Åbo Akademi
Process Chemistry Centre

Annual Report 2012 – 2013

Edited by Maria Ljung, Anders Brink, Rose-Marie Latonen,
Päivi Mäki-Arvela, Anna Sundberg

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

Åbo Akademi Process Chemistry Centre (PCC)

The PCC is a National Centre of Excellence in Research appointed by the Academy of Finland for the years 2000-2005 and 2006-2011.

The PCC consists of the teams:

- *Combustion and Materials Chemistry (lead by Prof. Mikko Hupa)*
- *Wood and Paper Chemistry (Prof. 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.

The PCC Industrial Advisory Board (2013): Örjan Andersson (Novia), Ilmo Aronen (Raisio), Stig-Erik Bruun (Chemigate), Heidi Fagerholm (Kemira), Lars Gädda (Forestcluster), Ari Jokilaakso (Outotec), Bertel Karlstedt (Nordkalk), Nina Kopola (Suominen Yhtymä), Timo Leppä (Chemical Industry Federation of Finland), Lars Peter Lindfors (Neste Oil), Leena Paavilainen (Metla), Ismo Reilama (Metsä-Botnia), Bengt-Johan Skrifvars (Top Analytica), Kenneth Sundberg (Tikkurila), Kari Toivonen (Elomatic) and Petri Vasara (Pöyry).

The PCC Scientific Advisory Board (2013): Professor Raimo Alén (University of Jyväskylä), Professor Jiri Janata (Georgia Institute of Science and Technology, Atlanta) and Professor Lars J. Pettersson (Royal Institute of Technology (KTH), Stockholm).

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PCG Annual Report 2012 - 2013

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1. Introduction to the Activities in 2012-2013

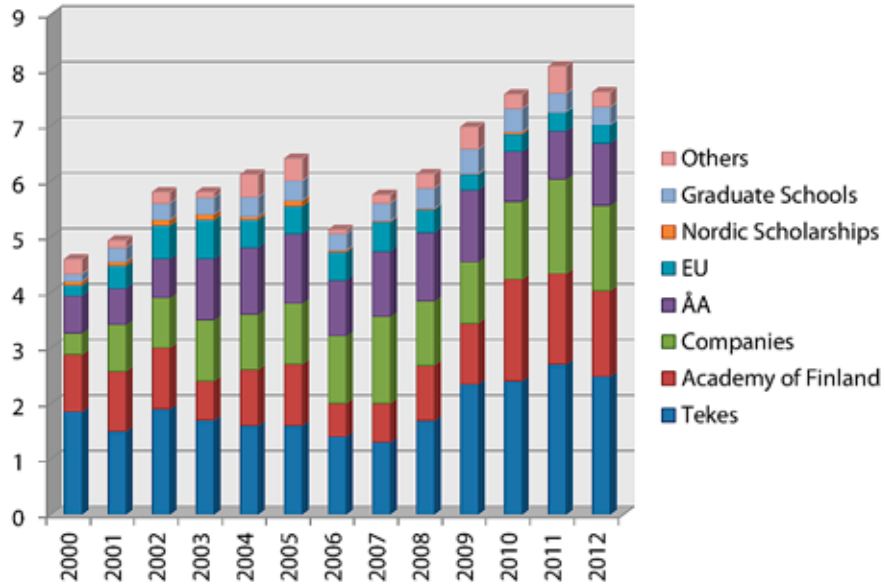
Background

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 has continued its activities with a new research programme working in close collaboration with a number of industrial companies and research organizations around the world.

The Year 2012 in Numbers

In 2012 altogether 20 senior researchers and 45 full-time PhD candidates worked in the 50 major research projects of the Centre. In addition, a number of shorter term visitors, Master's students and support personnel participated in our activities.

The Figure below shows the funding of the Centre since the year 2000. The key external funding sources in 2012 were the Tekes – the Finnish Funding Agency for Technology and Innovation together with Industrial Companies, and the Academy of Finland. In the year 2012 the Centre no longer received the Centre of Excellence funding from the Academy of Finland. However, this decrease in funding was partly compensated by a special strategic support from Åbo Akademi University, and this made it possible for the Centre to continue its activities with full capacity



The funding of the Åbo Akademi Process Chemistry Centre 2000-2012

The table below gives some key numbers of our academic activities in 2012. Our research resulted in altogether 145 papers in scientific publication series with the full referee system. 10 doctoral theses and 14 masters' theses were finished.

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

Theses and other publications by the Åbo Akademi Process Chemistry Centre 2000-2012

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 2012 the PCC was involved in the organization of a major international meeting. *The 15th Nordic Symposium on Catalysis* was held in Mariehamn, the Åland Islands from June 10 to June 12. The symposium attracted some 200 participants from 20 countries. The programme included three plenary lectures, four Nordic keynote lectures, 58 oral presentations and 91 posters. The main topics of the symposium were "Catalysis of renewables" and "Catalysis, Nordic countries and Baltic Sea". These topics reflect global trends and local circumstances: mankind faces one of its biggest challenges ever, when shifting from fossil resources to renewable feedstocks in the production of chemicals and fuel components. Environmental issues are crucial for the Baltic Sea region: the Baltic Sea is surrounded by nine heavily industrialized countries and it has a very vulnerable ecosystem. Catalysis is one of the key technologies in keeping the air clear and the water clean, providing the possibility for this unique nature to survive.

Doctoral Students

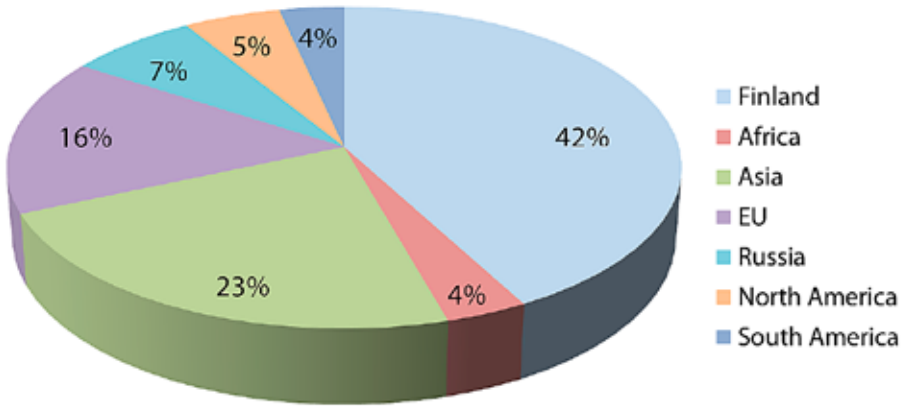
A central part of our research activities is done as doctoral theses works. Altogether about 45 PhD thesis projects are actively underway at the Centre. Our doctoral students are very international (see the graph below). More detailed information of the background of our PhD students is given in the Appendix 1 on page 165 of this Annual Report.

At the moment, 35% 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 2012 41 students were participating in the activities of the GSCE, 12 of them from our Centre. The GSCE has continued funding for the four-year period 2012-2015.

In 2012 the PCC PhD students further participated in the graduate schools of: Pulp and Paper Science and Technology (PaPSaT), Chemical Sensors and Micro Analytical Systems (CHEMSEM), Environmental Science and Technology (EnSTe), Nanoscience (NGS-NANO), and the Graduate School for Biomass Refining (BIOREGS).



Nationality of the PhD students at PCC 2012-2013. For more detailed information see Appendix 1 on page 165

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 2012 the board met eight times.

Since the very beginning the Centre board has been supported by two important Advisory Boards, the Scientific Advisory Board (SAB) consisting of three Professors and an Industrial Advisory Board. In 2012-2013 our Scientific Advisory Board consists of the Professors *Jiri Janata* from the Georgia Institute of Science and Technology in Atlanta, *Raimo Alén* from the University of Jyväskylä and *Lars Pettersson* from the Royal Institute of Technology in Stockholm, Sweden.

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 2012 the PCC had five lectures in its Distinguished Lecturer Series:

- March 2012: Prof. *Arkady A. Karyakin*, M.V. Lomonosov Moscow State University, Russia: "Advanced Biosensors Based on New Technologies"
- June 2012: Prof. *Fritz Scholz*, Ernst-Moritz-Arndt-Universität Greifswald, Germany: "The Interaction of OH Radicals with Metal Electrodes: Implications for Electrochemistry and Surface Science"
- October 2012: Prof. *Emil Paleček*, Institute of Biophysics, Czech Academy of Science, Brno, Czech Republic: "Electrochemical Sensing of Biomacromolecules"
- October 2012: Prof. *Chris Hardacre*, Queen's University Belfast, Northern Ireland: "Designing Catalysts for Low Pressure and Temperature Acid and Amide Formation"
- December 2012: Prof. *Richard K. Brow*, Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO, USA: "Corrosion of Specialty Glasses"

Acknowledgements

This report will be published at the annual seminar of the PCC held on August 29, 2013 at the Åbo Akademi ICT Building in Turku. The report gives an overview of the recent activities at the Centre. It has a complete list of the journal articles, theses and other publications produced by the Centre in the calendar year 2012. 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 Mia Mäkinen. The layout was done by Paul Söderholm.

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

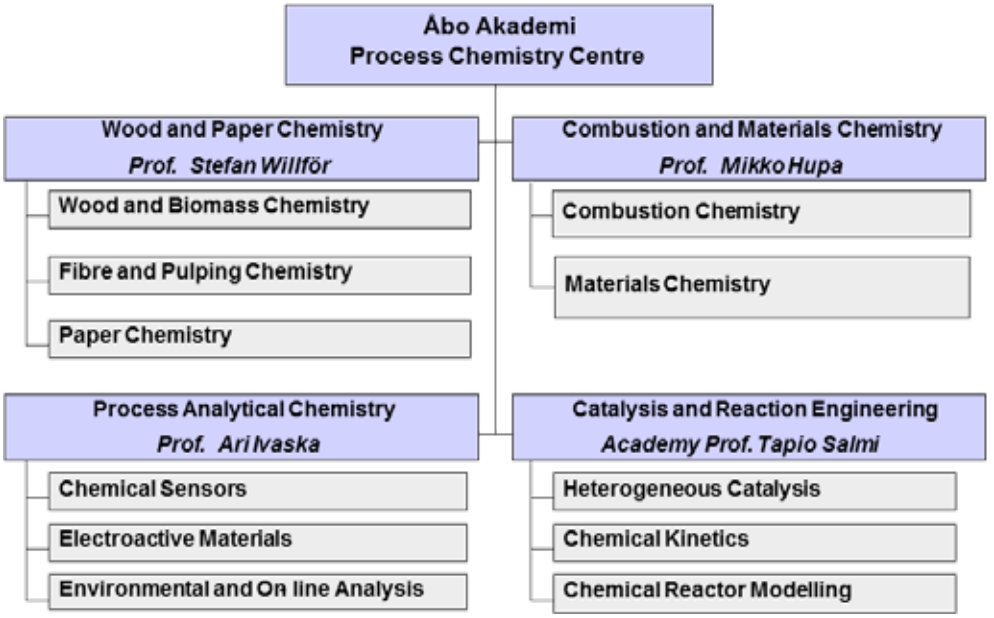
On behalf of the Board of the Åbo Akademi Process Chemistry Centre,

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

- Raimo Alén, Finland
- Jiri Janata, USA
- Lars Pettersson, Sweden

Industrial Advisory Board

- Örjan Andersson, Novia
- Ilmo Aronen, Raisio
- Stig-Erik Bruun, Chemigate
- Heidi Fagerholm, Kemira
- Lars Gädda, Forestcluster
- Ari Jokilaakso, Outotec
- Bertel Karlstedt, Nordkalk
- Nina Kopola, Suominen Yhtymä
- 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, cellulose, 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 2012 was obtained mainly from Tekes and the Fibic SHOK, the industry, EU, and Academy of Finland.

The following new projects started during 2012:

- Development of biocomposites from plant materials via chemo-enzymatic processes

We have a close cooperation with Metla, the Finnish Forest Research Institute, in the form of two joint senior research positions and a scientific advisor. Their field of research includes new products and biomaterials from the forest and other natural resources. We also have 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 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

	Chunlin Xu
Senior researchers	Azamat Boymirzaev
	Risto Korpinen
	Robin Manelius
	Lari Vähäsalo
Researchers	Sylwia Bialczak
	Daniel Dax
	Wenwen Fang
	Jarl Hemming
	Matti Häärä
	Victor Kisonen
	Ekaterina Korotkova
	Jens Krogell
	Ann-Sofie Leppänen
	Hanna Lindqvist
	Jun Liu
	Linda Nisula
	Sebastian von Schoultz
	Tao Song
	Anders Strand
Technician	Leif Österholm
Secretary	Agneta Hermansson

Links

http://www.abo.fi/institution/en/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 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 2012.

Our consortium project Future Fuels for Sustainable Energy Conversion, FUSEC, which was started in the spring of 2011, had a very important year with a number of research topics under study. 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 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.

We participate in the project BRISK - Biofuels Research Infrastructure for Sharing Knowledge. Brisk is a 11 Million Euro four-year initiative with 9 Million Euro funded under EC FP7 (Ref: 284498). The initiative runs from October 2011 to September 2015. BRISK is coordinated by the Royal Institute of Technology (KTH), Stockholm, and includes partners from Austria, Denmark, Finland, Germany, Greece, Italy, Netherlands, Norway, Poland, Spain, Sweden, Switzerland, Turkey and the UK. BRISK aims to develop a European Research Infrastructure for Thermochemical Biomass Conversion, supporting R&D in innovative processes to convert sustainable feedstocks (agricultural/forestry wastes and energy crops) into liquid, gaseous or solid fuels. Our biomass characterization laboratory has several pieces of equipment that are part of the BRISK infrastructure program. So far we have had visitors from SINTEF in Norway making use of our facilities and we have had access to the pilot facilities at the International Flame Research Foundation in Livorno, Italy.

Another part of our on-going activities deals with high-temperature inorganic materials of interest to various applications. In 2012 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. These studies have later been 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 2012 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
	Anders Brink
	Edgardo Coda Zabetta
	Kaj Fröberg
	Leena Hupa
	Christian Mueller
	Bengt-Johan Skrifvars
	Heimo Ylänen
Senior researchers	Dorota Bankiewicz
	Mikael Bergelin
	Nikolai DeMartini
	Markus Engblom
	Susanne Fagerlund
	Daniel Lindberg
	Jonathan Massera
	Xiaoju Wang
	Johan Werkelin
	Patrik Yrjas
	Maria Zevenhoven
	Di Zhang

Doctoral students
& researchers

Jan-Erik Eriksson
Sui Jingxin
Max Johansson
Oskar Karlström
Tooran Khazraie
Tor Laurén
Juho Lehmusto
Bingzhi Li
Na Li
Camilla Molin
Magnus Perander
Rishabh Sarna
Christoffer Sevonius
Linus Silvander
Berndt Södergård
Emil Vainio
Leena Varila
Hao Wu
Niklas Vähä-Savo

Technicians	Peter Backman
	Luis Bezerra
	Jaana Paananen
Coordination	Maria Ljung
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 and hydrolytic hydrogenation of hemicelluloses as well as hydrogenation and oxidation of mono- and disaccharides, preparation of percarboxylic acids, isomerisation and esterification reactions, enantioselective hydrogenation and cleaning of exhaust gas originating from biofuels. A new finnish-Brazilian project on the use of microalgae as sources for biofuels and health-promoting chemicals was started. 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). The new 4-year research project on multiscale modelling of chemical processes (MUMO) was successfully continued. New kinds of structured catalysts were under development, such as solid foams, which are developed together with the group in Combustion and Materials Chemistry (PCC) and foreign partners. The development of green process technology is advanced in many fields, particularly in the development of new continuous processes for biofuels and chemicals, such as direct synthesis of hydrogen peroxide. 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; typical examples are production of chemical intermediates, such as ethylene oxide and chloromethane.

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
Senior researchers	Atte Aho
	Andreas Bernas
	Heidi Bernas
	Pierdomenico Biasi
	Valerie Eta
	Nicola Gemo
	Henrik Grénman
	Jan Hájek
	Olatunde Jogunola
	Mats Rönnholm
	Victor Sifontes Herrera
	Anton Tokarev
	Pasi Tolvanen
	Pasi Virtanen
Doctoral students	Steliana Aldea
& researchers	Ikenna Anugwom
	Cesar de Araujo Filho
	Sigmund Fugleberg
	Juan García Serna
	Lidia Godina
	Imane Hachemi

	Sari Hyvärinen
	Teuvo Kilpiö
	Alexey Kirilin
	Antonina Kupareva
	Ewelina Leino
	Gerson Martin
	Toni Riittonen
	Jussi Rissanen
	Bartosz Rozmysłowicz
	Eero Salminen
	Sabrina Schmidt
	Stefano Sterchele
	Timo Petteri Suominen
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
	Johan Bobacka (pro tem)
	Kalle Levon (adjunct)
	Andrzej Lewenstam (part-time)

Docents	Leo Harju
	Carita Kvarnström
	Tom Lindfors
	Li Niu
	Tomasz Sokalski
Senior researchers	Zhanna Boeva
	Maija Blomquist
	Adriana Ferancová
	Kim Granholm
	Rose-Marie Latonen
	Zekra Mousavi
	Yasuhito Sugano
Laboratory Manager	Paul Ek
Doctoral students	Jesús Arroyo
& researchers	Marceline Akieh-Pirkanniemi
	Patrycja Bober
	Cristina Dumitriu
	Tingting Han
	Jerzy Jasielec
	Grzegorz Lisak
	Ulriika Vanamo
	Ning He
	Sylwia Strzalkowska
	Pingping Su
	Michał Wagner
	Zhe Yang
	Kai Yu

Secretary & coordinator	Victoria Mäkimartti
Technicians	Sten Lindholm
	Lassi Väinölä

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

3. Research

The starting points to the common research plan of the Centre are outlined below.

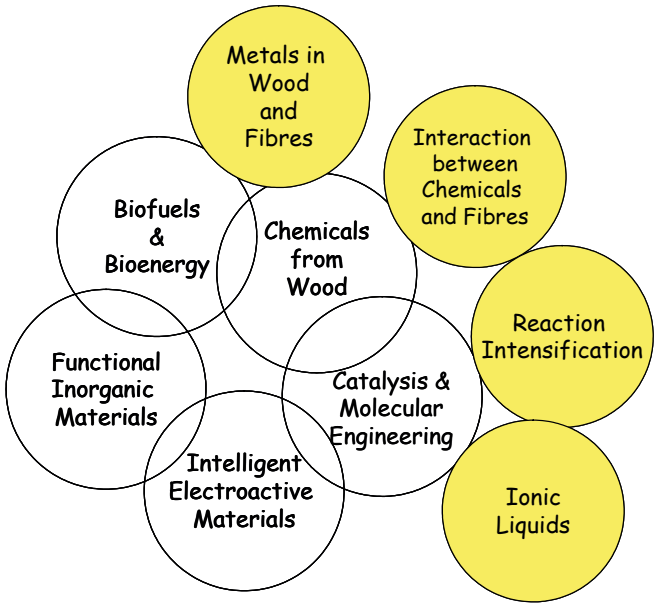
A general long-term trend in the industrial production is the move towards renewable and natural raw materials. Chemistry and chemical technology is going to change its direction towards long-term sustainability, implying:

- 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 is "Sustainable Chemistry in Production of Pulp and Paper, Fuels and Energy, and Functional Materials".



ÅA-PCC Research Areas

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

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

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

3.1 Ionic Liquids

Even though some of the earliest 'prototype' 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 solutions, 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 – millions and millions of formulations - 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 relative 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
- Synthesis of platform chemicals 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 University of Technology (the group of Doc. Mihkel Koel).

Important achievements have been obtained in 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. Later on, we also found out that even upon 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. In connection to this, also a new type of reactor, the SpinChem® reactor, well suited for enhanced contacting of liquids and solids has been utilized. As a result of these studies, a patent has been filed.

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 has been two-fold: to develop techniques more suitable for small-scale installations (particularly biogas plants) by taking advantage of novel ionic liquid formulations and to develop a methodology allowing for a fare comparison of various CO_2 capturing technologies. In essence, besides 'classical' ionic liquids that bind carbon dioxide either chemically or physically, switchable ionic liquids and polymeric ionic liquids have been studied and compared with traditional alkanol-amine systems. A doctoral student recently defended her thesis on this topic.

Ionic Liquids as an 'Enabling' Media:

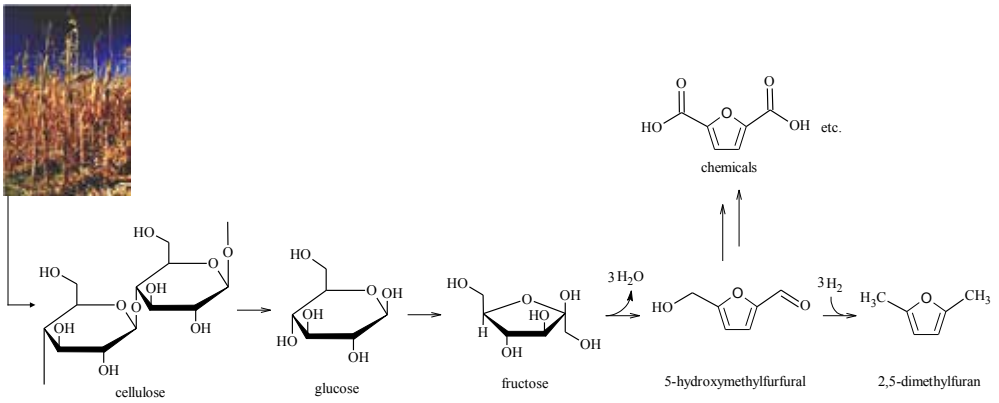
1. FUSILCA - Supported Ionic Liquid Catalyst used in the transformation of unsaturated aldehydes and synthesis of furanic fuels and chemicals;
2. OPTBIO, NoTre - Ionic liquid pre-treatment techniques for fermentable sugars; & Novel Treatment Processes of Lignocellulosics for Fermentable Building Blocks
3. BIOGASUP - Biogas cleaning for vehicle grade fuel
4. 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 University of Eastern Finland that in future could be utilized in the routine analysis of molecules originated from the bio resources.

Biogas is one of the feasible, delocalized near-future solutions to the mobility needs of the society. Moreover, it does not contribute to the depletion of fossil fuel resources and is relatively easy to implement, both as production sites and to be used as a fuel in internal combustion engines. One of the biggest challenges has been the lack of economic and robust small-scale gas purification technologies needed to yield vehicle-grade fuel. Since biogas primarily consists of methane (just like natural gas), the established gas-cleaning technologies, based on aqueous alkanol amines, 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., Virtanen, P., Sjöholm, R., Willför, S., Mikkola, J-P., Selective extraction of hemicelluloses from spruce using switchable ionic liquids, *Carbohydrate Polymers* 87 (2012) 3, 2005-2011 (Elsevier Ltd., ISSN: 0144-8617)
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- Salminen, E., Virtanen, P., Kordás, K., Mikkola, J-P., Alkaline modifiers as performance boosters in citral hydrogenation over Supported Ionic Liquid Catalysts (SILCAs), *Catalysis Today* 116 (2012), 126-131 (Elsevier B.V., ISSN: 0920-5861)

Cellulose Derivatives in Ionic Liquids

Main funding: PCC, Åbo Akademi

Olatunde Jogunola, Jyri-Pekka Mikkola, 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:

- Jogunola, O., Salmi, T., Kangas, M., Mikkola, J-P., Determination of the kinetics and mechanism of methyl formate synthesis in the presence of a homogeneous catalyst, *Chemical Engineering Journal* 203 (2012), 469-479 (Elsevier B.V., ISSN: 1385-8947)
- Jogunola, O., Salmi, T., Wärnå, J., Mikkola, J-P., Kinetic and diffusion study of acid-catalyzed liquid-phase alkyl formate hydrolysis, *Chemical Engineering Science* 69 (2012) 1, 201-210 (Elsevier Ltd,, ISSN: 0009-2509)
- Jogunola, O., Salmi, T., Wärnå, J., Mikkola, J-P., Kinetic studies of alkyl formate hydrolysis using formic acid as a catalyst, *Journal of Chemical Technology and Biotechnology* 87 (2012), 286-293 (Blackwell Publishing, ISSN: 0142-0356)

Electrochemical Characterization of Cellulose in Ionic Liquids

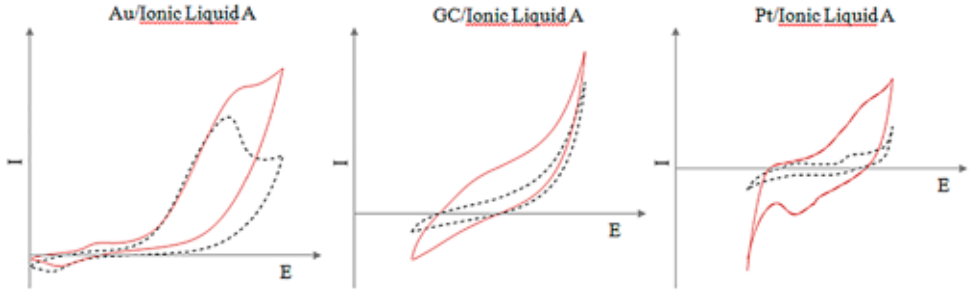
Main funding: Åbo Akademi Process Chemistry Centre

Yasuhito Sugano, Steliana Aldea, Ari Ivaska, Jyri-Pekka Mikkola

Cellulose is one of the promising renewable biopolymers of high demand for applications such as production of functional materials and bulk chemicals for industrial need (e.g. ethanol, functional polymers). Dissolution of cellulose in electrolytes enables us to make opportunity for direct electrochemical reaction of cellulose molecule at the electrode surface. Ionic liquids (ILs) are one of the most powerful and interesting solvent systems for cellulose dissolution. Several types of ILs have been synthesized and characterized in order to design and regulate the dissolution conditions of cellulose. However, there has been no research focusing on the electrochemistry of cellulose using ILs. The focus in this project has been to verify the electrochemical interaction between cellulose and the electrode materials in ILs. The fundamental characterization of cellulose in IL solvent

systems is important for further innovative use of cellulose in electrochemical applications and ILs in the bio refinery field. As the initial step in this research work, we have characterized electrochemical properties of cellulose in ILs using different reaction conditions. New insights in optimization of appropriate reaction conditions in IL based solvent systems have been obtained.

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



Red line: Cellulose, Black dash line: Background

Electrochemical response of cellulose with different combinations of electrodes and ionic liquids

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. The PCC has unique experimental devices for *in situ* studies of reactions under the influence of ultrasound and microwaves. The chemical applications are several, such as esterification, catalytic oxidation as well as hydrogenation of aldehydes and ketones, leaching of minerals and 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, such as ethylene oxide and chloromethane. The research has revealed that considerable process intensification can be achieved through the application of microreactors instead of conventional technology.

