Åbo Akademi
Process Chemistry Centre

Annual Report 2013 – 2014

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

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Åbo Akademi Process Chemistry Centre (PCC)

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

The PCC consists of the teams:

- *Combustion and Materials Chemistry (lead by Prof. Mikko Hupa)*
- *Wood and Paper Chemistry (Prof. Stefan Willför)*
- *Catalysis and Reaction Engineering (Prof. Tapio Salmi)*
- *Process Analytical Chemistry (Prof. Johan Bobacka)*

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 (2014): Örjan Andersson (Novia), Ilmo Aronen (Raisio), Stig-Erik Bruun (Chemigate), Heidi Fagerholm (Kemira), Christine Hagström-Näsi (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 Fibre), Bengt-Johan Skrifvars (Top Analytica), Kenneth Sundberg (Tikkurila), Kari Toivonen (Elomatic) and Petri Vasara (Pöyry).

The PCC Scientific Advisory Board (2014): 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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Cover design: Kimmo Aro, KMG Turku
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ISSN 1459-8213
Newprint Oy, Loimaa 2014

PCG Annual Report 2013 – 2014

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1. Introduction to the Activities in 2013-2014

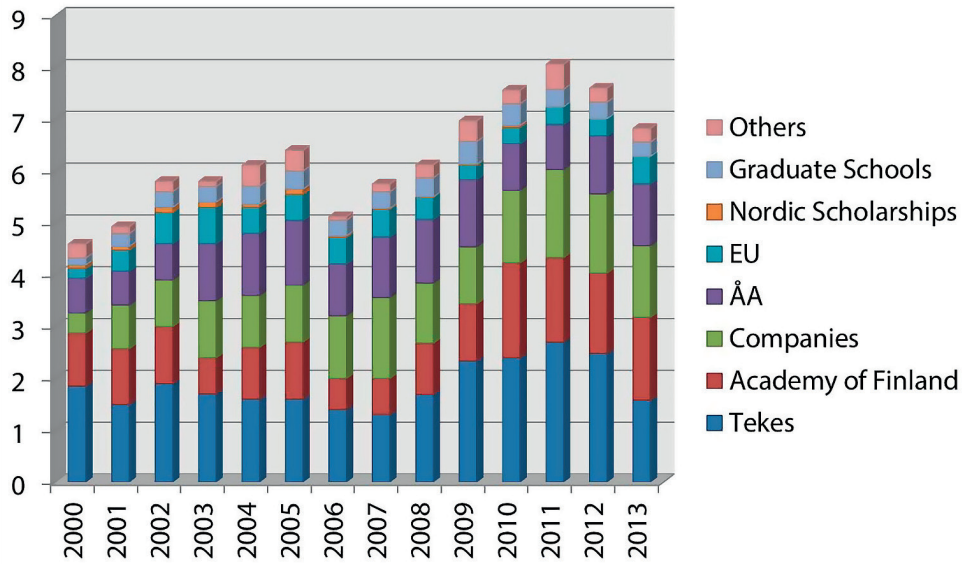
Background

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 2013 in Numbers

In 2013 altogether 20 senior researchers and 50 full-time PhD candidates worked in the 50 major research projects of the Centre. In addition, a number of shorter term visitors, Master's students and support personnel participated in our activities.

The figure below shows the funding of the Centre since the year 2000. The key external funding sources in 2013 were Tekes – the Finnish Funding Agency for Technology and Innovation together with industrial companies, and the Academy of Finland. Since 2012 the Centre has no longer received the Centre of Excellence funding from the Academy of Finland. However, this decrease in funding was partly compensated by a special strategic support from Åbo Akademi University and also from other sources, and this made it possible for the Centre to continue its activities with full capacity.



The funding of the Åbo Akademi Process Chemistry Centre 2000–2013

From the Academic point of view the year 2013 was extremely productive. The table below gives some key numbers of our academic activities in 2013. Once again, the Centre broke its own all-time record by publishing 154 papers in scientific publication series with the full referee system. Further, another remarkable record was achieved in 2013: 15 PhD theses were defended during the year.

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

Theses and other publications by the Åbo Akademi Process Chemistry Centre 2000-2013

Our researchers also wrote popular texts in daily newspapers and journals and appeared on several radio and TV programs.

Organizing International Conferences

Catalysis is one of the key research topics at PCC. A demanding application area of catalysis is the manufacture of fine chemicals. The conference series Catalysis Applied to Fine Chemicals started a long time ago and PCC had a great pleasure for us to host CAFC10, June 16 – 19, 2013 in Turku/Åbo, Finland. The event took place in the Arken building of Åbo Akademi.

CAFC held in Turku in June, 2013.

The congress is devoted to the application of any type of catalyst - homogeneous, heterogeneous, enzymatic - to the synthesis of fine chemicals, with special emphasis on the selectivity issues. The aim was to bring together researchers from both academia and industry, working in the synthesis of fine chemicals with various catalysts, to share their expertise in the field as a way to open new collaborations that help to solve the forthcoming problems in the chemical industry, and to implement more sustainable synthetic methods based on catalytic processes.

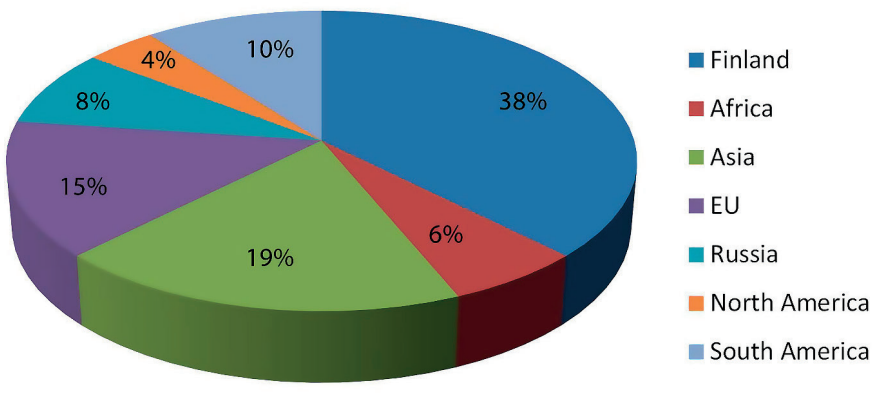
We were delighted to get almost 180 abstracts, which underwent a reviewing process. The result became 46 oral presentations and around 120 posters. Six top scientists were selected to give plenary lectures at the conference. The number of participants was around 200, representing 33 countries. The participants enjoyed the rich scientific content and beautiful Finnish summer – the conference excursion took place on the Pikku-Pukki Island and the representatives of the city honoured the event with their presence (www.cafc10.org)

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 Appendix 1 on page 158 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 2013, 41 students were participating in the activities of the GSCE, 6 of them from our Centre. In 2014 GSCE received additional funding from the Åbo Akademi doctoral network



Nationality of the PhD students at PCC 2013-2014. For more detailed information see Appendix 1 on page 158

programme which allowed for an additional six new students to be recruited from the beginning of the year.

Johan Gadolin Scholarships Program

Our Johan Gadolin Scholarship Programme was founded in 2007. It was funded by the Åbo Akademi Foundation during the years 2007-2011 and after that by other sources.

In the Johan Gadolin Scholarship Programme we have been able to invite PhD students and post doctoral researchers to join the Åbo Akademi Process Chemistry Centre (PCC) for a period between 3 to 12 months. So far, 44 fellows from 21 different countries and 37 different universities worldwide have participated in the programme, an additional 4 fellows have participated with their own funding. The visitors have participated in on-going research projects at the Centre. The cooperation between the PCC and the Johan Gadolin fellows has so far produced more than 60 scientific articles and more than 60 conference proceedings.

Åbo Akademi Foundation recently decided to grant new funding for the Johan Gadolin Scholarships Programme. This new funding will strongly activate the programme and in the next two years we expect to have continuously 2-4 visiting Johan Gadolin fellows at our Centre.

Research plans

The overall title of our research program 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 still presented divided in these nine research areas.

At the moment we are revising our research programme, and from the year 2015 we expect to follow a new overall research plan. The core of the new plans will still build on our strengths in experimental and modelling capabilities to explore chemical details in novel processes and products which use biomass-based raw-materials.

Boards and Task Forces

In 2014, the PCC is led by an executive board consisting of the four research group leaders, Professors Mikko Hupa, Stefan Willför, Johan Bobacka and Tapio Salmi. Dr. Hanna Lindqvist works with the coordination of the PCC and functions as secretary of the board. In 2013 the board met five times.

Since the very beginning the PCC Board has been supported by two important Advisory Boards; the Scientific Advisory Board (SAB) and an Industrial Advisory Board (IAB). In 2013-2014 our Scientific Advisory Board consists of the Professors *Jiri Janata* from 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 2013 the PCC had one lecture in its Distinguished Lecturer Series:

- October 2013: Prof. *Richard G. Compton*, Oxford University, United Kingdom: "Electrochemical Studies of Nanoparticles"

Acknowledgements

This report will be published at the annual seminar of the PCC held on August 20, 2014 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 2013. It also has an activity calendar listing the main events where members of the Centre have contributed or participated during that year.

The report is edited by an editorial team consisting of Hanna Lindqvist, Anders Brink, Rose-Marie Latonen, Päivi Mäki-Arvela 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 another year of interesting and inspiring work together.

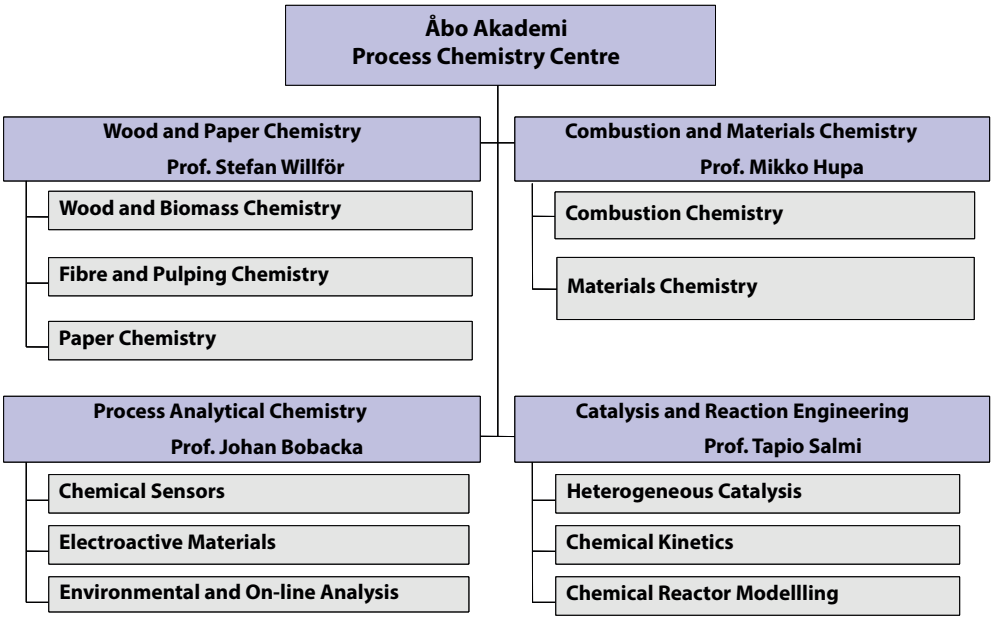
On behalf of the Board of the Åbo Akademi Process Chemistry Centre,

Mikko Hupa

Chairman

2. Organization and personnel

2.1 Organization



Åbo Akademi Process Chemistry Centre Organization

Executive Board

- Prof. Mikko Hupa (Chairman)
- Prof. Johan Bobacka
- Prof. Tapio Salmi
- Prof. Stefan Willför

- Coordination:
  Maria Ljung (–04/2014)
  Hanna Lindqvist (05/2014–)

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
- Christine Hagström-Näsi, 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 Fibre
- 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 value-added end-uses. Remaining wood substances can then further be recovered or utilized as energy.

External research support during 2013 was obtained mainly from Tekes and the Fibic SHOK, the industry, EU, and Academy of Finland.

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 close cooperation with KTH and the Wallenberg Wood Science Centre in Sweden.

We have chaired and coordinated the EU-supported COST Action FP0901, "Analytical methods for Biorefineries, 2009-2013". This Action had participants from 27 COST and 4 non-COST countries. We are also partners in the "European Polysaccharide Network of Excellence" (EPNOE) network and in the "Refining lignocellulosics to advanced polymers and fibers" Nordforsk researcher network.

Personnel

Professors	Stefan Willför
	Bjarne Holmbom (Emeritus)
Docents	Patrik Eklund (Organic Chemistry)
	Andrey Pranovich
	Annika Smeds
	Anna Sundberg
	Chunlin Xu
Senior researchers	Risto Korpinen
	Ann-Sofie Leppänen
	Bin Li

	Hanna Lindqvist
	Anders Strand
	Lari Vähäsalo
Researchers	Sylwia Bialczak
	Daniel Dax
	Jarl Hemming
	Matti Häärä
	Victor Kisonen
	Ekaterina Korotkova
	Jens Krogell
	Jun Liu
	Linda Nisula
	Sebastian von Schoultz
Technician	Leif Österholm
Secretary	Agneta Hermansson

Links:

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

2.3 Combustion and Materials Chemistry

"Alternative" and "Non-Fossil" fuels, such as biomasses and various wastes or waste-derived fuels, are heavily entering the bioenergy 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 2013 several new measurement technologies for combustion processes were developed and tested. A collaborative work with Tampere University of Technology resulted in the first direct measurements of released alkali vapours from burning biomass particles. The work sheds new light on the complex behaviour of alkali metal compounds in combustion.

A completely new technique was developed for accurate measurements of sulphur trioxide, SO_3, in flue gases. The technique is based on controlled absorption of the SO_3 in suitable alkali salts and appears to be sensitive enough to detect a few ppm SO_3 in flue gases without being disturbed by the presence of SO_2. Sulphur trioxide is a precursor for the low temperature corrosion in flue gases and presently of great interest when more efficient flue gas heat recovery systems are being developed.

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 2013.

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 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. The project is ending in 2014, and there is a great interest to have a continuation of the activities.

We participate in the project BRISK - Biofuels Research Infrastructure for Sharing Knowledge. Brisk is an 11 Million Euro four-year initiative with 9 Million Euros 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 programme. 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. We have continued our studies on bioactive glasses with optimized properties. Our on-line measurement system to establish the dissolution chemistry of bioactive glasses has produced data on the instantaneous 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 2013 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. In 2013

our electrochemistry work led to several activities for medical applications. The activity of wound healing has led to a patented innovation, and a project supported by Tekes (TUTLI) was initiated to prepare for commercialization of the innovation.

Personnel

Professor	Mikko Hupa
Docents	Rainer Backman (external)
	Anders Brink
	Edgardo Coda Zabetta (external)
	Kaj Fröberg
	Leena Hupa
	Christian Mueller (external)
	Laeticia Petit (external)
	Bengt-Johan Skrifvars (external)
	Heimo Ylänen (external)
Senior researchers	Dorota Bankiewicz
	Mikael Bergelin
	Nikolai DeMartini
	Markus Engblom
	Susanne Fagerlund
	Oskar Karlström
	Juho Lehmusto
	Bingzhi Li
	Daniel Lindberg
	Jonathan Massera
	Johan Werkelin
	Patrik Yrjas
	Maria Zevenhoven
	Di Zhang
	Xiaoju Wang
Doctoral students	Leena Björkvik
& *researchers*	Jan-Erik Eriksson
	Sui Jingxin
	Max Johansson
	Tooran Khazraie
	Tor Laurén
	Na Li
	Camilla Molin
	Magnus Perander
	Rishabh Sarna
	Christoffer Sevonius
	Linus Silvander
	Berndt Södergård
	Emil Vainio
	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 core of the research of the group is focused on heterogeneous catalysis, chemical kinetics, modelling 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. Simultaneously, we explore the research on reactive solids, mainly solid-liquid reactions, since they have numerous industrial applications, from pharmaceuticals to mining products. New theories have been developed at PCC for non-ideal reactive solids and they have got a lot of international attention. New catalytic systems have been taken in use, particularly supported nanogold and bimetallic catalysts, which are developed in collaboration with domestic and foreign universities. The research in biomass fractionation with ionic liquids has given revolutionary results, concerning the efficiency and selectivity of fractionation. Supported Ionic Liquid Catalysts (SILCA) are used for transformation of fine chemicals – the catalytic effect is based on immobilized metal nanoparticles. Several new molecules originating from biomass are under investigation. The research collaboration in the catalyst characterization is very intensive with University of Turku, University of Oulu and University of Umea.

Molecularly oriented kinetic studies are 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 epoxidized vegetable oils, isomerization and esterification processes, enantioselective hydrogenation and cleaning of exhaust gas originating from biofuels. The collaboration with Latin America has been expanded and deepened. Finnish-Brazil and Finnish-Chile projects are in progress in the field of microalgae as sources for biofuels and health-promoting chemicals and the student exchange with Venezuela is flourishing.

We approach reaction mechanisms and reaction kinetics from first principles, i.e. quantum chemical calculations, which can elucidate the adsorption states and adsorption stoichiometry on solid metal surfaces. The complex interaction of reaction and diffusion in porous media was studied experimentally and with sophisticated simulations includ-

ing 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 have been 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 are used to explore the possibilities to process intensification. The leading principle is multiscale modelling: to achieve real reaction intensification, the modelling efforts should cover the approaches from quantum chemistry to computational fluid dynamics (CFD). The four-year research project on multiscale modelling of chemical processes (MUMO) was successfully finished. New kinds of structured catalysts are under development, such as solid foams, which are developed together with the group in Combustion and Materials Chemistry (PCC) and foreign partners. The development of green process technology is advanced in many fields, particularly in the development of new continuous processes for 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 valuable chemical intermediates, such as ethylene oxide, chloromethane and chloroethane.

Personnel

Professors	Tapio Salmi (Academy Professor)
	Dmitry Murzin
	Johan Wärnå
	Jyri-Pekka Mikkola (together with Umeå University)
Docents	Kalle Arve
	Matias Kangas
	Narendra Kumar
	Päivi Mäki-Arvela
	Fredrik Sandelin
	Esa Toukoniitty
Laboratory manager	Kari Eränen
Senior researchers	Atte Aho
	Ikenna Anugwom
	Andreas Bernas
	Heidi Bernas
	Pierdomenico Biasi
	Valérie Eta
	Sigmund Fugleberg
	Nicola Gemo
	Henrik Grénman
	Jan Hájek
	Teuvo Kilpiö
	Alexey Kirilin

	Olatunde Jogunola
	Sébastien Leveneur
	Mats Rönnholm
	Victor Sifontes Herrera
	Anton Tokarev
	Pasi Tolvanen
	Pasi Virtanen
Doctoral students	Cesar de Araujo Filho
& researchers	Steliana Aldea
	Juan Garcia Serna
	Lydia Godina
	Imane Hachemi
	Sari Hyvärinen
	Antonina Kupareva
	Ewelina Leino
	Gerson Martin Curvelo
	Andrea Perez Nebreda
	Ricardo Pezoa Conte
	Toni Riittonen
	Jussi Rissanen
	Bartosz Rozmysłowicz
	Eero Salminen
	Sabrina Schmidt
	Stefano Sterchele
	Timo Petteri Suominen
Technician	Elena Murzina
Secretary	Lotta Malminen

Links

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

2.5 Process Analytical Chemistry

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

Process analytical chemistry is needed for efficient control of industrial processes, including (i) analysis of raw materials, (ii) determination of product quality, (iii) monitoring of effluents, and (iv) analysis of hazardous components for safety reasons. The main challenge of process analytical chemistry is the development of robust and automated analytical systems that can work continuously for a long time with a minimum of service

needed. In addition to sophisticated analytical instrumentation, there is a growing need for inexpensive analytical tools such as chemical sensors that are easy to use on a large scale in various fields of applications.

An important research direction at the Process Analytical Chemistry group is the development of chemical sensors for applications in process analysis, environmental monitoring and healthcare diagnostics. Solid-contact ion-selective electrodes have become a major research topic in our group over the last two decades. A unique feature of ion-selective electrodes is that they provide information about the free ion concentration (ion activity), while most other analytical methods which give the total concentration.

Our research on chemical sensors is supported by electrochemical and spectro-electrochemical characterization of electroactive materials including conducting polymers, fullerenes, carbon nanotubes and graphene. Advanced nonequilibrium mathematical modells are developed for accurate description of the potentiometric response of ion-selective electrodes. Electroactive materials are also studied as electrochemically controlled separation membranes, which is relevant for water purification. Furthermore, present research is focused on ion-exchange reactions and complexation of metal ions to biomass, which is relevant for the development of biorefineries.

Personnel

Professors	Johan Bobacka
	Ari Ivaska (Emeritus)
	Kalle Levon (FiDiPro)
	Andrzej Lewenstam (part-time)
Docents	Leo Harju
	Carita Kvarnström
	Rose-Marie Latonen
	Tom Lindfors
	Li Niu
	Tomasz Sokalski
	Di Wei
Senior researchers	Marceline Akieh-Pirkanniemi
	Maija Blomquist
	Patrycja Bober
	Zhanna Boeva
	Kim Granholm
	Jerzy Jasielec
	Grzegorz Lisak
	Zekra Mousavi
	Pingping Su
	Yasuhito Sugano
	Michał Wagner

Laboratory Manager	Paul Ek
Doctoral students	Jesús Arroyo
& researchers	Cristina Dumitriu
	Ning He
	Konstantin Milakin
	Jadielson Lucas da Silva Antonio
	Sylwia Strzalkowska
	Ulriika Vanamo
	Kai Yu
Secretary & coordinator	Victoria Mäkimartti
Technicians	Sten Lindholm
	Lassi Väinölä

Links

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

The personnel at Åbo Akademi PCC

3. Research

The starting points of 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:

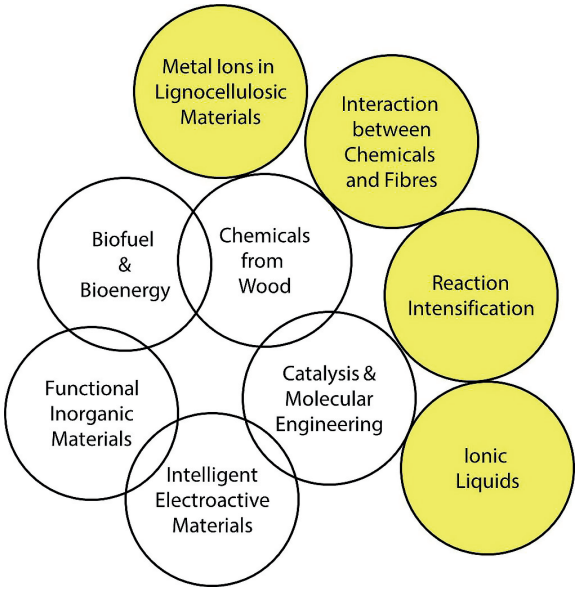
- using renewable raw materials instead of fossil resources (mainly oil)
- producing natural, biocompatible materials and chemicals, thus replacing synthetic, artificial ones
- understanding "nature's wisdom" in chemistry, thus recognizing and utilizing chemical solutions and mechanisms that have developed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

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



ÅA-PCC Research Areas

The basis of our work is naturally our special competence and our scientific toolbox, which we have developed during the course of many years. This toolbox 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 articles 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 Jyväskylä University (Doc. Manu Lahtinen), Moscow State University (the group of Prof. Leonid Kustov) or Tallinn Technical University (the group of Doc. Mihkel Koel).

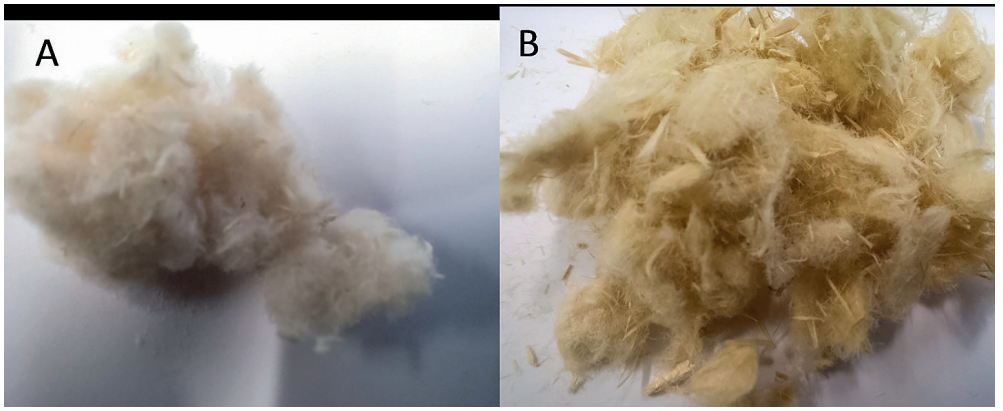
Important achievements have been obtained in preparation and use of supported ionic liquid catalysts (SILCA). The pores of the support material are filled with a thin ionic liquid layer, where e.g. an organometallic complex or an enzyme is solvated. Upon need, with further treatments, the organometallic 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 heterogenized 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).

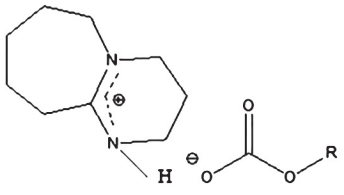
Fractionation and biorefining of lignocellulose is one of the areas where a lot of activities are on-going throughout the world. At PCC we have recently developed an entire new family of 'switchable' ionic liquids capable of selective removal of hemicelluloses, lignin and extractives from wood. These techniques enable separation of reasonably pure cellulose to be used for other applications from industrial size chips. In the beginning of our studies the treatment time was unnecessary long, and shorter treatment times would constitute a more cost effective process in an industrial scale. Furthermore, the use of large amounts of SILs and drying of the wood would also add to the process cost. Thus, an addition of water to the wood- SIL mixture and/or the use fresh non-dried wood was attempted, since it was observed that water does not significantly influence the wood dissolution efficiency of the SIL. Consequently, this can be seen as an approach to reduce the SIL consumption and as an adaptation to industrially feasible operational conditions. The search to optimize conditions for selective fractionation of woody biomass into its various fractions was continued by using an alkanol amine (MEA) and an organic superbase (DBU) derived SIL. The Short-Time-High-Temperature (STHT) approach involves the addition of water to obtain a 1:3:5 (wood:water:SIL) weight ratio mixtures. The aqueous SIL-wood mixture was kept at 160°C under normal atmospheric pressure for two hours without stirring. While the mixture was still hot, the undissolved wood fraction was separated using vacuum filtration. The undissolved wood material was washed several times with isopropyl alcohol at about 40°C until no visual evidence of any traces of the SILs remaining on the undissolved fraction could be seen. The chip weight was reduced by 35 wt-% and 30 wt-% for the birch and spruce chips, respectively. Upon addition of isopropyl alcohol the precipitated solid materials contained mostly lignin and about 10 wt-% and 25 wt-% hemicelluloses were recorded for spruce and birch, respectively. The results presented indicate selective lignin removal in a short time using SIL as a solvent, and the main hemicelluloses that were removed were mainly pectins, thus, resulting in a hemicelluloses rich pulp as product. 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 was 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

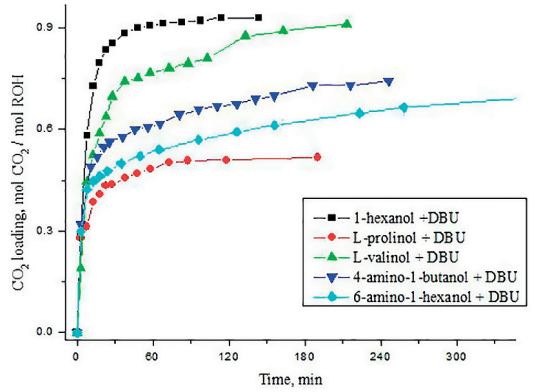


Undissolved fluffy material recovered from the STHT treatment for treatment of birch (left) and spruce (right).

'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 are used as efficient absorbents for CO_2.



