

(UK); Enel Ingegneria e Innovazione (Italy); Fundación Ciudad de la Energía (Spain); International Flame Research Foundation (Italy)

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

Main funding: European Commission 7th Framework Programme

Anders Brink, Mikko Hupa, Johan Werkelin

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

PCC is involved in two of the three Joint Research Activities. In addition two facilities for second generation biofuel characterization are offered within the Transnational Access framework. The project period of the BRISK project is 1.10 2011 -30.9 2015.

Cooperation:
Royal Institute of Technology, KTH – Coordinator (Sweden); Åbo Akademi University, Finland; Aston University (United Kingdom); BIOENERGY 2020+ (Austria); Cardiff School of Engineering (United Kingdom); Centre for Research and Technology Hellas (Greece); Danmarks Tekniske Universitet (Denmark); Delft University of Technology (The Netherlands); Energitekniskt Centrum i Piteå (Sweden); Energy Center of the Netherlands (The Netherlands); Fundación Ciudad de la Energia (Spain); INERCO

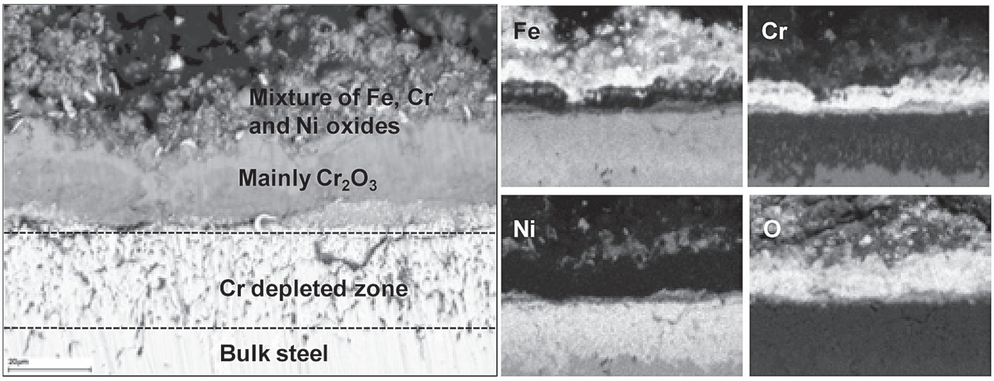
Ingeniería, Tecnología y Consultoría (Spain); International Flame Research Foundation (Italy); Joint Research Centre (The Netherlands); L'Agenzia ENEA (Italy); Norges Teknisk-Naturvitenskapelige Universitet (Norway); PALL Filtersystem (Germany); Paul Scherrer Institute (Switzerland); Stiftelsen for Industriell og Teknisk Forskning (Norway); Technische Universität München (Germany); Technische Universität Wien (Austria); TUBITAK MRC Energy Institute (Turkey); Universidad de Zaragoza (Spain); Università degli Studi di Napoli Federico II (Italy); Wroclaw University of Technology (Poland)

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

Main funding: Tekes

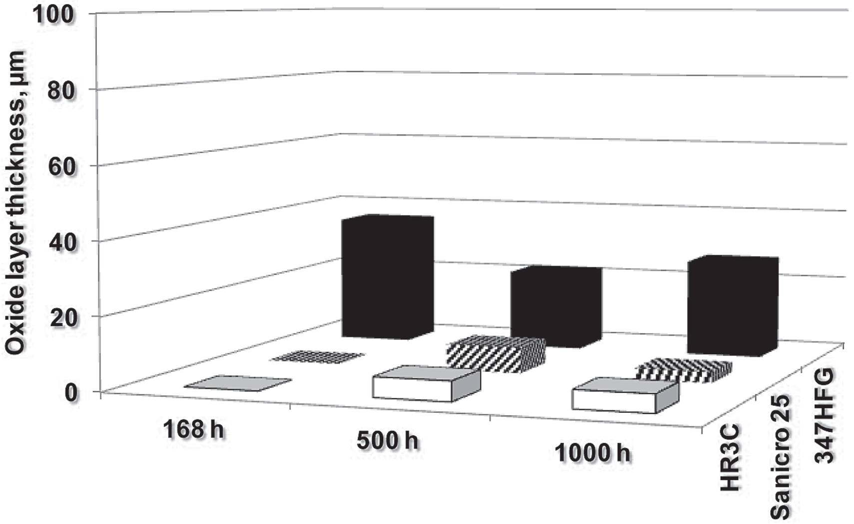
Patrik Yrjas, Dorota Bankiewicz, Mikko Hupa

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



A SEM picture of Sanicro 25 after 168 h exposure with 85CaO-14CaSO$_4$*-1KCl in air at 650°C*

The corrosion results are commonly presented as bar diagrams, and this is also illustrated in the figure below showing the corrosion of three different steels at three different exposure times and 650°C.



Oxide layer thickness after exposures in $60\%CO_2$*-*$30\%H_2O$ *with* $CaCO_3$*-*$CaSO_4$ *at 650°C*

Cooperation:
VTT; Aalto University; Fortum; Foster Wheeler Energia

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

Funding: Swedish Energy Agency, Industry

Patrik Yrjas, Daniel Lindberg, Mikko Hupa

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

Åbo Akademi participates with extensive fuel and additive analyses in combination with thermodynamic equilibrium calculations. The research will be done in close contact with the industrial partners together with SP Technical Research Institute of Sweden, which is the other research organisation in the project.

Cooperation:
Vattenfall; Metso Power; E.ON.; Sandvik Heating Technology; Outokumpu; SP Technical Research Institute of Sweden

Systems Optimization of Manufacturing of Biofuels and Steel in an Integrated Site (SYMBIOSIS)

Main funding: Academy of Finland

Anders Brink, Oskar Karlström, Bingzhi Li, Mikko Hupa

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

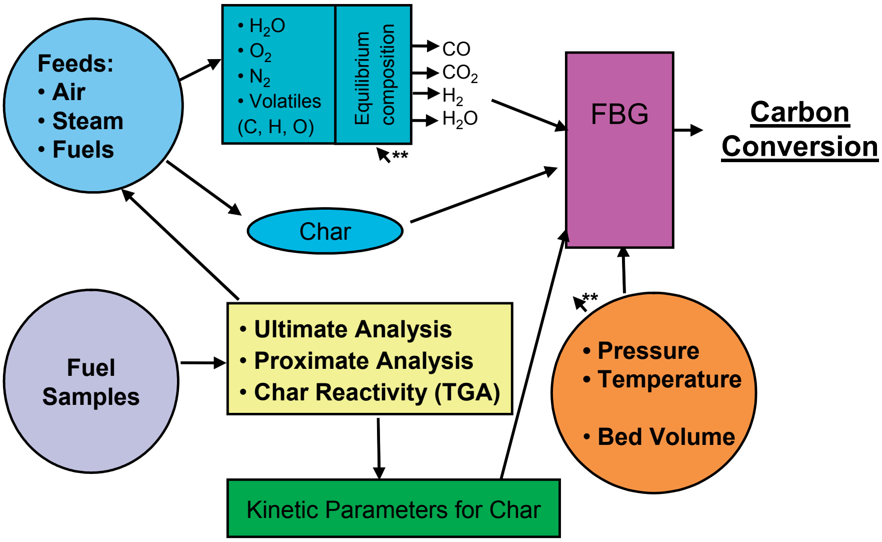
Cooperation:
Åbo Akademi University, Thermal and Flow Engineering

Biofuel Gasifier Feedstock Reactivity – Explaining the Conflicting Results (GASIFREAC)

Main funding: Academy of Finland

Nikolai DeMartini, Maria Zevenhoven, Tooran Khazraie, Mikko Hupa

GASIFREAC started in September, 2010 and is a three-year project. The objective of this project is to do pioneering work on the form and behavior of inorganics during the stages of char formation and conversion and to model the impact of these changes on the gasification kinetics. The rate data will be used as part of the fluidized-bed gasification reactor model “Carbon conversion predictor” (see figure below), to add a predictive capability regarding the effect of fuel ash composition on the gasification kinetics of biomass char.



The principles of the Carbon conversion predictor

The catalytic activity of the ash material in biomass char is significantly reduced towards the end of char gasification. On the basis of literature, the mechanisms are only partially understood and the impact of ash forming elements has not been taken into account in most kinetic models. The experimental work will be carried out in two pressurized TGA to obtain kinetic data at well-defined conditions for kinetic modeling. Interrupted experiments will be carried out to study changes in char morphology that will also impact conversion kinetics. Techniques to be utilized will include chemical fractionation, SEM and other microscopic techniques; and BET. Biomass samples will be gasified as received in addition to being gasified after acid washing and doping with different cations or salts. New carbon conversion parameters and models will be developed to scale up the improved understanding for the purposes of large-scale fluidized bed gasification reactor design needs.

Cooperation:
University of Jyväskylä; VTT Technical Research Centre of Finland

3.8 Intelligent Electroactive Materials

Our research in the field of intelligent electroactive materials is focused on the development and characterization of novel materials and their applications in chemical sensors, membranes, charge storage devices and solar cells. Functional composite materials are being developed from conducting polymers, fullerene, carbon nanotubes and graphene. The materials are combined and tailored to meet specific demands and further engineered into functional devices. These novel materials and devices are characterized by a broad range of electrochemical and spectroscopic methods, as well as surface analysis and imaging techniques. Experimental studies are supported by advanced mathematical modelling.

Recently, graphene oxide was electrochemically incorporated into conducting polymer films in a simple one-step process. The graphene oxide was subsequently reduced to graphene in the conducting polymer matrix, resulting in a conducting polymer-graphene composite. Conducting polymer-fullerene composites were also synthesized in a one-step electrochemical process by utilizing water-soluble complexes between fullerene and sulfonated calixarene. Ordered, hollow, three-dimensional structures of poly(3,4-ethylenedioxythiophene) (PEDOT) were obtained by electrochemical polymerization around well-ordered polystyrene spheres. Composites based on conducting polymers and cellulose beads were also synthesized. Furthermore, electrically conducting inks based on PEDOT doped with poly(styrene sulfonate) (PSS) were developed in order to obtain improved PEDOT:PSS films in terms of conductivity and surface adhesion in aqueous environments. Extensive research is focused also on electropolymerization, thiolation and electrospinning of polyaniline. These materials are extremely interesting for applications in the fields of electrochemical sensors, analytical separations and charge-storage devices.

Lowering of the detection limit of ion-selective electrodes (ISEs) continues to be a significant issue in electroanalytical chemistry. Along these lines, measuring procedures were developed so that ISEs based on solid-state (PbS/Ag_2S) membranes could be successfully applied in direct measurements of ultra-low concentrations of lead (Pb^{2+}) in natural waters. Initial research efforts were also made towards single-use potentiometric sensors.

