Åbo Akademi
Process Chemistry Centre

Annual Report 2008 – 2009

Edited by Maria Ljung, 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. Bjarne Holmbom)*
- *Kinetics and Catalysis (Prof. Tapio Salmi)*
- *Process Analytical Chemistry (Prof. Ari Ivaska)*

The PCC conducts research in detailed physico-chemical processes in environments of industrial importance, in order to meet the needs of tomorrow's process and product development. This approach, with the focus on the detailed understanding of the process chemistry, we have called Molecular Process Technology.

The PCC Industrial Advisory Board (2009): Örjan Andersson (Novia), Ilmo Aronen (Raisio), Håkan Gros (Danisco), Lars Gädda (Forestcluster), Markku Karlsson (UPM-Kymmene), Bertel Karlstedt (Nordkalk), Eeva-Liisa Lakomaa (Vaisala), Timo Leppä (Chemical Industry Federation of Finland), Lars Peter Lindfors (Neste Oil), Jarkko Partinen (Outotec), Ismo Reilama (Metsä-Botnia), Bengt-Johan Skrifvars (Top Analytica), Kenneth Sundberg (Ciba Finland), Kari Toivonen (Elomatic) and Petri Vasara (Pöyry).

The PCC Scientific Advisory Board (2009): Professor Douglas Reeve (University of Toronto), Professor Jean-Claude Charpentier (CNRS, Lyon) and Professor Jiri Janata (Georgia Institute of Science and Technology, Atlanta).

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Åbo Akademi PCC Annual Report 2008–2009

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1. Preface and Introduction 2008

Background

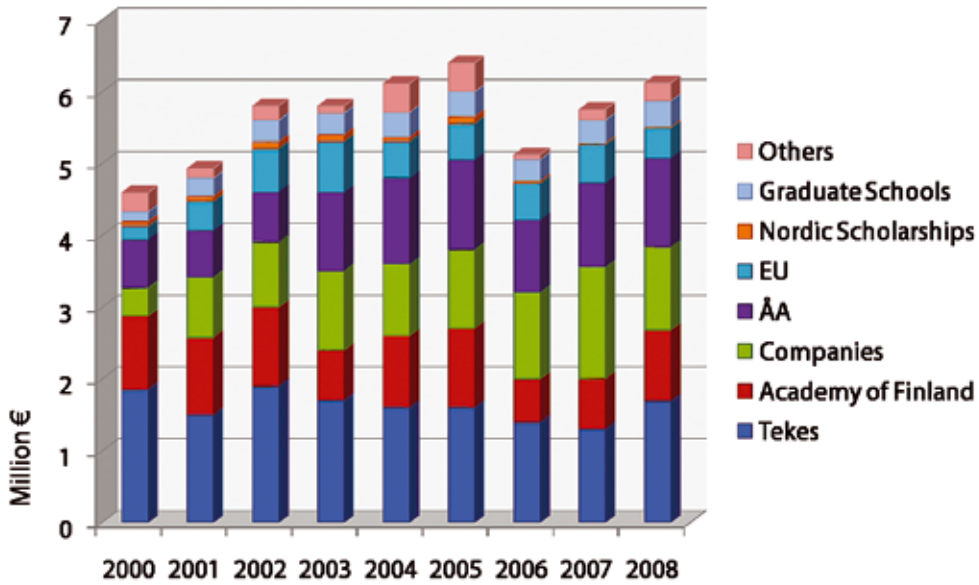
At the Åbo Akademi Process Chemistry Centre (PCC) we study detailed physico-chemical processes in complex environments of industrial importance, in order to meet the needs of tomorrow's process and product development. This approach, with the focus on the detailed understanding of the process chemistry, we have called *Molecular Process Technology*.

The PCC was formed in 1998 by joining four research groups at the Faculty of Chemical Engineering at Åbo Akademi into one research centre with common objectives and research strategy. In 2008–2009 altogether about 30 senior researchers and around 50 PhD candidates worked in the 56 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 year 2008 was the third year of our second six-year period (2006–2011) as a National Centre of Excellence in research appointed by the Academy of Finland.

The Year 2008 in Numbers

Economically, the year 2008 was a good one for the Centre. The overall funding was maintained on the same level as previously.



The funding of the Åbo Akademi Process Chemistry Centre 2000–2008

The detailed negotiations between the Academy of Finland and the PCC concerning the last three years of the six-year period as Centre of Excellence were concluded in the fall of 2008. The Academy of Finland, Tekes and Åbo Akademi University confirmed their support to the Centre for the next three years 2009–2011. In general the level of the basic support to the Centre was maintained on the same level as before.

From an academic point of view the year 2008 was productive. The table below gives the key numbers. Altogether 33 academic theses were finalised: nine doctoral theses, five licentiate thesis and 19 masters' theses.

Our research again resulted in altogether more than 100 papers in scientific publication series with the full referee system, and 195 other publications, reports and articles.

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

Theses and other publications by the Åbo Akademi Process Chemistry Centre 2000–2008

Besides the technical publications the PCC published two Newsletters. Our researchers also wrote popular texts in daily newspapers and journals and appeared on several radio and TV programs in the year 2008. The web pages of the PCC were renewed in 2008 to conform to the common visual image of the Centre.

Boards and Task Forces

The PCC is led by an executive board consisting of the four research group leaders, Professors Bjarne Holmbom, Mikko Hupa, Ari Ivaska and Tapio Salmi. Maria Ljung works with the coordination of the PCC and functions as secretary to the board. In 2008 the board met 10 times.

The board was supported by a Scientific Advisory Board (SAB) appointed by the Academy of Finland and an Industrial Advisory Board. In 2008 our Scientific Advisory Board consisted of the Professors Douglas Reeve from the University of Toronto, Jean-Claude Charpentier from CNRS in Lyon and Jiri Janata from the Georgia Institute of Science and Technology in Atlanta. In addition, Professor Johanna Buchert from the VTT Technical Research Centre of Finland represented the Academy of Finland and Jarmo E. Heinonen

represented Tekes, the Finnish Funding Agency for Technology and Innovation in this Board. In 2008 the Scientific Advisory Board visited the Centre in September in connection with the Annual Seminar of the Centre (September 9–10, 2008).

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.

Further, our Centre activities were supported by two internal task forces. One of the task forces has taken care of collecting all common information and statistics of the Centre, including working with the editing of this Yearbook. In 2008 the following people were participating in this task force: Anders Brink, Carita Kvarnström, Päivi Mäki-Arvela and Anna Sundberg.

The other task force has been responsible for internal communication and joint researcher meetings between the different research groups of the Centre. In 2008 the following joint meetings were organized:

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

- Matias Kangas: Structure-performance effects in zeolite catalyzed skeletal isomerization
- Michal Wagner: Electropolymerization of poly(para-phenylene) in ionic liquids
- Di Zhang: Glass-based biomaterials
- Chunlin Xu: Spruce galactoglucomannan: A potential raw material for hydrocolloids and novel advanced natural materials

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

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

In 2008 this task forces consisted of the following people: Markus Engblom, Tom Lindfors, Robin Manelius and Esa Toukoniitty.

The Centre had five well-visited lectures in its Distinguished Lecturer Series:

- Prof. *Philippe Bühlmann*, University of Minnesota, Minneapolis, MN, USA: "Electrochemical sensors for biological and environmental applications", February 7, 2008

- Dr. *Aldo R. Boccaccini*, Department of Materials, Imperial College London, UK: "Progress in the development and characterisation of bioactive scaffolds for tissue engineering", April 17, 2008
- Prof. *Akiyoshi Osaka*, Okayama University, Japan: "Current biomedical materials projects in Okayama U – Anion-substituted apatite and formation of c-axis oriented apatite nano-rods", September 4, 2008
- Prof. *Alexander Kuhn*, Université Bordeaux 1, France: "Rational design of electrodes for bioanalysis", November 6, 2008
- Prof. *J.W. Niemantsverdriet* (Hans), Eindhoven University of Technology, the Netherlands: "Synthetic fuels by the Fischer-Tropsch synthesis: Active and deactivating catalysts", November 20, 2008

Marcus Wallenberg Prize to Process Chemistry Centre

An absolute highlight of the year was when the Marcus Wallenberg Foundation in Sweden awarded their 2008 Marcus Wallenberg Prize to Prof. Bjarne Holmbom and Mr. Christer Eckerman. The Marcus Wallenberg Prize is the most prestigious international prize in the area of forest related R&D. Bjarne and Christer receive the prize "for their breakthrough research and innovation creating a platform for large-scale separation, isolation, purification and applications of chemical components in wood."

The Marcus Wallenberg Foundation noted: "By methodical research of the highest quality, the Laureates have significantly contributed to creating a platform for the forest products industry to improve and broaden its role and commercial prospects with a range of new products and implications e.g. for chemicals, energy, production efficiency and sustainability."

Awards, Best Presentations

The Åbo Akademi Alumni Society (Akademiföreningen Åbo Akademiker r.f.) granted its 2008 Scholarship to Johan Werkelin at the PCC. Johan successfully defended his PhD Thesis with the title "Ash Forming Elements and their Forms in Woody Biomass Fuels" in the fall of 2008.

Daniel Lindberg received the Harry Elving Prize for the best doctoral thesis at Åbo Akademi University 2007. Daniel's thesis was entitled "*Thermochemistry and Melting Properties of Alkali Salt Mixtures*".

Di Zhang received the 2008 Chinese Government Award for Outstanding Self-financed Student Abroad. Di Zhang's PhD thesis was entitled "*In vitro* characterization of bioactive glasses" and she successfully defended her thesis in September 2008.

Dorota Bankiewicz received the "Richard Bryers Best Paper Award" at the Conference "Impacts of Fuel Quality on Power Production and the Environment" in October 2008 in Banff, Alberta, Canada. Her paper was entitled "High temperature corrosion of steam tube materials exposed to zinc salts" and her co-authors in the paper were Patrik Yrjas and Mikko Hupa.

Susanne Fagerlund received the Award for Best Annual Report and Presentation at the Graduate School of Chemical Engineering (GSCE) Annual Meeting in November 2008 in Oulu.

New Positions

Another major recognition to the PCC researchers was the appointment of Professor Tapio Salmi to the prestigious position of Academy Professor. Academy Professor is the highest researcher position granted by the Academy of Finland and it was granted to Tapio after a very tight competition – only three of 60 applicants were appointed this time. The Director of the Academy of Finland appointed Tapio Salmi to Academy Professor for a five-year period 1.1.2009 – 31.12.2013.

This decision caused other changes in the positions at the Centre. After a careful selection procedure Dr. Johan Wärnå was appointed professor in chemical reaction engineering for the same period as Salmi's Academy Professorship, and Dr. Matias Kangas became academy lecturer (reader) in reaction engineering.

Further, Academy researcher, Dr. Jyri-Pekka Mikkola was selected among around 20 applicants to a professorship at the University of Umeå, Sweden. In order not to lose one

of its key researchers, Åbo Akademi suggested arrangement of a joint professorship (samprofessur) Åbo-Umeå for Jyri-Pekka. The proposal was accepted by the Rectors of both universities, and Jyri-Pekka was appointed professor in technical chemistry, sustainable development, starting from August, 1, 2008.

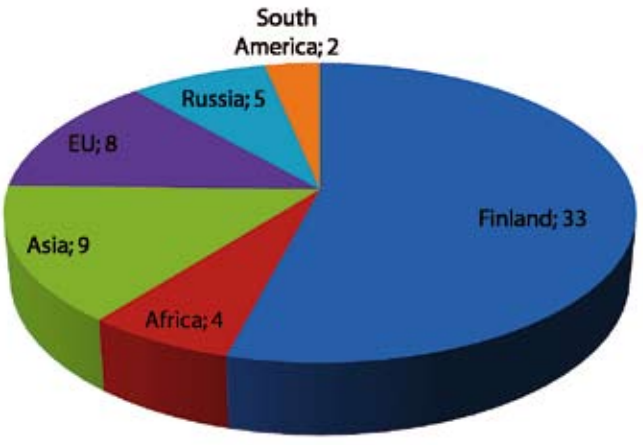
Graduate Schools and EU Projects

As in previous years, a central part of our research activities is done as part of the doctoral theses works. At the moment altogether about 60 PhD thesis projects are underway in the Centre. Many of the PhD works are done with support from the national graduate schools. At the moment the PCC is responsible for the coordination of the national Graduate School in Chemical Engineering (GSCE). The GSCE consists of altogether 26 participating laboratories at four universities: Helsinki University of Technology and Lappeenranta University of Technology, the University of Oulu and Åbo Akademi University. The Ministry of Education has granted the GSCE a continuation for the years 2007–2011 with funding for 30 full-time student positions and a coordinator. In 2008 40 students were participating in the activities of the GSCE, 10 of them from our Centre.

The PCC groups have further participated in the graduate schools of Materials Research (GSMR), Pulp and Paper Science and Technology (PaPSaT), Chemical Sensors and Micro Analytical Systems (CHEMSEM), Environmental Science and Technology (EnSTe), Nanoscience (NGS-NANO) and the Biomaterial Graduate School (BGS).

The doctoral students at the PCC are very international, and their diversity is presented in the graph below. At the moment, 41% of the PCC doctoral students are female.

In 2003 a first Nordic Graduate School was started up and is coordinated by our Centre. The Nordic Graduate School in Biofuel Science and Technology is part of the Nordic Energy Research activities funded by the Nordic Council of Ministers. This school is



Nationality of the PhD students at PCC 2008–2009

a collaborative effort by Chalmers University of Technology, the Technical University of Denmark, the Norwegian University of Science and Technology and Åbo Akademi University. This school received funding for an additional four-year period 2007–2010, thus making the continuation of this fruitful Nordic collaboration possible. The PCC acts as the coordinator for this collaborative School.

In 2008 we participated in altogether 7 EU projects. These EU projects were all wide consortia with a number of research partners in different European countries.

Bioraff

For the period 2006–2011 as Centre of Excellence we had made a completely new common overall research plan. The new overall title of our research program for the years 2006–2011 is "Sustainable Chemistry in Production of Pulp and Paper, Fuels and Energy, and Functional Materials". This plan divides our research in nine research areas. In this Annual Report all our research activities are now divided into these nine research areas.

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

Our most important project in this area has the title Chemistry in Forest Biorefineries, "Bioraff", which was started up in 2006. In this project we address a number of aspects in such concepts using tree based feed stocks, *forest biorefineries*. This project in which we collaborate with several outside groups is the largest PCC project under way and funded by Tekes and ten industrial companies. The partners and Tekes confirmed their support to this project for a next three-year period 2009–2011. The Bioraff project is coordinated by Professor Markku Auer and all four groups of the PCC actively participate in the project.

Acknowledgements

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

As previously, this annual report gives an overview of the activities in 2008 at the Centre. The report has a complete list of the journal articles, theses and other publications produced by the Centre in 2008. It also has an activity calendar listing the main events where members of the Centre have contributed or participated during the year.

The report is edited by an editorial team consisting of Maria Ljung, Anders Brink, Rose-Marie Latonen, Päivi Mäki-Arvela and Anna Sundberg. The layout was done by Paul Söderholm.

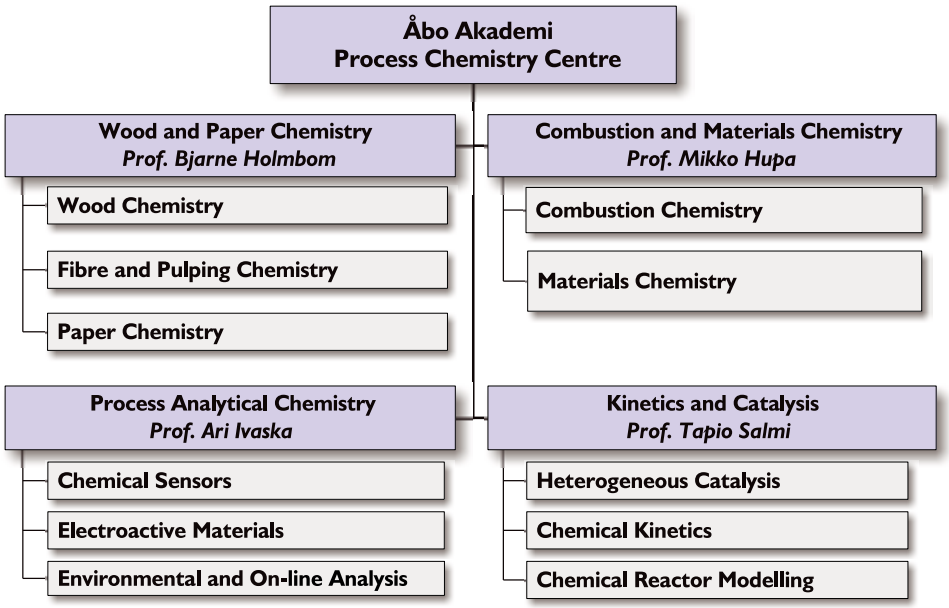
On behalf of the Board of the Åbo Akademi Process Chemistry Centre,

Mikko Hupa

Chairman

2. Organization and personnel

2.1 Organization



Åbo Akademi Process Chemistry Centre Organization

Executive Board

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

- Coordination: Maria Ljung

Industrial Advisory Board

- Örjan Andersson, Novia
- Ilmo Aronen, Raisio
- Håkan Gros, Danisco
- Lars Gädda, Forestcluster
- Markku Karlsson, UPM-Kymmene
- Bertel Karlstedt, Nordkalk
- Eeva-Liisa Lakomaa, Vaisala
- Timo Leppä, Chemical Industry Federation of Finland
- Lars-Peter Lindfors, Neste Oil
- Jarkko Partinen, Outotec
- Ismo Reilama, Metsä-Botnia
- Bengt-Johan Skrifvars, Top Analytica
- Kenneth Sundberg, Ciba Finland
- Kari Toivonen, Elomatic
- Petri Vasara, Pöyry

2.2 Wood and Paper Chemistry

The ultimate goal of our group's research is to promote sustainable and multipurpose use of wood, especially for pulp, paper, and fibre products, but also for high-value specialty biochemicals within the Forest Biorefinery concept.

We develop and apply advanced analytical techniques to obtain knowledge at the molecular level on the various components of wood, bark, and fibers and their reactions, interactions, and functions in pulping and papermaking. We also apply similar analytical techniques to non-wood natural raw materials and biochemicals, as well as their processing into renewable products. Lately, much of our research has been devoted to the extraction, recovery, functionalization, and utilization of hemicelluloses from wood, bark, and pulping liquors. Furthermore, we search for new bioactive substances in wood and bark, especially different polyphenols. These polyphenols have great potential in health-promoting foods and pharmaceutical products and as natural antioxidants and biocides.

External research support during 2008 was obtained mainly from the Academy of Finland, Tekes, and EU. Several industrial companies and foundations also supported our research.

The following new projects started during 2008:

- Improving the strength and runnability of wet paper by controlled wet end chemistry (ChemRun)
- Extraction of hemicelluloses from wood with pressurized water (HemU)
- Towards understanding of paper properties
- Bioactive and wood-associated stilbenes as multifunctional antimicrobial and health promoting agents (BioStimul)
- Biomass derived novel functional foamy materials (BioFoam)
- Lignin valorization (LigniVal)
- Global process efficiency

Furthermore, in the beginning of 2009 the following projects were started:

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

We have also participated actively in three EU-supported COST Actions and we have coordinated an application for a new Action:

- E 39: Forest, trees and human health and wellbeing
- E41: Analytical tools with applications for wood and pulping chemistry
- IE 0601: Wood science for conservation of cultural heritage
- Analytical methods for Biorefineries (application, decision due in summer 2009)

Personnel

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

Links:

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2.3 Combustion and Materials Chemistry

Combustion technologies are in state of new challenges. Completely new techniques are being developed for cleaner and more efficient combustion. "Alternative" and "Non-Fossil" fuels such as biomasses and various wastes or waste-derived fuels are heavily entering the scene especially in Europe. A large part of our Combustion and Materials Chemistry research activities is connected to the development of cleaner and more efficient combustion technologies. Our recent work has dealt with development of laboratory methods and modelling tools for prediction of the detailed behaviour of various combustion processes. The tools were tested in a number of measurement and sampling campaigns in full-scale combustion processes in many locations in Europe. These tools were used to assist the equipment manufacturing companies in their work to design novel combustion devices.

Another part of our ongoing activities dealt with inorganic materials of interest to various applications. In 2008 we continued our studies on bioactive glasses with optimized properties, we studied novel glazes which are easier to keep clean, and we applied our

electrochemical measurement systems to support the development of better fuel cell electrode materials and more effective electric capacitors.

Our project consortium Chemistry in Biofuel Combustion, ChemCom, 2008–2010 combines most of our combustion research activities into one coordinated large project. It is supported by Tekes and a consortium of international industrial companies: Andritz, Foster Wheeler Energia, Metso Power, Metsä-Botnia, UPM, Clyde Bergemann and International Paper.

We were partners in two EU projects in the year 2008. We continue coordinating the Nordic Graduate School in Biofuel Science and Technology. This graduate school is funded by the Nordic Energy Research Program and it has become an important platform to continue our long-term collaboration in the area of biofuel research with Chalmers University of Technology in Sweden, with the Technical University of Denmark and the Norwegian University of Science and Technology.

In 2008 we further worked with several projects connected to the development of fuel cell electrodes. We are making tests of electrode catalysts as well as applicability tests for other fuel cell electrode materials using our in-house measurement techniques. We also participate in a national project activity to study so called supercapacitors. These, also called ultracapacitors or electrochemical double layer capacitors can be used as energy storage, and are from a performance or energy density viewpoint situated somewhere between traditional capacitors and batteries.

Personnel

Professor	Mikko Hupa
Docents	Kaj Fröberg
	Leena Hupa
	Christian Mueller
	Bengt-Johan Skrifvars
	Heimo Ylänen
Senior researchers	Mikael Bergelin
	Anders Brink
	Nikolai DeMartini
	Linda Fröberg
	Pia Sjöberg-Eerola
	Johan Werkelin

	Patrik Yrjas
	Maria Zevenhoven
	Di Zhang
Doctoral students	Dorota Bankiewicz
& *researchers*	Markus Engblom
	Susanne Fagerlund
	Stig-Göran Huldén
	Max Johansson
	Oskar Karlström
	Tor Laurén
	Juho Lehmusto
	Bingzhi Li
	Na Li
	Isak Lindén
	Johan Lindholm
	Sam Myllynen
	Minna Piispanen
	Patrycja Piotrowska
	Linus Silvander
	Berndt Södergård
	Pasi Vainikka
	Emil Vainio
	Xiaoju Wang
	Hao Wu
Technicians	Peter Backman
	Luis Bezerra
	Jan-Erik Eriksson
	Hema Reddy Koyya
	Piia Leppäsalo
	Jaana Paananen
Secretarial staff	Eva Harjunkoski
	Mia Mäkinen

Coordination	Maria Ljung
Computer support	Peter Ekholm

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http://www.abo.fi/gsce

2.4 Kinetics and Catalysis

The research is focused on heterogeneous catalysis, chemical kinetics, modeling of chemical reactors as well as exploring new reaction environments and development of green process technology. Our know-how is continuously developed on catalyst preparation, characterization and screening. New catalytic systems have been taken in use, particularly supported nanogold catalysts, which are developed in collaboration with University of Helsinki (the group of Academy Professor M. Leskelä). The NANOCAT project financed by EU was finished and an extensive final report was published. Our focus was very much on the use of various supported carbon catalysts impregnated with precious metals. The catalysts, for instance, Pd carbon nanotubes were efficient and selective in the preparation of health-promoting components. A new concept for the production of biofuels through catalytic decarboxylation was patented abroad and extensive work was performed on the catalytic pyrolysis of wood. Supported Ionic Liquid Catalysts (SILCA) were used for transformation of fine chemicals – the catalytic effect is based on immobilized metal nanoparticles. New molecules originating from biomass are under investigation. Research collaboration in catalyst characterization is very intensive with University of Turku and University of Oulu.