Cellulose Derivatives in Ionic Liquids

Main funding: Åbo Akademi PCC, Åbo Akademi

Jyri-Pekka Mikkola, Olatunde Jogunola, Pia Damlin, Johan Wärnå, Sakari Teerikoski, 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. Shifting to the ionic liquid technology can considerably intensify the existing process and new derivates can be prepared.

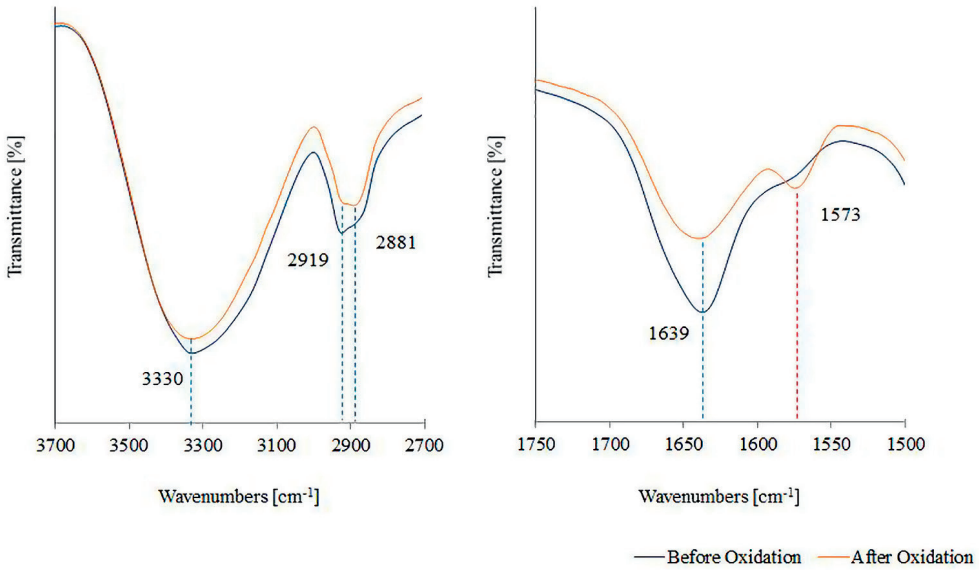
The focus of the research project is in the etherification and esterification of cellulose. Breakthroughs have been made in the selection of suitable ionic liquids for cellulose acetylation and carboxymethylation. A special attention was paid to the development of a detailed scheme for the substitution kinetics of cellulose. Detailed kinetic modelling based on probabilistic theories and rate retardation was carried out. The new model is able to describe the detailed substitution kinetics even in cases when several substituents are added to the anhydroglucose unit of cellulose or hemicellulose.

Electrochemical Characterization of Cellulose in Ionic Liquids

Main funding: Åbo Akademi PCC

Yasuhito Sugano, 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 bio refinery field. As the initial step in this research work, we have studied



FTIR spectra of cellulose samples before and after electrochemical oxidation in an ionic liquid.

electrochemical properties of cellulose in ILs using different reaction conditions. Moreover, we have characterized the structure of each reaction product for designing of a new cellulose modification system based on electro-catalysts and ionic liquids.

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

3.2 Reaction Intensification

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

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

Structured Reactors

Main funding: Åbo Akademi PCC, Academy of Finland, EU

Jyri-Pekka Mikkola, Teuvo Kilpiö, Victor Sifontes Herrera, Atte Aho, Kalle Arve, Erfan Behravesh, Leena Hupa, Mikko Hupa, 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 batch-wise, 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. Ruthenium-impregnated carbon cloths showed a high activity in the hydrogenation of various sugars, such as arabinose and galactose to corresponding sugar alcohols. A new sub-project was started with the aim of preparation of ceramic catalytic foams. The first results were very promising and the ruthenium and platinum impregnated foams will be used in conventional and enantioselective hydrogenation. Extensive mathematical modelling of structured reactors was continued.

Image of a solid foam prepared at PCC.

Cooperation:
TU Dresden, Germany; University of Tver, Russia; several EU partners

Publications:

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- Mäki-Arvela, P., Murzin, D. Yu., Effect of catalyst synthesis parameters on the metal particle size, *Applied Catalysis A: General*, 451 (2013), 251-281 (Elsevier B.V., ISSN: 0926-860X)
- Simakova, O. A., Davis, R. J., Murzin, D. Yu., Biomass processing over gold catalysts, *SpringerBriefs in Molecular Science*, Springer, 2013, 1-54, ISSN: 2191-5407, ISBN: 978-3-319-00905-6

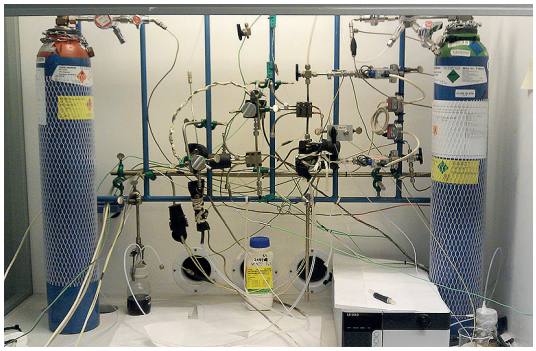
Micro- and Milliscale Reactor Technology

Main funding: Åbo Akademi PCC, GSCE, Academy of Finland

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

Micro- and millireactors enable an efficient performing of chemical processes because of enhanced mass and heat transfer. We have introduced the concept of microreactors on Finnish soil. Different kinds of microreactor systems have been constructed; e.g. for catalytic gas-phase systems and for liquid and liquid-liquid reactors. The catalyst coating

technology was developed and we are now able to perform various reactions in gas-phase microreactors and conduct kinetic studies. Gas-phase microreactors were successfully used to make chemical intermediates, such as ethylene oxide, methyl chloride and ethyl chloride. Silver-based microreactor combined to micro-gas chromatography gave excellent results in the preparation ethylene oxide, while zinc doped alumina turned out to be the best catalyst for preparation of methyl chloride. In general, the microreactor coating technology by using aluminium oxide as well as micro- and mesoporous materials was successfully developed; we are able to prepare catalytically active and mechanically strong coatings. The catalyst materials showed a high activity and selectivity in the halogenation process and very high yields and selectivities of methyl and ethyl chloride were obtained. Separation technology based on selective condensation was developed for the product mixture in the synthesis of methyl chloride. A detailed mathematical model was developed for catalyst layers in the microreactor structures. The model describes the reaction-diffusion phenomena in the porous structure very well. Separation technology was developed for the product mixture in the synthesis of methyl chloride. A new millireactor system was constructed for liquid-phase reactions and it was successfully used for the homogeneously catalyzed hydrolysis of hemicelluloses – the work will go on in future with various hemicelluloses and extensive mathematical modelling based on the concept of laminar flow with radial and axial diffusion is in progress. A new MICATOX project was commenced, in a close collaboration with Lappeenranta University of Technology and Aalto University.



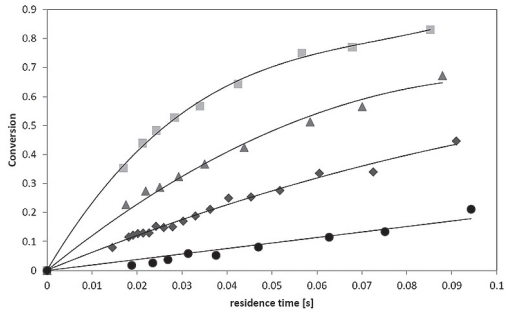


Figure 5: Influence of temperature and residence time on methanol conversion in microreactor. (■) 340 °C; (▲) 320 °C; (♦) 300 °C; (●) 280 °C.

Microreactor system for preparation of alkyl chlorides (left) and an example of the microreactor performance (right).

Cooperation:

Lappeenranta University of Technology; University of Oulu; Aalto University; Università di Napoli, Italy; Institute of Chemical Process Fundamentals (Czech Academy of Sciences), Czech Republic; CPE Lyon, France

Publications:

- Salmi, T., Hernandez Carucci, J., Roche, M., Eränen, K., Wärnå, J., Murzin, D., Microreactors as tools in kinetic investigations: ethylene oxide formation on silver catalyst, *Chemical Engineering Science*, 87 (2013), 306-314 (Pergamon, ISSN: 0009-2509)

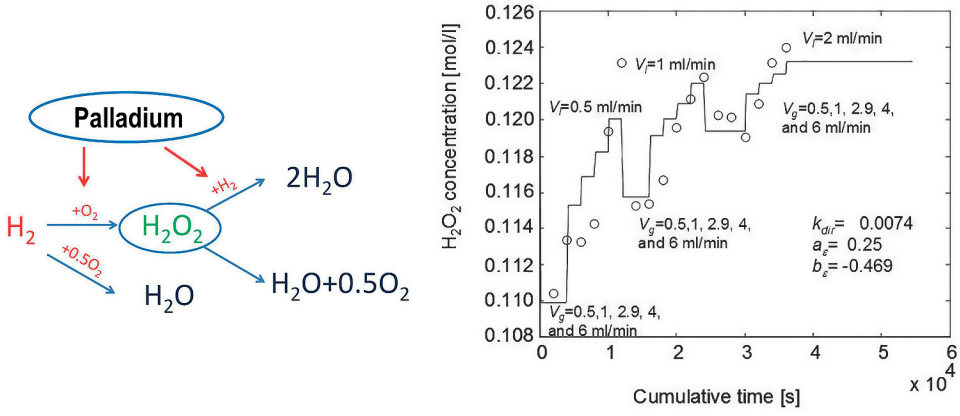
- Schmidt, S. A., Kumar, N., Shchukarev, A., Eränen, K., Mikkola, J-P., Murzin, D. Yu., Salmi, T., Preparation and characterization of neat and $ZnCl_2$ modified zeolites and alumina for methyl chloride synthesis, *Applied Catalysis A: General*, 468 (2013),120-134 (Elsevier B.V., ISSN:0926-860X)
- Schmidt, S. A., Kumar, N., Reinsdorf, A., Eränen, K., Wärnå, J., Murzin, D. Yu., Salmi, T., Methyl chloride synthesis over Al_2O_3 catalyst coated microstructured reactor – thermodynamics, kinetics and mass transfer, catalyst, *Chemical Engineering Science*, 95 (2013), 232-245 (Pergamon, ISSN: 0009-2509)

Multiphase Reactors

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

Johan Wärnå, Teuvo Kilpiö, Pasi Tolvanen, Adriana Freites, Sébastien Leveneur, Pierdomenico Biasi, Nicola Gemo, Gianluca Gallina, Juan Garcia Serna, Irene Huerta, Paolo Canu, Lionel Estel, 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. The research in hydrogen peroxide direct synthesis was summarized in two monumental theses (Pierdomenico Biasi and Nicola Gemo). Production of epoxidized vegetable oils under the presence and absence of microwaves was studied extensively and a new technology was developed, based on microwave technology, to enhance the epoxidation rate. The products are valuable chemical intermediates and bio-lubricants. Advanced mathematical models were developed; the models include kinetics, catalyst deactivation, transport phenomena as well as residence time distributions. This work was summarized in the extensive thesis of Teuvo Kilpiö: the works forms a platform for modelling and simulation of complex three-phase processes.



Hydrogen peroxide synthesis (left) and parameter estimation results for a study of direct decomposition (left).

Cooperation:
Università di Padova, Padova, Italy; INSA Rouen, France; Universidade de Valladolid, Spain

Publications:

- Biasi, P., Garcia-Serna, J., Salmi, T., Mikkola, J-P., Hydrogen peroxide direct synthesis: enhancement of selectivity and production with non-conventional methods, *Chemical Engineering Transactions*, 32 (2013), 673-678 (Italian Association of Chemical Engineering – AIDIC, ISSN: 1974-9791)
- Biasi, P., Garcia-Serna, J., Bittante, A., Salmi, T., Direct synthesis of hydrogen peroxide in water in a continuous trickle bed reactor optimized to maximize productivity, *Green Chemistry*, 15 (2013), 2502-2513 (RSC Publications, ISSN: 1463-9262)
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- Madsen, A. T., Rozmyslowicz, B., Mäki-Arvela, P., Simakova, I. L., Eränen, K., Murzin, D. Yu., Fehrmann, R., Deactivation in continuous deoxygenation of C18 fatty feedstock over Pd/Sibunit, *Topics in Catalysis*, 56 (2013) 9-10, 714-724 (Springer New York LLC, ISSN: 1022-5528)

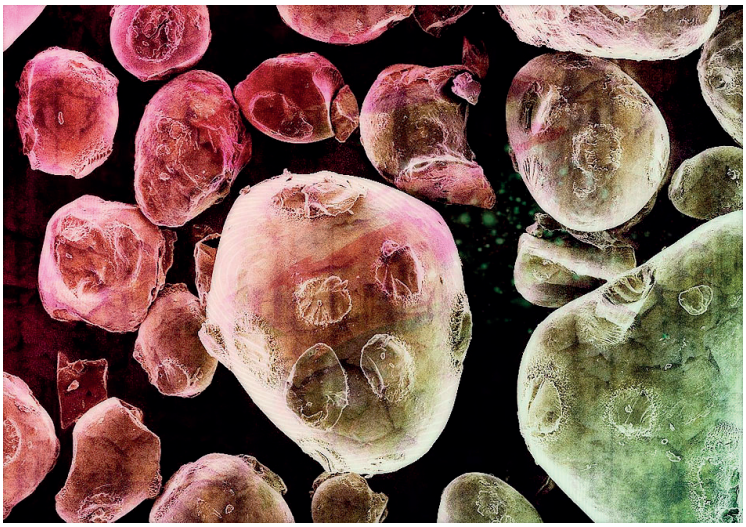
Batch and Semibatch Reactors for Reactive Solids

Main funding: Åbo Akademi PCC, Nordkalk

Henrik Grénman, Pia Damlin, Jyri-Pekka 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 the starch oxidation process, where an interesting two-stage reaction sequence was discovered. Solid particles change their morphology during the reaction; for instance, craters appear on the surface. Furthermore, the solid particle distribution changes as the reaction progresses. A new mathematical model was developed to describe these effects: morphology change, change of porous layer thickness change as well as change of the particle size distribution. The new theory for solid-fluid kinetics has been presented at numerous conferences and articles in the best journals in chemical engineering.



SEM image of starch particles.

Cooperation:

Raisio; Nordkalk

Publications:

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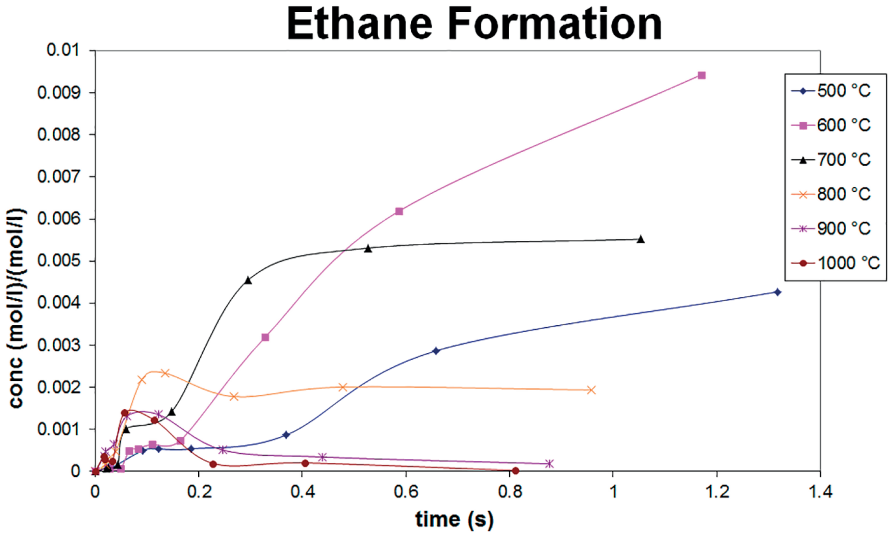
Complex Reaction Kinetics and Thermodynamics

Main funding: Academy of Finland, GSMR

Johan Wärnå, Jyri-Pekka Mikkola, Matias Kangas, Olatunde Jogunola, Valerie Eta, Ewelina Leino, Antonina Kupareva, Andreas Bernas, Heidi Bernas, Timo Petteri Suominen, Päivi Mäki-Arvela, Tapio Salmi, Dmitry Murzin

Reaction kinetics and equilibria as well as solubilities and mass transfer effects of complex reaction networks are measured experimentally and modelled quantitatively. Development of the methodology for analysis of complex reaction networks is an essential part of the project, particularly for heterogeneously and homogeneously catalyzed reactions and solid-liquid reactions. The main case studies were hydroformylation, esterification, oxidation of aldols, various catalytic hydrogenations, 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.



Modelling of ethane formation at high temperatures in a tube reactor.

Cooperation:

VTT, Recoil, Forchem; Université de Bourgogne, France; University of Oulu, INSA Rouen, France

Publications:

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3.3 Metal Ions in Lignocellulosic Materials

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 papermaking 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 papermaking 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 papermaking 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 papermaking 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 papermaking processes and in the energy conversion processes. The role and importance of individual metal ions in the different material cycles comprising the entire papermaking 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, Kim Granholm, 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.

A method based on column chromatography has been developed for determination of ion exchange (IE) constants for pairs of metal ions for different types of wood, pulp and bark samples. Bark was found to have higher selectivity than wood and pulp for the metal ions studied. Of the 14 different metal ions studied, the toxic transition metal ions Pb, Cu, and Cd were most strongly bound to all the materials used in this work. The validity of the column method was tested by means of different mixtures of metal ions as the loading solution. The IE constants obtained by the column method showed a good agreement with those obtained by the batch method reported earlier by our group. The IE constants were also determined for synthetic cation exchanger (CE) based on weak and strong acids. The IE constants of most pairs of metal ions are highest for the weakly acidic CE followed by bark, wood, pulp, and strongly acidic CE.

Summary of ion exchange (IE) constants lgK^{M}_{Mg} for different lignocellulosic materials. The loading solution contained Pb, Cu, Cd, Zn, Ni, Mn, Ba, Sr, Ca, Mg, K, Na and Li ions

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

-: not determined; *SW: softwood; **HW: hardwood

Publications:

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3.4 Interaction between Chemicals and Fibres

Our daily life would not function without paper! Besides the most obvious – toilet paper and tissue – we also use a lot of other paper grades with special properties. Paper with good barrier properties for liquid and food packages, strong and stiff cardboard for boxes, good-quality printing paper for our traveling tickets bought on-line and cheap paper for the morning newspaper and the Clas Ohlson catalogue. A very important aspect of paper is that it can be printed on, often with high quality, so that the package also functions as information-carrier. Paper is furthermore environmentally friendly; it is made from renewable resources and when it has been used it can easily be recycled or burned and if left in nature it will degrade quite quickly.

A modern paper machine is about 10 m wide and can run up to 2,000 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 thereby good production economy. 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 systems based on several analytical instruments and devices that can predict and give early warnings of problems is a key factor in maintaining a smooth production. Flow cytometry (FCM) has been shown to be an excellent tool to detect and analyze agglomeration in process waters and estimate the hydrophobicity of particles. FCM can, for example, be used to assess the sorption of wood pitch onto fillers in the presence and absence of galactoglucomannans (GGMs). Using FCM, we could detect that addition of GGMs changes the interactions between colloidal wood pitch and cationic fillers, which has been difficult to prove using traditional methods. The formed agglomerates were less hydrophobic in the presence of GGMs and hence the risk of depositions should be lower. To control the chemistry in the wet-end of a paper machine and to know the composition of substances in the process waters is crucial for smooth operations.

By combining FCM with on-line turbidity monitoring, x-ray diffraction, and scanning electron microscopy, we were able to monitor the build-up of calcium oxalate crystals in an actual mill. By this system, the performance and function of different anti-scale products can be tested on-site at real conditions, confirming the results from laboratory trials. This would help the mills to choose the correct anti-scale agent adapted to their system.

The interactions between chemicals and fibres is very complex, due to the release of a vast variety of substances from the fibres and that many different chemicals are needed to ensure that the final product has the desired properties. In order to meet the high demands on production efficiency and product quality, the industry need fast and accurate analytical systems. We also need to develop new, more efficient and more environmentally friendly additives.

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 FCM methods for the analysis of pulp and paper mill samples. The capability of FCM to detect and analyze agglomeration has turned out to have a great advantage compared to more traditional analytical techniques. In this project, we will develop and build a system that will produce the same type of valuable information as the FCM technique. The system will be installed on-line in order to get real time information of a paper process. The aim is also to develop 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 Oy

Publications

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Interactions between Wood Pitch, Galactoglucomannans and Mineral Particles

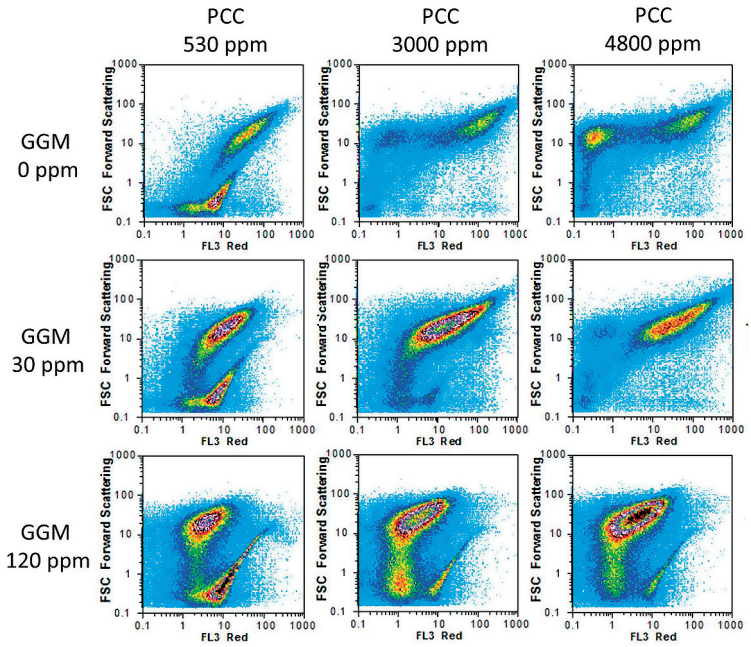
Main funding: Åbo Akademi

Hanna Lindqvist, Anders Strand, Lari Vähäsalo, Sylwia Bialczak, Stefan Willför, Anna Sundberg

The lipophilic extractives, commonly called pitch, are mostly found in colloidal form in papermaking processes which use thermomechanical pulp. The colloidal pitch is the most problematic as uncontrolled aggregation leads to problems like deposits, runnability problems as well as spots and holes in the paper. FCM is a rapid and efficient way to study interactions between different kinds of particles, such as colloidal pitch particles, mineral particles and hemicelluloses.

In this study, GGMs, hemicelluloses originating from spruce, were mixed with pitch emulsions and mineral particles. When GGMs were mixed with pitch, the mean hydrophobicity of the colloidal pitch droplets decreased only slightly, even if GGMs are known to sterically stabilize colloidal pitch droplets against aggregation by salts. However, the presence of GGM decreased the mean hydrophobicity of the aggregates formed by

pitch and scalenohedral precipitated calcium carbonate (PCC). This indicated that the interactions between colloidal pitch and the cationic PCC were hindered by the steric stabilization provided by GGM to some extent. However, the GGM could not completely prevent interactions between cationic mineral surfaces and pitch at any of the tested concentrations. These results further support the conclusion that a high concentration of water-soluble GGMs in the process waters is essential for avoiding pitch problems in papermaking.



Light scattering (FSC) versus hydrophobicity (FL3) of colloidal pitch droplets and scalenohedral precipitated calcium carbonate (PCC) particles, with 0, 30 and 120 ppm galactoglucomannans (GGM), plotted in logarithmic scale.

Cooperation:

VTT Finland, Kemira Oy, Mid Sweden University, Åbo Akademi PCC

Publications:

- Lindqvist, Hanna, Improvement of wet and dry web properties in papermaking by controlling water and fibre quality, Doctoral thesis, 2013 (Painosalama Oy, ISBN: 978-952-12-2948-0)
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Calcium Oxalate Scaling in Mechanical Pulping and Bleaching

Main funding: Industry

Matti Häärä, Lari Vähäsalo, Anna Sundberg, Stefan Willför

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

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

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

SEM-micrographs of calcium oxalate crystals precipitated in peroxide-bleached groundwood pulp filtrate by titration with sodium oxalate solution without additives (left), in the presence of the new product (50 ppm, middle), in the presence of the reference product (50 ppm, right).

Cooperation:

Sappi Fine Paper Europe; Kemira Oy

Publications:

- Häärä, M., Sundberg, A., Willför, S., Sample pretreatment for oxalate analysis and the effect of peroxide bleaching parameters on oxalate formation, *Nordic Pulp and Paper Research Journal*, 28 (2013) 1, 42-50 (Mid Sweden University, ISSN: 0283-2631)

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 utilization of renewable wood and bark raw materials in environmentally sound processes, as well as he use of novel or 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 utilization, 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. We have also evaluated suitable analytical methods for obtaining correct mass balances for the fractionation processes. 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 polymerization 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, amphiphilic barrier properties that can be utilized in specialty paper grades, food packaging or even in textiles. One interesting approach is using chemo-enzymatic processes to fabricate PANI-biocomposites suitable for applications in biosensors and biomedical engineering. Another approach we use is targeted functionalization that is applied to activate the polysaccharides for further anchoring desired functional groups and thereafter the functionalized hemicelluloses can be sorbed onto cellulose surfaces. Hemicellulose-based hydrogels have also been shown to have great potential in wastewater treatment. We have as well worked with nanocellulose produced from spruce sawdust, which has been converted into transparent films with good mechanical strength.

Polyphenols and lignin, not only from wood but also from bark, continue to be in focus in some projects. One important aim is to find and develop new mild, selective, and environmentally benign oxidation methods for wood based compounds. Another approach aims at producing lignin for use in biocomposites.

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 could exchange ideas, methods, and experiences.

Future Biorefinery II (FuBio)

Main funding: Tekes, FIBIC 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). The PCC has been active in both programs.

FuBio JR2 is divided in different research work packages, where the 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, the PCC was involved in WP3 (New products). The main research areas concerning the 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 approach for ionic liquids was described in chapter 3.1 Ionic Liquids.

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

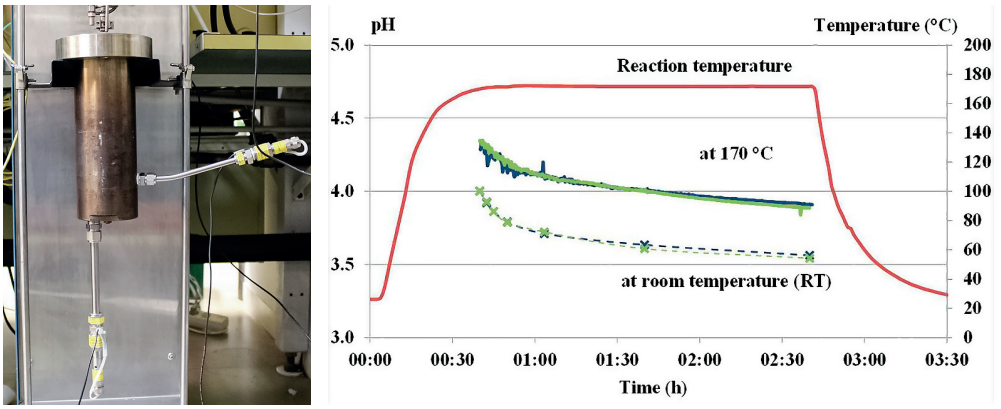
- high-yield extraction of high-molar-mass (polymeric) GGM from spruce wood and modelling of the extraction process
- pH measurement and pH control inline in the extraction reactor
- with plain water and without buffer addition if possible
- providing as small as possible chemical altering of the residual material, which is important to a following extraction of lignin (lignin extraction)
- purification (delignification) of obtained hemicellulose fractions
- to study the influence on mass-transfer limitations: internal cell wall diffusion, effect of particle size and shape, surface, challenges with simultaneous extraction and hydrolysis, measuring and controlling the pH in the reactor at high temperatures during the extraction

- Chemical modification of spruce galactoglucomannans (GGM) to obtain hydrophobic barrier properties for coating of paper and board
- Chemical characterization for the use of wood extractives for health-related applications and final proof-of-concept studies. Special emphasis has been laid on understanding the polymerization process and products that certain compounds seem to undergo.
- Study metal ion affinities of cationic cellulose beads that are prosperous materials for analytical separations and drug release and were prepared in the program

Control of pH

Nowadays modern biorefineries aim to utilize as much as possible of a wide range of different renewable raw materials. A common method for obtaining various hemicelluloses from wood is with pressurized hot water. Unfortunately, due to the water auto-ionization at the high temperatures used in the hot-water extractions and acetic acid formation from detached acetyl groups from the hemicelluloses (especially from spruce hemicelluloses), pH drops rapidly during the extraction. This decrease in pH will induce an autohydrolysis of the hemicellulose chains with a loss in molar mass of the hemicelluloses and increase of monomeric sugars in the extracts. If the native molar-mass of the hemicelluloses could be preserved while extracting them from the wood, more options regarding the end products, whether it would be controlled degradation towards ethanol production or other platform chemicals or high-molar-mass demanding products such as films etc., would be possible. Today synthesizing polymeric sugars from sugar monomers is very demanding and to synthesize hemicelluloses with the same molar-mass as can be extracted is definitely not economical feasible. Therefore, at this point, the option of choosing end products is unavailable. This shows the importance of the extraction pH when trying to extract long-chain hemicelluloses. If the pH could be controlled during the hot-water extraction it may reduce or even prevent the hemicellulose chain degradation.