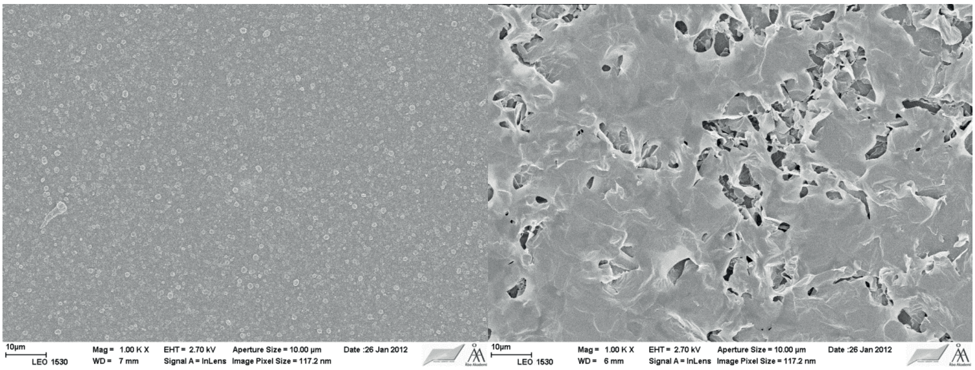
The development of printed enzymatic power supplies was continued and a prototype of a sugar-powered BioBattery consisting of two serially connected cells was successfully produced.

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

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

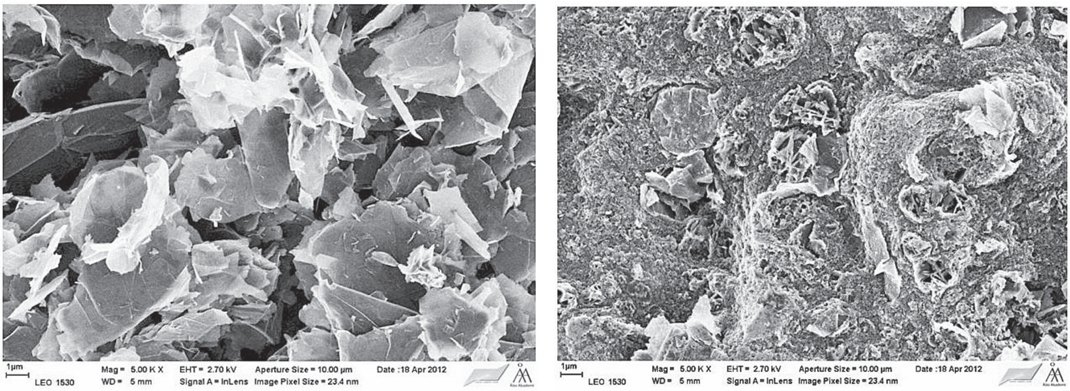
Zhanna Boeva, Tingting Han, Ning He, Rose-Marie Latonen, Tom Lindfors, Grzegorz Lisak, Ulriika Vanamo, Li Niu, Júlia Szücs, Michał Wagner, Hossein Wakili, Anna Österholm, Andrzej Lewenstam, Johan Bobacka, Ari Ivaska

A simple, one-step method for direct electrochemical incorporation of graphene oxide (GO) into conducting polymer films without additional dopants has been developed. The GO solution which is used in this project has a large number of negatively charged oxygen-containing functional groups that can act as counter ions during electropolymerization. The electropolymerization process of poly(3,4-ethylenedioxythiophene) (PEDOT), poly(pyrrole) (PPy), poly(aniline) (PANI) and poly(N-methylaniline) (PNMA) has been investigated. All films exhibited a good and reversible electroactivity. The incorporation of GO was confirmed with cyclic voltammetry, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), Raman, FTIR and X-ray photon spectroscopy (XPS). The reduction of GO to graphene in the PEDOT and PPy films have been carried out electrochemically at a negative anodic potential in 0.1 M KCl. It was verified with XPS that GO is reduced to graphene in the CP matrices.



SEM images of PPy prepared from an aqueous solution of KCl (left) and GO (right)

Chemical synthesis of organic dispersions of electrically conducting polyaniline and graphene has been studied for use in printed devices, supercapacitors and as hydrophobic ion-to-electron transducer materials in all-solid-state solid-contact ion-selective electrodes for ultratrace measurements. The composites were dispersible in N-Methylpyrrolidone (NMP) and fundamental characterization was carried out with scanning electron microscopy (SEM), Raman, FTIR and X-ray photon spectroscopy (XPS), thermo gravimetric analysis (TGA/DTA), cyclic voltammetry and electrical conductivity measurements.



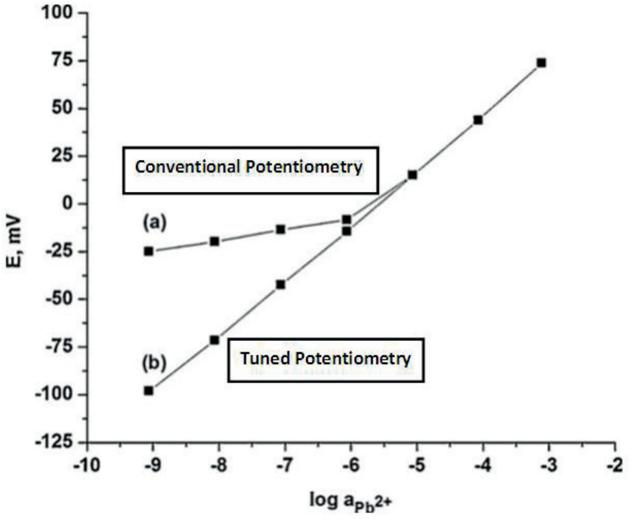
SEM images of pristine graphene (left) and polyaniline-graphene composite (right); magnification: 5000x

The hydrophobicity and high electrochemical stability of polyazulene (PAz) is utilized as new ion-to-electron transducer material to prepare all-solid-state solid-contact ion-selective electrodes (SCISEs) with superior response characteristics for ultratrace measurements. The project has expected to generate valuable knowledge about a new generation of hydrophobic, conditioning- and calibration-free SCISEs with low detection limit and water uptake, and stable response characteristics.

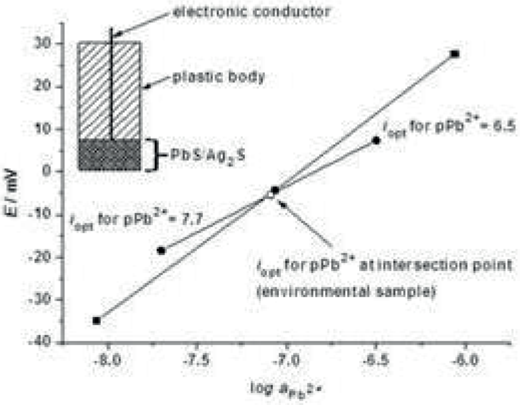
Ordered, hollow, three-dimensional poly(3,4-ethylenedioxythiophene) (PEDOT) structures having high capacitance has been developed for use as ion-to-electron transducer layers in solid-contact ion-selective electrodes (SCISEs). The 3-D structures are prepared by electropolymerization of PEDOT around mono- and multilayers of well-organized spherical polystyrene (PS) particles with the diameter of 750 nm. After dissolving the PS particles in an organic solvent, hollow 3-D structures of PEDOT with high active surface area are formed which have higher capacitance compared to 'normal' non-hollow PEDOT films. In another approach, the hydrophobicity of the PEDOT layer is increased by leaving the embedded PS particles undissolved in the PEDOT matrix. The results of the research will be used in constructing new types of conditioning-free SCISEs with stable response characteristics.

Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) water-based inks were modified with ethylene glycol containing quaternary ammonium salts in order to achieve improved PEDOT:PSS films in terms of conductivity and surface adhesion in aqueous environment. Quaternary ammonium cations were added to crosslink PEDOT:PSS particles in a similar manner as previously achieved in our group by using multivalent cations such as magnesium and calcium. The crosslinking effect results in electrochemically stable PEDOT:PSS films deposited on glassy carbon electrodes in aqueous electrolytes. The deposited PEDOT:PSS films were studied by performing: potential scanning in different water solutions, stability tests and impedance spectroscopy. Additionally, our PEDOT:PSS films were tested as a solid-contact material for ion-selective electrodes. Since, we can freely modify the ink composition to address all the issues with PEDOT:PSS printing we are able to obtain chemical sensors by different printing technologies.

Novel methods of lead(II) determination in various natural waters were developed and tested in synthetic and environmental samples. Fist method, time and concentration dependent conditioning coupled with a recovery of lower detection limit by reversing ion flux from the membrane to the conditioning solution used with solid-contact (polybenzopyrene doped with eriochrome black T coated with PVC-based membrane) ion-selective electrodes. Second method, a tuned galvanostatic polarization used with solid-state (PbS/Ag_2S) crystalline membrane electrodes to lower the detection limit and reliably measure lead in diluted samples. The last one was used in the determination of Pb^{2+} in ground water collected from disused mine in Finnish Archipelago. The results were favourably compared to the analysis perform on the same sample by inductively coupled plasma mass spectrometry and differential pulse anodic stripping voltammetry.



Conventional and tuned potentiometry



Tuned galvanostatic polarization method used with solid-state electrode in determination pf lead(II) in an environmental sample

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Cooperation:

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China; Budapest University of Technology and Economics, Budapest, Hungary; M.V. Lomonosov Moscow State University, Chemistry Department, Division of Polymer Science, Laboratory of Polyelectrolytes and Biopolymers; Åbo Akademi University; Department of Physics, Åbo, Finland, Georgia Institute of Technology, School of Chemistry and Biochemistry; AGH, University of Science and Technology, Kraków, Poland; St. Petersburg State University, St. Petersburg, Russia

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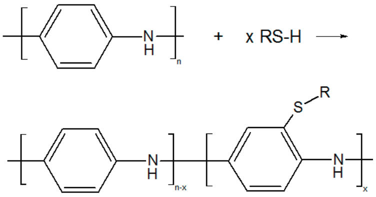
Health Diagnostics with Chemical Sensors

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

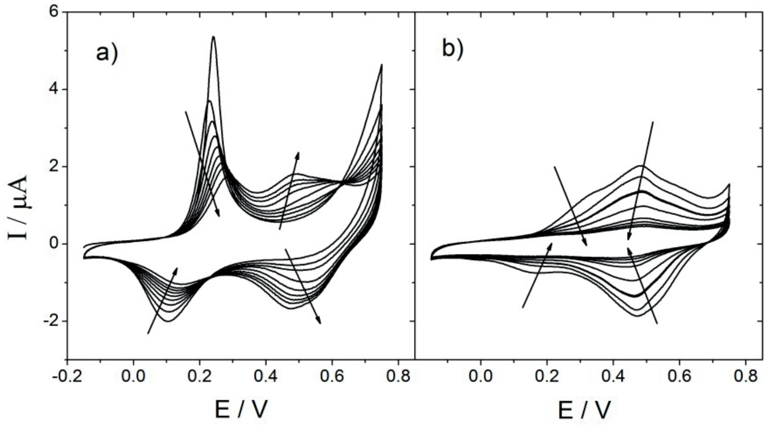
Maija Blomquist, Ulriika Vanamo, Adriana Ferancová, Kalle Levon, Andrzej Lewenstam, Johan Bobacka, Ari Ivaska

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 labeling.