Detailed kinetic studies were carried out in many applications, particularly in the hydrolysis of hemicelluloses as well as hydrogenation and oxidation of mono- and disac-

charides, preparation of percarboxylic acids, hydroformylation reactions, enantioselective hydrogenation and cleaning of exhaust gas originating from biofuels. Special attention was paid on the description of the reaction mechanisms based on first principles, i.e. quantum chemical calculations, which can elucidate the adsorption states and adsorption stoichiometry on solid metal surfaces. The complex interaction of reaction and diffusion in porous media was studied experimentally and with sophisticated simulations including particle-size distributions. The concept was applied to catalytic two- and three-phase systems as well as reactions of solids with liquids. New computational tools were taken in use in the simulation of kinetics, diffusion and flow pattern.

A lot of effort is devoted to the development of continuous reactor technology: we have constructed several continuous reactors, the star among them being the parallel screening tube reactor system equipped with GC-MS analysis (financed by Academy of Finland). Microwave and ultrasound equipment were used to explore the possibilities to process intensification. The leading principle is multiscale modelling: to achieve real reaction intensification, the modeling efforts should cover the approaches from quantum chemistry to computational fluid dynamics (CFD). New kinds of structured catalysts were taken in use, such as solid foams, which are developed together with the group in Combustion and Materials Chemistry (PCC) foreign partners. The development of green process technology is advanced in many fields, particularly in the development of new continuous processes for biofuels and chemicals. Heterogeneous catalysts can replace homogeneous ones and a clean and continuous technology can replace the old concept, we demonstrate in the synthesis of peracetic and perpropionic acid. One-pot synthesis, which combines heterogeneous catalyst and an enzyme in a single reactor unit, is an area for which intensive research work is going on and the expectations are high. Micro- and millireactors provide a technology jump; we use them for catalyst development, kinetic screening and continuous production of chemicals in gas and liquid phase.

Personnel

Professors	Tapio Salmi (Academy Professor)
	Dmitry Murzin
	Lars-Eric Lindfors (Emeritus)
	Jyri-Pekka Mikkola (together with Umeå University)
	Johan Wärnå
Docents	Kalle Arve
	Narendra Kumar

	Päivi Mäki-Arvela
Laboratory manager	Kari Eränen
Senior researchers	Steliana Aldea
	Andreas Bernas
	Heidi Bernas
	Betiana Campo
	Pia Damlin
	Jan Hájek
	Matias Kangas
	Mats Rönnholm
	Anton Tokarev
	Esa Toukoniitty
Doctoral students	Atte Aho
& researchers	Ikenna Anugwom
	Pierdomenico Biasi
	Valérie Eta
	Sigmund Fugleberg
	Henrik Grénman
	José Rafael Hernández Carucci
	Sari Hyvärinen
	Olatunde Jogunola
	Teuvo Kilpiö
	Alexey Kirilin
	Bright Kusema
	Mats Käldström
	Sébastien Leveneur
	Elena Murzina
	Elena Privalova
	Serap Sahin
	Victor Sifontes Herrera
	Olga Simakova
	Timo Petteri Suominen

	Antti Taskinen
	Pasi Tolvanen
	Pasi Virtanen
Secretary	Lotta Malminen

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2.5 Process Analytical Chemistry

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

The main targets and challenges of analytical chemistry, and process analytical chemistry in particular, is the development of robust and automatic analytical systems that can be

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

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

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

Personnel

Professors	Johan Bobacka
	Ari Ivaska
	Andrzej Lewenstam (part-time)

Docents	Leo Harju
	Carita Kvarnström
	Tom Lindfors
	Tomasz Sokalski
Senior researchers	Gordon Driver
	Dongxue Han
	Anna Kisiel
	Rose-Marie Latonen
	Beatriz Meana Esteban
Doctoral students	Marceline Akieh
& researchers	Maija Blomquist
	Paul Ek
	Kim Granholm
	Henrik Gustafsson
	Tingting Han
	Jerzy Jasielec
	Grzegorz Lisak
	Ulriika Mattinen
	Zekra Mousavi
	Pingping Su
	Fredrik Sundfors
	Michał Wagner
	Zhijuan Wang
	Anna Österholm
Secretary & Coordinator	Anne-Leena Gröning
Technicians	Sten Lindholm
	Lassi Väinölä

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http://www.abo.fi/public/en/analytisk_kemi

3. Research

For the second period 2006–2011 as a Centre of Excellence a completely new common research plan was planned. The starting points of this planning are outlined below.

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

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

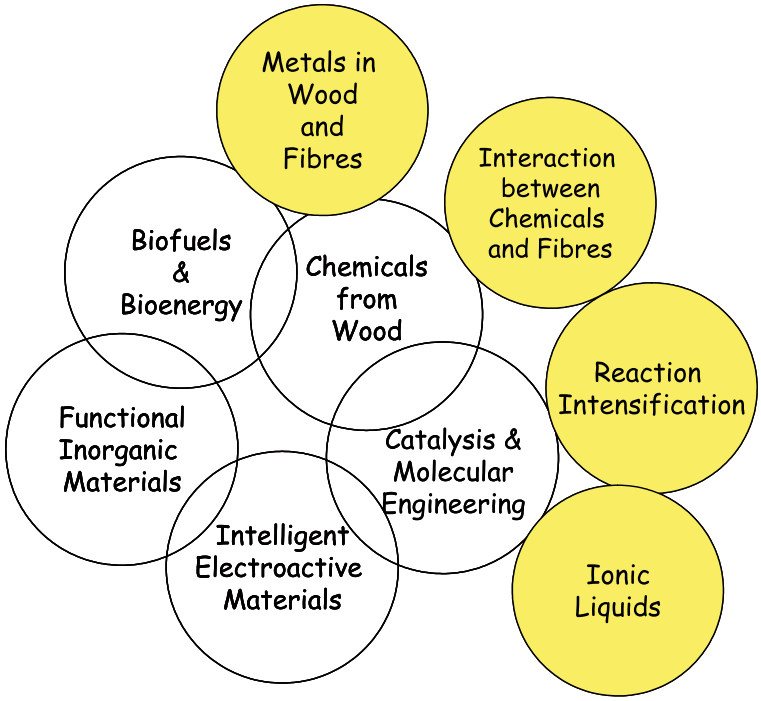
This approach can lead to "truly green" chemistry and chemical technology in harmony with nature, yet fulfilling urgent needs of mankind. In this development, deep understanding of the detailed chemistry – "Molecular Process Technology" – will be of crucial importance. A large part of our future research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

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

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

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

The basis of our future work will naturally be our special competence and our scientific tool-box, which we have developed during the course of many years. This tool-box consists of unique analytical capabilities, other experimental laboratory techniques, advanced chemical engineering models and a good understanding of the technical state and chal-



ÅA-PCC Research Areas 2006–2011

lenges of modern industrial processes. It also contains a long and successful experience in researcher training and fluent national and international networks.

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

3.1 Ionic Liquids

Ionic liquids (ILs) have emerged as a novel class of materials and neoteric solvents that are applied in many fields such as solvents for electrochemistry and organic synthesis, as materials for recovery of metals from aqueous solution, synthesis of nano-structured materials and sequestration of carbon dioxide, to entrapment and activation of enzymatic and metal species for catalytic applications. The vast number of anticipated possibilities to form various ionic liquids, at least a million or even 10^{18}, gives the possibilities almost beyond our imagination, enabling task-specific configurations for different technology disciplines.

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

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

- Synthesis, development and characterization of novel, ionic liquid analogues
- Catalysis by novel supported ionic liquids
- Cascade catalysis in terms of combined enzymatic and metal catalysis supported in ionic liquids
- Bio-transformations in ionic liquids
- Electrochemical studies and applications of ionic liquids

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

The main achievements have been obtained in two fields: preparation and use of supported ionic liquid catalysts (SILCA). The pores of the support material are filled with an ionic liquid and an organometallic complex is formed. In the further treatment, the metal is reduced, and we obtain, for instance, palladium nanoparticles. It has turned out that this kind of novel heterogeneous catalyst is efficient in reduction of carbonyl groups, as demonstrated by selective catalytic hydrogenation of citral. The potential of SILCAs is huge, since they provide a way to heterogenize homogeneous catalysts thus providing the benefits of both homogeneous catalysis (high activity and high selectivity) and heterogeneous catalysis (easily separable catalysts).

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

SILCA Catalysts and Ionic Liquids as Reaction Media

Main funding: Academy of Finland

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

Ionic liquids are the hot topic of chemical research. At PCC, a new project was started in 2005 concerning ionic liquids as reaction and catalyst media. Several new ionic liquids

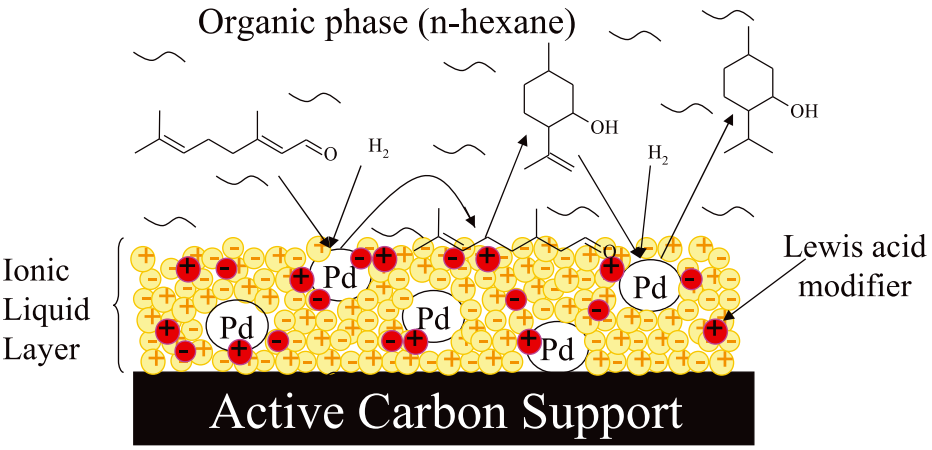
have been prepared and characterized. The project is focused on the use of ionic liquids in catalyst supports; we have successfully demonstrated that ionic liquids can be used to heterogenize homogeneous catalysts. Kinetic studies have been carried out for hydrogenation of fine chemicals on SILCA. The use of SILCA in hydroformylation was explored. An extensive study of the physical properties of selected ionic liquids has been continued and kinetic modelling of hydrogenation processes on SILCA advanced.

Cooperation:

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

Publications:

- Virtanen, Pasi (Category 4.1.2)



A Lewis acid modified Supported Ionic Liquid Catalyst used in citral transformation

Cellulose Derivatives in Ionic Liquids

Main funding: PCC

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

Ionic liquids are excellent reaction media for making cellulose derivatives, because cellulose can be dissolved in non-toxic, non-volatile ionic liquids. This implies that a big technology jump is taken: classical methods for preparing cellulose derivatives are based on the use of suspended cellulose in a solvent, which implies that the reaction is heterogeneous with all cumbersome mass transfer limitations involved. In dissolved state, cellulose reacts eagerly, and a new world of derivatives is opened. The existing processes can be considerably intensified by shifting to the ionic liquid technology and new derivates can

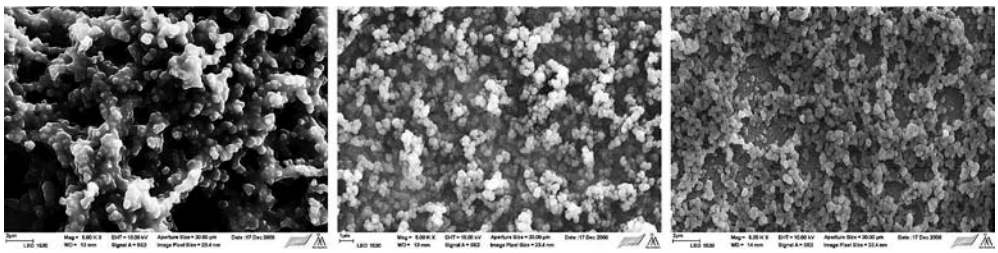
be prepared. The focus of the research project is in the etherification and esterification of cellulose.

Ionic Liquids in Electrosynthesis and in Characterization of Organic Electroactive Materials

Main funding: Academy of Finland, DAAD

Anna Österholm, Carita Kvarnström, Ari Ivaska

Room temperature ionic liquids have been studied as media for electrosynthesis of conducting polymers and for functionalization and characterization of carbon nanotubes and fullerenes. Smoother film morphology was often observed when the electrosynthesis was performed in ionic liquid media. Electrochemical doping of conducting polymers and thin films of fullerenes has also been performed in different ionic liquids. They showed an increased redox cycling response which means an increased degree of doping and a higher stability compared to films doped in organic electrolytes. Ionic liquids made it also possible to study a bigger number of fullerene redox reactions due to that the polymer films often dissolve in presence of an organic solvent at higher negative potential. The characterization has mainly been electrochemistry combined with simultaneous in situ FTIR and UV-vis spectroscopy.



SEM pictures showing a smoother morphology of PAz films electrochemically polymerized in presence of BMP-Tf_2N (middle) and BMIM-PF_6 (right) ionic liquids compared to acetonitrile (left).

Cooperation:

Institute of Solid State and Material Research, Dresden, Germany

Publications:

- Wei, D., Baral, J.K., Österbacka, R., Ivaska, A. (a) (Category 4.2)
- Wei, D., Baral, J.K., Österbacka, R., Ivaska, A. (b) (Category 4.2)
- Wei, D., Ivaska, A. (Category 4.2)

3.2 Reaction Intensification

The aim of the project is to develop new reactor systems and new technologies which lead to an essential decrease of the size of a chemical plant. The following areas are of interest: monolith reactors, fibrous catalyst structures as well as ultrasonic and microwave technology. The group has unique experimental devices for in situ studies of reactions under the influence of ultrasound and microwaves. The chemical applications are several, such as esterification, catalytic oxidation as well as hydrogenation of aldehydes and ketones, leaching of minerals and delignification of wood. A new breakthrough was obtained in the use of ultrasound technology in the chemistry of cellulose: it turned out that the dissolution of cellulose in ionic liquids can be considerably enhanced by the use of acoustic exposure. Thus the process intensification aspect was combined to the research tasks in ionic liquids (section 3.1) and chemicals from wood.

A special emphasis is focused on multiphase reactors, where a gas phase, a liquid phase and a solid catalyst are present. Modern computational techniques and reactor structures, such as CFD and microreactors are applied. We constructed two new microreactor systems, for catalytic gas-phase reactions and for liquid-phase reactions. Detailed mathematical modelling was applied on the reactor systems. Both systems work technically and it turned out that microreactors are efficient tools for rapid screening of reaction kinetics, particularly for gas-phase reactions. The main application was in environmental catalysis, and in the production of chemicals.

Structured Reactors

Main funding: Academy of Finland

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

Fibre catalysts and monoliths provide an attractive alternative for traditional catalyst technologies, since they combine the immobility of the catalyst to a short diffusion path, which guarantees a minimized mass transfer resistance. Fibre catalysts and monoliths enable a continuous operation for processes, which traditionally have been carried out batchwise, particularly synthesis of fine chemicals. Three kinds of fibre catalysts have been investigated: polymer-based fibres as well as silica and carbon fibres. The former ones have applications in esterification, etherification and aldolization reactions, while the latter ones are used after metal impregnation in oxidation and hydrogenation reactions. Esterification of carboxylic acids, hydrogenation of aldehydes and ketones has been used as model reactions. Compared to conventional catalysts, a clearly improved performance has been achieved, since the internal mass transfer limitation is suppressed.

Cooperation:

Lappeenranta University of Technology

Publications:

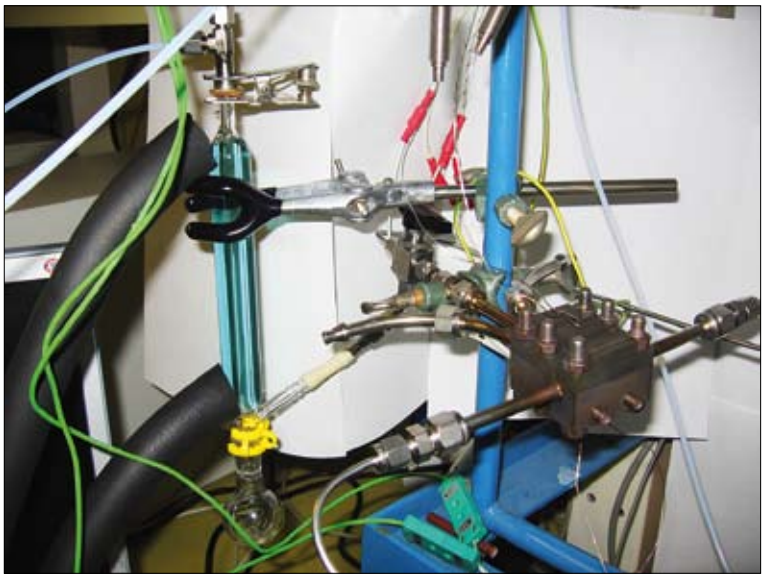
- Salmi, T., Murzin, D.Yu., Eränen, K., Mäki-Arvela, P., Wärnå, J., Kumar, N., Villegas, J., Arve, K. (Category 4.2)
- Toukoniitty, B., Mikkola, J.-P., Murzin, D.Yu., Salmi, T. (Category 4.2)

Microreactors and Millireactors

Main funding: Tekes, Academy of Finland

Kari Eränen, Mats Rönnholm, José Rafael Hernández Carucci, Sara Björkqvist, Ville Halonen, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

We have introduced the concept of microreactors on Finnish soil. Two different kinds of microreactor systems were constructed; one for catalytic gas-phase systems and another one 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. For homogeneous liquid-phase reactions the work was successful (e.g. determination of reaction kinetics) but liquid-liquid reaction systems need further development to achieve very precise kinetics. The applications of microreactors range from environmental catalysis to the production of fine chemicals. Extensive modelling work after modelling of microreactors was continued.



Microreactor for production of chemicals

Cooperation:

Lappeenranta University of Technology; University of Oulu; PCAS Finland; Kemira

Publications:

- Hernández Carucci, J. R., Arve, K., Eränen, K., Murzin, D.Yu., Salmi, T. (Category 4.2)

Multiphase Reactors

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

Johan Wärnå, Mats Rönnholm, Andreas Bernas, Henrik Grénman, Sigmund Fugleberg, Blanka Toukoniitty, Heidi Bernas, Jyrki Kuusisto, Atte Aho, Anton Tokarev, Pierdomenico Biasi, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

The project concerns advance modelling of multiphase reactors, involving various flow models in the bulk phases of the reactor as well as modelling of simultaneous reaction and diffusion in porous catalyst pellets: in process scale-up, the crucial step is the shift from small particles used in laboratory experiments to large particles characteristic for fixed bed reactors. The main applications are catalytic three-phase hydrogenation and oxidation, ring opening and reactions of solids with gases and liquids. A new model was developed for delignification of wood. The model can be used for process intensification as well as prediction of the behaviour of cellulose production.

Cooperation:

Danisco; Forchem; Perstorp; Kemira; Raisio; Lappeenranta University of Technology; Università di Padova, Padova, Italy

Publications:

- Aho, A., Kumar, N., Eränen, K., Holmbom, B., Hupa, M., Salmi, T., Murzin, D.Yu. (Category 4.2)
- Aho, A., Kumar, N., Eränen, K., Salmi, T., Hupa, M., Murzin, D.Yu. (Category 4.2)
- Bernas, A., Wärnå, J., Mäki-Arvela, P., Ahlkvist, J., Still, C., Lehtonen, J., Murzin, D.Yu., Salmi, T. (Category 4.2)
- Mäki-Arvela, P., Kuusisto, J., Mateos Sevilla, E., Simakova, I., Mikkola, J-P., Myllyoja, J., Salmi, T., Murzin, D.Yu. (Category 4.2)

- Mäki-Arvela, P., Sahin, S., Kumar, N., Mikkola, J-P., Eränen, K., Salmi, T., Murzin, D.Yu. (Category 4.2)
- Tokarev, A.V., Murzina, E.V., Seelam, P.K., Kumar, N., Murzin, D.Yu. (Category 4.2)

Batch and Semibatch Reactors

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

Henrik Grénman, Steliana Aldea, Sébastien Leveneur, Jyrki Kuusisto, Jyri-Pekka Mikkola, Andreas Bernas, Pasi Tolvanen, Johan Wärnå, Dmitry Murzin, Tapio Salmi

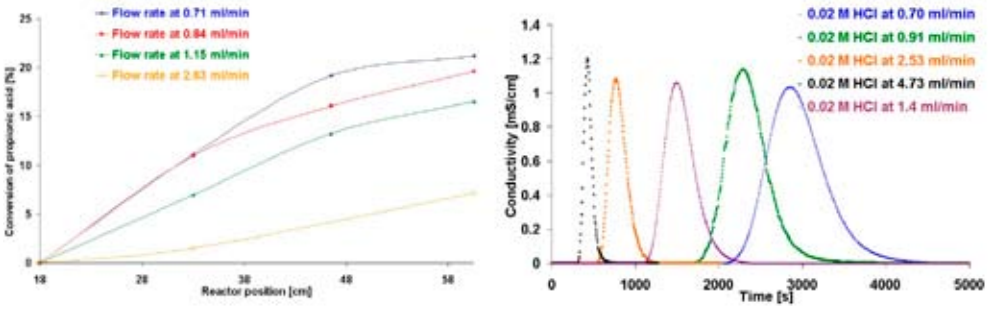
Batch and semibatch reactors are frequently used in the production of fine and specialty chemicals. The aim of the project is to develop experimental equipment and procedures for obtaining kinetic data and to carry out advanced modelling of chemical kinetics and mass transfer in (semi)batch reactors. Typical case studies are reactions of solid materials with organic compounds in liquid phase as well as decomposition of organic materials in liquid phase. The project has contributed to essentially increased production capacities.

Cooperation:

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

Publications:

- Grénman, H., Ramirez, F., Eränen, K., Wärnå, J., Salmi, T., Murzin, D.Yu. (Category 4.2)
- Kuusisto, J., Mikkola, J.-P., Sparv, M., Wärnå, J., Karhu, H., Salmi, T. (Category 4.2)
- Leveneur, S., Salmi, T., Murzin, D.Yu., Estel, L., Wärnå, J., Musakka, N. (Category 4.2)
- Salmi, T., Kuusisto, J., Wärnå, J., Mikkola, J-P. (Category 4.2)
- Salmi, T., Murzin, D.Yu., Mäki-Arvela, P., Wärnå, J., Eränen, K., Mikkola, J-P., Denecheau, A., Alho, K. (Category 4.2)
- Tolvanen, P., Mäki-Arvela, P., Eränen, K., Wärnå, J., Holmbom, B., Salmi, T., Murzin, D.Yu. (Category 4.2)



Continuous production of perpropionic acid in a fixed bed reactor. Concentration profiles and modelling of the residence time distribution.

Complex Reaction Kinetics and Thermodynamics

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

Johan Wärnå, Mats Rönnholm, Jyri-Pekka Mikkola, Matias Kangas, Pasi Tolvanen, Olatunde Jogunola, Valerie Eta, Esko Tirronen, Andreas Bernas, José Rafael Hernandez Carucci, Sébastien Leveneur, Kalle Arve, 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.

