Johan Gadolin Process Chemistry Centre

at

Åbo Akademi University

Annual Report 2017-2018

Edited by

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*Picture from the **PCC** annual meeting in August 2017*
Photo: Atte Aho

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Painosalama, Turku/Åbo

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1. Overview of JGPCC activities in 2015-2018

Background and news

The Johan Gadolin Process Chemistry Centre (***PCC***) began its journey already 1998 as a centre with common objectives and research strategy. We have now worked for nearly four years with the status of Centre of Excellence at Åbo Akademi University for the period 2015-2018. As we have an excellent historic overview later in this report, I will just briefly comment the activities during 2017 and 2018.

The core of our current research plan, "**Future Refining of Forest Biomass – the Molecular Process Technology Approach**" is built on our strengths in experimental and modelling capabilities to explore chemical details in novel processes and products that use biomass-based raw materials. The focus is on modification of the biomass components and their use in high-value applications such as structural biocomposites, 3D biomaterials in biomedical applications, immunostimulatory glycoclusters, and various fine and specialty chemicals. The weight is not only on polysaccharides but very much also on lignin and trace elements, both utilization and fate in modern biorefineries. Great thanks goes to our Work Package leaders who have coordinated the activities and reporting.

Our Johan Gadolin Scholarship Programme has also continued to be successful and is well integrated to our research plan. The role of our Forum for Society (FS) chaired by Lars Gädda is important to help us interact with society and industry and this kind of cooperation will be continued as ***PCC*** looks forward towards our future after 2018.

PCC is active in three out of the four research profile areas Åbo Akademi University has in its current strategy, namely "Molecular Process and Material Technology (MPMT)", "Drug development and diagnostics", and the also the newest "The Sea". The university also supports these areas with special funding and in consequence, to this we have Professor Thomas "Rosi" Rosenau from the University of Natural Resources and Applied Life Sciences (BOKU), Vienna, Austria, as an Adjunct Professor at ***PCC***. Professor Rosenau's area of expertise is very broad and includes e.g. oxidation chemistry, cellulose chemistry, lignin chemistry, chemical synthesis and analytics. Furthermore, Henrik Grénman from ***PCC*** has one of the tenure track professorships, Associate Professor in Molecular Process and Material Technology at the Faculty of Science and Engineering, supported by the university in conjunction to the MPMT profile area.

Our cooperation with the Turku Centre for Biotechnology (CBT), Biocity Turku, and the newly established Health Campus Turku has been very successful. Biocity Turku has seven research programs, where ***PCC*** and its members are active in four and have cooperation with also some of the others. The main program where ***PCC*** is active is the Advanced Bioresources and Smart Bioproducts – Towards Sustainable Bioeconomy, "Smartbio" (director: Academy Professor Eva-Mari Aro, University of Turku (UTU), vice-director: Professor Stefan Willför). Then our groups are also members or associated members of the Biomaterial and Medical Device Research Programme (director: Professor Pekka Vallittu, University of Turku, vice-director: Professor Leena Hupa) and Diagnostic Technologies and Applications (directors: Professor Tero Soukka, UTU,