Structured Reactors

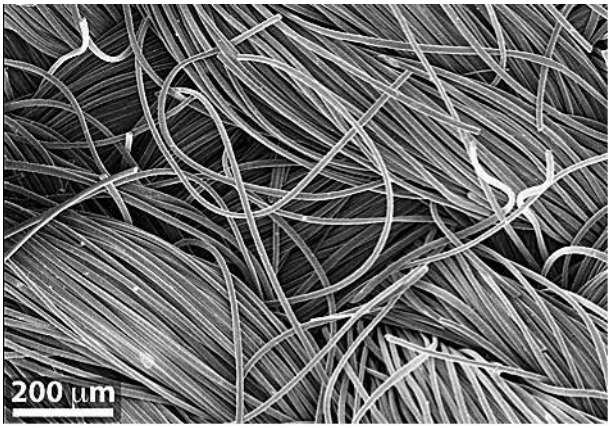
Main funding: Academy of Finland, EU

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:

- Sifontes Herrera, Victor, *Hydrogenation of L-arabinose, D-galactose, D-maltose and L-rhamnose* (Doctoral Thesis, Åbo Akademi University, Turku, ISBN: 978-952-12-2731-8)
- Kilpiö, T., Biasi, P., Bittante, A., Salmi, T., Wärnå, J., Modeling of direct synthesis of hydrogen peroxide in a packed bed reactor, *Industrial & Engineering Chemistry Research* 51 (2012), 13366-13378 (ACS Publications, ISSN: 0888-5885)
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- Sifontes Herrera, V., Saleem, F., Kusema, B., Eränen, K., Salmi, T., Hydrogenation of L-arabinose and D-galactose mixtures over a heterogeneous Ru/C catalyst, *Topics in Catalysis* 55 (2012), 550-555 (Springer-Verlag, ISSN: 1022-5528)

Micro- and Milliscale Reactor Technology

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

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, several EU partners

Publications:

- Salmi, T., Roche, M., Hernandez Carucci, J., Eränen, K., Murzin, D.Yu., Ethylene oxide- kinetics and mechanism, *Current Opinion in Chemical Engineering* 1 (2012), 321-327 (Elsevier Ltd, ISSN: 2211-3398)

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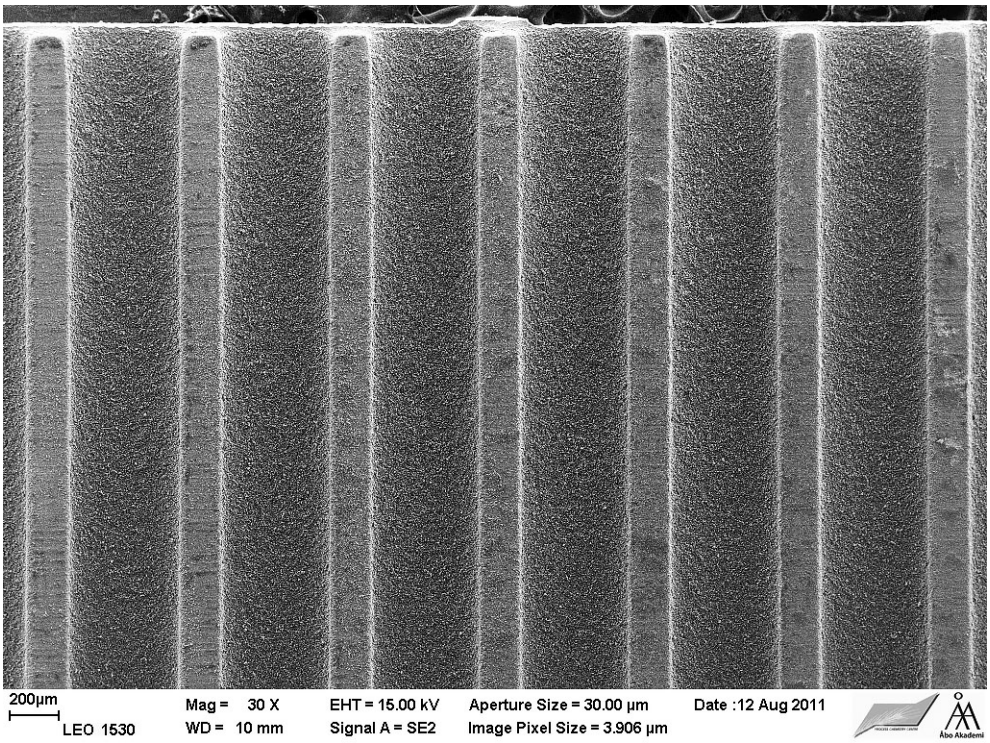

A SEM image of microreactor element

Multiphase Reactors

Main funding: PCC, Academy of Finland, 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., Menegazzo, F., Pinna, F., Salmi, T.O., Direct synthesis of hydrogen peroxide in a trickle bed reactor: Comparison of Pd-based catalysts, *Industrial & Engineering Chemistry Research* 51 (2012) 26, 8883-8890 (ACS Publications, ISSN: 0888-5885)
- Biasi, P., Gemo, N., Hernandez Carucci, J.R., Eränen, K., Canu, P., Salmi, T., Kinetics and mechanism of H_2O_2 direct synthesis over a Pd/C catalyst in a batch reactor, *Industrial & Engineering Chemistry Research* 51 (2012) 26, 8903-8912 (ACS Publications, ISSN: 0888-5885)
- Gemo, N., Biasi, P., Canu, P., Salmi, T., Mass transfer and kinetics of H_2O_2 direct synthesis in a batch slurry reactor, *Chemical Engineering Journal* 207-208 (2012), 539-551 (Elsevier B.V., ISSN: 1385-8947)
- Gemo, N., Biasi, P., Salmi, T., Canu, P., H_2 solubility in methanol in the presence of CO_2 and O_2, *The Journal of Chemical Thermodynamics* 54 (2012), 1-9 (Elsevier Ltd., ISSN: 0021-9614)
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Batch and Semibatch Reactors for Reactive Solids

Main funding: Raisio Foundation, Nordkalk

Henrik Grénman, J-P. Mikkola, 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; INSA Rouen, France

Publications:

- Gemo, N., Biasi, P., Canu, P., Salmi, T., Mass transfer and kinetics of H_2O_2 direct synthesis in a batch slurry reactor, *Chemical Engineering Journal* 207-208 (2012), 539-551 (Elsevier B.V., ISSN: 1385-8947)
- Leveneur, S., de Araujo Filho, C., Estel, L., Salmi, T., Modeling of a liquid-liquid-solid heterogeneous reaction system: Model system and peroxyvaleric acid, *Industrial & Engineering Chemistry Research* 51 (2012), 189-201 (ACS Publications, ISSN: 0888-5885)

Complex Reaction Kinetics and Thermodynamics

Main funding: Academy of Finland, Industry

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; Université de Bourgogne, France; University of Oulu, INSA Rouen, France

Publications:

- Cortese, R., Duca, D., Sifontes Herrera, V., Murzin, D.Yu. L-arabinose conformers adsorption on ruthenium surfaces: A DFT study, *Journal of Physical Chemistry C* 116 (2012), 14908-14916 (ACS Publications, ISSN: 1932-7447)
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- Suominen, P., Brink, A., Salmi, T., Parameter estimation of complex chemical kinetics with covariance matrix adaptation evolution strategy, *MATCH Communications in Mathematical and in Computer Chemistry* 68 (2012) 2, 469-476 (Faculty of Science, University of Kragujevac, ISSN: 0340 - 6253)

3.3 Metals in Wood and Fibres

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

This project is to study the occurrence of metal ions in different part of the wood materials 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. The chemical form of the metals 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 to the type of metal ions and their contents in different fuels. Study on metal ions 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 materials and the reactions of the metal ions with wood fibres and other chemicals in different stages of the paper making processes 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

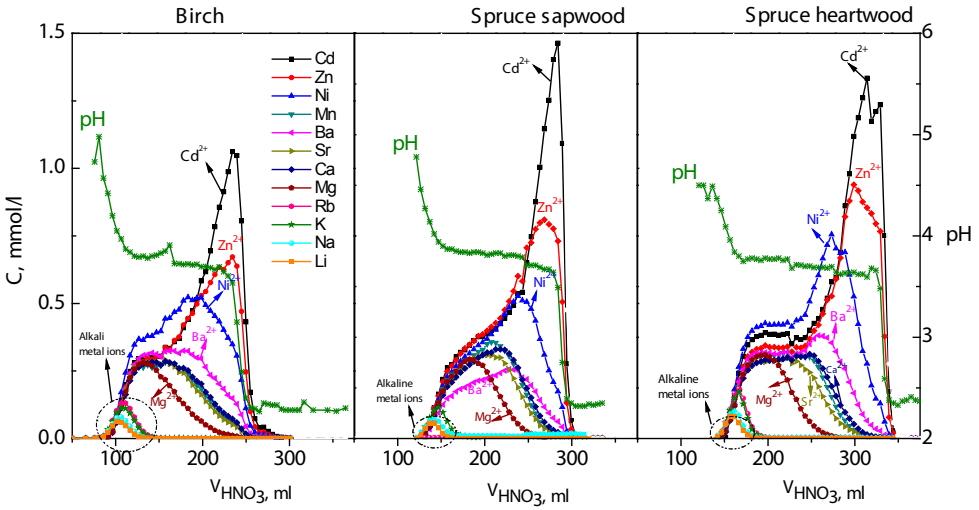
Pingping Su, Leo Harju, Andrey Pranovich, Ari Ivaska, Bjarne Holmbom

The main objective of this project has been to study the reactions of metal ions with functional groups in various wood based materials. A column chromatographic method and a batch method have been used to study the affinities of metal ions to different types of pulp, wood and bark materials. The mechanism of these methods 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, pulp and bark samples. By combination of the sorption experiments with several different metal ion mixtures, the following affinity order was established, e.g. for spruce sapwood particles:

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

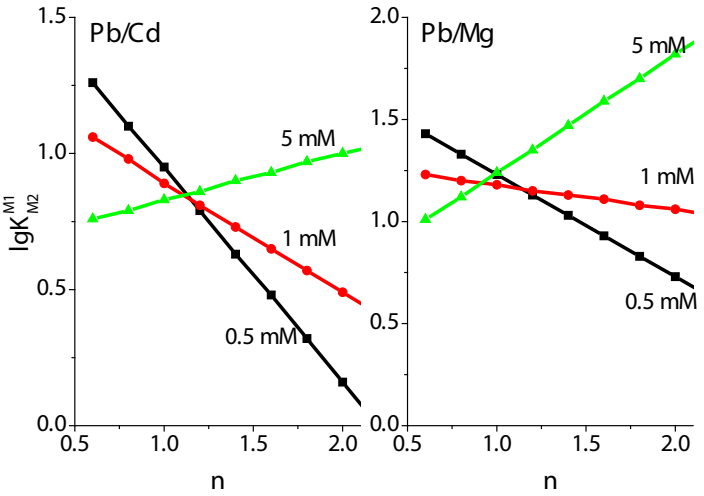
The affinity orders were almost the same for the bark (spruce inner bark and outer bark), the wood particles from birch, spruce sapwood and spruce heartwood, and pulps both from mechanical and kraft processes.

Ion exchange equilibrium constants for sorption of metal ions to pulps by the batch method have also been determined. The distribution of metal ions between the solid and solution phases and mass balance of metal ions during the course of the sorption experiments were



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

also studied. A graphic method was used for the determination of the stoichiometric ratio of the ion exchange reactions occurring between two divalent metal ions in pulp. The stoichiometric ratio of the ion exchange reaction between two divalent metal ions was found to be close to 1:1. The ion exchange constants are slightly dependent on pH and also on concentration of the metal ions. For the same pair of metal ions studied, the ion exchange constants determined in TMP, unbleached and oxygen-delignified softwood kraft pulps are rather similar. Compared with a strongly acidic cation exchanger, the pulps studied show clearly better selectivity to the metal ions studied. Especially the pulps have better selectivity to heavy metal ions, e.g. lead and copper, than to the alkaline earth metal ions.



Determination of the stoichiometric coefficient, n, of the Pb/Cd and Pb/Mg ion exchange reactions in unbleached softwood kraft pulp.

Publications:

- Su, Pingping, *Sorption of metal ions to wood, pulp and bark materials* (Doctoral Thesis, Åbo Akademi University, Turku, ISBN: 978-952-12-2777-6)

- Boonjob, W., Zevenhoven, M., Ek, P., Hupa, M., Ivaska, A., Miró, M., Automatic dynamic chemical fractionation method with detection by plasma spectrometry for advanced characterization of solid biofuels, *Journal of Analytical Atomic Spectrometry* 27 (2012) 5, 841-849, RSC Publishing, ISSN: 0267-9477)
- Su, P., Ek, P., Ivaska, A., Determination of metal ions in single wood fiber by LA-ICP-MS, *Holzforschung* 66 (2012) 7, 833-840 (Walter de Gruyter GmbH, ISSN: 0018-3830)
- Su, P., Granholm, K., Pranovich, A., Harju, L., Holmbom, B., Ivaska, A., Metal ion sorption to birch and spruce wood, *BioResources* 7 (2012) 2, 2141-2155 (North Carolina State University, ISSN: 1930-2126)

3.4 Interaction between Chemicals and Fibres

Paper is still an inevitable part of our daily life, even if the consumption of some types of paper has decreased in Europe. Important types of paper products are, for example, toilet paper, paper for printers, liquid packages for milk and juice, cardboard boxes for shipping goods acquired 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.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 estimate the hydrophobicity of particles. It is furthermore a very rapid method. Flow cytometry can, for example, be used to assess the sorption of extractives onto fillers in the presence and absence of galactoglucomannans (GGMs). Flow cytometry can also be combined with on-line turbidity monitoring in order to evaluate different types of anti-scale chemicals that are commonly used to eliminate calcium oxalate precipitation. Calcium oxalate deposition is one of the major deposit problems occurring in pulping and papermaking industry.

Additives are used in papermaking to improve the properties of the product or to ensure a smooth production. We are aiming at replacing some of the synthetic polymers with natural polymers that may be modified in order to achieve the best result. In some cases it is important to know if the additives are sorbed onto the fibres, penetrates through the paper or forms a film on the fibre network. With surface sensitive methods, such as ToF-SIMS, it was possible to detect natural and modified GGMs at the surface of papers. An iminated GGM formed a film when added to paper by sorption or spraying; this was not seen for natural GGM or cationized GGM. This opens opportunities for targeted functionalization of the paper surface.

The wood pitch that is retained in the paper will affect the surface and printing proper-

ties; but the extractives may also cause odour and taste problems, especially if the paper is used as packaging material for food or cigarettes. It is important that the content of extractives remaining in chemical pulp is correctly quantified. This has been shown to be challenging, since the extractives are modified by oxidation and radical reactions during pulping, bleaching and storage. Extraction with ASE and quantification with size exclusion chromatography was shown to be the best method. The conditions during storage were also very important. Samples should preferably be stored at low temperature in closed containers to avoid alteration of the extractives and to be able to correctly quantify the extractives.

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

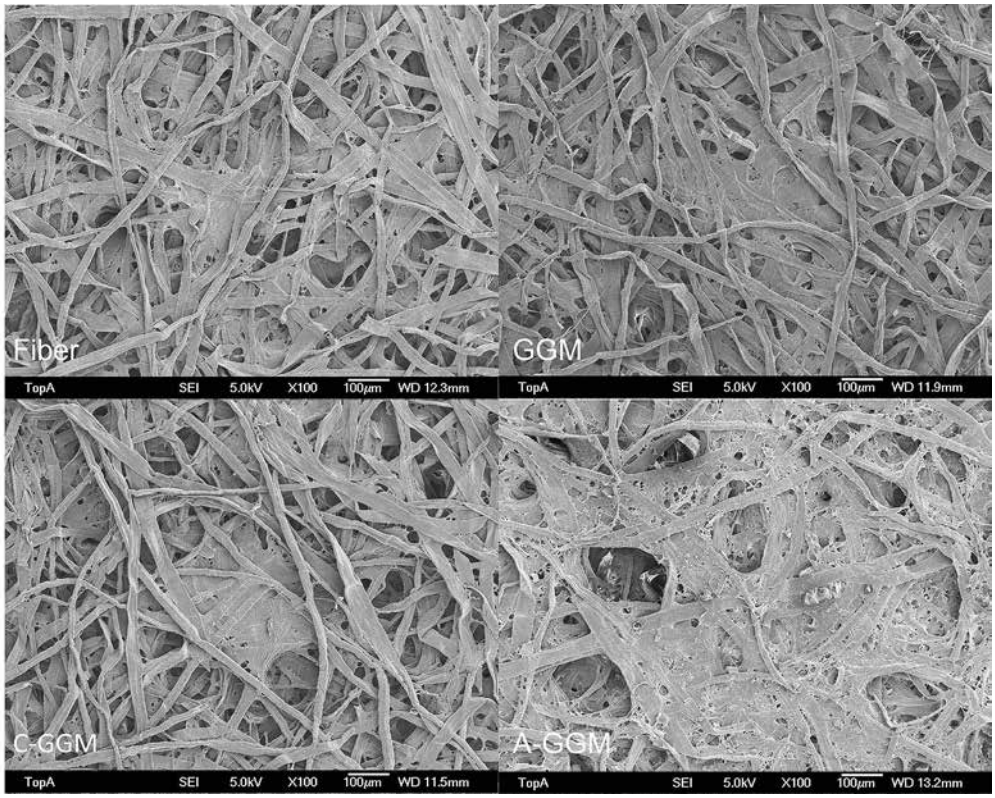
The runnability of the paper machine should be without disturbances such as web breaks and deposits to ensure an efficient production and a good quality product. The aim is to identify and develop new ideas and concepts for more efficient chemistry in papermaking, emphasizing the wet-end chemistry, and especially to use natural hemicelluloses as raw material for additives.

Natural galactoglucomannans (GGMs) was modified to obtain cationic of amphiphilic properties. These were added to papers either by spraying on top of a freshly formed paper sheet or by sorbtion onto chemical fibres before papermaking. By using ToF-SIMS, a surface specific technique, it was possible to identify characteristic peaks for each of the added GGMs. ToF-SIMS and FE-SEM suggested that the native and cationic GGMs penetrated into the sheet while the amphiphilic, iminated GGM formed a layer on the surface of the sheet. Iminated GGMs could therefore be used for functionalization of the paper surface.

Cooperation:
VTT; Åbo Akademi University, Top-Analytica

Publications:

- Lindqvist, H., Salminen, K., Kataja-aho, J., Retulainen, E., Fardim, P., Sundberg, A., The effect of fibre properties, fines content and surfactant addition on dewatering, wet and dry web properties, *Nordic Pulp and Paper Research Journal* 27 (2012) 1, 104-111 (SPCI, Swedish association of Pulp and Paper Engineers, ISSN: 0283-2631)
- Retulainen, E., Salminen, K., Lindqvist, H., Oksanen, A., Sundberg, A., Improving the wet web strength and runnability, *Appita Journal* 65 (2012) 3, 255-261 (Appita Inc., ISSN: 1038-6807)
- Hubbe, M.A., Sundberg, A., Mocchiutti, P., Ni, Y., Pelton, R., Dissolved and colloidal substances (DCS) and the charge demand of papermaking process waters and suspensions: A review, *BioResources* 7 (2012) 14, 6109-6193 (North Carolina State University, ISSN: 1930-2126)



FE-SEM images of papers. Top left: only chemical fibres, top right: addition of natural GGM by spraying on a freshly formed sheet, down left: addition of cationic GGM by spraying, and down right: addition of an iminated GGM. Magnification x 100, the bar is 100 µm. The GGM and the cationized GGM penetrated into the paper while the iminated GGM formed a film on top of the fibre network.

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

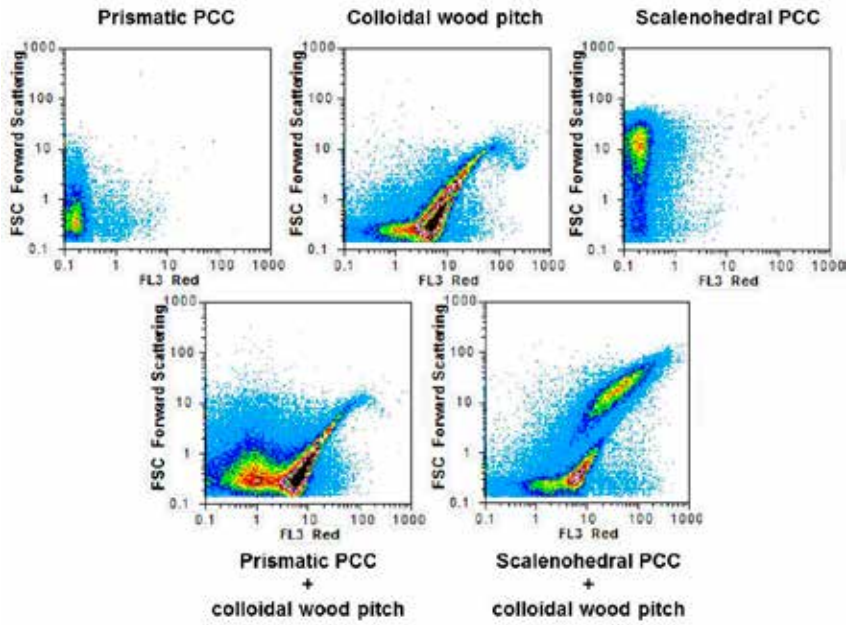
Interactions of Wood Pitch and Fillers Assessed by Flow Cytometry

Main funding: Åbo Akademi Process Chemistry Centre

Anders Strand, Anna Sundberg, Lari Vähäsalo, Stefan Willför

With flow cytometry (FCM) it is possible to estimate the particle size and also the hydrophobicity of the particles. An increase in particle size is seen as an increase in forward scattering and an increase in hydrophobicity as an increase in FL3. If most particles have FL3 > 2 they can be considered as hydrophobic.

FCM data showed that wood pitch emulsion consists of hydrophobic particles, even if the most hydrophobic pitch components are shielded from the surrounding water by a surface layer of resin and fatty acids. Both samples of precipitated calcium carbonate (PCC) were hydrophilic.



Flow cytometry (FCM) of a colloidal wood pitch emulsion, prismatic PCC, scalenohedral PCC and mixtures of wood pitch and PCC. An increase in particle size is seen as an increase in the forward scattering and an increase in hydrophobicity as an increase in FL3. Particles are considered hydrophobic if most particles have FL3 > 2

Additions of prismatic PCC to a pitch emulsion resulted in a new population seen by FCM, due to interactions between the pitch and the PCC. However, the FCM results imply that the prismatic PCC particles were not completely covered by pitch. Additions of scalenohedral PCC to the pitch emulsion resulted in a population of pitch-PCC parti-

cles with an even higher FL3 value than colloidal pitch. The prismatic PCC was anionic, while the scalenohedral PCC was cationic. Attraction between the anionic charges of the colloidal pitch and the cationic charges of the scalenohedral PCC lead to strong interactions. The pitch most likely accumulated within the scalenohedral structure, and seemed to completely cover the surface of the particles. The large difference in hydrophobicity between the pitch populations formed with the prismatic PCC and the scalenohedral PCC showed that the type of charge of the mineral particle is crucial for the interactions between mineral particles and colloidal pitch. Addition of galactoglucomannans resulted in a lower hydrophobicity of the pitch-PCC population. GGM thus diminished the adsorption of colloidal wood pitch onto the cationic PCC, but could not completely prevent the interactions between pitch and scalenohedral PCC.

Cooperation:
Åbo Akademi University PCC

Publications:

- Strand, A., Zasadowski, D., Norgren, M., Hedenström, E., Willför, S., Sundberg, A., Selective froth flotation of pitch components from spruce TMP process water, *Appita Journal* 65 (2012) 4, 337-346 (Appita Inc., ISSN: 1038-6807)

Calcium Oxalate Scaling in Mechanical Pulping and Bleaching

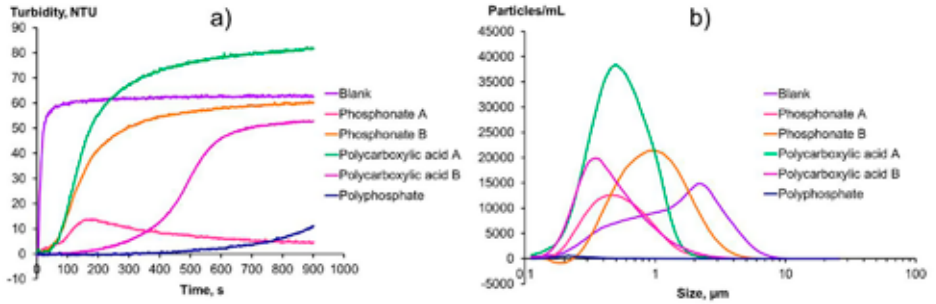
Main funding: Industry

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

Calcium oxalate scaling is one of the major deposit problems occurring in pulping and papermaking industry. Oxalic acid, that enters the process with the wood raw material, and is formed in the oxidative bleaching stages, can form a calcium salt with a very low solubility in water. The resulting calcium oxalate precipitates often cause both production and quality related problems.

Within this project we have looked at the formation of oxalic acid from different wood substances and the effect of peroxide bleaching parameters. Oxalate analysis methods have also been addressed. Apart from the ion concentrations, calcium oxalate precipitation in pulping processes is governed by many different process water parameters like pH, temperature, conductivity, and other dissolved and colloidal substances, and these have also been investigated in this project.

Different types of anti-scale chemicals are commonly used to eliminate calcium oxalate precipitation by threshold inhibition, crystal modification, and dispersion mechanisms. Screening of these chemicals in laboratory scale is often challenging. Recently we have combined on-line turbidity monitoring and flow cytometry (FCM) analysis in order to evaluate product performance more reliably. X-ray diffraction (XRD), and scanning electron microscopy (SEM) have further been utilized to identify and visualise the crystal forms in the precipitates.