Cooperation:

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

Publications:

- Bernas, A., Mäki-Arvela, P., Lehtonen, J., Salmi, T., Murzin, D.Yu. (Category 4.2)
- Bernas, H., Plomp, A. J., Bitter, J. H., Murzin, D.Yu. (Category 4.2)
- Busygin, I., Nieminen, V., Taskinen, A., Sinkkonen, J., Toukoniitty, E., Sillanpää, R., Murzin, D.Yu., Leino, R. (Category 4.2)

- Busygin, I., Wärnå, J., Toukoniitty, E., Murzin, D.Yu., Leino, R. (Category 4.2)
- Grénman, H., Ramírez, F., Eränen, K., Wärnå, J., Salmi, T., Murzin, D.Yu. (Category 4.2)
- Hernández Carucci, J.R., Arve, K., Eränen, K., Murzin, D.Yu., Salmi, T. (Category 4.2)
- Kangas, M., Salmi, T., Murzin, D.Yu. (Category 4.2)
- Leveneur, S., Salmi, T., Murzin, D.Yu., Estel, L., Wärnå, J., Musakka, N. (Category 4.2)
- Murzin, D.Yu., Leino, R. (Category 4.2)
- Murzin, D.Yu. (a) (Category 4.2)
- Murzin, D.Yu. (b) (Category 4.2)
- Murzin, D.Yu., Simakova, I.L. (Category 4.2)
- Eta, V., Mäki-Arvela, P., Mikkola, J.-P., Kordas, K., Murzin, D.Yu., Salmi, T. (Category 4.2.2)

3.3 Metals in Wood and Fibres

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

This project studies the occurrence of metal ions in different parts of the wood material used for pulp and papermaking and in 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 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. Chemical forms of 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 of the type of metal ions and their content in different fuels. The studies of metals give important information to predict their behaviour in different parts of the papermaking process and in energy conversion processes, so that the negative effects can be eliminated and the positive effects enhanced.

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

Chemical Microscopy and Chemical Microanalysis of Wood Tissues and Fibres

Main funding: Academy of Finland, Tekes (Bioraff)

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

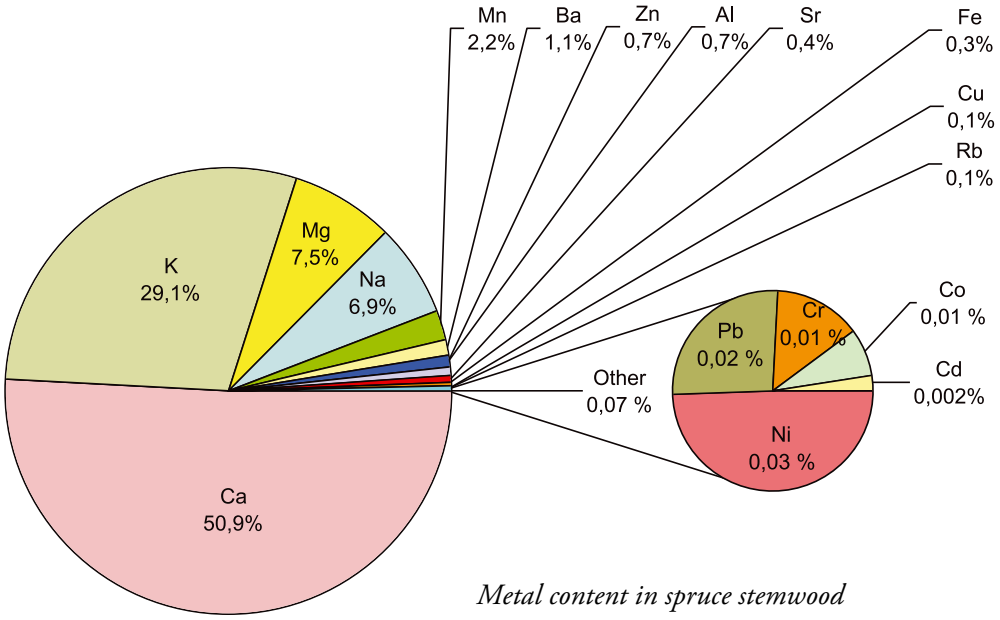
The metal composition of the wood reflects both the metabolism of the plant and environmental conditions. Metals in wood are either

- bound as ions to carboxyl groups in hemicelluloses and pectins
- involved in complex formation with lignin moieties
- present as salts with different solubility

Knot-free wood discs from straight and symmetric spruce and aspen trees were studied in order to examine the distribution of organic and inorganic constituents in different morphological parts of the trees. Samples were taken from differentiated wood, sapwood (from both earlywood SE and latewood SL), heartwood (from both earlywood HE and latewood HL) and juvenile wood. Sampling of wood tissues from different morphological parts of the trees (spruce and aspen) was performed according to the figure shown below.

Altogether 17 natively occurring metals in wood have been analysed. Different morphological parts of spruce contained 2–3 times more Mn compared to those from aspen. In spruce, earlywood from both sapwood and heartwood as well as juvenile wood, contain the highest concentrations of Mn. Spruce also contains more Ca than aspen, especially in heartwood earlywood (HE) and juvenile wood (JUV).

We have also developed and applied a new method for labelling of anionic groups with metal ions in wood sections in order to assess their special distribution by Time-of-Flight Secondary-Ion Mass Spectrometry (ToF-SIMS). Laser ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) has been applied for verification of ToF-SIMS results and for semi-quantification of anionic groups in wood tissues.



Metal content in spruce stemwood

Publications:

- Fardim, P., Holmbom, B. (Category 4.2.2)
- Tokareva, E., Pranovich, A., Holmbom, B. (Category 4.3)

Application of Liquid Nitrogen in Chemical Analysis

Main funding: Industry

Paul Ek, Sten Lindholm, Ari Ivaska

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

A flow through cell has been designed for analysis of hydride forming elements. In this construction liquid nitrogen is used to freeze the hydride gases allowing continuous accumulation of the hydrides and thereby increasing the sensitivity of the method.

Publications:

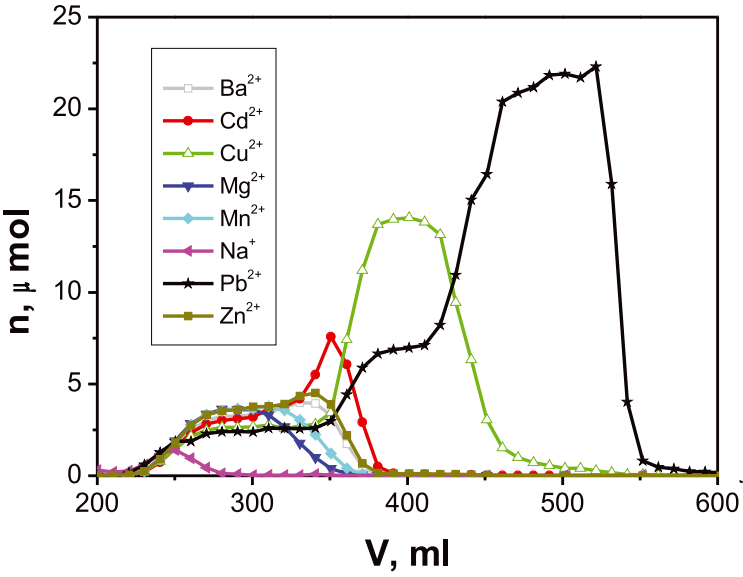
- Granfors, M. (Category 4.1.3)

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

Main funding: Tekes, Åbo Akademi Foundation Research Institute

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

The main objective of the project has been to study complex forming reactions of metal ions in the pulping process in order to obtain selective and effective chelation, especially at high pH values. Chelation is an important step when hydrogen peroxide is used in the bleaching process because transition metals break down hydrogen peroxide. The LA-ICP-MS technique has been used to study the distribution of metals in single wood fibres. A column chromatographic method has been developed for the study of metal ion affinities to different types of pulps. Equilibrium constants for ion exchange reactions between metal ions and pulps have been determined by a batch technique.



Desorption of preloaded metal ions from hardwood kraft pulp. The number of micromoles (n) of Ba^{2+}, Cd^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Na^{+}, Pb^{2+} and Zn^{2+} as function of the volume (V) of eluate in the collected fractions.

Free calcium ions in black liquors have been determined using a calcium ion selective electrode. A differentiation between calcium bound to phenolic and carboxylic groups was made by titration of black liquor with EDTA.

Publications:

- Karhu, Jouni (Category 4.1.1)
- Granholm, K., Harju, L., Bobacka, J., Ivaska, A. (Category 4.3)
- Granholm, K., Su, P., Harju, L., Ivaska, A. (Category 4.3)
- Su, P., Granholm, K., Harju, L., Ivaska, A. (Category 4.3)

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

Main funding: Åbo Akademi University, Process Chemistry Centre

Leo Harju, Kjell-Erik Saarela, Johan Rajander

Ion beam analyses have mainly been developed for the determination of elemental content mainly in biological and environmental samples. Thick target particle induced X-ray emission (PIXE) enables reliable and sensitive analysis of especially heavy metal ions in a great variety of materials. With particle induced gamma emission (PIGE) light elements like C, N and O can be determined. Our main research interest has been the study of wood, bark, needles and leaves of different tree species e.g. pine, spruce, birch, aspen, willow and eucalyptus and how the chemical composition of these materials is affected by natural and anthropogenic factors. Also the elemental content in ashes of these wood-based materials has been determined. Other types of environmental materials like soils, mushrooms, mosses, lichens and marine algae have been examined.

Cooperation:

Åbo Akademi University (Accelerator Laboratory); Turku PET Centre

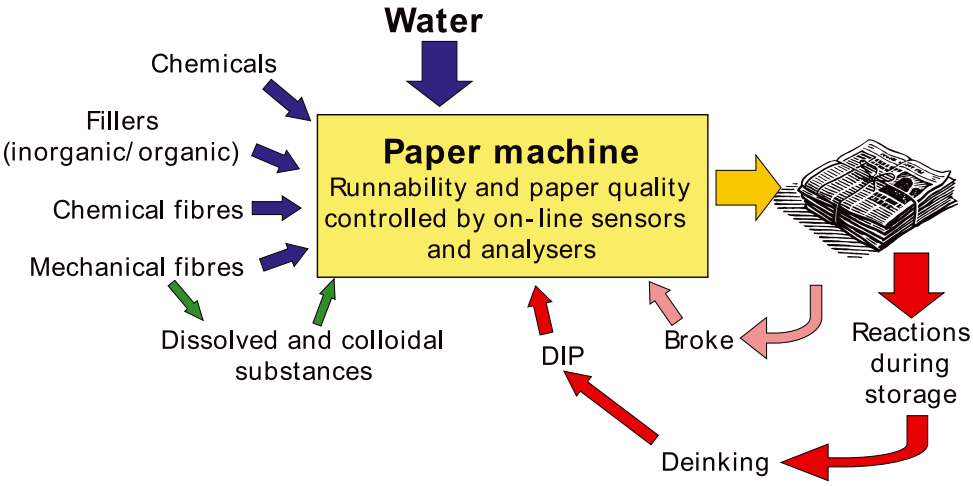
3.4 Interaction between Chemicals and Fibres

The wet end of the paper machine is a very complex system. The consistency of the fibers is only about 0.2–0.8%, and other components such as fillers, fines, and a wide variety of added chemicals are also present in the water. Dissolved and colloidal substances are further released from the pulp or from broke and recycled fiber material, which sometimes includes tacky polymers from recycled coated paper. The pH, conductivity and ions present in the process waters will affect the amount and the composition of the substances released.

The chemicals added will interact with the fibres and the released substances. This will affect the runnability of the paper machine and the quality of the produced paper. The

paper machines of today have a speed of about 2000 m/min, which requires a fast dewatering and a sufficient initial wet strength to avoid web breaks.

Mistakes made in the wet end of paper machines are difficult to correct afterwards, and are impossible to correct especially when the mistakes result in fouling and the machines become unstable to operate. Therefore, it is of utmost importance to know how chemicals added to the furnish will interact with each other. One key issue is to develop specific analytical methods, to be able to predict the runnability of a paper machine.



A variety of fibres and chemicals interact in the wet end of paper machines

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

Main funding: Tekes, Industry

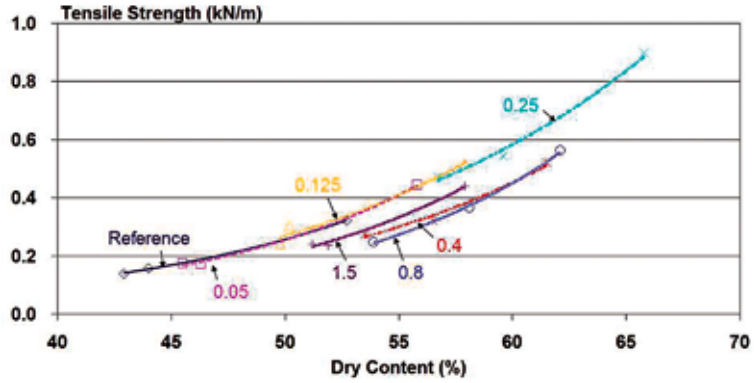
Hanna Lindqvist, Anna Boedeker, Johan Isaksson, Paula Heikkilä, Bjarne Holmbom, Anna Sundberg

The initial strength of wet paper is critical for the runnability of paper machines. Lower wet strength causes web breaks and may also impair the quality of the paper. Dissolved and colloidal (DisCo) substances in white water are known to affect the properties of dry paper, but no systematic information is found in the literature on how additives and DisCo substances affect the wet-web rheology and paper machine runnability. Wet paper cohesion is a complex combination of friction and surface tension forces and emerging hydrogen bonding.

In the first step of this project, the effects of a surfactant, pH, and different types of electrolytes were determined. Addition of a surfactant decreased the dewatering time and increased the dry content of the sheets. The initial wet web strength and the residual

tension increased, primarily due to the increased dry content of the sheets. The concentration of the surfactant should not exceed CMC. The main goal of this project is to control strength and runnability of wet paper by tailored wet-end chemistry.

Isolation of wood substances was performed in cooperation with Metla.



Wet tensile strength after addition of a non-ionic surfactant. The sheets were pressed to different dry contents.

Cooperation:

VTT Jyväskylä; Kemira; Metso Paper; Stora Enso; UPM-Kymmene; Metla

Publications:

- Saarimaa, V., Sundberg, A., Holmbom, B. (Category 4.2)

Beet Pulp

Main Funding: EU

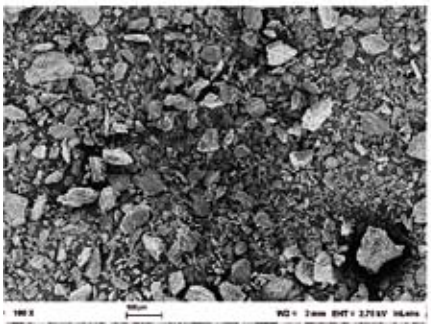
Markku Auer, Robin Manelius, Sara Niemi, Bjarne Holmbom

Sugar beet production in the European Union amounts today to about 116 million tons per year. The EU beet sector represents 400 000 beet growers. During production of beet sugar, beet pulp will end up as waste, amounting to about 6 million tons of dry matter per year in the EU.

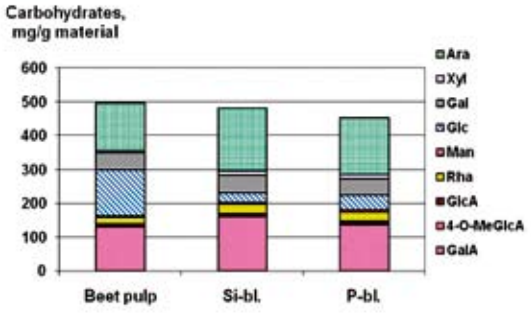
The project aims at valorisation of beet pulp into a high-added-value product: to transform beet pulp into vegetal micro-fillers for paper and board production. Today, mineral additives are incorporated into many paper grades to improve, for example, optical properties. However, the mechanical properties of paper are impaired by mineral fillers and they are, additionally, detrimental to parts of the papermaking equipment in that they are abrasive. This project proposes to replace these mineral fillers, as a whole or partly, in paper by bleached particles made of beet pulp. In the research, particular emphasis is laid on bleaching of this additive to meet the paper and board specifications. The environmental

aspects, in the use of this bio-material, are also investigated as well as the integration of the production process of this additive into the sugar production is also studied.

From the paper and board makers´ perspective these vegetal additives would bring several advantages, for example competitiveness and environmental friendliness, in comparison to currently used mineral fillers.



SEM picture of micronized beet pulp particles



Hemicelluloses and pectins represent a large part of the beet pulp mass. The remaining sucrose in beet pulp is removed during sodium bisulphate bleaching (Si-bl.) and peroxide bleaching (P-bl.).

Cooperation:

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

Global Process Efficiency

Main funding: Kemira

Lari Vähäsalo

The physiochemical phenomenon involved in paper machine water systems is often extremely complex. However, processes are normally monitored using very simple sensors and analyzers. Bulk parameters, such as turbidity, are one of the most common parameters that is used to monitor a paper machine wet end. It is clear that such measurements do not give a very good understanding or control of the multitude of phenomena occurring simultaneously. Flow Cytometry has turned out to be an outstanding analytical method for the analysis of the physiochemical state of the paper machine water systems. The method has given new type of understanding of the molecular level phenomena that

influences particle aggregation and deposition. However, for the time being this method is not economically sound to be implemented on-line.

The aim of this project is to identify key phenomena that are the most critical for the runnability of a paper machine. The goal is to develop problem-specific analytical methods, simple enough to be implemented as an on-line analyzer. Several parameters, such as microbiological activity and charge profiles etc., are of interest.

Cooperation:

Kemira

Publications:

- Holmbom, B., Vähäsalo, L. (Category 4.3)

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

Main funding: PaPSaT Graduate School

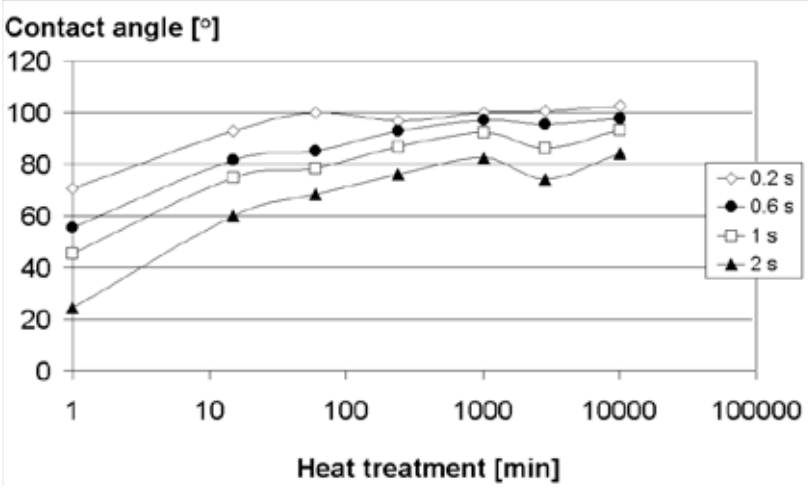
Sylwia Bialczak, Bjarne Holmbom, Anna Sundberg

During production, storage and usage, paper components undergo chemical reactions, which will affect the paper properties. In this study, TMP paper was submitted to accelerated ageing by treatment at 60°C. The content and composition of extractives was analyzed by gas chromatography after extraction with acetone:water (9:1). The surface properties of the paper were investigated by XPS/ESCA and contact angle measurements. The content of acetone:water soluble extractives decreased significantly during ageing. Already after 2 days of ageing, only 20% of the original extractives could be found in the GC analysis. The contact angle increased with ageing, indicating a change in the surface coverage of extractives. In the XPS studies, the surface oxygen content was found to increase during ageing.

The ultimate goal for this project is to create a deeper, solid base for technical development of better paper products.

Cooperation:

Åbo Akademi University (Paper Coating and Converting, Physical Chemistry)



The contact angle increases after heat treatment of the paper, which will affect the printing properties.

Phase Distribution of Resin and Fatty Acids in Colloidal Wood Pitch Emulsions at Different pH Levels

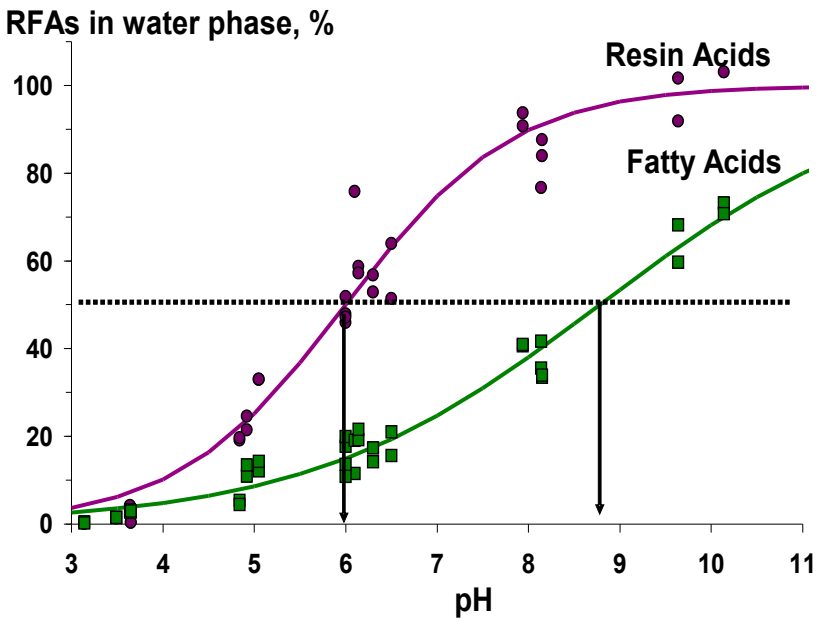
Main funding: Åbo Akademi Process Chemistry Centre

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

The phase distribution of resin and fatty acids (RFAs) between the water phase and the lipophilic phase in colloidal pitch emulsions is very important for phenomena related to pitch stability, deposition and washing of pulp. The phase distribution was therefore determined as a function of pH for emulsions with different pitch composition, at different temperatures and salt concentrations. The experimental data were used for calculation of pK_{lw}, i.e. the pH at which 50% of the component is in the water phase.

At pH 3, all RFAs were associated with the colloidal droplets. When increasing the pH, the RFAs were gradually released. The resin acids were released at a lower pH than the fatty acids. Dehydroabietic acid had the lowest pK_{lw} of all RFAs. The phase distribution of the fatty acids depended much on the chain length and the amount of double bonds. Only very little saturated fatty acids with 20 or more carbon atoms were found in the water phase even at pH 11.

Addition of NaCl or $CaCl_2$ increased the pK_{lw}-values. At high $CaCl_2$ concentration, insoluble aggregates between RFAs and Ca-ions were formed, which were not found in the water phase even at high pH.



Distribution of resin and fatty acids (RFAs) between the colloidal, lipophilic phase and the water phase at 50°C and low NaCl concentration. The arrows show the pK_{lw}. No additional fatty acids were added to the pitch emulsion.

Cooperation:

Åbo Akademi Process Chemistry Centre

Publications:

- Qin, M., Holmbom, B. (Category 4.2)

Wood Resin Components in Birch Kraft Pulping and Bleaching

Main funding: Industry

Eija Bergelin, Bjarne Holmbom

Process disturbances caused by wood resin are common in birch kraft pulp mills in form of foaming and deposition of wood resin on surfaces of process equipment. Deresination is difficult in kraft pulping of birch wood due to the high proportion of neutral, unsaponifiable resin components. Brown-stock washing efficiency affects the chemical consumption in bleaching, as well as the load to the chemical recovery area. Efficient washing is critical for the economy (energy efficiency) and pollution control in subsequent bleaching.

The main objectives are to clarify deresination mechanisms in debarking and washing. In birch debarking, problems are caused by defragmentation of the outer bark. Betulinol behaviour is assessed by material balances over debarking. This can clarify the behaviour

and distribution of betulinol in debarking. The aim of the brown-stock washing evaluation is to clarify resin removal in relation to resin distribution, surface tension and critical micelle concentrations.

Cooperation

UPM; Metsä-Botnia

Publications:

- Bergelin, Eija (Category 4.1.1)
- Bergelin, E., Holmbom, B. (Category 4.2)

3.5 Chemicals from Wood

Today, a majority of the organic chemicals and materials in our daily life are synthetic products of oil or natural gas. Concern about the future availability, an increasing interest for environmentally sound solutions, and a hardening legislation has created a deep interest in renewable alternatives and the concept of establishing biorefineries.