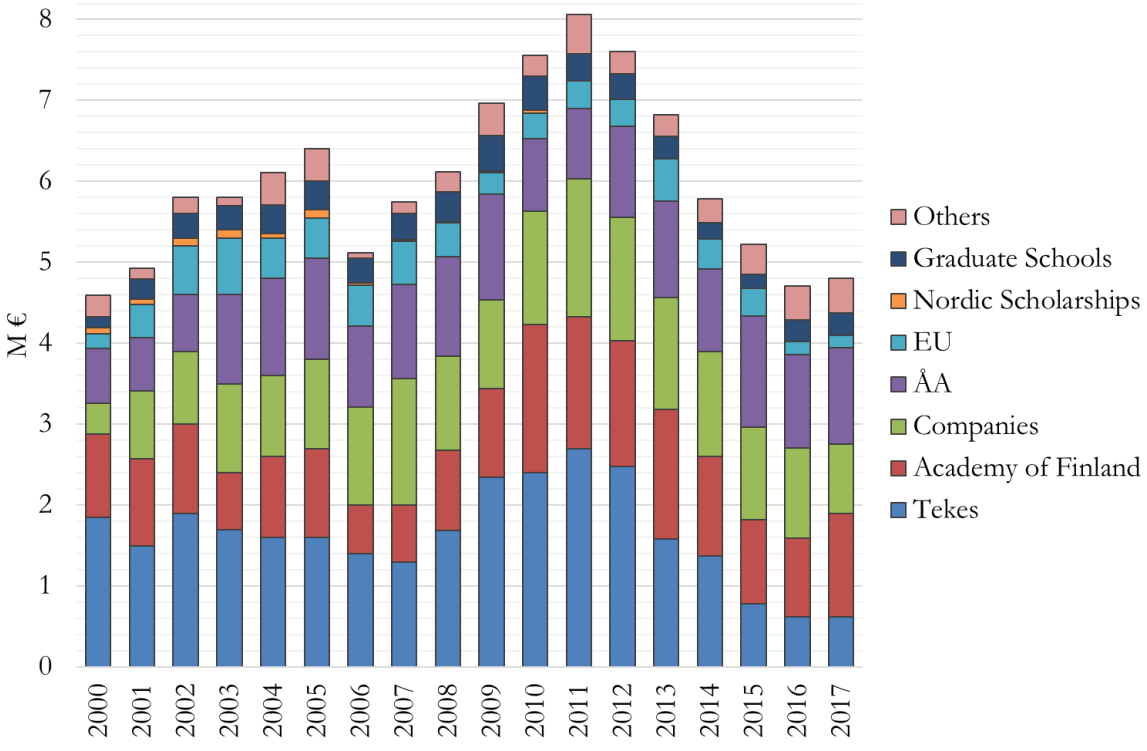
and Jessica Rosenholm (ÅA), vice-directors: Professor Johan Bobacka and Pekka Hänninen, UTU).

As always, ***PCC*** and its members have been very active in applying for funding on both national and international level. In 2018, Åbo Akademi University opened a new internal call for a Centre of Excellence Programme. For this new call, ***PCC*** decided to build a new research plan around "Molecular Process TechnoEconomy". The new research program requires a strongly multidisciplinary approach bridging chemistry, chemical engineering, and techno-economic evaluation from a system perspective. Thus we also expanded the participating groups to include two new ones, namely those of Professors Kim Wikström (Industrial Management) and Niklas Sandler (Pharmacy). ***PCC*** is one the few centers in Europe, where all these fields co-operate intensively within the same faculty. Unfortunately, ***PCC*** did not get to the second round in this call. However, we will continue the discussion on how to proceed as a center also in the future.

The year 2017 in numbers

In 2017, more than 100 senior researchers and full-time PhD candidates worked in the research projects of the Centre. In addition, a number of shorter term visitors, Master's students, and support personnel participated in our activities.

The figure below shows the funding of the Centre since the year 2000. The key external funding sources in 2017 were Åbo Akademi University, the Academy of Finland, and Tekes (nowadays Business Finland) together with Industrial Companies. The decrease in funding since the top-year 2011 has raised the demand level of the Centre to maintain its high-level productivity of research. This situation is a consequence of the overall funding situation for research in Finland, but 2017 seems as a turn point that again has changed this negative trend. It is noteworthy that although the funding is back at the level we had when ***PCC*** first started, our production is still excellent and thus the production per invested euro is better than ever.