Effect of some common anti-scale agent components (100 ppm) on calcium oxalate precipitation, a) Precipitation rate estimated by turbidity monitoring, and b) Particle size distribution by flow cytometry analysis (Calcium: 2 mmol/L; Oxalate: 1 mmol/L)

Cooperation:
Sappi Fine Paper Europe, Kemira

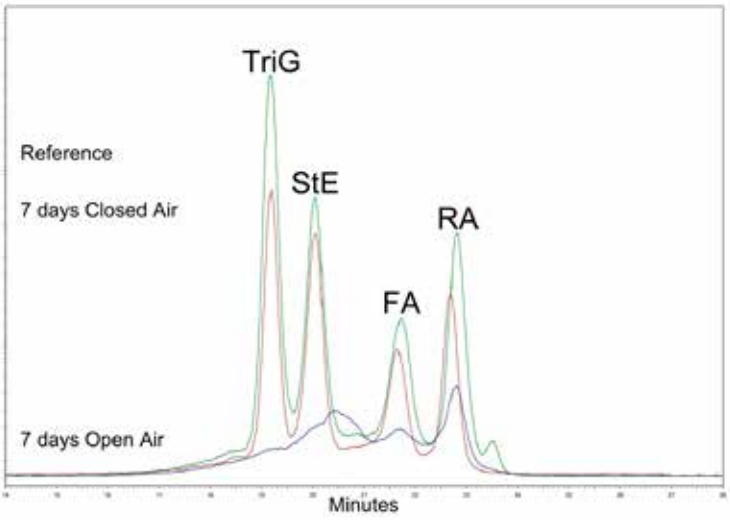
Towards Chemical Understanding of Paper Properties - Role of Different Fibre Constituents on Sorption and Optical Properties

Main funding: PaPSaT Graduate School

Sylwia Bialczak, Stefan Willför, Bjarne Holmbom, Anna Sundberg

Paper produced from mechanical pulp contains almost all of the original wood components. The lipophilic extractives, or wood pitch, 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. However, 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

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

Polymerized Extractives in Birch Kraft Pulp

Main funding: Industry

Sylwia Bialczak, Stefan Willför, Anna Sundberg

A part of the lipophilic extractives remain in chemical pulp, especially from birch. These extractives are difficult to analyse, since they have undergone oxidation and radical reactions during the harsh conditions during cooking and bleaching. The extractives may cause problems in following processes and their quantification is important.

In this work, we concluded that extraction in an accelerated solvent extractor (ASE) with acetone:water:acetic acid (95:5:1) gave a good yield of fatty acid soaps and were faster and more efficient than soxhlet extraction. High performance size exclusion chromatography (HP-SEC) gave a higher yield of extractives, also high-molar mass extractives, but the individual groups of extractives could not be quantified. With gas chromatography is was possible to quantify only a small part of the extractives, since many of the components were altered during the processes. The content of extractives decreases during the bleaching sequence, especially during the alkaline washing steps, but the amount of altered extractives increases.

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 obtained understanding of processes and the chemistry behind these are also used for other biomass sources, such as sugarcane bagasse and straw.

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.

Future Biorefinery II (FuBio)

Main funding: Tekes, Forestcluster Ltd

Ikenna Anugwom, Jesús Arroyo, Johan Bobacka, Tao Song, Jens Krogell, Petri Kilpeläinen, Ekaterina Korotkova, Jarl Hemming, Patrik Eklund, Tingting Han, Bjarne Holmbom, Ari Ivaska, Victor Kisonen, Ann-Sofie Leppänen, Jyri-Pekka Mikkola, Dmitry Murzin, Päivi Mäki-Arvela, Andrey Pranovich, Markku Reunanen, Tapio Salmi, Annika Smeds, Anna Sundberg, Maunu Toivari, Pasi Virtanen, Risto Korpinen, Jan-Erik Raitanen, Chunlin Xu, 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) ended in 2011 and 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 programs.

FuBio JR2 is divided in different 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). In FuBio Cellulose, 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.

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 plain water and without buffer addition if possible

- providing as small as possible chemical altering of the residual material, which is important to a following extraction of lignin (lignin extraction)

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

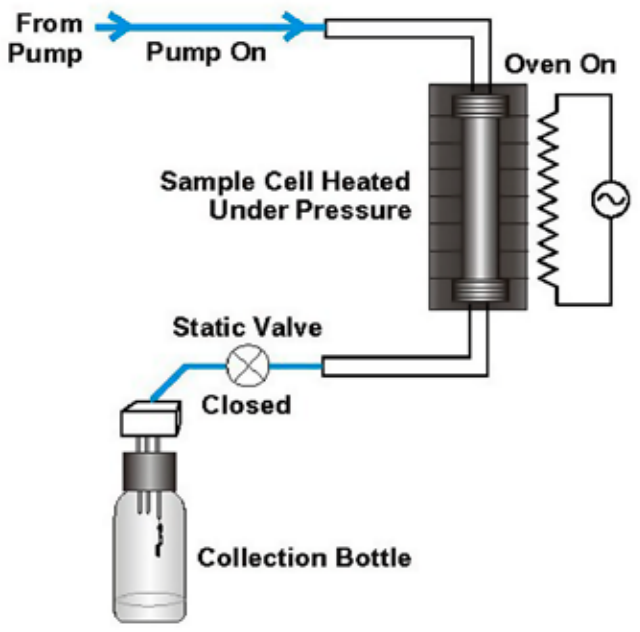
- internal cell wall diffusion
- effect of particle size and shape
- surface
- challenges with simultaneous extraction and hydrolysis
- measuring and controlling the pH in the reactor at high temperatures during the extraction

Experimental condition applied in this study:

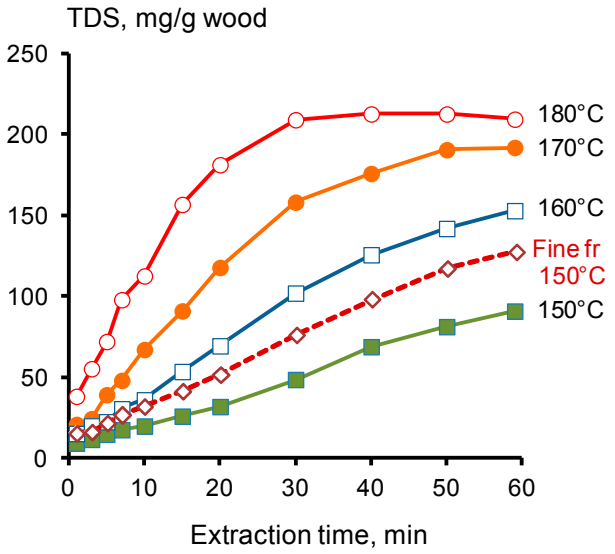
- ASE 350, Zr-type cell
- Temperature: 150°C
- Solvent: distilled water
- Fine fraction 0.05-0.1 mm of ground spruce sapwood

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.

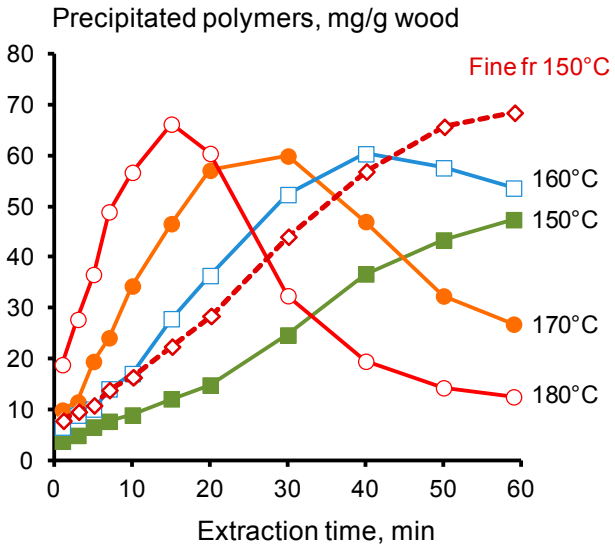
It was established that after 60 min extraction, the yield of polymeric GGM, isolated by precipitation in EtOH:H_2O (85:15 v/v), was c. 70 mg/g of the dried wood. This is about half of TDS (ca 140 mg/g of dried wood) isolated from spruce sapwood by hot-water extraction at given conditions. The "quality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



Principle of Accelerated Solvent Extraction

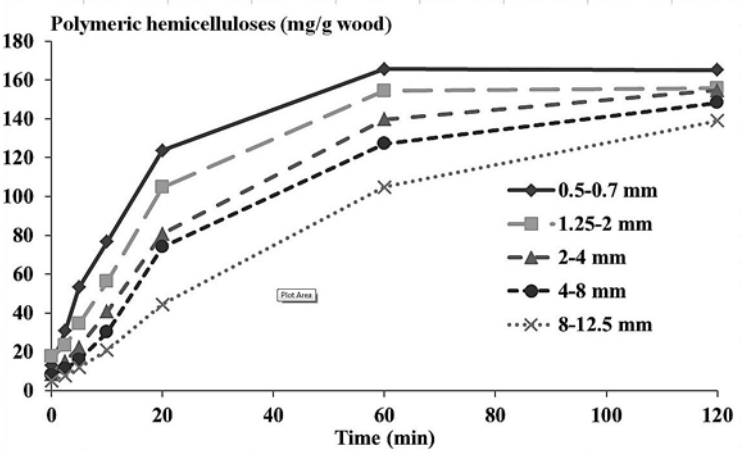


TDS of extracts obtained at different temperatures (particle size 0.25-1.0 vs fine fraction 0.05-0.1)



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

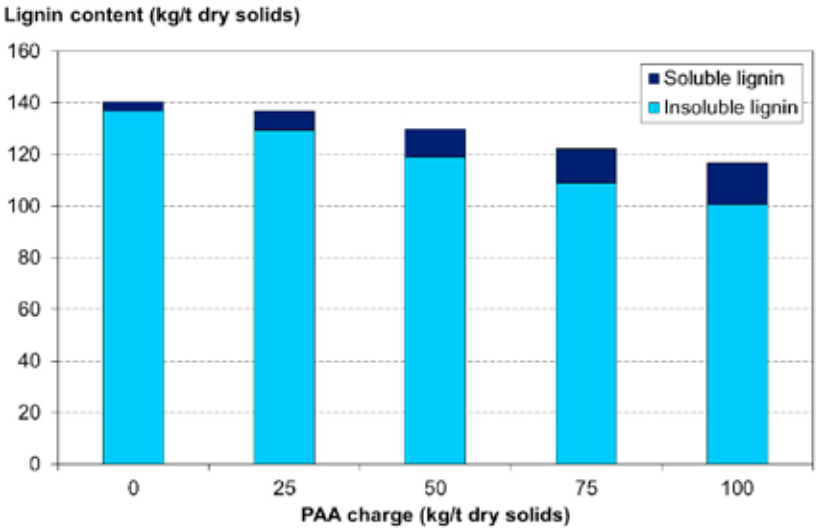
These studies were extended also to a wider particle size range and a batch extractor system. This work confirmed that it is possible to extract about 30 % of the total wood material and particularly almost all hemicelluloses with plain water at 170 °C. Particle size had a large effect on both the extraction rate and the extraction yield. Smaller size wood particles gave a faster initial (first 20 minutes) extraction and slightly higher yield after two hours of extraction. The reaction order was established to be of pseudo first order for larger particles (2mm – 12.5 mm) and 1.5st order for smaller particles (0.5 mm – 2 mm). The effective diffusion coefficient was determined to be $9.11*10^{-10}$ m^2/s. The average molar mass of the extracted hemicelluloses drops rapidly during the first 10 minutes of the extraction and is further not much affected by the difference in wood particle sizes. For a maximum yield of polymeric non-cellulosic carbohydrates without too much degradation, about 20 minutes at 170 °C were shown to be the optimal time. After that the autohydrolysis becomes more extensive and monomeric sugars and the formation of other degradation products dominate.



Total polymeric hemicelluloses in extracts obtained from different size spruce wood particles at 170°C.

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 are 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) are applied because deacetylation of hemicelluloses occurs in alkaline conditions and will decrease the water solubility of the hemicelluloses.

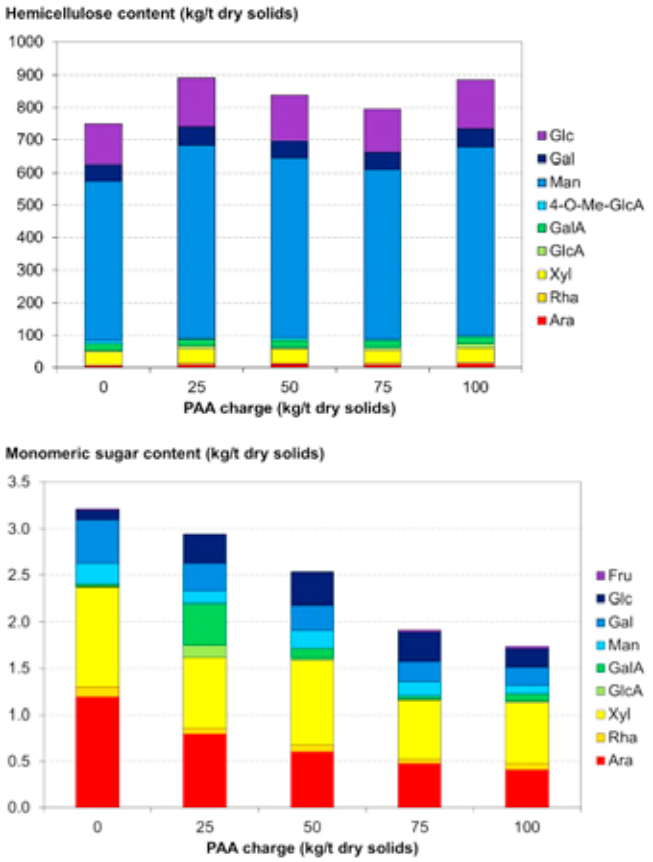
Industrial Norway spruce (*Picea abies*) sawdust was extracted using a flow-through PHWE process. Thereafter the obtained hemicellulose-rich extract was ultrafiltered using 10 kDa cut-off membranes and a concentrate fraction containing high molecular weight hemicelluloses having relatively high dry solids content was obtained. The concentrate fraction was treated with PAA. 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.

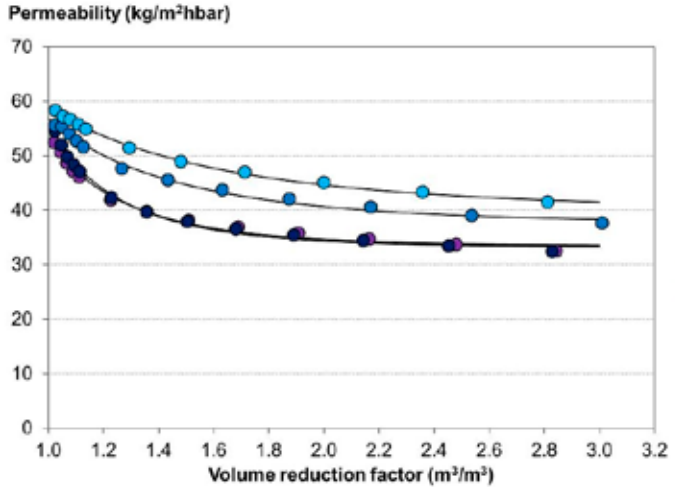
The hemicellulose content was not affected by PAA treatment which is an important issue. Additionally, the monomeric sugar content was not increased. This clearly suggests that PAA is a suitable bleaching chemical for PHW extract purification.



Hemicellulose (top) and monomeric sugar (bottom) content of PAA treated concentrate

Norway spruce extract having TDS 0.99% was treated with ClO_2 using the following charges: 0, 10, 30 and 50 kg ClO_2/t dry solids. The pH value of the extract was adjusted with 1 M H_2SO_4 to approximately 2.8. 4 g o.d. extract was treated at 60 °C and 60 min time in addition to 15 min heating time. The extract was concentrated by ultrafiltration subsequent to ClO_2 treatment. Millipore Amicon 8400 stirred dead-end type filtration system was used in the concentration stage. The filtration temperature was 60 °C and the pressure 2 bar obtained by N_2 gas. 300 g extract was concentrated to 100 g. After the concentration stage the extract was further diafiltered using the same ultrafiltration system. 100 g purified water was added and filtrated using the same filtration conditions as above.

The permeability of the spruce extract concentration was enhanced considerable by ClO_2-charge (see Figure below). Also, the permeability during diafiltration was enhanced with increased ClO_2-charge (not shown).



Permeability as a function of volume reduction factor and ClO_2-charge during extract concentration

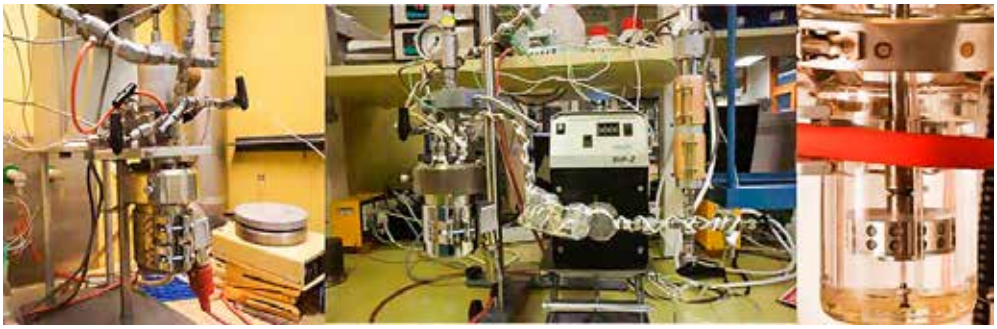
Chlorine number of the extract was determined and it was found to be 210.94 kg Cl_2/t. The amount of chlorine dioxide needed to fully oxidise the extract can be calculated by using the oxidation power of bleaching chemicals, oxidation equivalents (OXE). The ClO_2 charge should thus theoretically be 80.26 kg/t or 8.03% on o.d. extract for complete oxidation. Thus, the ClO_2-charges used in the experiments, 10 kg/t, 30 kg/t and 50 kg/t correspond 12.6%, 37.4% and 62.3% of the complete oxidation of the extract.

The solids content, lignin content, hemicellulose content, extractives content and average molecular weight of the samples was determined. The lignin content was decreased substantially by increased ClO_2 charge. When the ClO_2 charge was 50 kg/t the lignin content of the concentrate fraction decreased to approximately 5.4% on o.d. extract. Extractives were almost entirely degraded with increased ClO_2 charge. The hemicellulose content of the different fractions was maintained constant indicating a very selective delignification. Also, the average molecular weight of the concentrate fraction was not changed.

It can be concluded that ClO_2 is superb bleaching chemical to purify spruce extract: lignin and extractives are removed while the hemicellulose content and the length of the hemicellulose chains are maintained. Additionally, the filtration capacity is enhanced.

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.

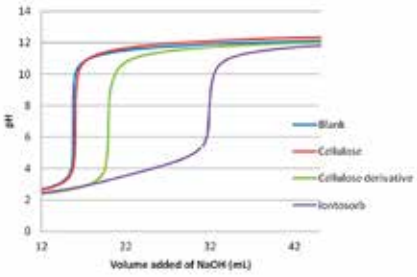


Sample wood processing with SILs. 1) Classical batch reactor to 2) loop reactor and 3) 'SpinChem' reactor

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. Cellulose beads are prosperous materials for analytical separations and drug release. Cellulose beads contain acidic groups that were studied by potentiometric titration. The titration data was evaluated by the FITEQL software giving detailed information about the different acidic groups on the cellulose beads and modified cellulose beads. Modified cellulose beads have more than ten times the amount of acidic group than cellulose beads.

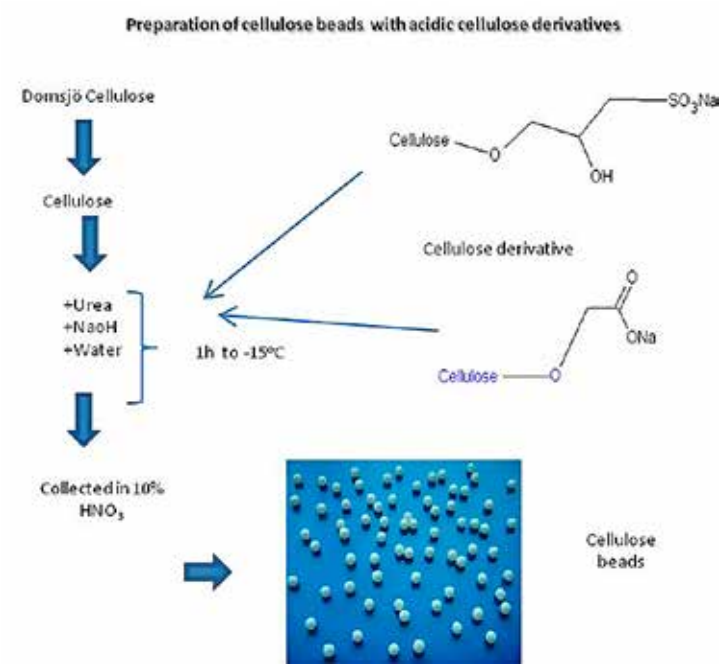


	Cellulose		Cellulose derivative		Iontosorb	
	lg K	Concentration (μeq/g)	lgk	Concentration (μeq/g)	lg K	Concentration (μeq/g)
$R_1^-H^+$	2.8	112.8	2.7	94.3	3.7	750.6
$R_2^-H^+$	4.5	6.8	5.4	17.9	4.7	538.2
$R_3^-H^+$	6.0	2.5	9.6	45.0	8.7	25.4
Total		122.1		157.2		1314.2

Potentiometric acid titration for cellulose and cellulose derivative with acidic groups

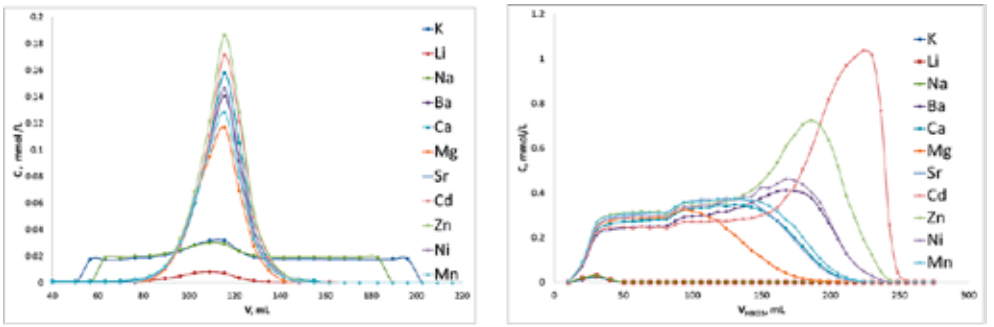
The cellulose matrix obtained from Domsjö fabriker AB was treated with HCl and ethanol to eliminate any lignin residue and cellulose with 3-sulpho-2-hydroxypropyl groups were

inserted in the preparation of cellulose beads. The new modified cellulose can be used as a cation exchanger and present unique characteristics which can be used for better and higher sorption.



Preparation of cellulose with acidic cellulose derivatives

The cellulose beads were used as a stationary phase in column chromatography in order to study metal ion affinities. The mechanism is mainly ion exchange by complexation of metal ions to the cellulose, which contains carboxylic groups as a functional group. It was observed that divalent ions show better sorption than monovalent ions and the modified cellulose beads with acidic groups show a higher operating capacity.



Concentration of metal ions in the collected fractions as a function of the elution volume for a chromatographic column filled with cellulose beads (left) and modified cellulose beads with acidic group (right).

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

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Environmentally Sound Extraction of Biomass with Green Solvents

Main funding: Metla

Petri Kilpeläinen, Andrey Pranovich, Jarl Hemming, 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. Work on optimising extraction parameters for up-scaling to pilot scale extractions of birch hemicelluloses have also been part of the activities.

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

Publication:

- Kilpeläinen, P., Leppänen, K., Spetz, P., Kitunen, V., Ilvesniemi, H., Pranovich, A., Willför, S., Pressurised hot water extraction of acetylated xylan from birch sawdust, *Nordic Pulp and Paper Research Journal* 27 (2012) 4, 680-688 (SPCI, Swedish association of Pulp and Paper Engineers, ISSN: 0283-2631)

New Value-Added Natural Chemicals and Renewable Materials from Wood

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

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, Ekaterina Korotkova, Stefan Willför

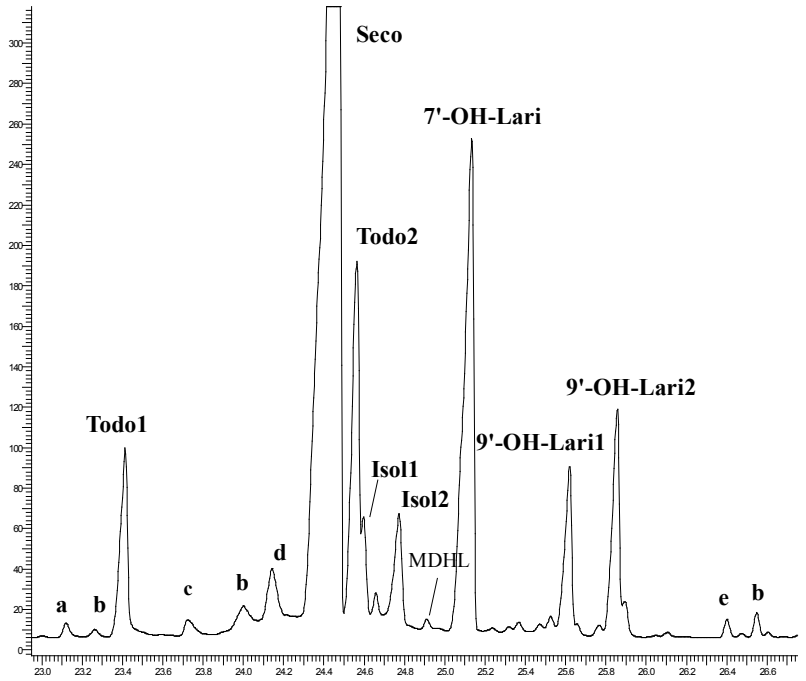
This project aims at identifying natural tree compounds that can be upgraded to new value-added natural biochemicals or renewable materials. Chemical or enzymatic modifications in combination with state-of-the-art analytical methods are means used to produce potential bioactive or technically interesting 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. The work on wood lignans was also useful in a study of the content, composition, and stereochemical characterisation of lignans in berries and seeds, which gave new insights into the polyphenols in such food species. Our isolated lignans were also used in a study where versatile peroxidase was used as a biocatalyst tool for generating new polymeric biomolecules by homogeneous and heterogeneous cross-linking.



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)". Industrial production of pinosylvins and other extractable pine compounds using different selective extraction techniques (organic solvents, supercritical water, sequential extraction etc.) and different sources were evaluated.