In the PCC, we are especially interested in developing new processes in the forest industry, where side-streams and waste materials of today could give value-added and sustainable alternatives to oil-based products in a near future. To achieve this goal we isolated, characterised, and tested potential chemical substances from waste material sources such as bark, knotwood from over-sized chips, and process waters going to biological treatment plants. For wood-derived polyphenols, we study the transformation of readily available knotwood lignans to other, rare and more valuable, substances, either chemically or by catalytic means. Furthermore, some economical and technical evaluations of feasibility have been carried out for selected processes.

Polyphenols, such as knotwood lignans and spruce bark stilbenes, have been identified as potential antioxidants both for technical and biological purposes. Pine wood and spruce bark stilbenes exhibit antibacterial and decay resistance potential.

An utilisation of wood-derived hemicelluloses, such as O-acetyl galactoglucomannans (AcGGM) from spruce and arabinogalactans (AG) from larch, is another important target within PCC. Interesting areas of applications are in papermaking or in the textile industry, and for medical applications, i.e. areas that deal with cellulose surfaces. The potential lies within a possible surface modification using native or modified AcGGM or AG. Specialty paper grades, abrasion-resistant clothing, antibacterial bandage, barriers against oxygen gas, water vapour, or fat barriers in food packages are high-value products

of interest. Hemicellulose-based biodegradable films or health promoting agents, such as prebiotic substances, as well as emulsion stabilization in food or various technical applications are other potential areas of use. Recovered hemicelluloses can also be used as a renewable source for development of sugar-based fine chemicals.

Chemistry in Forest Biorefineries (Bioraff)

Main Funding: Tekes

Markku Auer, Atte Aho, Paul Ek, Mikael Forssén, Kim Granholm, Leo Harju, Paula Heikkilä, Bjarne Holmbom, Mikko Hupa, Sari Hyvärinen, Ari Ivaska, Mats Käldström, Jyri-Pekka Mikkola, Dmitry Murzin, Päivi Mäki-Arvela, Andrey Pranovich, Tapio Salmi, Tao Song, Pingping Su, Anna Sundberg, Timo Petteri Suominen, Elena Tokareva, Johan Werkelin, Stefan Willför, Chunlin Xu, Maria Zevenhoven

In recent years, biorefinery-related issues have become one of the major research topics due to the increasing pressures to counteract assumed global environmental effects from fossil raw materials. The aim of the Bioraff project is a broader and more efficient use of forest resources. This renewable resource should be used in a more intelligent manner than previously. The focus of the project is in wood and process chemistry. Through increased knowledge of wood constituents and wood process chemistry at a molecular level, a knowledge base is created for more intelligent use of forest raw materials for specialty biochemicals and biomaterials as well as for liquid fuels and power.

The project comprises the following working themes:

1. Polysaccharides from wood
2. Sugar-based fine chemicals
3. Cellulose derivatives
4. Polyphenols from knots and barks
5. Metal ions and functional groups in trees and pulps
6. Fuel analysis and presence of trace elements in bio-fuels
7. Options for catalysts for catalytic production of bio based liquid fuels
8. Gasification of biorefinery streams for synthesis and energy

Fine and specialty chemicals

In addition to naturally occurring constituents, chemical modification of isolated wood components will provide new options. For example, new physiologically active compounds can be derived from wood using heterogeneous catalysis; sitostanol can be produced by catalytic hydrogenation from sitosterol, conjugated linoleic acids can be synthesized via isomerization of linoleic acids, and other lignans can be obtained from hydroxymatairesinol through hydrogenolysis. Dissolution of cellulose is possible in ionic liquids, giving new possibilities for the production of grafted cellulosic materials. Galactoglucomannan (GGM) is the dominating softwood hemicellulose. During refining of mechanical pulp, part of the GGM is dissolved in the process water. This GGM can be recovered from the waters by ultrafiltration.

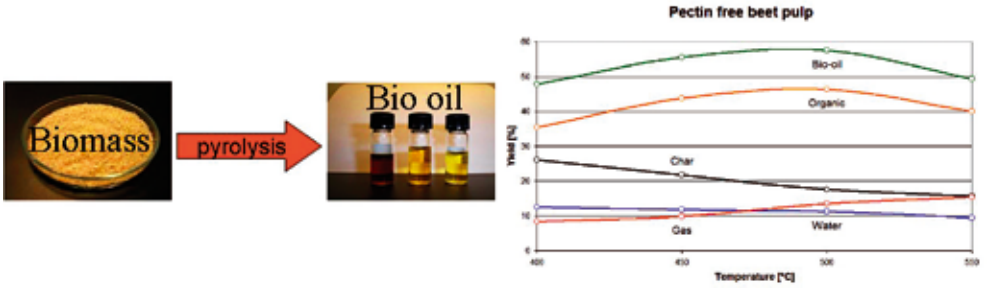
In black liquor, roughly half of the dissolved organic material is lignin and the rest is mainly sugar acids, other organic acids and methanol. Presently, black liquor is used as fuel in the recovery boiler, but separation of lignin from black liquor, may lead to new uses of lignin; as raw material for adhesives, dispersants, phenolic compounds and carbon fiber.

Cooperation:

KCL; Top Analytica (research partners exchanging information on issues related to biorefining); Danisco; Dynea Chemicals; Fortum; Metsä-Botnia; M-real; Neste Oil; Pöyry; Stora Enso; UPM-Kymmene (industrial partners)

Publications:

- Aho, A., Kumar, N., Eränen, K., Backman, P., Hupa, M., Salmi, T., Murzin, D.Yu. (a) (Category 4.2)
- Aho, A., Kumar, N., Eränen, K., Backman, P., Hupa, M., Salmi, T., Murzin, D.Yu. (b) (Category 4.2)
- Aho, A., Kumar, N., Eränen, K., Holmbom, B., Hupa, M., Salmi, T., Murzin, D.Yu. (Category 4.2)
- Aho, A., Kumar, N., Eränen, K., Salmi, T., Hupa, M., Murzin, D.Yu. (Category 4.2)



Product distribution of the pyrolysis of pectin free beet pulp

Future Biorefinery (FuBio)

Main funding: Tekes, Forestcluster Ltd

Stefan Willför, Ikenna Anugwom, Markku Auer, Johan Bobacka, Nikolai DeMartini, Christer Eckerman, Patrik Eklund, Tingting Han, Paula Heikkilä, Bjarne Holmbom, Mikko Hupa, Ari Ivaska, Victor Kisonen, Ann-Sofie Leppänen, Jyri-Pekka Mikkola, Dmitry Murzin, Päivi Mäki-Arvela, Andrey Pranovich, Markku Reunanen, Tapio Salmi, Rainer Sjöholm, Annika Smeds, Anna Sundberg, Pasi Virtanen, Lari Vähäsalo, Johan Werkelin, Maria Zevenhoven

The FuBio project is a top-down planned research program that will lay the foundation for a new knowledge 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. Thus the focus is on future forest biorefineries. The project is divided into five research themes:

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

A sixth theme will cover day-to-day management of the program and generate reports on specific topics (e.g. black liquor gasification and pyrolysis).

Theme 1 focuses on two selected technologies, pressurized hot water treatment and ionic liquids, enabling novel fractionation of woody biomass into fractions with high potential

for further refining. Additionally, also separation of hydroxy acids from black liquor will be studied. The aim is to generate novel hemicellulose and cellulose fractions. In addition, "sulphur-free lignin" will be generated.

The target of Theme 2 is to develop technologies enabling modification of cellulose molecules fibres from traditional, emerging, and future biorefineries. These up-graded cellulose products will be an essential part of novel materials, as well as find solutions in various relatively large scale applications within the wood products, packaging, graphical printing, tissue, and selected other value chains.

Theme 3 aims at designing novel value chains, in which wood-derived hemicelluloses are converted into novel biopolymers, and to develop and test the technologies needed to enable such value chains in reality. Such biopolymers could potentially be used e.g. in packaging, as coatings and films and to improve runnability. The availability and feasibility of the hemicelluloses are closely dependent on clever co-utilisation of the fibre/cellulose fraction.

The target of Theme 5 is to find, separate, refine, and test extracts and compounds from trees or wood processing side-streams for their functional and biomedical activity, especially their antioxidative, antimicrobial, and health-promoting properties. Such extracts and compounds could also be applied as protection agents for technical products such as wood, paper, board, etc. Product roadmaps and regulation issues for selected promising applications, such as natural antioxidants for product protection, will also be layed out. This theme will eventually provide the knowledge base for development of new health-promoting products.

Cooperation:

Forestcluster Ltd; VTT; KCL; Metla; Lappeenranta University of Technology; Helsinki University of Technology; University of Jyväskylä; University of Helsinki; University of Turku; University of Tampere; University of Joensuu; Metsäliitto; Myllykoski; Metso; Kemira; Ciba Finland; Andritz; Tamfelt; Pöyry; Stora Enso; UPM-Kymmene; Danisco; Orthotopix; Separation Research

New Value-added Natural Chemicals from Wood

Main funding: Academy of Finland

Chunlin Xu, Ann-Sofie Leppänen, Jan-Erik Raitanen, Patrik Eklund, Rainer Sjöholm, Markku Reunanen, Paula Heikkilä, Annika Smeds, Stefan Willför

The ultimate goal of this project is to identify, characterise, valorise, test, and evaluate new

value-added natural biochemicals mainly from wood, but also from other biomass sources, as active compounds in various biomaterials and pharmaceutical and technical applications. Especially different valuable polyphenols and hemicelluloses are of interest.

Strong emphasis has also been laid on developing and evaluating analytical techniques for wood extractives and polyphenols in general. The occurrence and structure of different polyphenols and volatile organic carbons (VOC's) in selected industrially important tree species has been studied. We have obtained new, important data on the occurrence of lignans in natural waters, as well as in different non-wood plants by utilising our improved analytical techniques. The antimicrobial properties of knotwood extracts were also studied. By far the most consistent antibacterial and antifungal properties were associated with extracts of pine species and especially their pinosylvin content. The pinosylvin studies have been continued 2008–2009 within the Tekes (EU structural funds) project "Bioactive and wood-associated stilbenes as multifunctional antimicrobial and health-promoting agents (BIOSTIMUL)". Norlignans, with structures resembling those of the pinosylvins, have also been synthesised from the abundant knotwood lignan hydroxymatairesinol and are being evaluated for several bioactive properties.

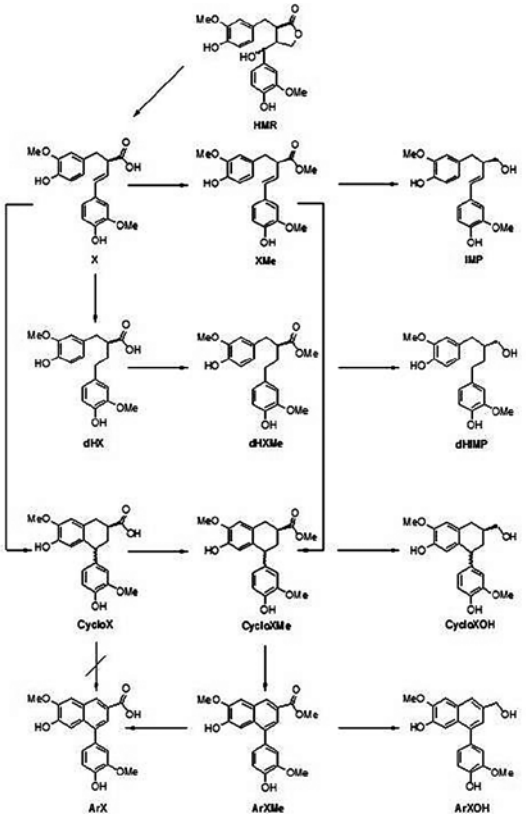
The physico-chemical properties and acid stability of spruce GGM have been intensively studied bringing forth new information and ideas for the use of such wood-derived hemicelluloses. Functionalization of GGM through acetylation, carboxymethylation, sulphonation, and combinations thereof, has been carried out to improve specific properties. Native hemicelluloses, such as GGM, hardwood xylans, and larch arabinogalactans also have potential to be used as a feed source for ruminants. Promising preliminary in vitro tests are now followed up by in vivo tests in cooperation with MTT and Metla.

Cooperation:

UPM-Kymmene; Ciba; Raisio; Metso Paper; M-real; Nordic Jam; Granula; Bio-Vita; University of Helsinki; University of Kuopio; Metla; University of Turku; University of Jyväskylä; VTT; MTT; Metla; KCL; University of Peshawar, Pakistan; Zonguldak Karaelmas University, Turkey; University of Maribor, Slovenia; University of Agricultural Sciences and Veterinary Medicine, Romania; Romanian Academy "P. Poni" Institute of Macromolecular Chemistry, Romania; "Al. I. Cuza" University, Romania; Universidad Miguel Hernández, Spain; Slovak Academy of Sciences, Slovakia; Health Sciences University of Hokkaido, Japan; Central Research Laboratories, Yomeishu Seizo, Japan; Tampere University of Technology; North Carolina State University, Raleigh, NC, USA; United States Department of Agriculture, USA; Technical University of Luleå, Sweden; European Polysaccharide Network of Excellence (EPNOE)

Publications:

- Xu, Chunlin (Category 4.1.1)
- Mikkonen, K.S., Yadav, M.P, Cooke, P., Willför, S.M., Hicks, K.B., Tenkanen, M. (Category 4.2)
- Piispanen, R., Willför, S., Saranpää, P., Holmbom, B. (Category 4.2)
- Willför, S., Sundberg, K., Tenkanen, M., Holmbom, B. (Category 4.2)
- Xu, C., Pranovich, A., Vähäsalo, L., Hemming, J., Holmbom, B., Schols, H.A., Willför, S. (Category 4.2)
- Xu, C., Willför, S., Holmbom, B. (Category 4.2)
- Balas, A., Hemming, J., Willför, S., Popa, V.I., Holmbom, B., (Category 4.3)
- Willför, S. (Category 4.3)
- Xu, C., Pranovich, A., Hemming, J., Holmbom, B., Albrecht, S., Schols, H.A., Willför, S. (Category 4.3)
- Xu, C., Sundberg, K., Petterson, C., Holmbom, B., Willför, S. (Category 4.3)



Synthesis pathway for different norlignans

Targeted Functionalization of Spruce Galactoglucomannans with Aid of Galactose Oxidase (FunMan)

Main funding: Academy of Finland

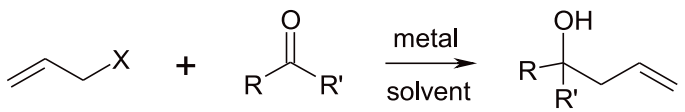
Ann-Sofie Leppänen, Outi Niittymäki, Patrik Eklund, Rainer Sjöholm, Markku Reunanen, Chunlin Xu, Stefan Willför

The project focuses on spruce galactoglucomannans (GGM), which is a new potential product from forest biorefineries. The key technologies studied are targeted and controlled oxidation of GGM with galactose oxidase (GO), and further chemical functionalization of the oxidized GGM. The usefulness of GGM in various applications is evaluated. The goal is to develop novel innovative applications for a side-product from the processing of spruce.

Pure spruce GGM was prepared from TMP and its fine structure characterized. The oxidation reaction with GO was studied in detail using methyl-α-D-galactopyranoside and D-raffinose as substrates. Reaction products were isolated and their structures analyzed. GGM was oxidized with GO in the optimized conditions and the product analyzed by NMR and GC-MS. The poor solubility of the oxidized product in NMR solvents lead to the investigation of a GC-MS technique utilizing NaBD4 reduction of the product to result deuter labelling of the oxidized galactose prior to acid methanolysis and GC-MS analysis. The further chemical modification of oxidized GGM was tested using oxidized methyl-α-D-galactopyranoside as a model compound in a Barbier type reaction. The formed aldehyde can be further modified by the metal-mediated allylation reaction. This synthetic route, where enzymatic oxidation is followed by chemical modification, could make it possible to selectively modify galactose-containing polysaccharides. The aim is to develop a reaction protocol for allylation of oxidized methyl-α-D-galactopyranoside that also could be applied on GGM.

Cooperation:

University of Helsinki



Metal mediated allylation of carbonyl groups

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

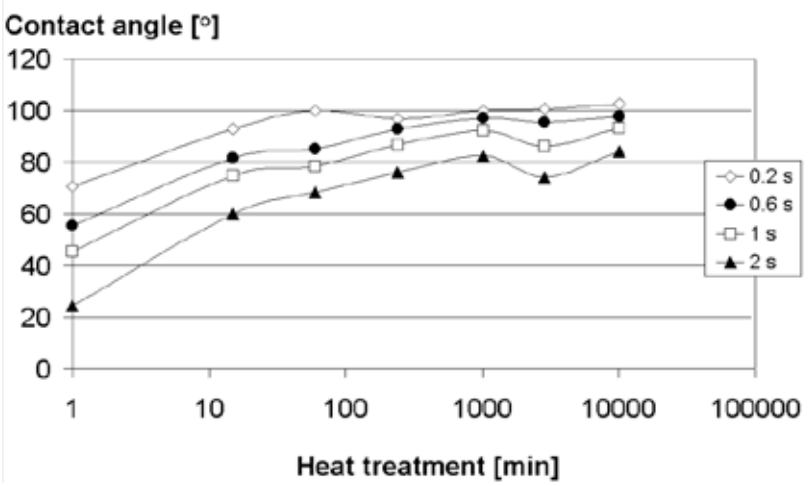
Main funding: Tekes

Annika Smeds, Markku Reunanen, Jarl Hemming, Stefan Willför

The objective of the project is to develop novel functional solid foamy materials from renewable natural polymers and biomass. This will be achieved by combining advanced polymer modification and analytical technologies to processing operations such as extrusion, injection moulding, rotational moulding, and coating. Biomass-derived feedstock materials (proteins, suberin, lignin, cellulose, galactoglucomannans, Polydextrose, and process wastes) will be converted by chemo-enzymatic technologies to compatible constituents for variable solid foam applications. The final aim is to replace man-made, synthetic and expensive components currently used in porous composite structures and foams with renewable polymers and materials. Since foam provides an excellent directional matrix for fibre orientation, fibre-reinforced structures will also be investigated. The interfacial tailoring depends on the type of processing and the polymer modification indicated above must be designed a target, such as matrix-fibre bonding, polymer-surfactant rheology and foaming control, etc. These processing technologies are then characterized in order to establish a measurable success of the research.

Cooperation:

VTT; University of Helsinki; Åbo Akademi University Centre for Functional Materials (FUNMAT); UPM; Consolis Technology; Danisco Sweeteners; FinnFoam; Forcit; Termex Eriste; Laihian Mallas; Taivalkosken Mylly; Weekend Snacks; Lignival project



FTIR spectra of native (DS=0.3) and acetylated (DS=2.7) GGM

Extraction of Hemicelluloses from Wood with Pressurised Water (HemU)

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

Tao Song, Andrey Pranovich, Bjarne Holmbom

The aim of the research is to develop new industrially feasible techniques for extraction of the main wood components, preserving their structure as well as possible, with selective extraction of hemicelluloses as the first target. Spruce chips and ground spruce wood have been extracted using an Accelerated Solvent Extraction (ASE) apparatus. The obtained extract solutions have been analysed in detail for dissolved hemicelluloses, monosaccharides and lignin. Hydrolysis of glycosidic bonds as well as acetyl groups has also been assessed. Selective extraction of galactoglucomannan (GGM), the main hemicellulose type in spruce, in high yield has been achieved with plain water in the temperature range of 160–180°C.

The extracted hemicelluloses are partly hydrolysed, even to monosaccharides, but high-molar-mass hemicelluloses can also be recovered in considerable amounts at optimised conditions. By using buffers it is possible to obtain a more flat pH profile, thus inhibiting acid hydrolysis of acetyl groups as well as hemicellulose chain cleavage. Consequently, GGM with higher molar mass can be extracted. The wood particle size has a considerable effect on the extraction yield.

Cooperation:

METLA; Lappeenranta University of Technology; EPNOE partners

Publications:

- Song, T., Pranovich, A., Sumerskiy, I., Holmbom, B. (Category 4.2)
- Song, T., Pranovich, A., Sumerskiy, I., Holmbom, B. (Category 4.3)

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

Main funding: Tekes, WoodWisdom Net

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

The aim of this large European project is to develop an Integrated Bark Biorefinery, in which softwood bark is efficiently used as a biomass feedstock for production of industrial and consumer products or suitable intermediates, and energy. A central part of the work is to develop and evaluate the Integrated Bark Biorefinery as an economical and technological concept.

In our laboratory, chemically well-characterized softwood bark extracts and components have been prepared for further product development at other particiapting laboratories. Separation processes for stilbenes and tannins have been explored using industrial spruce bark samples. Stilbene glucosides can be extracted using water at room temperature. The extraction is more effective when the bark is milled. Improvements of the extraction was also achieved by increasing the water to bark ratio, and by addition of ethanol. Separation of the stilbene glucosides from co-extracted monosaccharides was achieved by using XAD-7 resin. The tannins can be extracted by ASE with water in the temperature range 25–125°C. Freeze-drying and grinding of the bark facilitate also the tannin extraction.

Methods for determination of tannins in extracts have been evaluated. The acid-butanol method was found to be a more reliable and convenient method than the traditional PVP method. Acid degradation of the tannins in the presence of phloroglucinol followed by GC analysis is a promising method for rapid and convenient structural analysis of tannins.

Hemicelluloses and pectins can be extracted efficiently from spruce bark with water at temperatures of 150–170°C. The hemicelluloses in spruce bark are mainly composed of arabinose, xylose and glucose, while the dominating spruce GGM type is only a minor hemicellulose in bark.

Cooperation:

VTT; Fraunhofer Institut, Karlsruhe, Germany; Royal Institute of Technology (Wood Chemistry), Stockholm, Sweden; Technaro, Germany

Lignin Valorisation (Lignival)

Main funding: Tekes

Annika Smeds, Jan-Erik Raitanen, Paula Heikkilä, Patrik Eklund, Rainer Sjöholm, Markku Reunanen, Stefan Willför

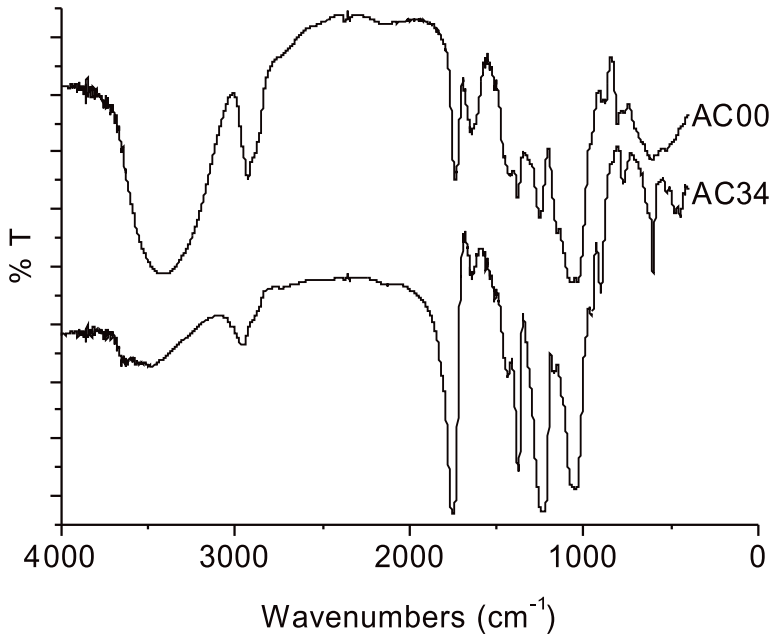
Lignin is an abundant natural biopolymer and thus a promising raw material for environmentally friendly production of materials. In Finland, the energy value of lignin is effectively utilised in the recovery boilers of the kraft mills. However, about 20 % of the black liquor lignin could be withdrawn from the recovery system without harming its energy balance. In order to be economically feasible, this necessitates that the withdrawn lignin can be upgraded into products whose value clearly surpasses the energy value of the lignin raw material, calculated to be 167 €/t. Sulphur free lignins from various experimental processes differ from kraft lignin and may find applications that are not feasible for kraft lignin. In addition, low-molecular aromatic compounds such as lignans

are an interesting source of phenolic materials to be used as such or in combination with the polymeric lignins.