The funding of the Johan Gadolin Process Chemistry Centre 2000-2017

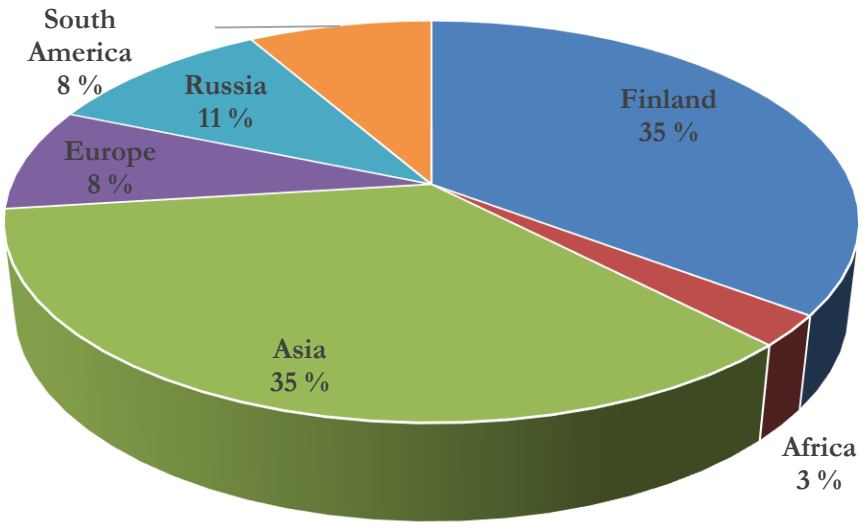
From the academic point of view, the year 2018 was again very productive. The table below gives some key numbers of our academic activities in 2017 and up to September 2018. Once again, the Centre kept a very high production rate and published 122 papers in scientific publication series with the full referee system in 2017. The year 2018 will evidently be even better. The number of theses is still on a satisfying level, although especially the number of Master's theses could be higher.

Theses and peer reviewed journal articles by the Johan Gadolin Process Chemistry Centre.

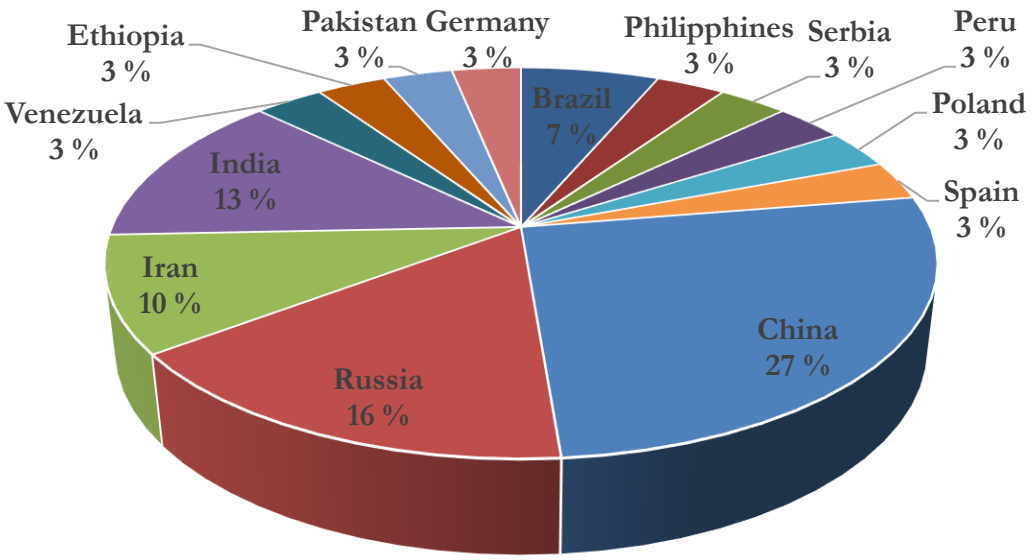
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Doctoral Theses	5	7	8	2	11	8	8	8	9	7
Masters' Theses	21	23	27	26	17	15	20	23	19	17
Journal Articles	60	71	94	77	106	109	113	116	101	118
	2010	2011	2012	2013	2014	2015	2016	2017	2018 (09)	
Doctoral Theses	6	10	10	15	16	12	6	6	4	
Masters' Theses	15	11	14	12	16	25	10	18	12	
Journal Articles	138	126	130	139	136	152	146	122	123	

Doctoral students

A central part of our research activities is done as doctoral theses works. Altogether 48 PhD thesis projects are actively underway at the Centre. Our doctoral students are very international (see the graph below) and I believe ***PCC*** is the most international unit in our university.