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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- Smeds, A.I., Eklund, P.C., Monogioudi, E., Willför, S.M., Chemical characterization of polymerized products formed in the reactions of matairesinol and pinoresinol with the stable radical 2,2-diphenyl-1-picrylhydrazyl, *Holzforschung* 66 (2012) 3, 283-294 (Walter de Gruyter GmbH, ISSN: 0018-3830)

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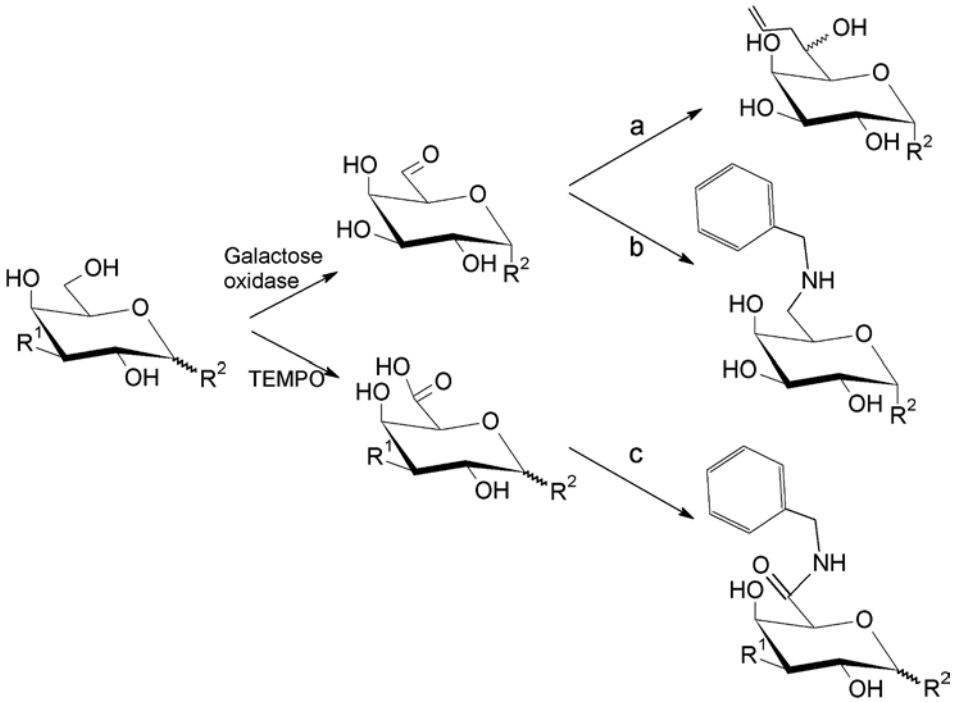
Chemical Modification of Water-Soluble Spruce O-Acetyl-Galactoglucomannan

Main funding: Graduate School for Biomass Refining (BIOREGS)

Ann-Sofie Leppänen, Haolin Lu, Jun Liu, Xiaoju Wang, 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.

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.

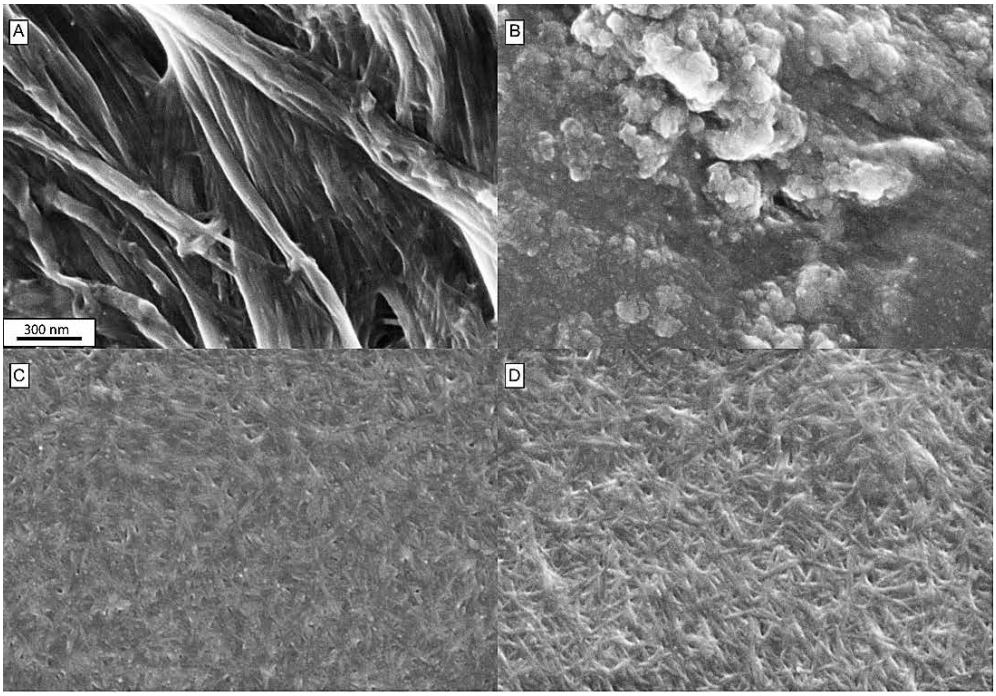


Selective chemical modifications of GGM in water: Enzymatic oxidation followed by a) indium mediated allylation and b) reductive amination, and chemical oxidation followed by c) amidation. R1 = - OH or GGM backbone; R2 = GGM backbone

In addition to enzymatic oxidation, chemical oxidation has also been used for the activation of specific hydroxyls for further modification. GGMs were oxidized on C-6 of hexoses by TEMPO-mediated oxidation. Different degrees of oxidation were successfully obtained by varying the reaction parameters. The formed uronic acids were then further modified by a carbodiimide mediated amidation reaction, which opens a window for introducing various functionalities selectively on C6 of hexoses. The affinity of the modified polysaccharides to cellulose surfaces has also been investigated.

A green chemo-enzymatic pathway for synthesis of conducting polyaniline (PANI) composites was also developed. Laccase-catalyzed polymerization in combination with anionic polysaccharides was used to produce polysaccharide/PANI composites, which could be processed into flexible films or coated onto cellulose surfaces. Different polysaccharide templates were assessed, including κ-carrageenan, native spruce GGM, and TEMPO-oxidized cellulose (nanofibrillated cellulose, NFC) and GGM. The resulted conducting biocomposites derived from natural materials provide a broad range of potential applications, such as in biosensors, electronic devices, and tissue engineering.

Cooperation:
University of Helsinki; Royal Institute of Technology (KTH), Wallenberg Wood Science Centre, Stockholm, Sweden



SEM images of (a) filter paper; (b) κ-CGN/PANI coated on filter paper; (c) NFC film; (d) NFC/PANI film.

Design of Hemicellulose Block Copolymers and Their Applications

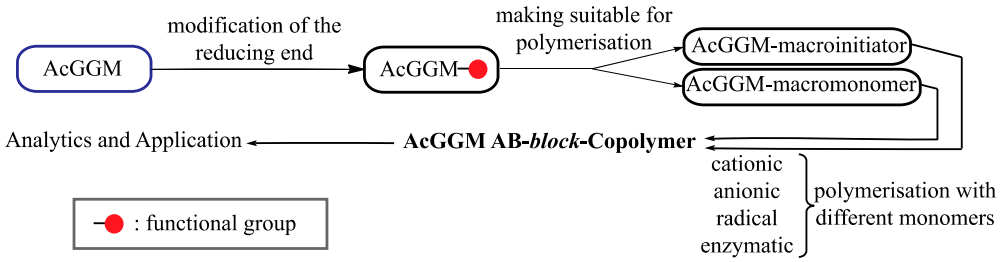
Main funding: Aides à la formation recherche (AFR)

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

The aim of this work is to modify spruce O-acetyl galactoglucomannans (AcGGM) in order to get AB-block-copolymers. Two approaches have been designed.

In the first approach, a class of nonionic polysaccharides-based surfactants were synthesized from AcGGM using naturally-occurring saturated fatty acids, CH3(CH2)nCOOH (n = 7, 12, and 16). Different synthesis routes were applied to yield amphiphilic derivatives with either a grafted or block structure. Fatty acids activated with 1,1'-carbonyldiimidazole (CDI) were grafted to the backbone of AcGGM molecules on their hydroxyl groups. Alternatively, synthesized amino-activated fatty acids using ethylenediamine were reacted with the reducing end of GGM. The resultant products may find potential applications in such areas as food, cosmetic, and paint formulations.

The other approach is described as such: in a first reaction, the reducing end of the polysaccharide chain has to be tailored for polymerization purpose; subsequently, a polymerization of a monomer can be performed to result in AB-block-copolymers with different properties and different fields of application. In the following illustration the synthesis path is shown in a simplified way:



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

Development of Biocomposites

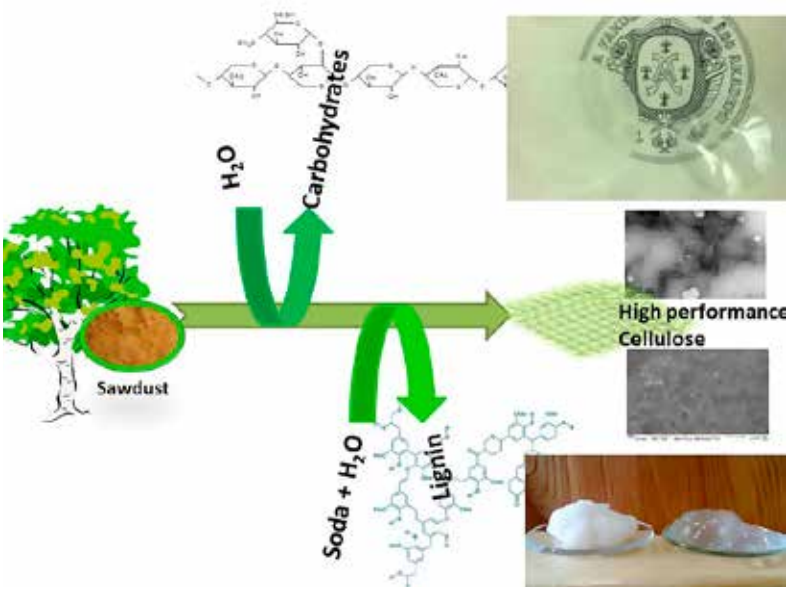
Main funding: Graduate School for Biomass Refining (BIOREGS), Chinese Council Scholarship, Knut and Alice Wallenberg Foundation

Chunlin Xu, Ann-Sofie Leppänen, Jun Liu, Risto Korpinen, Stefan Willför

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

For the first time, applicability of sawdust has been explored to develop nanofibrillated cellulose (NFC) from the biorefinery concept. The residual cellulose of wood processing waste, sawdust, which was left over after sequential hot-water extraction processes to isolate hemicelluloses and lignin in a novel forest biorefinery concept, was explored as the starting material for preparation of a highly value-added polymeric material, NFC. The residual cellulose in sawdust was converted to a transparent NFC suspension in water through the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)/NaClO/NaBr oxidization approach. The resultant NFC with a dimension of 5-10 nm in width and hundreds of nanometres in length were further processed into NFC films. This study has demonstrated the feasibility of producing NFC and its films with high mechanical properties from a wood waste – birch sawdust by a process incorporated into a novel biorefinery platform recovering also polymeric hemicelluloses for other applications.

We have also developed a novel approach for fabricating PANI-biocomposites. Firstly, we developed chemo-enzymatic processes to utilize natural polysaccharides as templates instead of conventional synthetic polymers for laccase-catalyzed polymerization of aniline. Various polysaccharides and their derivatives, including naturally anionic κ-carrageenan (κ-CGN), native spruce O-acetyl galactoglucomannan (GGM), TEMPO-oxidized cellulose derived NFC, and GGM (GGMPolyU) were assessed as anionic templates. Moreover, these templates could be directly processed with PANI and utilized as construction components of the final PANI-biocomposites. More specifically, the use of κ-CGN, a naturally occurring anionic polysaccharide from algae, resulted in a κ-CGN/PANI hy-



Upgrading of birch sawdust to value-added materials.

drogel, which could be casted into film or processed to coatings. Wood-derived cellulose and GGM were subjected to TEMPO-oxidation to introduce carboxylic acids at the C6 positions of the sugar units prior to PANI synthesis. Notably, the resulted NFC/PANI hydrogel could be directly processed to a flexible film or other forms of biocomposites with good mechanical strength, which may find potential applications in biosensors and biomedical engineering.

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

Cooperation:

Åbo Akademi University PCC and FUNMAT; Royal Institute of Technology (KTH), Wallenberg Wood Science Center, Stockholm, Sweden; University of Helsinki; Aalto University

Publications:

- Parikka, K., Leppänen, A.-S., Xu, C., Pitkänen, L., Eronen, P., Österberg, M., Brumer, H., Willför, S., Tenkanen, M., Functional and anionic cellulose-interacting polymers by selective chemo-Enzymatic carboxylation of galactose-containing polysaccharides, *Biomacromolecules* 13 (2012), 2418–2428 (ACS publications, ISSN: 1525-7797)

- Xu, C., Spadiut, O., Araújo, A.C., Nakhai, A., Brumer, H., Chemo-enzymatic assembly of clickable cellulose surfaces via multivalent polysaccharides, *ChemSusChem* 5 (2012) 4, 661-665 (WILEY-VCH Verlag GmbH, ISSN: 1864-564X)

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

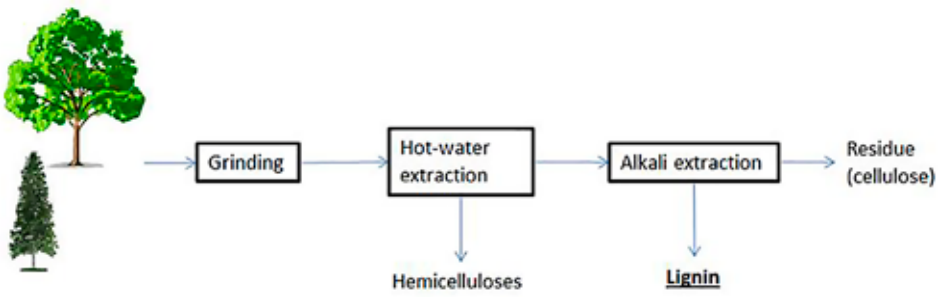
Main funding: International Doctoral Programme in Bioproducts Technology (PaPSaT)

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. The work so far has concentrated on obtaining a thorough understanding of how different parameters, such as temperature, pH, and sequential extraction, affect the extraction and purification of lignin from spruce.

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 organic waste is produced. However, economical- and image factors and are often working against valorising waste materials and therefore products, such as organic fillers and food supplements, 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 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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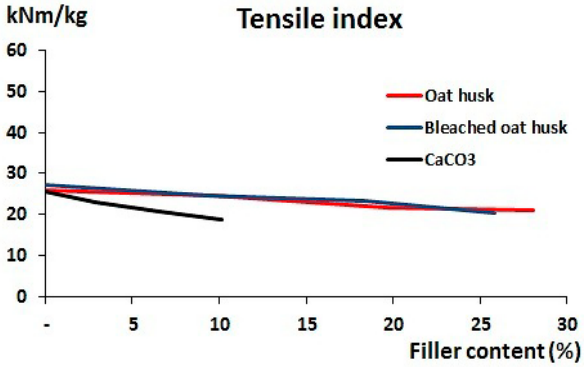
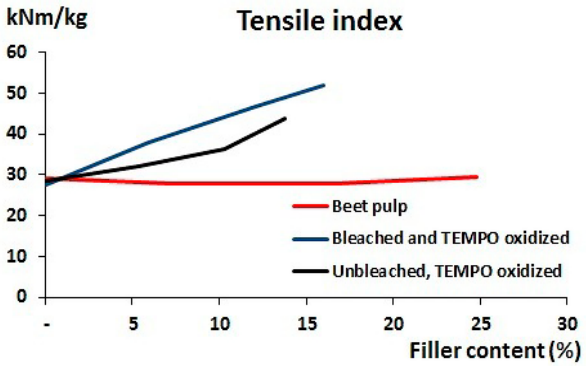
The agro side streams can be used, for example, as filler materials for paper. The paper making properties for the organic fillers are, generally, good but there are significant differences in the papermaking properties depending on the source and modification of the raw material (Figures A and B below).





Variations in tensile strength of paper depending on raw material and chemical treatment 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. Left: Tensile strength of paper with a filler made of unbleached or bleached oat husk compared to a traditional filler. Right: Tensile strength of fillers made from untreated or oxidized (bleached- or unbleached) beet pulp.

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 (see figures below). One aim of the project is, thus, to test different means of tailoring them to suit the planned applications.

Bleaching experiments with wheat bran

Bleaching experiments with beet pulp

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.

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

COST Action FP0901, "Analytical Methods for Biorefineries"

Main funding: EU RTD 7th Framework Programme

Stefan Willför, Anna Sundberg, Anders Strand, Annika Smeds, Andrey Pranovich

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 (twice). 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. The final meeting and seminar of the Action will be arranged by PCC in September 2013 at Åbo Akademi University. More information can be found at www.abo.fi/costfp0901.

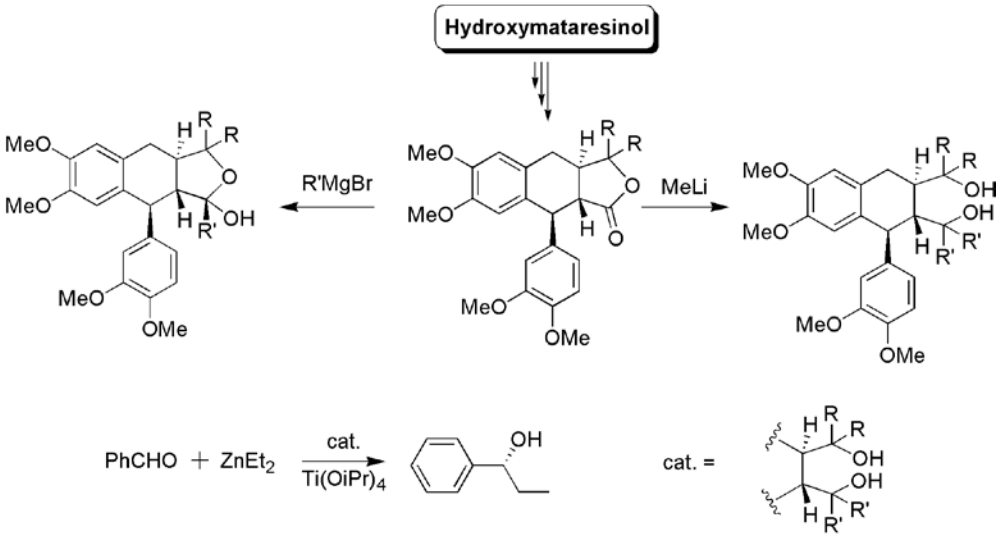
Cooperation:
Universities, laboratories, research institutes, and companies from 27 EU COST and 4 affiliated countries

Lignans as Versatile Chiral Auxiliaries and Chiral Catalysts (LIGNOCATS)

Main funding: Academy of Finland

Patrik Eklund, Yury Brusentsev, 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: Åbo Akademi 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

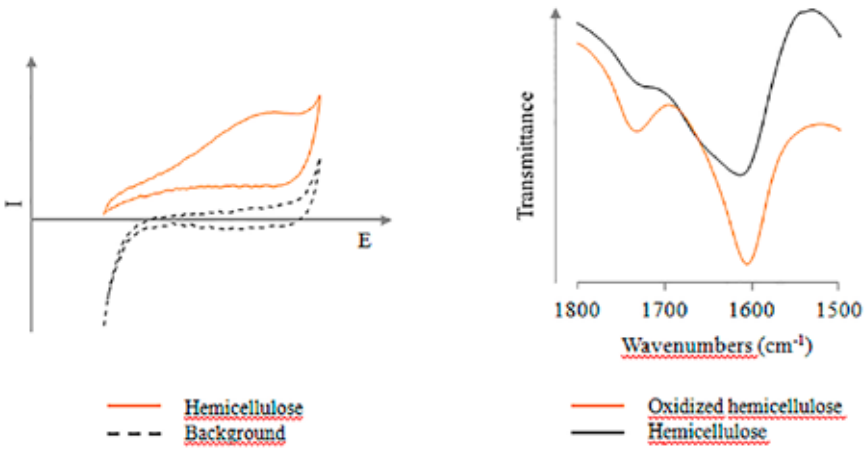
Sequential extraction of sugarcane bagasse with 1) toluene: ethanol (2:1), 2) hot water at temperatures between 170 and 200°C, and 3) alkaline peroxide yielded fractions rich in extractives, water-soluble hemicelluloses together with lignin, and alkali-soluble hemicelluloses. The total extractable material was slightly more than half of the dry sugarcane bagasse weight. The non-extractable residue mostly consisted 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 and two manuscripts are in preparation.

Electrochemistry of Polysaccharides derived from Biomass

Main funding: Åbo Akademi PCC

Yasuhito Sugano, Ari Ivaska

Utilization of biomass as an alternative energy resource has been expected to play an important role in building of a sustainable society. Especially production of biodegradable functional polymers in bio refineries can be expected to be produced from the main components of biomass (i.e. cellulose and hemicelluloses). The functional biopolymers and their physical properties can be designed by modifying chemical groups of the molecules. Oxidation of cellulose, for example, is one major approach in designing functional materials and further modifications of them. It has been studied by using chemicals and a catalyst. It has been reported that cellulose oxidized by 2,2,6,6,-tetramethylpiperidine-1-oxyl radical (TEMPO) is more hydrophilic than the original cellulose. In this project, we have studied the electrochemistry of polysaccharides to obtain fundamental knowledge about electrochemical interaction between the polysaccharide and the electrode substrate. We have been able to show that not only cellulose but also some hemicelluloses can be oxidized electrochemically. No systematic research about the electrochemistry of polysaccharides has been made until now. So, this project has potential to pioneer a new front in electrochemistry and claim a unique approach for electrochemical modification, functionalization and innovative utilization of polysaccharides derived from biomass in the bio refinery field.



Electrochemical response of one hemicellulose at Au electrode and the FTIR spectra of that material

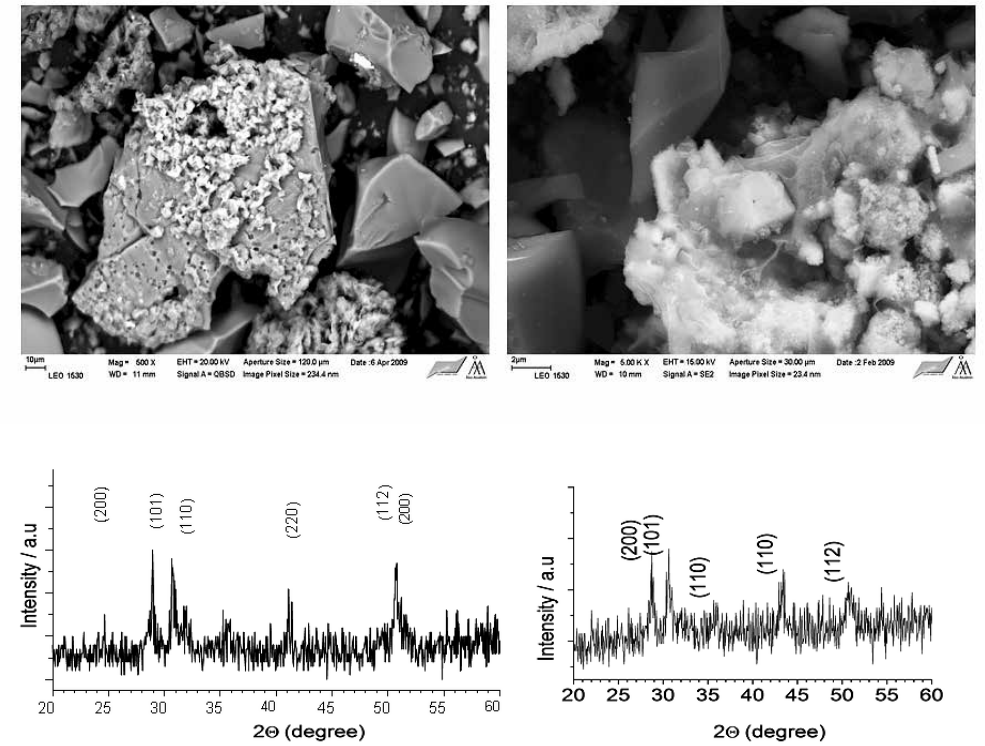
3.6 Catalysis and Molecular Engineering

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, and pyrolysis of biomass.



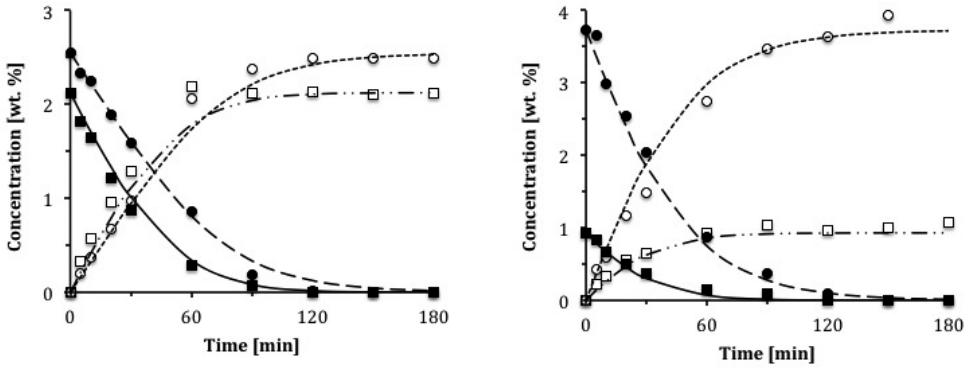
SEM images from the recycled catalyst surface showing crystallites of MgO and KCl deposited on zirconia surface (above) and XRD patterns from ZrO_2-KCl (left) and ZrO_2, KCl and MgO (right) catalysts below

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

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.