The structure of macromolecular lignin is highly heterogeneous due to variations in lignin composition, size, cross-linking and functional groups. These, in turns, are caused by differences in raw material, pulping and isolation conditions. However, in order to facilitate the industrial use, lignins having a simplified structure and controllable reactivity are needed. Lignins and lignans can be modified by chemical, physical and enzymatic means. The chemistry behind different reactions is investigated through model substances such as lignans. Co-polymerisation of lignin and lignans can also introduce new functionalities to the materials. The present project aims at identifying suitable processing technologies for selected available or emerging lignin raw materials to modify them into materials applicable for the target products: coating layers with barrier properties for packaging, and composite materials.

Cooperation:

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



Lignan model compounds for studying radical and laccase induced polymerisation reactions in lignin

Lignans as Versatile Chiral Auxiliaries and Chiral Catalysts (LIGNO-CATS)

Main funding: Academy of Finland

Patrik Eklund, Yury Brutsentsev, Rainer Sjöholm, Stefan Willför, Annika Smeds, Jan-Erik Raitanen

The objective of the project is to develop and evaluate novel lignan-based chiral reagents and catalysts for applications in modern organic synthesis and stereoselective reactions. Recent progress and development of Finnish biorefinery processes has shown that enantiopure natural products belonging to the class of lignans can be isolated from spruce knotwood in large quantities (up to tons). This unique possibility has prompted us to use the lignan hydroxymatairesinol as a valuable starting material for the synthesis of new lignans and lignan derivatives, and recently as chiral reagents and catalysts. Although several natural products such as tartaric acids and carbohydrates have successfully been derivatized to well-working chiral ligands, this is the first research project to develop natural lignans into chiral ligands and catalysts.

The development of novel lignan-based chiral ligands and catalysts is divided in four separate lines. 1) Synthesis and evaluation of TADDOL-like ligands (chiral 1,4-diols). 2) Synthesis and evaluation of phosphorous-containing ligands 3) Synthesis and evaluation of chiral Brönsted acid catalysts. 4) Synthesis and evaluation of lignan-based stoichiometric reagents for enantioselective reactions and for resolution of racemates. The chemical structure of hydroxymatairesinol allows us to prepare numerous different derivatives by suitable synthetic modifications. The synthetic modifications will include reductions, oxidations, metathesis, aryl-aryl couplings, Grignard reactions etc. The lignan skeleton is thus transformed into chiral ligands with different degree of flexibility or with fixed "biting angels" or with atropoisomeric properties or with a combination of these. The properties of the different types of the chiral ligands and the catalysts are then evaluated, and/or submitted to further derivatisation (water solubility, immobilization, optimizing "biting angles" etc). The synthesis and the properties of the novel catalysts is supported by molecular modeling. Also, some of the testing and evaluation of the catalysts will be performed by international collaborating researchers, making research visits between laboratories possible. The final applications of the catalysts will be focused on stereoselective carbon-carbon bond formations and enantioselective hydrogenations/reductions.

Wood Extractives as Starting Materials for Synthesis: From the Spruce Lignan Hydroxymatairesinol to Other Valuable Bioactive Lignans and Lignan Derivatives

Main funding: PCC, EU

Rainer Sjöholm, Patrik Eklund, Stefan Willför, Annika Smeds, Jan-Erik Raitanen, Heidi Markus

The main goal is to develop methods for the transformation of naturally occurring lignans, mainly hydroxymatairesinol (HMR) to other, rare and more valuable known lignans as well as to new, previously unknown ones. In parallel to this, advanced analytical methods have been developed for qualitative as well as quantitative analysis of lignans from different sources.

Future plans include chemical transformation of the most common lignans, i.e. HMR, matairesinol (MR), secoisolariciresinol (SECO) and the norlignan imperanene (IMP) into new molecules and materials with defined areas of application. The inherent enantiopurity of the lignans will be utilized for development of methods for synthesis of: 1) *Chiral ligands for enantioselective metal-catalysed reactions*. These find applications in many different types of reactions, e.g. enantioselective additions to carbonyl compounds, conjugate additions, transesterifications, cyclopropanations and cycloadditions. Many of these reactions are used in the preparation of e.g. pharmaceuticals, 2) *Chiral crown ethers.* These can have applications in complexation of metal ions for analytical purposes, as well as in complexation (recognition) of small organic molecules, i.e. for use as sensors. Applications in chromatography may also be found, 3) *Chiral dendrimers*. These are expected to interact with guest molecules in a way that the interaction can be detected by spectrometric and electrochemical methods, 4) *Chiral stationary phases for HPLC.* Part of the results from groups 2 and 3 fall under this heading, as the modified lignans are easily immobilised e.g. on silica. The unmodified lignans can be immobilised as such for applications in chiral separations.

In this project, forest products are utilised as the starting material and the reactions presented can be seen as the ultimate steps within the forest biorefinery concept.

Publications

- Eklund, P.C., Backman, M.J., Kronberg, L.Å., Smeds, A.I., Sjöholm, R.E. (Category 4.2)

Chemicals from Wood

Main funding: Raisio Foundation, EU

Heidi Markus, Päivi Mäki-Arvela, Jyri-Pekka Mikkola, Narendra Kumar, Ville Nieminen, Dmitry Murzin, Tapio Salmi, Bjarne Holmbom, Rainer Sjöholm

A new, environmentally friendly pathway for preparing of anti-mutagenic and anti-carcinogenic components is based on the use of chemicals derived from wood and their transformation via heterogeneous catalysis. New catalysts are synthesized, characterized and tested under relevant reaction conditions. Preparation of conjugated linoleic acid and hydrogenolysis of hydroxymatairesinol to matairesinol through heterogeneous catalysis has become feasible. We have been the first ones, who have demonstrated that it is possible to make conjugated linoleic acid with the aid of heterogeneous catalysts and in the absence of solvents. New Pd/active carbon nanotube catalysts were obtained for the production of hydroxymatairesinol.

Publications:

- Bernas, H., Plomp, A. J., Bitter, J. H., Murzin, D.Yu. (Category 4.2)
- Nieminen, V., Honkala, K., Taskinen, A., Murzin, D. Yu. (Category 4.2)

3.6 Catalysis and Molecular Engineering

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

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

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

Among the new materials which are actively researched at PCC are various micro- and

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

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

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

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

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

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

(e.g. hydroformylation products). Advanced dynamic models including complex kinetics, catalyst deactivation and regeneration as well as flow modeling (classical and CFD) were applied. The effect of ultrasound and microwave irradiation on catalytic processes was studied intensively and gave encouraging results (see chapter 3.2).

Micro and Mesoporous Materials

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

Narendra Kumar, Matias Kangas, José Villegas, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

Synthesis of new catalysts with different micro- and mesoporous materials has been carried out. The effect of ultrasonic treatment on zeolite crystallization has been studied. In situ metal modification has been applied in preparation of metal modified zeolites and molecular sieve catalysts. The prepared catalysts are characterized with modern techniques, such as XRD, SEM, TEM, AFM and TPD. The catalysts are applied in several projects, for instance in hydrocarbon transformations as well as in preparation of fine chemicals. The deactivation and regeneration of zeolite materials is investigated. Sensor materials have been synthesized and successfully applied. Quantum chemical calculations, FTIR and solid state NMR have been used to characterize the active sites on zeolites.

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

Publications:

- Kangas, M., Kumar, N., Harlin, E., Salmi, T., Murzin, D.Yu. (Category 4.2)
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- Reinik, J., Heinmaa, I., Mikkola, J-P., Kirso, U. (Category 4.2)
- Sarkadi-Pribóczki, É., Kumar, N., Kovács, Z., Murzin, D.Yu. (Category 4.2)
- Villegas, J.I., Kangas, M., Byggningsbacka, R., Kumar, N., Salmi, T., Murzin, D.Yu. (Category 4.2)

Environmental Catalysis

Main funding: Academy of Finland

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

The project addresses fuel consumption and emissions from vehicles. The objectives are to show the potential for a continuous catalyst system to comply with EU standard of year 2005 for diesel and lean-burn cars. An Ag/alumina catalyst converter, developed by our laboratory, has been installed in a prototype common rail diesel vehicle. This converter has shown high potential in NO_x reduction during stationary and transient vehicle tests. Detailed NO_x reaction mechanisms are investigated by transient techniques, combined with isotopic jumping, and the surface-induced gas-phase reactions are studied using modified reactor systems. Radicals formed during the complex heterogeneous-homogeneous HC-SCR cycle are trapped in a growing Argon matrix at 10 K and analyzed, in collaboration with University of Jyväskylä, by means of electron-paramagnetic resonance and infrared spectroscopy. Microreactors were successfully used in development of HC-SCR catalysts.

Cooperation:

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

Publications:

- Hernández Carucci, J.R., Arve, K., Eränen, K., Murzin, D.Yu., Salmi, T. (Category 4.2)

Clean Fuels and Components

Main funding: Neste Oil, Tekes

Matias Kangas, Heidi Bernas, Ikenna Anugwom, Andreas Bernas, Mathias Snåre, Siswati Lestari, José Villegas, Mats Käldström, Narendra Kumar, Päivi Mäki-Arvela, Dmitry Murzin, Tapio Salmi

Cleaner fuels and fuel components are needed in the future. The project focuses on several applications, such as ring opening of cyclic hydrocarbons and skeletal isomerization of alkenes. Catalyst synthesis, catalyst screening as well as kinetic investigations are included. New catalyst configurations have been patented. A chemometric approach was success-

fully applied to interpret complex fuel mixtures. Modelling of kinetics and diffusion in zeolites is in progress. Furthermore, a possibility is explored for production of fuels from renewable resources. New technology was developed for cleaning fuels from sulphuric components with ionic liquids.

Cooperation:

Neste Oil

Publications:

- Kangas, M., Kumar, N., Harlin, E., Salmi, T., Murzin, D.Yu. (Category 4.2)
- Kangas, M., Salmi, T., Murzin, D.Yu. (Category 4.2)
- Lestari, S., Simakova, I., Tokarev, A., Mäki-Arvela, P., Eränen, K., Murzin, D.Yu. (Category 4.2)
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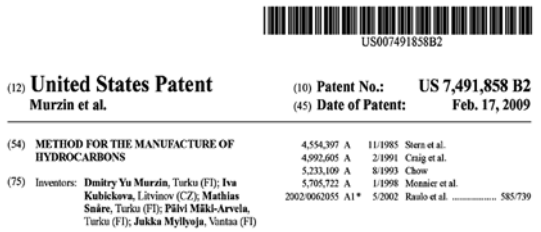

US007491858B2

(12) **United States Patent**
Murzin et al.

(10) **Patent No.: US 7,491,858 B2**
(45) **Date of Patent: Feb. 17, 2009**

(54) **METHOD FOR THE MANUFACTURE OF HYDROCARBONS**

(75) Inventors: **Dmitry Yu Murzin**, Turku (FI); **Iva Kubickova**, Litvinov (CZ); **Mathias Snåre**, Turku (FI); **Päivi Mäki-Arvela**, Turku (FI); **Jukka Myllyoja**, Vantaa (FI)

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Continuous reactor for hydrogenation and decarboxylation and patent in decarboxylation

Valorization of Chemicals Derived from Biomass

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

Jyrki Kuusisto, Jyri-Pekka Mikkola, Anton Tokarev, Narendra Kumar, Bright Kusema, Victor Sifontes, Heidi Bernas, Olga Simakova, Olawamuiwa Oladele, Jan Hájek, Bartosz Rozmysłowicz, Betiana Campo, Päivi Mäki-Arvela, Hannu Karhu, Dmitry Murzin, Tapio Salmi

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

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

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

Cooperation:

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

Publications:

- Kuusisto, J., Mikkola, J.-P., Sparv, M., Wärnå, J., Karhu, H., Salmi, T. (Category 4.2)
- Murzina, E.V., Tokarev, A.V., Kordas, K., Karhu, H., Mikkola, J-P., Murzin, D.Yu. (Category 4.2)
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- Tolvanen, P., Mäki-Arvela, P., Eränen, K., Wärnå, J., Holmbom, B., Salmi, T., Murzin, D.Yu. (Category 4.2)

Asymmetric Catalysis

Main funding: Academy of Finland

Esa Toukoniitty, Blanka Toukoniitty, Igor Busygin, Päivi Mäki-Arvela, Ville Nieminen, Serap Sahin, Alexey Kirilin, Matti Hotokka, Rainer Sjöholm, Reko Leino, Dmitry Murzin, Tapio Salmi

Enantioselective catalytic hydrogenation of ketones provides a pathway to a cleaner synthesis of optically active compounds, which are used as intermediates for pharmaceuticals. The aim of the project is to develop new catalytic technologies for the production of enantiomerically pure compounds through selective catalytic hydrogenation in the presence of catalyst modifiers. A particular emphasis is put on the development of better catalyst modifiers in collaboration with the research group at the laboratory of Organic Chemistry, Åbo Akademi University (Professor Reko Leino). Molecular modelling is used as a tool to increase the understanding in enantioselective hydrogenation. New multicentered adsorption models have been applied to enantioselective hydrogenation. The enantioselective hydrogenation has been performed in a batch and in a continuous reactors and the transient behaviour of the system has been modelled quantitatively. Chemo-bio synthesis work in one pot was initiated and it was demonstrated that the concept works.

Cooperation:

University of Turku

Publications:

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- Murzin, D.Yu. (Category 4.2.2)

3.7 Biofuels and Bioenergy

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

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

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

The PCC also develops modeling capabilities to make it possible to predict the combustion process for non-conventional fuels and, in particular, mixtures of two or more different fuels. Computational Fluid Dynamics, CFD, has opened excellent opportunities to study biofuel conversion in realistic furnace environments. To be useful in biofuel conversion processes these advanced CFD models however require tailored submodels to describe

the many important aspects of the practical biofuel processes. We develop submodels for fuel particle oxidation, the chemistry of the unwanted pollutants, the fuel and ash particle behaviour, and fouling and corrosion phenomena in furnaces.

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

The biorefinery concepts imply the option of production of bio-based liquid fuels for use in vehicles by processes based on pyrolysis or gasification. All of the interesting process concepts require fundamental understanding of the conversion chemistry itself, but also of the behaviour of the many impurities in the biomass materials being used as feedstock. The PCC wants to contribute to the development of process concepts of liquid biofuel production.

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

Chemistry in Biomass Combustion (ChemCom 2.0)

Main funding: Tekes

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

ChemCom 2.0 started in January 2008 and will continue until the end of 2010. The project focuses on fundamental chemical questions and solutions in combustion and gasification of solid biofuels and black liquor. However, although biofuels and black liquor are in focus, also waste fuel combustion (REF, RDF, MSW, sludges, etc.) and oxyfuel combustion will be investigated. In ChemCom 2.0 we will take advantage of the results that have been achieved in ChemCom 2005–2007, and turn them to the best possible account. Especially, a heavy input on modelling of both bubbling fluidised beds and recovery boilers have been done and several different submodels have been produced.

As a consequence, one of the main needs and also objectives of ChemCom 2.0 is the validation of these models, in combination with identifying shortcomings of the models and improving them. This is of highest importance since CFD modelling is nowadays utilized in the analysis of the reasons of practical furnace problems, and as a design tool in retrofit applications and in designing new furnaces. Data for the validation is gathered by measuring critical parameters during measurement campaigns in one recovery boiler and in one bubbling fluidised bed, in combination with laboratory testing and fuel analyses. Although, modelling and model validation has a large role in this project, also other issues will be emphasized to clarify fundamental chemical phenomena in combustion and gasification processes. Such issues are the behaviour and release of ash forming matter and trace metals, corrosion issues, gaseous emissions, thermodynamic data development and calculations, combustion and gasification rate studies of biofuel and black liquors, etc. These subjects, among others, are in ChemCom 2.0 organised by using four overall topics:

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

Cooperation:

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

Publications:

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- Laurén, Tor (Category 4.1.2)
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- Senthoorselvan, S., Gleis, S., Hartmut, S., Yrjas, P., Hupa, M. (Category 4.2.1)

Measuring gas composition inside a boiler

Multi-Phase Chemistry in Process Simulation (VISTA)

Main funding: Tekes/Masi

Anders Brink, Bingzhi Li, Mikko Hupa

In the project common methods for combining the thermodynamic multi-phase approach with computational fluid dynamics, reactor simulations and process simulations

are being developed. The thermodynamic multi-phase method is combined with flow simulation to predict multi-variant operation windows for high-temperature processes. In the project the use of multi-component streams and source terms in process flowsheet simulation is also developed. At Åbo Akademi University, the project focus on process problems related to high load flows of reacting particles.

Cooperation:

VTT (Coordinator); Helsinki University of Technology; University of Oulu; Andritz; Fortum Nuclear Services; Outotec; Outokumpu Stainless; Luvata; Ovako Bar; Rautaruukki; UPM-Kymmene

Publications:

- Brink, A., Engblom, M., Hupa, M. (Category 4.2)
- Li, B., Brink, A., Hupa, M. (Category 4.2.1)

Modelling Interfacial Partitioning in Multi-Phase Systems (Inter)

Main funding: Tekes/Masi

Anders Brink, Bingzhi Li, Mikko Hupa

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

Cooperation:

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

Publications:

- Li, B., Brink, A., Hupa, M.(Category 4.2.1)

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

Main funding: Academy of Finland/Ketju

Johan Lindholm, Anders Brink, Mikko Hupa

In the project new flame retardants in the family of novel azoalkane flame retardants are developed. In addition, the goal is to create a base for constructing a novel tool-box that will be helpful in rendering any polymeric material flame retardant. The approach is based on synthesis of novel model flame retardant compounds; new fire test methodologies; and new techniques for evaluating results, including mathematical modelling and simulation that will further increase the knowledge in fire retardancy theory and applications

Cooperation:

Åbo Akademi University (Polymer Technology)

Publications:

- Lindholm, J., Brink, A., Hupa, M. (Category 4.3)

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

Main funding: Tekes/Climbus

Patrik Yrjas, Tor Laurén, Mikko Hupa

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

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

Cooperation:

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

Publications:

- Aho, M., Vainikka, P., Taipale, R., Yrjas, P. (Category 4.2)

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

Main funding: Tekes/Climbus

Patrik Yrjas, Pasi Vainikka, Tor Laurén, Mikko Hupa

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

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

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

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

Cooperation:

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

Publications:

- Vainikka, P., Laurén, T., Hupa, M., Yrjas, P., Taipale, R. (Category 4.2.1)

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

Main funding: Tekes

Patrik Yrjas, Micaela Westén-Karlsson, Mikko Hupa

The project started in February 2007 and will continue until February 2010. The aim is to optimize the material solutions to withstand corrosion and erosion phenomena in power plant boilers. The formation mechanisms and composition of the oxide layers is to be determined together with their mechanical characteristics both in the laboratory tests and in full scale. The purpose is to improve the materials within two temperature intervals i.e. 400–600˚C (high temperature corrosion) and below 160°C (dewpoint corrosion). The focus is on finding economical and durable material solutions and also to develop methods to repair eventual material damages that may occur by time.

Cooperation:

VTT; Helsinki University of Technology, Turku Energia – Åbo Energi ; Oitin Valu; Ekokem; Ingmar Westerlund Consulting; Foster Wheeler Energia; Kuopion Konepaja; Fortum

Publications:

- Westén-Karlsson, Micaela (Category 4.1.2)

Demonstration of Direct Solid Recovered Fuel (SRF) Co-combustion in Pulverized Fuel Fired Power Plants and Implementation of a Sustainable Waste-to-energy Technology in Large-scale Energy Production (Recofuel)

Main funding: EU/TREN/04/FP6/S07.32813/503184

Maria Zevenhoven, Mikko Hupa

This project focuses on demonstrating the use of solid recovered fuels together with coal and brown coal in full scale pulverized fuel fired boilers for producing energy. The studies include assessments of fuel feeding possibilities, boiler operational problems such as slagging fouling and corrosion, and emissions control of toxic elements.

The ÅAU part consists of theoretical and lab scale studies of the combustion behavior of various types of SRF. Also the behavior of ash forming elements and toxic metals are studied. The theoretical studies involve thermochemical evaluations of ash forming elements including the toxic metal partitioning during combustion.

Cooperation:

RWE Umwelt (coordinator), Germany; University of Stuttgart IVD, Germany; KEMA Nederland, the Netherlands; RWE Power, Germany; National Technical University of Athens (NTUA), Greece; Institut für Abfall-, Abwasser- und Infrastruktur-Management (INFA), Germany; Public Power Corporation (PPC), Greece; Essent Energie, the Netherlands; Centro Elettrotechnico Sperimentale Italiano Giancinto Motta (CESI), Italy; TAUW, the Netherlands; Institute for Nuclear Power (VINCA), Serbia

Utilization of Combustible Waste – A Study of Environmental and Financial Consequences

Main funding: Finnish Environment Institute (SYKE)

Maria Zevenhoven, Mikko Hupa

According to an agreement within the European Union, in 2016, biodegradable waste dumping will have to decrease to 35% of the level of 1994. This means that Finland will have to change the way waste is treated.

This project studies the feasibility of energy recovery from different biodegradable waste streams. Hereto different typical Finnish areas have been chosen to be studied more closely, i.e. an urban area, a sub-urban area, a rural area etc.

An inventory will be made of waste streams, possible waste treatment technologies and their environmental and financial consequences. Also potential future technologies will be taken into account.

Cooperation:

Finnish Environment Institute (SYKE); University of Helsinki; Helsinki University of Technology; Tampere University of Technology

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

Main funding: Tekes

Patrik Yrjas, Mikko Hupa

The project started in May 2008 and will continue until the end of 2010. The principal scientific objectives are to develop and validate improved high performance alloys to withstand the impact of hot corrosion and other high temperature damage in biomass and waste combustion. Also the intent is to develop and demonstrate advanced online

corrosion monitoring probes and to combine the results from computational materials modelling, online corrosion monitoring and laboratory testing for life prediction of new advanced alloys, and to validate the results by comparison to field testing. Further, one part of the project is to clarify material challenges and alternatives for oxyfuel combustion- ÅA will support these objectives by making laboratory corrosion tests under different process conditions, by changing the gas atmosphere, synthetic ash compositions, etc. The materials meant for testing will be provided by the project partners.

Cooperation:

VTT; Helsinki University of Technology; Fortum; Foster Wheeler Energia

3.8 Intelligent Electroactive Materials

The research activities in the area of electroactive materials comprise conjugated polymers, donor-acceptor molecules, fullerenes and carbon nanotubes. New conjugated oligomers and polymers are synthesized electrochemically, one of the main interests being multifunctional conducting polymers. The functionalization is made in order to obtain specific properties like good solubility, complexing and self-doping properties, n- and p-dopability and low band gap.

Different parameters can be controlled during electrochemical polymerization and functionalization so that a desired structure and film thickness can be obtained. The functionalization of the polymer material can be modified to meet the demands of a certain application. When used in sensors different complexing agents (ionophores) will be covalently bound to the polymer or to the monomeric unit. When used in photovoltaic devices, covalent bonding of alkyl chains is made to obtain solubility of the polymer material or covalent bonding of functional groups (containing oxygen) in order to control the size of the band gap of the polymer.

Mixtures or bilayers of fullerenes and a conducting polymer are the main components in the structure of plastic solar cells. Special efforts are made to produce well organized surfaces and layers in order to optimize the interfaces between the layers.