Origin of PhD students at Johan Gadolin Process Chemistry Centre.



Nationality of foreign PhD students at Johan Gadolin Process Chemistry Centre.

In addition to projects, CoE funding, and grants, the Åbo Akademi doctoral network program and therein the Graduate School in Chemical Engineering (GSCE) and Doctoral Network of Materials Research (DNMR) are important sources of funding for the PhD students in ***PCC***.

Johan Gadolin Scholarship Program

Our Johan Gadolin Scholarship Program was founded in 2007. It was funded by the Åbo Akademi Foundation during the years 2007-2011 and continued for 2012- 2013 on other sources of funding, after which the Åbo Akademi Foundation decided to continue funding for the Johan Gadolin Scholarships Program for at least the period 2014-2019.

In the Johan Gadolin Scholarship Program we have been able to invite PhD students and post doctoral researchers to join ***PCC*** for a period between 3 to 9 months. So far, 89 fellows from 32 different countries and 76 different universities worldwide have participated in the program. Also 11 fellows joined the JGS with their own funding. The visitors have participated in on-going research projects at the Centre. The cooperation between the ***PCC*** and the Johan Gadolin fellows has so far produced more than 200 scientific articles

Boards and task forces

PCC is led by an executive board consisting of the five research group leaders: Professors Stefan Willför, Johan Bobacka, Tapio Salmi, Reko Leino, and Leena Hupa. Dr. Otto Långvik worked with the coordination of the ***PCC*** and functions as secretary of the board until he got a new appointment outside ÅAU and now Dr. Markus Engblom has the honors of being the coordinator.

Since the very beginning, the ***PCC*** board has been supported by two important Advisory Boards; the Scientific Advisory Board (SAB) and the former Industrial Advisory Board, which now is called the Forum for Society. 2015-2018 our Scientific Advisory Board consists of the Professors *Jiri Janata* from the Georgia Institute of Science and Technology in Atlanta, USA, *Raimo Alén* from the

University of Jyväskylä, Finland, *Lars Pettersson* from the Royal Institute of Technology in Stockholm, Sweden, *Andreas Seidel-Morgenstern* from Max Planck Institute, Germany and *Jan-Erling Bäckvall* from Stockholm University, Sweden.

In 2017-2018, the ***PCC*** had four lectures in its Distinguished Lecturer Series:
February 13, 2017: Prof**. Thomas Rosenau**, University of Natural Resources and Life Sciences, BOKU, Vienna, Austria: "Celluloses I and II – some news from an old polymer"

May 9, 2017: Prof. **Dermot Diamond,** National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland: "Long-Term Autonomous Biochemical Sensing in Remote Locations: From Broken Promises to a New Beginning?"

June 1, 2017: **Alain Walcarius**, Research Director at CNRS, Director of the Laboratory of Physical Chemistry and Microbiology for the Environment (LCPME), Head of the "Analytical Chemistry and Electrochemistry" (ELAN): "Electrogeneration of nanostructured and functionalized silica films"

February 15, 2018: Prof. **David Crich**, Wayne State University, Detroit, MI, USA: "Shaping Next Generation Aminoglycoside Antibiotics for Treatment of Multidrug-Resistant Diseases"

Acknowledgements

This report will be published at the Annual Symposium of the ***PCC*** held on November 22, 2018 at Åbo Akademi University Arken Building in Turku. The report gives an overview of the recent activities at the Centre.

An editorial team consisting of Lucas Lagerquist, Rose-Marie Latonen, Otto Långvik, Päivi Mäki-Arvela, Anna Sundberg, Johan Werkelin, and Pasi Virtanen edited the report and layout.