Micro and Mesoporous Materials

Main funding: Åbo Akademi

Narendra Kumar, Sabrina Schmidt, 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

Publications:

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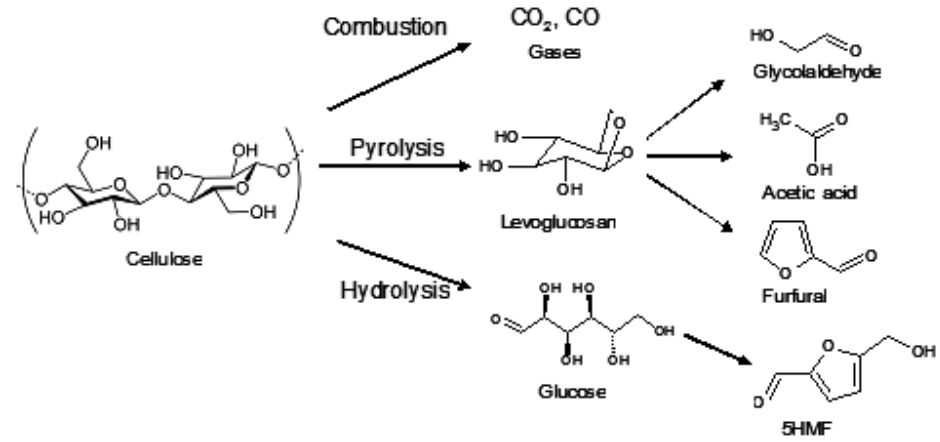
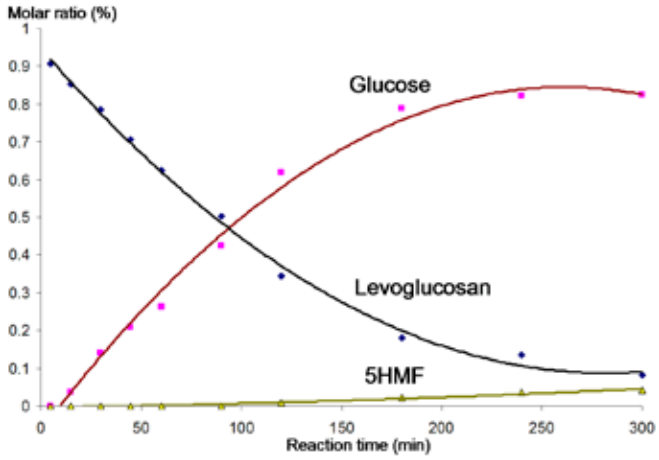




Common ways for biomass processing and catalytic transformation of levoglucosan into glucose

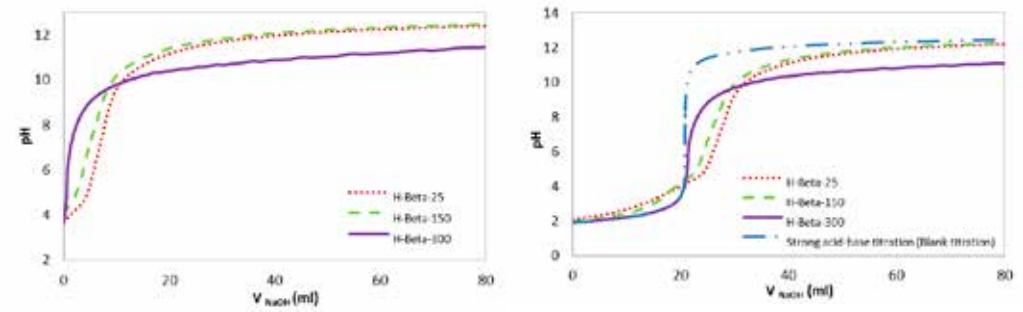
Synthesis, Characterization and Application of Polypyrrole/Zeolite Nanocomposites

Main funding: PCC

Kai Yu, Ari Ivaska, Narendra Kumar

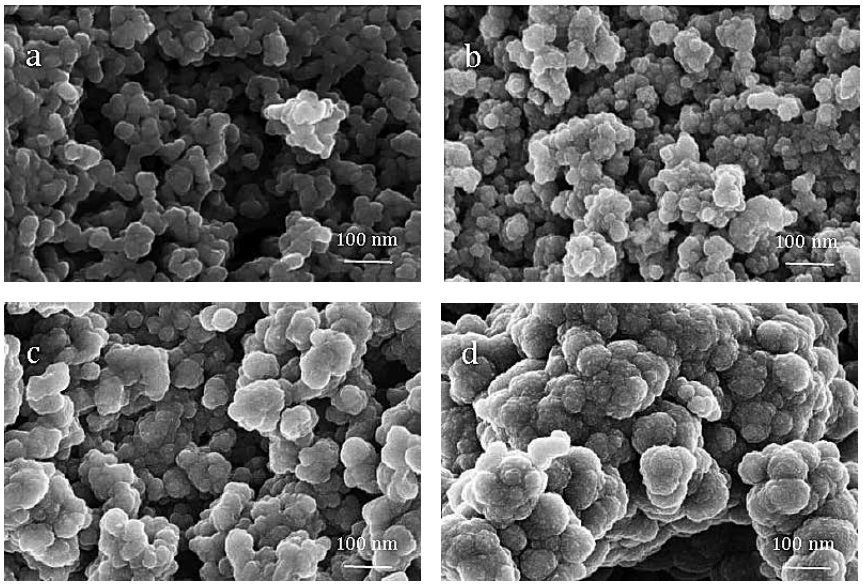
Various amounts of polypyrrole (PPy) were synthesized on zeolite frameworks by a chemical oxidative method using $FeCl_3$ as the oxidizing agent in water at ambient temperature. The proton forms of BEA zeolites with SiO_2/Al_2O_3 ratios of 25, 150 and 300 were employed as the host for PPy in this study. Before the polymerization reaction, the acid sites present in the host zeolites were determined with potentiometric titration. For that purpose the zeolite powders were dispersed in sodium nitrate solution, which were then titrated with a standard solution of sodium hydroxide and the titration curves shown below (left) were generated. Data analysis was based on linearization of the titration curves. Parallel experiments were done by adding nitric acid in the suspensions prior the titration in order to protonate the acid sites inside the zeolite structures before performing the titration. The titration curves shown on the right below were obtained. Various acid sites were found in the target zeolites, and both the protonation constants and the

concentrations of these acid sites were determined. Some released components from the zeolite structures may have influenced the potentiometric titration and therefore the ICP-OES technique was used to study the concentrations of dissolved aluminum and silicon in the zeolite suspensions after titration.

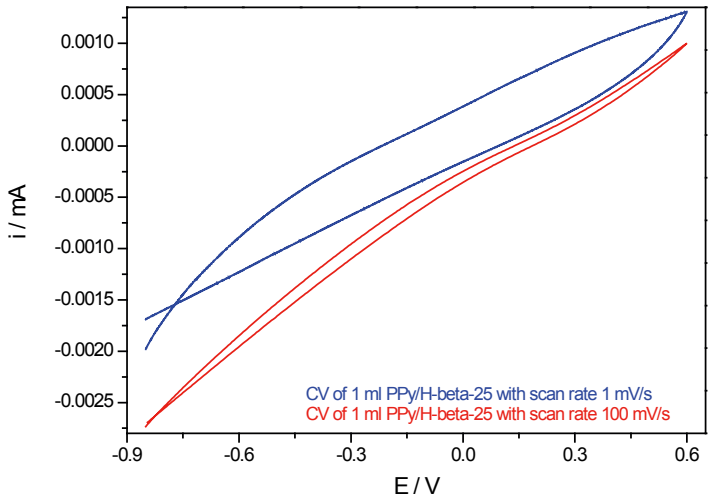


Potentiometric titration curves of host zeolites, pure zeolites (left), with added HNO_3 (right)

Both the anionic groups on the acidic sites of host zeolites and chloride ions from the oxidizing agent were functioning as dopants during the chemical polymerization process of pyrrole. For comparison, bulk PPy powders were synthesized without host zeolites by having only purified pyrrole and $FeCl_3$ in the aqueous polymerization solution. Nitrogen adsorption-desorption technique (Dubinin and Raduskevich), XRD, SEM, TEM and FTIR-ATR were used to characterize the resulting black powdery composite samples and these studies indicated that PPy was synthesized both in the inner and outer part of the zeolite structures. Conductivity measurements showed that depending on the amount of pyrrole and zeolite used during polymerization the electrical conductivities of the composites varied in the range 6.2×10^{-6} - 1.3 S cm^{-1}.



SEM images of a) pure H-beta-25, b) 1 ml PPy/H-beta-25 composite, c) 2 ml PPy/H-beta-25 composite and d) 3 ml PPy/H-beta-25 composite



Cyclic voltammogram of 1 ml PPy/H-beta-25 composite electrode obtained in 0.1 M NaCl solution with scan rate of 1 and 100 mV/s, respectively

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Valorization of Components Derived from Biomass

Main funding: Academy of Finland, Tekes, EU, Industry

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 Hajek, 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

Publications:

- Simakova, Olga, *Catalysis by gold for biomass transformations* (Doctoral Thesis, Åbo Akademi University, Turku, ISBN: 978-952-12-2793-6)
- Bernas, A., Salmi, T., Murzin, D.Yu., Mikkola, J-P., Rintola, M., Catalytic transformation of abietic acid to hydrocarbons, *Topics in Catalysis* 55 (2012) 7-10, 673-679 (Springer, ISSN: 1022-5528)
- Bernas, H., Bernas, A., Mäki-Arvela, P., Leino, R., Murzin, D. Yu., Hydrogenation of geraniol over ruthenium- Binap catalysts, *Catalysis Science & Technology* 2 (2012), 1901-1907 (RSC Publishing, ISSN: 2044-4753)
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- Kusema, B., Mikkola, J-P., Murzin, D.Yu., Kinetics of L-arabinose oxidation over supported gold catalyst with *in-situ* catalyst electric potential measurements, *Catalysis Science & Technology* 6 (2012) 2, 423-431 (RSC Publishing, ISSN: 2044-4761)
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- Riittonen, T., Madnani, D., Toukoniitty, E., Mikkola, J-P., Leino, A-R., Kordás, K., Sapi, A., Arve, K., Wärnå, J., One-pot liquid-phase catalytic conversion of ethanol to 1-butanol over aluminium oxide - the effect of the active metal on the selectivity, *Catalysts* 2 (2012), 68-84 (MDPI AG, ISSN: 2073-4344)
- Rozmysłowicz, B., Mäki-Arvela, P., Tokarev, A., Leino, A-R., Eränen, K., Murzin, D.Yu., Influence of hydrogen in catalytic deoxygenation of fatty acids and their derivatives over Pd/C, *Industrial & Engineering Chemistry Research* 51 (2012), 8922-8927 (ACS Publications, ISSN: 0888-5885)
- Simakova, O., Murzina, E., Leino, A-R., Mäki-Arvela, P., Willför, S., Murzin, D.Yu., Gold catalysts for selective aerobic oxidation of the lignan hydroxymatairesinol to oxomatairesinol: Catalyst deactivation and regeneration, *Catalysis Letters* 142 (2012) 8, 1769-1772 (Elsevier Inc., ISSN: 1011-372X)
- Simakova, O., Smolentseva, E., Estrada, M., Murzina, E., Beloshapkin, S., Willför, S., Simakov, A., Murzin, D.Yu., From woody biomass extractives to health promoting substances: Selective oxidation of the lignan hydroxymatairesinol to oxomatairesinol over Au, Pd and Au-Pd heterogeneous catalysts, *Journal of Catalysis* 291 (2012), 95-103 (Elsevier Inc., ISSN: 0021-9517)

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- Tkachenko, O., Tarasov, A., Kumar, N., Simakova, O., Campo, B., Kustov, L., Murzin, D.Yu., Comparative study of Au modified Beta, MCM-22, Mordenite, ZSM-5, MCM-41, Ce-MCM-41 catalysts in piperonyl alcohol oxidation, *Current Catalysis* 1 (2012), 58-66 (Bentham Science Publishers, ISSN: 2211-5447)
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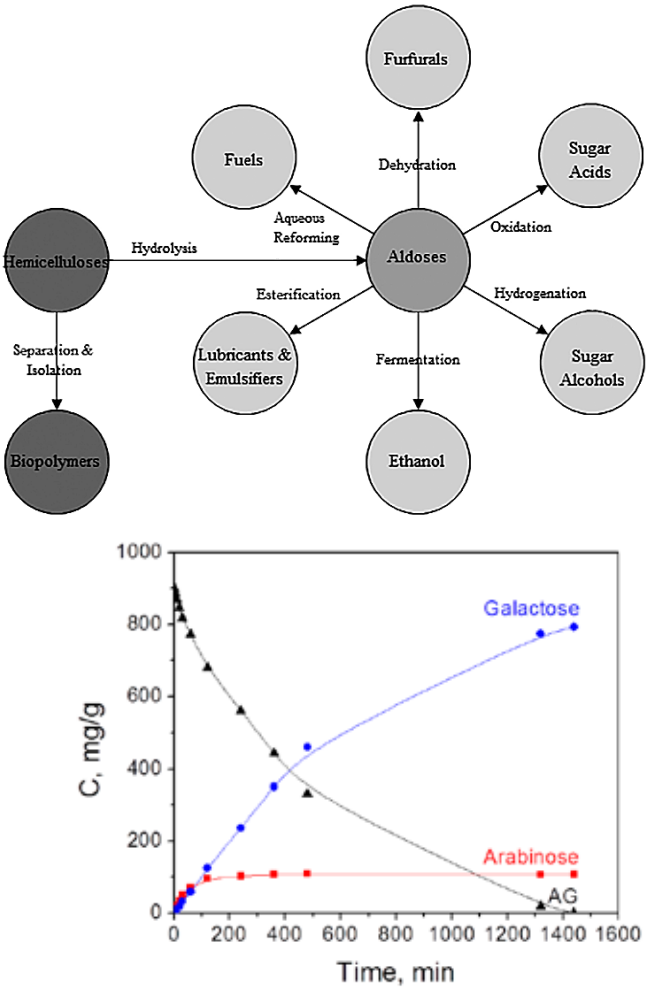

Different catalytic routes for the transformaiton of hemicelluloses to chemicals (above) and kinetics for acid hydrolysis of arabinogalactan to arabinose and galactose (below)

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 2012, 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

Publication:

- Kirilin, A.V., Tokarev, A.V., Kustov, L.M., Salmi, T., Mikkola, J-P., Murzin, D.Yu., Aqueous phase reforming of xylitol and sorbitol: comparison and influence of substrate structure, *Applied Catalysis A: General* 435-436 (2012), 172-180 (Elsevier B.V., ISSN: 0926-860X)

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 also been of interest.

The PCC further 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 and they resulted in several key journal publications in 2012.

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.

A new area of interest has been the so called torrefaction of biomasses. Torrefaction implies a mild pyrolysis – a heat treatment of the biomass in an inert gas atmosphere in the temperature range 200-300°C. At these conditions the biomass dries and loses some volatile matter which leads to new properties such as higher heating value and hydrophobicity (moisture resistance). In 2012 the PCC initiated several studies to better understand the chemical changes taking place during torrefaction processes.

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)

Publication:

- Jalkanen, J-P., Johansson, L., Kukkonen, J., Brink, A., Kalli, J., Stipa, T., Extension of an assessment model of ship traffic exhaust emissions for particulate matter and carbon monoxide, *Atmospheric Chemistry and Physics* 12 (2012), 2641–2659 (Copernicus GmbH (Copernicus Publications), European Geosciences Union (EGU), ISSN: 1680-7316)

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, WP3 Emission Control and WP5 Intelligent Automation and Control.

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

Publication:

- Kaario, O., Brink, A., Wehrfritz, A., Larmi, M., Analyzing local combustion environment with a flamelet model and detailed chemistry, Proceedings: *SAE 2012 World Congress & Exhibition*, April 24-26, 2012, Detroit, MI, USA, 2012-01-0150

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

Publication:

- Suominen, P., Brink, A., Salmi, T., Parameter estimation of complex chemical kinetics with covariance matrix adaptation evolution strategy, *MATCH Communications in Mathematical and in Computer Chemistry* 68 (2012) 2, 469-476 (Faculty of Science, University of Kragujevac, ISSN: 0340 - 6253)

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

Main funding: European Commission 7th Framework Programme

Anders Brink, Oskar Karlström, Dorota Bankiewicz, Mikko Hupa

The RELCOM project (1.12 2011-30.11 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, UK (Coordinator); Åbo Akademi University; 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 (IFRF), Italy

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

Main funding: European Commission 7th Framework Programme

Anders Brink, Oskar Karlström, Johan Werkelin, Mikko Hupa

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.

The PCC is involved in two of the three Joint Research Activities. In addition to this 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), Sweden (Coordinator); Åbo Akademi University; Aston University, UK; BIOENERGY 2020+, Austria; Cardiff School of Engineering, UK; 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 (IFRF), Italy; Joint Research Centre, the Netherlands; L'Agenzia ENEA, Italy; Norges Teknisk-Naturvitenskapelige Universitet, Norway; PALL Filtersystem Corporation, Germany; Paul Scherrer Institute, Switzerland; Stiftelsen for Industriell og Teknisk Forskning, Norway; Technische Universität München, Germany; Technische Universität Wien, Austria; TUBITAK MRC Energy Institute, Turkey; Universidad de Zaragoza, Spain; Università degli Studi di Napoli Federico II, Italy; Wroclaw University of Technology, Poland

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

Main funding: Academy of Finland

Anders Brink, Oskar Karlström, Bingzhi Li, Magnus Perander, 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

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 proper-

ties 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

Chemical Energy-based Processing of Future Complex Materials (ChemEner) - Development of Sustainable Furnace and Boiler Processes

Main funding: Tekes

Daniel Lindberg, Mikko Hupa

The subproject of the ÅA Process Chemistry Centre in the ChemEner proposal is focused on developing submodels for describing the chemistry of minor elements, such as heavy metals, in the furnaces and boilers firing biomass and waste fuels, as well as developing the thermodynamic databases to needed as input for successful implementation of these models. The focus will be on new thermal conversion techniques, such as waste gasification or different thermal treatment methods to separate harmful components from the ash to render it useable for other applications. The project is a unique collaboration between experts in the field high temperature combustion and materials chemistry with experts from the field of pyrometallurgy and process technology. New synergies between high temperature process chemistry and pyrometallurgy will further strengthen the high-level knowledge in high temperature thermodynamics in Finland, which will give an additional competitive edge for the Finnish industry and export business.

Cooperation:
Aalto University, Finland; VTT, Finland; École Polytechnique de Montréal, Canada; GTT-Technologies, Aachen, Germany ; Metso Power; Processflow; Outotec

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

In this project it has been essential to gain knowledge about the combustion and volatiles

release behaviour of the different fuels and fuel mixtures. This is of special relevance for "new" and "difficult-to-use" fuels (e.g. short rotation crops, energy grasses, residues from agricultural industries).

The project aimed to efficiently analyse the underlying processes during biomass combustion. For biomass combustion plants, CFD modelling has proved to be a highly efficient tool for process analyses as a basis to optimise plant design concerning flue gas burnout, CO emissions, plant efficiencies and availabilities. Results of this project form an important contribution to this modelling. Solid fuel combustion itself, NO_x formation as well as ash, aerosol and deposit formation have been focussed upon.

An important problem related to the utilization of some biomass fuels is their contents of metal species, especially components containing alkali metals that are partly volatilized and molten during combustion and then condensed when the gas temperature falls below a certain level, either homogeneously into a fume, or heterogeneously on condensation nuclei or walls, eventually forming deposits on heat transfer surfaces, and, depending on the cleaning devices employed, escaping into the surroundings with known deleterious health effects. The latter is particularly important in small combustors where the gas cleaning equipment is more primitive compared to larger plants.

The fuels also may contain other precursors to pollutants, such as nitrogen as part of the organic structure that may be oxidized into nitrogen oxides with a well-known inconvenience to the environment. An improved knowledge of the transformations of nitrogen compounds released from the fuel and carried to the exhaust gas form a basis for reduction procedures to convert the N-compounds into free nitrogen instead of nitrogen oxides. Furthermore, many biomasses are obtained with high content of moisture and they may be directly used in a boiler without drying. This influences the progress of combustion and has to be taken into account to predict the behavior of a fuel during conversion, particularly in case of grate firing. The inclusion of the information regarding the primary release from the fuel particles into a description of the conversion process in a furnace has also been very important. In some cases it may be advantageous to prepare the biomass feedstock upstream the combustion process – both in combustors using one fuel and in processes with co-combustion of two or more fuels. For the design of such processes the physical and chemical characteristics of the fuels are of utmost importance.

Within the project's close cooperation between the project partners, advanced fuel analysis and characterisation methods, concerning the combustion of different biomass fuels in various plant technologies of different size ranges, were further developed. It has provided a basis for an improved understanding of the combustion behaviour and to collect the data in an advanced fuel database

Advanced CFD-based simulation routines considering different phenomena like single particle conversion, solid biomass combustion on the grate, release of ash forming elements, gas phase combustion and NO_x formation have been developed as efficient, future process analysis and plant design tools

In 2012 NTNU has visited ÅA's facilities and coordinated experiments and results may lead to joint publications

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

Publications:

- Karlström, O., Brink, A., Hercog, J., Hupa, M., Tognotti, L., One-parameter model for the oxidation of pulverized bituminous coal chars, *Energy & Fuels* 26 (2012) 2, 968-975 (ACS Publications, ISSN: 0887-0624)
- Brink, A., Inder Singh, R., Karlström, O., Koschack, R., Hupa, M., Biomass conversion in bubbling fluidized beds - CFD modeling and field measurements, Proceedings: *21st International Conference on Fluidized Bed Combustion*, June 3-6, 2012, Naples, Italy, Vol. II, 899-905, ISBN: 978-88-89677-83-4

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, Oskar Karlström, Juho Lehmusto, Na Li, Hao Wu, Dorota Bankiewicz, Bingzhi Li, Emil Vainio, Niklas Vähä-Savo, Christoffer Sevonius, 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 control
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

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

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- Vähä-Savo, N., DeMartini, N., Hupa, M., Fate of biosludge nitrogen in black liquor evaporation and combustion, *TAPPI Journal* 11 (2012) 9, 53-59 (TAPPI Publishing, ISSN: 0734-1415)
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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 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

Publication:

- Khazraie Shoulaifar, T., DeMartini, N., Ivaska, A., Fardim, P., Hupa, M., Measuring the concentration of carboxylic acid groups in torrefied spruce wood, *Bioresource Technology* 123 (2012), 338-343 (Elsevier Ltd., ISSN: 0960-8524)

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.

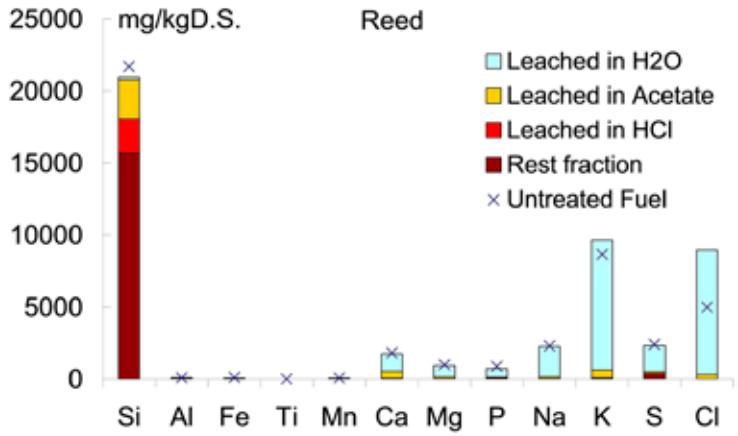
In case of Brazil, the use of sugar cane to produce bioethanol contributes to reduce the country's petroleum dependence. Nowadays 7 million hectares of field is used in Sugar cane farming in Brazil and it is estimated that the area will grow 12% a year over the next five years. In the production of bioethanol, 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, Fibre and Cellulose Technology

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 PCC 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

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 biomedical tools. The materials under investigation include conducting polymers, fullerene, carbon nanotubes and graphene. 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.

Composite materials based on conducting polymers and graphene were developed for future applications in supercapacitors and batteries, printable chemical sensors and biodiagnostics. Polycyclic aromatic hydrocarbons with 40-60 carbon atoms, mimicking small cut-outs of graphene, were also electrosynthesized and characterized.

Conducting polymers were studied as electroactive membranes for separation of metal ions and optically active compounds. This approach allows electrochemical control over the separation process. Research on functionalization of polyaniline via thiolation was also continued, the major application being potentiometric DNA sensors. Related to this topic, also fibers containing polyaniline were successfully prepared by electrospinning.

Extensive research on solid-contact ion-selective electrodes (ISEs) and reference electrodes was continued. An all-solid-state reference electrode with excellent potential stability was developed. This achievement will be of utmost importance for further development and use of all-solid-state potentiometric sensor systems in real-life applications. The water uptake and transport properties of membrane materials used in ion-selective electrodes were studied both experimentally and by using mathematical modelling in order to improve the potential stability and analytical performance of ISEs.

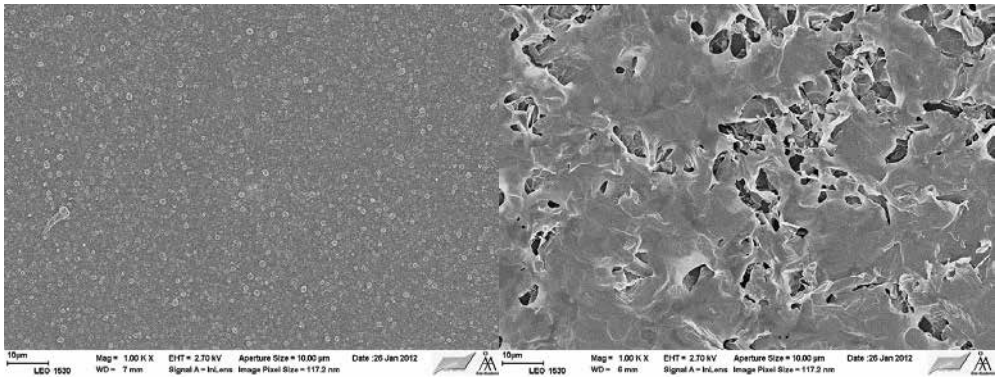
The development of printed enzymatic power supplies and printed supercapacitors was continued. The goal is that printing technology will enable low-cost manufacturing of a disposable sugar-powered BioBattery. Research on catalyst materials for the development of a cost-minimised highly efficient and durable PEM-Electrolyzer stack was also performed. Furthermore, projects related to the commercialization of a bio-based galvanic skin treatment patch and a microcurrent wound treatment patch are in progress.