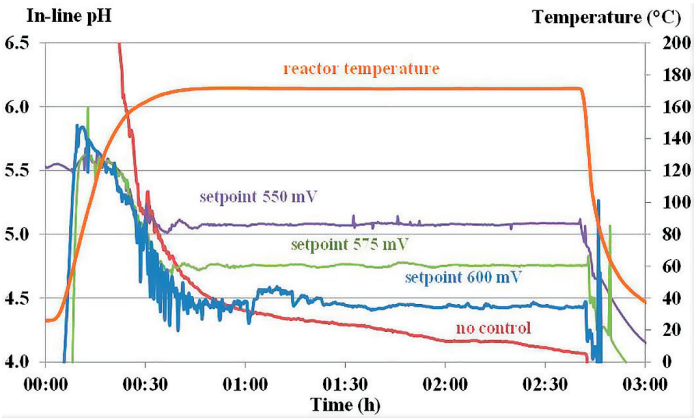
A high-temperature pH measuring and –controlling system was developed, calibrated, and validated for measuring pH during hot-water extraction of hemicelluloses from wood.



Reactor (left) with installed pH electrode on the bottom of reactor and reference electrode on the side. In-line pH at 170 °C during wood extraction and at room temperature after samples cooled down (right).

The aim was to measure in-line pH during extraction in order to control the extraction pH. An yttria-stabilized Zr/ZrO_2 electrode with an Ag/AgCl reference electrode was used for measuring the potential. Phthalate and phosphate buffers were used to calibrate the system at 100, 160, 170, and 180 °C.

A Dulcometer® D1Cb mV controller was connected to the pH meter. The controller regulated a HPLC pump pumping 0.5 M NaOH into the reactor. With this setup it was possible to decide a mV set point for any extraction that the controller with the HPLC pump and the alkali would attempt to withhold.



Control of pH at different set points during wood extractions.

The preliminary pH control results clearly show that it is possible to counter the natural pH drop with automated addition of alkali with the installed controller-HPLC pump system and maintain a desired pH throughout the extraction. The extracts were analyzed for TDS, carbohydrates, average molar mass of the extracted hemicelluloses, and acetic acid.

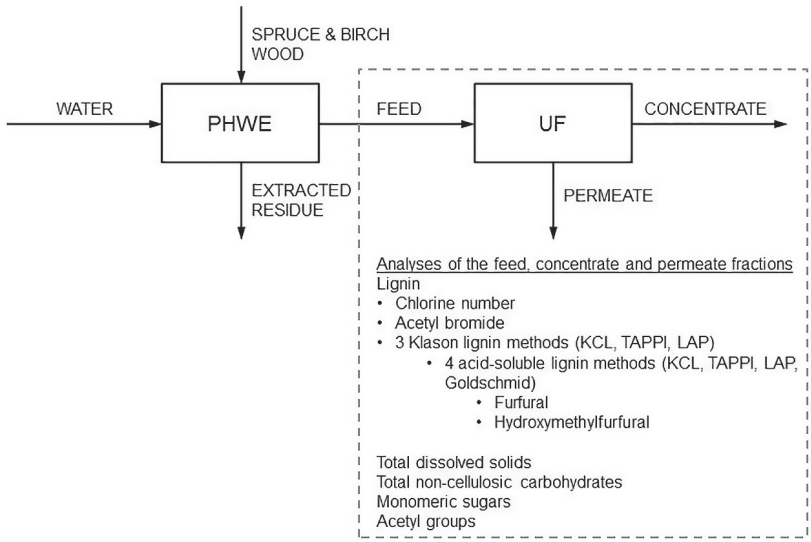
In general, the results show that with higher in-line pH, smaller amounts of non-cellulosic carbohydrates are extracted. It seems that relative low pH is required for total hemicellulose extraction. An explanation could be that with lower pH the hemicellulose chains are detached from the wood matrix by hydrolysis of the glycosidic bonds within the hemicellulose chains, and not breaking of the bonds between the hemicelluloses and the cellulose-hemicellulos-lignin matrix. At higher pH the hydrolysis would be weaker with less chain-splitting and less dissolved hemicelluloses as result. The again, molar mass analysis shows that with a higher in-line pH the extracted hemicellulose chains are longer. With an extraction pH of 5.15 the molar mass of the extracted hemicelluloses is significantly higher than the hemicelluloses in the other extracts. Comparing to the no control extraction, the molar mass of the extracted hemicelluloses are 50 % larger already after 20 minutes and after two hours the difference is as much as 135 %.

Evaluation of analytical methods

Various lignin determination methods were applied to hemicellulose-rich industrial Norway spruce (*Picea abies*) and Nordic birch (*Betula spp.*) sawdust extracts obtained after pressurized hot-water extraction (PHWE) and membrane ultrafiltration (UF). In focus were the chlorine number method, the acetyl bromide method, and four modifications of the Klason lignin determination, such as the KCL, TAPPI, LAP, and the Goldschmid

methods. The furfural and hydroxymethylfurfural concentrations in the acid hydrolysates were also determined. Mass balances of the fraction were calculated with respect to contents of dry solids and lignin including the acid soluble lignin. The reliability of the methods was evaluated based on the lignin mass balances and the gross chemical composition of the extracts. Though the results were dependent on the method applied, the lignin mass balance calculations yielded similar results, in general.

The experimental steps concerning isolation and analyses of this work are illustrated in the figure.



Flow diagram of the experimental steps concerning isolation and analyses.

The hemicellulose concentration in the permeate (passing the membrane) is low with low molar mass, while the concentrate contains the high-molar-mass hemicellulose fraction retained by the 10 kDa membrane. The dry solids content in the concentrate was significantly higher than in the feed due to a high volume reduction. Samples from the obtained extract fractions were freeze-dried before the analyses.

The chemical composition of the spruce feed and permeate fractions substantially exceeded 100% when the lignin content obtained by the KCl no., AcBr, and LAP methods was added, as seen in Table A. The chemical composition of the spruce concentrate was adequate with all other lignin determination methods except with LAP. The AcBr method resulted in too high lignin content in all birch fractions. Additionally, the LAP method gave too high lignin content in the birch feed fraction (not shown).

Gross chemical composition of spruce hot-water extract and its ultrafiltrate (UF) fractions. The sugar units are calculated as anhydrosugars.

Compounds, methods	Feed (% w w^{-1})		Fractions of UF (% w w^{-1}) Concentrate		Permeate	
Carbohydrates						
Ara	3.8		0.5		3.9	
Rha	0.7		0.3		0.7	
Xyl	14.8		4.2		15.7	
GlcA	0.9		0.3		0.9	
GalA	2.4		2.3		1.8	
4-*O*-Me-GlcA	1.7		1.0		1.6	
Man	40.0		51.3		36.6	
Gal	8.3		5.6		10.5	
Glc	10.2		13.2		9.8	
Acetyl groups						
RID	4.5		6.1		4.0	
Lignin						
Cl no.	19.7	107.1[1)]	14.2	99.0[1)]	20.4	105.9[1)]
AcBr	21.3	108.7[2)]	17.9	102.6[2)]	21.9	107.4[2)]
KCL	14.8	102.2[3)]	12.9	97.7[3)]	16.4	101.9[3)]
TAPPI	16.1	103.5[4)]	13.4	98.2[4)]	14.5	100.0[4)]
LAP	26.2	113.6[5)]	19.6	104.3[5)]	31.1	116.6[5)]
Goldschmid	16.0	103.4[6)]	13.4	98.1[6)]	14.2	99.7[6)]

1) carbohydrates + acetyl (RID) + lignin (Cl no.), 2) carbohydrates + acetyl (RID) + lignin (AcBr), 3) carbohydrates + acetyl (RID) + lignin (KCL), 4) carbohydrates + acetyl (RID) + lignin (TAPPI), 5) carbohydrates + acetyl (RID) + lignin (LAP), 6) carbohydrates + acetyl (RID) + lignin (Goldschmid)

Though the tested methods gave deviating results, the lignin mass balances in respect to the total dry solids content and the total lignin content of the studied fractions showed only minor differences. However, the total lignin content in the birch PHWE extract and corresponding ultrafiltration (UF) fractions could not be determined precisely. When lignin mass balances are monitored during UF, satisfactory information is gained by all studied method, except the AcBr method for birch. Only the modified Klason methods KCL, TAPPI, and Goldschmid gave accurate results. Though these techniques developed for fibrous samples are time-consuming, their application can be recommended also for characterization of fractions of PHWE. It is strongly advised that the lignin determination methods should be critically evaluated prior to biorefinery studies dealing with various raw materials.

Cooperation:
FIBIC; VTT; Metla; Lappeenranta University of Technology; Aalto University; University of Jyväskylä; University of Helsinki; University of Turku; University of Tampere; University of Eastern Finland; Metsä Fibre; Metso; Kemira; Andritz; Pöyry; Stora Enso;

UPM-Kymmene; Orthotopix; Pharmatest Services; Arbonova; Separation Research; Royal Institute of Technology (KTH), Wallenberg Wood Science Centre, Stockholm, Sweden

Publications:

- Song, Tao, Extraction of polymeric galactoglucomannans from spruce wood by pressurized hot water, Doctoral thesis, 2013 (Painosalama Oy, ISBN: 978-952-12-2922-1)
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- Song, T., Pranovich, A., Holmbom, B., Separation of polymeric galactoglucomannans from hot-water extract of spruce wood, *Bioresource Technology*, 130 (2013), 198-203 (Elsevier B.V., ISSN: 0960-8524)

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. The aim of the extractions was to extract polymeric and water-soluble acetylated xylans. Extractions were performed using birch sawdust, which was extracted with pressurized hot water (PHWE) flow-through extraction vessel in laboratory and in pilot scale.

Birch sawdust was extracted using pressurized hot water at temperatures between 140 and 200°C. There was a constant flow of heated water through the sawdust inside the extraction vessel. These results were used to find optimal extraction conditions for further extractions. PHWE was also performed using acetate buffer to prevent excess hydrolysis of xylans. PHW extractions were performed at temperatures in ranges from 160°C to 180°C. The molar masses of the extracted xylans were somewhat higher than without pH buffer. The xylan yield was lower when pH was controlled with acetate buffer. Birch sawdust was also packed to extraction vessel to lower liquid to wood ratio. Extractions were performed at 180°C with packing degrees from typical 0.2 kg/L to 0.7 kg/L. The xylans yield increased according to packing degree. Part of sawdust was sieved to three different fractions from 0.063–0.2 mm to 0.63-2.0 mm. With typical 0.2 kg/L, the smallest fraction 0.063-0.2 mm had the highest hemicellulose concentration. When sawdust was packed to 0.5-0.6 kg/L, extraction yields were similar with all particle sizes. Birch sawdust was also extracted with a pilot scale PHWE flow-through system. The extraction yields and extraction profiles were similar in both laboratory and pilot scale. Laboratory- and pilot scale extractions were done in same conditions at 160°C.

All birch extracts contained mostly polymeric, oligomeric, and monomeric xylan. There were also some lignin-derived compounds present in the extracts especially with the highest extraction temperatures. About half of lignin and almost all cellulose were present in extracted sawdust after extraction at 180°C. Lignin related compounds and cellulose fractions obtained from PHWE could be used later in further processes.

Publications:

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- Penttilä, P.A., Kilpeläinen, P., Tolonen, L., Suuronen, J-P., Sixta, H., Willför, S., Serimaa, R., Effects of pressurized hot water extraction on the nanoscale structure of birch sawdust, *Cellulose*, 20 (2013) 5, 2335-2347 (Springer Netherlands; Cellulose Division, ISSN: 0969-0239)

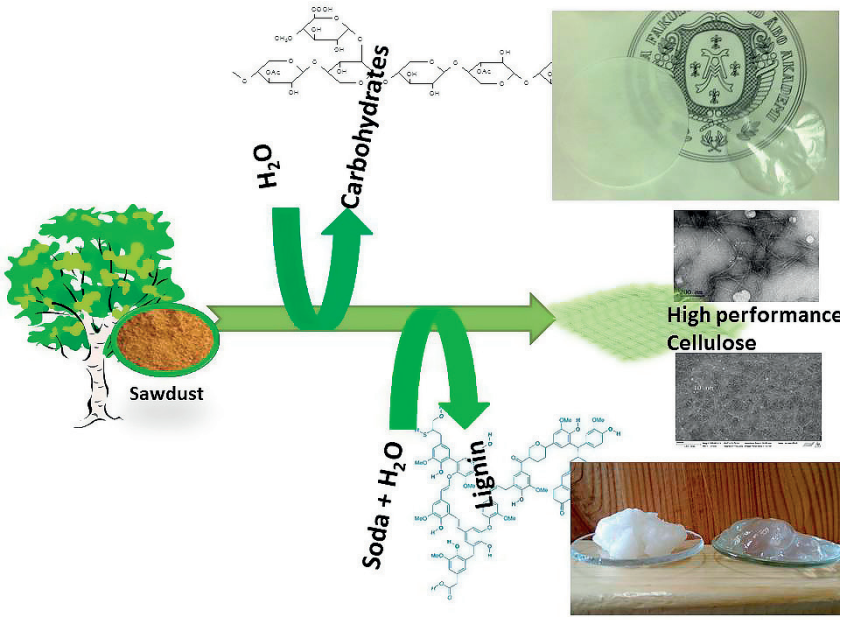
Development of Biocomposites

Main funding: Graduate School in Chemical Engineering (GSCE), Graduate School for Biomass Refining (BIOREGS), Chinese Council Scholarship, Johan Gadolin Foundation, Knut and Alice Wallenberg Foundation

Chunlin Xu, Jun Liu, Ann-Sofie Leppänen, Risto Korpinen, Bin Li, Xiaoju Wang, Patrycja Bober, Tom Lindfors, Rose-Marie Latonen, Stefan Willför

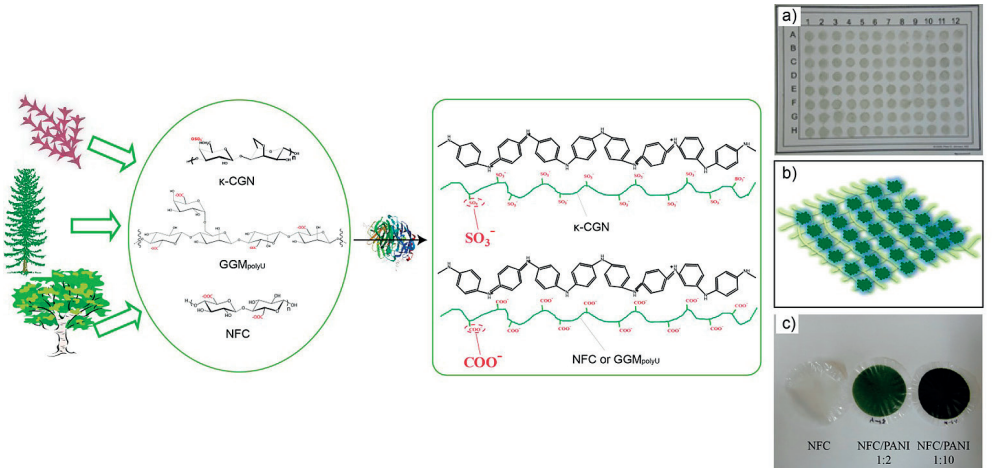
The objective of this research is to develop novel advanced materials from biorenewable sources. Biocomposites and new materials based on wood components offer a huge potential in a large variety of applications. With the use of chemo-enzymatic and chemical tools, the product characteristics can be vastly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



Upgrading of birch sawdust to value-added materials.

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 matrix of the final PANI-composites. Notably, the resulted composite hydrogel could be directly processed to a flexible film or other forms of composites with good mechanical strength, which may find potential applications in biosensors and biomedical engineering.



Schematic illustration of the synthesis of conductive polyaniline using anionic polysaccharides as templates.

Moreover, NFC can also be used as a template in the polymerization of pyrrole and thus the composites of NFC/polypyrrole and NFC/polypyrrole/silver nanoparticle can be prepared. The resulted conducting composite can be directly processed to flexible free-standing films with good mechanical strength and antimicrobial properties, which may find potential applications in biosensors and biomedical engineering.

We have also developed a novel approach to prepare cellulose nanocrystal. Different from the conventional approach where strong acids, e.g. sulphuric acid were usually used for acid hydrolysis of wood fibres, the current approach has applied formic acid for hydrolysis. The benefit is that formic acid can be easily recovered and reused in the hydrolysis process.

Cooperation:
University of Helsinki; FUNMAT, Åbo Akademi University; PCC, Åbo Akademi University; Royal Institute of Technology (KTH), Wallenberg Wood Science Center, Sweden; University of Eastern Finland

Publications:

- Leppänen, A–S., Xu, C., Liu, J., Wang, X., Pesonen, M., Willför, S., Anionic polysaccharides as templates for synthesis of conducting polyaniline and as structural matrix for conducting biocomposites, *Macromolecular Rapid Communications*, 34 (2013) 13, 1056-1061 (Wiley - V C H Verlag GmbH & Co. KGaA, ISSN: 1521-3927)

Chemical Modification of Water-Soluble Spruce O-Acetyl Galactoglucomannan

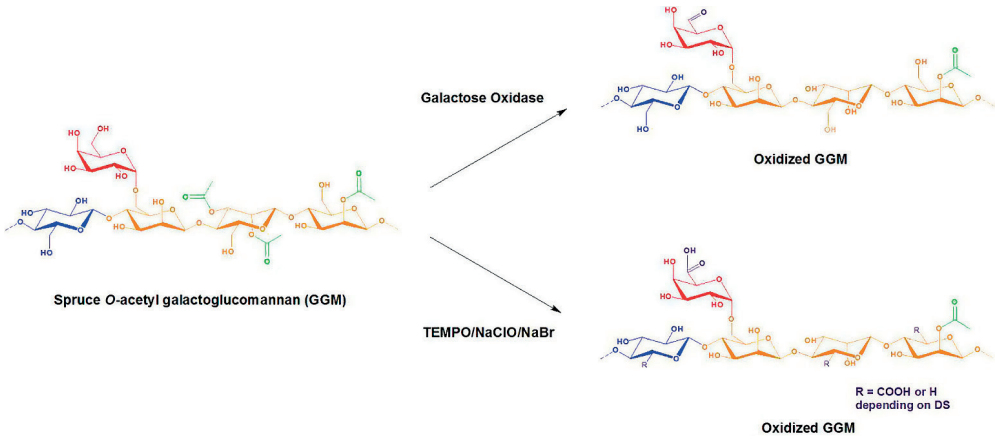
Main funding: Graduate School for Biomass Refining (BIOREGS), Knut and Alice Wallenberg Foundation

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

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 fibre integrity are circumvented. Therefore, targeted functionalization is applied to activate the polysaccharides for further anchoring desired functional groups and thereafter the functionalized hemicelluloses can be sorbed onto cellulose surfaces. This approach enables the assembly of (bio) chemically active cellulose surfaces for applications in tailoring functional biocomposites with untapped potentials.

O-acetyl galactoglucomannan (GGM) is the major hemicellulose type in softwoods and a water soluble polymer. It is a potential raw material for natural biochemical and biomaterials. GGM has a high affinity onto cellulose fibres. By regioselective modification, i.e. on the primary alcohol of the galactose side groups or as well as other free hexose units, the high affinity to cellulose is preserved and modified GGM can be used for the

functionalization of cellulose. Moreover, the utilization of aqueous systems as solvents is a step towards more environmentally friendly synthetic procedures.



Selective oxidation of GGM in water.

One way of performing selective modification of galactose units in GGM is to use enzymatic modification combing with chemical reactions. The primary alcohol of galactose can be selectively oxidized to its aldehyde form, which is more reactive and ready for further chemical functionalization, e.g. indium mediated allylation and reductive amination. Thus, a broad spectrum of functional groups can be introduced.

Another approach is to use regioselective chemical approach, i.e. 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation which can selectively oxidize the free primary alcohols of hexoses. The formed uronic acids are then further modified by a carbodiimide-mediated amidation reaction, which opens up a window for introducing various functionalities selectively on C6 of hexoses. The affinity of the modified polysaccharides to cellulose surfaces has also been investigated.

The uronic acid form of GGM was also applied in the synthesis of conducting polyaniline where the GGM derivative was used as synthesis template.

Cooperation:

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

Publications:

- Leppänen, Ann-Sofie, Regioselective modifications of galactose-containing polysaccharides in aqueous media, Doctoral thesis, 2013 (Painosalama Oy, ISBN: 978-952-12-2942-8)
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- Lu, Haolin, Sorption of enzymatically and chemically modified spruce galactoglucomannans and guar gum to cellulose fibres, Master's thesis, 2013

Renewable Materials as Barriers for Functional Packaging

Main funding: Tekes (FIBIC/FuBio II project), Graduate School for Biomass Refining (BIOREGS), Knut and Alice Wallenberg Foundation

Victor Kisonen, Chunlin Xu, Stefan Willför

The objective of this research is to develop functional derivatives of *O*-acetyl galactoglucomannan (GGM) for applications in packaging. Different amphiphilic GGM derivatives, e.g. benzoate, succinate, and phthalate esters were prepared and evaluated as barriers, e.g. for grease, oxygen, water, and aroma compounds using carton board as a model packaging substrate. As obtained from non-food based side-stream resources, GGM and GGM esters project a sustainable and modern conception for barrier purposes in food packaging.

Moreover, the composites of GGM esters and cellulose nanofibres were also tested for the study of barrier properties.

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

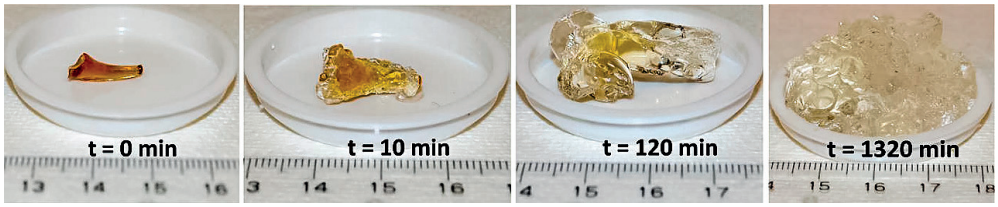
Design of Hemicellulose-based Hydrogels for Wastewater Treatment

Main Funding: Aides à la formation recherche (AFR)

Daniel Dax, María Soledad Chávez, Regis Teixeira Mendonça, Julio Sánchez, Chunlin Xu, Stefan Willför

O-acetyl galactoglucomannan (GGM) from Norway spruce (*Picea abies*) is a water-soluble and biodegradable polysaccharide with a high industrial potential and can be extracted from spruce wood by pressurized hot-water extraction (PHWE) or isolated from mechanical pulp wastewaters. Due to its relatively low molar mass and its availability in large quantities, GGM represents an interesting starting material for the synthesis of functional materials. In this study GGM (7 kDa or 28 kDa) was implemented in a transesterification reaction with glycidyl methacrylate using DMAP as a catalyst. The reaction conditions were investigated using different amounts of DMAP and different solvents. The GGMs with different degrees of substitution were in a second reaction used as cross-linker in a free radical polymerization. Methacrylate monomers bearing a quaternary ammonium group with chlorine as counter ion were applied. The physical properties of the GGM-based hydrogels could be tailored by adjusting the polymerization parameters. Ascribed to the potential of the used synthetic cationic polymers to act as ion exchange substrates, the produced GGM hydrogels were applied to remove toxic metal species from water.

Cooperation:
Centro de Biotecnología, University of Concepción, Chile; Polymer Department, University of Concepción, Chile



Photographs of a GGM-based hydrogel in dry form (left) and fully swollen form (right).

Publications:

- Dax, D., Eklund, P., Hemming, J., Sarfraz, J., Backman, P., Xu, C., Willför, S., Amphiphilic spruce galactoglucomannan derivatives based on naturally-occurring fatty acids, *BioResources*, 8 (2013) 3, 3771-3790 (North Carolina State University, Dep. of Wood and Paper Science; ISSN: 1930-2126)
- Dax, D., Xu, C., Långvik, O., Hemming, J., Backman, P., Willför, S., Synthesis of SET-LRP-induced galactoglucomannan-diblock copolymers, *Journal of Polymer Science Part A: Polymer Chemistry*, 51 (2013), 5100-5110 (Wiley & Sons, Inc., ISSN: 1099-0518)

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

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

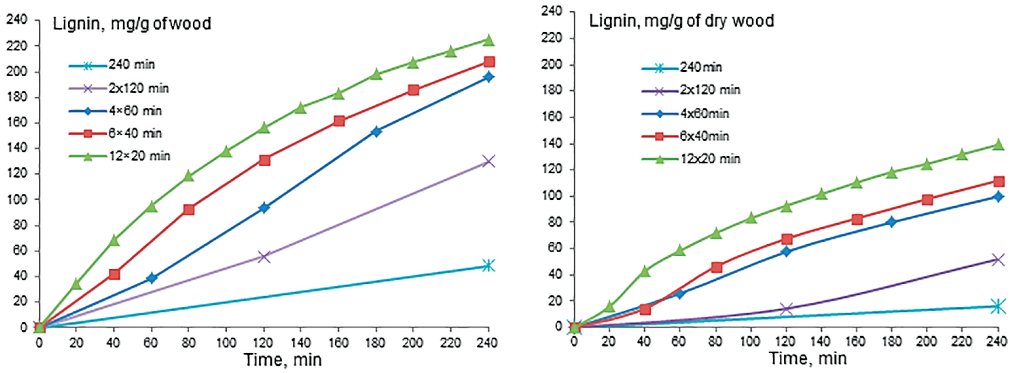
Ekaterina Korotkova, Andrey Pranovich, Stefan Willför

Lignin is one of the most abundant natural polymers. Due to its phenolic structure, lignin has great potential in different areas such as producing of fertilizers, adhesives, composites, biodegradable films, resins, polymer additives, surfactants, and as base material for the various other biochemicals.

Nowadays lignin can be isolated mainly as a by-product in pulp and paper industry. The composition of lignins varies a lot depending on the wood species, way of isolation and purification. Lignin is mainly separated from wood as lignosulfonates in sulfite pulping and as kraft lignin in kraft pulping. 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 used as a by-product and is further purified for use in different chemical and material applications. A problem with kraft lignin is the condensed structure and therefore low reactivity, as well as the high sulfur content.