We want to thank all our collaborating partners in Finland and all over the world for another year of interesting and inspiring work together.
On behalf of the Board of the Johan Gadolin Process Chemistry Centre,

Stefan Willför

Chairman

Greetings from Forum for Society (FS) to 2018 annual report

Our Forum for Society (FS) consists of representatives of the key industrial companies, as well as members of the society co-operating with the Centre. The members of FS have appreciated the possibility to take part and to follow up activities and results of the research performed within Johan Gadolin ***PCC***.

FS expresses its gratitude to The Executive Board of ***PCC*** and especially its chairman prof. Stefan Willför and coordinator Otto Långvik for their efforts to direct and coordinate the ***PCC*** research. Without the practical efforts and work done by the Working Package leaders, all researchers and support personnel could this Centre of Excellence never have been so productive and achieved all reported results since its start. The organizing and funding of this important Centre of Excellence done by Åbo Akademi and Åbo Akademi University Foundation is also gratefully acknowledged by Forum for Society.

The focus and core of ***PCC*** research as defined in current research plan "Future Refining of Forest Biomass – the Molecular Process Technology Approach" address relevant and important questions when our society develops and takes steps towards the future Bioeconomy. Modifications of forest biomass components and their use in addressed various high-value added applications are thus very important.

However, the Forum for Society Members want also to remind that ***PCC*** members must always remember the importance of the competences and technology needs of the more traditional chemical industry in areas as *e.g.* catalysis, unit operations, analytics and in-depth basic chemistry knowledge.

FS will contribute to the planning of the future Centre of Excellence through a genuine and open dialogue. This requires a pro-active approach by the organizers and participants of the future Centre of Excellence. An organization of the future activities and research within the three following topics, could be one starting point at least from FS point of view:
Cutting-edge and exploratory research to establish the necessary knowledge platform needed for developing future competitive technologies for the future more bio-related society including both existing industry and future new ventures. The right research topics ought to raise from the vast knowledge base within Åbo Akademi and from understanding of important future developments of both markets and society.

Application research in areas important for partnering industries. This application research ought to fit both within the Centre's knowledge and competences areas and areas where partnering industries lack competences and resources. An extensive dialogue between the Centre of Excellence and the partnering industry is thus needed to secure success in desired application research.

Trouble shooting activities for partnering industry in areas suitable for competences and resources. This activity requires well planned and directed marketing activities towards the industry actors.

Forum for society wish success for the future planning efforts of this very successful Centre of Excellence.

Tapio Salmi Academy Professor again!

Academy Professor is the highest researcher position in Finland. The national research agency, Academy of Finland received a total of 193 Academy Professor applications. The final funding decisions were made by the Academy's General Subcommittee based on the panel review reports. Finally 10 new Academy Professors were appointed. Tapio Salmi, professor in chemical reaction engineering at our university and working at ***PCC*** became one of the new Academy Professors. He is the only one among the new Academy Professors representing chemical sciences. The five-year term will start 1.1.2019. Besides the full-term grant for the professor's salary, Academy of Finland will also finance the Academy Professors' research costs (equipment and researchers' salaries).

Academy Professors are internationally leading-edge researchers and recognized experts in their field who are expected to have great scientific impact in the scientific community and in society at large. Academy Professors are also expected to significantly advance research in their field and to develop creative research environments.

Tapio Salmi is one of the very few professors in Finland who has been appointed Academy Professor twice, the former term was in 2009-2013. The research topic for the new term (2019-2023) is