Electroactive Materials Based on Conjugated Polymers, Carbon Nanotubes, C_{60} and Graphene for Chemical Sensors, Biodiagnostics, Printed Electronics, Supercapacitors and Batteries

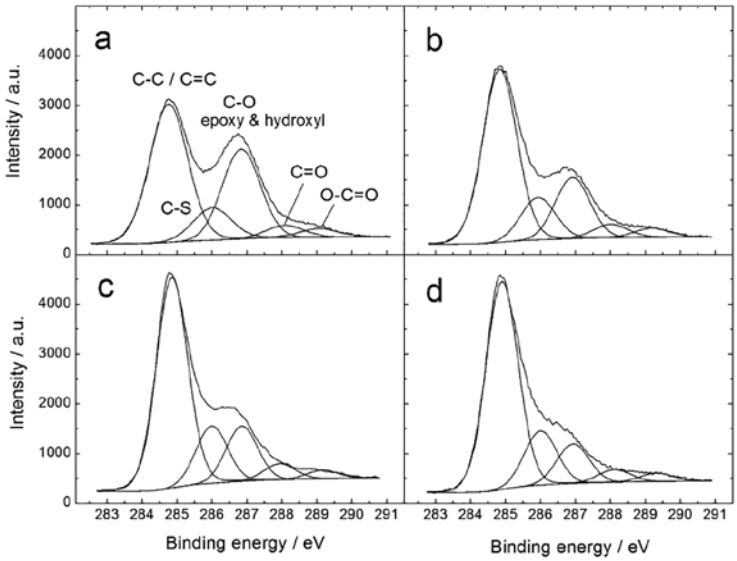
Main funding: Academy of Finland, Research Institute of Åbo Akademi University Foundation, ERASMUS

Patrycja Bober, Zhanna Boeva, Cristina Dumitriu, Tingting Han, Ning He, Carita Kvarnström, Rose-Marie Latonen, Tom Lindfors, Li Niu, Sylwia Strzalkowska, Júlia Szücs, Michał Wagner, Zhe Yang, Anna Österholm, Andrzej Lewenstam, Johan Bobacka, Ari Ivaska

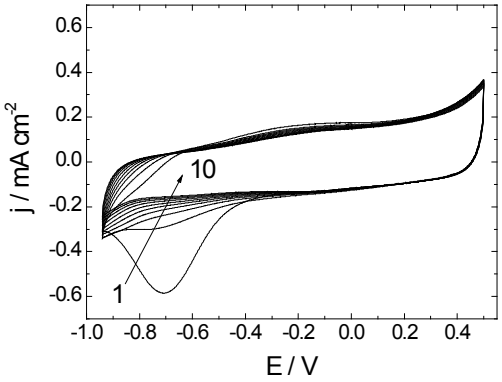
Composites of electrically conducting polymers and graphene oxide (GO), reduced graphene oxide (RGO) or graphene have been synthesized electrochemically and chemically. The composite materials developed are aimed to be used in supercapacitors and batteries, printable chemical sensors and biodiagnostics.

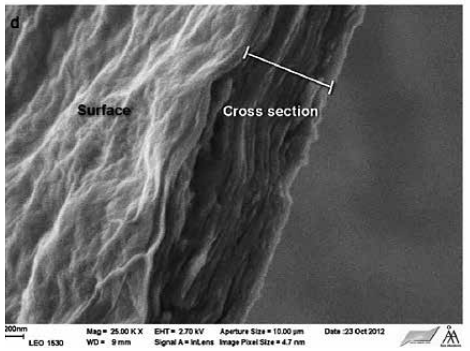


SEM images of PPy prepared from an aqueous solution of KCl (left) and GO (right)

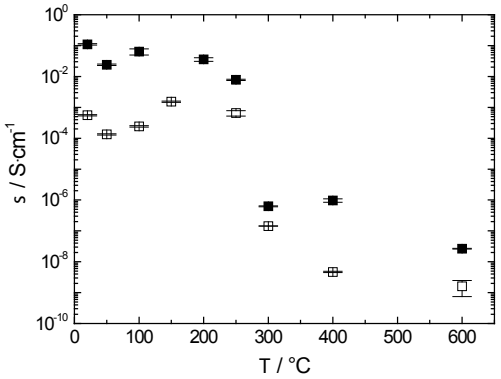


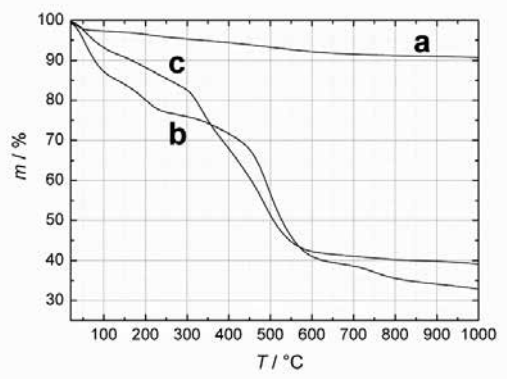
C1s XPS spectra of PEDOT-GO films electrochemically reduced at -0.85 V in 0.1 M KCl for (a) 0 min (χ^2=1.4), (b) 10 min (χ^2=2.1), (c) 20 min (χ^2=5.0) and (d) 30 min (χ^2=5.5)





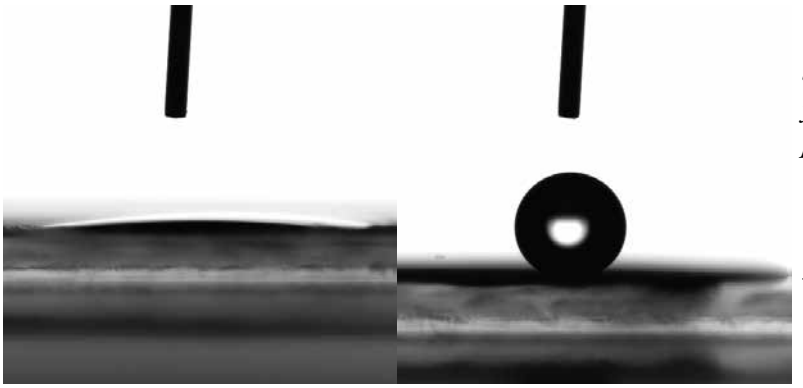
Electrochemical reduction of a PEDOT-GO film in 0.1 M KCl by cyclic voltammetry for 10 cycles (v=10 mVs^{-1}), (left). Cross sectional SEM image of the PEDOT-RGO film showing its layer by layer structure (magnification: 25000x), (right)



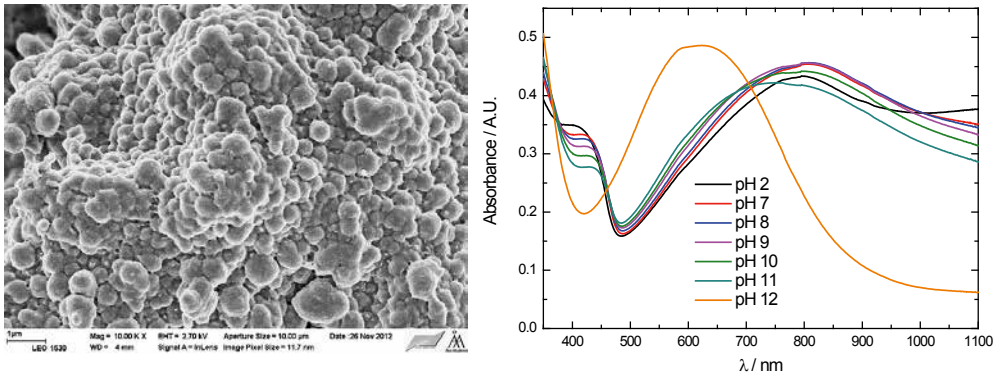


The electrical conductivity (σ) as function of temperature for the composite material of polyaniline and graphene (■) and only polyaniline (□); n=3 (left). Thermogravimetric curves of (a) graphene, (b) polyaniline and c) polyaniline-graphene recorded with the heating rate of 10°C min^{-1}(right).

The hydrophobicity and high electrochemical stability of polyazulene has been utilized to prepare all-solid-state solid-contact ion-selective electrodes (SCISEs) with superior response characteristics for ultratrace measurements.



Water contact angles of polyazulene films pretreated for 10 min at 1.0 V (left) and -0.4 V (right)

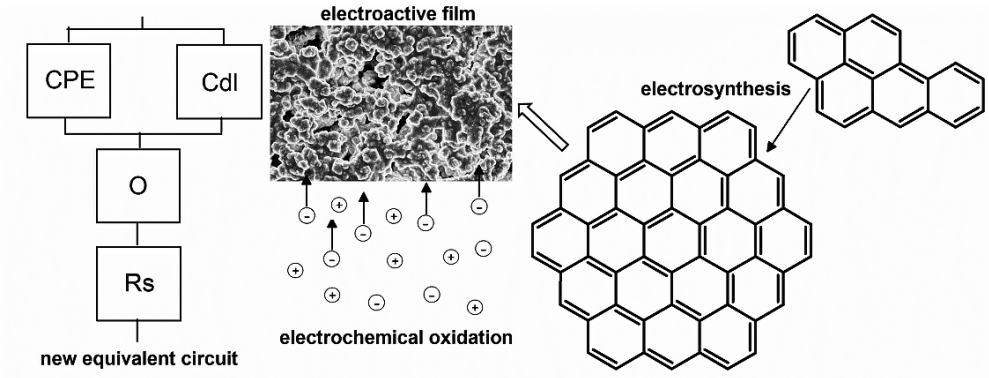


SEM image and water contact angle of a polyaniline-perfluorooctanesulfonic acid film (left). The stability of the electrically conducting form of the film measured with UV-Vis spectroscopy (right)

Hydrophobic polyaniline materials were also studied in this project. The stability of the electrically conducting emeraldine salt form could be extended to pH>10.

Polycyclic aromatic hydrocarbons (PAHs) are interesting compounds from both fundamental and applied research points of view, because these molecules can be considered as well-defined cut-outs of graphene. Starting from relatively small PAHs it is possible to electrochemically synthesize in one easy step electroactive films consisting of larger PAH molecules. In the present work benzo(a)pyrene was used as the monomer and by potential cycling in propylene carbonate, porous films were obtained consisting of PAH molecules with an average number of carbon atoms in the range 40-60, evidenced by Raman and infrared spectroscopy. Electrochemical activity during oxidation of the resulting amorphous poly(benzopyrene) (PBP) films was determined by in situ conductance measurements and electrochemical impedance spectroscopy. Additionally, based on impedance spectra a new equivalent circuit was proposed which accurately describes the electrochemical properties of the synthesized PBP films. The model was verified by comparing calculated conductivity values with experimental values obtained from in situ conductance measurements. It was found that PBP films exhibit fast ion transport with electrical conductivity of ~6.6 mS cm^{-1}. The results presented in this work imply that PBP is an interesting material for electrochemical applications.

Cooperation:
State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China; Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry and Research Group of Technical Analytical Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary; M.V. Lomonosov Moscow State University, Chemistry Department, Division of Polymer Science, Laboratory of Polyelectrolytes and Biopolymers; Turku University Centre for Materials and Surfaces (MATSURF), Laboratory of Materials Chemistry and Chemical Analysis, University of Turku, Finland; Åbo Akademi University, Department of Natural Sciences and Center for Functional Materials, Physics, Finland; Georgia Institute of Technology, School of Chemistry and Biochemistry,



Proposed hypothetical average molecule in a new electrosynthesized porous electroactive film together with equivalent electrical circuit description its electrochemical properties

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USA; AGH, University of Science and Technology, Kraków, Poland; St. Petersburg State University, St. Petersburg, Russia

Publications:

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- Kupis, J., Mattinen, U., Kisiel, A., Błaż, T., Migdalski, J., Lewenstam, A., Biomimetic membranes made of conducting polymers doped with adenosine diphosphate (ADP), *Electrochimica Acta* 77 (2012), 23-28 (Elsevier Ltd., ISSN: 0013-4686)
- Latonen, R-M., Österholm, A., Kvarnström, C., Ivaska, A., An electrochemical and spectroelectrochemical study of polyazulene/BBL-PEO donor-acceptor composite layers, *Journal of Physical Chemistry C* 116 (2012) 44, 23793-23802 (ACS Publications, ISSN: 1932-7447)
- Nasybulin, E., Cox, M., Kymissis, I., Levon, K., Electrochemical codeposition of poly(thieno[3,2-b] thiophene) and fullerene: an approach bulk heterojunction organic photovoltaic device (OPVd), *Synthetic Metals* 162 (2012) 1-2, 10-17 (Springer, ISSN: 0379-6779)
- Nasybulin, E., de Albuquerque, I., Levon, K., Electrochemical synthesis of oligothiophenes by radical termination of the growing macromolecular chain, *Electrochimica Acta* 63 (2012), 341-345 (Elsevier Ltd., ISSN: 0013-4686)
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- Wang, Y., Levon, K., Influence of dopant on electroactivity of polyaniline, *Macromolecular Symposia* 317-318 (2012) 1, 240-247 (Wiley-VCH Verlag, ISSN: 1521-3900)
- Österholm, A., Lindfors, T., Kauppila, J., Damlin, P., Kvarnström, C., Electrochemical incorporation of graphene oxide into conducting polymer films, *Electrochimica Acta* 83 (2012), 463–470 (Elsevier Ltd., ISSN: 0013–4686)

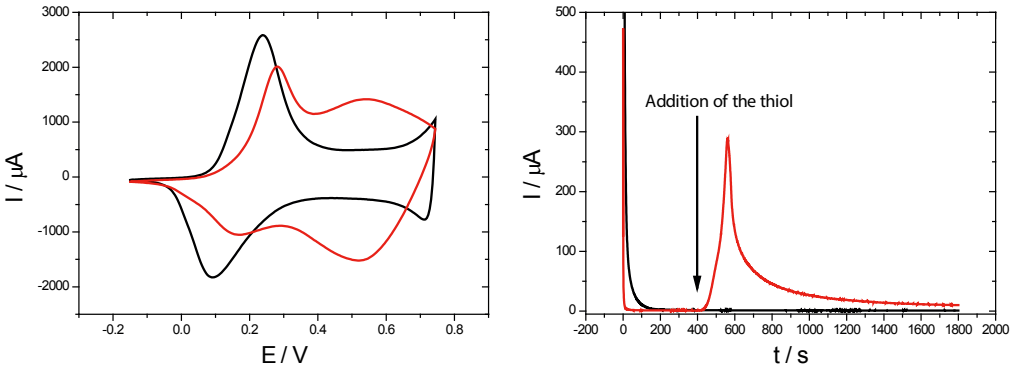
Health Diagnostics with Chemical Sensors

Main funding: Tekes (FiDiPro), Industry

Maija Blomquist, Ulriika Vanamo, Adriana Ferancová, Sara Suominen, Zhanna Boeva, Kalle Levon, Andrzej Lewenstam, Johan Bobacka, Ari Ivaska

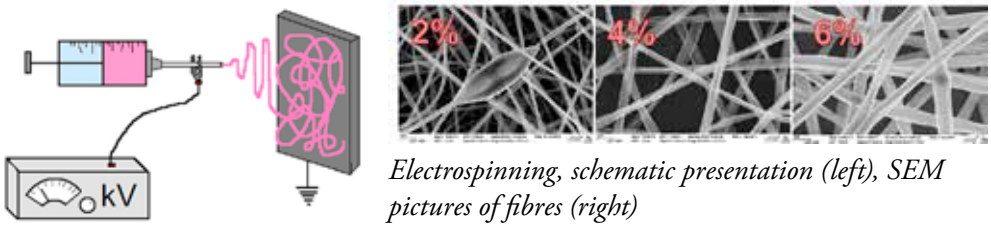
Fast and easy-to-use DNA hybridization sensors are needed to shorten the analysis time, and for the point-of-care devices. Conducting polymers as sensor substrate are promising and very fast signal transducers. The aim of this project is to study conducting polymer substrates as signal transducer and immobilization platform for potentiometric ion-sensitive electrodes for DNA hybridization. DNA hybridization sensors are very specific and can be used to detect genetic diseases and viruses. Potentiometry offers a unique method for monitoring DNA hybridization without additional labeling which is a time-consuming and expensive step.

The substrate for probe DNA used in this study is polyaniline on glassy carbon or glass substrate prepared by electrochemical polymerization or by electrospinning. Immobilization of the probe DNA to conducting polymer substrate is done by using thiolation by immersion, by constant potential, by potential cycling or by flow-injection analysis. Shorter thiol compounds are also immobilized on the surface to hinder non-specific binding. The project focuses on the impact of thiolation on the conducting polymer, optimization of thiolation time, method and concentration as well as on the design of the electrode. Thiolation changes the electrochemical properties of polyaniline depending on the nature of the thiol and it is hence highly important to characterize the substrate and evaluate the effect of thiol binding.



CV (left) and chronoamperometry (right) response of PANI film at 0.6 V in 0.1 M KCl, without an addition of thiol (—) and after an addition of thiol, c_{MCE} = 0.1 M (—)

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



Electrospinning, schematic presentation (left), SEM pictures of fibres (right)

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

Publications:

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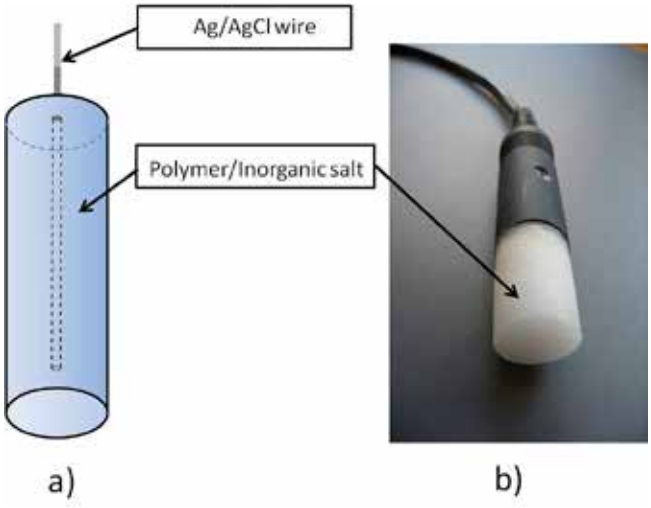
Intelligent Monitoring for Health and Well-being (WP 202 Intelligent Technology Platforms)

Main funding: Tekes (Salwe Ltd, IMO)

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

A new type of all-solid-state reference electrodes was designed and characterized. The electrodes are based on a polymer/inorganic salt composite and a silver/silver chloride reference element. A rigorous testing procedure was used to reveal possible influence of pH, solution composition, as well as the concentrations and mobility of ions. The tests demonstrated the insensitivity of the electrodes to the matrix effects, excellent stability of the potential readings, and significantly reduced leakage of inorganic salt. It was shown that the composite reference electrodes showed comparable or better performance than high-quality commercial reference electrodes. The reference electrodes described here are of analytical quality allowing for continuous, prolonged, and intensive usage.

The results from this project were the basis of a patent priority application "A reference electrode and an arrangement for an electrochemical measurement" (No. 20126315) filed on 14/12/2012.



A schematic picture (a) and a photo (b) of the composite reference electrode

Cooperation:
AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Cracow, Poland

Water Uptake of Membrane Materials Used in Ion-selective Electrodes

Main funding: Academy of Finland

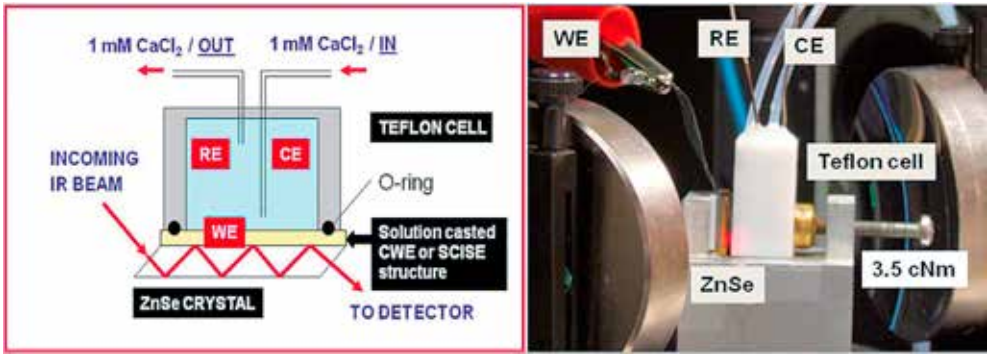
Ning He, Rose-Marie Latonen, Haolin Lu, Tom Lindfors

Fundamental aspects of the water uptake of both commonly used and new ion-selective membrane (ISM) materials have been studied in this project. Its main goal has been 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 mesoporous silica films. Different types of fluorescent water sensitive dyes have been 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 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, as well as for applications where it is important to detect diffusion of water through different types of polymeric materials.



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

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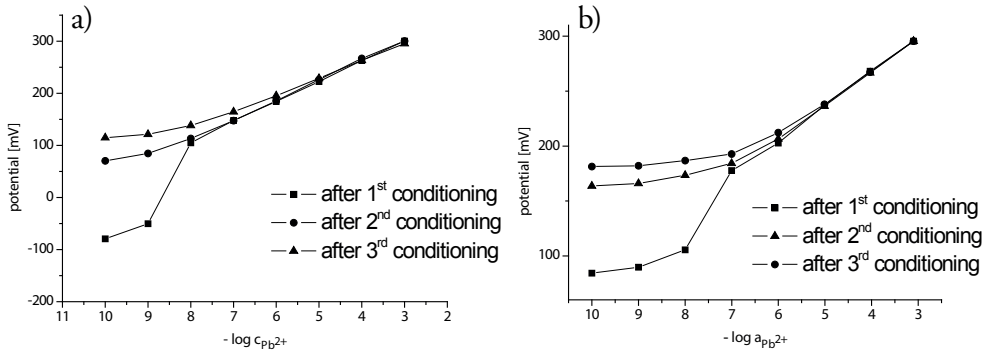
Cooperation:
Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry and Research Group of Technical Analytical Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary; Åbo Akademi University, Laboratory of Physical Chemistry, Finland; Åbo Akademi University, Laboratory of Organic Chemistry, Finland; University of Turku, Faculty of Medicine, Laboratory of Biophysics, Finland

Modelling of Transport Properties of All-solid-state Ion-selective Electrodes with a Conducting Polymer

Main funding: Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM), Graduate School in Chemical Engineering (GSCE), Institute of Åbo Akademi University Foundation

Jerzy Jasielec, Grzegorz Lisak, Tomasz Sokalski, Johan Bobacka, Andrzej Lewenstam

All-solid-state electrodes are increasingly used in clinical, industrial and environmental analysis. The wide range of applications requires deep theoretical description of such electrodes. The focus of this project has been development of the numerical tool for qualitative prediction of electrochemical behaviour for the solid-contact ion selective electrodes at low concentrations of the analyte. For that purpose a general approach to the description of electro-diffusion processes, namely Nernst-Planck-Poisson (NPP) model was used to model all-solid-state ISEs with a conducting polymer. The results obtained from this model were verified by experimental data of lead(II)-selective electrodes based on a polymeric PVC membrane with polybenzopyrene doped with Eriochrome Black T used as the solid contact.



Calibration curves for ISE, with CP as the solid contact, a) obtained from numerical experiment, b) experimental response of SC Pb^{2+}-ISE.

The numerical experiments showed the enrichment of the polymer matrix with the primary ion. This process is strongly dependent on the time of conditioning.

The qualitative agreement of theoretical and experimental results is observed. Both of these results show the process of enriching the polymer with the main ion, which leads to the changes in the detection limit and slope. The CP enrichment process is shown by the theory and indicated by the experiment. Both theoretical and experimental results show, that for the presented system calibration curves have the following characteristics:

– after the first conditioning - the super-Nernstian response,
– after the second conditioning - Nernstian response with lower detection limit,
– and after the third conditioning - Nernstian response with higher detection limit.

The detection limit obtained in the experiment is higher and the super-Nernstian jump is smaller than the one obtained from the calculations. The difference between the experiment and calculations may be due to the following reasons: many of the parameters of the system are unknown, and the values used in the numerical experiments are estimated. Because the parameters are inter-connected, it is very difficult and time-consuming to find the proper/optimal set of parameters by trial and error method. The quantitative agreement can be obtained by using the stochastic methods to search the optimal parameters. One

of such methods namely Hierarchical Genetic Strategy (HGS) has been already combined with the NPP model. Our results deliver for the first time consistent interpretation of the responses of solid-contact ion-selective electrodes with polymer membranes.

Cooperation:
AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Cracow, Poland

Publications:

- Lisak, Grzegorz, *Ion selective electrodes for determination of low and ultra-low concentrations of lead(II) in natural waters* (Doctoral Thesis, Åbo Akademi University, Turku, ISBN: 978-952-12-2752-3)
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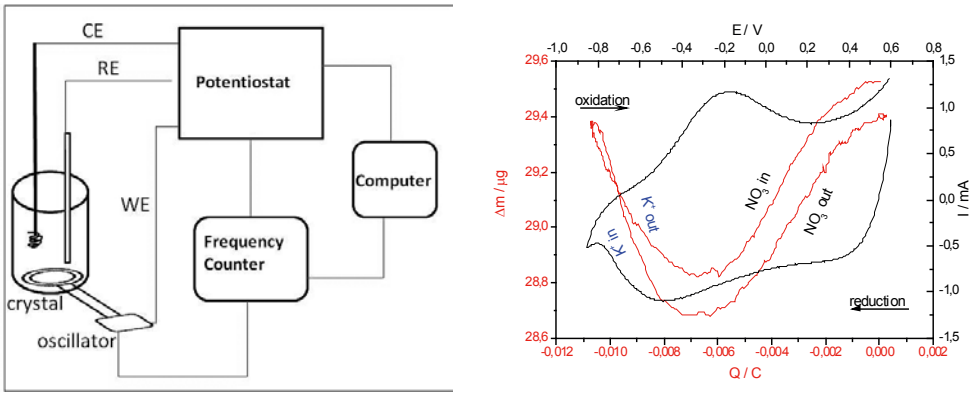
Electroactive Membranes for Separation of Metal Ions and Optically Active Compounds

Main funding: Graduate School in Chemical Engineering (GSCE)

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

The resolution of optically active compounds is crucial especially in the pharmaceutical and biotechnology sectors. Optically active drugs are problematic because one enantiomeric form of the drug is more effective than the other form or one enantiomeric form may counteract the effect of the other. Enantioseparation is commonly done by chromatographic methods. Also, liquid membranes have been used in enantioseparation but the efficiency has been really low. Membranes composed of conducting polymers can be a simple and efficient approach in separating these enantiomers. Chirality in conducting polymers can be induced either by attaching a chiral substituent on the polymer backbone or by doping the polymer during synthesis with a chiral dopant anion. The properties of the membrane can be tuned via electrochemical means to improve the separation efficiency of enantiomers. Selective transport of one form of a chiral compound can be induced by using electrical stimuli applied to the polymer membrane. This will switch the chiral conducting polymer between its reduced and oxidized state.