The substrate for probe DNA is a conducting polymer layer on glassy carbon or glass substrate prepared by electrochemical polymerization or by electrospinning. The immobilization of the probe DNA to conducting polymer substrate is done by using thiolation. Shorter thiol compounds are used as spacers to hinder non-specific binding. The first part of the project focuses on the impact of thiolation on conducting polymer, quantitative determination of thiolation on the surface and optimizing of the electrode design. Thiolation changes the electrochemical properties of polyaniline.

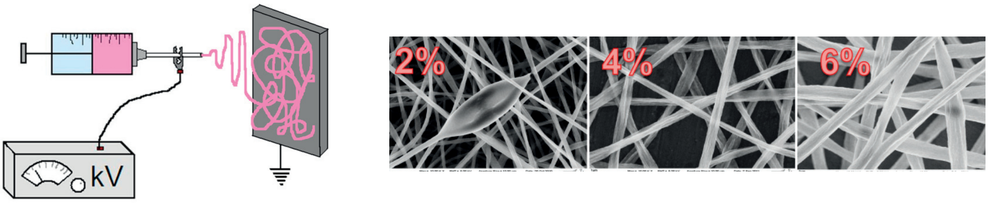


Thiolation scheme of polyaniline



Cyclic voltammogram of polyaniline in a solution of 1.0 M H_2SO_4 and 0.1 M 2-mercaptoethanol. Left: cycles 1 to 10, Right: cycles 11-100 (every 10^{th} scan is shown)

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



Electrospinning: Left: schematic presentation Right: SEM pictures of fibres

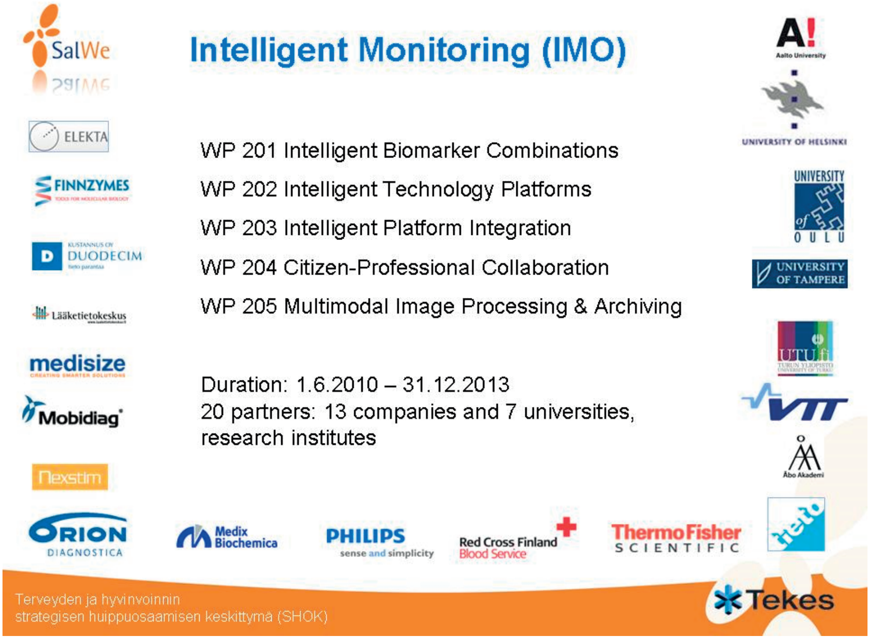
Cooperation:
Polytechnic Institute of New York University; Perkin Elmer, ThermoFisher Scientific, Labmaster Ltd, TYKSLAB, Radiometer

Intelligent Monitoring for Health and Well-being (WP 202 Intelligent Technology Platforms)

Main funding: Tekes (Salwe Ltd, IMO), project partners

Kim Granholm, Zekra Mousavi, Marcin Guzinski, Peter Lingenfelter, Tomasz Sokalski, Johan Bobacka, Andrzej Lewenstam

The goal of this project is to develop novel sensors, and multi-electrode electrochemical platforms, for electrochemical sensing of ions, small metabolites and biomarkers. The main field of application is the clinical and environmental analysis and early warning systems. For such applications electrochemical all-solid-state integrated sensors, e.g. all-solid-state ion-selective electrodes, characterized by a simple construction, low production cost and low power requirements are beneficial.



Intelligent Monitoring (IMO)

WP 201 Intelligent Biomarker Combinations
WP 202 Intelligent Technology Platforms
WP 203 Intelligent Platform Integration
WP 204 Citizen-Professional Collaboration
WP 205 Multimodal Image Processing & Archiving

Duration: 1.6.2010 – 31.12.2013
20 partners: 13 companies and 7 universities, research institutes

Terveyden ja hyvinvoinnin strategisen huippuosaamisen keskittymä (SHOK)

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

Cooperation:
Åbo Akademi University Foundation Research Institute (Johan Gadolin Post-doctoral Fellowships); Academy of Finland; AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Cracow, Poland

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

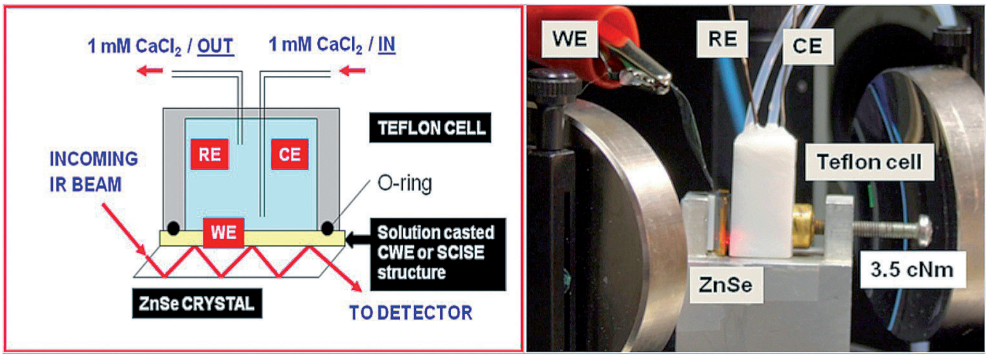
Main funding: Academy of Finland, Graduate School in Chemical Engineering (GSCE), Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM)

Ning He, Jerzy Jasielec, Tom Lindfors, Tomasz Sokalski, Andrzej Lewenstam

Fundamental aspects of the water uptake of both commonly used and new ion-selective membrane (ISM) materials are studied in this project. Its main goal is to develop useful experimental methods to identify membranes with low water uptake, which could be beneficial for ultra-trace analysis with solid-contact ion-selective electrodes (SCISEs). The low water uptake of ISMs will prevent the formation of detrimental water layers (or scattered clusters of water) at the interfaces of the SCISEs. One of the main techniques to study the water is FTIR-ATR spectroscopy due to its ability to distinguish between different types of water in the ISM.

The project has received funding from the Academy of Finland since 1.8.2009 in the form of a 5-year Academy Research Fellowship granted to the research leader of this project (Tom Lindfors). 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 electrodes. This is the first time these three parameters have been successfully measured simultaneously. It is currently studied if there is a correlation between the water uptake and low detection limit of SCISEs. The project has also focused on quantifying the water uptake of plasticized poly(vinyl chloride) (PVC) and silicone rubber (SR) based ISMs with the oven based coulometric Karl Fischer technique.

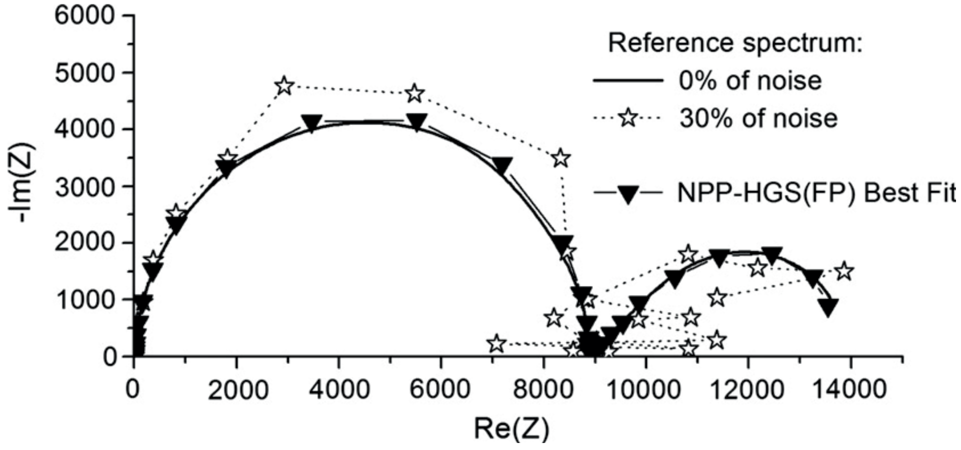
The water uptake of ISMs will also be monitored by fluorescent dyes embedded in thin nanostructured silica substrates. Different types of fluorescent water sensitive dyes are used for monitoring the water uptake of plasticized PVC and SR based ISMs. The distribution of water transported through the ISMs is monitored by measuring the changes in the intensity of the fluorescence signal at the substrate/ISM interface, thus mimicking the water uptake of SCISEs. It was recently shown that low water content at the substrate/ISM interface correlated with superior potential stability of SR based SCISEs. It is therefore crucial to use materials with low water uptake in the fabrication of SCISEs. The ingenious experimental approach introduced in this sub-project makes it possible to monitor the time-dependent distribution of water at the substrate/ISM interface and to identify if water forms an aqueous layer or minor/major isolated pools of water at this interface. The fundamental research carried out in this project will later be very useful for understanding the response characteristics of SCISEs and to construct electrodes with good long-term stability.



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.

The Nernst–Planck–Poisson (NPP) model is used to numerically simulate electrochemical impedance spectra (EIS) of ion-selective electrodes (ISEs). By using the Hierarchical Genetic Strategy with real number encoding (HGS(FP)) the reverse problem is solved. The NPP–HGS(FP) method allows estimation of physicochemical parameters of ISEs with plastic membranes, which is illustrated here by using NPP–HGS(FP) for obtaining the values of the diffusion coefficients of ions in the ISE membrane phase.

The NPP–HGS(FP) method allows calculation of the most accurate solution of the inverse problem and can be effectively used to facilitate the process of finding the parameters for optimal ISE performance.



The results of NPP–HGS(FP) compared with the reference spectrum with 30% of noise.

The method presented here not only allows for interpretation of the EIS spectra but also for accounting for the mechanism of the processes occurring at the interface in terms of physicoelectrochemically valid concepts.