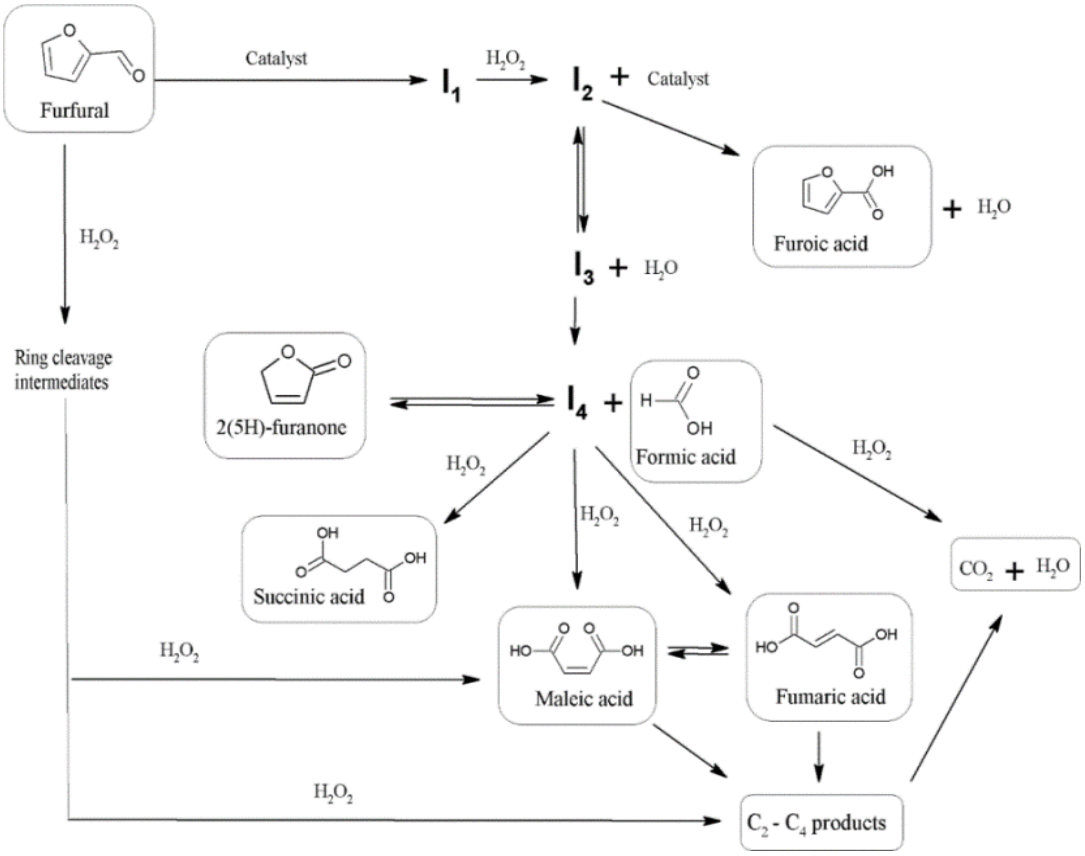
Towards a deep understanding of multiphase molecular processes by application of transient experimental techniques and mathematical modelling

Conventional methods for investigating the rates of chemical reactions are based on the measurement of concentration changes as a function of the reaction time. Conventional kinetic methods are however not sufficient for studying chemical processes in which solid heterogeneous catalysts and several phases (gas-liquid-solid) are involved. Two key questions need to be answered: what are the reactive surface species and how do they interact on the catalyst surface in elementary reaction steps, which lead to the overall reactions observable in the gas or liquid bulk phases?
Throughout the years, advanced transient methods have been developed and successfully applied to study the mechanisms of heterogeneously catalyzed gas-phase reactions: step response and pulse methods and isotope exchange techniques. Numerous industrially relevant catalytic processes are much more difficult to investigate on a deeper molecular level, because they are multiphase systems

involving both gas and liquid phases. In situ and transient experiments in the liquid phase are much more demanding than for gas-phase experiments. Attenuated total reflection infrared spectroscopy will be used to investigate the surface species in liquid-phase catalytic reactions. New and modified transient techniques will be applied to get a better understanding on three-phase reaction mechanisms. As the intrinsic reaction mechanism on the molecular level is revealed, the research takes the next step: the development of mathematical models, i.e. rate expressions for the elementary steps and the overall reactions. The kinetic parameters of the model can be determined from experimental data and supporting information will be obtained from quantum chemical calculations. This approach contributes to the design of significantly improved chemical reactors based on solid structures and the use of 3D printing technology.