Carbon nanotubes (CNTs) have been used to modify electrode surfaces to give increased electrochemical catalytic activity to the substrate. Modification has been done by using Au-nanoparticles together with some organic mediators and ionic liquids.

Techniques used for characterization of the thin films are cyclic voltammetry, in situ FTIR, Raman and UV-Vis spectroscopy, in situ electron spin resonance spectroscopy and in situ conductivity measurements. Impedance spectroscopy, electrochemical quartz

crystal microbalance, scanning electron microscopy and atomic force microscopy are also used.

New electroactive materials are essential tools for the development of chemical sensors. Our research on chemical sensors is focused on the use of conducting polymers as transducers and sensing membranes in combination with supramolecular receptors in order to obtain durable all-solid-state chemical sensors. Integration of the transducer and recognition elements into the same phase and ultimately into the same macromolecule will form the basis of durable chemical sensors.

Conducting polymers and carbon nanotubes are used in combination with polymeric ion-selective membranes to obtain solid-contact ion-selective electrodes (SC-ISEs) with improved analytical performance, such as high potential stability and low detection limit. The water uptake of polymeric ion-selective membranes is an important parameter that has been studied. Recent efforts have also resulted in a solid-contact reference electrode that will simplify the production and use of electrochemical sensors.

One objective is also to understand the detailed mechanisms of ion recognition and signal transduction in potentiometric ion sensors and membranes in general. In order to achieve this goal, experimental electrochemical studies are complemented with theoretical modeling of membrane potentials by using the Nernst-Planck-Poisson system of differential equations.

In addition to applications in chemical sensors and solar cells, conducting polymers are also used as immobilization matrix for enzymes in the development of biofuel cells.

Chemical Sensors Based on Conjugated Polymers and Carbon Nanotubes

Main funding: Academy of Finland; Åbo Akademi University Process Chemistry Centre; Åbo Akademi Foundation; Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM)

Maija Blomquist, Tingting Han, Tom Lindfors, Zekra Mousavi, Pia Sjöberg-Eerola, Andrzej Lewenstam, Johan Bobacka, Ari Ivaska

Chemical sensors for determination of Ag^+ and Cl^- were developed further by using poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3-octylthiophene) (POT) as sensing membranes. In addition to conjugated polymers, the ion-to-electron transduction properties of functionalized carbon nanotubes were studied. Conducting composite materials based on PEDOT doped with negatively charged carbon nanotubes was used as solid contact in ion sensors. Ion-selective organic electrochemical junction transistors (IS-OEJT) were developed further.

Derivatives of polyaniline were electrosynthesized and characterized by electrochemical and spectroscopic techniques. Special emphasis is given to the proton selectivity of PANI and the development of an optical method based on the sequential injection analysis technique for measuring pH with PANI nanoparticles.

Cooperation:

Universitat *Rovira i Virgili*, Tarragona, Spain

Publications:

- Sjöberg-Eerola, Pia (Category 4.1.1)
- Han, Tingting (Category 4.1.3)
- Sundblom, Sören (Category 4.1.3)
- Väänänen, Virpi (Category 4.1.3)
- Lindfors, T., Harju, L. (Category 4.2)
- Mousavi, Z., Latonen, R-M., Alaviuhkola, T., Bobacka, J., Pursiainen, J., Ivaska, A. (Category 4.2)
- Berggren, M., Forchheimer, R., Bobacka, J., Svensson, P-O., Nilsson, D., Larsson, O., Ivaska, A. (Category 4.2.2)

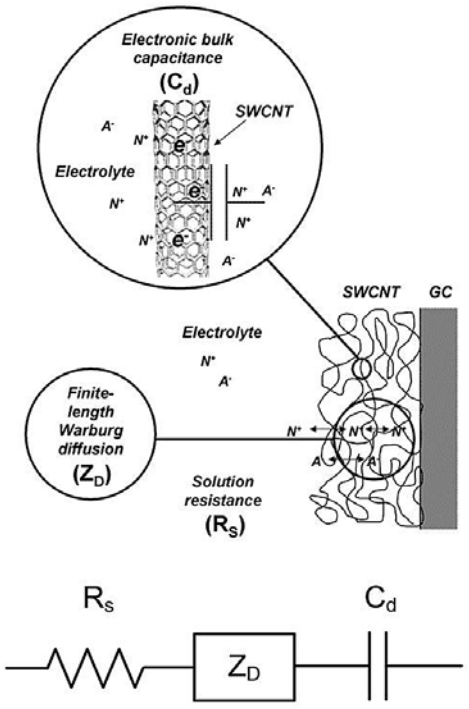


Illustration of ion-to-electron transduction of carbon nanotubes (SWCNT) deposited on glassy carbon (GC) and in contact with an electrolyte (N+A-). The corresponding equivalent electrical circuit is also shown (bottom).

Water Uptake of Membrane Materials Used in Ion-selective Electrodes

Main funding: Åbo Akademi University Process Chemistry Centre; Academy of Finland; Hungarian Academy of Sciences

Tom Lindfors, Fredrik Sundfors

The water uptake of both commonly used and new ion-selective membrane (ISM) materials was studied with FTIR-ATR spectroscopy within this project. Its main goal is to develop useful experimental methods for identifying membranes with low water uptake, which could be beneficial for ultra trace analysis with solid-contact ion-selective electrodes (SC-ISEs). The low water uptake of ISMs will probably prevent the formation of detrimental water layers (or scattered clusters of water) at the interfaces of the SC-ISEs. The power of the FTIR-ATR technique is its ability to distinguish between different types of water in the ISM.

The project was started in May 2008 and has resulted in three manuscripts, which all will be submitted before 05/2009 to high quality analytical chemistry journals. It was shown by FTIR-ATR measurements that the water uptake of ISMs based on plasticized poly(vinyl chloride) and poly(acrylate) was much higher on longer time scales than for silicon rubber based ISMs. In most cases, the water uptake was best described by a model including two diffusion coefficients describing diffusion of faster and slower water. The water uptake studies resulted in the preparation of the first silicon rubber based calcium-selective SC-ISEs with the solid-contact layer consisting of an electrically conducting polymer. The detection limit of these ISEs was 10^{-9} M Ca^{2+} (40 ppt).

Cooperation:

Budapest University of Technology and Economics, Budapest, Hungary

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

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

Jerzy Jasielec, Andrzej Lewenstam, Grzegorz Lisak, Ulriika Mattinen, Konstantin Mikhelson, Jill Nylund, Maria Peshkova, Tomasz Sokalski, Johan Bobacka

The goal of the MASTRA project is to develop robust solid-state ion sensors with low detection limit and a solid-state reference electrode based on recent advances in materials science and sensor technology. The solid state sensors and reference electrode will be

combined into a miniaturized potentiometric device for determination of toxic heavy metals and other ions of importance to human health and welfare.

The research in 2008 was focused on the development of conducting polymer-based solid-state reference electrodes and common platforms for both solid-state reference and solid-state ion sensors to be used for lowered detection limits. A first version of a solid-state reference electrode was developed. A general base for mathematical interpretation of the sensor signal was created in order to develop an in-depth understanding of the signal formation mechanism.

Cooperation:

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

Publications:

- Jasielec, Jerzy (Category 4.1.3)
- Mattinen, Ulriika (Category 4.1.3)
- Nylund, Jill (Category 4.1.3)
- Bobacka, J., Ivaska, A., Lewenstam, A. (Category 4.2)
- Grysakowski, B., Lewenstam, A., Danielewski, M. (Category 4.2)
- Peshkova, M.A., Sokalski, T., Mikhelson, K.N., Lewenstam, A. (Category 4.2)
- Sjöberg-Eerola, P., Nylund, J., Bobacka, J., Lewenstam, A., Ivaska, A. (Category 4.2)
- Sokalski, T., Kass, M., Mueller, C., Ivaska, A. (Category 4.2)
- Ivaska, A. (Category 4.2.2)
- Lewenstam, A., Blaz, T., Migdalski, J., Duda, L. (Category 4.6)

Electroactive Ion-Exchange Films for Removal of Heavy Metals from Wastewater

Main funding: Magnus Ehrnrooth Foundation

Marceline Akieh, Ari Ivaska, Johan Bobacka

Conducting polymers were studied as electrochemically controllable ion-exchange membranes for the transport of metal ions. The transport of certain metal ions was enhanced by applying potential pulses to a polypyrrole-based membrane containing immobilized doping anions.

Cooperation:

University of Wollongong, Australia

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

Main funding: EU 6th Framework Programme

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

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

The fundamental project objective is to increase understanding and overcome the present limitations of biofuel cell and biosensor devices based on biological electron transfer systems. The initial target systems will be based on development of prototype biosensors for the intermittent determination of glucose and catecholamine neurotransmitter levels in clinical samples, and of a biofuel cell functioning on in-vivo available biofuels.

Cooperation:

National University of Ireland, Galway, Ireland; VTT; Hebrew University of Jerusalem, Israel; University of Southampton, UK; University of Rome "La Sapienza", Italy; BVT Technologies, Czech Republic

Printed Enzymatic Power Supplies with Integrated Capacitor Structures (PEPSiC)

Main funding: Tekes

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

The main goal of this research proposal is to produce a printable fully enzymatic biofuel cell based on the use of enzymes as catalyst on both electrodes. The power supply is developed to meet the demand of for instance RFID applications integrated into medical instruments. As this cell type is a low-price and truly disposable alternative, smart-pads or band aids can also be possible points of use, since the components selected will be non-toxic and non-allergenic, and since the product can be disposed with normal hospital waste without need for any recycling. Due to this, the technology is also applicable more generally in the packing industry. Common targets to be reached are; 1) a fully enzymatic power supply, 2) a printable supercapacitor, 3) a biofuel cell based power supply with an integrated supercapacitor, 4) a cell voltage exceeding 1.2 V, 5) a peak current of at least 50 mA for 0.3 seconds, 6) the size (area) less than 10 cm^2, thickness no more than 0.5 mm.

A number of critical components have been identified. Regarding the structural components of the cell, the first point of focus is the selection of a suitable substrate (outer shell) material having sufficient oxygen diffusion and moisture retention properties. The second issue is related with the electrode structure and immobilization of the enzyme and mediator in a way which enables both maximum enzymatic activity and a maximal active surface area. The third issue is related to the separation of the anode and cathode side by use of a suitable membrane material with desired mechanical and chemical properties. The fourth and final major issue is related to the integration of the printed capacitor structure and a suitable separation from the actual fuel cell compartment, as the electrolytes most likely are different in composition.

In order to get large enough potential differences between the anode and cathode compartment, suitable enzyme/mediator pairs are needed on both sides. The redox potential of the anodic enzyme/mediator pair should be as low as possible, while the redox potential of the cathodic enzyme/mediator pair should be as high as possible. Besides the potential, specific activity and stability of the enzymes are also important issues and are also addressed.

Cooperation:

VTT; Helsinki University of Technology; Ciba Speciality Chemicals; Joutsenpaino; Tervakoski; Stora Enso; Evox-Rifa

Publications:

- Smolander, M., Boer, H., Valkiainen, M., Roozeman, R., Bergelin, M., Eriksson, J-E., Zhang, X-C, Koivula, A., Viikari, L. (Category 4.2)
- Keskinen, J., Sivonen, E., Bergelin, M., Eriksson, J-E., Valkiainen, M., Smolander, M., Koivula, A., Boer, H. (Category 4.2.1)

A thin film biobattery

Active Nanocomposite Materials

Main funding: Tekes

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

The main goal of this research project is to develop tailored functional nanocomposite materials as anode material for a new generation of lithium-ion batteries with enhanced energy density. The numerous issues related to these new anodes hinder their development for long life industrial battery application such as HEV or standby (for sustainable energy device). In order to overcome these issues, the originality of this work is to combine new high tech nanocomposite synthesis methods with new surface functionalization of the active material. The novel composites would combine the high activity of the nanomaterial with the high surface area and cohesion of the agglomerate, while the polymer matrix would provide protection towards ageing and volume changes. Targeted volumetric capacity of the new material is at least 3 times higher than the standard graphite anode, while

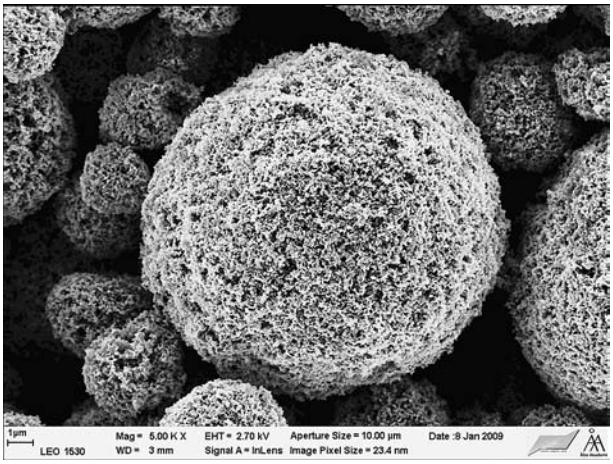
the life time of the anodes would be comparable. Currently, substitutes to the present graphite anodic material are known but they suffer from significant volume changes during battery cycling resulting rapid fading especially at elevated temperatures.

The project is divided in three main tasks.

- The composites are synthesized using three different production techniques: induction nucleation, spray pyrolysis and CVS as well as applying a new coating technique.
- The physical structure and electrochemical properties of the various produced composites are characterised, both in their native form and during electrochemical cycling. Further, loadability, potential stability and ageing issues will be addressed.
- The optimisation of the various production techniques also require development of modelling techniques for composite material synthesis in order to thoroughly understand the process of particle formation, growth and agglomeration.

Cooperation:

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



Scanning electron microscope image of novel lithium-ion battery anode material

Advanced Material Solutions for PEM Fuel Cells

Main funding: Tekes

Mikael Bergelin, Max Johansson, Mikko Hupa

The objective of the project is to develop materials for PEM-FC and DMFC stack components. The main emphasis is in the development of components to PEMFC stacks in 1 to 50 kW power range needed for industrial vehicles and working machines. The project will concentrate in the development and testing of the components where the industrial

competence and commitment is highest. The other components needed to test the components in fuel cell single cells and stacks will be purchased from the world market.

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

The main setback of carbon paper and cloth production processes is the high cost of the heat treatment processes needed for the carbonization of the PAN precursor fibre and the carbonization and graphitization of the binders needed for the paper or cloth. An attempt will be made to use conductive polymers, e.g. polyaniline (PANI), polypyrrole (PPy) or polythiophene (PEDOT) as binders. The membrane electrode assembly is typically produced by printing or coating an ink consisting of the catalyst material, dissolved proton conducting membrane and solvent on the membrane or the MPL of the GDL. Typical application techniques are screen printing and spray coating. An alternative method to produce high performance MEAs with ultralow Pt content of less than 0, 1 mg/cm^2 will be attempted. The Pt catalyzed GNF fabrics developed in the project will be laminated with commercial or experimental GDLs and LT or HT electrolyte membranes. The use of GNF fabrics as the catalyst support facilitates the location of the Pt catalyst exactly at the GDL membrane interface. Within the project bipolar-plate related development will also be made.

Cooperation:

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

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

Main funding: Tekes; Industry; Academy of Finland; Graduate School in Chemical Engineering (GSCE); Graduate School of Materials Research (GSMR); Graduate School in Nanosciences (NGS-NANO); Fortum Foundation

Anna Österholm, Henrik Gustafsson, Rose-Marie Latonen, Beatriz Meana Esteban, Zhijuan Wang, Michał Wagner, Carita Kvarnström, Ari Ivaska

New electrosynthetic routes have been established for the production of n- and p-dopable conducting polymers and for low band gap fused ring polymers. The charge transfer in the resulting electronically conducting films has been studied in situ by the electrochemical quartz crystal microbalance and by in situ conductivity measurements as well as with different in situ spectroelectrochemical techniques (UV-vis, Raman and FTIR).

Surface modification techniques have been used to obtain densely-packed structures with well-ordered architecture of conducting polymer films and carbon nanotubes on metal and semiconductor surfaces. Surface modification is especially useful for applications where nano-sized dimensions are demanded. The aim of this project is to synthesize and fabricate conducting polymer and carbon nanotube films with versatile structure and function by the surface modification technique. These materials will be applied in multilayer structures as hole transporting layers in organic solar cells.

Electrochemical characterization of fullerene structures and other electron donor-acceptor molecules in solution, as LB films and in bilayer structures like poly(azulene) (PAz) combined with C_{60} have been studied. Kinetic/mechanistic studies in water and in organic solvents have been performed. The techniques applied are electron voltage spectroscopy EVS and in situ spectroelectrochemistry mainly FTIR and Raman spectroscopy. Characterization and comparison of the photoinduced and the electrochemically induced changes in thin polymer and fullerene films will be made. The development of the electron transfer layers and the connection to the electrodes in the solar cell is a central issue in this project. The focus will be on synthesis on n-type semiconducting polymers. An n-type water soluble semiconducting polymer, poly(benzimidazobenzophenanthroline) (BBL), has been studied for this purpose. In the future other acceptor-like materials, benzapyrene and other graphite-like molecules, will also be studied.

Hybrid electron donor-acceptor materials for solar cell applications have been developed. A combination consisting of inorganic wide band gap TiO_2 as the electron acceptor and organic low band gap conducting polymer PAz, as the electron donor have been studied. These hybrid materials have been characterized by cyclic voltammetry, in situ UV-vis spectroelectrochemistry, both ex situ and in situ FTIR spectroscopy, Raman and XRD spectroscopy techniques and by Scanning Electron Microscopy. Characterization of the performance of these hybrid materials in solar cell structures will be performed by photocurrent measurements.

Cooperation:

University of Turku (Analytical Chemistry); Johannes Kepler University of Linz, Austria; Institute of Solid State and Material Research, Dresden, Germany; Albert-Ludwigs Universität, Institut für Physikalische Chemie, Freiburg, Germany; Romanian Academy of Sciences, Bucharest, Romania; State Key Laboratory of Electroanalytical Chemistry (SKLEAC), Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China; Polytechnic University of Cartagena, Spain; Tampere University of Technology; University of Helsinki; Rautaruukki; UPM-Kymmene; Licentia; Panipol; KSV Instruments

Publications:

- Blomquist, Susanna (Category 4.1.3)
- Gustafsson, H., Kvarnström, C., Ivaska, A. (Category 4.2)
- Meana Esteban, B., Sundfors, F., Espindola, P., Kvarnström, C., Heinze, J., Ivaska, A. (Category 4.2)
- Wang, Z., Zhang, Y., Kuehner, D., Shen, Y., Xu, X., Ivaska, A., Niu, L. (Category 4.2)
- Wang, Z., Li, M., Su, P., Zhang, Y., Shen, Y., Han, D., Ivaska, A., Niu, L. (Category 4.2)
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- Österholm, A., Meana Esteban, B., Kvarnström, C., Ivaska, A. (b) (Category 4.2)
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3.9 Functional Inorganic Materials

The two main goals of our recent materials research have been:

(i) to improve the understanding of the properties and especially surface characteristics

of silicate based glasses and ceramics for various novel applications, and

(ii) to explore the detailed mechanisms of the high temperature corrosion of various steels in combustion environments containing corrosive alkali compounds.

The use of bioactive glasses as implants for tissue regeneration and regeneration is based on selective and controlled leaching of the glass surface to allow formation of a layered structure of silica and hydroxyapatite on the glasses. The hydroxyapatite layer reacts further with components in body fluid and is bonded to tissue. In our research we have established the influence of the glass composition on the layer formation. Further, we have studied how the surface area affects the layer formation. For example, in porous load-bearing composites of bioabsorbable polymer and bioactive glass fibres, the glass thin glass fibres should be tailored to react at the same rate as bone is grown into the scaffold in order to maintain the desired long-term strength.

Novel types of glasses have been studied as matrix materials for short-lived beta-emitting radioisotopes aimed for localized internal treatment of tumours. These radiotherapy glasses contain elements, which are activated prior to the injection of the glasses as microspheres or crushed fractions into tumours. The largest challenge in finding a suitable glass composition is the requirements that only the beta-emitting radioisotope is activated, and the glass gradually dissolves after the radioactivity has ceased to levels which do not harm healthy tissues. Thus, controlled reactivity in body fluids is essential also for glasses aimed for radiotherapy.

Glass and glazed surfaces are generally regarded as easy-to-clean surfaces. However, the increased demands for the ware in service, have called for enhanced cleanability and also for self-cleaning surfaces. In some specific applications also antibacterial properties are desired. The self-cleaning surfaces are typical examples of the possibilities offered by nanotechnology. The focus on the research of functionalizing glass and glaze surfaces for enhanced cleanability at PCC has been in establishing their long-term chemical and mechanical resistance in typical conditions present in the application. Also, the influence of the additional surface films on the appearance and topography has been taken into account.

Increasing the power production efficiency in combustion devices and boilers by allowing higher material temperatures in e.g. superheaters has called for development of better high temperature materials for steam power plants. The presence of various alkali salts such as potassium and sodium chlorides, sulphates or carbonates is the main reason to severe high temperature corrosion of the hottest surfaces of combustion devices burning biofuels. Our laboratory corrosion exposure technique, together with microscopic and

analytical techniques, has been used to establish the corrosion tendency of a given salt deposit on various steel qualities. For detailed understanding of the corrosion mechanisms we have especially focused on the role of partial melting of the salt deposit on its corrosion properties.

Porous, Load-Bearing Composite Made of Bioabsorbable Polymer and Bioactive Glass Fibres (Biowaffle)

Main funding: Tekes, Combio

Leena Hupa, Hanna Arstila, Erik Vedel, Zhang Di, Heimo Ylänen, Jaana Paananen, Susanne Fagerlund, Annika Westberg, Mikko Hupa

Novel composite materials consisting of bioactive glass fibres and bioabsorbable polymer fibres have been developed. The composites are manufactured as fabrics or as load-bearing porous implants. The main tasks are to characterize fibre drawing properties of bioactive glasses and the in vivo and in vitro reactivity of the glass fibres. The goal is to tailor the fibre composition for desired response in various applications of the composite materials.