Cooperation:

Budapest University of Technology and Economics, Budapest, Hungary; Åbo Akademi University, Laboratory of Physical Chemistry, Finland; AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Cracow, Poland; Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM); Åbo Akademi Foundation Research Institute

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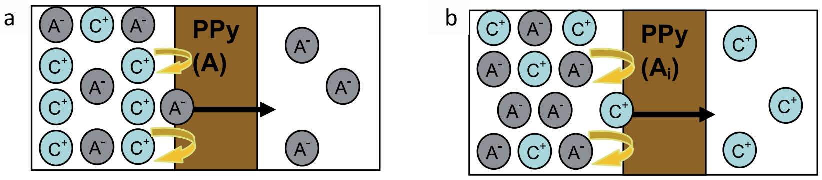
Electroactive Membranes for Separation of Metal Ions

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

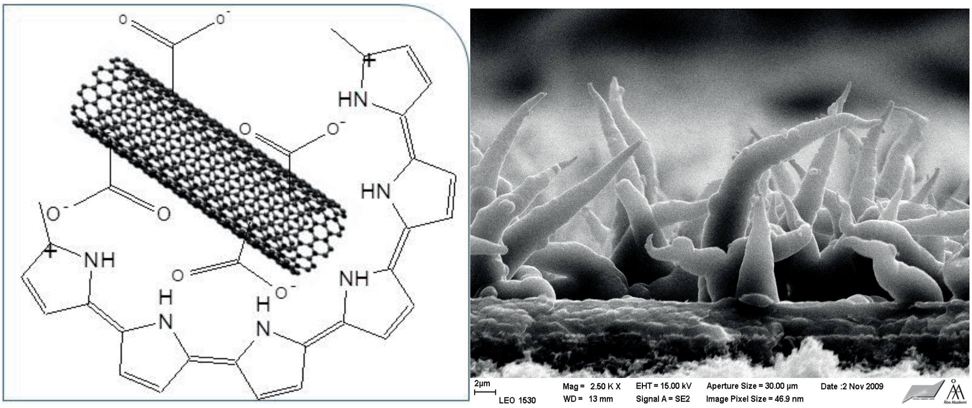
Marceline Akieh, Rose-Marie Latonen, Jesús Arroyo Condori, Jiayi Huang, Ari Ivaska, Johan Bobacka



$$PPy^+A^- + e^- \rightleftharpoons PPy^0 + A^- \qquad PPy^+A_i^- + e^- + C^+ \rightleftharpoons PPy^0A_i^-C^+$$

Polypyrrole membranes for separation of anions and cations. A is a mobile anion and A_i an immobile anion.

Conducting polymer membranes can be used in the separation of metals from aqueous solution. Cation exchange properties of conducting polymer can be induced by doping the polymer with a bulky size anion. Conducting polymers and carbon nanotubes (CNTs) have unique and interesting electrochemical properties, and it has been shown that combining both materials gives composites that synergistically unite their individual characteristics. A polypyrrole doped with acid-treated multi-walled carbon nanotubes, PPy(CNT), composite membrane has been prepared and the permeability towards metal (toxic) ions only when electrochemically stimulated have been studied. The performance of this composite membrane is compared to that of PPy doped with para-toluene sulphonate (PPy(pTS)).



Left: Polypyrrole doped with acid-treated MWCNTs. Right: SEM image of the PPy(pTS) membrane

Cooperation:

University of Wollongong, Australia

Publications:

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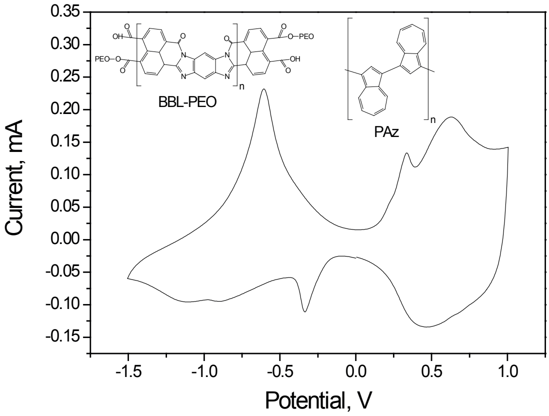
Electroactive Materials for Optical & Photovoltaic Devices – Ordered Structures of Organic Electronic Materials

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, Michał Wagner, Zhe Yang, Kai Yu, Anna Österholm, Ari Ivaska

New electrosynthetic routes have been established for the production of n- and p-dopable conducting polymers. The focus has been on synthesis of n-type semiconducting polymers. A new n-type water dispersible poly(benzimidazobenzo-phenanthroline) (BBL) functionalized with poly(ethyleneoxide) (PEO) side-chains have been studied. The effect of side-chain length of four BBL-PEO films with varying PEO length has been investigated. 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 and the formed PBP films 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. The development of electron transfer layers and their connection to the electrodes in the solar cell has also been a central issue in this project. Poly(3,4-ethylenedioxythiophene) (PEDOT) and ZnO nanoparticles have been studied as electron transfer layers on alumina.

As one step further in development of materials for use in solar cells, different type of donor-acceptor material combinations have been studied. Composite layers 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 nanostructured TiO_2 as the electron acceptor and PAz as the electron donor have been studied. Furthermore, organic donor-acceptor materials composed of PEDOT or PAz functioning as electron donors has been combined with the electron accepting BBL-PEO in a composite structure. In the future BBL-PEO will be studied in combination with nanoporous PAz made by template assisted polymerization. The new conducting polymer films and donor-acceptor composites studied in this project have been characterized by a large variety of analysis techniques: cyclic voltammetry, *in situ* UV-vis spectroelectrochemistry, both *ex situ* and *in situ* FTIR spectroscopy, Raman and XRD spectroscopy, impedance spectroscopy, Electron Spectroscopy for Chemical Analysis (ESCA) and Scanning Electron Microscopy.



A cyclic voltammogram of BBL-PEO/PAz composite in $TBAPF_6$-acetonitrile electrolyte solution (50 mV/s). Insets: the structure of BBL-PEO and PAz

Cooperation:

Laboratory of Materials Chemistry and Chemical Analysis, University of Turku; Tampere University of Technology; University of Helsinki; Rautaruukki; KSV Instruments, Systems Biology Worldwide

Publications:

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Printed Enzymatic Power Supplies with Embedded Capacitor on Next Generation Devices (PEPSecond)

Main funding: Tekes

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

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

Optimization of cell components and manufacturing methods will further be conducted to allow for R2R manufacturing with a minimum of separate steps required. Interfacing of the BioBattery with potential applications is currently being investigated, and suitable simple electronic interfaces are being tested. The complexity of the interface is strongly dependent on the point of use, and hence two alternatives of different nature are realized.

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.

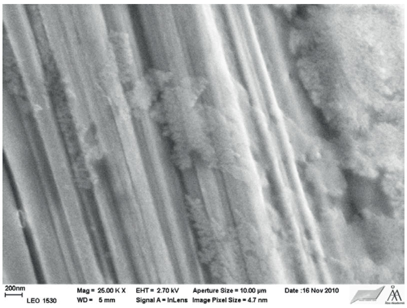
Cooperation:

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

Publications:

- Wang, X., Latonen, R-M., Sjöberg-Eerola, P., Eriksson, J-E., Bobacka, J., Boer, H., Bergelin, M., Direct electron transfer of Trametes hirsuta laccase in a dual-layer-architecture of poly(3,4-ethylenedioxythiophene) films, *Journal of Physical Chemistry C* 84 (2011) 13, 5919-5929 (ACS Publications, ISSN: 1932-7447)

- Wang, X., Sjöberg-Eerola, P., Immonen, K., Bobacka, J., Bergelin, M., Immobilization of *Trametes hirsuta laccase* into poly(3,4-ethylenedioxythiophene) and polyaniline polymer-matrices, *Journal of Power Sources* 196 (2011) 11, 4957-4964 (Elsevier, ISSN: 0378-7753)



SEM image of GOx enzyme clusters immobilized on Carbon fibers

BioBattery Prototype consisting of two serially connected cells

Pressurized PEM Electrolyzer (Primolyzer)

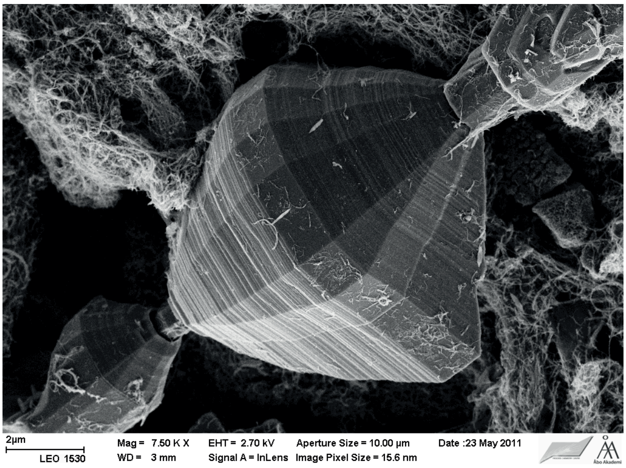
Main funding: EU

Mikael Bergelin, Max Johansson, Mikko Hupa

The primary objective of the PrimoLyzer project is to develop, construct, and test a cost-minimised highly efficient and durable PEM-Electrolyzer stack aimed for integration with µCHP technology. The research tasks within the project have concentrated around developing mixed metal oxide (MMO) anode catalyst and CNT supported PtPd cathode catalyst facilitating MEA performance of 1.2 A/cm^2 at 1.64 V_{DC} and extrapolated durability of 20,000 h. The performance target for the anode catalyst is 1.2 A/cm^2 at 1.45 V (RHE) with a loading of 1.0 mg/cm^2 and for the cathode catalyst 1.2 A/cm^2 at – 40 mV (RHE) with a noble metal loading of 0.5 mg/cm^2. At ÅA/PCC nanostructured IrO_2 and different binary $Ir_xRu_yO_z$ MMO catalysts manufactured by VTT have been characterized by TGA, SEM and cyclic voltammetry in 0.5 M $H_2SO_{4.}$ The oxygen evolution reaction (OER) onset potential and the limiting current have been studied in a potential window of 1.0-2.5 V (RHE). The OER onset data showed that the activity of IrO_2 prepared by Adams fusion are close to the commercial reference and the activity increases with increasing amount of Ru in the mixed oxides. The catalysts prepared by FSP are less active but show similar trend in Ru content. The limiting current measurements show an opposite trend in Ru content: the more Ru the lower the limiting current. Once more, the FSP catalysts are less active than those prepared by the Adams method. The superior performance of $IrRu_3O_8$ catalyst has been verified at MEA level.

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

Cooperation:
IRD (Denmark); ECN (The Netherlands); VTT; ÅA-PCC; Fumatech, Germany; Hynergreen, Spain



SEM image of Pt particles on graphitized MWCNT support

3.9 Functional Inorganic Materials

The main topics of our materials research have been characterization and improving the understanding of the chemical durability and 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 and stimulate tissue regeneration in medical applications. In body the bioactive glass partly dissolves and forms a superficial layer of silica and hydroxyapatite that bonds the glass chemically to bone. The ionic dissolution products induce growth of novel tissue support also vascularization of the neotissue. In addition, the ionic dissolution products may have antibacterial properties. Today, many of the applications of bioactive and biocompatible glasses studied deal with their uses as porous scaffolds and thin fibres often combined with bio-stable and biodegradable polymers. Accordingly, the interactions between the materials in the composites are of utmost importance for desired function of the composite in the body. We have studied the mechanisms of glass dissolution and layer formation on glasses and composites to get a more comprehensive knowledge of all parameters affecting bioactivity and biodegradability of glasses. Our research efforts included also defining the crystallization characteristics of glasses. This information is essential when sintering porous scaffolds from powdered fractions or drawing continuous glass fibres from melt.