The research will be focused on selected oxidation reactions of bio-derived and bio-degradable molecules. The key molecules are monomers from biomass, hydrogen, oxygen, water and hydrogen peroxide. Oxidation of carbonyl and hydroxyl groups in molecules originating from biomass is of significant industrial importance. Two environmentally friendly oxidation agents will be used: molecular oxygen and hydrogen peroxide.

The research effort provides both new methodology and new technology (liquid-phase transient techniques) and new, molecular-level results (reaction mechanisms, kinetic data, kinetic models). The main part of the work will be done at ***PCC***. A strong international network has been established to achieve the goal, besides domestic collaboration, experts from France, Germany and Italy will contribute to the work. The new era of chemical industry shall be based on strong fundamental research, Professor Salmi states.



Example of a complex reaction system to be studied by transient techniques.

1.1 Experiences of the Johan Gadolin Scholarship researchers

Dahiana Andrea Avila Salazar

I am Dahiana Andrea Avila Salazar, I studied chemistry at the National University of Colombia. In 2016 I completed my Master's degree in Chemistry at University of Siegen, Germany. Currently, I am doing my PhD in Glass Chemistry at Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Germany, supervised by Prof. Delia Brauer. My research focuses on the dissolution mechanism of phosphate glasses for structural design of optimized glasses of tailored solubility as well as on glass structure characterization by solid-state NMR spectroscopy. I was awarded a Johan Gadolin Scholarship for a period of four months under the supervision of Prof. Leena Hupa which provided me with a unique learning experience both in the personal and professional field. In Turku, I had the opportunity to address my research from different scientific and technological perspectives owing to the diverse expertise of the cooperative team at the Inorganic Chemistry Department. I am positive that I will publish the results obtained in my "Dynamic dissolution kinetics in phosphate glasses" project. On the other hand, there were a number of extra factors such as getting to know great people, the culture and amazing landscapes in Finland which made my stay quite an experience.

Maria Khaydukova

My name is Maria Khaydukova. I got my PhD in Saint Petersburg State University (Russia) in 2016. My research topic was devoted to the development of multisensor systems and their analytical application. After getting the PhD I decided to extend my knowledge and try myself in a different field but where my background can be useful. Therefore I contacted Dr. Zhanna Boeva from the department of Analytical Chemistry at Åbo Akademi University and we decided to apply for the Johan Gadolin scholarship. I would like to underline that the application process is simple and transparent. I received a scholarship for 3 months. It gave me an opportunity to work in the well-known research group with very helpful and friendly members. During my stay, I learned a lot about conducting polymers and their application for biosensors. I obtained new knowledge and skills which I would like to apply in my future research work. It is valuable to mention that normal life in Finland is simple for foreigners since almost everyone can communicate with you in English. I highly recommend Åbo Akademi University for efficient work and Turku for a peaceful life.

Katharina Schuhladen

My name is Katharina Schuhladen and I am a PhD student in material science at the Friedrich-Alexander-University of Erlangen-Nuremberg (Germany). I have received a scholarship at the Johan Gadolin Process Chemistry Center (***PCC***) for a period of five months, under the supervision of Prof. Leena Hupa. My primary research interest is the use of bioactive glasses in the repair of soft tissue, especially in borate glasses, since they are able to stimulate wound healing. Therefore, the aim of my research visit in Finland was the fabrication of a new family of bioactive borosilicate and borate glasses, to use them after my visit for the fabrication of polymer composites containing these glass powders for wound healing and soft tissue engineering applications. Beside the fabrication, I was able to do some dissolution experiments using different media, which are of great interest in the design of an application in wound healing. Beside the possibility to enjoy the wonderful country, I was able to expand my knowledge about bioactive glasses and had the possibility to work with great people.