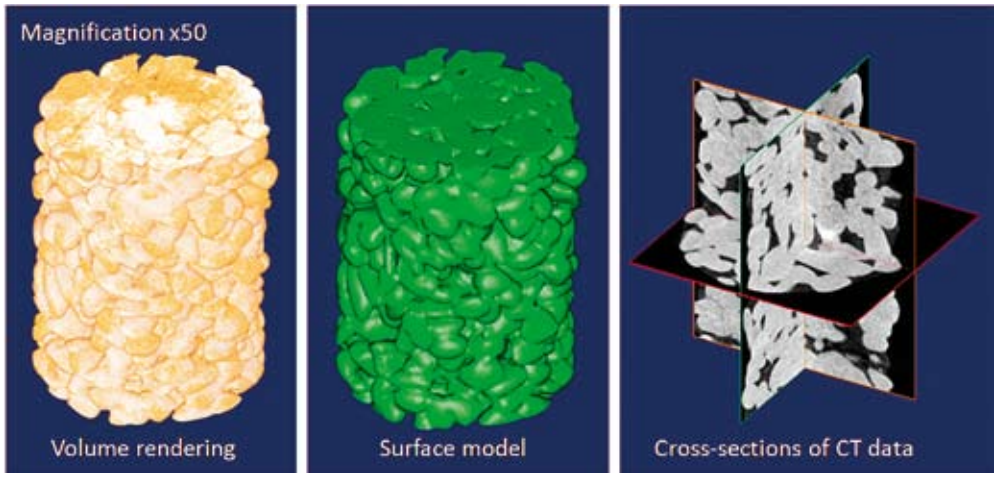
Cooperation:

Technical University of Tampere (Biomedical Engineering); University of Turku (Orthopaedics and Traumatology); University of Oulu (Surgery); Vivoxid; Bioretec; ConMed Linvatec Biomaterials; BbS-Bioactive Bone Substitutes

Publications:

- Arstila, Hanna (Category 4.1.1)
- Vedel, Erik (Category 4.1.1)
- Zhang, Di (Category 4.1.1)
- Westberg, Annika (Category 4.1.3)
- Arstila, H., Hupa, L., Karlsson, K.H., Hupa, M. (Category 4.2)
- Arstila, H., Tukiainen, M., Taipale, S., Kellomäki, M., Hupa, L. (Category 4.2)
- Arstila, H., Vedel, E., Hupa, L, Hupa, M. (Category 4.2)
- Karlsson, K.H., Hupa, L. (Category 4.2)
- Leppäranta, O., Vaahtio, M., Peltola, T., Zhang, D., Hupa, L., Hupa, M., Ylänen, H., Salonen, J.I., Viljanen, M.K., Eerola, E. (Category 4.2)

- Munukka, E., Leppäranta, O., Korkeamäki, M., Vaahtio, M., Peltola, T., Zhang, D., Hupa, L., Ylänen, H., Salonen, J.I., Viljanen, M.K., Eerola, E. (Category 4.2)
- Taipale, S., Ek, P., Hupa, M., Hupa L. (Category 4.2)
- Vedel, E., Arstila, H., Ylänen, H., Hupa, L, Hupa, M. (Category 4.2)
- Zhang, D., Arstila, H., Vedel, E., Ylänen, H., Hupa, L., Hupa, M. (Category 4.2)
- Zhang, D., Hupa, M., Aro, H.T., Hupa, L. (Category 4.2)
- Zhang, D., Hupa, M., Hupa, L(Category 4.2)
- Zhao, D., Moritz, N., Vedel, E., Hupa, L., Aro, H.T. (Category 4.2)



3D models of an implant sintered of Glass 1–98 particulates based on micro-CT data. The implant has an interconnected 23 vol-% porosity (© Niko Moritz, University of Turku)

A Special Material for Local Treatment of Malignant Tumours (Holmbag)

Main funding: Tekes

Leena Hupa, Zhang Di, Na Li, Mikko Hupa

Melt derived glasses are studied as a carrier matrix for holmium for in situ therapeutic radiation of cancer tumours. When injected into the tumours, the glasses provide a high localized dose of beta radiation and minimize the irradiation of surrounding healthy tissues. The glasses are conventionally melted with an appropriate amount of holmium oxide. Before injection of the crushed particles or spherulized micro-spheres into the tumour, the holmium is activated. Conventional bioactive glasses cannot be used as the carrier matrix, because they contain components which would give rise to undesired long-term radioactivity due to the activation (oxides of sodium, potassium and calcium). The

main task is to choose a carrier matrix, which allows the manufacture of glass particles or microspheres with a controlled radioactivity and a desired biodegradability.

Cooperation:

Turku Biomaterials Centre; University of Turku (Orthopaedic Research Unit); Vivoxid; MAP Medical Technologies; DelSiTech

Publications:

Cacaina, D., Ylänen, H., Simon, S., Hupa, M. (Category 4.2)

Enhanced Functionality of Self-cleaning and Antibacterial Surface Coatings

Main funding: Nordic Innovation Centre, MINT

Leena Hupa, Minna Piispanen, Linda Fröberg, Jaana Paananen, Mikko Hupa

Coatings which combine self-cleaning and antibacterial properties are tested on glazed ceramics and glasses. The coatings are manufactured through a flame-based nanoparticle deposition process. Flame-based processes are commonly known to be fast and cost-effective and thus ideal for industrial use. The main goal is to test and develop the coatings for industrial production.

Cooperation:

Tampere University of Technology (Physics); Glass Research Institute, Växjö, Sweden; Lund University (Nanocrystals Group), Lund, Sweden; Technological Institute of Iceland, Reykjavik, Iceland; University of Helsinki (Inorganic Chemistry, Applied Chemistry and Microbiology, Micronova); Beneq; Ido Bathroom

Publications:

Fröberg, L., Hupa, L. (Category 4.2)

4. Publications

4.1 Theses

4.1.1 Doctoral Theses (9)

Arstila, Hanna, Crystallization characteristics of bioactive glasses

Bergelin, Eija, Wood resin components in birch kraft pulping and bleaching – Material balances, reactions and deposition

Kangas, Matias, Chemical reaction engineering in skeletal isomerization

Karhu, Jouni, Equilibria and balances of metal ions in kraft pulping

Sjöberg-Eerola, Pia, All-solid-state ion sensors. Single piece and solid-contact sensors for chloride and lithium ions

Vedel, Erik, Predicting the properties of bioactive glasses

Werkelin, Johan, Ash-forming elements and their chemical forms in woody biomass fuels

Xu, Chunlin, Physicochemical properties of water-soluble spruce galactoglucomannans

Zhang, Di, *In vitro* characterization of bioactive glasses

4.1.2 Licentiate Theses (5)

Laurén, Tor, Methods and instruments for characterizing deposit build-up on heat exchangers in combustion plants

Leveneur, Sébastien, Catalytic synthesis and decomposition of peroxypropionic acid – Green catalytic synthesis of green compounds (with *Institut National des Sciences Appliquées de Rouen*)

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

Westén-Karlsson, Micaela, Assessment of a laboratory method for studying high temperature corrosion caused by alkali salts

Yli-Niemi, Outi, Latex factors affecting sticky formation in wet end and in drying section

4.1.3 Master of Science Theses (19)

Blomquist, Susanna, Elektrokemisk och spektroelektrokemisk undersökning av de ledande polymererna poly (3.4-etylen-dioxytiofen) och poly(3.4-metylendioxytiofen)

Granfors, Mikael, Bestämning av kvicksilver genom ackumulering av guldfälla kombinerad med DCP-AES

Han, Tingting, Study on electrochemical properties of glassy carbon, carbon nanotube/glassy carbon, fullerene/glassy carbon and single wall carbon nanotube paper electrodes

He, Ning, Mesoporous materials for application in drug loading and controlled release (*Mesoporösa material för läkemedelsimpregnering och kontrollerad upplösning*, in English)

Jasielec, Jerzy, JEDS – computer program for simulation of electro-diffusion processes

Karlström, Oskar, Bestämning av bränslespecifika parametrar för modellering av biomasspartikelförbränning (*Determining fuel specific parameters for modelling of biomass particle burning*, in Swedish)

Koyya, Hema Reddy, Determination of yield and selectivity for a complex chemical system in a continuous gas-liquid reactor (*Bestämning av utbyte och selektivitet for ett komplicerat kemiskt system i en kontinuerlig gas-vätskereaktor*, in English)

Kurman Rivero, Adriana, Kinetics of biofuels-assisted SCR of NO_x over silver-alumina coated microchannels (*Kinetiken för biobränsleassisterad selektiv katalytisk reduktion av NO_x i silveraluminiumoxidbelagda mikrokanaler*, in English)

Martin Curvelo, Gerson, Hydrogenation of beta-sitosterol to beta-sitostanol over different Pd-catalysts (*Hydrering av beta-sitosterol to beta-sitostanol på olika palladiumkatalysatorer*, in English)

Mattinen, Ulriika, Solid-state reference electrode

Michelsson, Linda, Assessing the stability of pitch in a paper mill using mechanical pulp (*Utvärdering av hartsstabilitet i ett pappersbruk som använder mekanisk massa*, in English)

Nyberg, Thomas, Utfällning av silikater ur lut

Nylund, Jill, Kloridselektiva elektroder med fast kontakt samt deras respons vid låga koncentrationer

Patola, Markus, A study of filler retention with dynamic drainage jar and focused beam reflectance measurements (*Bestämning av fyllmedelsretention med en laboratorieavvattnare och en laserbaserad flockningsmätare*, in English)

Päärni, Riikka, Bränntemperaturens inverkan på brända kalkens släckningsreaktivitet (*Influence of the burning temperature on the reactivity of the corroded lime*, in Swedish)

Sundblom, Sören, Bestämning av surheten hos zeoliter med *in situ* FTIR

Udd, Annika, Bestämning av SO_2 och SO_3 i kalcineringsgas

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Väänänen, Virpi, Undersökning av jonselektiva elektroder med fast kontakt

4.2 Articles in Refereed International Scientific Journals and Series (101)

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Willför, S., Holmbom, B., Eklund, P., Sjöholm, R., Smeds, A., Effect of the extraction method on the lignan yield from different plant materials, *Planta Medica* 74 (2008) 9, 24

Willför, S., Production of high value chemical products from pulp and paper mills: Wood hemicelluloses – a potential source of value-added natural polymers, Proceedings: *2nd Annual Conference: Biorefining for the Pulp and Paper Industry*, December 2–3, 2008, Helsinki, Finland, Intertech Pira, UK

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Ylänen H., Bioactive glasses now and tomorrow, Proceedings: *2nd International Conference on Ceramics* (ICC2), Global Roadmap for Ceramics, Ceramics for Health and Biotechnologies, June 29–July 4, 2008, Verona, Italy

Zdrodowska, B., Czerwinska, K., Raczynska, A., Bieganowski, P., Wagner-Czauderna, E., Lewenstam, A., Maj-Żurawska, M., Ion selective electrodes in speciation analysis of calcium and magnesium in milk, Proceedings: *International Conference on Electrochemical Sensors* (Mátrafüred 08), October 5–10, 2008, Dobogókö, Hungary, 95

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Zevenhoven, M., Hupa, M., Lehtovaara, J., Storholm, S., Ash forming matter in peat – The role of iron, Proceedings: *Scandinavian-Nordic Section of the Combustion Institute Topical Meeting: Measuring Techniques in Combustion*, October 23–24, 2008, Gothenburg, Sweden

Österholm, A., Petr, A., Kvarnström, C., Dunsch, L., Ivaska, A., *In situ* ESR-UV-vis-NIR spectroelectrochemical investigation of charge carriers in polyazulene, Proceedings: *International Conference on Science and Technology of Synthetic Metals* (ICSM 2008), July 6–11, 2008, Porto de Galinhas, Brazil

4.4 Åbo Akademi Reports (19)

Arstila, H., Crystallization characteristics of bioactive glasses, Report 08-07, *Åbo Akademi Process Chemistry Centre, Combustion and Materials Chemistry*, ISBN 978-952-12-2161-3, UNIPRINT, Åbo, Finland, 2008 (academic dissertation)

Bernas, A., Eränen, K., Salmi, T., Synthesis and separation of chemical intermediates, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, Åbo, Finland, 38 p.

Bernas, H., Mäki-Arvela, P., Eränen, K., Salmi, T., Murzin, D.Yu., Decarboxylation of fatty acids in a fixed bed reactor I, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, Åbo, Finland, 34 p.

Bernas, H., Mäki-Arvela, P., Wärnå, J., Eränen, K., Salmi, T., Catalysts, kinetics and reactor modelling in dehalogenation, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, Åbo, Finland, 9 p. and appendices

Holmbom, B., Sundberg, A., Willför, S., Lindqvist, H., Holmback, J., Jin, H., Vähäsalo, L., Auer, M., New functions for paper chemicals and fibers – ”FunPaC”, Final Report, C1-08, *Åbo Akademi Process Chemistry Centre, Laboratory of Wood and Paper Chemistry,* Åbo, Finland

Jogunola, O., Mikkola, J-P., Eränen, K., Salmi, T., Quick screening method to determine the complexing power of some additives in methyl formate hydrolysis, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, Åbo, Finland, 19 p.

Jogunola, O., Salmi, T., Wärnå, J., Mikkola, J-P., Tirronen, E., Kinetics of methyl formate hydrolysis in the absence and presence of complexating agents, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, Åbo, Finland, 30 p.

Kumar, N., Murzin, D.Yu., Salmi, T., Käldström, M., Synthesis, characterization and catalytic application of ÅA-MM novel mesoporous molecular sieve catalysts embedded with a zeolite structure, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, Åbo, Finland, 80 p.

Laurén, T., Methods and instruments for characterizing deposit buildup on heat exchangers in combustion plants, Report 07-05, *Åbo Akademi Process Chemistry Centre, Combustion and Materials Chemistry*, ISBN 978-952-12-2009-8, UNIPRINT, Åbo, Finland, 2008 (licentiate thesis)

Lestari, S., Mäki-Arvela, P., Bernas, H., Eränen, K., Salmi, T., Murzin, D.Yu., Decarboxylation of fatty acids in a fixed bed reactor, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, Åbo, Finland, 18 p.

Ljung, M. (ed.), *Graduate School in Chemical Engineering Yearbook 2008*, Åbo Akademi University 2008, ISSN 1238-2647, UNIPRINT, Åbo, Finland, 2008

Ljung, M., Brink, A., Kvarnström, C., Mäki-Arvela, P., Sundberg, A. (eds.), *Åbo Akademi Process Chemistry Centre Annual Report 2007–2008*, Åbo Akademi University 2008, ISSN 1459-8213, Priimus Paino, Loimaa, Finland, 2008

Murzin, D. (ed.), NANOCAT – Tailored nanosized metal catalysts for improving activity and selectivity via engineering of their structure and local environment, final report (EU contract 506621), *Åbo Akademi Process Chemistry Centre*, 90 p.

Musakka, N., Bernas, A., Mikkola, J-P., Salmi, T., Selective transformation of some organic compounds, *Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering*, Åbo, Finland, 34 p.

Vedel, E., Predicting the properties of bioactive glasses, Report 08-01, *Åbo Akademi Process Chemistry Centre, Combustion and Materials Chemistry*, ISBN 978-952-12-2054-8, UNIPRINT, Åbo, Finland, 2008 (academic dissertation)

Werkelin, J., Ash-forming elements and their chemical forms in woody biomass fuels, Report 08-06, *Åbo Akademi Process Chemistry Centre, Combustion and Materials Chemistry*, ISBN 978-952-12-2125-5, UNIPRINT, Åbo, Finland, 2008 (academic dissertation)

Westén-Karlsson, M., Assessment of a laboratory method for studying high temperature corrosion caused by alkali salts, Report 08-03, *Åbo Akademi Process Chemistry Centre, Combustion and Materials Chemistry*, ISBN 978-952-12-2116-3, UNIPRINT, Åbo, Finland, 2008 (licentiate thesis)

Zevenhoven, M., Hupa, M., The environmental impact and cost efficiency of combustible waste utilisation- The potential and difficulties of ongoing technology, Report 08-05, *Åbo Akademi Process Chemistry Centre, Combustion and Materials Chemistry*, ISBN 978-952-12-2127-9, UNIPRINT, Åbo, Finland, 2008

Zhang, D., *In vitro* characterization of bioactive glass, Report 08-04, *Åbo Akademi Process Chemistry Centre, Combustion and Materials Chemistry*, ISBN 978-952-12-2121-7, UNIPRINT, Åbo, Finland, 2008 (academic dissertation)

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

Bränds i Åbo och annanstans, *Meddelanden från Åbo Akademi*, January 18, 2008 (Tapio Salmi)

Energin från skogen kunde fördubblas. Energin som lämnas kvar motsvarar Finlands oljeförbrukning, *Åbo Underrättelser*, September 9, 2008

Jyri-Pekka Mikkola är Åbo-Umeå samprofessor, *Kemia-Kemi* 35 (2008) 7, 51 (Tapio Salmi)

Kestämätön tuote ei sovi kestävän kehityksen linjaukseen, *Turun Sanomat*, April 10, 2008, (J-P. Mikkola, Esa Toukoniitty)

Nobelfilm i Krakow, *Åbo Underrättelser*, January 18, 2008 (Tapio Salmi)

Näin syntyi Europacat 2007, *Kemia-Kemi* 35 (2008) 2, 48–49 (Tapio Salmi)

Ongelma lienee eristeissä, ei katalysaattoreissa, *Turun Sanomat*, December 17, 2008 (Kalle Arve)

Åbo-Umeå samprofessor, *Meddelanden från Åbo Akademi*, October 31, 2008 (Tapio Salmi)

4.6 Patents (1)

Lewenstam, A., Blaz, T., Migdalski, J., Duda, L., Reference electrode for electrochemical measurements, and in particular potentiometric measurements, *EPO Application* 06716825.2, 2008

4.7 Awards (7)

Bankiewicz, Dorota, Richard W. Bryers Award for Best Paper (Bankiewicz, D., Yrjas, P., Hupa, M., High temperature corrosion of steam tube materials exposed to zinc salts), in conference: Impacts of Fuel Quality on Power Production and the Environment Conference, September 29–October 3, 2008, Banff, Alberta, Canada

Fagerlund, Susanne, Award for Best Annual Report and Presentation, Graduate School of Chemical Engineering, November 13–14, 2008, Oulu, Finland

Holmbom, Bjarne & Eckerman, Christer, 2008 Marcus Wallenberg Prize, Marcus Wallenberg Foundation, Stockholm, Sweden

Lindberg, Daniel, Harry Elving Prize for the best doctoral thesis at Åbo Akademi University 2007

Mikkola, J-P., Umeå University – Young Researcher Award 2008

Salmi, Tapio, American Chemical Society (ACS)-PRF Grant

Werkelin, Johan, ÅA-alumnernas forskarstipendium 2008, Akademiföreningen Åbo Akademiker r.f., Åbo, Finland

Zhang, Di, 2008 Chinese Government Award for Outstanding Self-financed Students Abroad, China Scholarship Council

5. Courses

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

Chemistry in Combustion Processes I

Course Supervisor: Mikko Hupa

Course Coordinator: Markus Engblom

Time: March

Place: Åbo Akademi University

Cooperation: Graduate School in Chemical Engineering (GSCE)

Lecturers: Mikko Hupa
Edgardo Coda Zabetta, Foster Wheeler
Markus Engblom
Bengt-Johan Skrifvars, Top Analytica
Johan Werkelin
Maria Zevenhoven

Process Analytical Chemistry

Course Supervisor: Johan Bobacka

Time: March

Place: Åbo Akademi University

Cooperation: Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM)
Graduate School in Chemical Engineering (GSCE)
Graduate School of Materials Research (GSMR)

Lecturers: Ari Ivaska
Johan Bobacka
Kari Saloheimo, Outotec
Stig Fröberg, Neste Oil

Advanced Techniques for Characterization of Heterogeneous Catalysts

Course Supervisor: Dmitry Murzin

Time: May

Place: Åbo Akademi University

Cooperation: Graduate School in Chemical Engineering (GSCE)

Lecturers: Andrey V. Simakov, Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México

Dmitry Murzin

Tapio Salmi

Chemistry in Combustion Processes II

Course Supervisor: Mikko Hupa

Course Coordinator: Maria Zevenhoven

Time: November

Place: Åbo Akademi University

Cooperation: Graduate School in Chemical Engineering (GSCE)

Nordic Graduate School in Biofuels Science and Technology (biofuelsGS-2)

Lecturers: Mikko Hupa

Markus Engblom

Bengt-Johan Skrifvars, Top Analytica

Johan Werkelin

Maria Zevenhoven

Wood Extractives in Pulping and Papermaking

Course Supervisor: Bjarne Holmbom

Time: November

Place: Åbo Akademi University

Cooperation: PaPSaT Graduate School

Lecturers: Bjarne Holmbom

Anna Sundberg

Stefan Willför

Eija Bergelin

Armando J. D. Silvestre, University of Aveiro, Portugal

Pedro Fardim, Laboratory of Fibre and Cellulose Technology

Lari Vähäsalo

Chemical Kinetics

Course supervisors: Tapio Salmi

Dmitry Murzin

Time: December

Place: Åbo Akademi University

Cooperation: Graduate School in Chemical Engineering (GSCE)

Graduate School of Materials Research (GSMR)

Lecturers: Tapio Salmi

Dmitry Murzin

Demonstrators and assistants:

Johan Wärnå

Matias Kangas

Åbo Akademi Process Chemistry Centre Internal Workshops

Workshop I: Instrumental Methods - Part I, October 14, 2005

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

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

- Dr. Mikael Bergelin: Non-optical microscopy
- Docent Carita Kvarnström: FTIR & Raman spectroscopy

- Docent Rainer Sjöholm: NMR spectroscopy
- Dr. Lari Vähäsalo: Flow cytometry

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

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

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

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

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

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

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

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

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

- Doc. Eric Bertoft, ÅA, Dept. of Biochemistry and Pharmacy:

Advances in understanding of the structure of amylopectin, the major starch component

- Prof. Pia Vuorela, ÅA, Dept. of Biochemistry and Pharmacy:

Microfractionation and bioassays in natural product drug discovery

- Prof. Bjarne Holmbom: Bioraff

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

- Matias Kangas: Structure-performance effects in zeolite catalyzed skeletal isomerization
- Michal Wagner: Electropolymerization of poly(para-phenylene) in ionic liquids
- Di Zhang: Glass-based biomaterials
- Chunlin Xu: Spruce galactoglucomannan: A potential raw material for hydrocolloids and novel advanced natural materials

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

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

6. Other Activities

6.1 Organization of Conferences, Courses and Seminars

Location, Meeting, Date, Number of Participants

Espoo, Finland, Graduate School in Chemical Engineering (GSCE) Spring Seminar, April 15–16 (50)

Gothenburg, Sweden, Nordic Graduate School in Biofuels Science and Technology (biofuelsGS) course: Analytical Techniques in Combustion I, October 20–24 (30)

Gothenburg, Sweden, Scandinavian-Nordic Section of the Combustion Institute (SNCI) Topical Meeting 2008: Measuring Techniques in Combustion, October 23–24 (53)

Oulu, Finland, Graduate School in Chemical Engineering (GSCE) Annual Seminar, November 13–14 (50)

Turku, Finland, Åbo Akademi Process Chemistry Centre Annual Seminar, September 9–10 (130)

Turku, Finland, ChemCom Researcher Day, February 13 (22)

Turku, Finland, ChemCom 2.0 Technical Spring Meeting, May 19–20 (43)

Turku, Finland, ChemCom 2.0 Technical Fall Meeting, December 3–5 (47)

Turku, Finland, EU/COST, Final seminar of COST Action E41 & Workshop of Action E50, May 19–21 (93)

Verona, Italy, 2nd International Congress on Ceramics (ICC2), June 29–July 4

Vilnius, Lithuania, 7th ScanBalt Forum and Biomaterials Days, September 24–26

Visby, Sweden, Nordic Graduate School in Biofuels Science and Technology (biofuelsGS) Annual Meeting, September 14–16 (25)

6.2. Participation in Major Conferences, Meetings and Courses

Location, Meeting/Organizer, Contribution, Number of Participants

January

Naples, Italy, Early Stage Research Training in Integrated Energy Conversion for a Sustainable Environment (INECSE) Semi Annual Meeting, 3

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

Tampere, Finland, International Flame Research Foundation (IFRF) Finnish Flame Research Committee IV LIEKKI Day, 4

Temecula, CA, USA, Winter Conference on Plasma Spectrochemistry, *Paul Ek*

Tver, Russia, EU project meeting, 4

Tver, Russia, Visit and meeting at Tver Technical University, *Mikko Hupa, Dmitry Murzin*

February

Berlin, Germany, Wood Wisdom Net/ProBark kick-off meeting, *Bjarne Holmbom*

March

Aveiro, Portugal, University of Aveiro, Professor´s evaluation, Guest seminar, *Bjarne Holmbom*

Espoo, Finland, Tekes Fuel Cell Annual Seminar 2008, 1

Foz do Iguaçu, Brazil, 6th Spring Meeting of the International Society of Electrochemistry, lecturer, *Johan Bobacka*

Helsinki, Finland, Data, Information and Knowledge in Chemical Technology, Tekes, invited lecture, *Tapio Salmi*, 1, 3

Kish Island, Iran, 2nd Conference on Nanostructures (NS2008), keynote lecture, *Ari Ivaska*, 2

Noordwijkerhout, the Netherlands, IXth Netherlands Catalysis and Chemistry Conference (NCCC IX), 1

Nottingham, UK, 4th International Meeting on Starch Structure and Functionality (Starch 2008), 1

Santiago de Chile, Chile, Academy of Finland Finland-Chile Seminar, *J-P. Mikkola, D. Murzin*