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

Lignin extraction from wood in an Accelerated Solvent Extractor (ASE) using hot water with addition of alkali is a promising way to obtain new, more reactive types of lignin for future applications. The work so far was concentrated on obtaining a thorough understanding of how different parameters, such as sequential extraction, alkali concentration, and pre-extraction affect the extraction and purification of lignin from spruce sapwood. Two concentrations of alkali were studied – 1% and 2% aqueous NaOH. Extraction was performed for 4 hours total time, but different extraction sequences were studied: 1×240 min, 2×120 min, 4×60 min, 6×40 min, and 12×20 min. It was found that higher alkali concentration allows extracting more lignin from spruce wood (Figure 1 a and b). The extraction sequence has great influence on the process – shorter extraction times extracted up to 10 times more lignin compared to longer extraction times. Xylose and galactose were the most abundant carbohydrate impurities in the isolated lignins. The average molar mass of lignin increased with the extraction time and concentration of alkali.



Yield of lignin extracted with 2% NaOH concentration (left) and 1% NaOH concentration (right).

COST Action FP0901, "Analytical Methods for Biorefineries"

Main funding: EU RTD 7th Framework Programme

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

COST is an intergovernmental framework for European Cooperation in Science and Technology, allowing the coordination of nationally funded research on a European level. FP0901 was chaired (Prof. Stefan Willför) and coordinated by Åbo Akademi University. The scientific program of the final meeting, which was arranged by the PCC in Åbo, explored the outcomes from FP0901 during the life span 2009-2013. About 70 persons attended the meeting, which also received some media attention in Finland.

Trees, annual and perennial plants, recycled fibres, 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 mate-

rial of Biorefineries, renders the analyses of the feed constituents, processes, and valorized products challenging. The main objectives of FP0901 were to develop new and evaluate existing analytical methods related to forest-based and agro-industrial biorefineries. Especially analytical pretreatments were in focus. Critical steps were the representativeness of the sampling and samples, the extraction, fractionation, and sample storage methods applied. New methods were applied and evaluated for their relevance. Other emphasised areas were 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 number of COST countries that participated in FP0901 was 27, with four active non-COST members (two reciprocal agreements). The number of registered participants was +130, of which about 100 were actively participating. The number of female participants and ESRs (early stage researchers) were very good, both being close to 50%. The number of true joint publications was 65 (25 international peer-review articles, 40 conference papers and STSM (short term scientific mission) reports), and additionally 156 presentations at FP0901 workshops. The industry also showed appreciable interest in the Action, however mainly as watchers and only sparsely directly involved in the actual activities. From scientific and networking aspects, the main success stories were definitely the successful STSM visits. 24 regular STSMs were accomplished and 12 of these by female ESRs. One reciprocal STSM was accomplished from Austria to New Zealand. The analytical Round Robin type activities were also important and allowed the Action to develop and get closer to reaching the goals. Basically, the objectives of FP0901 were fulfilled at least partly. It was also delightful that especially ESR's and also young female researchers found suitable activities within the Action. The Chair, Steering Group, and some MC members actively promoted the Action at conferences and meetings (also outside EU), as well as in direct contacts with the industry. FP0901 had joint activities both with other Actions, EU projects, and broad international cooperation.

Cooperation:

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

Publications:

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Selective Oxidation of Unprotected Carbohydrates, Polyols and Phenolic Compounds from the Biorefinery Feedstock (SELOX)

Main funding: Academy of Finland

Patrik Eklund, Reko Leino, Leif Kronberg, Dominique Agustin, Stefan Willför

In recent years, the use of wood in lignocellulose-feedstock based biorefineries has become more and more important. Still much attention is focused on the use of lignin and cellulose for the production of fuels and materials. However, more sophisticated methods for isolation and purification of single compounds, or mixture of specific compounds, has emerged. In many cases, wood-based compounds may need further chemical modification to meet the requirements of different applications. Oxidation is one of the most important and frequently used types of reaction in this context. Oxidations can introduce chemical complexity by introduction of new functional groups, cyclisations etc. However, selective oxidations of complex wood based compounds from the biorefinery feedstock are much more difficult compared to oxidations of hydrocarbons from the petrochemical feedstock. Often, modern catalytic transition metal-based oxidation reactions are not compatible with the polyolic structures of unprotected carbohydrates and polyols.

The objective of this research is to find and develop new mild, selective, and environmentally benign oxidation methods for wood based compounds. The oxidations will be based on catalytic methods, oxidation by molecular oxygen, oxidation by ozone, and

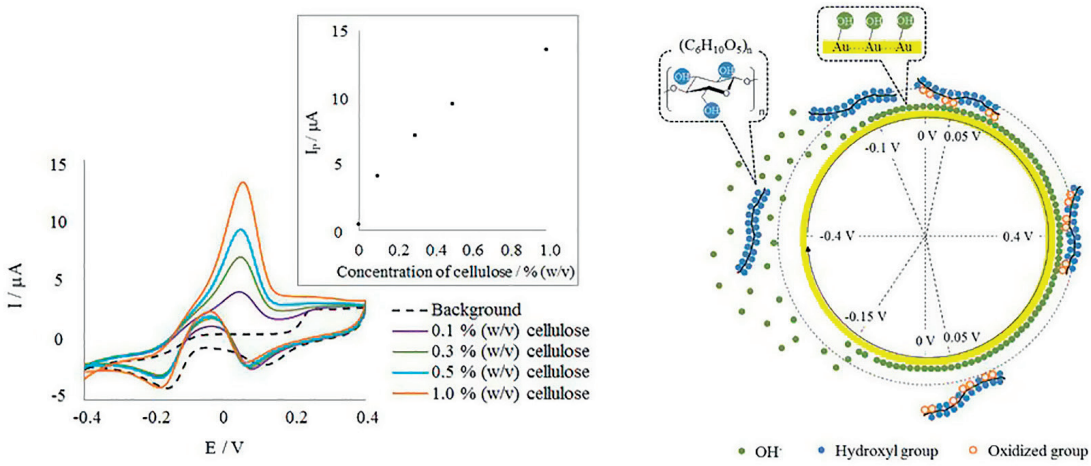
oxidations by oxo-molybdenym catalysts, preferably in aqueous solution. Due to our previous research activities and knowledge in the field, hemicelluloses, lignans, norlignans, stilbenes and carbohydrates from the biorefinery feedstock, these compounds will be used as model substrates for the oxidations. The isolation and purification of these substrates has been developed at Åbo Akademi University, and the substrates are readily available to our group. The research will be focused on the development of methods for oxidation, but the oxidized substrates will be fully characterized and their properties and possible future applications will be evaluated. The research will be divided into four work programs performed at the Laboratory of Organic Chemistry (Åbo Akademi University, Finland) and at Laboratoire de Chimie de Coordination (Institut Universitaire de Technologie Paul Sabatier, France). The research team consists of five senior researchers with experience in wood chemistry, natural product chemistry, chemistry of transition metal complexes, chemical synthesis, and oxidations. The project will employ both post-doctoral researchers and PhD-students.

Electrochemistry of Polysaccharides Derived from Biomass

Main funding: Åbo Akademi PCC

Yasuhito Sugano, Rose-Marie Latonen, Johan Bobacka, Ari Ivaska

Utilization of biomass as an alternative resource has been expected to play an important role in building of a sustainable society. Especially biodegradable functional polymers in biorefineries can be expected to be produced from main components of the 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 of the major approaches for designing the functional materials and further modifications. It has so far been studied by using chemicals and a catalyst. Cellulose oxidized by 2,2,6,6,-tetramethylpiperidine-1-oxyl radical (TEMPO) has been reported to be more hydrophilic than the original cellulose. In this project, we have studied electrochemistry of polysaccharides to obtain fundamental knowledge of the electrochemical properties of polysaccharides. It has been found that not only cellulose but also some hemicelluloses can be oxidized electrochemically. There has so far not been any systematic research about electrochemistry of polysaccharides. This research has a 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.



Electro-catalytic oxidation of cellulose: Cyclic voltammograms of cellulose (left) in different concentration at Au electrode in 1.3 M NaOH. Cellulose can be electro-catalytically oxidized at the electrode surface irreversibly. A schematic representation of oxidation of cellulose (right) during one potential cycle is shown.

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 isomerisation, dimerisation, oxidation, pyrolysis of biomass.

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

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

The materials were characterized with modern techniques, such as SEM, TEM, XRD, AFM, TPD, and FTIR. An electrochemical method, cyclic voltamperometry, which is

mainly used for bulk metals, was developed to characterize supported metals with low metal loading.

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

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

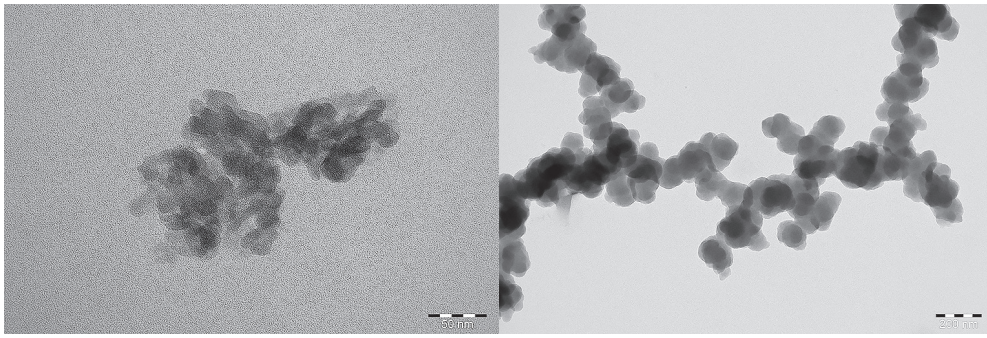
Micro and Mesoporous Materials

Main funding: Åbo Akademi

Narendra Kumar, Sabrina Schmidt, Kai Yu, 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



Transmission electron micrograph (TEM) of pristine H-Beta-25 zeolite (left) and of polypyrrole/H-Beta-25 semiconductor composite material (right).

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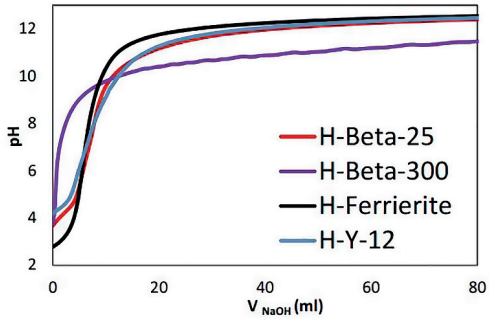
Electrodeposition of Composite Consisting of Polypyrrole and Microporous Zeolite

Main funding: Åbo Akademi PCC

Kai Yu, Narendra Kumar, Jingjing Li, Ning He, Jorma Roine, Ari Ivaska

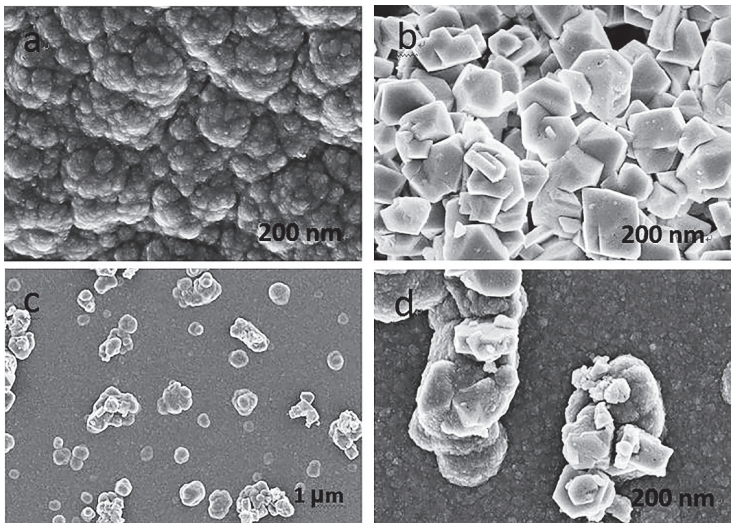
Polypyrrole/zeolite composites were synthesized by electrochemical polymerization of pyrrole monomer in an aqueous suspension of purely microporous zeolite particles at ambient temperature (22±1°C). The applied electrodeposition methods were constant potential, constant current and potential cycling. The proton form of Beta zeolites with SiO_2/Al_2O_3

ratios of 25 and 300 and Y zeolites with SiO_2/Al_2O_3 ratios of 12 and 80 were used as the host for polypyrrole (PPy) in this work. The acidic properties and the chemical composition of these zeolites were studied by potentiometric acid-base titration and inductively coupled plasma optical emission spectrometry (ICP-OES) prior to the polymerization.

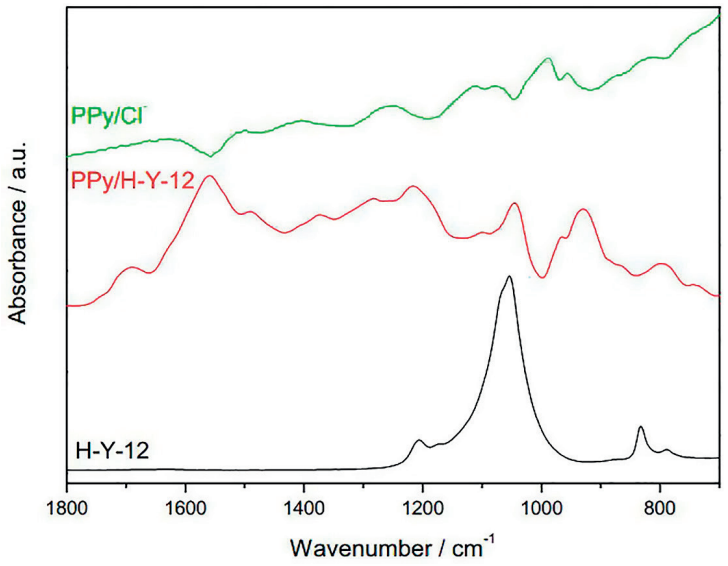


Potentiometric titration curves of host zeolites

The obtained polypyrrole/zeolite composite films deposited on platinum and indium tin oxide (ITO) glass electrodes were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) and Raman spectroscopy. Their electrochemical behaviour was studied by cyclic voltammetry. These measurements indicate that the polymerization of pyrrole took place both on the inner and outer surfaces of the host zeolite structures where the cationic PPy was charge-balanced by the anionic groups present in the zeolite framework.



SEM images of a) Polypyrrole/Cl- film (200 nm), b) H-Y-12 zeolite (200 nm), c) Polypyrrole/H-Y-12 composite film (1 µm) and d) Polypyrrole/H-Y-12 composite film (200 nm) synthesized on Pt disk by constant potential method



FTIR-ATR spectra of Polypyrrole/H-Y/12 composite film synthesized on Pt electrode by applying constant potential in comparison to the spectra of PPy/Cl- and H-Y/12

Valorization of Components Derived from Biomass

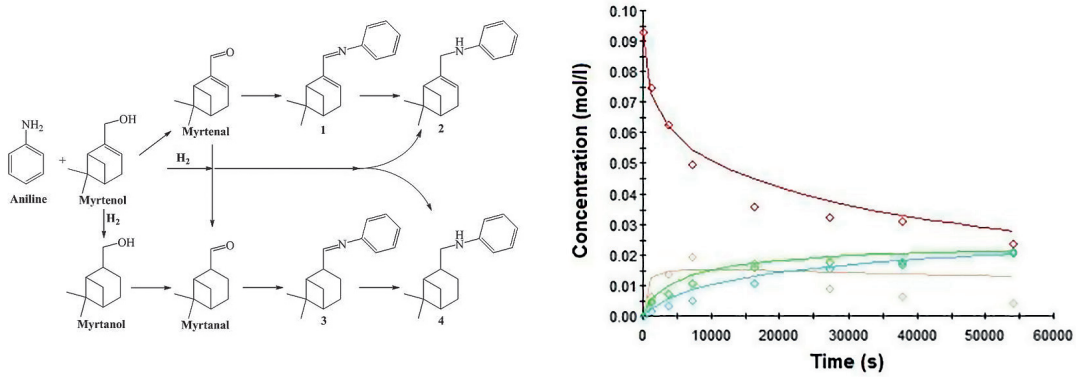
Main funding: Academy of Finland, Tekes, GSMR

Jyri-Pekka Mikkola, Anton Tokarev, Narendra Kumar, Lydia Godina, Andrea Perez Nebreda, Yulia Demidova, Victor Sifontes Herrera, Andreas Bernas, Heidi Bernas, Alexey Kirilin, Antonina Kupareva, Toni Riittonen, Bartosz Rozmysłowicz, Cesar de Araujo Filho, Irina Simakova, Jan Hájek, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

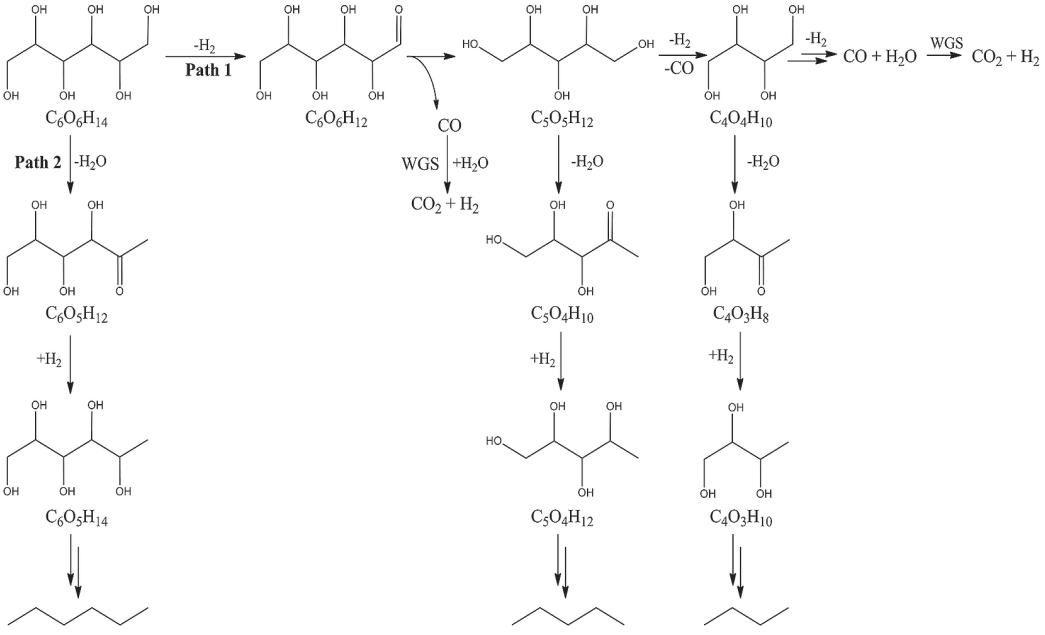
Wood is one of the most versatile materials, being at the same time a renewable resource, for chemical derivatives of wood, which serve as raw materials for a large number of other chemical and reprocessing industries. Chemical wood pulping processes extract many chemicals from wood - depending on the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

The project concerns valorization of components originating from biomass. Catalytic production of biobutanol, catalytic hydrogenation of several types of sugars over supported metal catalysts, heterogeneous catalytic isomerisation of linoleic acid, valorization of glycerol tall oil as well as hydrogenolysis of hydroxymatairesinol are studied in this project. Within the framework of this project hydrogenation and oxidation of mono and disaccharides is studied. The work of catalytic hydrogenolysis and hydrolysis of hemi-

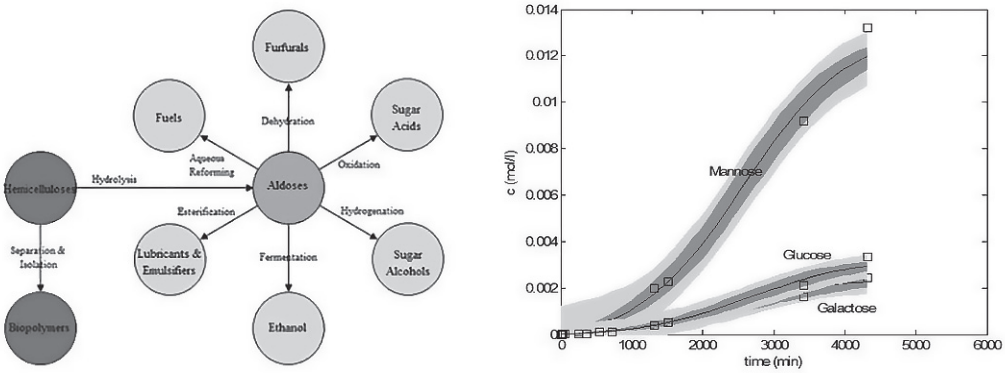
celluloses is in progress. The main raw materials being studied are arabinogalactan and O-acetylgalactoglucomannan molecule. Besides development of new active and selective catalysts, various aspects of reaction engineering, e.g. catalyst deactivation and reaction kinetics are considered.



Reaction scheme (left) and kinetic data (right) for one-pot myrtenol amination with aniline over Au catalysts.



Aqueous phase reforming of sugar alcohols to hydrogen and hydrocarbons.



Different catalytic routes for the transformation of hemicelluloses to chemicals (left) and kinetics for acid hydrolysis of galactoglucomannan to glucose, galactose and mannose (right).

Cooperation:

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

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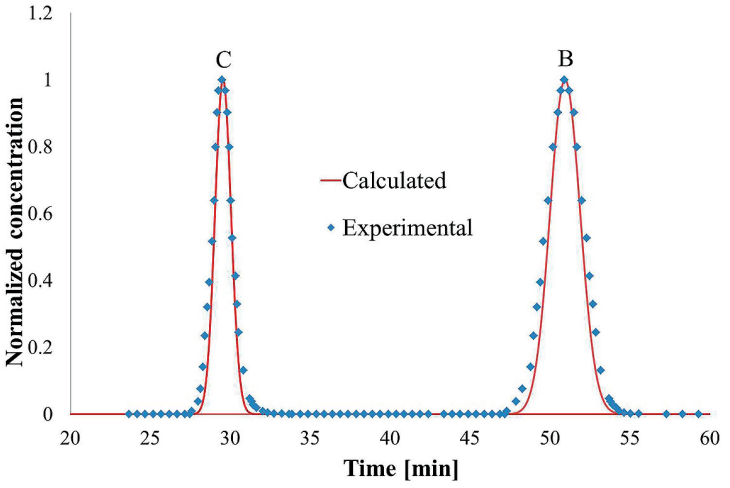
Asymmetric Catalysis and Chromatographic Separation

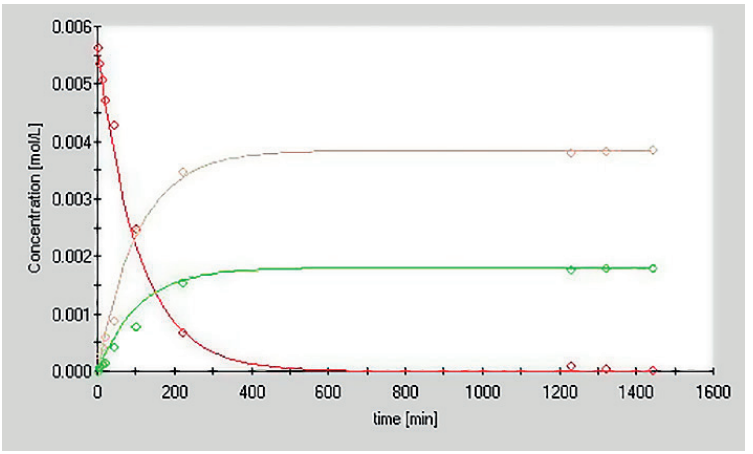
Main funding: Academy of Finland

Gerson Martin Curvelo, Carla Pereira, Päivi Mäki-Arvela, Rainer Sjöholm, Reko Leino, Henrik Saxén, Frank Pettersson, Alirio Rodrigues, Dmitry Murzin, Tapio Salmi

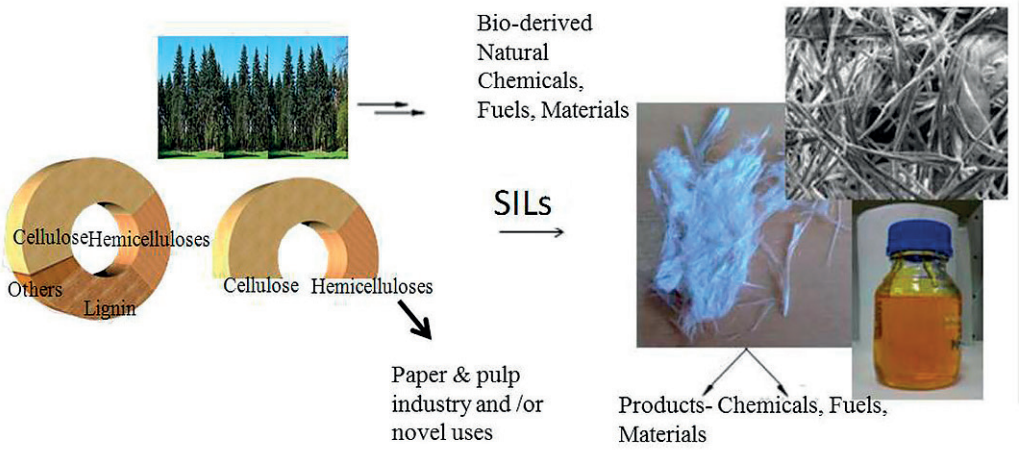
Enantioselective catalytic hydrogenation of ketones provides a pathway to a cleaner synthesis of optically active compounds, which are used as intermediates for pharmaceuticals. The aim of the project is to develop new catalytic technologies for the production of enantiomerically pure compounds through selective catalytic hydrogenation in the presence of catalyst modifiers. Molecular modelling is used as a tool to increase the understanding in enantioselective hydrogenation. New multicentered adsorption models have been applied to enantioselective hydrogenation. The enantioselective hydrogenation has been performed in a batch and in a continuous reactor and the transient behaviour of the system has been modelled quantitatively. The work is mainly focused on the combination of enantioselective hydrogenation and chromatographic separation in order to elaborate a green process concept, which minimizes waste production and maximizes the production of desired enantiomers. The experimental work has shown that it is possible, and a completely new technology for enantioselective hydrogenation was developed, based on the use continuous fixed bed reactors and chromatographic separation.



Experimental (points) and simulated elution profiles (solid lines) of (R)- and (S)-ethyl mandelate at 4.65 g/L obtained in single-component pulse experiments at 25 °C. ([B] = (R)-ethyl mandelate, [C] = (S)-ethyl mandelate)



Model prediction for the hydrogenation of ethyl benzoylformate. Points: experimental; line: calculated. Reaction conditions: 0.85 mmol of ethyl benzoylformate, 220 mg of 5 wt% Pt/Al2O3 (<90 μm), 150 mL of toluene, 25 °C, [CD] = 0.16 mmol/L and pH2 = 1 atm.



Flowsheet for wood fractionation with switchable ionic liquids.

Cooperation:

University of Porto

Publications:

- Långvik, O., Mäki-Arvela, P., Aho, A., Saloranta, T., Murzin, D. Yu., Leino, R., Regioselective hydrogenation of 1,2-indanedione over heterogeneous Pd and Pt catalysts, *Catalysis Letters*, 143 (2013), 142-149 (Springer New York LLC, ISSN:1011-372X)
- Martin, G., Mäki-Arvela, P., Murzin, D. Yu., Salmi, T., Solvent effects in the enantioselective hydrogenation of ethyl benzoylformate, *Catalysis Letters*, 143 (2013) 10, 1051-1060 (Springer New York LLC, ISSN: 1011-372X)
- Mavrynsky, D., Murzin, D. Yu., Leino, R., Kinetic studies on sec-alcohol racemisation with dicarbonylchloro(pentabenzyl-cyclopentadienyl) and dicarbonylchloro(penta-phenyl-cyclopentadienyl) ruthenium catalysts, *ChemCatChem*, 5 (2013), 2436-2445 (Wiley - V C H Verlag GmbH & Co. KGaA, ISSN:1867-3880)

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.

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 at our Centre has been very fruitful and

led to several widely cited key publications. 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.

Torrefaction of biomass is a relatively new area in our research. Torrefaction implies 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 2013 the PCC initiated several studies to better understand the chemical changes taking place during torrefaction processes.