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 ceramics. Effort has been put to find out suitable procedures and methods to measure the thin surface films accurately. We have compared different characterization methods to measure nanoparticles deposited on surfaces via 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 and ceramic refractory qualities. For detailed understanding of the corrosion mechanisms we have especially focused on the role of partial melting of the salt deposit on its corrosive properties. 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.

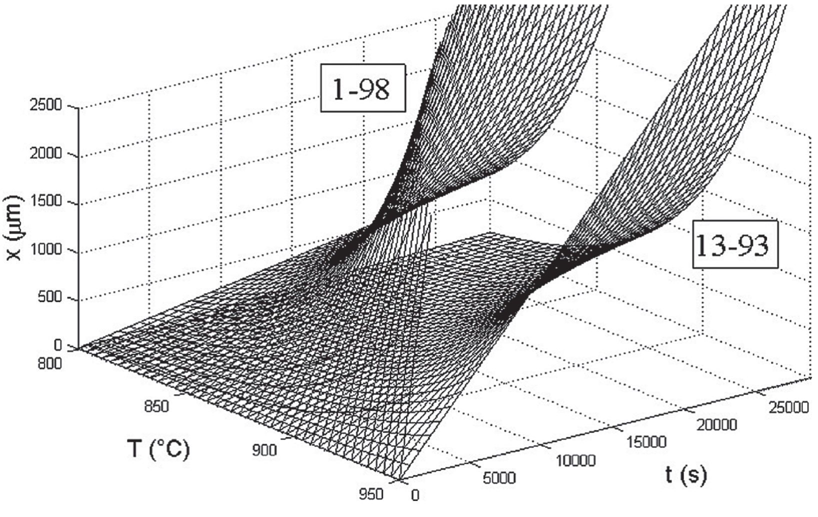
Bioactive Glasses and Their Properties

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

Leena Hupa, Jonathan Massera, Zhang Di, Susanne Fagerlund, Leena Varila, Camilla Molin, Mizhang Zhao, Chao Gao, Paul Ek, Mikko Hupa

The main goal of our bioactive glass research is to characterize the influence of glass composition on various surface properties and bulk properties of glasses. The dissolution kinetics of the glasses in vitro and was one of the main research areas. The dissolution was measured in pure water and buffered solutions using different flow rates at different temperatures. The results are of importance for the behaviour of the glass at the moment of implantation and but five also fundamental information of the dissolution rate of the glasses in aqueous solutions. The results can be used to compare the anticipated behaviour of novel bioactive glasses. Ideally, the glass should dissolve gradually with a rate that matches the growth rate of new tissue.

We also continued to measure the thermal properties of the glasses. Our goal was to get detailed information on the crystallization tendency of the glasses in manufacturing porous implants by sintering of crushed glass or drawing continuous glass fibres. The crystal growth rate as functions of temperature and time for thermal treatments of glasses 13-93 and 1-98 are shown in the figure below. Both glasses allow thermal treatments but clear differences in the crystal growth rate can be seen between the two glass compositions.



Crystal growth as a function of time and temperature for glasses 13-93 and 1-98 during thermal treatments

Cooperation:

University of Turku (Orthopaedics and Traumatology, Dentistry); University of Erlangen-Nuremberg, Germany; École Nationale Supérieure de Chimie de Rennes, Rennes, France; Lehigh University, US ; Vivoxid

Publications:

- Keränen, P., Moritz, N., Alm, J.J., Ylänen, H., Kommonen, B., Aro, H. T. Bioactive glass microspheres as osteopromotive inlays in macrotextured surfaces of Ti and CoCr alloy bone implants: trapezoidal surface grooves without inlay most efficient in resisting torsional forces, *Journal of the Mechanical Behavior of Biomedical Materials* 4 (2011) 7, 1483-1491 (Elsevier Ltd, ISSN: 1751-6161)
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Surface Coatings on Ceramics and Glasses

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

Leena Hupa, Minna Piispanen, Jonathan Massera

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

Cooperation:

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

Publications:

- Piispanen, M., Hupa, L., Comparison of self-cleaning properties of three titania coatings on float glass, *Applied Surface Science* 258 (2011) 3, 1126-1131 (Elsevier B.V, ISSN: 0169-4332)
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4. Publications 2011

4.1 Theses

4.1.1 Doctoral theses (10)

Enestam, Sonja, Corrosivity of hot flue gases in the fluidized bed combustion of recovered waste wood

Eta, Valerie Ayamba, Catalytic synthesis of dimethylcarbonate from carbon dioxide and methanol

Granholm, Kim, Sorption/desorption reactions of metal ions with pulp

Jogunola, Olatunde Zambakiu, Reaction intensification of formic acid production

Kusema, Bright T., Catalytic transformation of arabinogalactan its oligomers and monomers into valuable chemicals

Käldström, Mats, Cellulose valorization by heterogeneous catalysis

Piispanen, Minna, Characterization of functional coatings on ceramic surfaces

Tokareva, Elena, Spatial distribution of components in wood by ToF-SIMS

Vainikka, Pasi, Occurrence of bromine in fluidised bed combustion of solid recovered fuel

Österholm, Anna, Electronic and structural properties of polyazulene materials: an in situ spectroelectrochemical investigation

4.1.2 Licentiate theses (1)

Lindholm, Johan, On experimental techniques for testing flame retardants in polymers

4.1.3 Master's theses (11)

Alanko, Tiina, Bränsleegenskaper hos fyra energigräs

Arroyo Condori, Jesús, Enantiometric separation using chiral conducting polymer membranes

Huang, Jiayi, Electrochemically controlled membranes based on PEDOT for the transport of ions

Korotkova, Ekaterina, Intensification of galactoglucomannan hot-water extraction from Norway spruce

Lu, Xiomin, Effects of metal ions and wood pitch on retention and paper properties

Rasela, Sina, Extraction and chemical characterisation of pine bark

Solana Marañón, Marta, CO_2 absorption and desorption with switchable solvents

Sui, Jinxing, Glucose oxidase enzyme based bioanodes - an investigation of the effect of immobilization strategy on the glucose oxidation activity

Trybus, Katarzyna, A chemical analysis of the contents of metals in the soil profile of the Slovak Tatra mountains

Varila, Leena, Reactions of bioactive glasses and their composites in aqueous solutions

Zhang, Biao, Preparation and characterization of zeolite catalysts based on microreactor elements

4.2 Publications

4.2.1 Articles in refereed international scientific journals and series (120)

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4. Akieh, M., Varga, Á., Latonen, R-M., Ralph, S., Bobacka, J., Ivaska, A., Simultaneous monitoring of the transport of anions and cations across polypyrrole based composite membranes, *Electrochimica Acta* 56 (2011) 10, 3507-3515 (Pergamon-Elsevier, ISSN: 0013-4686)

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10. Bao, Y., Song, J., Mao, Y., Han, D., Yang, F., Niu, L., Ivaska, A., Graphene oxide-templated polyaniline microsheets toward simultaneous electrochemical determination of DA/AA/UA, *Electroanalysis 23* (2011) 4, 878-884 (John Wiley & Sons, ISSN: 1040-0397)

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sorbents by sulphuric acid treatment of spruce sawdust, *Khimiya rastitelnogo syrya (Chemistry of Plant Raw Materials)* 4 (2011), 33-38 (Barnaul, ISSN: 1029-5151)

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4.4 Edited Conference Proceeding and Reports (6)

Aldea, S., Snåre, M., Eränen, K., Mikkola, J-P., Murzin, D.Yu., Salmi, T., Process intensification for nano-calcium carbonate production, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering,* 2011

Anghelescu-Hakala, A., Asikainen, J., Auer, M., Harlin, A., Haavisto, S., Hartman, J., Heikkilä, M., Heikkinen, S., Hyvärinen, S., Kataja-Aho, J., Kilpeläinen, P., Kisonen, V., Mehtiö, T., Mänttäri, M., Pajari, H., Richard, P., Rautkoski, H., Ropponen, J., Setälä, H., Sievänen, J., Spetz, P., Tenkanen, M., Tiitola, P., Vuoti, S., Vähä-Nissi, M., Willför, S., *FuBio: Theme 3 Final Report 1.3.2009-31.3.2011* (ed. A-L Kokko), Forest Cluster Ltd, Espoo, Finland, 2011, 72 pp.

Bobacka, J., *9th Spring Meeting of the International Society of Electrochemistry. Electrochemical Sensors: From nanoscale engineering to industrial applications,* May 8-11, 2011, Turku, Finland, Book of Abstracts, International Society of Electrochemistry

Ljung, M. (ed.), *Graduate School in Chemical Engineering Yearbook 2011,* Åbo Akademi University 2011, ISSN: 1238-2647, Uniprint, Åbo, Finland, 2011

Ljung, M., Brink, A., Latonen, R-M., Mäki-Arvela, P., Sundberg, A. (eds.), *Åbo Akademi Process Chemistry Centre Annual Report 2010-2011,* Åbo Akademi University 2011, ISSN: 1459-8213, Newprint, Loimaa, Finland, 2011

Salmi T., Murzin, D., Wärnå, J. (eds.), *Catalysis in Multiphase Reactors (CAMURE-8) & International Symposium on Multifunctional Reactors (ISMR-7),* May 22-25, 2011, Naantali, Finland, Book of Abstracts, ISBN: 978-952-12-2586-4

4.5 General articles (in newspapers etc.) (16)

En visit till Università degli studi di Padova, *Meddelanden från Åbo Akademi* 1 (2011), ISSN: 0359-8632, Tapio Salmi

FKS firade sitt 120-årsjubileum, *Kemia – Kemi* 7 (2011), 64, ISSN: 0355-1628

Förnyelsebara äventyr - vår framtid?, *Umevatoriet* (2011), March 17, Jyri-Pekka Mikkola

Internationell kemiingenjörskonferens i Nådendal blev en succé, *Meddelanden från Åbo Akademi* 12 (2011), 18-19, ISSN: 0359-8632, Tapio Salmi

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Kemipris till ÅA-professor (T. Salmi), *Meddelanden från Åbo Akademi* 6 (2011), 11, ISSN: 0359-8632

Kolme uranuurtajaa palkittiin (P. Simula, A.O.K. Nieminen, T. Salmi), *Kemia – Kemi* 3 (2011), 54-55, ISSN: 0355-1628

Guldets glimt, *Åbo Underrättelser* (January 2011), ISSN: 0785-398X, Tapio Salmi

Magnus Ehrnroothin säätiön kemian palkinto 2011 akatemiaprofessori Tapio Salmelle, Åbo Akademi, *Sphinx, The yearbook of Societas Scientiarum Fennica* (2011), ISSN: 0783-5892

Puusta voisi lypsää maitoa märehtijöiden avulla, *Maaseudun tulevaisuus,* Liite 3/2011, 24.10.2011 (2011), 16, Marketta Rinne, Kaisa Kuoppala, Riitta Sormunen-Cristian, Erkki Joki-Tokola, Stefan Willför