Electrically conducting polymers (ECPs) exhibit ion exchange behaviours with the ion exchange capacity similar to that of conventional ion exchange membranes. The diverse ion exchange properties exhibited by ECPs have led to the development of electrochemically controlled membrane systems for separation of metal ions between two solutions. The ion exchange properties of ECPs depend on the type, size and valency of the doping anion used during electropolymerization and it has been found that when small anions, such as Cl-, have been incorporated into the polymer film during polymerization the charge neutrality during p-doping is maintained by transfer of anions between the film and the solution. On the other hand, when the polymer film has been prepared in presence of large counterions, such as dodecylbenzenesulfonate, polyvinylsulfonate, polystyrenesulfonate, cyclodextrins or nafion having a polymeric character or multiple electrostatic interactions making them relatively immobile, the polymer film becomes a cation exchanger. This is because charge compensation takes place through cation transfer between the film and the surrounding electrolyte. Films prepared with monovalent anions of moderate size usually show mixed ion exchange behaviour, i.e. both anions and cations are involved in charge compensation during redox cycling. Therefore, in order to understand the fundamental ion transport property of the polymer film it is important also to determine the identity of the mobile ion/ions. The Electrochemical Quartz Crystal Microbalance (EQCM) technique is a powerful tool in identification of ion exchange properties of ECP films and it has widely been used for monitoring mass changes of ECPs on an electrode surface in situ during potential cycling. The set-up for performing EQCM experiments is shown in the figure below. The apparent molar masses of species causing the mass change during potential cycling can be calculated from the mass change of a fresh polymer film vs. charge curves in the different electrolyte solutions. Non-permselective behaviour of the studied polymer films was observed in all of the studied electrolytes. A PPy film showing mixed ion exchange behaviour in KNO_3 solution is shown in the right figure below.



Set-up of EQCM experiments CE = counter electrode, RE = reference electrode, WE = working electrode (left). EQCM graph of PPy films immersed in 0.1 M KNO_3 (right)

Cooperation:
University of Wollongong, Australia

Publications:

- Akieh-Pirkanniemi, Marceline Neg, *Electroactive ion exchange membranes: Based on conducting polymers* (Doctoral Thesis, Åbo Akademi University, Turku, ISBN: 978-952-12-2820-9)

Commercialization of Green, Bio-based Galvanic Skin Treatment Patch with Ambient Disposal for Personal Wellbeing Markets (COSPAD)

Main funding: Tekes

Mikael Bergelin, Jan-Erik Eriksson, Mikko Hupa

The target of this project is to enable the commercialization of an environmentally friendly and easily disposable cosmetics patch for galvanic treatment by validating its technical, market and business feasibility. In doing so, this project aims to demonstrate that compared to competing single-use products on the market our solution enables longer effective treatment periods, superior environmental performance, as well as the lowest material and manufacturing costs. The product concept for galvanic treatment is based on bio-based power source technology developed within the PEPSic and PEPSecond projects.

There is an increasing business potential for novel concepts in the high-volume consumer markets for cosmetics products. One of the emerging but steadily growing market areas within the homecare cosmetics sector are galvanic skin treatments. At the moment a majority of the total volume of galvanic treatments is given to consumers by trained skin care professionals using special equipment, but in order to make the galvanic treatment widely accessible and inexpensive for the consumers, there is a clear need for home-use purpose-made disposable skin care products, and recently some products have entered the cosmetics market.

In order to ensure the competitiveness of our solution we need to scientifically verify the administration of electrical stimulation and to quantify the enhanced transfer of active agents to the relevant tissues. In addition we will validate the environmental performance of the product while defining its uniqueness and optimizing its material and manufacturing costs. Finally, our goal is to identify commercialization partners for introducing this technology from laboratory to pilot manufacturing for first market trials and adoption.

The key objectives of this project are to:

1. define product concept and its uniqueness
2. define regulatory market requirements, customer needs and competitive edge
3. build functional product prototypes for testing and demonstration
4. perform life cycle analysis and materials safety study
5. demonstrate proof of treatment effects
6. define preliminary specification for a pilot manufacturing process
7. establish relationships with potential customers and commercialization partners

Cooperation:
VTT, Tampere Technical University, ABEnzymes, Joutsenpaino, Lumene, Stora Enso, Tervakoski

Microcurrent Wound Treatment Patch with Increased Functionality (MC-Patch)

Main funding: Tekes

Mikael Bergelin, Jan-Erik Eriksson, Mikko Hupa

Chronic wounds affect nearly 1% of population and up to 10% of institutionalized patients. By the year 2030, 366 million people worldwide are estimated to suffer from diabetes further increasing the prevalence of ulcers. Conventional treatment of ulcers has so far been passive; 1) remove or control the impediments for healing and 2) cover the wound area with occlusive dressing to allow nature to take its course. For ulcers that fail to heal, the treatment in the end often leads to surgical debridement under anaesthesia. A new therapeutic approach utilizes electrical stimulation of the wound by increasing the healing rate via application of direct current. Recent studies published in Nature did show drastically faster wound healing and at wider area when electrical stimulation was applied. It is also expected that the most efficient external stimulation would mimic and enhance the naturally occurring potential difference formed between the wound area and the surrounding intact skin.

The first accelerated wound healing products have recently entered the market, but their functionality is to date very limited. The lack of possibility for control of the current-flow, both in terms of magnitude and direction, results in a situation where the stimulus current does not penetrate into the actual wound tissue, but rather mainly flows along the wound surface. This severely limits the accelerating effect on the healing process, as the bio-mimicking potential difference between the more positively charged wound and more negatively charged intact skin will not be achieved. Further, one major problem in wound care is associated with monitoring of the healing process. The present approach requires disturbing the wound by removal of the dressing and visual inspection of the wound area to assess the onset of formation of granulation tissue and to ensure that the wound is not becoming infected. Development of a tool that would allow objective online monitoring without disturbance would be of great importance.

By combining together the know-how of the project partners regarding bio-medical technology, materials- and electrode array-design, printed intelligence and power source development, we are aiming to develop a significantly more advanced, bio-mimicking multifunctional accelerated wound healing patch. Due to the present IPR protection status further details regarding design and functional aspects are omitted. The patch cost, dimensions and its malleability will be kept reasonable, and the manufacturing simple, utilizing mainly printing techniques. The true commercialization potential and -path of the patch will be investigated, and calculations will be made to assess realistic manufacturing costs from materials, investment, subcontracting and marketing viewpoint. It is

expected that the proposed patch design is far more advanced in its therapeutic action than any commercially available stand-alone patch at present.

Cooperation:
Aalto University, Tampere University of Technology, Tampere University Hospital, Finnmedi, Joutsenpaino, Kiilto, Tervakoski

Publications:
- 1 patent application

Printed Supercapacitors (PRISU)

Main funding: Tekes

Mikael Bergelin, Max Johansson, Mikko Hupa

Conventionally supercapacitors (= ultracapacitor, electric double layer capacitor, EDLC) are separate components used in applications where relatively high peak power is needed, such as in vehicles and wind power plants. However, smaller supercapacitors have also been developed and are primarily now applied e.g. in memory back-ups. The power density (kW/kg) of the supercapacitors is typically 10-fold compared with Li-ion batteries. Analogously the charge time of a supercapacitor can be of the order of few seconds. The cycle life of a supercapacitor can exceed 1,000,000 cycles which is superior to battery cycle life (500–3,000 cycles). The drawback of supercapacitors compared to batteries is that the energy density is considerably lower, only 10 % of the energy density typical to Li-ion batteries. In practical applications the cycle period of supercapacitor systems is normally from about one second to about one minute.

Supercapacitors are relatively new components since they did not become widely known until the 2000´s. There are no considerable differences in the basic structure between most commercial suppliers (e.g. Maxwell, Nesscap, Matsushita and Batscap). Some manufacturers have innovative solutions such as asymmetric structures, metal oxide or aerogel electrodes or various electrolytes for niche applications (Evans Capacitor Company, PowerStor, ESMA, Advanced Capacitor Technologies Inc.). Because the field of supercapacitors is quite new, there still exist possibilities for new innovative structure, material or manufacturing solutions.

The scope of this project is to facilitate the supercapacitor manufacturing process by utilization of printing technology. This enables low-cost manufacturing process that is important in order to widen the application range of supercapacitors. Another significant advantage is the ability to design energy storage components of required physical shape. Since the focus of the project is in the development of inexpensive alternatives, activated carbon and manganese oxide electrodes are to be used. Electrode performance enhancement by carbon nanotubes and graphene will also be explored. The electrolytes will be applied as gel or bound to polymers. The basic structure of the supercapacitor cells will be designed to be applicable both in small and large scale components.

Cooperation:
VTT, Aalto University, Confidex, Kemet, Cabus

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

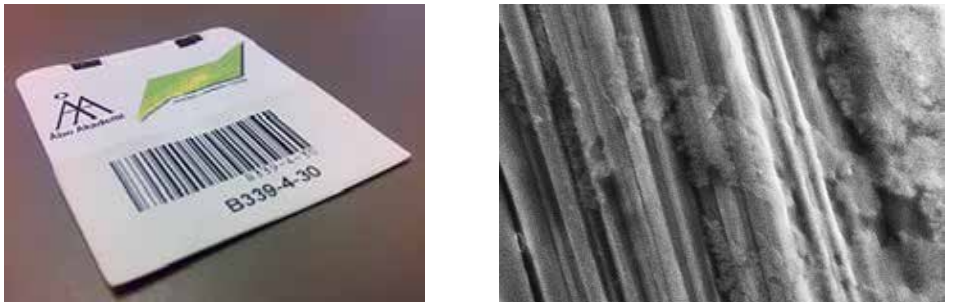
Main funding: Tekes

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.



BioBattery Prototype consisting of two serially connected cells (left), SEM image of GOx enzyme clusters immobilized on carbon fibres (right)

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

Publications:

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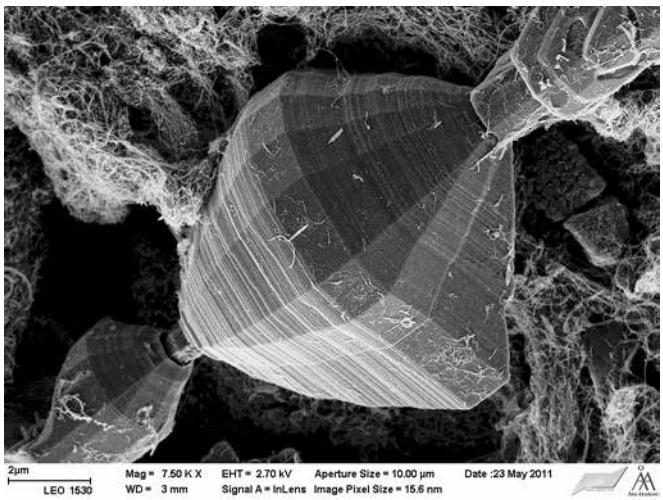
Pressurized PEM Electrolyzer (Primolyzer)

Main funding: EU

Mikael Bergelin, Max Johansson, Mikko Hupa

The primary objective of the PrimoLyzer project is to develop, construct, and test a cost-minimised highly efficient and durable PEM-Electrolyzer stack aimed for integration with μCHP technology. The research tasks within the project have concentrated around developing mixed metal oxide (MMO) anode catalyst and CNT supported PtPd cathode catalyst facilitating MEA performance of 1.2 A/cm2 at 1.64 VDC and extrapolated durability of 20,000 h. The performance target for the anode catalyst is 1.2 A/cm2 at 1.45 V (RHE) with a loading of 1,0 mg/cm2 and for the cathode catalyst 1.2 A/cm2 at – 40 mV (RHE) with a noble metal loading of 0,5 mg/cm2. At ÅA/PCC nanostructured IrO2 and different binary IrxRuyOz 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:



SEM image of Pt particles on graphitized MWCNT support

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 levelThe 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

3.9 Functional Inorganic Materials

Our research covers a wide range of inorganic materials from metals and refractory ceramics used in boilers for energy generation to glasses and ceramics used as implants of tissue engineering scaffolds in the human body. Typically, these materials are either manufactured or used at high temperatures. Thus, understanding the chemical and physical processes taking place at high temperatures is one of our key competences and research focuses. We have been developing new compositions for materials but also comparing the properties of commercial qualities at laboratory conditions imitating the final use of the materials. Although inorganic materials are often utilized as structural materials, their mechanical performance may be limited by their chemical interaction with the surrounding environment. Besides the bulk material properties, a thorough understanding of the surface properties in different environments is a key characteristic for the functionality of the materials.

Implants and tissue engineering scaffolds based on bioactive glasses have been one of our research focuses during the past three decades. Today, bone grafting materials made out of bioactive glasses developed at our laboratory are commercially available. Ideally, the bioactive glass gradually dissolves in the body environment while stimulating and guiding growth of new bone. In general, tissue engineering scaffolds giving optimal environment for in vitro or in vivo regeneration of neotissue are studied intensely. These structures are often highly porous thus giving place for the ingrowth of tissue and its proper vascularization. One important goal of our bioactive glass research has been tailoring the glass composition to enable manufacture of porous scaffolds which have a controlled release of ions that triggers and stimulates the tissue regeneration and growth. This requires a close control of high temperature properties and in vivo dissolution kinetics of the glasses and glass-ceramics. Our research tasks include also development of glass fibers for different sensing and trauma healing applications.

High temperature materials in combustion devices and boilers face new challenges by requirements of increased power production efficiency and reduced emissions. However, higher material temperatures needed e.g. in superheaters or the utilization of biofuels, waste derived fuels and different fuel mixtures may give rise to severe corrosion of the hottest surfaces. 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 in the presence of ashes and volatiles that contain various alkali salts such as potassium an sodium chlorides, sulphates and carbonates or

zinc and lead compounds. 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. In addition, the detailed mechanism of chromium oxide protective film formation on stainless steel and corrosion at high temperatures has been one key research area. During the past year we have also developed a laboratory procedure for estimating and comparing the effect of erosion by bed particles on the boiler materials at elevated temperatures.

Bioactive Glasses and Their Properties

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

Leena Hupa, Jonathan Massera, Zhang Di, Susanne Fagerlund, Leena Varila, Anna Iisa, Paul Ek, Mikko Hupa

Controlled dissolution of ions was a key issue of our bioactive glass and glass-ceramics research. In addition, the interaction of bioactive glasses in composites together with biostable and biodegradable polymers, the effect of the sample form and surface condition of the samples on the reactions in aqueous solutions were studied. The main goal was to gain fundamental information of the effect of fluid flow, interfacial conditions as well as glass composition on the ion release kinetics. This information is essential for tailoring glasses to various implants and tissue engineering scaffolds. As the scaffold manufacture from bioactive glasses via different high temperature procedures is closely correlated with the thermal stability of the glasses, we have measured the thermal properties to get detailed information on the crystallization kinetics of the glasses. The figure below shows examples of various products prepared from our bioactive glasses via melt quenching (monoliths and particulates), sintering (coatings, porous implants and scaffolds), melt or preform spinning (continuous fibers), and sol-gel synthesis (nanomeshes). In tailoring the oxide composition of the glasses for these products their surface area to volume ratio has to be taken into account to achieve an adequate strength, desired biological effect and controlled dissolution rate. The knowledge of the effect of glass composition on the various properties gained over the years gives as fundamental tools needed for the manufacture of bioactive glass based products.

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

Publications:

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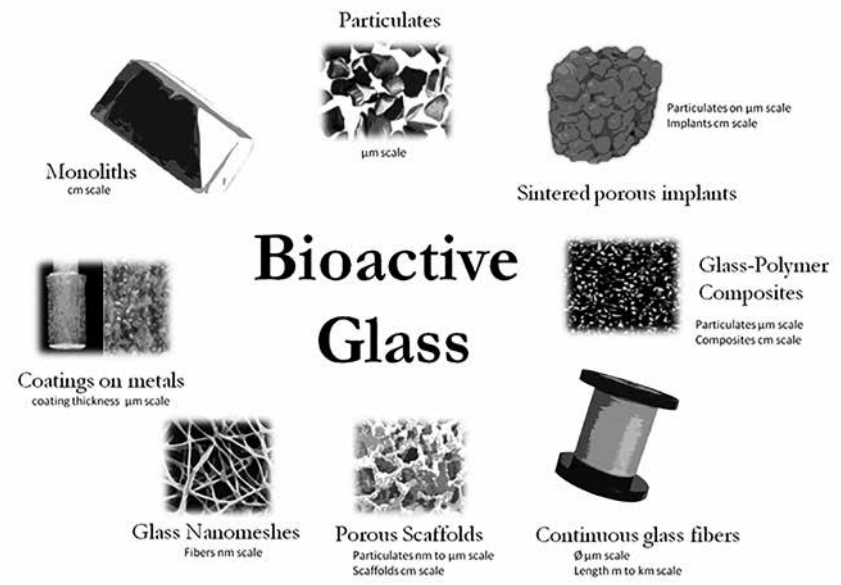

Examples of product forms manufactured from our bioactive glasses with various methods

Nanostructured Glass and Ceramic Coatings

Main funding: ÅA-PCC, Academy of Finland (MoreBags)

Leena Hupa, Leena Varila, Camilla Molin, Eveliina Viljamaa

Our nanostructured materials research includes manufacture and characterization of coatings and nanoparticles which give biomaterial surfaces desired properties such as enhanced tissue attachment of medical implants. We have manufactured via sol-gel synthesis bioactive glass nanomeshes and nanoparticles that have been incorporated to biopolymer surfaces. The goal is to tailor novel composite implants that biodegrade in a controlled manner and show optimal tissue interaction immediately after implantation.

One further goal has been to develop reliable characterization methods to identify the composition, thickness and structure of different nanostructured or long-term chemical and mechanical durability for glazed and glass surfaces.

Cooperation:
University of Turku (Dentistry); Central Glass & Ceramic Research Institute, Kolkata, India

Corrosion and Erosion of Refractories

Main funding: ÅA-PCC, FUSEC project partners

Leena Hupa, Na Li, Ismoil Bello, Johan Lindholm, Henri Holmblad

We have developed laboratory testing procedure for characterization of corrosion of refractories in boilers using challenging fuel combinations such as biofuels and wood and waste derived fuels. The corrosion was studied as infiltration of alkaline synthetic ashes, mainly potassium containing salts into different commercial refractories at the temperature range 500-900°C. The goal is to find out the primary mechanisms of the interactions of the ash components and refractories. For erosion testing we have developed a laboratory scale equipment in which the material surfaces are eroded at a controlled angle with sand or other bed particles at a controlled rate and at a controlled temperature. The erosion resistance is characterized as erosion depth and rate of materials consumption per surface area. The equipment will be used for erosion and corrosion testing of both metal and ceramic materials.

Cooperation:
Foster Wheeler

4. Publications 2012

4.1 Theses

4.1.1 Doctoral theses (10)

Akieh-Pirkanniemi, Marceline Neg, Electroactive ion exchange membranes: Based on conducting polymers

Bankiewicz, Dorota, Corrosion behaviour of boiler tube materials during combustion of fuels containing Zn and Pb

Blomqvist, Maija, Electrochemical and spectroelectrochemical characterization of alkylated and thiolated polyanilines

Fagerlund, Susanne, *In vitro* dissolution rate of glasses with respect to future clinical applications

Lisak, Grzegorz, Ion selective electrodes for determination of low and ultra-low concentrations of lead(II) in natural waters

Piotrowska, Patrycja, Combustion properties of biomass residues rich in phosphorus

Sifontes Herrera, Victor, Hydrogenation of L-arabinose, D-galactose, D-maltose and L-rhamnose

Simakova, Olga, Catalysis by gold for biomass transformations

Su, Pingping, Sorption of metal ions to wood, pulp and bark materials

Wang, Xiaoju, Enzyme electrode configurations: for application in biofuel cells

4.1.2 Licentiate theses (0)

4.1.3 Master's theses (14)

Alanko, Tiina, Bränsleegenskaper hos fyra energigräs

Becher, Nora, Reaktionstechnische Untersuchung zur Hydrolyse von Xylan (in collaboration with TU Dresden)

Engblom, Niklas, Product gas cooling in waste gasification – Deposition and corrosion

Fang, Wenwen, Calcium oxalate precipitation in pulping and papermaking

Faten Diaz, Sara, Isomerisation of pinene oxides to fine chemicals over metal modified zeolites

Guo, Jiaqi, Synthesis of value-added saccharides via oxidative decarboxylation

Molin, Camilla, Electrospinning of bioactive glass nanofibers

Saleem, Farhan, Hydrogenation of L-arabinose and D-galactose mixtures over a heterogeneous catalyst

Santochi Pereira da Silva, Paulo, Methods for interpreting black liquor single particle combustion data for NO emission modeling

Sevonius, Christoffer, Konstruktion av en fluidbäddreaktor i laboratorieskala – De första resultaten av applomereringsförsök

Sundqvist, Sofia, Inverkan av metaller på koksens reaktivitet och gasemissioner vid förbränning och förgasning av biomassor

Vakili, Hossein, Solid-contact ion sensors for determination of pharmaceutically important cations

Viljanen, Sari, Undersökning av elektroder tryckta på papper som substrat för jonselektiva elektroder

Zmudzka, Magdalena, A comparative study of potentiometric reference electrodes

4.2 Publications

4.2.1 Articles in refereed international scientific journals and series (125)

1. Aho, A., DeMartini, N., Pranovich, A., Krogell, J., Kumar, N., Eränen, K., Holmbom, B., Salmi, T., Hupa, M., Murzin, D. Yu., Pyrolysis of pine and gasification of pine chars - Influence of organically bound metals, *Bioresource Technology* 128 (2012), 22-29 (Elsevier Ltd, ISSN: 0960-8524)

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Zecca, M., Centomo, P., Sterchele, S., Campetrini, S., Biasi, P., Salmi, T., Polymer supported heterogeneous catalysts for direct synthesis of hydrogen peroxide in absence of selectivity enhances, Proceedings: *15th Nordic Symposium on Catalysis*, June 10-12, 2012, Mariehamn, Åland, ISBN: 978-952-12-2745-5, P21

Österholm, H., Kumar, N., Lindblad, M., Tiitta, M., Murzin, D.Yu., Synthesis and characterization of zeolites embedded in mesoporous molecular sieves, Proceedings: *15th International Congress on Catalysis (ICC 2012)*, July 1-6, 2012, Munich, Germany, 1.01.1573

4.4 Edited Conference Proceeding and Reports (8)

Aldea, S., Process intensification for nano-calcium carbonate production (PINK), *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, 2012, 20 p.

Bernas, A., Ketonization of carboxylic acids, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, 2012, 31 p.

Ljung, M. (ed.), *Graduate School in Chemical Engineering Yearbook 2012*, Åbo Akademi University 2012, ISSN: 1238-2647, Uniprint, Åbo, Finland, 2012

Ljung, M., Brink, A., Latonen, R-M., Mäki-Arvela, P., Sundberg, A. (eds.), *Åbo Akademi Process Chemistry Centre Annual Report 2011-2012*, Åbo Akademi University 2012, ISSN: 1459-8213, Newprint, Loimaa, Finland, 2012

Reinsdorf, Arne, *Grosser Beleg zum Thema: Synthese von Methylchlorid – Modellierung und experimentelle Validierung*, TU Dresden and Åbo Akademi Process Chemistry Centre, 2012, 49 p. + app.