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 green house 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 Oy; AGCO SISU POWER Oy; Ecocat Oy 4 Gasum Oy; Metso Power Oy; Metso Automation Oy; Wapice Oy; Wärtsilä Finland Oy; Centre for Metrology and Accreditation; Lappeenranta University of Technology; Tampere University of Technology; Aalto University; Turku University of Applied Sciences; University of Oulu; University of Vaasa; VTT Technical Research Centre of Finland; Åbo Akademi University

COST Action CM901: Detailed Chemical Kinetic Models for Cleaner Combustion

Main funding: EU RTD 7th Framework Programme

Anders Brink, Mikko Hupa

The key objective of this Action is to promote at the European level the development of cleaner and more efficient combustion technologies through the implementation of theoretically grounded and more accurate chemical models. This is motivated by the fact that the current models which have been developed for the combustion of hydrocarbons and oxygenated compounds present in natural gas, kerosene, gasoline, diesel and bio-fuels

do a reasonable job in predicting auto-ignition and flame propagation parameters, and the formation of the main regulated pollutants. However their success rate deteriorates sharply in the prediction of the formation of minor products (alkenes, dienes, aromatics, aldehydes) and soot nano-particles, which have a deleterious impact on both the environment and on human health. The work in this action is organized into six working groups. AAU is active in WG3.

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

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

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

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

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

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

Publications:
- Nowak, B., Karlström, O., Backman, P., Brink, A., Zevenhoven, M., Voglsam, S., Winter, F., Hupa, M., Mass transfer limitation in thermogravimetry of biomass gasification, *Journal of Thermal Analysis and Calorimetry* 111 (2013) 1, 183-192 (Springer, ISSN: 1388-6150)

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, Jaana Paananen, Mikko Hupa

The RELCOM project (1.12 2011 to 30.11 2015) is designed to undertake a systematic and focused series of applied research, development and demonstration activities involving both experimental studies and combustion modelling work to enable full-scale early demonstration oxyfuel plant to be designed and specified with greater confidence as well as providing improved assessment of the commercial risks and opportunities.

The key tasks within the project are:

- Underpinning technology investigation including: fuel and combustion charac-

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

Åbo Akademi University's main activities in this project are related to underpinning technology investigation. Three different tasks are undertaken: fuel characterization, corrosion testing and sub-model development.

Cooperation:
University of Glamorgan – Coordinator, UK; Åbo Akademi University; E.On New Build & Technology Ltd., UK; Technische Universität München, Germany; Electricitée de France S.A. , France; University of Leeds, UK; Instytut Energetyki, Poland; Universität Stuttgart, Germany; Katholieke Universiteit Leuven, Belgium; Doosan Power Systems Ltd., UK; Enel Ingegneria e Innovazione SpA, Italy; Fundación Ciudad de la Energía, Spain; International Flame Research Foundation, Italy

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

Main funding: European Commission 7th Framework Programme

Anders Brink, Oskar Karlström, Maria Zevenhoven, 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 framework European researchers will have free access to a larger number of installations. The BRISK project is creating new opportunities via the equivalent of around 3,400 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 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:
Kungliga Tekniska Högskolan – Coordinator, Sweden; Åbo Akademi University; Aston University, UK; BIOENERGY 2020+ GmbH, 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, Italy; L'Agenzia ENEA, Italy; Norges Teknisk-Naturvitenskapelige Universitet, Norway; PALL Filtersystem Corporation, Germany; Paul Scherrer Institute, Switzerland; Stiftelsen for Industriell og Teknisk Forskning, Norway; Technische Universität München, Germany; Technische Universität Wien, Austria; TUBITAK MRC Energy Institute, Turkey; Universidad de Zaragoza, Spain; Università degli Studi di Napoli Federico II, Italy; Wroclaw University of Technology, Poland

Publications:
- Houshfar, E., Wand, L., Vähä-Savo, N., Brink, A., Løvås, T., Experimental study of a single particle reactor at combustion and pyrolysis conditions, *Chemical Engineering Transactions*, 35 (2013), 613-618 (The Italian Association of Chemical Engineering, ISSN: 1974-9791)

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 complicate the solution of the optimization problem. A challenge is thus to cast the problem into a solvable form and to develop specific numerical methods for tackling it. It is expected that the optimization will require hybrid techniques, such as memetic algorithms, to avoid the curse of dimensionality in the solutions. A systematic optimization approach of the integrated biofuel and steelmaking plants may give rise to completely new process alternatives, where the energy and raw materials are used much more efficiently than today.

Cooperation:
Thermal and Flow Engineering Laboratory

Publications:

- Karlström, O., Brink, A., Hupa, M., Biomass char nitrogen oxidation - single particle model, *Energy & Fuels*, 27 (2013), 1410-1418 (ACS Publications, ISSN: 0887-0624)
- Karlström, O., Brink, A., Hupa, M., Time dependent production of NO from combustion of large biomass char particles, *Fuel*, 103 (2013), 524-532 (Elsevier Ltd., ISSN: 0016-2361)

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 project 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 is 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 (main project partners); École Polytechnique de Montréal, Canada; GTT-Technologies, Aachen, Germany; Metso Power/ Valmet Power; Processflow; Outotec

Publications:

- Jones, F., Niklasson, F., Lindberg, D., Hupa, M., Effects of reduced bed temperature in laboratory- and full-scale fluidized-bed boilers: particle, deposit, and ash chemistry, *Energy & Fuels*, 27 (2013) 8, 4999-5007 (ACS Publications, ISSN: 0887-0624)
- Jones, F., Tran, H., Lindberg, D., Zhao, L., Hupa, M., Thermal stability of zinc compounds, Energy & *Fuels*, 27 (2013) 10, 5663-5669 (ACS Publications, ISSN: 0887-0624)
- Jones, F., Bisaillon, M., Lindberg, D., Hupa, M., The presence of zinc in Swedish waste fuels, *Waste Management*, 33 (2013) 12, 2675-2679 (Elsevier Ltd., ISSN: 0956-053X)
- Jones F.C., Blomqvist E.W., Bisaillon M., Lindberg D.K., Hupa M., Determination of fossil carbon content in Swedish waste fuel by four different methods, *Waste Management & Research: The Journal of the International Solid Wastes and Public Cleansing Association*, ISWA, 31 (2013) 10, 1052-1061 (ISWA, ISSN: 0734-242X)

Behaviour and Properties of Molten Ash in Biomass and Waste Combustion

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

Daniel Lindberg

Many challenges in the deeper understanding of the chemistry in a number of industrial high-temperature processes are connected to the molten phase. The behaviour of systems containing molten phases is very difficult to predict by any theoretical methods. Thermodynamic properties of molten phases consisting of a number of components are not very well known. There are many indications that the presence of even small amounts of a molten phase may have a dramatic importance to the kinetics of many industrially important high-temperature reaction systems. However, little systematic generic research has been published on the detailed role of composition and amount of liquid phases in reacting systems.

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

We will develop new electrochemical methods to detect the formation of a melt in ionic mixtures as compliments to thermal analysis. The physical properties of the relevant molten ash components are modelled to combine these properties with other predictive tools, such as thermodynamic equilibrium modeling. These properties will also assist in modeling the thermal gradients in ash deposits in real boilers.

A variety of experimental and theoretical approaches will pave the road to more quantitative connections between the presence and composition of a molten phase and the rate of processes such as sintering, solid-gas reactions or oxidation of steels and alloys.

From the application point of view, the expected results from the project will support solving specific industrial problems, such as materials corrosion and fouling in reactors and furnaces.

Publications:

- Lindberg, D., Backman, R., Chartrand, P., Hupa, M., Towards a comprehensive thermodynamic database for ash-forming elements in biomass and waste combustion - Current situation and future developments, *Fuel Processing Technology*, 105 (2013) 1, 129-141 (Elsevier B.V., ISSN: 0378-3820)
- Vainikka, P., Lindberg, D., Moilanen, A., Ollila, H., Tiainen, M., Silvennoinen, J., Hupa, M., Trace elements found in the fuel and in-furnace fine particles collected from 80MW BFB combusting solid recovered fuel, *Fuel Processing Technology*, 105 (2013) 1, 202-211 (Elsevier B.V., ISSN: 0378-3820)

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

Main funding: Academy of Finland

Mikko Hupa, Daniel Lindberg

New technologies are being developed to increase the efficiency of thermal biomass conversion for electricity and heat production as well as for producing new chemicals, such as various gasification or pyrolysis-based technologies However, many aspects of the chemistry of the fuel impurities are not fully understood at reducing conditions. In the present project we will study corrosion of construction materials of future thermal conversion technologies, the chemistry of the important fuel impurities, such as sulphur, halogens, alkalis, lead and zinc and their effects on deposition formation and emissions. Various experimental and modeling tools will be utilized to study these phenomena specifically for reducing conditions. The expected results from the project will support solving specific industrial problems, such as prevention of potential harmful emissions and materials corrosion and fouling in future thermal conversion concepts, such as gasifiers and different types of furnaces.

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, Tooran Khazraie, Magnus Perander, Rishabh Sarna, Asad Sultan, Jingxin Sui, Mia Mäkinen

FUSEC was a three-year (April 2011– March 2014) joint research project between several industrial companies operating in the area of biomass and waste to energy. The project, which was coordinated by Top Analytica, consisted of the research efforts of five Finnish companies with the additional support from two international companies (the companies

are mentioned under "Funding"). The research efforts included company-specific tasks and a major common research program – the FUSEC Core Program, which was coordinated by Åbo Akademi University, included additionally 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).

FUSEC Core Program focused 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 (NO_x, SO_2, PM2.5, etc.)

E. Furnace process prediction

F. Recovery boiler control (incl. changing BL quality)

The above listed subject themes and the problems connected to these were tackled within five work packages in which the actual project plan was 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

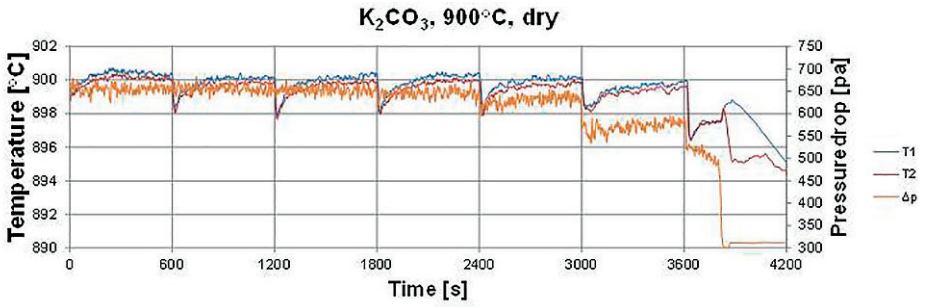
WP 5. Information and international co-operation

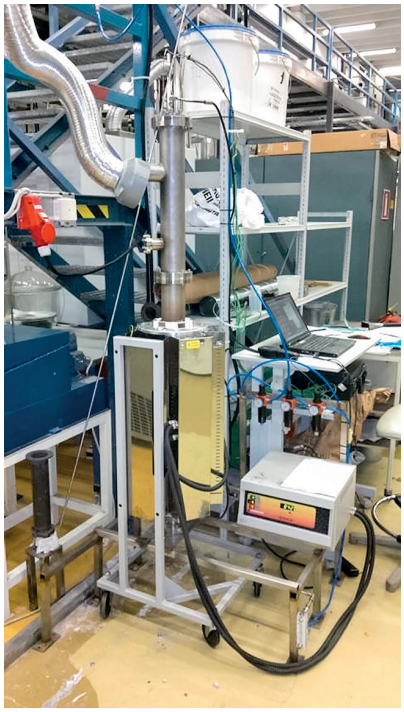
Cooperation:

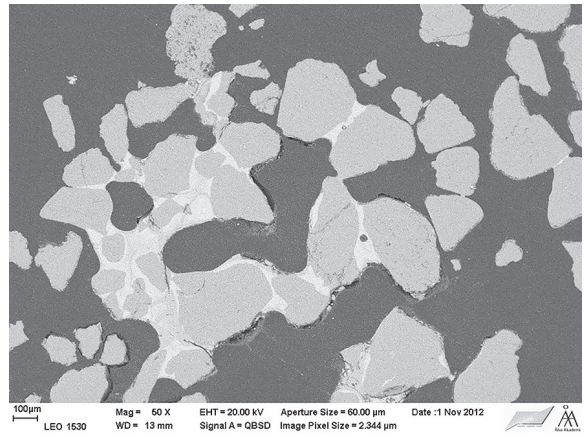
Tampere University of Technology; Lappeenranta University of Technology; Aalto University; VTT Technical Research Centre of Finland

Publications:

- Bankiewicz, D., Enestam, S., Yrjas, P., Hupa, M., Experimental studies of Zn and Pb induced high temperature corrosion of two commercial boiler steels, *Fuel Processing Technology*, 105 (2013) 1, 89-97 (Elsevier B.V., ISSN: 0378-3820)







Agglomeration of quartz sand in a laboratory fluidized bed due to addition of K_2CO_3 at 900°C.

- Bankiewicz, D., Yrjas, P., Lindberg, D., Hupa, M., Determination of the corrosivity of Pb-containing salt mixtures, *Corrosion Science*, 66 (2013), 225-232 (Elsevier Ltd., ISSN: 0010-938X)
- Enestam, S., Bankiewicz, D., Tuiremo, J., Mäkelä, K., Hupa, M., Are NaCl and KCl equally corrosive on superheater materials of steam boilers?, *Fuel* 104 (2013), 294-306 (Elsevier Ltd., ISSN: 0016-2361)
- Enestam, S., Backman, R., Mäkelä, K., Hupa, M., Evaluation of the condensation behavior of lead and zinc in BFB combustion of recovered waste wood, *Fuel Processing Technology*, 105 (2013) 1, 161-169 (Elsevier B.V., ISSN: 0378-3820)
- Karlström, O., Brink, A., Biagini, E., Hupa, M., Tognotti, L., Comparing reaction orders of anthracite chars with bituminous coal chars at high temperature oxidation conditions, *Proceedings of the Combustion Institute* 34 (2013) 2, 2427-2434 (Elsevier Inc.; Combustion Institute, ISSN: 1540-7489)
- Lehmusto, J., Skrifvars, B.-J., Yrjas, P., Hupa, M., Comparison of potassium chloride and potassium carbonate with respect to their tendency to cause high temperature corrosion of stainless 304L steel, *Fuel Processing Technology*, 105 (2013) 1, 98-105 (Elsevier B.V., ISSN: 0378-3820)
- Piotrowska, P., Zevenhoven, M., Hupa, M., Giuntoli, J., de Jong, W., Residues from the production of biofuels for transportation: Characterization and ash sintering tendency, *Fuel Processing Technology*, 105 (2013) 1, 37-45 (Elsevier B.V., ISSN: 0378-3820)

- Sevonius, C., Yrjas, P., Hupa, M., Defluidization caused by potassium salts in a laboratory bubbling fluidized bed, *Proceedings: 38th International Technical Conference on Clean Coal and Fuel Systems*, June 2-6, 2013, Clearwater, FL, USA, 267-276, ISBN: 9781627486415
- Singh, R.I., Brink, A., Hupa, M., CFD modeling to study fluidized bed combustion and gasification, *Applied Thermal Engineering*, 52 (2013), 585-614 (Elsevier Ltd., ISSN: 1359-4311)
- Vainio, E., Fleig, D., Brink, A., Andersson, K., Johnsson, F., Hupa, M., Experimental evaluation and field application of a salt method for SO_3 measurement in flue gases, *Energy & Fuels*, 27 (2013) 5, 2767-2775 (ACS Publications, ISSN: 0887-0624)
- Vainio, E., Yrjas, P., Zevenhoven, M., Brink, A., Laurén, T., Hupa, M., Kajolinna, T., Vesala, H., The fate of chlorine, sulfur, and potassium during co-combustion of bark, sludge, and solid recovered fuel in an industrial scale BFB boiler, *Fuel Processing Technology*, 105 (2013) 1, 59-68 (Elsevier B.V., ISSN: 0378-3820)

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

Main funding: Academy of Finland

Nikolai DeMartini, Magnus Perander, 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 behaviour 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.

Calcium and potassium are the main catalytically active species in biomass. Calcium tends to be more catalytically active earlier in the char gasification and drops off, apparently as calcium oxide crystals grow. Potassium shows increasing catalytic activity towards the end of char conversion before the conversion rate drops precipitously just before full char conversion. At ÅAU, we have removed metals from biomasses (mostly spruce wood, but also spruce bark and miscanthus) and doped Ca and K to organic anionic sites (such as carboxylic and phenolic sites). These biomass samples have been pyrolysed and gasified in CO_2 at different pressures and temperatures. Gasification in H_2O with these same samples is on-going at VTT. This data is being utilized at the University of Jyväskylä to develop parameters for kinetic modeling of the influence of inorganic ions on the char gasification rate. These new models will be utilized in in the updated "Carbon conversion predictor" and compared with conversion measurements performed in a pilot-scale fluidized bed gasifier at VTT as part of a Nordic project.

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

Publications:

- 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 (2013), 22-29 (Elsevier B.V., ISSN: 0960-8524)
- Vähä-Savo, N., DeMartini, N., Hupa, M., Fate of char nitrogen in catalytic gasification – formation of alkali cyanate, *Energy & Fuels*, 27 (2013)11, 7108-7114 (ACS Publications, ISSN: 0887-0624)

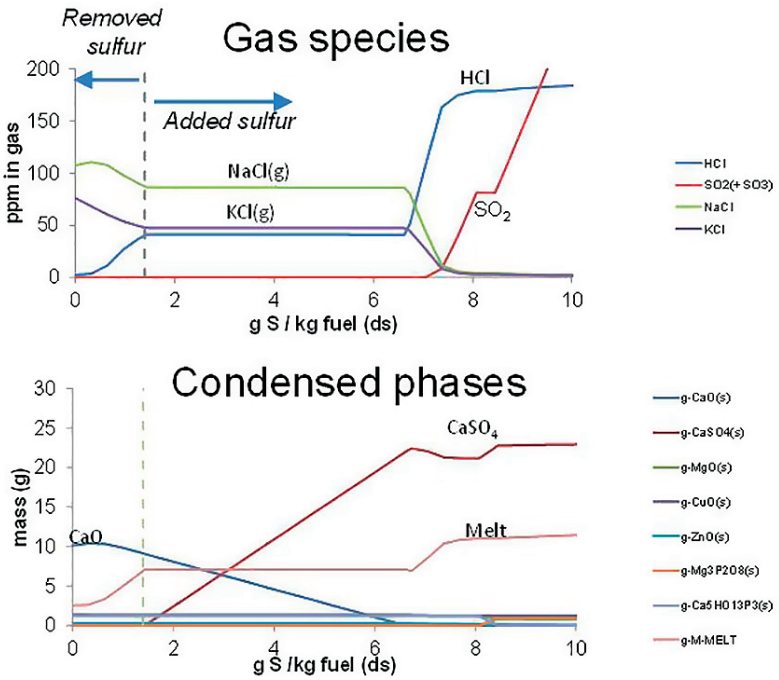
Fuel Additives to Reduce Corrosion at Elevated Steam Data in Biomass Boilers

Funding: Swedish Energy Agency, Industry

Patrik Yrjas, Daniel Lindberg, Mikko Hupa

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

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



Gaseous species and condensed phases for sulfur addition at 850°C and oxidizing conditions.

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

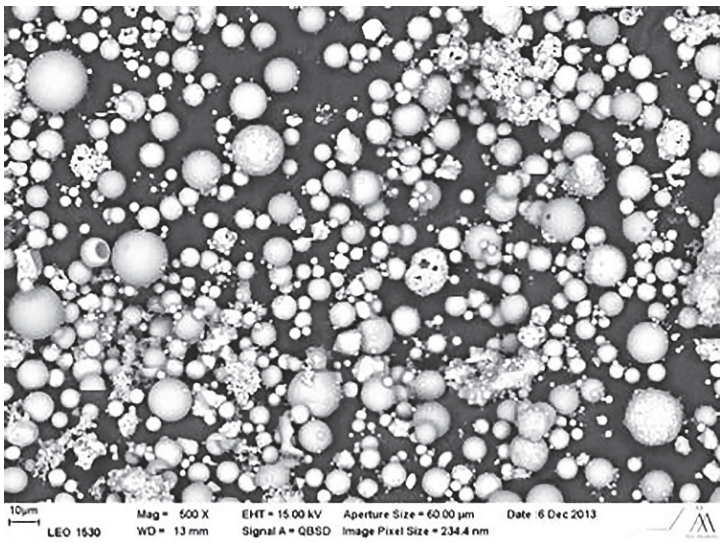
Sustainable Utilization of Ash, Slag and Pyrolysis Residuals – TUULI

Funding: Tekes, Industry

Patrik Yrjas, Daniel Lindberg, Tor Laurén, Camilla Molin, Mikko Hupa

The project started in late 2012 and will continue until spring 2015. The target of the project is to create a viable business ecosystem between ash and slag producers, handlers and utilizers. The aim is to study how ash and slag properties can be developed by means of mechanical and chemical processing as well as by optimising incineration conditions. The utilization potential of processed ash fractions will be examined in a wide range of applications. The benefits of the project will be a better holistic understanding of thermal residues, which improves the possibility to considerably lessen the quantity of ash placed in landfills, to lessen the quantity of virgin raw materials in other businesses, to develop new processes for ash handling and utilization and to strengthen the participants' competitiveness at foreign markets

The role of Åbo Akademi is to test, analyze and predict the risks for the combustion process when changing fuel input to improve ash quality. The combustion tests were done in Piteå, Sweden within the EU-BRISK project. ÅA also evaluates the behaviour of ash minerals through thermodynamic equilibrium modeling. Also, a literature study on heavy metal separation from ashes has been done.



Fly ash when co-firing 96% torrefied wood with 4% coal.

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

3.8 Intelligent Electroactive Materials

Intelligent electroactive materials and composites were developed further by utilizing conducting polymers, fullerene, carbon nanotubes, graphene and nanofibrillated cellulose. Various materials and devices were characterized by a broad range of electrochemical and spectroscopic methods, as well as surface analysis and imaging techniques. Experimental studies were supported by advanced mathematical modelling. The main application areas of these materials include chemical sensors, membranes, charge storage devices and biomedical tools. Our activities in this field range from basic characterization of novel materials to commercial exploitation of new devices.

Composites of electrically conducting polymers and graphene oxide (GO), reduced graphene oxide (rGO) or graphene were synthesized electrochemically and chemically. By using nanofibrillated cellulose (NFC) as template for conducting polymers and Ag-nanoparticles it was possible to obtain biocompatible, electrically conductive, flexible and anti-bacterial freestanding composite papers. Furthermore, conducting polymers were studied as electroactive membranes for separation of metal ions. Functionalization of polyaniline via thiolation was studied further in order to develop potentiometric sensors for DNA hybridization.

Research on solid-contact ion-selective electrodes (ISEs) was continued. The water uptake and transport properties of membrane materials used in ISEs were studied further in order to improve the potential stability and analytical performance of ISEs. Chronopotentiometry with solid-state PbS/Ag_2S electrodes was used to determine low concentrations of lead in environmental samples. Potentiometric sensors were also combined with paper-based microfluidic transport of the sample solution. Theoretical work was focused on a general approach to the description of electro-diffusion processes, by using the Nernst-Planck-Poisson (NPP) model, to allow for the description of complexing reactions occurring in ion-selective membranes.

A composite all-solid-state reference electrode was fabricated by injection moulding and chemical polymerization methods. Rigorous testing 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 had comparable or better performance than high-quality commercial reference electrodes.

The development of printed supercapacitors was continued. The goal is that printing technology will enable a low-cost manufacturing process that will widen the application range of supercapacitors. Furthermore, projects related to the commercialization of a bio-based galvanic skin treatment patch for personal wellbeing markets and a microcurrent wound treatment patch with increased functionality are in progress.

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

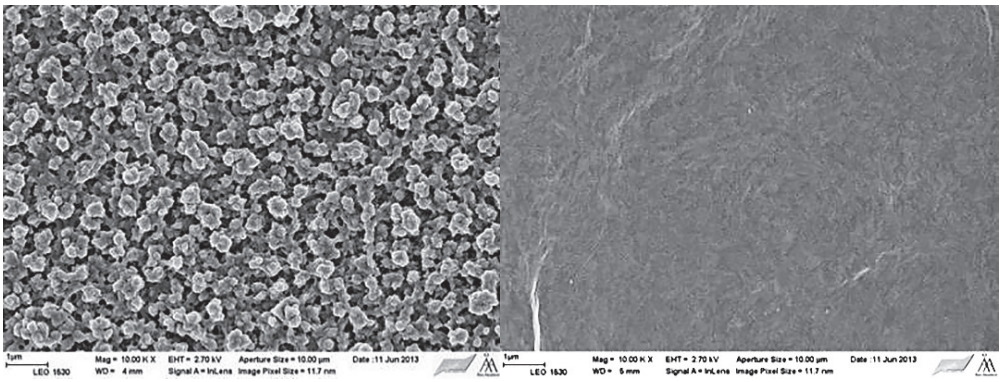
Main funding: Academy of Finland, Johan Gadolin Scholarship, Research Institute of Åbo Akademi University Foundation, ERASMUS

Patrycja Bober, Zhanna Boeva, Cristina Dumitriu, Ning He, Rose-Marie Latonen, Tom Lindfors, Jun Liu, Konstantin Milakin, Jadielson Lucas da Silva Antonio, Michał Wagner, Chunlin Xu, Johan Bobacka, Ari Ivaska

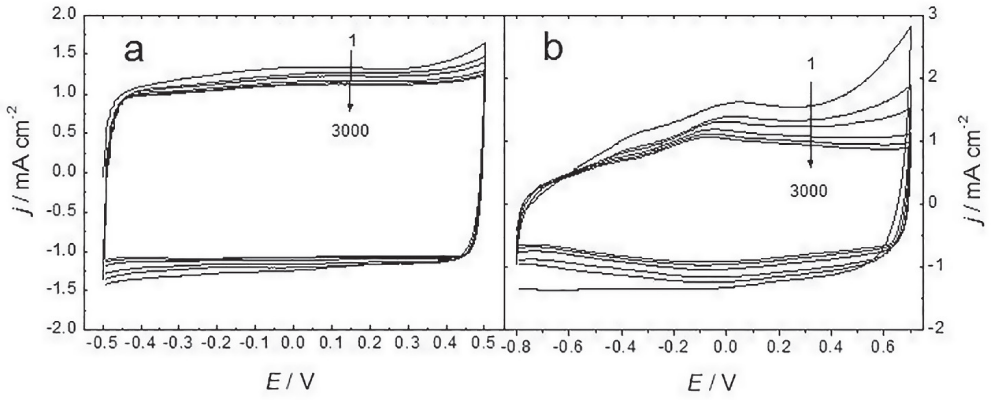
Composites of electrically conducting polymers and graphene oxide (GO), reduced graphene oxide (rGO) or graphene have been synthesized electrochemically and chemically. The composite materials developed are aimed to be used in supercapacitors and batteries, printable chemical sensors and biodiagnostics.

Electrochemical reduction of GO to rGO in nanostructured composite films of polyaniline (PANI) and GO has improved the electroactivity of the composite by 30%. At the same time the redox capacitance of the composite films increased by 15% to 77 mF cm^{-2}. Furthermore, the PANI composite films showed good cycling stability during 10,000 potential cycles. The PANI composite films are aimed to be used in solid-state chemical sensors and capacitor applications, where the electrochemical deposition procedure suits well for deposition of thin layers on well-defined small surfaces.

A one-step electrochemical synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) in an aqueous dispersion of reduced graphene oxide (rGO) has also been successfully accomplished. A uniformly porous and open surface morphology was obtained and the films behaved almost like ideal capacitors and had a very good potential cycling stability.