Woody biomass catalytic pyrolysis research at Åbo Akademi University, *Pyrolysis Network Newsletter* 29 (2011), ISSN: 2040-2759, Atte Aho

Yliopisto takaisin yliopistoksi, *Acatiimi* 29 (2011), 36-37, ISSN: 1455-1608, Tapio Salmi

ÅA samarbetar med Indien kring biobränslen, *Åbo Underrättelser* (2011), ISSN: 0785-398X, Jyri-Pekka Mikkola

Åbo Akademi palkitsi kemistejä, *Kemia – Kemi* 6 (2011), 60, ISSN: 0355-1628

4.6 Patents and invention disclosures (4)

Konkol, Y., Bernoulli, J., Vuorikoski, H., Halleen, J., Pranovich, A., Holmbom, B., Water-soluble polysaccharides extracted from wood of coniferous tree species in the treatment and/or prevention of prostatic diseases and lower-urinary-tract symptoms (2011)

Korpinen, R., Ilvesniemi, H., Kitunen, V., Willför, S., Pranovich, A., Behandling av biomassor med alkalisk och trycksatt genomflödesextraktion (2011)

Vähäsalo, L., Pulse assisted dispersion field flow fractionator (2011)

Willför, S., Bergelin, M., Pranovich, A., Eriksson, J-E., Johansson, M., Bobacka, J., The use of hot-water extracted water soluble sulphur-free lignin as corrosion inhibitor of copper in chloride rich acidic environments (2011)

4.7 Awards granted in 2011 (6)

Grénman, Henrik, Harry Elving Prize, best doctoral thesis at Åbo Akademi, Åbo Akademi University 2011

Hupa, Mikko, member of Academia Scientiarum Fennica

Mäki-Arvela, Päivi, Riddartecknet av Finlands Vita Ros orden

Retulainen, E., Salminen, K., Lindqvist, H., Oksanen, A., Sundberg, A., Improving the wet strength and runnability, Jasper Mardon Memorial Prize for significant contribution to the science and technology of papermaking, Best Conference Paper, *65th Appita Annual Conference*, April 10-13, 2011, Rotorua, New Zealand

Salmi, Tapio, Magnus Ehrnrooth Prize for research in chemistry, physics and mathematics, Societas Scientiarum Fennica – Finnish Society of Science and Letters 2011

Werkelin, Johan, Harry Elving Prize, teacher's prize, Åbo Akademi University 2011

5. Courses 2011

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

Chemical Thermodynamics in Furnaces

Course Supervisor: Mikko Hupa
Course Coordinator: Daniel Lindberg
Time: January-February
Place: Åbo Akademi University
Cooperation: Graduate School in Chemical Engineering (GSCE)
Fund for the Association of Finnish Steel and Metal Producers
Lecturers: Daniel Lindberg
Mikko Hupa
Gunnar Eriksson, GTT-Technologies, Aachen
Rainer Backman, Umeå University
Pertti Koukkari, VTT
Pekka Taskinen, Aalto University
Patrice Chartrand, Ecole Polytechnique de Montréal
Dan Boström, Umeå University
Sonja Enestam, Metso Power
Iina Vaajamo, Aalto University
Ville-Valtteri Visuri, University of Oulu

Computer-aided Chemical Reaction Engineering

Course Supervisor: Tapio Salmi
Time: April
Place: Åbo Akademi University
Cooperation: Graduate School in Chemical Engineering (GSCE)
Lecturers: Paolo Canu, University of Padova
Heikki Haario, Lappeenranta University of Technology
Tapio Salmi
Johan Wärnå
Andreas Bernas
Henrik Grénman

Chemistry in Combustion Processes I

Course Supervisor: Mikko Hupa
Course Coordinator: Markus Engblom
Time: October-November
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

Modern Analytical Tools for Pulp and Paper

Course Supervisors: Stefan Willför, Anna Sundberg
Course Coordinator: Ekaterina Korotkova
Time: November-December
Place: Åbo Akademi University
Cooperation: International Doctoral Programme in Bioproducts Technology (PAPSAT)
Lecturers: Stefan Willför
Anna Sundberg
Eija Bergelin, Nab Labs
Karin Fackler, Vienna University of Technology
Chunlin Xu, ÅA/KTH
Andrey Pranovich
Elena Tokareva
Lari Vähäsalo
Anna-Stina Jääskeläinen, VTT
Ari Ivaska
Patrik Eklund

Chemical Kinetics

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

6. Other Activities 2011

6.1 Organization of Conferences, Courses and Seminars

February

Turku, Finland, Process Chemistry Centre Winter Colloquium, 90

Turku, Finland, 40 Years of Inorganic Chemistry at Åbo Akademi University – Jubilee Seminar, 100

May

Naantali, Finland, Catalysis in Multiphase Reactors CAMURE-8 & International Symposium on Multifunctional Reactors ISMR-7, 160

Turku, Finland, 9th Spring Meeting of the International Society of Electrochemistry (ISE), 230

Turku, Finland, ERANET ScitoBiCom semiannual meeting, 30

Oulu, Finland, Graduate School in Chemical Engineering Spring Seminar (GSCE), 35

June

Turku, Finland, International Flame Research Foundation (IFRF) Joint Committee Meeting

August

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

November

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

6.2 Participation in Conferences, Major Meetings and Courses

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

January

Baltimore, USA, 25th International forum for Process Analytical Technology (IF-PAC-2011), invited lecture, *Ari Ivaska*

Espoo, Finland, National selection committee of students to technical sciences, chairman, *Tapio Salmi*

Oulu, Finland, University of Oulu, Department of Process and Environmental Engineering, guest lecture, *Tapio Salmi*

Paris, France, Beet Pulp final meeting, 1

Paris, France, COST FP0901 Characterisation of raw biomass and processed materials for biorefinery, bioenergy and biofuels production, Chairman, *Stefan Willför*, 1

Piteå, Sweden, Swedish-Finnish Flame Days, 3

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

Turku, Finland, ÅA/CLL Kemin söker nya vägar – tillbaka till naturen (invited lecture), *Bjarne Holmbom*

Turku, Finland, ÅA/CLL Puusta pitemmälle (invited lecture), *Bjarne Holmbom*

Utrecht, Netherlands, COST-meeting, Utilization of Biomass for Sustainable Fuels and Chemicals, *Tapio Salmi*

February

Dresden, Germany, TU Dresden, Symposium in honour of Prof. Dr. Dr.habil. *Ruediger Lange*, invited lecture, *Tapio Salmi*

Kokkola, Finland, Nanomaterials in Catalysis, KETEK, invited lecture, *Tapio Salmi*

Paris, France, Dean's convention on the technical education in Europe, *Päivi Mäki-Arvela*

Tirichirappalli, India, International workshop on design and operating experience of coal/lignite/pet coke in large utility circulating fluidized bed combustion boilers, *Mikko Hupa*

Zaragoza, Spain, European Winter Conference of Plasma Spectroscopy, 1

March

Anaheim, CA, USA, 241st ACS National Meeting & Exposition, The Anselme Payen Award Symposium: Polysaccharides for Sustainable Chemistry, invited lecturer, *Stefan Willför*

Espoo, Finland, Biofuels: Production, Properties and Use, invited lecturer, *Mikko Hupa*

Espoo, Finland, Finnish Flame Research Committee Annual Meeting, *Anders Brink*

Gliwice, Poland, Clean Industrial Fuel Utilization, International Flame Research Foundation, 1

Helsinki, Finland, Catalysis – From Theory to Industrial Applications, Finnish Catalysis Society, invited speaker, *Dmitry Murzin*, organizer, *Päivi Mäki-Arvela,* 2

Helsinki, Finland, Coal Combustion Products Workshop, European Chemicals Agency REACH, *Mikko Hupa*

Moscow, Russia, Conference: Experience and results of investigations, performed under leadership of invited scientists from diaspora, invited lecturer, *Dmitry Murzin*

Stockholm, Sweden, 3rd Nordic Wood Biorefinery Conference, Program Advisory Group member, *Bjarne Holmbom*, 4

Stockholm, Sweden, Forest Cluster – Innventia Seminar, Science, creativity and innovations, invited lecture, *Bjarne Holmbom*

Trois Rivières, Quebec, Canada, Quebec Wood Export Bureau Seminar, invited lecturer, *Bjarne Holmbom*

Turku, Finland, Microfabrication technology, Annual Seminar, Koneteknologiakeskus, 1

Turku, Finland, Graduate School of Materials Research Seminar, 3

Zagreb, Croatia, XXII Conference of Croatian Chemists and Chemical Engineers, plenary, *Dmitry Murzin*

April

Espoo, Finland, Aalto University, Biorefinery Lecture Series, invited lecturer, *Bjarne Holmbom*

Espoo, Finland, Forest Cluster Graduate School Bioeconomy Seminar, invited lecturer, *Stefan Willför*

Helsinki, Finland, CLEEN Summit Meeting and Annual Meeting, 2

Palermo, Italy, Polycat EU project meeting, *Heidi Bernas*

St. Petersburg, Russia, Russian Chemical Society in St Petersburg, invited lecturer, *Andrey Pranovich*

May

Amsterdam, the Netherlands, Colloids and Materials 2011, 1

Awaji, Japan, Shikata Discussion 2011, International Symposium on Electroanalytical Chemistry, invited lecture, *Ari Ivaska*

Budapest, Hungary, COST 543 Event, invited lectures, *Tapio Salmi, J-P. Mikkola*

Cincinnati, OH, USA, PaperCon Conference, 1

Firenze, Italy, AIDIC Conference, chairman *Tapio Salmi*, members of scientific committee, *J-P. Mikkola, Sébastien Leveneur,* 4

Krakow, Poland, Xth Conference on Electroanalysis in Theory and Practice, 1

Kyoto, Japan, IUPAC International Congress on Analytical Sciences 2011 (ICAS2011), *Ari Ivaska*

Lisboa, Portugal, 9th Carbohydrate Bioengineering Meeting, 1

Naantali, Finland, CAMURE-ISMR Conference, Chairman of the Scientific Committee *Tapio Salmi,* 19

San Diego, CA, USA, International Symposium on Capillary Chromatography, 1

Seattle, WA, USA, 33rd Symposium on Biotechnology for Fuels and Chemicals, invited lecturer, *Stefan Willför*

Turku, Finland, Finnish Conference of Environmental Science, Introduction to panel discussion, *Bjarne Holmbom*

Turku, Finland, 9th Spring Meeting of the International Society of Electrochemistry, keynote lecture, *Andrzej Lewenstam*, 22

June

Arlington, USA, 4th Congress on Ionic Liquids, 3

Braga, Portugal, Gas-liquid-solid reactors conference, session chairman, *Tapio Salmi*, 2

Dobogókö, Hungary, Mátrafüred International Conference on Electrochemical Sensors, invited lecture, *Tom Lindfors*, 3

Kirkniemi, Finland, Sappi Europe Seminar, invited lecturer, *Bjarne Holmbom*

Novosibirsk, Russia, Current Topics in Organic Chemistry (dedicated to Professor Valentin Koptyug), plenary lecture, *Dmitry Murzin*