Stockholm, Sweden, 1st Nordic Wood Biorefinery Conference, invited lecturers, *Bjarne Holmbom, Mikko Hupa*, 4

Vilamoura, Portugal, 8th European Conference on Industrial Furnaces and Boilers, 2

Örnsköldsvik, Sweden, Processum Biorefinery Initiative, invited lecture, *J-P. Mikkola,* 1

April

Borovets, Bulgaria, CONOPEX Meeting, keynote lecture, *Ari Ivaska*

Delft, the Netherlands, Delft University of Technology, Advanced Course in Biocatalysis, *Päivi Mäki-Arvela*

Espoo, Finland, Finnish Society for Industrial Ecology and Geological Survey of Finland Seminar: Towards Sustainable Energy: the Nordic Way of Renewables, invited speaker, *J-P. Mikkola*

Espoo, Finland, Graduate School in Chemical Engineering (GSCE) Spring Seminar, 8

Helsinki, Finland, Millennium Prize Committee Meeting, *Mikko Hupa*

Helsinki, Finland, Nanotechnology, Materials and New Production Finland, 4

Helsinki, Finland, TKK-HU Biorefinery Lecture Series, invited lecturer, *Bjarne Holmbom*

Kokkola, Finland, AEL Course: Metallianalyytikon päivityspaketti, LA-ICP-MS-tekniikan käyttö määritettäessä metallien jakautumista puu- ja paperinäytteissä, *Paul Ek*

Krakow, Poland, ERA Chemistry Workshop "Chemistry of raw material change; Chemical transformation of biomass", invited lecturer, *Bjarne Holmbom*, 2

Madrid, Spain, Universidad Carlos III de Madrid, invited lectures, *Mikko Hupa*

Pisa, Italy, International Flame Research Foundation (IFRF) Executive Committee Meeting, *Mikko Hupa*

Richmond, VA, USA, 22nd Conference on the Catalysis of Organic Reactions, 4, 4

Wageningen, the Netherlands, Pectins and Pectinases Symposium, 1

May

Amsterdam, the Netherlands, World Biomaterials Congress (WBC 2008), 1

Espoo, 6th Fundamental Mechanical Pulp Research Seminar, 1

Espoo, Finland, Scandinavian Society of Glass Technology, 58th Annual Meeting, Espoo, Finland, 5

Hamburg, Germany, 9th International Conference on Circulating Fluidized Beds, invited lecturer, *Mikko Hupa*, 3

Hamburg, Germany, International Energy Agency-Fluidised Bed Conversion (IEA-FBC) Executive Committee Meeting, *Mikko Hupa*

Helsinki, Finland, AEL Course, Polttotekniikat ja päästöt, *Mikko Hupa*

Jinan, China, Shandong Institute of Light Industry, Guest seminar, *Bjarne Holmbom*

Mariehamn, Åland, Tekes Microreactor Technology Symposium, 4, 10

Marrakech, Morocco, Chemical Product and Process Modeling, Engineering Conferences International, invited lecture, *J-P. Mikkola*

Pardubice, Czech Republic, Erasmus teacher exchange, *Kalle Arve*

Paris, France, European Meeting on Magnesium (EuroMag Paris 2008), plenary lecture, *Andrzej Lewenstam*

Stockholm, Sweden, Swedish Black Liquor Gasification Research Programme Scientific Advisory Board Meeting, *Mikko Hupa*

Tarragona, Spain, Dept. of Analytical Chemistry and Organic Chemistry, Universitat *Rovira i Virgili,* invited lecturer, *Johan Bobacka*

Tartu, Estonia, 5th Baltic Conference on Electrochemistry: Functional Materials in Electrochemistry – from Fundamental Problems to Molecular Electronics and Modern Power Sources (BEC-5), 1

Tianjin, China, 2nd International Papermaking & Environmental Conference, plenary lecturer, *Bjarne Holmbom*, 5

Turku, COST Action E41 Final Seminar, invited lecturer, *Bjarne Holmbom*

Turku, Finland, Bio-organic meeting, University of Turku, invited lecture, *Tapio Salmi*, 1, 3

June

Clearwater, FL, USA, Clearwater Clean Coal Conference, invited lecturer, *Mikko Hupa*

Delft, the Netherlands, Early Stage Research Training in Integrated Energy Conversion for a Sustainable Environment (INECSE) Semi Annual Meeting + SFERA course, 2

Eindhoven, the Netherlands, 7th International Conference on Coatings on Glass and Plastics, 1

Helsinki, Finland, Helsinki University Tvärminne Seminar, 1

Helsinki, Finland, Millennium Prize Ceremony, *Mikko Hupa*

La Grande Motte, France, 11th Meeting of the European Society of Sonochemistry (ESS11), 1, 2

Munich, Germany, International Flame Research Foundation (IFRF) Joint Committee Meeting & Workshop, 2

Novosibirsk, Russia, Modern Trends in Catalysis, plenary lecturer, *Dmitry Murzin*

Oulu, Finland, COST Action 543 Summer School, lecturer, session chairman and organisation, *J-P. Mikkola*, invited lectures*, Tapio Salmi, Anton Tokarev*, 4, 5

Prague, Czech Republic, 12th International Conference on Electroanalysis, *Andrzej Lewenstam*

Sao Paulo, Brazil, Academy of Finland Brazil-Finland Cooperation Meeting, *Mikko Hupa*

Singapore, 9th International Hydrocolloids Conference, 1

Trenčin, Slovakia, 9th European Society of Glass Conference (9th ESG), 4

Vantaa, Finland, Academy of Finland Energy & Power Seminar, 1

Vasa, Finland; Umeå, Sweden, Vasa-Umeå Summer School in Sustainable Chemistry, 10, 14

Verona, Italy, 2nd International Congress on Ceramics (ICC2), 1

Zvenigorod, Russia, Vth Russian Conference on Zeolites, 1, 1

July

Graz, Austria, 8th International Symposium on Functional π-Electron Systems, *2*

Porto de Galinhas, Pernambuco, Brazil, International Conference on Science and Technology of Synthetic Metals (ICSM 2008), 3

Prague, Czech Republic, 9th European Workshop on Laser Ablation in Elemental and Isotopic Analysis, *1*

Seoul, Korea, 14th International Congress on Catalysis, 9, 5

August

Aalborg, Demark, Course: Rheological and Electrical Properties of Glass-forming Liquids, 2

Athens, Greece, 7th Joint Meeting of AFERP, ASP, GA, PSE & SIF (Natural Products with Pharmaceutical, Nutraceutical, Cosmetic and Agrochemical Interest), 2

Hornbaek, Denmark, Topsoe Catalysis Forum, plenary lecturer, *Dmitry Murzin*

Prague, Czech Republic, 18th International Congress of Chemical and Process Engineering (CHISA2008), member of scientific committee, *Tapio Salmi*, session chairman, *J-.P. Mikkola,* keynote lecture *Pasi Virtanen*, 12, 7

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

Stockholm, Sweden, *10th European Workshop on Lignocellulosics and Pulp* (EWLP 2008), 7

Turku, Finland, 5th International New Exploratory Technologies Conference (NEXT 2008), Keynote lecture, *Johan Bobacka*, 2

Varna, Bulgaria, 10th International Symposium on Heterogeneous Catalysis, plenary lecture, session chairman, *Dmitry Murzin*, member of scientific advisory board, *Tapio Salmi*

September

Almeria, Spain, Summer School on Functional Materials, invited lecture, *Dmitry Murzin*

Athens, Greece, 6th European Federation for the Science and Technology of Lipids Congress, invited lecture and chairman, *Dmitry Murzin*

Banff, Alberta, Canada, Impacts of Fuel Quality on Power Production and the Environment Conference, 4

Belfast, Northern Ireland, 5th International Conference on Environmental Catalysis, 3, 2

Delhi, India, 14th Annual International Sustainable Development Research Conference, session chairman, invited lecture, *J-P. Mikkola*

Husum, Sweden, Vinnova Vinnväxt Kick-off Seminar, invited lecture, *J-P. Mikkola*

Krakow, Poland, Annual Congress of the Polish Magnesiological Society, *Andrzej Lewenstam*

Krakow, Poland, International Seminar on Diffusion and Reactions: Multiscale Phenomena (DIFREA 2008), *Andrzej Lewenstam*

Kyoto, Japan, 20th International Symposium on Chemical Reaction Engineering (ISCRE-20), session chairman *Tapio Salmi*, 3, 2

Lahti, Finland, Tekes Biorefinery Symposium, invited lecture, *Tapio Salmi*, 1, 3

Lammi, Finland, National Graduate School in Nanoscience (NGS-Nano) Meeting, 1

Livorno, Italy, International Flame Research Foundation (IFRF) & Early Stage Research Training in Integrated Energy Conversion for a Sustainable Environment (INECSE) Combustion Course, 2

Paris, France, 4th Federation of European Zeolite Association Conference (FEZA), Paris, France, 2, 2

Seville, Spain, 59th Annual Meeting of the International Society of Electrochemistry, 8

Turku, Finland, Åbo-Umeå Seminar in Industrial Chemistry, 4, 30

Turku, Finland, Turku Biomaterials Day, 1

Valetta, Malta, XVIII International Conference on Chemical Reactors (Chemreactor-18), 11, 7, plenary lecture, session chairman, *Dmitry Murzin*

Vilnius, Lithuania, 7th ScanBalt Forum and Biomaterials Days, 2

Visby, Sweden, Nordic Graduate School in Biofuels Science and Technology (biofuelsGS) Annual Meeting, 8

Åbo Akademi Faculty of Technology Alumni Day, chairman*, Mikko Hupa*, lecturer, *Bjarne Holmbom*

October

Buzios, Brazil, 21st International Symposium on Ceramics in Medicine, 1

Dobogókö, Hungary, *International Conference on Electrochemical Sensors* (Mátrafüred 08), invited lecture, *Andrzej Lewenstam,* keynote lecture, *Ari Ivaska, 9*

Espoo, Hanaforum Seminar on Forest Industry Future, invited lecturer, *Bjarne Holmbom*

Gothenburg, Sweden, 13th Nordic Symposium on Catalysis, 7, 4

Gothenburg, Sweden, Course: SEM 2008, Chalmers University of Technology, 1

Gothenburg, Sweden, Nordic Graduate School in Biofuels Science and Technology (biofuelsGS) course: Analytical Techniques in Combustion I, 3

Gothenburg, Sweden, Scandinavian-Nordic Section of the Combustion Institute (SNCI) Topical Meeting 2008: Measuring Techniques in Combustion, 5

Helsinki, Finland – Nynäshamn, Sweden, Finnish Catalysis Society 20 Years Anniversary Cruise Meeting, invited lecture, *Tapio Salmi*

Lisbon, Portugal, 57th International Energy Agency-Fluidised Bed Conversion (IEA-FBC) meeting, chairman, *Mikko Hupa*

Nagoya, Japan, 15th International Conference on Flow Injection Analysis Including Related Techniques (ICFIA 2008) & 25th Anniversary Meeting of Japanese Association for Flow Injection Analysis, keynote presentation, *Ari Ivaska*

Oulu, Finland, Guest lecturer, University of Oulu, *Tapio Salmi*

Stockholm, Sweden, Marcus Wallenberg Prize Symposium, lecturers, *Bjarne Holmbom* and *Christer Eckerman*

Turku, Finland, Book, Science and Food Fair, invited lecturer, *Bjarne Holmbom*

Uppsala, Sweden, Sensor Technology Course, 2

November

Berlin, Germany, 3rd International Symposium on Carbon for Catalysis (CarboCat-III), 1

Hangzhou, China, 1st International Organic Electrochemistry and Industry Symposium, plenary lecture, *Ari Ivaska*

Helsinki, Forest Tech Europe 2008, invited lecturer, *Bjarne Holmbom*, 2

Oulu, Finland, Graduate School in Chemical Engineering (GSCE) Annual Seminar, session chairman, *Tapio Salmi*, *Mikko Hupa*, 10

Pisa, Italy, International Flame Research Foundation (IRFR) TOTem 31, 1

Stockholm, Sweden, Sodahuskonferensen, 2

Stockholm, Sweden, Swedish Black Liquor Programme Scientific Board Meeting, *Mikko Hupa*

Turku, Finland, Åbo Akademi Leadership Conference "Kompetens 2008", invited lecturer, *Bjarne Holmbom*

Wesel, Germany, Clyde Bergemann Powergroup Annual Meeting, invited lecturer, *Mikko Hupa*

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

December

Freising, Germany, International Flame Research Foundation (IFRF) TOTem 32, invited lecture, *Mikko Hupa*, 2

Helsinki, 2nd Annual Biorefining for the Pulp and Paper Industry 2008, invited lecturer, *Stefan Willför*

Karlstad, Sweden, ForeNew´s Workshop, University of Karlstad, invited lecturer, *Bjarne Holmbom*

Moscow, Russia, 1st Nanotechnology International Forum (Rusnanotech 2008), *Dmitry Murzin*

Rouen, France, INSA-Rouen, invited lecture, *Tapio Salmi*

Singapore, Biomass to Fuels & Chemicals Workshop, invited lecturer, *Päivi Mäki-Arvela*

Turku, Finland, Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM) Annual Meeting, 1

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

Vienna, Austria, ERA-NET Bioenergy Workshop on Clean Combustion, invited expert, *Mikko Hupa*

6.3. Visitors and Visits

Visitors to PCC

Adam, Jiři, University of Pardubice, Pardubice, Czech Republic (September–November)

Almkvist, Gunnar, Swedish University of Agricultural Sciences (SLU), Sweden (March)

Biasi, Pierdomenico, Università di Padova, Padova, Italy (March–September)

Blanchard, Boris, Université de Poitiers, Poitiers, France (April–June)

Brazda, Lukaš, Institute of Chemical Technology, Prague, Czech Republic (September–December)

Ciepiela, Filip, AGH University of Science and Technology, Kraków, Poland (January–May)

Dönmez, Emrah, Bartin University, Bartin, Turkey (October–January)

Garcia Mora, Alexandro Eduardo, University of Chile, Santiago, Chile (August–September)

Giuntoli, Jacopo, Delft University of Technology, Delft, the Netherlands (August–December)

Goanta, Adrian, Technische Universität München, München, Germany (August–December)

Guan, Hongyu, State Key Laboratory of Electroanalytical Chemistry, Changchun, China (January–September)

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

Jakobitz, Christopher, Technische Universität Dresden, Dresden, Germany (December)

Jasielec, Jerzy, AGH University of Science and Technology, Kraków, Poland (January–May)

Kilic, Ayben, Bartin University, Bartin, Turkey (January–July)

Kirilin, Alexey, Mendeleev Institute of Chemical Technology, Moscow, Russia (August–December)

Lamand, Frédéric, Université Blaise Pascal, Aubiere, France (June–August)

Lestari, Siswati, University of Queensland, Brisbane, Australia (August–December)

Link, Siim, Tallinna Tehnikaülikool, Tallinn, Estonia (March–August)

Madnani, Dipak Kumar, Indian Institute of Technology, Delhi, India (May–July)

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

Monedero, Esperanza, Universidad de Castilla-La Mancha, Spain (May–December)

Peshkova, Maria, St. Petersburg University, St. Petersburg, Russia (April–June; November–December)

Reinik, Janek, Keemia-füüsika instituut, Tallinn, Estonia (January–April)

Rozmysłowicz, Bartosz, Poznan University of Technology, Poznan, Poland (January–April, September–December)

Rubino, Teresa, Università di Palermo, Palermo, Italy (August–December)

Rupp, Matthias, Universität Karlsruhe, Karlsruhe, Germany (March–July)

Simakova, Irina, Boreskov Institute of Catalysis, Novosibirsk, Russia (February, May, September)

Stepien, Milena, AGH University of Science and Technology, Kraków, Poland (January–May)

Sumersky, Ivan, St. Petersburg Forest Technical Academy, St. Petersburg, Russia (July–September)

Vitjuk, Artem, Mendeleev Institute of Chemical Technology, Moscow, Russia (May)

Wang, Zhijuan, State Key Laboratory of Electroanalytical Chemistry, Changchun, China (January–March)

Ziolkowski, Bartosz, Poznan University of Technology, Poznan, Poland (January–May)

Zule, Janja, Pulp and Paper Institute, Ljubljana, Slovenia (May)

Visits by PCC members

Bankiewicz, Dorota, Institute for Energy Systems, Technische Universität München, München, Germany (September–December)

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

Grénman, Henrik, Ian Wark Research Institute, University of South Australia, Adelaide, Australia (March–August)

Leveneur, Sébastien, INSA-Rouen, Rouen, France (June)

Lindfors, Tom, University of Technology and Economics, Budapest, Hungary, (August–October)

Murzin, Dmitry, Eindhoven University of Technology, Eindhoven, the Netherlands (March)

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

Sundfors, Fredrik, University of Technology and Economics, Budapest, Hungary, (August–November)

Tokareva, Elena, University of Glasgow, Scotland, UK (August)

Xu, Chunlin, Shandong Institute of Light Industry, Shandong, China (January)

6.4. External PhD Examinations and Reviews

Ahola, Juha, University of Oulu, Oulu, Finland, opponent, *Johan Wärnå*

Almkvist, Gunnar, Swedish University of Agricultural Sciences (SLU), Sweden, opponent, *Bjarne Holmbom*

Bleda Martinez, Maria Jesus, University of Alicante, Alicante, Spain, Evaluation of PhD thesis, *Ari Ivaska*

Editorial board member for Foundations of Science, *Andrzej Lewenstam*

Editorial board member for Journal of Electroanalytical Chemistry, *Ari Ivaska*

Editorial board member for Analytical Letters, *Ari Ivaska*

Editorial board member for Journal of Elementology, *Andrzej Lewenstam*

Editorial board member for Magnesium Research, *Andrzej Lewenstam*

Editorial board member for Philosophy of Science, *Andrzej Lewenstam*

Editorial board member for The Open Analytical Chemistry Journal, *Andrzej Lewenstam*

Elected to Societas Scientiarum Fennica, *Tapio Salmi, Dmitry Murzin*

ERA-Chemistry and the Irish Research Council for Science, Engineering and Technology evaluator of project proposals, *Johan Bobacka*

Evaluation of a Slovenian Research Centre of Excellence, Slovenia, *Johan Bobacka*

Evaluation of Docentship competence (*Konstantin Popov*), University of Oulu, Oulu, Finland, *Ari Ivaska*

Evaluation of Docentship competence (*Sami Franssila*), University of Helsinki, Helsinki, Finland, *Ari Ivaska*

Evaluation of Professorship competence (*Magnus Paulsson),* Mittuniversitet, Sundsvall, Sweden, *Bjarne Holmbom*

Evaluation of research proposals from EPFL, Lausanne, *Tapio Salmi*

Guest Editor of the topical issue "Solid-state potentiometric sensors" of the Journal of Solid State Electrochemistry, *Johan Bobacka*

Guest Editor, Topics in Catalysis, *Dmitry Murzin*

Kahlert, Heike, Ernst-Moritz-Arndt-Universität Greifswald, Greifswald, Germany, Evaluation of the Habilitation Thesis, *Johan Bobacka*

Kang, Jinguo, University of Wollongong, Wollongong, Australia: external examiner, *Annika Smeds*

Khalaj-Zadeh, Asghar, University of Toronto, Toronto, Canada, external examiner, *Mikko Hupa*

McLean, Douglas, University of Tasmania, Tasmania, Australia, external examiner, *Anna Sundberg*

Mouraou, Jérôme, INPG, Institute National Polytechnique Grenoble, France, opponent, *Bjarne Holmbom*

Mäkelä, Tapio, Åbo Akademi University, Turku, Finland, opponent, *Ari Ivaska*

Pedersen, Kim Hougaard, Technical University of Denmark, Kongens Lyngby, Denmark, opponent, *Mikko Hupa*

Pettersson, Anita, Chalmers University of Technology, Gothenburg, Sweden, opponent, *Mikko Hupa*

Principal Investigator Programme Grant, Science Foundation Ireland, evaluator of a grant proposal, *Johan Bobacka*

Reshetnikov, Sergei, Boreskov Institute of Catalysis, Novosibirsk, Russia, opponent, *Dmitry Murzin*

Invited lecturers

Bühlmann, Philippe, University of Minnesota, Minneapolis, MN, USA, February

Boccaccini, Aldo, Department of Materials, Imperial College London, UK, April

Fisher, Galen B., Delphi Corporation, Auburn Hills, MI, USA, May

Kuhn, Alexander, Université Bordeaux I, Bordeaux, France, November

Osaka, Akiyoshi, Okayama University, Japan, September

Niemantsverdriet, J.W. (Hans), Eindhoven University of Technology, the Netherlands, November

Shvarev, Alexey, Oregon State University, Corvallis, OR, USA, December

6.5 Publicity

Television and Radio

Finnish national TV, *Prisma* science program, January, *J-P. Mikkola*

Interviews on national and local TV news, May, *Stefan Willför*

Press Info, Åbo Akademi University, September, *Bjarne Holmbom*

Puusta pitemmälle – tekniikan huippututkimusta Turussa, Academy of Finland public discussion at Turku Science Fair, October, *Bjarne Holmbom*

Swedish national TV, RegionalNytt, February, *J-P. Mikkola*

Swedish TV, February, *Matias Kangas*, *J-P. Mikkola*

Ylen Ykkönen (national radio), interview with *Bjarne Holmbom*

Newspapers and General Journals

2008 Wallenberg Prize honors Holmbom and Eckerman, *Paper 360°*, May 2008

Det gröna guldet är framtidens energi, *Meddelande för Åbo Akademi*, February 1, 2008

Energin från skogen kunde fördubblas. Energin som lämnas kvar motsvarar Finlands oljeförbrukning, *Åbo Underrättelser*, September 9, 2008

Finlands Akademi stöder katalysforskning, *Meddelanden från Åbo Akademi*, February 15, 2008

Inte längre så kvistigt med kvistar*, Teknik & Ekonomi*, May 9, 2008

Kansainvälisesti arvostettu kemiantekniikan palkinto Åbo Akademiin, *Turun Sanomat*, September 3, 2008

Kemian huippututkijoille akatemiaprofessuurit (Tapio Salmi, Mart Saarma, Maarit Karppinen), *Kemia-Kemi* 35 (2008) 5, 82

Kuusen sisäoksista saattaa tulla arvo-osa? *MetsäRaha*, 5/2008

Marcus Wallenberg Prize awarded to Finnish Scientists, *Paperi ja Puu,* 4/2008

Nu får de lön för mödan, *Åbo Underrättelser*, October 4, 2008

Nya marknader ett måste, *Åbo Underrättelser*, May 22, 2008

Paperitehtaista tulee biojalostamoja turkulaistutkijoiden johdolla, *Turun Sanomat*, May 22, 2008

Prisbelönt ÅA-teknolog oroas över brist på frihet, *Åbo Underrättelser*, September 3, 2008

Skogsindustrins slagg kan bli till nyttiga näringstillskott, *Hufvudstadsbladet*, October 4, 2008

”Små grupper mera kreativa”. Bjarne Holmbom tror på innovativ forskning under fria former, *Meddelanden från Åbo* Akademi, December 12, 2008

Snart blir skogens kvistar energi. Johan Werkelin vid laboratoriet för Oorganisk kemi vid Åbo Akademi forskar i aska, *Åbo Underrättelser*, February 21, 2008

Suomalaistutkijat pokkaavat Wallenbergin, *Metsälehti,* 9/2008

Suomalaistutkijat saivat Wallenberg-palkinnon kuninkaalta, *Paperi ja Puu,* 7/2008

Trees are Nature´s Miracle Chemical Factory, *The Griffin* (UPM-Kymmene customer magazine), 3/2008

Västerbottens-Kuriren, interview together with Professor Leif Jönsson, October, *J-P. Mikkola*

Wallenbergpriset till forskare vid Åbo Akademi, *Meddelanden från Åbo Akademi,* May 9, 2008