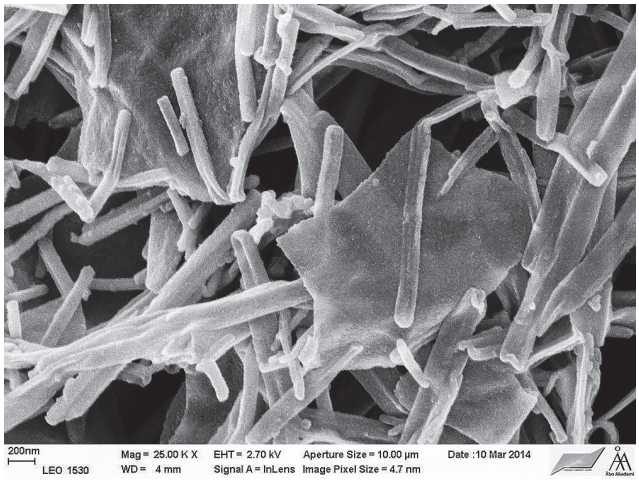


Comparison of the SEM image of the PEDOT-rGO composite (left) with PEDOT-GO composite (right)



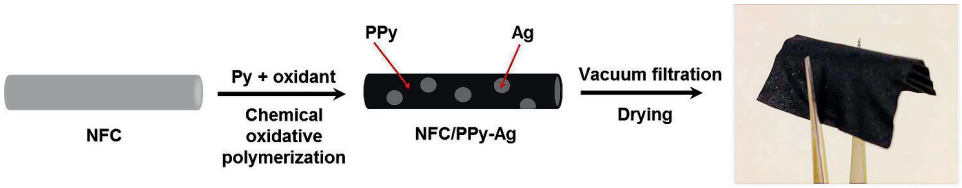
Cyclic voltammograms of the PEDOT-rGO composite film measured during the potential cycling stability test in 0.1 M KCl under nitrogen, v=100 mV s^{-1}. The 1, 50, 200, 1000, 2000 and 3000th cycles are shown.

Conducting composites of a polypyrrole-hydro-sponge (PPy-HP) and GO have been synthesized chemically. These composite materials have a 3D nanostructure and due to their large surface area they could be suitable materials in supercapacitor applications.



SEM images of PPy-HP + GO prepared from methyl orange aqueous solution and GO aqueous dispersion of 25 mg L^{-1}.

Nanofibrillated cellulose (NFC), originated from softwood fibres, prepared by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) mediated oxidation results in a fibre size of 5-10 nm in width and hundreds of nanometres in length. NFC has shown high strength, stiffness and good film forming properties. By using NFC as template for conducting polymers or GO/rGO or both, electroconductive freestanding films or ink formulations can be made for different applications such as supercapacitors, printable chemical sensors and for biodiagnostics. By using NFC as template for PPy and Ag-nanoparticles, biocompatible, electroconductive, flexible and anti-bacterial free-standing composite papers have been prepared by a one-step chemical polymerization procedure.



Preparation of freestanding conductive and anti-bacterial composite papers based on NFC, PPy and Ag-nanoparticles.

Cooperation:

Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry and Research Group of Technical Analytical Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary; M.V. Lomonosov Moscow State University, Chemistry Department, Division of Polymer Science, Laboratory of Polyelectrolytes and Biopolymers; 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, USA; AGH, University of Science and Technology, Kraków, Poland; St. Petersburg State University, St. Petersburg, Russia

Publications:

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- Dumitriu, C., Mousavi, Z., Latonen, R., Bobacka, J., Demetrescu, I., Electrochemical synthesis and characterization of poly(3,4-ethylenedioxythiophene) doped with sulfonated calixarenes and sulfonated calixarene–fullerene complexes, *Electrochimica Acta*, 107 (2013), 178-186 (Pergamon; International Society of Electrochemistry, ISSN: 0013-4686)
- Ferancová, A., Rengaraj, S., Kim, Y., Vijayalakshmi, S., Labuda, J., Bobacka, J., Sillanpää, M., Electrochemical study of novel nanostructured in2s3 and its effect on oxidative damage to DNA purine bases, *Electrochimica Acta*, 92 (2013), 124-131 (Pergamon; International Society of Electrochemistry, ISSN: 0013-4686)
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- Lindfors, T., Österholm, A., Kauppila, J., Gyurcsányi, R.E., Enhanced electron transfer in composite films of reduced graphene oxide and poly(N-methylaniline), *Carbon*, 63 (2013), 588-592 (Pergamon, American Carbon Society, ISSN: 0008-6223)
- Lindfors, T., Österholm, A., Kauppila, J., Pesonen, M., Electrochemical reduction of graphene oxide in electrically conducting poly(3,4-ethylenedioxythiophene) composite films, *Electrochimica Acta*, 110 (2013), 428-436 (Pergamon; International Society of Electrochemistry, ISSN: 0013-4686)
- Määttänen, A., Vanamo, U., Ihalainen, P.,Pulkkinen, P., Tenhu, H., Bobacka, J., Peltonen, J., A low-cost paper-based inkjet-printed platform for electrochemical analyses, *Sensors and Actuators B: Chemical*, 177 (2013), 153-162 (Elsevier S.A., ISSN: 0925-4005)

- Wagner, M., Kvarnström, C., Ivaska, A., Bobacka, J., Electrochemical activity of novel porous carbon based material synthetized from polycyclic aromatic hydrocarbons, *Electrochimica Acta*, 105 (2013), 384–393 (Pergamon; International Society of Electrochemistry, ISSN: 0013-4686)
- Wagner, M., Lisak, G., Ivaska, A., Bobacka, J., Durable PEDOT:PSS films obtained from modified water-based inks for electrochemical sensors, *Sensors and Actuators B: Chemical*, 181 (2013) May, 694-701 (Elsevier S.A., ISSN: 0925-4005)
- Wagner, M., O'Connell, C.D., Harman, D.G., Sullivan, R., Ivaska, A., Higgins, M.J., Wallace, G.G., Synthesis and optimization of PEDOT:PSS based ink for printing of nanoarrays by Dip-Pen Nanolithography, *Synthetic Metals*, 181 (2013) October, 64-71 (Elsevier S.A., ISSN: 0379-6779)

Paper-based Sensors

Main funding: Åbo Akademi Foundation, Åbo Akademi PCC

Grzegorz Lisak, Jingwen Cui, Sylwia Strzalkowska, Johan Bobacka

In modern analysis of ions it is recommended to minimize any pre-treatment and manipulation of the sample. Operations, such as dilution, pre-concentration, standard additions and even a time delay may influence the speciation of ions in the sample. Ion-selective electrodes offer the possibility to continuously follow ion distribution and to measure in untreated samples, if the fouling of the electrodes will be resolved or diminished. I order to do that, a specific sampling method was introduced to allow measurement of ions and at the same time to protect the electrodes from interfering matter, e.g. larger solid impurities (industrial and foodstuff samples) or blood cells (clinical samples). In this method, a solid-contact ion-selective electrode and a solid-contact reference electrode are pressed against a filter paper into which the sample solution is absorbed. The filter paper acts both as a sampling unit and as a sample container during potentiometric sensing. The paper substrates containing standard and sample solutions are disposable, while the sensors are used multiple times.

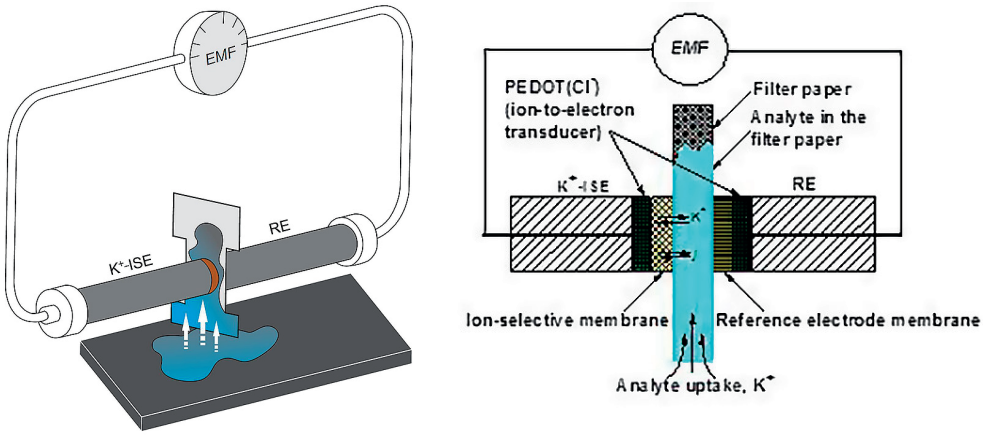


Illustration of the potentiometric setup utilizing paper-based sampling: general view (left), close up of the electrodes and the cross-section of filter paper (right).

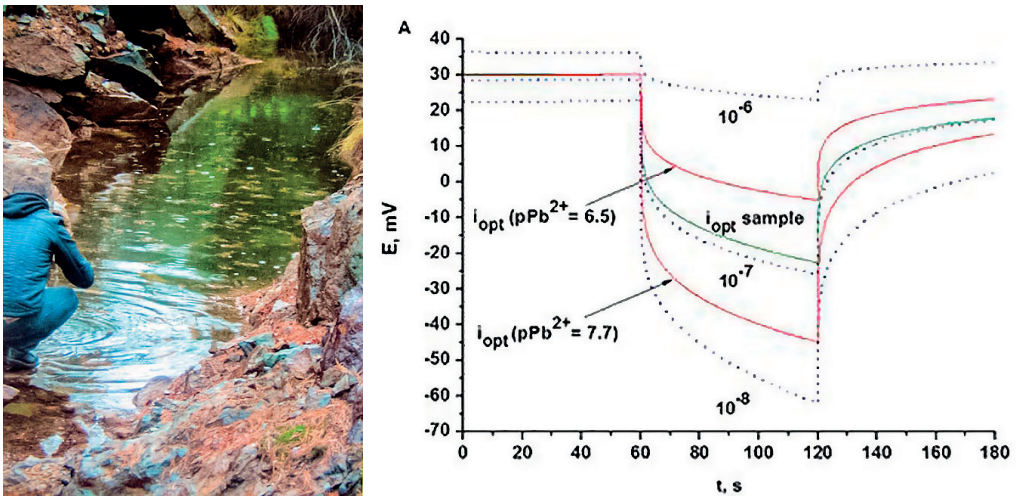
Ion Sensors with Low Detection Limit for Trace Analysis of Heavy Metals in Environmental Samples

Main funding: Åbo Akademi Foundation

Grzegorz Lisak, Filip Ciepiela, Marcin Guzinski, Tomasz Sokalski, Leo Harju, Ari Ivaska, Andrzej Lewenstam, Johan Bobacka

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

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



Ground water sampling in the Finnish Archipelago for measurements of lead(II) using the TGP method (left). Procedure used in the TGP method to measure low and ultra-low concentrations of heavy metals (e. g. Pb^{2+}) in untreated environmental samples (right).

For the first time, chronopotentiometry (TGP method) with solid-state PbS/Ag_2S electrodes was used to lower the detection limit in order to determine lead concentrations in unprocessed environmental samples. The tuned galvanostatic polarisation method offers an attractive possibility to determine analytes at low concentrations not attainable by classical potentiometry. The main advantage of the TGP method is in the possibility of performing measurements in non-filtered environmental samples despite the presence of

solid impurities, which the other applied methods suffer from. It offers as well the possibility of using such sensors which are known to be troublesome in direct potentiometric measurements because of their intrinsic instability as in the case of the Pb^{2+}-ISE with solid-state membrane.

Cooperation:
AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Cracow, Poland; Department of Chemical Technology, Chemical Faculty, Gdansk University of Technology, Gdansk, Poland

Publications:

- Lisak, G., Ciepiela, F., Bobacka, J., Sokalski, T., Harju, L., Lewenstam, A., Determination of lead(II) in groundwater using solid-state lead(II) selective electrodes by tuned galvanostatatic polarization, *Electroanalysis*, 25 (2013) 1, 123-131 (Wiley - V C H Verlag GmbH & Co. KGaA, ISSN: 1040-0397)
- Guziński, M., Lisak, G., Sokalski, T., Bobacka, J., Ivaska, A., Bocheńska, M., Lewenstam, A., Solid-contact ion-selective electrodes with highly selective thioamide derivatives of p-tert-butylcalix[4] arene for the determination of lead(II) in environmental samples, *Analytical Chemistry*, 85 (2013) 3, 1555-1561 (ACS Publications, ISSN: 0003-2700)
- Guzinski, M., Lisak, G., Kupis, J., Jasinski, A., Bochenska, M., Lead(II)-selective ionophores for ion-selective electrodes: A review, *Analytica Chimica Acta*, 791 (2013), 1-12 (Elsevier B.V., ISSN: 0003-2670)

Health Diagnostics with Chemical Sensors

Main funding: Tekes (FiDiPro), Industry

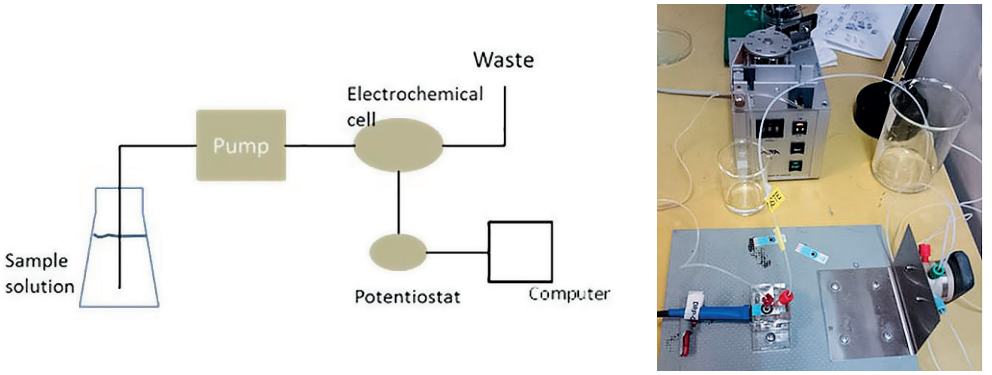
Maija Blomquist, Ulriika Vanamo, Sara Suominen, Zhanna Boeva, Kalle Levon, Andrzej Lewenstam, Johan Bobacka, Ari Ivaska

Fast and easy-to-use DNA hybridisation 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 labelling 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.

An electrochemical flow system with screen-printed electrodes offers a faster analysis technique compared with manually made experiments. Screen-printed electrodes enable even multielectrode analysis procedures. The miniaturization of analytical instrumentation and small volumes of reagents and samples are additional benefits. Optimization of electropolymerization of aniline on screen-printed electrodes, thiolation time and method as well as hybridization in the flow cell are studied in this part of the project.



The electrochemical flow system used: shown as schematics (left) and in a photograph (right). The electrochemical flow cell and the potentiostat are connected with a cable. The peristaltic pump feeds the sample solution to the flow cell.

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

Publications:

- Suominen, Sara, *An Electrochemical flow system with screen-printed electrodes for thiolated polyaniline for biosensor applications*, Master's thesis, 2013
- Blomquist, M., Bobacka, J., Ivaska, A., Levon, K., Electrochemical and spectroscopic study on thiolation of polyaniline, *Electrochimica Acta*, 90 (2013), 604-614 (Pergamon; International Society of Electrochemistry, ISSN: 0013-4686)
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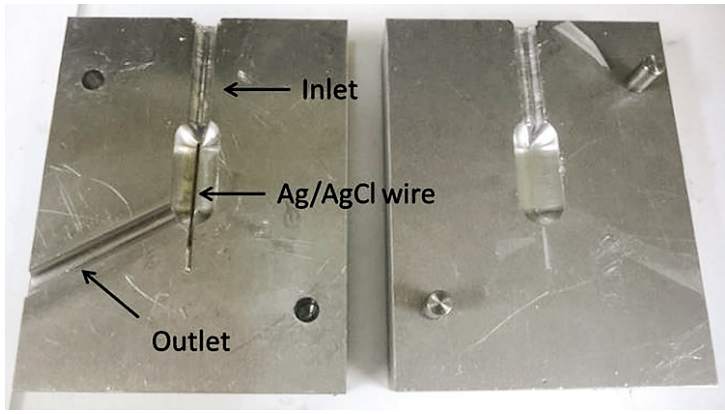
Intelligent Monitoring for Health and Well-being (WP 202 Intelligent Technology Platforms)

Main funding: Tekes (Salwe Ltd, IMO)

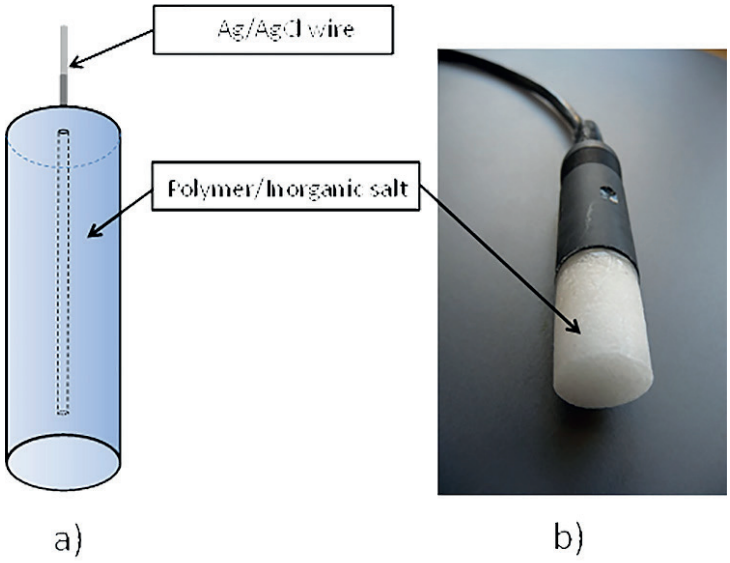
Kim Granholm, Zekra Mousavi, Tomasz Sokalski, Johan Bobacka, Andrzej Lewenstam

A new type of all-solid-state composite reference electrodes (SSC) was designed and char-

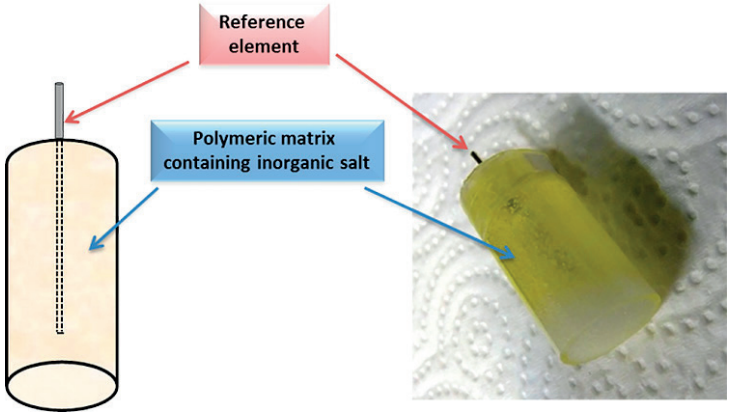
acterized. The electrodes are based on a polymer/inorganic salt composite and a silver/silver chloride reference element. The new all-solid-state reference electrodes were made using injection molding and chemical polymerization methods.



Photograph of a mould used in the injection moulding of reference electrode.

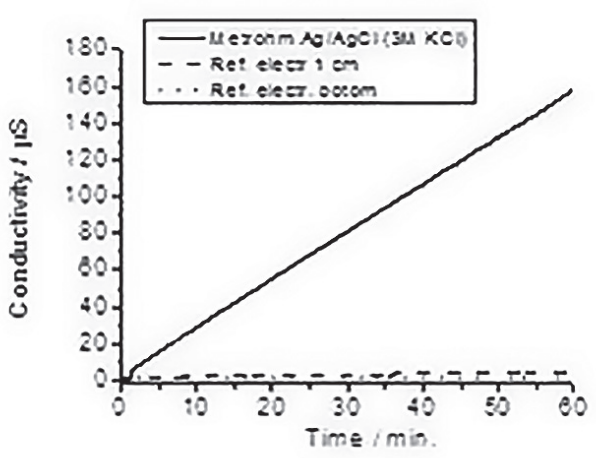


A schematic picture (a) and a photo (b) of the composite reference electrode (SSC) made by injection molding method.

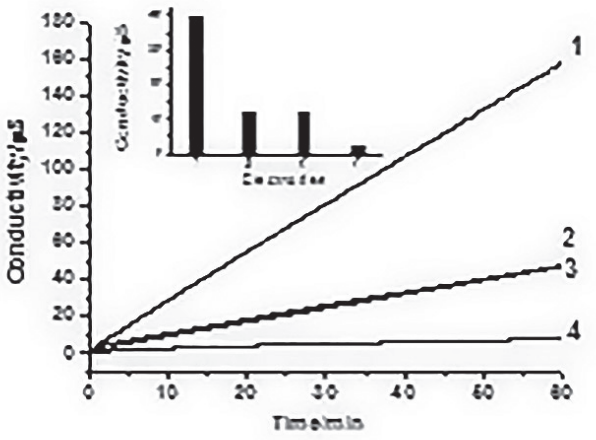


Schematic illustration (left) and picture (right) of a reference electrode (SSC) made by chemical polymerization.

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.



Release of KCl from reference electrodes made by injection molding estimated by conductometric measurement.



Leakage from the Metrohm Ag/AgCl/3 M KCl reference electrode (1), SSC1 reference electrode made by chemical polymerization (2), Orion Ross Ultra double junction reference electrode(3), and SSC2 reference electrode (4). The inset shows the conductivity after 60 minutes.

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.

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

Publications:

- Granholm, K., Mousavi, Z., Sokalski, T., Lewenstam, A., Analytical quality solid-state composite reference electrode manufactured by injection moulding, *Journal of Solid State Electrochemistry*, October (2013), 1-6 (Springer, ISSN: 1432-8488)
- Mousavi, Z., Granholm, K., Sokalski, T. Lewenstam, A., An analytical quality solid-state composite reference electrode, *Analyst*, 138 (2013) 18, 5216-5220 (RSC Publications, ISSN: 0003-2654)

Patents:

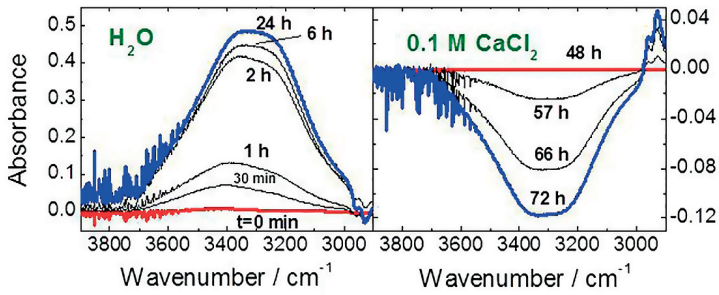
- Patent priority application, A reference electrode and an arrangement for an electrochemical measurement, No. 20126315, filed on 14/12/2012
- European patent application, A reference electrode and an arrangement for an electrochemical measurement, No. PCT/FI2013/051163, filed on 12/12/2013

Water Uptake of Polymeric Materials

Main funding: Academy of Finland

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

Fundamental aspects of the water uptake of both commonly used and new ion-selective membrane (ISM) materials have been studied. The 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). It has recently been shown that low water content at the substrate/ISM interface correlates with superior potential stability of SCISEs. One of the main techniques to study the water is FTIR-ATR spectroscopy due to its ability to distinguish between different types of water in the ISM. The developed spectroelectrochemical method for simultaneous measurement of the water uptake, impedance spectra and open circuit potential has been utilized for studying different polymeric materials. The project has also focused on quantifying the water uptake of plasticized poly(vinyl chloride) (PVC) and silicone rubber (SR) based ISMs with the oven based coulometric Karl Fischer technique.



FTIR-ATR spectra of CaISM(PVC-IV) membrane showing the growth of OH-stretching bands in deionized water (DIW) for 24 h (left) and in 0.1 M $CaCl_2$ for 24 h after being in DIW for 48 h showing transmembrane flux of water from the membrane to the solution phase due to lower osmotic pressure in $CaCl_2$.

The water uptake technique has also been applied for the composite materials based on polyaniline and perfuorinated ionomer Nafion of different compositions and compared to commercially available ready-made Nafion membranes. The membranes based on Nafion and the composite of polyaniline and Nafion are very hydrophilic compared to the membranes used for ion-selective electrodes and therefore the water uptake technique had to be adopted to the fast measurements. The use of MCT detector for modified water uptake method has possessed to record the spectra every 20 s and to evaluate water uptake of the polymeric composites in the form of freestanding films and to resolve fast water sorption.

Cooperation:
Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry and Research Group of Technical Analytical Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary; M.V. Lomonosov Moscow State University, Chemistry Department, Division of Polymer Science, Laboratory of Polyelectrolytes and Biopolymers

Publications:

- He, N., Lindfors, T., Determination of water uptake of polymeric ion-selective membranes with the coulometric Karl Fischer and FT-IR-attenuated total reflection techniques, *Analytical Chemistry*, 85 (2013) 2, 1006-1012 (ACS Publications, ISSN: 0003-2700)

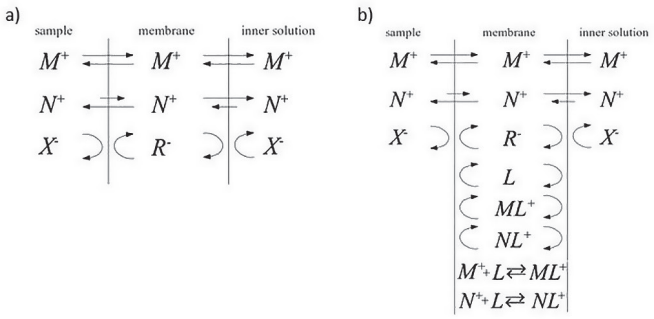
Modelling of Transport Properties of the Neutral Carrier Ion-Selective Electrodes

Main funding: Tekes (Salwe Ltd, IMO)

Jerzy Jasielec, Tomasz Sokalski, Andrzej Lewenstam

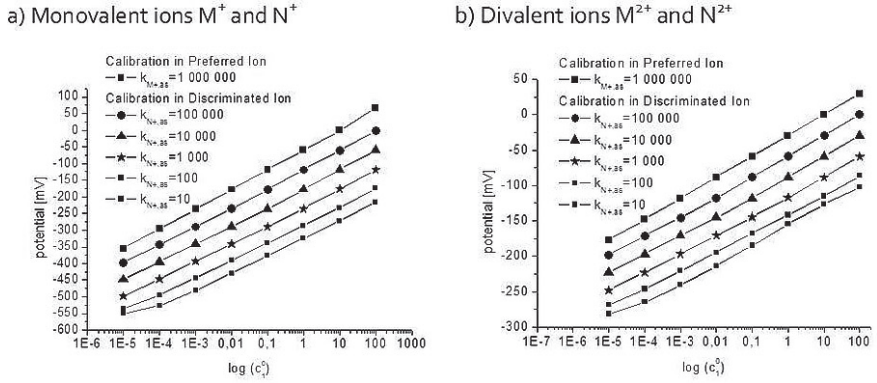
Electrodes containing neutral ionophores are used in clinical, industrial and environmental analysis. The wide range of applications requires deep theoretical description of such electrodes. The focus of this project has been the development of the general approach to the description of electro-diffusion processes, namely Nernst-Planck-Poisson (NPP) model to allow the description of the complexing reactions occurring in the ion-selective membranes. Systems analyzed in all previous works devoted to the NPP modelling of ISE, did not include the information about the ligands and complexes they are forming. Such description is strictly valid for ion-exchanger type of ISE (see figure below). In the case of the neutral carrier (ionophore) membranes the reactions $M^+ + L \Leftrightarrow ML^+$ and $N^+ + L \Leftrightarrow NL^+$ have to be taken into account (see figure below). Such complexes may have crucial influence on the formation of membrane potential. In this work we present the effects of including the reaction in the NPP model with and without the assumption of the constant uniform ligand concentration in the membrane.

For the Neutral Carrier membranes, not only the partition coefficients, but also the stability constants of the complexation reactions influence the selectivity coefficient $K_{MN}^{pot} = (k_N / k_M)(\beta_N / \beta_M)$. The stability constants of reactions $M^+ + L \Leftrightarrow ML^+$ and $N^+ + L \Leftrightarrow NL^+$ are given as $\beta_M = k_{M,as} / k_{M,dis}$ and $\beta_N = k_{N,as} / k_{N,dis}$, respectively.



Systems considered in this work: M^+ represents preferred ion, N^+ - discriminated ion, X^- - counter ion, R^- - anionic site in the membrane, L – ligand, ML^+ is the complex of ligand and preferred ion and NL^+ is the complex of ligand and discriminated ion. a) system with no reactions (ion-exchanger), b) system with the complexation reactions (neutral carrier).