Oulu, Finland, Nanocatalysis in (photo)catalysis, Scandem-Annual Meeting of Scandinavian Microscopy Society, 1

Stockholm, Sweden, European Ceramic Society Conference (ECerS XII), 4

St. Petersburg, Russia, Renewable Wood and Plant Resources: Chemistry, Technology, Pharmacology, Medicine, vice-Chairman and co-organizer, *Andrey Pranovich*, plenary lecturer, *Bjarne Holmbom*, invited lecturer, *Stefan Willför,* participants, 9

Tianjin, China, 16th International Symposium on Wood, Fiber and Pulping Chemistry (ISWFPC), 3

Thessaloniki, Greece, International Conference on Hydrogen Production, 1

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

July

Burgas, Bulgaria, Symposium in Honour of Docent Narendra Kumar, invited lecture, *Tapio Salmi*

Dijon, France, 11th International Conference on Carbon Dioxide Utilization, 5

New London, NH, USA, Gordon Research Conference - Environmental Nanotechnology, 1

Prague, Czech Republic, 75th Prague Meeting on Macromolecules, 2

August

Dresden, Germany, Summer School Spectroelectrochemistry, invited lecture, *Ari Ivaska*, 3

Glasgow, Scotland, UK, European Congress on Catalysis X (EuropaCat X), plenary session chairman, *Dmitry Murzin,* 6

Helsinki, Finland, 14th IUPAC International Symposium on MacroMolecular Complexes (MMC-14), invited lecture, *Ari Ivaska*

Jyväskylä, Finland, Jyväskylä Summer School, invited lecturer, *Mikko Hupa*, 2

Otaniemi, Finland, AgroBio Kick-off Meeting, 1

Paris, France, 1st European Training Course, training module organiser and invited lecturer, *Stefan Willför*

Wageningen, the Netherlands, 2nd International Polysaccharide Conference (EPNOE 2011), 1

September

Beijing, China, 6th Asia Pacific Chemical Reaction Engineering Symposium, 2

Berlin, Germany, European Congress on Chemical Engineering (ECCE), session chairman, *Tapio Salmi*, 8

Berlin, Germany, Conference über Ionenanalyse (CIA-2011), plenary lecture, *Ari Ivaska*

Caparica, Portugal, 11th International Chemical and Biological Engineering Conference CHEMPOR, 1

Espoo, Finland, Multiscale Modelling of Chemical Systems (MUMO), annual meeting, *Tapio Salmi*

Espoo, Finland, SusEN Research Program Seminar 2011, invited lecture, *Mikko Hupa*, 2

Helsinki, Finland, NordForsk Seminar, 6

Lecce, Italy, XXIV Congresso Nazionale delle Societe Chimica Italiane, 1

Oxford, England, UK, International Conference on the Chemistry of Glasses and Glass-Forming Melts, 1

Sitges, Spain, 1st International Conference on Ionic Liquids in Separation and Purification Technology, 4

Stockholm, Sweden, European Corrosion Congress (EUROCORR-2011), 2

St. Petersburg, Russia, St. Petersburg Institute of Technology, invited lecture, *Tapio Salmi*

Tallinn, Estonia, International Conference on Materials and Technologies for Green Chemistry, 6

Turku, Finland, 250 Years of Chemistry Education in Finland, invited lecture, *Tapio Salmi,* 40

Turku, Finland, Organic Chemistry at Åbo Akademi 90 years, *Tapio Salmi, Dmitry Murzin*

Turku, Finland, FUSEC Kick-off Meeting, 30

Viterbo, Italy, Italic 6 Science & Technology of Biomasses: Advances and Challenges, 4

Viterbo, Italy, COST FP0901 Joint Analysis Effort, chairman, *Stefan Willför*, 1

Zaragoza, Spain, EU COST action CM0901- Detailed Chemical Combustion Models for Cleaner Combustion, 2nd Annual Meeting, 1

October

Helsinki, Finland, Finska kemistsamfundet 120 years, invited lecture, *Tapio Salmi*

Jyväskylä, Finland, NGS-NANO Graduate School Annual Seminar, 2

Moscow, Russia, Roskatalys, invited lecturer, *Dmitry Murzin,* 3

Moscow, Russia, 10 Years of "Catalysis in Industry" Journal, invited lecturer, *Dmitry Murzin*

Riga, Latvia, Pinosylvins as Novel bioactive agents for food applications (Woodwisdom ERA-NET), project kick-off meeting, 1

Sitges, Spain, 5th International Conference on polyphenols and health, 1

Stockholm, Sweden, EU-BRISK project kick-off meeting, *Mikko Hupa*

Torremolinos, Spain, 1st International Congress on Catalysis for Biorefineries, 2

Turku, Finland, Turun työväenopisto, Invited lecture series in honour of the International Year of Chemistry 2011, *Tapio Salmi, Bjarne Holmbom, Mikko Hupa, Ari Ivaska*

Zürich, Switzerland, ETH, invited lecturer, *Dmitry Murzin*

November

Delft, the Netherlands, Technische Universiteit Delft, guest lecture, *Tapio Salmi*

Hamburg, Germany, vTI, Tag der Holzwirtschaft: Wood extractives – a rich source of specialty chemicals and bioactive compounds, invited lecturer, *Bjarne Holmbom*

Liege, Belgium, 5th International Conference on Advanced Computational Methods in Engineering, 1

Lochow, Poland, Surface Modification for Chemical and Biochemical Sensing (SM-CBS'2011), plenary lecture, *Andrzej Lewenstam*

Lyon, France, Polycat EU project meeting, *Heidi Bernas, Dmitry Murzin*

Prague, Czech Republic, 43rd Symposium on Catalysis, plenary lecture, *Dmitry Murzin,* 2

Rio de Janeiro, Brazil, Energy Seminar, Academy of Finland, Conicyt Chile and CNPq

Brazil seminar, delegate member, *J-P. Mikkola*

Stockholm, Sweden, Sodahuskonferensen 2011, 1

Tezpur, India, International Congress on Renewable Energy (ICORE 2011), keynote speakers, session chairpersons, *Narendra Kumar, Päivi Mäki-Arvela*

Trondheim, Norway, Scandinavian-Nordic Section of the Combustion Institute, 3

December

Helsinki, Finland, University of Helsinki, Department of Chemistry, invited lecture, *Tapio Salmi*

Helsinki, Finland, AEL-INSKO, Polttotekniikat ja päästöt, invited lecture, *Mikko Hupa*

Kuala Lumpur, Malaysia, Green Process Engineering, 1

Lille, France, Green chemistry for industry, *Tapio Salmi,* 2

Strasbourg, France, WoodChem 2011, 1

Trondheim, Norway, Symposium in honour of Professor *Anders Holmen*, NTNU, invited lecture, *Tapio Salmi*

Turku, Finland, Graduate School of Materials Research Seminar, 3

Turku, Finland, FUSEC semi-annual meeting, 30

Victoria Falls, Zimbabwe, 6th International Conference of the Africa Materials Research Society, 1

Wuhan, China, Sino-Australian Symposium on Advanced Coal and Biomass Utilisation Technologies, invited lecture, *Mikko Hupa*

6.3 Visitors and Visits

Visitors to the PCC

Azhar, Shoaib, Royal Institute of Technology (KTH), Wallenberg Wood Science Center, Stockholm, Sweden (January)

Banerjee, Prothiba nath, CSJM University, Kanpur, India (August-December)

Becher, Nora, Germany (May-December)

Bittante, Alice, Italy (January-December)

Bochenska, Maria, Poland (May-June)

Djinovic, Petar, Slovenia (October)

Dumitriu, Cristina, Romania (October-December)

Faten Diaz, Sara, Spain (March-September)

Ferancová, Adriana, Slovakia (February-July)

García Serna, Juan, Spain (June-July)

Gelmi, Amy, Australia (August; September)

Gemo, Nicola, Italy (February-December)

Guzinski, Marcin, Poland (January-June)

Hrobal, Vlastimil, Czech Republic (June-August)

Janzon, Ron, Johann-Heinrich-von-Thünen-Institut, Hamburg, Germany (June-November)

Kupis, Justyna, Poland (February-March)

Lawoko, Martin, Royal Institute of Technology (KTH), Wallenberg Wood Science Center, Stockholm, Sweden (April)

Lhermerout, Gabriel, France (August-November)

Mammitzsch, Frank, Germany (September-December)

Martón, Aurel, Hungary (October-November)

Mikhelson, Konstantin, Russia (February-May)

Nowak, Benedikt, Austria (March-May)

Reinsdorf, Arne, Germany (September-December)

Singh Jassar, Ravi Inder, India (August-December)

Sterchele, Stefano, Italy (November)

Sumiersky, Ivan, St. Petersburg Forest Technical Academy, Russia (January)

Xiao, Mizhang, China (January-October)

Zhang, Qi, USA (October-December)

Visits by PCC Members

Biasi, Pierdomenico, Università di Padova, Italy (September-October)

Fagerlund, Susanne, Nanyang Technological University, Singapore (January-April)

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

Hupa, Mikko, Wuhan, China (December)

Ivaska, Ari, Japan (May)

Ivaska, Ari, USA (January)

Jasielec, Jerzy, AGH University of Science and Technology, Krákow, Poland (November-December)

Kirilin, Alexey, University of Wisconsin, Madison, WI, USA (October-December)

Laurén, Tor, United Kingdom (June; August; November)

Leppänen, Ann-Sofie, Royal Institute of Technology (KTH), Wallenberg Wood Science Center, Stockholm, Sweden (April)

Lindberg, Daniel, Canada (November)

Lindfors, Tom, Hungary (April; November-December)

Lisak, Grzegorz, Poland (July)

Murzin, Dmitry, Germany-Czech Republic (November)

Piotrowska, Patrycja, Umeå University, Sweden (January-March)

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

Salmi, Tapio, Germany (September)

Strand, Anders, Mid Sweden University, Sundsvall, Sweden (September)

Wagner, Michal, Australia (January-July)

Xu, Chunlin, Royal Institute of Technology (KTH), Wallenberg Wood Science Center, Stockholm, Sweden (November)

Zhang, Di, Lehigh University, Bethlehem, PA, USA (January-February)

6.4 External PhD Examinations and Reviews

Czech Academy of Sciences, Institute of Chemical Process Fundamentals, scientific board member, *Tapio Salmi*

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

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

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

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

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

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

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

Editorial Board Member for *Magnesium Research, Andrzej Lewenstam*

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

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

Evaluation of Professorship in Thermal and Catalytic Conversion of Biomass, Royal Institute of Technology (KTH), Stockholm, member of evaluation panel, *Tapio Salmi*

Evaluation of proposals in EU Framework Nano, *Päivi Mäki-Arvela*

Evaluation of proposals in the Swedish Science Council, Natural Sciences and Technology, Stockholm, *Päivi Mäki-Arvela*

Evaluation of research programme, Slovenian Research Agency (ARRS), Slovenia, *J-P. Mikkola*

Evaluation of Värmeforsk basic research programme 2008-2011, Energimyndigheten, Sweden, *Mikko Hupa*