Salmi T., Murzin, D., Wärnå, J., Bernas, A., (eds.), *15th Nordic Symposium on Catalysis*, June 10-12, 2012, Mariehamn, Åland, Book of Abstracts, ISBN: 978-952-15-2745-5, Painosalama, Turku, Finland, 2012

Salmi, Tapio (ed.), *FabTech Microreactor Project – Final report*, Åbo Akademi Process Chemistry Centre, Aalto University and Lappeenranta University of Technology, 2012

Tolvanen, P., Kinetic study of organic reactions, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, 2012

4.5 General articles (in newspapers etc.) (13)

Banbrytande forskning inom biomassa: kemikalier från hemicellulosor – från katalysatorutveckling till design av nya reaktorstrukturer, *Katalysnytt* 22, 2/2012, Tapio Salmi

Brev från Aten, *Ny Tid* 47/2012, 23.11.2012, Tapio Salmi

Den skenbara storhetens vansinne, *Åbo Underrättelser*, 17.4.2012, Tapio Salmi

En grekisk Odyssé, *Meddelanden från Åbo Akademi*, 18/2012, Tapio Salmi

En matnyttig konferens, *Meddelanden från Åbo Akademi* 11/2012, Tapio Salmi

Familjen Curie och det internationella kemiåret, *Åbo Underrättelser*, 13.1.2012, Tapio Salmi

Fenomenet Marie Curie, *Ny Tid* 6/2012, 10.2.2012, Tapio Salmi

Finns det ett liv efter oljan?, *Ikaros*, 3 (2012), 37-38 (Folkets Bildningsförbund, ISSN 1796-1998), Stefan Willför

Fresh ideas and valuable visits, *Åbo Akademi University News Bulletin* 1/2012, Tapio Salmi

Groundbreaking research in biomass, *Public Service Review: Europe*, issue 24, Tapio Salmi

Huippua vai ei, *Academy of Finland, researcher's blog*, 9.2.2012, Tapio Salmi

Katalyskonferensen blev en succé, *Kemia–Kemi* 8 (2012), ISSN: 0355-16288, Tapio Salmi

Vem behövs, vad behövs vid Universitet, *Acatiimi,* 9/2012, Tapio Salmi

4.8 Patents and invention disclosures (8)

Bergelin, M., Eriksson, J-E., Ylänen, H.O., Xu, C., Leppänen, A-S., Willför, S., Köppä, S., Kekonen, A., Johansson, M., Viik, J., Hyttinen, J., A multifunctional wound treatment system consisting of a galvanic wound stimulation electrode array, an antimicrobial agent to reduce risk of infection and a handheld interfaceable bio-impedance measuring device allowing monitoring of the healing process, ID U/18/2012, Åbo Akademi University

Mäkelä, S., Polari, L., Saarinen-Aaltonen, N., Yatkin, E., Smeds, A., Eckerman, C., Prevention of breast and prostate cancer through modulation of tissue pro-inflammatory state and estrogen synthesis by pine extract and its active components, Invention disclosure K/22/2012, University of Turku

Riittonen, T., Kumar, N., Mikkola, J-P., Manufacturing of alkyl ethers, Patent Application FI20126071, Åbo Akademi

Sokalski, T., Lewenstam A., Mousavi, Z., Granholm, K., All-solid-state reference electrode, Finnish Patent Appl. 2012 20126315

Virtanen, P., Anugwom, I., Mikkola, J-P., Mäki-Arvela, P., Method for Fractionating of Lignocellulosic Material and Novel Ionic Liquids Therefor, Patent: PCT/FI2011/050959; FI 20106086 (Åbo Akademi/ForestCluster)

Vähäsalo, L., Saari, E., Joensuu, I., Pulse assisted dispersion field flow fractionator, Invention Disclosure

Wu, M., Kordás, K., Zoltán, K., Kukovecz, A., Sapi, A., Huuhtanen, M., Mikkola, J-P., Toth, G., Keiski, R., Patent: PCT/FI2011/050925; FI 20106142

Xu, C., Leppänen, A-S., Willför, S., Bergelin, M., Johansson, M., A natural bio adhesive to facilitate contact between a galvanic stimulation electrode array and wound tissue, May 3, 2012, ID U/03/2012, Åbo Akademi University

4.8 Awards granted in 2011 (3)

Engblom, Markus, Tekniktävling, Department of Chemical Engineering, Åbo Akademi, 3rd Prize

Salminen, K., Kataja-aho, J., Lindqvist, H., Retulainen, E., Rantanen, T., Sundberg, A., The effects of certain polymers on tensile strength and tension relaxation of wet web, *Jasper Mardon Memorial Award,* PaperCon Conference 2011, May 1-4, 2011, Cincinnati, OH, USA. Award presented by TAPPI at the *PaperCon Conference 2012*, April 22-25, 2012, New Orleans, LA, USA

Tolvanen, Pasi, Tekniktävling, Department of Chemical Engineering, Åbo Akademi, 3rd Prize

5. Other Activities 2012

5.1 Organization of Conferences, Courses and Seminars

January

Turku, Finland, PCC Winter Colloquium

April

Espoo, Finland, GSCE Spring Seminar

June

Mariehamn, Åland, Industrial Chemistry and Reaction Engineering Summer School

Mariehamn, Åland, 15th Nordic Symposium on Catalysis

August

Turku, Finland, PCC Annual Seminar

November

Athens, Greece, ERASMUS Course: Renewables: Towards New Reactors

Oulu, Finland, GSCE Annual Seminar

Turku, Finland, Course: Wood Extractives – Friend or Foe in Industry

Turku, Finland, Course: Reaction Kinetics

5.2 Participation in Conferences, Major Meetings and Courses

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

January

Brussels, Belgium, Reliable and Efficient Combustion of Oxygen/Coal/Recycled Flue Gas Mixtures (RELCOM) project kick-off meeting, 1

Lappeenranta, Finland, Finnish Flame Research Committee VI Liekkipäivä, 4

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

Ås, Norway, CenBio Annual Meeting, invited lecture, *Mikko Hupa*

February

Geelong, Victoria, Australia, 7th Annual International Electromaterials Science Symposium, invited lecture, *Ari Ivaska*

Lanzarote, Canary Islands, Spain, Zing Conferences: Electrochemistry Conference 2012, 6

Lyon-Villeurbanne, France, Utilization of Biomass for Sustainable Fuels & Chemicals (UBIOCHEM) Workshop, 2

Lyon, France, 12th International Conference on Microreaction Technology (IMRET12), 3

Prague, Czech Republic, Institute of Chemical Process Fundamentals, invited lecturer, *Dmitry Murzin*

Padova, Italy, University of Padova, invited lecturer, *Tapio Salmi*

Pori, Finland, Outotec Research Centre, invited lecturer, *Tapio Salmi*

Pori, Finland, Chamber of Commerce, SataRekry recruitment event, *Tapio Salmi, Henrik Grénman*

March

Graz, Austria, European Research Infrastructure for Thermo-Chemical Biomass Conversion (BRISK), kick-off meeting, 1

Helsinki, Finland, Prof. C-J. Fogelholm Retirement Seminar, invited lecture, *Mikko Hupa*

Pittsburgh, PA, USA, Carnegie Mellon University, invited lecturer, *Dmitry Murzin*

Pulheim, Germany, VGB Scientific Advisory Board, 79th Meeting, 1

San Diego, CA, USA, 243rd American Chemical Society National Meeting, invited speaker, *Dmitry Murzin*, 2

Tampere, Finland, Micro Current Wound Treatment Patch with Increased Functionality project kick-off meeting, 2

Turku, Finland, Materials Science and Technology Seminar, 1

Turku, Finland, FABTech Microtechnology Seminar, 5

Turku, Finland & Umeå, Sweden, Catalyst Characterization, Finnish-Indian-Swedish Symposium on Heterogeneous Catalysis, invited speakers: *Jyri-Pekka Mikkola, Päivi*

Mäki-Arvela, Tapio Salmi, Dmitry Murzin, Narendra Kumar, Pasi Virtanen, Toni Riittonen, Anton Tokarev, Andreas Bernas, Johan Wärnå

April

Annapolis, MA, USA, 24th Biennial Conference of the Organic Reactions Catalysis Society (ORCS), 3

Corfu, Greece, 12th Eurasian Conference on Chemical Science, 1

Detroit, MI, USA, SAE World Congress, 1

Funchal, Madeira, Portugal, XIV Iberic Meeting of Electrochemistry & XVII Meeting of the Portuguese Electrochemical Society, keynote lecture, *Ari Ivaska*

Heraklion, Greece, EU Polycat project meeting, 2

Joensuu, Finland, SciFest, 2

Lisbon, Portugal, AFORE Training School, Invited lecture, *Bjarne Holmbom*

May

Bucharest, Romania, 3rd Regional Symposium on Electrochemistry- South-East Europe (RSE-EES3), plenary lecture, *Ari Ivaska*

Dresden, Germany, TU Dresden, invited lecturer, *Tapio Salmi*

Haikko, Finland, FuBio2 meeting, 3

Jönköping, Sweden, Nordic Wood Biorefinery Conference, 1

Magdeburg, Germany, Max-Planck-Institut, invited lecturer, *Tapio Salmi*

Marrakech, Morocco, 6ème Journées Francophones sur les Réacteurs Gaz-Liquides et Gaz-Liquides-Solides (GLF-F6), *Olatunde Jogunola*

Prague, Czech Republic, 63rd Annual Meeting of the International Society of Electrochemistry, 4

Seattle, WA, USA, 221st Electrochemical Society Meeting (221st ECS), 4

Turku, Finland, Johan Gadolin Day, invited lecturer, *Victor Sifontes Herrera*

Trondheim, Norway, ERANET ScitoBiCom Semiannual Meeting, 4

Tver, Russia, Tver Technical University, invited lecturer, *Dmitry Murzin*

Qingdao, China, Qingdao Institute of BioEnergy and Bioprocess Technology, Chinese Academy of Sciences, Invited lecture, *Chunlin Xu*

June

Ankara, Turkey, 10th International Symposium on Pharmaceutical Sciences, plenary lecture, *Ari Ivaska*

Helsinki, Finland, Millennium Prize Event, 2

Hódmezövásárhely, Hungary, 7th International Workshop on the Electrochemistry of Electroactive Materials (WEEM), 9

Ixtapa-Zihuatanejo, Guerrero, México, International-Mexican Congress on Chemical Reaction Engineering

Maastricht, the Netherlands, 11th ESG Conference, 4

Madrid, Spain, Catalysis for Clean Energy and Sustainable Chemistry (CCECS), 2

Maffliers, France, 17th International Flame Research Foundation (IFRF) Members Conference, 3

Mariehamn, Åland Islands, 15th Nordic Symposium on Catalysis

Milan, Italy, 20th EU Biomass Conference & Exhibition, 1

Naples, Italy, 21st International Conference on Fluidized Bed Combustion, 5

Paris, France, 6th International Society of Antioxidants in Nutrition and Health (ISANH) Congress on Polyphenols Applications (Paris Polyphenols), 1

Portorož, Slovenia, 14th International Conference on Electroanalysis, 6

Seoul, Korea, International Conference on Hydrogen Production, 1

Stockholm, Sweden, 8th International Paper and Coating Chemistry Symposium, 3

Turku, Finland, Pressurized PEM Electrolyzer (Primolyzer) end meeting, 3

Turku, Finland, Nordic Environmental Chemistry Conference (NECC2012), plenary lecture, *Mikko Hupa*

July

Atlanta, GA, USA, International Conference on Science and Technology of Synthetic Metals, 4

Madrid, Spain, 26th International Carbohydrate Symposium, 2

Montpellier, France, International Commission on Glass course, 1

Munich, Germany, 15th International Congress on Catalysis, Poster symposium session chairman, *Dmitry Murzin*, 6

Nantes, France, Plant and Seaweed Polysaccharides Symposium 2012, 2

Thessaloniki, Greece, International Conference on Advances in Catalysis for Biomass Valorization (CAT4BIO), 4

August

Espoo, Finland, 12th European Workshop on Lignocellulosics and Pulp (EWLP), 5

Espoo, Finland, Workshop for COST Action FP0901 'Analytical tools for biorefineries', 3

Foz do Iguaçu, PR, Brazil, 4th International IUPAC Conference on Green Chemistry

Prague, Czech Republic, 20th International Congress of Chemical and Process Engineering (CHISA 2012), keynote lecturers and chairs *Tapio Salmi*, *Päivi Mäki-Arvela*, 13

Oulu, Finland, Nanotechnology Platform for Electronics and Photonics Workshop, invited speaker, *Jyri-Pekka Mikkola*

Turku, Finland, 17th International Workshop on Quantum Systems in Chemistry and Physics

Warsaw, Poland, 34th Combustion Symposium, 2

September

Edinburgh, Scotland, 29th European Conference on Surface Science, 1

Goslar, Germany, 10th International Symposium on Crystallization in Glasses and Liquids, 1

Helsinki, Finland, Fuel Cell Annual Seminar, 4

Krakow, Poland, XI Conference on Electroanalysis - Theory and Practice, 3

Maastricht, the Netherlands, 22nd International Symposium on Chemical Reaction Engineering (ISCRE22), 6

Novosibirsk, Russia, 4th Annual Russian-Korean Conference - Current Issues of Natural Products Chemistry and Biotechnology, plenary lecturer, *Dmitry Murzin*

Paris, France, Rhodia, invited lecturer, *Dmitry Murzin*

Pescara, Italy, Convegno Nazionale GRICU 2012, Ingegneria Chimica: dalla macroscala alla nanoscala, 1

Puchberg, Austria, Impacts of Fuel Quality on Power Production and the Environment, plenary lecture, *Mikko Hupa*

St. Petersburg, Russia, Renewable Resources Chemistry Meeting Vice-Chairman and co-organizer *Andrey Pranovich*, 20

Tlemcen, Algeria, International Symposium on Catalysis and Speciality Chemicals (ISCSC 2012), 1

Białystok, Poland, 55th Congress of the Polish Chemical Society, 2

Yichang, Hubei, China, XIII International Conference on the Physics of Non-Crystalline Solids, 2

October

Fukuoka, Japan, 2nd Symposium on Biotechnology Applied to Lignocellulosics (Lignobiotech-II), 1

Fukuoka, Japan, 57th Lignin Symposium, 1

Helsinki, Finland, 4th Nordic Wood Biorefinery Conference, 2

Honolulu, HI, USA, Pacific Rim Meeting on Electrochemical and Solid-State Science (PRiME 2012), 6

Pisa, Italy, European Research Infrastructure for Thermo-Chemical Biomass Conversion (BRISK), 1

Pittsburgh, PA, USA, 2012 American Institute of Chemical Engineers Annual Meeting, 1

St. Petersburg, Russia, IX International Conference: Mechanisms of Catalytic Reactions, keynote lecturer, *Dmitry Murzin*

Tampere, Finland, Finnish Recovery Boiler Committee Soodakattilapäivä, 1

Tampere, Finland, Tiedeviikko Tampereella, Työväenmuseo Werstas, 1

Tokyo, Japan, University of Tokyo, invited lecturer, *Andrey Pranovich*

Turku, Finland, Åbo Akademi University Graduate School Annual Seminar, 4

Turku, Finland, Department of Chemical Engineering Alumni Day, invited lecturers, *Stefan Willför, Mikko Hupa, Tapio Salmi*

November

Bergen, Norway, 8th Topical Meeting of the Scandinavian-Nordic Section of the Combustion Institute, 2

Berlin, Germany, EU Polycat Meeting, 1

Berlin, Germany, Fritz-Haber-Institut, invited lecturer, *Dmitry Murzin*

Delft, the Netherlands, TU Delft Process Technology, International Program Committee, *Tapio Salmi*

Helsinki, Finland, Academy of Finland, Seminar of LASTU research program, 1

Mülheim, Germany, Institute for Coal Research, invited lecturer, *Dmitry Murzin*

Rio de Janeiro, Brazil, Academy of Finland, Brazilian CNPq and Conicyt Chile, invited lecturer, *Jyri-Pekka Mikkola*

Tampere, Finland, Scanbalt Biomaterials Days, 3

Thessaloniki, Greece, Cost UBIOCHEM-III, Workshop: Sustainable Production of Fuels/Energy, Materials & Chemicals from Biomass, 5

Turku, Finland, Workshop on Hemicelluloses

Umeå, Sweden, Processum Annual Meeting, invited speaker, *Jyri-Pekka Mikkola*

December

Copenhagen, Denmark, ERANET SciToBiCom final meeting, 3

Mondorf-les-Bains, Luxembourg, XX International Conference on Chemical Reactors (Chemreactor-20), 1, keynote and chairman, *Dmitry Murzin*

Risø, Denmark, Nordic Conference on Ceramic and Glass Technology, 1

Termas de Catillo, Chile, VI Coloquio de Macromoléculas, plenary lecture, *Ari Ivaska*

5.3 Visitors and Visits

Visitors to the PCC

- Becker, Manuel, BOKU, Austria (January–February)
- Banerjee, Protibha Nath, National Sugar Institute, Kalyanpur, Kanpur, Uttar Pradesh, India (January-December)
- Boga, Dilek Ayse, University of Utrecht, the Netherlands (April)
- Bourhis, Kevin, Politecnico di Torino, Turin, Italy (June-July)
- Demidova, Yulia, Boreskov Institute of Catalysis, Novosibirsk, Russia (May, September-December)
- Egorova, Anastasia, St. Petersburg Institute of Technology, Russia (June)
- Fortes, Mariana, University of Rio de Janeiro, Brazil (June-July)
- Garcia Serna, Juan, University of Valladolid, Spain (June-July)
- Gemo, Nicola, University of Padova, Italy (January–April)
- Gulbrandsen, Tore Aarhus, Norwegian University of Science and Technology (NTNU), Norway (March)
- Hagebols, Erik, University of Aberdeen, Scotland (January– May)
- Hasse, Benjamin, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany (January-March)
- Houshfar, Ehsan, NTNU, Trondheim, Norway (May)
- Huerta Illoza, Irene, University of Valladolid, Spain (September-December)
- Inder Singh, Ravi, Guru Nanak Dev Engineering College, Ludhiana, Punjab, India (January-July)
- Ivanova, Anna, St. Petersburg Institute of Technology, Russia (June)
- Janceva, Sarmite, Latvian State Institute of Wood Chemistry, Latvia (November)
- Lauberts, Maris, Latvian State Institute of Wood Chemistry, Latvia (November)
- Leino, Anne-Riikka, University of Oulu (December)

- Mammitzsch, Frank, Technical University of Dresden, Germany (January-March)
- Poljanšek, Ida, University of Ljubljana, Slovenia (May-June)
- Reinsdorf, Arne, Technical University of Dresden, Germany (January-February)
- Stekrova, Martina, Institute of Chemical Technology, Czech Republic (September-December)
- Vieira Viegas, Carolina, University of Rio de Janeiro, Brazil (June-July)
- Vilaplana, Fransisco, Royal Institute of Technology (KTH), Sweden (October-November)
- Wang, Liang, NTNU, Trondheim, Norway (May)
- Zbuzek, Michal, Institute of Chemical Technology, Prague, Czech Republic (March-April)

Visits by PCC Members

- Hyvärinen, Sari, Tallinn University of Technology, Estonia (August-September)
- Hupa, Mikko, TAPPI Kraft Recovery Short Course, St. Petersburg, FL, USA (January)
- Karlström, Oskar, International Flame Research Foundation, Pisa, Italy (October)
- Korotkova, Ekaterina, Tver State Technical University, Russia (April)
- Lindberg, Daniel, École Polytechnique de Montréal, Montréal, Canada (November)
- Pranovich, Andrey V., St. Petersburg Forest Technical University, Russia (April)
- Rozmysłowicz, Bartosz, University of Rio de Janeiro, Brazil (January-February)
- Salminen, Eero, Bucharest University, Romania (October)
- Strand, Anders, Mid Sweden University, Sweden (March-April)
- Xu, Chunlin, Chinese Academy of Sciences, China (May)
- Xu, Chunlin, Wallenberg Wood Science Center, KTH, Sweden (June and October)

5.4 External PhD Examinations and Reviews

Board member, Helmholtz Energie-Alliaz: Energieeffiziente Chemische Mehrphasenprozesse, *Tapio Salmi*

Board member, Raisio Research Foundation, *Tapio Salmi*

Chairman, National Committee for Student Selection for Technical Universities and Faculties in Finland, *Tapio Salmi*

Editorial Board Member for *Electroanalysis* (Wiley), *Andrzej Lewenstam*

Editorial Board Member for *Foundations of Science*, (Springer-Kluwer), *Andrzej Lewenstam*

Editorial Board Member for *Journal of Elementology* (UWM), *Andrzej Lewenstam*

Editorial Board Member for *Magnesium Research* (Libbey), *Andrzej Lewenstam*

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

Editorial Board Member for *Philosophy of Science*, (Semper), *Andrzej Lewenstam*

Evaluation committee member for the appointment of a professor at NTNU, Faculty of Natural Sciences and Technology, Norway, *Jyri-Pekka Mikkola*

Evaluation committee member for the appointment of a professor at KTH, Chemical Technology, Sweden, *Tapio Salmi*

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

Evaluation of research proposal for EPSRC, UK, *Johan Bobacka*

Evaluation of research proposals for the Slovenian Research Agency, *Johan Bobacka*

Evaluation of scientific competence for lecturership, Aalto University, Helsinki, *Päivi Mäki-Arvela*

Evaluation of docentship, Environmental catalysis and isotope studies in catalysts, University of Oulu, *Päivi Mäki-Arvela*

Evaluator for research programmes and projects for the Slovenian Research Agency (ARRS), *Jyri-Pekka Mikkola*

Evaluator of appointment as Assistant Professor, Luleå University of Technology, Sweden, *Jyri-Pekka Mikkola*

Evaluation of Associate Professorship, Mid Sweden University, Sweden, *Bjarne Holmbom*

Evaluator of Qatar National Research Fund, *Jyri-Pekka Mikkola*

Evaluator of the Latvian Science Foundation, *Jyri-Pekka Mikkola*

Evaluator or research programmes and projects of the Portuguese Science and Technology Foundation, *Tapio Salmi*

Evaluators of research projects, Latvian Council of Science, *Bjarne Holmbom, Andrey Pranovich*

Evaluator of research projects, Mistra (Foundation for Strategic Environmental Research), Stockholm, Sweden, *Bjarne Holmbom*

Evaluator of research projects for NWO, the Netherlands, *Dmitry Murzin, Tapio Salmi*

Expert for the Netherlands NWO biomass related program, *Dmitry Murzin*

Expert for the Qatar Research Council, *Dmitry Murzin*

Expert, Haldor Topsoe PhD scholarship program, *Dmitry Murzin*

Guest Editor, *Advances in Chemical Engineering, Dmitry Murzin*

Guest Editor, *Topics in Catalysis, Dmitry Murzin, Tapio Salmi, Päivi Mäki-Arvela*

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

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

Member of scientific committee, 20th International Congress of Chemical and Process Engineering (CHISA 2012), Prague, Keynote lecture, session chairman, *Tapio Salmi*

Member of scientific committee, 22nd International Symposium on Chemical Reaction Engineering (ISCRE22), Maastricht, the Netherlands, Session chairman, *Tapio Salmi*

Member of scientific committee, COST UBIOCHEM-III Workshop: Sustainable Production of Fuels/Energy, Materials & Chemicals from Biomass, Thessaloniki, Greece, *Dmitry Murzin*

Member of scientific committee, International Conference on Advances in Catalysis for Biomass Valorization (CAT4BIO), Thessaloniki, Greece, *Dmitry Murzin*

Member of scientific committee, IX International Conference: Mechanisms of Catalytic Reactions, St. Petersburg, Russia, *Dmitry Murzin*

Member of International Scientific Committee, 10th International Conference on Chemical & Process Engineering (ICheaP10), Florence, Italy, *Jyri-Pekka Mikkola, Tapio Salmi*

Member of the Review Panel of the Romanian National Research Council, *Chunlin Xu*

Member of the scientific committee, 15th Nordic Symposium on Catalysis 2012, Mariehamn, Åland, *Dmitry Murzin, Tapio Salmi, Reko Leino, Esa Toukoniitty*

Member of scientific committee, 6th International Symposium on the Molecular Aspects of Catalysis by Sulphides, Lyon, Session chairman, *Dmitry Murzin*

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

Member of the expert group "Vasa Preservation Council", Stockholm, Sweden, *Bjarne Holmbom*

Promotion of Associate Professor Samuel P. Kounaves to the rank of Professor with tenure at Department of Chemistry, Tufts University, Medford, MA, USA, *Ari Ivaska*

Promotion of Associate Professor Philippe Bühlmann to the rank of Professor with tenure at Department of Chemistry, University of Minnesota, MN, USA, *Ari Ivaska*

Rapporteur for the Romanian National Research Council, CNCS, *Jyri-Pekka Mikkola*

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

Session organizer, 15th International Congress on Catalysis, Munich, *Dmitry Murzin*

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

Vice President of the Scientific Committee, XX International Conference on Chemical Reactors (Chemreactor-20), Luxembourg, *Dmitry Murzin*

External Examinations

Ebrahimi, Fatemeh, Lappeenranta University of Technology, Finland, opponent, *Tapio Salmi*

Haase, Stefan, TU Dresden, Germany, reviewer*, Tapio Salmi*

Ikemoto, Heideki, Technical University of Denmark, Lyngby, Denmark, opponent, *Ari Ivaska*

Kassman, Håkan, Chalmers University of Technology, Sweden, examination committee for doctoral thesis*, Maria Zevenhoven*

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

Nørskov, Linda Skaare, DTU, Lyngby, Denmark, opponent, *Anders Brink*

Palmre, Vilja, University of Tarto, Estonia, opponent*, Ari Ivaska*

Piispanen, Mirja, University of Oulu, Finland, opponent*, Mikko Hupa*

Rebrov, Evgeny, Moscow Academy of Fine Chemicals Technology, Moscow, Russia, opponent, *Dmitry Murzin*

Sinha, Shalini, IIT Kanpur, India, reviewer*, Dmitry Murzin*

Telschow, Samira, Technical University of Denmark, Lyngby, Denmark, opponent, *Mikko Hupa*

Uddin, Jahir Ahmad, University of Helsinki, Finland, reviewer, *Dmitry Murzin*

Vaajamo, Iina, Aalto University, Finland, reviewer of licentiate thesis, *Daniel Lindberg*

Vidruk, Roksana, Ben Gurion University of the Negev, Israel, reviewer, *Dmitry Murzin*

Wang, Liang, NTNU Trondheim, Norway, member of assessment committee, first opponent, *Mikko Hupa*

Ylinen-Hinkka, Tiina, Aalto University, Espoo, Finland, reviewer, *Ari Ivaska*

Zasadowski, Dariusz, Mid Sweden University, Sweden, reviewer of licentiate thesis, *Anna Sundberg*

Invited Lecturers at ÅA-PCC

Alatalo Matti, Lappeenranta University of Technology, Finland

Ashman, Peter, University of Adelaide, Australia

Brow, Richard, Missouri University of Science and Technology

Hardacre Chris, Queen's University of Belfast, Northern Ireland

Lefferts, Leon, University of Twente, the Netherlands

Marek, Milos, VSCT, Czech Republic

5.5 Publicity

Television and Radio

Internationalisation of Finnish universities, panel discussion, Radio Vega, 24.8.2012, *Tapio Salmi*

Newspapers and General Journals

Presidentens utmärkelsetecken delades ut, *Meddelanden från Åbo Akademi* 3/2012, *Päivi Mäki-Arvela*

Vihreys on kemian alan tämän hetken avainsana, Academy of Finland (www.tietysti.fi), 15.3. 2012, *Sabrina Schmidt*, *Tapio Salmi*

Åbo Akademi Process Chemistry Centre Doctoral Theses in Progress 2013

Students from Outside Finland

Part-time and external students included

- Cesar de Araujo Filho (Brazil, *M*), MSc Federal University of Ceara, Fortaleza, Brazil, 2010
- Steliana Aldea (Romania, *F*), MSc University of Bucharest, Bucharest, Romania 2006, BSc ibid. 2002
- Ikenna Anugwom (Nigeria, *M*), MSc ÅA 2009, BSc Satakunta University of Applied Sciences, Pori, Finland
- Jesús Arroyo Condori (Peru, *M*), MSc ÅA 2011, BSc Universidad Nacional Mayor de San Marcos UNMSM, Peru 2010
- Sylwia Bialczak (Poland, *F*), MSc Poznan University of Technology, Poland 2007
- Daniel Dax (Luxembourg, *M*), MSc RWTH Aachen University, Aachen, Germany, BSc ibid.
- Wenwen Fang (China, *F*), MSc ÅA 2012, BSc Shandong Institute of Light Industry, China 2010
- Lidia Godina (Russia, *F*), MSc Mendeleyev University of Chemical Technology of Russia, Moscow, Russia 2012
- Imane Hachemi (Algeria, *F*), MSc University of Sciences and Technology Houari Boumediene (USTHB) 2012, BSc Ibid., Algiers, Algeria, 2009
- Tingting Han (China, *F*), MSc ÅA 2008, BSc Shandong Institute of Light Industry, China 2006
- 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)
- Jun Liu (China, *M*), MSc Tianjin University of Science and Technology, China 2012
- Donald MacNeil (Canada, *M*), MSc ÅA 2002, BEng Dalhousie University, Halifax, Canada 1994
- Gerson Martin Curvelo (Venezuela, *M*), MSc Universidad Simón Bolivar, Caracas, Venezuela 2008
- He Ning (China, *M*), MSc ÅA 2009, BSc Shandong Polytechnic University, China 2007
- Bartosz Rozmysłowicz (Poland, *M*), MSc ÅA & Poznan University of Technology, Poland 2009 (double degree)
- Rishabh Sarna (India, *M*), MSc ÅA 2012, BSc Indian Institute of Technology Roorkee 2010
- Sabrina Schmidt (Germany, *F*), Diplom Chemiker RWTH Aachen University, Aachen, Germany 2010
- Tao Song (China, *M*), MSc ÅA 2006, BSc Shandong Institute of Light Industry, China 2003
- Jingxin Sui (China, *M*), MSc ÅA 2011, BSc Shandong Institute of Light Industry, China 2009
- 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

- 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
- Magnus Perander (Pargas, *M*), MSc ÅA 2010
- 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
- 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