In earlier works devoted to the NPP description of the Neutral Carrier membranes, only fully associated complexes were taken into account. Inclusion of reaction terms gives the possibility of analyzing the influence of the stability constants on such systems. In order to research the ISEs selectivity using NPP model, calibrations in pure solutions of the preferred and the discriminated ion were performed. The results are shown below.



Calibration curves in pure solutions of the preferred and the discriminated ion: a) for monovalent ions, b) for polyvalent ions.

The predictions made using the Phase Boundary Model were confirmed by the results obtained with NPP model. The tenfold increase of the stability constant causes a tenfold increase of selectivity coefficient.

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

Publications:

- Jasielec, Jerzy, Modelling of potentiometric ion sensors, Doctoral thesis, 2013 (Painosalama Oy, ISBN 978-952-12-2938-1)
- Jasielec, J., Lisak, G., Wagner, M., Sokalski, T., Lewenstam, A., Nernst-Planck-Poisson model for the description of behaviour of solid-contact ion-selective electrodes at low analyte concentration, *Electroanalysis*, 25 (2013) 1, 133-140 (Wiley - V C H Verlag GmbH & Co. KGaA, ISSN: 1040-0397)

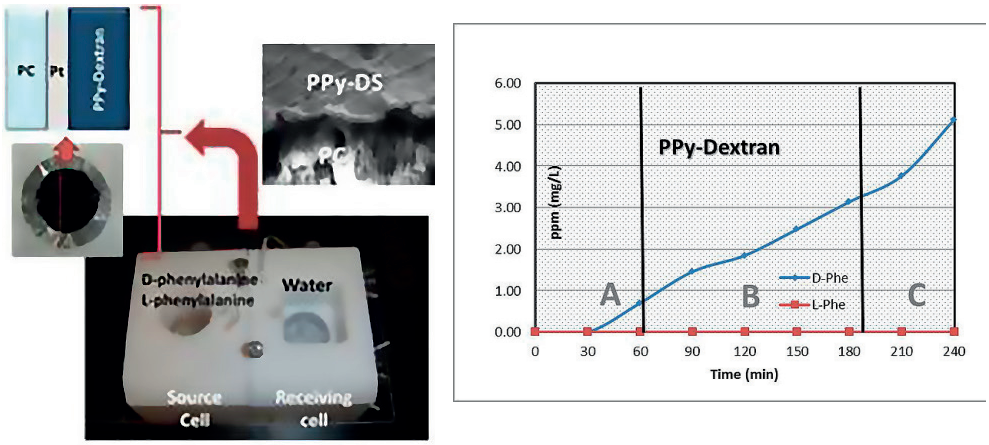
Electroactive Membranes for Separation of Metal Ions and Optically Active Compounds

Main funding: Åbo Akademi Foundation, Åbo Akademi PCC

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

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. Therefore, pharmaceutical industries demand pure enantiomeric compounds. Enantioseparation is commonly done by rather expensive methods such as high performance liquid chromatography (HPLC) and electrophoresis. In this project the use of electroactive membranes based on conducting polymers have been studied for separation of enantiomers.

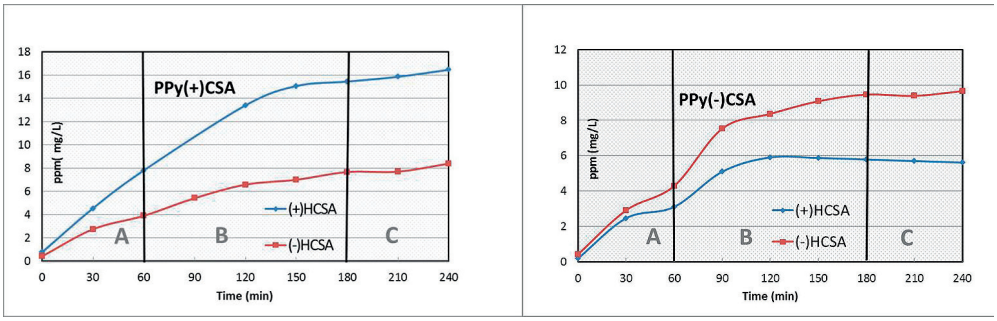
Chiral conducting polymers can be achieved by polymerizing a monomer attached to a chiral compound or by using chiral anionic polymers as dopants during polymerization of the conducting polymer. Selective transport of one form of a chiral compound through the membrane can be induced by using electrical stimuli applied to the polymer membrane. This will switch the chiral conducting polymer between its reduced and oxidized state.



Transport cell for the separation of optically active D/L-tryptophan (left). Transport profile for D/L- Phenylalanine across PPy-Dextran composite membrane (right). Region A: no applied potential, Region B: pulsed potential between +0.50 V and -0.80 V with a 50 s pulse width; Region C: no applied potential.

The transport cell used for enantioseparation is shown in the left figure below. The membrane separates the source solution from the receiving solution. Schematic of the cross section of a polypyrrole doped with sulfonated dextran (PPy-DS) composite membrane is shown in the same figure. The membrane is a composite membrane consisting of a conducting polymer film deposited on a platinised polycarbonate membrane as the support material. The figure at right shows the transport profile of D-phenylalanine and L-phenylalanine.

Transport of both enantiomeric forms of camphor sulphonic acid (HCSA) was also studied and the transport profiles are shown in the figures below. The conducting polymer polypyrrole (PPy) was doped with one of the enantiomeric forms, (+)HCSA or (-)HCSA, via electrochemical polymerization of pyrrole. These membranes were then used for transport studies by applying pulsed potential during the transport. As is shown in the left figure, when PPy was doped with (+)HCSA, selectivity was shown for its analogous form; and when PPy was doped with (-)HCSA, selectivity was shown for its corresponding form.



Electrochemically controlled transport of (+)CSA and (-)CSA across PPy membranes doped with (+)HCSA (left) and (-)HCSA (right). Source solution 0.1 M (+)HCSA/ 0.1 M (-) HCSA; receiving solution pure water. Region A: no applied potential, Region B: pulsed potential between +0.50 V and -0.80 V with a 50 s pulse width; Region C: no applied potential.

Cooperation:
University of Wollongong, Australia

Publications:

- Latonen, R-M., Akieh, M.N., Vavra, K., Bobacka, J., Ivaska, A., Ion exchange behavior of polypyrrole doped with large anions in electrolytes containing mono- and divalent metal ions, *Electroanalysis*, 25 (2013) 4, 991-1004 (Wiley - V C H Verlag GmbH & Co. KGaA, ISSN: 1040-0397)

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 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 optimising 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 University of Technology; ABEnzymes Oy; Joutsenpaino Oy; Lumene Oy; Stora Enso Oy; Tervakoski Oy

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 institutionalised 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. 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 Oy; Joutsenpaino Oy; Kiilto Oy; Tervakoski Oy

Publications:
- 3 notifications of invention, 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 Oy; Kemet Oy; Cabus Oy

Electrical Array with Dual Functionality Allowing for Electrically Controlled Anti-inflammatory Drug Delivery and Galvanic Wound Stimulation

Main funding: Academy of Finland, Postdoctoral researcher

Xiaoju Wang, Mikko Hupa

Chronic wounds cause patients severe emotional and physical stress and create a significant financial burden on patients and the whole healthcare system. The current project proposed a material and technological development for a wound dressing surface with both the delivery of electric stimulation for accelerated wound healing and the anti-inflammatory functionality integrated. The dual functionality can be realised *via* a novel electrode array design, which is as predicted by skin impedance modeling simulation to have a premium performance on delivering electric stimuli to the tissue around the wound site as well as with a good polarity control. The fabrication parameters for this electrode array *via* printing technology will be investigated in terms of delivery efficiency of the treatment current, including screening the suitable conductive ink species and optimization of the inks' composition. The integration of anti-inflammatory functionality to this electrode array surface will be realised *via* the modification of the partitioned electrodes in the array with electropolymerized conducting polymers and the doping of non-steroidal anti-inflammatory drugs (NSAIDs) into the conducting polymers during electropolymerization. This would facilitate the electrically controlled drug release in such conducting polymer based drug delivery system (DDS). Planned research efforts will also focus on the development of nano-structured conducting polymer based DDS, in order to enhance the delivery performance in terms of the drug loading and release efficiency of the devices. The resulted conducting polymer based DDS will be characterized with instrumentation supported by the infrastructure at PCC, in terms of the morphological features and the drug delivery performance of the devices. Based on the anticipated research outcome of the proposed project, a dressing product with increased functionality and more precise controllability can be then potentially developed for the point-of-use of medical care to the chronic wound.

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 or tissue engineering scaffolds in the human body. The link in common for these materials is their manufacturing and/or utilization at high temperatures. Functionality of the materials is related with their special physicochemical properties in the final application. Understanding the chemical and physical processes taking place at high temperatures and how these affect the performance of the material are our key competences and research focuses. We develop new compositions for materials but also study the behaviour and properties of commercial qualities at laboratory conditions imitating the final use of the materials.

Medical implants based on bioactive glasses have been one of our research focuses during the past three decades. Today, bone-grafting materials made of bioactive glass compositions developed at our laboratory are commercially available. Ideally, the bioactive glass gradually dissolves in the body while stimulating and guiding growth of new living tissue. Depending on the composition the glasses have also bacteriostatic properties. Basically, the interactions with living tissue are controlled by the dissolution characteristics of the glasses and thus by the glass composition. Our procedure for measuring and modelling ion dissolution rate from the glasses gives valuable information for development of compositions for novel applications. One important goal of our bioactive glass research has been tailoring the glass composition to enable manufacture of porous scaffolds releasing inorganic ions in a controlled manner. This requires a close control of high temperature properties and dissolution kinetics of the glasses. Our most recent research topic deals with development of bioactive glass fibres for different sensing and trauma healing applications. In addition, we study the interactions of the glasses with organic biopolymers in various composite structures and porous tissue engineering scaffolds.

Highly porous structures, foams, are used in a wide range of applications. We initiated studies for optimising the processing parameters and compositions giving desired properties for bioactive glass foams to be used in biomedical applications and for inert ceramics foams to be used catalyst support applications.

High temperature materials in combustion devices and boilers face new challenges by requirements of increased power production efficiency, reduced emissions and increasing utilization of renewable fuels. Higher material temperatures needed e.g. in superheaters, utilization of biofuels, waste derived fuels and different fuel mixtures may give rise to severe corrosion of the hottest boiler 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 alkali 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. We have also

developed a laboratory procedure for estimating and comparing the abrasive effect of bed particles in fluidized bed combustion on the boiler materials at elevated temperatures.

Bioactive Glasses and Their Properties

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

Leena Hupa, Di Zhang, Susanne Fagerlund, Leena Björkvik, Anna Iisa, Paul Ek, Mikko Hupa

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

Cooperation:
University of Turku, Institute of Dentistry; BioMediTech; University of Erlangen-Nuremberg, Germany

Publications:

- Huhtinen, R., Sandeman, S., Rose, S., Fok, E., Howell, C., Fröberg, L., Moritz, N., Hupa, L., Lloys, A., Examining porous bio-active glass as a potential osteo-odonto-keratoprosthetic skirt material, *Journal of Materials Science. Materials in Medicine*, 24 (2013) 5, 1217-1227 (Springer, ISSN: 1573-4838)
- Fagerlund, S., Hupa, L., Hupa, M., Dissolution patterns of biocompatible glasses in 2-amino-2-hydroxymethyl-propane-1,3-diol (Tris) buffer, *Acta Biomaterialia*, 9 (2013) 2, 5400-5410 (Acta Materialia Inc., ISSN: 1742-7061)

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

Main funding: Academy of Finland, Åbo Akademi PCC

Leena Hupa, Susanne Fagerlund, Leena Björkvik, Eveliina Viljamaa,Ulriika Vanamo, Sara Kiran, Johan Bobacka, Mikko Hupa

The MoreBAGS project aims to gain a thorough understanding of the mutual interactions of biodegradable and bioactive materials in aqueous solutions, such as simulated body fluid. The research has been done with binary and ternary composites of polymers and melt-derived bioactive glasses or sol-gel derived nanoparticles. In addition, bioactive glasses have been applied to the surface of load-bearing fibre-reinforced composite (FRC)

implant. The goal is to utilize these materials to tailor implants with a gradient structure giving controlled resorption and controlled guidance of tissue regeneration. The results will be utilized to develop implants with a FRC core giving long-term stability and with bioactive surface layers providing good bonding to tissue.

Local precipitation of hydroxyapatite on a polylactic acid fibre mesh containing bioactive glass nanoparticles after one week in simulated body fluid.

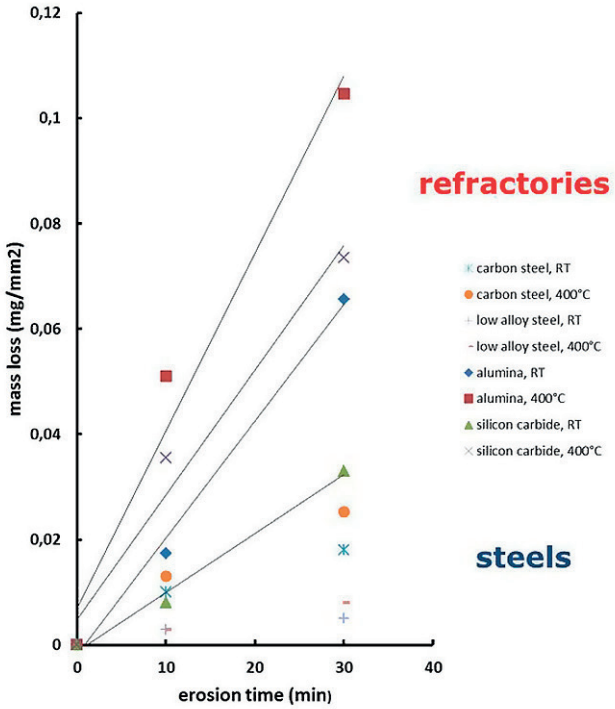
Cooperation:
University of Turku, Institute of Dentistry; Central Glass & Ceramic Research Institute, Kolkata, India

Corrosion and Erosion of Refractories

Main funding: Åbo Akademi PCC, FUSEC project partners

Leena Hupa, Na Li, Ismoil Bello, Henri Holmblad, Mikko Hupa

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



Mass loss from ceramic refractories and metals as a function of time after erosion with sand (6 m/s) at room temperature and 400°C.

Optical Fibres with Bioactive Surface

Main Funding: Academy of Finland

Jonathan Massera

In this three-year project, we proposed to develop new core-clad glass/glass-ceramic fibres combining the good optical quality of the core and the rapid tissue bonding of the glass used as the clad of the fibre for medical and sensing applications.

New silicate and phosphate-based bioactive glasses, containing Mg or Sr ions, have been developed. Within this project, we showed that it is possible i) to tailor the glass reactivity in simulated body fluid and ii) to obtain bioactive glasses with a crystallization kinetics favourable to fibre drawing. The addition of SrO in glass was found to induce formation of a Sr-substituted apatite layer, which yields to better cell attachment. SrO substitution for CaO, in both silicate and phosphate glasses, was found to lead to higher gingival fibroblast cells activity. The thermal properties of the newly developed glasses were fully measured and the crystallization mechanism investigated. The impact of partial to full glass crystallization on the bioactive properties of the glasses was investigated. While the bioactivity of crystallized silicate glasses was found to be reduced, it was completely suppressed in crystallized phosphate glasses. Single core fibres of the most promising glasses were successfully drawn in collaboration with Dr. I. Ahmed at the University of Nottingham (UK) and Prof. J. Ballato at Clemson University (USA). The fibre drawing process leads to preferential orientation of the P-O-P bonds in phosphate glass and to a faster Na release into solution. However, fibre drawing does not modify the glass

bioactivity. We demonstrated that it is possible to estimate *in vitro* the degree of reaction of a glass-fibre through the measurement of the changes in the fibre optical properties. The change in the light output is separated in 4 stages as shown in the figure. Up to 48h the light output remain constant due to the limited glass reaction in simulate body fluid (stage 1). Successively a slight decrease in the light output power is recorded due to the initial formation of a calcium-phosphate layer and small reduction in the fibre cross section (stage 2). Then the decrease in the light output becomes more rapid due to the presence of a thick layer inducing light scattering at the fibre surface (stage 3) and finally the decrease in the light intensity slows down as the formed layer act as barrier to the glass dissolution (stage 4).

Cooperation:
University of Turku Institute of Dentistry (Finland); nLIGHT corp., Finland; University of Nottingham, UK; University of Rennes, France; University of Bordeaux, France; Clemson University, SC, USA; Politecnico di Torino, Italy

Publications:

- Massera, J., Bourhis, K., Petit, L., Cardinal, T., Hupa, L., Hupa, M., Effect of the glass composition on the chemical durability of zinc-phosphate-based glasses in aqueous solutions, *Journal of Physics and Chemistry of Solids*, 74 (2013) 1, 121-127 (Elsevier Ltd.; ISSN: 0022-3697)
- Massera, J., Petit, L., Cardinal, T., Videau, J.J., Hupa, M., Hupa, L., Thermal properties and surface reactivity in simulated body fluid of new strontium ion-containing phosphate glasses, *Journal of Materials Science: Materials in Medicine*, 24 (2013) 6, 1407-1416 (Springer, ISSN: 1573-4838)

4. Publications 2013

4.1 Theses

4.1.1 Doctoral theses (15)

Biasi, Pierdomenico, Combination of catalyst development and chemical reaction engineering: a key aspect to improve the hydrogen peroxide direct synthesis

Jasielec, Jerzy, Modelling of potentiometric ion sensors

Jones, Frida, Characterisation of waste for combustion - with special reference to the role of zinc

Karlström, Oskar, Oxidation rates of carbon and nitrogen in char residues from solid fuels

Kilpiö, Teuvo, Mathematical modeling of laboratory scale three-phase fixed bed reactors

Kirilin, Alexey, Aqueous-phase reforming of renewables for selective hydrogen production in the presence of supported platinum catalysts

Lehmusto, Juho, The role of potassium in the corrosion of superheater materials in boilers firing biomass

Leppänen, Ann-Sofie, Regioselective modifications of galactose-containing polysaccharides in aqueous media

Li, Bingzhi, Modeling of fireside deposit formation in two industrial furnaces

Lindqvist, Hanna, Improvement of wet and dry web properties in papermaking by controlling water and fiber quality

Privalova, Elena, Towards novel biogas upgrading processes

Song, Tao, Extraction of polymeric galactoglucomannans from spruce wood by pressurized hot water

Strand, Anders, The pH-dependent phase distribution of wood pitch components in papermaking processes

Tolvanen, Pasi, Development of an environmentally friendly method of starch oxidation by hydrogen peroxide and a complex water-soluble iron catalyst

Wagner, Michal, Synthesis, characterization and chemical sensor application of conducting polymers

4.1.2 Licentiate theses (0)

4.1.3 Master's theses (12)

Aaltonen, Toni, Liquid phase hydration of 1-butene over an acidic ion-exchange resin catalyst

Bello, Ismail, Laboratory procedure for testing of erosion of boiler materials at elevated temperatures

Bittante, Alice, Study of liquid residence time distribution in a trickle bed reactor used for direct synthesis of hydrogen peroxide

Garcia de Sastro Insua, Ricardo Antonio, Acid hydrolysis of birch and spruce hemicelluloses by heterogeneous catalysts

Lawal, Adullahi Adekunle, Quantification of the release of K, Mg and Mn during rapid and slow devolatilization of pulverized biomass fuels in a wire-mesh reactor

Li, Zhiqiang, Optimisation of alkaline flow-through extraction of spruce wood for lignin recovery

Jingwei, Cui, Potentiometric sensing utilizing paper-based sampling

Liu, Xuan, Zeta potential measurement of zeolites, alumina and silica

Lu, Haolin, Sorption of enzymatically and chemically modified spruce galactoglucomannans and guar gum to cellulose fibers

Pérez Nebreda, Andrea, Acid hydrolysis of O-acetyl-galactoglucomannan in a continuous reactor

Sultan, Muhammad Asad, Laboratory method for soot blower tests in elevated temperatures

Suominen, Sara, An electrochemical flow system with screen-printed electrodes for thiolated polyaniline for biosensor applications

4.2 Publications

4.2.1 Articles in refereed international scientific journals and series (136)

1. Ahlkvist, J., Samikannu. A., Larsson, W., Mikkola, J-P., Catalytic transformation of Nordic pulp media into green platform chemicals, *Applied Catalysis A: General*, 454 (2013), 21-29 (Elsevier B.V., ISSN: 0926-860X)

2. Ahlkvist, J., Samikannu. A., Larsson, W., Wärnå, J., Salmi, T., Mikkola, J-P.,

Reaction network upon one-pot catalytic conversion of pulp, *Chemical Engineering Transactions*, 32 (2013), 649-654 (Italian Association of Chemical Engineering – AIDIC, ISSN: 1974-9791)

3. Aho, A., Käldsröm, M., Kumar, N., Eränen, K., Hupa, M., Holmbom, B., Salmi, T., Fardim, P., Murzin, D. Yu., Pyrolysis of beet pulp in a fluidized reactor, *Journal of Analytical and Applied Pyrolysis*, 104 (2013), 426-432 (Elsevier B.V., ISSN: 0165-2370)

4. 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 (2013), 22-29 (Elsevier B.V., ISSN:0960-8524)

5. Anttila, A-K., Pirttilä, A.M., Häggman, H.H., Harju, A., Venäläinen, M., Haapala, A., Holmbom, B., Julkunen-Tiitto, R., Condensed conifer tannins as antifungal agents in liquid culture, *Holzforschung*, 67 (2013) 7, 825-832 (Walter de Gruyter GmbH & Co. KG, ISSN: 0018-3830)

6. de Araujo Filho, C.A., Salmi, T., Bernas, A., Mikkola, J-P., Kinetic model for homogeneously catalyzed halogenation of glycerol, *Industrial & Engineering Chemistry Research*, 52 (2013) 4, 1523–1530 (ACS Publications, ISSN: 0888-5885)

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Stekrova, M., Kumar, N., Mäki-Arvela, P., Volcho, K., Salakhutdinov, N., Murzin, D. Yu., Isomerizations of α-pinene oxide and verbenol oxide over Fe- and Ce-supported catalysts, *10th Congress on Catalysis Applied to Fine Chemicals*, June 16-19, 2013, Turku, Finland, P25

Sterchele, S., Biasi, P., Centomo, P., Canton, P., Cepmestrini, S., Salmi, T., Zecca, M., Pd-Pt catalysts supported on an ion-exchange resin for direct synthesis of hydrogen peroxide, *EuropaCat XI*, September 1-6, 2013, Lyon, France, 3-T6-202

Strand, A., Zasadowski, D., Norgren, M., Hedenström, E., Willför, S., Sundberg, A., Selective froth flotation of pitch components from spruce TMP process water, Proceedings: *17th International Symposium on Wood, Fibre and Pulping Chemistry*, June 12-14, 2013, Vancouver, BC, Canada

Sugano, Y., Levon, K., Ivaska, A., Electrochemical oxidation of polysaccharides, *10th Congress on Catalysis Applied to Fine Chemicals*, June 16-19, 2013, Turku, Finland, P 119

Sugano, Y., Aldea, S., Ivaska, A., Mikkola, J-P., Electrochemical characterization of cellulose dissolved in ionic liquid, *5th Congress on Ionic liquids*, April 21-25, 2013, Algarve, Portugal, P273

Sulman, E., Doluda, V., Wärnå, J., Aho, A., Salmi, T., Murzin, D. Yu., Konieva, M., Matveeva, V., Bykov, A., Sidorov, A., Bronstein, L., Kinetics of lactose hydrogenation over Ru nanoparticles on hypercrosslinked polystyrene, *EuropaCat XI*, September 1-6, 2013, Lyon, France, 3-T6-209

Tolvanen, P., Mäki-Arvela, P., Murzin, D., Salmi, T., Development of an environmentally friendly method of starch oxidation, *Slovak Conference in Chemical Engineering*, May 25-29, 2013, Tatranske Matliare, Slovakia

Vainio, E., Brink, A., DeMartini, N., Laurén, T., Hupa, M., Development of a method to measure low quantities of SO_3/H_2SO_4 in recovery boiler flue gas ducts, *8th International Black Liquor Colloquium Black Liquor and Biomass to Bioenergy and Biofuels*, May 19-23, 2013, Belo Horizonte, Brazil

Vainio, E., Brink, A., Hupa, M., Simulation of the reduction of nitrogen species in air jets, *Finnish-Swedish Flame Days*, 17-18 April, 2013, Jyväskylä, Finland

Vanamo, U., Bobacka, J., Adjustment of the standard potential of solid-contact ion-selective electrodes - comparison between different types of ion-selective membranes, *6th International Workshop on Surface Modification for Chemical and Biochemical Sensing (SMCBS' 2013)*, November 8-12, 2013, Łochów, Poland, 102

Varila, L., Vanamo, U., Puska, M., Vallittu, P. K., Bobacka, J., Hupa, L., Polylactic acid/bioactive glass fibre meshes for craniofacial applications, *10th Pacific Rim Conference on Ceramic and Glass Technology*, June 3, 2013, San Diego, CA, USA

Vähä-Savo, N., DeMartini, N., Hupa, M., Ziesig, R., Tomani, P., Theliander, P., Properties of reduced lignin black liquors, *8th International Black Liquor Colloquium Black Liquor and Biomass to Bioenergy and Biofuels*, May 19-23, 2013, Belo Horizonte, Brazil

Wagner, M., Kvarnström, C., Ivaska, A., Bobacka J., Electrochemical properties of novel porous carbon based material synthesized from polycyclic aromatic hydrocarbons, *64th Annual Meeting of the International Society of Electrochemistry*, September 8–13, 2013, Santiago de Queretaro, Mexico

Xu, C., Leppänen, A-S., Kisonen, V., Parikka, K., Vilaplana, F., Brumer, H., Tenkanen, M., Willför, S., Mass spectrometry as a powerful tool for characterizing the complex structure of polysaccharides and their derivatives: case studies, Proceedings: *17th International Symposium on Wood, Fibre and Pulping Chemistry*, June 12-14, 2013, Vancouver, BC, Canada

Yu, K., Kumar, N., Ivaska, A., Synthesis, characterization and application of polypyrrole-zeolite nanocomposites, *14th International Symposium on Electroanalytical Chemistry (14th ISEAC)*, August 17-20, 2013, Changchun, China, P-164

Zasadowski, D., Strand, A., Sundberg, A., Willför, S., Edlund, H., Hedenström, E., Norgren, M., Selective flotation – Key for chemical recovery and better production processes,

Proceedings: *17th International Symposium on Wood, Fibre and Pulping Chemistry*, June 12-14, 2013, Vancouver, BC, Canada

Zhang, Z., Jain, H., Hupa, M., Hupa, L., *In vitro* degradation of tailored amorphous multi porous bio-scaffold, *13th Conference of the European Ceramic Society*, June 23-27, 2013, Limoges, France

Zhang, D., Li, N., Hupa, L., *In vitro* degradation of holmium containing lithium silicate glasses, *23rd International Conference on Glass*, July 1-5, 2013, Prague, Czech Republic

4.4 Edited Conference Proceeding and Reports (9)

Hajek, J., von Schoultz, S., Eränen, K., Salmi, T., Valorization of heavy tall oil fractions, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering Reports*, 2013, 36 pp.

Hupa, M., Frandsen, F., Gupta, R., Harding, S., Mueller, C., Wall, T., Wigley, F., Zevenhoven, M. (eds.), Proceedings: Impacts of Fuel Quality on Power Production and Environment, *Fuel Processing Technology*, 105 (2013), 1-222 (Elsevier B.V., ISSN: 0378-3820)

L'Huissier, M., Catalytic and non-catalytic kinetic model simulation of the oxidation of Fe(II) into Fe(III) as a part of the coagulation-flocculation step for water treatment, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering Reports,* 2013, 44 pp.