Evaluation of Assistant Professorship, Luleå University of Technology, *J-P. Mikkola*
Evaluation of Professorship, Mid Sweden University, *Bjarne Holmbom*

Finnish representative in the European Federation of Chemical Engineering (EFCE) working party Chemical Reaction Engineering, *Tapio Salmi*

Foreign corresponding member of the Russian Scientific Council on Catalysis, *Dmitry Murzin*

Lead guest editor, Hindawi Publishing Corporation, Special Issue for International Journal of Chemical Engineering, *Päivi Mäki-Arvela,* guest editor *Jyri-Pekka Mikkola*

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

Member of expert group for a series of Bioeconomy workshops to expand the Forest Cluster Ltd towards a Bioeconomy Cluster, *Stefan Willför*

Member of expert group for evaluation of the research programme “A Future for Vasa”, *Bjarne Holmbom*

Member of expert group for Review of the state and quality of scientific research in Finland (2012), Workshop for Pulp and Paper, *Stefan Willför*

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

Member of the scientific advisory board of Biofuel Technology Center SLU, Sweden, *J-P. Mikkola*

Member of the scientific advisory board, UNICRE, Czech Republic, *Dmitry Murzin*

President of the Federation of Nordic Catalysis Societies, *Kalle Arve*

President of the Finnish Catalysis Society, *Päivi Mäki-Arvela*

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

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

Scientific advisory board, Nordic ChemQuest, *J-P. Mikkola*

Steering Group of Bio4Energy research programme, *J.-P. Mikkola*

Vice chairman of European Federation of Catalysis Societies (EFCATS), *Dmitry Murzin*

External Examinations

Adamov, Alexey, University of Helsinki, examiner of doctoral thesis, *Ari Ivaska*

Altman Restrepo, Ernesto, Technische Universiteit Delft, the Netherlands, opponent, *Tapio Salmi*

Carlsson, Per, Luleå University of Technology, Sweden, opponent, *Mikko Hupa*

Casa Ferreira, Ana Maria, Universidad de Salamanca, Spain, opponent, *Ari Ivaska*

Jensen, Martin, Aalborg University, Denmark, opponent, *Leena Hupa*

Kontkanen, Maija-Liisa, University of Eastern Finland, Joensuu, evaluator of doctoral thesis, *Päivi Mäki-Arvela*

Kärnä, Minna, University of Jyväskylä, opponent, *J-P. Mikkola*

Lee, Roland, University of Tasmania, Australia, reviewer of PhD thesis, *Anna Sundberg*

Lilleberg, Björn, NTNU, Norway, opponent, *Anders Brink*

Madsen, Anders Theilgaard, Technical University of Denmark, opponent, *Tapio Salmi*

Malinen, Ilkka, University of Oulu, opponent, *Tapio Salmi*

Moreno Rueda, Teresa, Universidad de Valladolid, Spain, opponent, *Pierdomenico Biasi*

Pihlasalo, Sari, University of Turku, opponent, *Ari Ivaska*

Protasova, L., Technische Universiteit Eindhoven, the Netherlands, opponent, *Dmitry Murzin*

Rasmussen, Martin Hagsted, Technical University of Denmark, opponent, *Patrik Yrjas*

Razaq, Aamir, Uppsala University, Sweden, opponent, *Johan Bobacka*

Rekola, Jami, University of Turku, opponent, *Mikko Hupa*

Shah, Mayankkumar R., Technische Universiteit Eindhoven, the Netherlands, opponent, *Tapio Salmi*

Toftegaard, Maja Bog, Technical University of Denmark, opponent, *Mikko Hupa*

Turunen, Helka, University of Oulu, opponent, *Päivi Mäki-Arvela*

Urb, Gary, University of Tartu, Estonia, opponent, *J-P. Mikkola*

Wu, Hao, Technical University of Denmark, opponent, *Mikko Hupa*

Invited Lecturers at ÅA-PCC

Rudie, Alan W., US Forest Service, Forest Products Laboratory, Madison, WI, USA

Wallace, Gordon G., Australian Research Council Centre of Excellence for Electromaterials Science, Wollongong, Australia

6.5 Publicity

Television and Radio

Åktur, programme on local TV, *Anna Sundberg*

Newspapers and General Journals

FKS firade sitt 120-årsjubileum, *Kemia – Kemi* 7 (2011), 64, ISSN: 0355-1628

Internationell kemiingenjörskonferens i Nådendal blev en succé, *Meddelanden från Åbo Akademi* 12 (2011), 18-19, ISSN: 0359-8632

Kemiallista täsmäkirurgiaa: katalyysi muokkaa luonnon rakenteita, *Kemia – Kemi* 7 (2011), 47, ISSN: 0355-1628

Kemiforskningen i Finland och vid Åbo Akademi, *Meddelanden från Åbo Akademi* 4 (2011), 14-15, ISSN: 0359-8632

Kemiingenjörskonferens i Nådendal blev en succé, *Kemia – Kemi* 6 (2011), 57, ISSN: 0355-1628, Tapio Salmi

Kemipris till ÅA-professor (T. Salmi), *Meddelanden från Åbo Akademi* 6 (2011), 11, ISSN: 0359-8632

Kolme uranuurtajaa palkittiin (P. Simula, A.O.K. Nieminen, T. Salmi), *Kemia – Kemi* 3 (2011), 54-55, ISSN: 0355-1628

Magnus Ehrnroothin säätiön kemian palkinto 2011 akatemiaprofessori Tapio Salmelle, Åbo Akademi, *Sphinx, The yearbook of Societas Scientiarum Fennica* (2011), ISSN: 0783-5892

Åbo Akademi palkitsi kemistejä, *Kemia – Kemi* 6 (2011), 60, ISSN: 0355-1628

Appendix I

Åbo Akademi Process Chemistry Centre Doctoral Theses in Progress 2012

Students from Outside Finland

Part-time and external students included

- Steliana Aldea (Romania, *F*), MSc University of Bucharest, Bucharest, Romania 2006, BSc ibid. 2002
- Marceline Akieh (Cameroon, *F*), MSc Martin-Luther-Universität Halle-Wittenberg, Germany 2005, BSc University of Buea, Cameroon 1999
- Ikenna Anugwom (Nigeria, *M*), MSc ÅA 2009, BSc Satakunta University of Applied Sciences, Pori, Finland
- Sylwia Bialczak (Poland, *F*), MSc Poznan University of Technology, Poland 2007
- Pierdomenico Biasi (Italy, *M*), PhD Università di Padova, Italy 2009
- Daniel Dax (Luxembourg, *M*), MSc RWTH Aachen University, Aachen, Germany, BSc ibid.
- Tingting Han (China, *F*), MSc ÅA 2008, BSc Shandong Institute of Light Industry, China 2006
- Ning He (China, *M*), MSc ÅA 2009, BSc Shandong Polytechnic University, China 2007
- Jerzy Jasielec (Poland, *M*), MSc ÅA and AGH University of Science and Technology, Krákow, Poland 2008 (double degree)
- Tooran Khazraie Shoulaifar (Iran, *F*), MSc Sharif University of Technology, Tehran, Iran 2007, BSc Tehran University, Tehran, Iran 2002
- Alexey Kirilin (Russia, *M*), MSc D.I. Mendeleyev University of Chemical Technology of Russia, Moscow, Russia 2009
- Antonina Kupareva, (Russia, *F*) MSc Gubkin Russian State University of Oil and Gas, Moscow Russia 2008
- Ekaterina Korotkova (Russia, *F*), MSc ÅA (2011) & Tver State Technical University, Tver, Russia (2010) (double degree), BSc Tver State Technical University, Tver, Russia 2008
- Ron Lai (Canada, *M*), MSc University of British Columbia, Vancouver, Canada 1994
- Ewelina Leino (Poland, *F*), MSc Silesian University of Technology, Gliwice, Poland 2006
- Bingzhi Li (China, *M*), MSc ÅA 2006, BSc Shandong Institute of Light Industry, China 2004
- Na Li (China, *F*), MSc ÅA 2007, BSc Shandong Institute of Light Industry, China 2005
- Peter Lingenfelter (USA, *M*), MSc ÅA 2000, BSc Oberlin College, Oberlin, OH, USA 1995
- Grzegorz Lisak (Poland, *M*), MSc ÅA & 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 Privalova (Russia, *F*), MSc D.I. Mendeleev University of Chemical Technology of Russia, Moscow, Russia 2008
- Bartosz Rozmysłowicz (Poland, *M*), MSc ÅA & Poznan University of Technology, Poland 2009 (double degree)
- Sabrina Schmidt (Germany, *F*), Diplom Chemiker RWTH Aachen University, Aachen, Germany 2010
- 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
- Michał Wagner (Poland, *M*), MSc AGH University of Science and Technology, Krákow, Poland 2007
- Hao Wu (China, *F*), MSc ÅA 2007, BSc Shandong Institute of Light Industry, China 2005
- Zhe Yang (China, *M*), MSc Jilin University, China 2010
- Kai Yu (China, *M*), MSc ÅA 2010, BSc Shandong Polytechnic University, China 2008

Doctoral Students from Finland

Part-time and external students included

- Susanne Fagerlund (Åbo, *F*), MSc ÅA 2007
- Sari Hyvärinen (Viitasaari, *F*), MSc ÅA 2007
- Matti Häärä (Åbo, *M*), MSc ÅA 1994
- Oskar Karlström (Jomala, *M*), MSc ÅA 2008
- Petri Kilpeläinen (St. Michel, *M*), MSc University of Helsinki 2002
- Teuvo Kilpiö (Riihimäki, *M*), LicTech Helsinki University of Technology 1993
- Victor Kisonen (Masku, *M*), MSc University of Turku 2005
- Jens Krogell (Mariehamn, *M*), MSc ÅA 2009
- Juho Lehmusto (Åbo, *M*), MSc University of Turku 2007
- Ann-Sofie Leppänen (Nådendal, *F*), MSc ÅA 2004
- Christian Lindfors (Helsingfors, *M*), MSc Helsinki University of Technology 2008
- Hanna Lindqvist (Nagu, *F*), MSc ÅA 2004
- Sam Myllynen (Borgå, *M*), LicTech ÅA 2002
- Linda Nisula (Vasa, *F*), MSc ÅA 2003
- Toni Riittonen (Åbo, *M*), MSc University of Turku 2009
- Jussi Rissanen (Åbo, *M*), MSc University of Turku 2010
- Eero Salminen (Nystad, *M*), MSc University of Turku 2010
- Christoffer Sevonius (Sibbo, *M*), MSc ÅA 2012

- Anders Strand (Nykarleby, *M*), MSc ÅA 2008
- Timo Petteri Suominen (Tammerfors, *M*), MSc ÅA 2007
- Pasi Tolvanen (Hangö, *M*), MSc ÅA 2006
- Emil Vainio (Pargas, *M*), MSc ÅA 2009
- Ulriika Vanamo (Åbo, *F*), MSc ÅA 2008
- Leena Varila (Vasa, *F*), MSc ÅA 2011
- Niklas Vähä-Savo (Björneborg, *M*), MSc ÅA 2009