Ljung, M. (ed.), *Graduate School in Chemical Engineering Yearbook 2013*, Åbo Akademi University 2013, ISSN: 1238-2647, Juvenes Print, Åbo, Finland, 2013

Ljung, M., Brink, A., Latonen, R-M., Mäki-Arvela, P., Sundberg, A. (eds.), *Åbo Akademi Process Chemistry Centre Annual Report 2012-2013*, Åbo Akademi University 2013, ISSN: 1459-8213, Newprint, Loimaa, Finland, 2013

Murzin, D. Yu., Mäki-Arvela, P., Salmi, T. (eds.), Proceedings: 15th Nordic Symposium on Catalysis, Mariehamn, Åland, June 16-18, 2012, *Topics in Catalysis* 56 (2013) 9-10, 511-855 (Springer New York LLC, ISSN: 1022-5528)

Murzin, D. Yu. (ed.), *Advances in Chemical Engineering*, Chemical Engineering for Renewables Conversion, 42 (2013), 2-371 (Elsevier B.V., ISBN: 978-0-12-386505-2)

Tolvanen, P.,Viscosity steering of selected organic molecules, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering Reports*, 2013, 69 pp.

Verove, A., Epoxidation of vegetable oil assisted by microwaves, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering Reports*, 2013, 10 pp.

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

Banbrytande forskning inom biomassa: kemikalier från hemicellulosor - från katalysatorutveckling till design av nya reaktorstrukturer, *Redox 2013* (Kemistklubben vid Åbo Akademi), Tapio Salmi

Haikeat jäähyväiset lännelle, *Kanava*, 4 (2013), 31-35 (Otavamedia, ISSN: 0355-0303), Tapio Salmi

CAFC10–10th Congress on Catalysis Applied to Fine Chemicals – Katalys- och finkemikaliekonferens i Åbo blev en dynamisk internationell träffpunkt, *Kemia-Kemi* (2013), (Kempulssi Oy, ISSN: 0355-1628), Tapio Salmi

Har vi råd med små ämnen vid våra universitet?, *Ny Tid*, November 13 (2013), (Tigertext Ab, ISSN: 1456-0518), Tapio Salmi

4.8 Patents and invention disclosures (4)

Aldea S., Grénman, H., Mikkola, J-P., Murzin, D. Yu., Salmi, T., Snåre M., Framställning av saltpartiklar från utfällt kalciumkarbonat, *Finnish Patent Application* No. 20135191

Häärä, M., Vähäsalo, L., Monitoring of inorganic precipitate formation, U/12/2013

Korpinen, R., Raitanen, J.-E., Willför, S., Kleen, M., Kallraffinering och extraktion av biomassor, U/01/2013

Riittonen T., Kumar, N., Mikkola, J-P., Manufacturing of alkyl-ethers, 2012/2013, *Finnish Patent Application* No. 20126071

4.8 Awards granted (4)

Akieh-Pirkanniemi, Marceline Neg, Alfthanska priset (Alfthan Prize), awarded by Finska Kemistsamfundet

Salmi, Tapio and Murzin, Dmitry, Kanslerspriset (The Chancellor's Prize), research leaders of the year, awarded by the Chancellor of Åbo Akademi Jarl-Thure Eriksson

Saloranta, Tiina, Per Brahe-priset (Per Brahe Prize), awarded by the Åbo Akademi University Foundation

5. Other Activities 2013

5.1 Organization of Conferences, Courses and Seminars

February

Turku/Åbo, Finland, PCC Winter Colloquium

May

Baltic Sea, Graduate School in Chemical Engineering (GSCE) Spring Seminar

Turku/Åbo, PCC workshop on microscopic techniques

June

Repino, St Petersburg, Russia, Renewable Plant Resources and Organic Chemistry (RR-2013)

Turku/Åbo, Finland, 10th Congress on Catalysis Applied to Fine Chemicals

August

Turku/Åbo, Finland, PCC Annual Seminar

September

Turku, Finland, COST FP0901 Final Meeting

October

Turku/Åbo, Finland, Course: Non-cellulosic Plant Polysaccharides

Turku/Åbo, Finland, Course: Towards New Reactor Technology

November

Porvoo, Finland, Graduate School in Chemical Engineering (GSCE) Annual seminar

Turku/Åbo, Finland, Course: Modern Analytical Tools for Pulp and Paper

Turku/Åbo, Finland, Course: Reaction Kinetics (November-December)

5.2 Participation in Conferences, Major Meetings and Courses

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

January

Helsinki, Finland, Panel discussion on engineering education in Finland, *Tapio Salmi*

Palermo, Italy, UBIOCHEM Cost action CM09, 9

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

February

Krakow, Poland, European Winter Conference on Plasma Spectrochemistry, 1

March

Brno, Czech Republic, 66th IEA-FBC meeting, committee member, *Patrik Yrjas*

Helsinki, Finland, ChemBio Finland, Chemistry and Biotechnology exhibition, 1

Helsinki, Finland, Seminar of Finnish Catalysis Society, *Päivi Mäki-Arvela*

Houston, USA, North American Symposium on Chemical Reaction Engineering, NASCRE, 2

Karlsruhe, Germany, Helmholtz-Allianz für Energie-effiziente Dreiphasenreaktorsysteme, Halbjahrestreff, *Tapio Salmi*

Kolkata, India, Central Glass and Ceramic Research Institute, guest lecturers, *Leena Hupa and Susanne Fagerlund*

Lappeenranta, Finland, MICROFIN National Microtechnology Symposium, 5

Philadelphia, USA, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy 2013 (PITTCON 2013), invited lecturer, *Johan Bobacka*

Sorrento, Italy, Third International Conference on Multifunctional, Hybrid and Nanomaterials, 2

April

Algarve, Portugal, 5th Congress on Ionic liquids, 7

The Hague, the Netherlands, ECCE-EKAB, 9th European Congress of Chemical Engineering + 2nd European Congress of Applied Biotechnology, 6

Helsinki, Finland, Annual meeting of the Finnish Ceramic Society, 2

Helsinki, Finland, Societas Scientiarum Fennica, 175 year celebration, *Dmitry Murzin and Tapio Salmi*

Jyväskylä, Finland, Finnish-Swedish Flame Days, invited lecturer, *Mikko Hupa*, 7

Sitges, Spain, 1st International Conference on Desalination using Membrane Technology, 1

Trondheim, Norway, Cenbio Days, invited lecturer, *Nikolai DeMartini*

May

Aberdeen, Scotland, UK, All-Energy Conference, 1

Baltic Sea, Graduate School in Chemical Engineering (GSCE) Spring Seminar, 7

Belo Horizonte, Brazil, 8th International Black Liquor Colloquium Black Liquor and Biomass to Bioenergy and Biofuels, invited speaker, *Mikko Hupa*, 4

Dresden, Germany, 60 Jahre Chemische Verfahrenstechnik in TU Dresden, *Tapio Salmi*

Espoo, Finland, EURACHEM Workshop on Quality Assurance of Measurements from Field to Laboratory, invited lecturer, *Johan Bobacka*

Helsinki, Finland, Nordic Polymer Days, 1

La Rochelle, France, ISGC2 Green Chemistry Symposium, 2

Rouen, France, INSA-Rouen, Researchers meeting, *Tapio Salmi*

Sitges, Spain, Frontiers in Polymer Science 2013, 1

St. Petersburg, Russia, Technical University, guest lecture, *Tapio Salmi*

Tatranske Matliare, Slovak Congress on Chemical Engineering, 2

June

Clearwater, Florida, USA, Clearwater Clean Coal Conference 38th International Technical Conference on Clean Coal & Fuel Systems, 1

Kraków, Poland, XII Conference on Electroanalysis in Theory and Practice, 2

Lappeenranta, Finland, 23th European Congress of Computer Aided Process Engineering (ESCAPE), 2

Limoges, France, 13th Conference of the European Ceramic Society, 2

Milan, Italy, AIDIC, Conference on Chemical & Process Engineering, 3

Pisa, Italy, IFRF Joint Committee Meeting JC 160, 1

Pisa, Italy, ToTeM 39, 1

Repino, St. Petersburg, Russia, Renewable Plant Resources and Organic Chemistry (RR-2013), invited lecturer, *Stefan Willför and Bjarne Holmbom*, co-organizer: *Andery Pranovich*

San Diego, CA, USA, 10th Pacific Rim Conference on Ceramic and Glass Technology, 1

Southampton, UK, Southampton Electrochemistry Summer School "Instrumental Methods in Electrochemistry", 3

Stockholm, Sweden, Sustainable Chemistry and Process Technology for the Northern Baltic Region (POKE) network meeting

Tromsø, Norway, XXXVIII Colloquium Spectroscopicum Internationale, 1

Turku, Finland, 10th Congress on Catalysis Applied to Fine Chemicals, 17

Vancouver, Canada, 17th International Symposium on Wood, Fibre and Pulping Chemistry, ISWFPC, 2

July

Arkhangelsk (Solovetskij Island), Russia, V International Conference "Physical Chemistry of Plant Polymers", plenary lecture, *Andrey Pranovich*

Lund, Sweden, Second International Conference Catalysis for Renewable Sources: Fuel, Energy, Chemicals, plenary lecture, *Tapio Salmi*, 2

Prague, Czech Republic, 23rd International Congress on Glass, 4

August

Changchun, China, 14th International Symposium on Electroanalytical Chemistry (14th ISEAC), 4

Helsinki, Finland, FIBIC seminar, Ionic liquids and Food Processing, 3

Lund, Sweden, CECOST Graduate School, CISS 2013, 1

Lyngby, Denmark, Technical University of Denmark, Operational Challenges of Biofuel Utilization for Heat and Power Production and Bio Refinery, invited lecturers, *Mikko Hupa and Leena Hupa*, 2

September

Helsinki, Finland, Tekes seminar: Functional Materials Four Seasons, 7

Helsinki, Finland, Energy Seminar, *Päivi Mäki-Arvela*

Indianapolis, Indiana, USA, 246th ACS National Meeting and Exposition, 1

Leuven, Belgium, Composites week @ Leuven and TexComp-11 conference, 1

Lyon, France, EuropaCat, XIth European Congress on Catalysis, plenary lecture, *Dmitry Murzin*, 10

Nancy, France, WoodChem 2013, 1

Perugia, Italy, 4th annual meeting of the COST Action CM0901, 1

Ponferrada, Spain, 3rd Oxyfuel Combustion Conference, 2

Riva del Garda, Italy, International Conference on Diamond and Carbon Materials 2013, 2

Santiago de Queretaro, Mexico, 64th Annual Meeting of the International Society of Electrochemistry, 4

Turku, Finland, Final Seminar COST FP 0901 "Analytical Techniques for Biorefineries",

October

Birmingham, UK, BRISK EU-FP7 project, general assembly, 1

Bochum, Germany, Helmholtz-Allianz für Energie-effiziente Dreiphasenreaktorsysteme, Halbjahrestreff, *Tapio Salmi*

Budapest, Hungary, 1st EuCheMS Congress on Green and Sustainable Chemistry, 1

Cartagena, Spain, European Scientific Network for Artificial Muscles (ESNAM) Training School, 5

Espoo, Finland, CFD-päivä, 1

Fredericton, New Brunswick, Canada, 63rd Canadian Society of Chemical Engineering (CSChE) Conference, 1

Gothenburg, Sweden, Industrial Biotechnology for Lignocellulose Based Processes, Chalmers University of Technology, invited lecturer, *Stefan Willför*

Jyväskylä, Finland, Nanoscience Days 2013, 6

Lyon, France, SFGP2013 - XIVe congrès de la Société Française de Génie des Procédés, 1

Montreal, Quebec, Canada, Materials Science and Technology 2013, 1

Nice, France, 3rd EPNOE International Polysaccharide conference, 3

Turku, Finland, Turku Biomaterials Days, lecture, *Leena Hupa*, 4

Valencia, Spain, 4th International Workshop of COST Action CM0903, Sustainable production of fuels/energy, materials & chemicals from biomass, 9

Vantaa, Finland, Soodakattilapäivät, 1

Vasa, Finland, Sustainable Chemistry and Process Technology for the Northern Baltic Region (POKE) network meeting

November

Delft, Germany, TU Delft Process Technology Annual Seminar and International Advisory Board Meeting, *Tapio Salmi*

Łochów, Poland, 6th International Workshop on Surface Modification for Chemical and Biochemical Sensing (SMCBS 2013), keynote lecture, *Johan Bobacka*, 2

Porvoo, Finland, GSCE fall seminar, 7

Turku, Finland, 1st Royal Society of Chemistry RSC Finnish Section Annual Seminar, invited lecturers, *Andrey Pranovich and Dmitry Murzin*

December

Auckland, New Zealand, 12th International Conference on Frontiers of Polymers and Advanced Materials, 2

Långvik, Finland, Graduate School on Chemical Sensors and Microanalytical Systems (CHEMSEM) Annual Seminar, 1

Stockholm, Sweden, LignoFuel meeting, 2

Tallinn, Estonia, Sustainable Chemistry and Process Technology for the Northern Baltic Region (POKE) network meeting

5.3 Visitors and Visits

Visitors to the PCC

- Bober, Patrycja, Institute of Macromolecular Chemistry, Czech Republic (September–November)
- Boeva, Zhanna, Lomonosov Moscow State University, Russia (January–March, August-November)
- Bourhis, Kevin, Politecnico di Torino, Italy (June)
- Boymirzaev, Azamat, Namamgan Institute of Engineering and Technology, Uzbekistan (February–October)
- Das, Indranee, Central Glass and Ceramic Research Institute, Kolkata, India (September–November)
- Demidova, Yulia, Boreskov Institute of Catalysis, Novosibirsk, Russia (October)
- Dorofeeva, Elizaveta, Saint-Petersburg Technological Institute, Russia (August)
- Dumitriu, Cristina, Politehnica University Bucharest, Romania (August)
- Dönmez, Emrah, Suleyman Demirel University, Turkey (June–August)
- Efimkin, Dmitry, Mendeleev University of Chemical Technology, Moscow, Russia (June)
- Fomchenkov, Mikhail, Tomsk State University, Russia (September–October)
- Fortes, Mariana, University of Rio de Janeiro, Brazil (May–June)
- Freites, Adriana, Simon Bolivar University, Venezuela (September–December)
- Gallina, Gianluca, University of Padova, Italy (June–December)
- Garcia-Serna, Juan, University of Valladolid, Spain (March–October)
- Gemo, Nicola, Italy, University of Padova, Italy (June–December)
- Gudarzi, Davood, Lappeenranta University of Technology, (August)

- Hebda Edyta, Cracow University of Technology, Poland (April)
- Hilgert, Jakob, Max-Planck Institut für Kohlenforschung, Germany (August, November)
- Huerte Illoza, Irene, University of Valladolid, Spain (January–February)
- Iisa, Anna, University of Colorado, USA (May–July)
- Kaewthai Andrei, Nomchit, Rajamangala University Srivijaya, Thailand (September)
- Kholkina, Ekaterina, Saint Petersburg Technological Institute, Russia (August)
- Kiss, Andras, University of Pecs, Hungary (March–June)
- Konwar, Lakhya, Tespur University, Tezpur, India (November–December)
- Lane, Daniel, University of Adelaide, Australia (February–June)
- L'huissier, Margaux, Université de Rennes, Rennes, France (May–August)
- Li, Bin, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, China (August–December)
- Malinovskiy, Alexandr, Russian University of Chemical Technology, Mendeleev, Moscow, Russia (August)
- Mayran, Marielle, Ecole Polytechnique Universitaire de Montpellier, France (May–August)
- Milakin, Konstantin, Lomonosov Moscow State University, Russia (September–December)
- Nikitich, Marina, Tomsk State University, Tomsk, Russia (May)
- Paiva, Eduardo, Universidade Federal do Paraná, Paraná, Brazil (March–December)
- Rujana, Luis, Simon Bolivar University, Caracas, Venezuela (September–December)
- Russo, Vincenzo, University of Naples, Italy (November–December)
- Shaimardan, Minavar, A. B. Bekturov Institute of Chemical Sciences, Kazakhstan (June–July)
- Shpotyuk, Yaroslav, Université de Rennes, France (October–December)

- da Silva Antonio, Jadielson Lucas, University of Sao Paolo, Brazil (August–December)
- Sterchele, Stefano, University of Padova, Italy (May–December)
- Stekrova, Martina, Institute of Chemical Technology, Prague, Czech Republic (January–February)
- Strobl, Florian, Erlangen-Nuremberg University, Germany (January–March)
- Stzalkowska, Sylwia, University of Warsaw, Poland (January–October)
- Sugano, Yasuhito, Osaka University, Japan (January–December)
- Szucs, Julia, Budapest University of Technology and Economics, Hungary (January)
- Torbina, Viktoriia, Tomsk State University, Russia (September–October)
- Vajglova, Zuzana, Institute of Chemical Process Fundamentals, ASCR, Czech Republic (September–November)
- Vassallo-Breillot, Morgane, Ecole Polytechnique Universitaire de Montpellier, France (May–August)
- Verove, Antoine, INSA Rouen, France (May–August)
- Vieira Viegas, Carolina, University of Rio de Janeiro, Brazil (May–June)

Visits by PCC Members

- Dax, Daniel, University of Concepción, Chile (April-September)
- Fagerlund, Susanne, Central Glass and Ceramic Research Institute, Kolkata, India (March)
- He, Ning, Budapest University of Technology and Economics, Hungary (March-June, September-December)
- Hupa, Leena, Central Glass and Ceramic Research Institute, Kolkata, India (March)
- Ivaska, Ari, Spain (October)
- Laurén, Tor, Sweden (November)
- Lindfors, Tom, Budapest University of Technology and Economics, Hungary (April-May)

- Lindfors, Tom, Lomonosov Moscow State University, Russia (October)
- Lisak, Grzegorz, University of Wollongong, Australia (February-May, September-December)
- Liu, Jun, KTH Royal Institute of Technology, Sweden (January-April, September-October)
- Pranovich, Andrey V., St. Petersburg Forest Technical University, Russia (April)

5.4 External PhD Examinations and Reviews

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

Board member of Raisio Research Foundation, *Tapio Salmi*

Board member of European Federation of Catalysis Societies, *Päivi Mäki-Arvela*

Board member of Finnish Catalysis Society, *Tapio Salmi*

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

Chairman of the organizing committee, CAFC10-Catalysis Applied to Fine Chemicals, Turku, Finland, *Dmitry Murzin*

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

Editorial board member for *Nordic Pulp and Paper Research Journal*, Mittuniversitetet, Sweden, *Anna Sundberg*

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

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

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

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

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

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

Editorial Board Member for *ISRN Analytical Chemistry* (Hindawi), *Andrzej Lewenstam*

Editorial Board Member for *Advances in Analytical Chemistry* (S&AP), *Andrzej Lewenstam*

Evaluation of a project for the Natural Sciences and Engineering Research Council of Canada, *Jun Liu*

Evaluation of Professorship in Bio-based Materials, Aalto University, *Bjarne Holmbom*

Evaluation of Senior Researcher in Forest Products and Chemical Engineering, Department of Chemical and Biological Engineering, Chalmers University of Technology, Sweden, *Bjarne Holmbom*

Evaluation of scientific competence, National Research Foundation of South Africa, *Anna Sundberg, Stefan Willför*

Evaluation of VTT's Fibre value chain research, *Bjarne Holmbom*

Evaluation of project for The Knowledge Foundation, Sweden, *Bjarne Holmbom*

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

Evaluation of Docentship in Environmental catalysis in catalysts, University of Oulu, Finland, *Päivi Mäki-Arvela*

Evaluator of Docentship, Chalmers University, Sweden, *Dmitry Murzin*

Expert for the Qatar Research Council, *Dmitry Murzin*

Expert for the Danish Research Council, *Dmitry Murzin*

Expert (water, environment) for Ålands Landskapsstyrelse, April 2013, Åland, Finland, *Stefan Willför*

Expert in nomination of Dr Vesa Virtanen to Professor in Chemistry at the University of Oulu, *Ari Ivaska*

Finnish representative in the board of Nordtek, *Stefan Willför*

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

Guest Editor, Catalysis Today, *Dmitry Murzin*

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

Member of the board in selecting the candidates to the Chair in Physical Chemistry at Aalto University, *Ari Ivaska*

Member of the International Advisory Board, 2nd International Symposium on Green Chemistry, Renewable carbon and Eco-Efficient Processes, La Rochelle, France, *Dmitry Murzin*

Member of scientific committee, UBIOCHEM 4, Valencia, Spain, *Dmitry Murzin*

Member of the Scientific Meetings Committee (SMC) of the International Society of Electrochemistry (ISE), 2012–2014, *Johan Bobacka*

Member of the expert group "Vasa Preservation Council" 2012- , Stockholm, Sweden, *Bjarne Holmbom*

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 the COST action CM1206 (EXIL) 2013-, *Jyri-Pekka Mikkola*

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

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

Session chairman, CAFC10- catalysis applied to fine chemicals, Turku, Finland, *Tapio Salmi, Dmitry Murzin, Päivi Mäki-Arvela*

Session chairman, Europacat 12, Lyon, *Dmitry Murzin, Päivi Mäki-Arvela*

Suomen Vetytiekartta, report, *Mikael Bergelin*

Vice-president of the scientific committee, Catalysis for renewable sources-2, Lund, Sweden, *Dmitry Murzin*

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

External Examinations

Abejon, Ricardo, Universidad de Cantabria, Spain, opponent, *Tapio Salmi*

Alakurttila, Sami, University of Helsinki, Finland, opponent, *Stefan Willför*

Boro, Jutika, Tezpur University, India, evaluator, *Jyri-Pekka Mikkola*

Faba, Laura, University of Oviedo, Spain, opponent, *Dmitry Murzin*

Gräsvik, John, University of Umeå, Sweden, member of the committee, *Päivi Mäki-Arvela*

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

Hakola, Maija, University of Helsinki, Finland, reviewer, *Bjarne Holmbom*

Halonen, Niina, University of Oulu, Finland, pre-reviewer, *Ari Ivaska*

Karlsson, Anette, Mid Sweden University, Sweden, examination committee for doctoral thesis, *Bjarne Holmbom*

Krawczyk, Holger, Lund University, Sweden, examination committee for doctoral thesis*, Anna Sundberg*

Liimatainen, Jaana, University of Turku, Finland, opponent, *Stefan Willför*

Stepan, Agnes, Chalmers University of Technology, Sweden, examination committee for doctoral thesis, *Chunlin Xu*

Takkunen, Laura, University of Eastern Finland, Finland, reviewer*, Leena Hupa*

Varhimo, Pekka, Aalto University, Finland, reviewer, *Anna Sundberg*

Wang, Yong-Lei, Stockholm University, Sweden, evaluation committee, *Jyri-Pekka Mikkola*

Invited Lecturers at ÅA-PCC

Compton, Richard G, Oxford University, United Kingdom

De Marco, Roland, University of the Sunshine Coast, Australia

Han, Xiaojun, Harbin Institute of Technology, China

John, Lukasz, University of Wroclaw, Poland

Kaewthai Andrei, Nomchit, Rajamangala University Srivijaya, Thailand

Kuhn, Alexander, University of Bordeaux, France

Papayannakos, Nikos, National Technical University of Athens, Greece

Petterson, *Lars J,* KTH Royal Institute of Technology, Sweden

Serrano Ruiz, Juan Carlos, Abengoa Research, Spain

5.5 Publicity

Television and Radio

COST FP0901 final seminar, Radio Vega 17.9.2013, *Stefan Willför*

Participation in one of the films ”Jordklotet, Lyckan och Jag - tre filmer om hållbar utveckling”. Sustainability is presented from three different points of view; the natural resources, the society and the individual, *Stefan Willför*

TV interview, 18.2.2013, *Stefan Willför*

VAT'N – H_2O, press conference, 7.3.2013, *Stefan Willför*

Newspapers and General Journals

Alger blir grön diesel, Åbo Underrättelser, 26.2.2013, *Dmitry Murzin, Päivi Mäki-Arvela, Henrik Grénman*

Suomen kulttuurirahasto jakoi apurahat, Pohjoisen Itämeren alueen kestävää kemiaa ja prosessiteknologiaa käsittelevään Tieteen työpajaan, Turun Sanomat, 28.2.2013, *Tapio Salmi*

Åbo Akademin professoreille 50000 euron kansleripalkinto, Turun Sanomat, 9.10.2013, *Tapio Salmi, Dmitry Murzin*

Appendix I

Åbo Akademi Process Chemistry Centre Doctoral Theses in Progress 2014

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.
- Meheretu Jaleta Dirbeba (Ethiopia, M), MSc Addis Ababa University, Ethiopia 2013, BSc ibid. 2003
- Lidia Godina (Russia, *F*), MSc Mendeleyev University of Chemical Technology of Russia, Moscow, Russia 2012
- Imane Hachemi (Algeria, *F*), MSc University of Sciences and Technology Houari Boumediene (USTHB) 2012, BSc Ibid., Algiers, Algeria, 2009
- Tooran Khazraie Shoulaifar (Iran, *F*), MSc Sharif University of Technology, Tehran, Iran 2007, BSc Tehran University, Tehran, Iran 2002
- Antonina Kupareva, (Russia, *F*) MSc Gubkin Russian State University of Oil and Gas, Moscow Russia 2008
- Ekaterina Korotkova (Russia, *F*), MSc ÅA (2011) & Tver State Technical University, Tver, Russia (2010) (double degree), BSc Tver State Technical University, Tver, Russia 2008
- Ron Lai (Canada, *M*), MSc University of British Columbia, Vancouver, Canada 1994
- Ewelina Leino (Poland, *F*), MSc Silesian University of Technology, Gliwice, Poland 2006
- Na Li (China, *F*), MSc ÅA 2007, BSc Shandong Institute of Light Industry, China 2005
- Jun Liu (China, *M*), MSc Tianjin University of Science and Technology, China 2012
- Donald MacNeil (Canada, *M*), MSc ÅA 2002, BEng Dalhousie University, Halifax, Canada 1994
- Gerson Martin Curvelo (Venezuela, *M*), MSc Universidad Simón Bolivar, Caracas, Venezuela 2008
- Konstantin Milakin (Russia, M), MSc M.V. Lomonosov Moscow State University, Moskow, Russia 2011

- He Ning (China, *M*), MSc ÅA 2009, BSc Shandong Polytechnic University, China 2007
- Andrea Pérez Nebreda (Spain, F), MSc Universidad de Cantabria, Santander, Spain, 2013
- Ricardo Miguel Pezoa Conte (Chile, M), MSc University of Chile, Santiago, Chile, 2010
- 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
- Farhan Saleem, (Pakistan, M), MSc. ÅA, 2013, Bachelor in Chem. Tech. University of Karachi, Pakistan 2007
- Sabrina Schmidt (Germany, *F*), Diplom Chemiker RWTH Aachen University, Aachen, Germany 2010
- Jadielson Lucas da Silva Antonio (Brazil, M), BSc Federal Rural University of Pernambuco, Recife, Brazil 2010
- Jingxin Sui (China, *M*), MSc ÅA 2011, BSc Shandong Institute of Light Industry, China 2009
- Hao Wu (China, *F*), MSc ÅA 2007, BSc Shandong Institute of Light Industry, China 2005
- Kai Yu (China, *M*), MSc ÅA 2010, BSc Shandong Polytechnic University, China 2008

Doctoral Students from Finland

Part-time and external students included

- Stina Grönqvist (Tuusniemi, F), MSc ÅA 2000
- Sari Hyvärinen (Viitasaari, *F*), MSc ÅA 2007
- Matti Häärä (Åbo, *M*), MSc ÅA 1994
- Petri Kilpeläinen (St. Michel, *M*), MSc University of Helsinki 2002
- Victor Kisonen (Masku, *M*), MSc University of Turku 2005
- Jens Krogell (Mariehamn, *M*), MSc ÅA 2009
- Christian Lindfors (Helsingfors, *M*), MSc Helsinki University of Technology 2008
- 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
- Timo Petteri Suominen (Tammerfors, *M*), MSc ÅA 2007
- Ulriika Vanamo (Åbo, *F*), MSc ÅA 2008
- Leena Varila (Vasa, *F*), MSc ÅA 2011
- Niklas Vähä-Savo (Björneborg, *M*), MSc ÅA 2009