Nataliya Shcherban

I am Nataliya Shcherban, I work at L.V. Pisarzhevsky Institute of Physical Chemistry of National Academy of Sciences of Ukraine, Kyiv, Ukraine. In 2010 I completed my PhD degree in physical chemistry at L.V. Pisarzhevsky Institute of Physical Chemistry of NAS of Ukraine. Currently, I am senior researcher at the same Institute. My research focuses on synthesis, characterisation and applications of nanostructured porous materials (carbons, carbon nitride, micro-mesoporous aluminosilicates, silicon carbide, etc.). I was awarded a Johan Gadolin Scholarship for a period of three months under the supervision of Prof. Dmitry Yu. Murzin. In Turku, I had the opportunity to address my research from different scientific and technological perspectives owing to the diverse expertise of the cooperative team at Johan Gadolin Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering. Research work aimed on the development of physical and chemical principles of creation of new nanostructured and nanoporous materials based on micromesoporous zeolite-like structures, carbon including functionalized carbons and carbon nitride for use in catalysis and adsorption. Catalytic activity of different materials in a few catalytic reactions such as α-pinene oxide isomerization, betulin oxidation, Knoevenagel condensation between benzaldehyde with ethylcyanoacetate, aldol condensation of cyclopentanone with valeraldehyde was evaluated. The obtained scientific results were summarized in 5 papers related to the scholarship period. The scholarship gave me a unique learning experience both in the personal and professional field.

Dmitrii Riabukhin

My name is Dmitrii Riabukhin and I am from Russian Federation. I graduated with a PhD degree from Saint Petersburg State Forest Technical University. My primary research interest are superelectrophilic chemistry of formation heterocycles and organic synthesis based on nature compounds. I applied for the Johan Gadolin Scholarship at Åbo Akademi, because I wanted to get new experiences in laboratory job, to open new directions in chemistry, meet interesting people, and make new contacts. During my stay at the Johan Gadolin Process Chemistry Center, in laboratories of Wood and Paper Chemistry and Organic Chemistry, my work was focused on the experimental study of new synthetic approach of utilization natural lignans and lignins for preparation potentially useful materials. I got new skills and knowledge, which I would like to use for further research work in my home country. In my own opinion, scholarship in Åbo Akademi University is the best place and choice to understand that personal practical work experience abroad is invaluable. I highly recommend applying for Johan Gadolin Scholarship in Åbo Akademi, this place has left only positive moments in my heart.

Soma Papp

My name is Soma Papp, I'm a PhD student at Budapest University of Technology and Economics in Hungary. In Budapest I work in the Chemical Nanosensors Research Group, under the supervision of Prof. Róbert Gyurcsányi, where my work focuses on sensing with different kinds of nanopores. May it be quantitative counting and sizing of viruses or developing new concepts for ion-selective electrodes, I enjoy voyaging on the frontier of human knowledge and pioneering beyond. Here, in Turku together with Dr. Tom Lindfors we aimed for a goal no less ambitious than to improve the potential reproducibility of conducting polymer-based solid-contact ion-selective electrodes, a challenge long ongoing in the field of electroanalytical chemistry. During my 3 month long stay I was able to test many of our ideas, which took us several steps closer to the final solution. Although I travel a lot, I've never been to Finland before, yet I found an easy-going atmosphere here. In Åbo Akademi University I could work with really amiable and helpful people, who made the working days and lunchtimes enjoyable. Beside work I had many opportunities to enjoy the life in Turku. I loved the countless events, the museums and the beautiful riverside always full of life, while the scenery of the Turku Cathedral is the type of rare beauty which is impossible to forget. I encourage everyone to apply for Johan Gadolin scholarship and to visit Turku.

2. *PCC*, from local traditions to international top-level science

Bjarne Holmbom, Ari Ivaska

The Process Chemistry Centre (***PCC***)* was created in 1998 when we four: Mikko Hupa, Ari Ivaska, Tapio Salmi and Bjarne Holmbom held our first brainstorming meetings. From the very beginning we agreed and established that we are a chemical engineering group with strong focus on chemistry. However, the base of this strong chemistry-focused process engineering was created already 100 years ago, when our Department of Chemical Engineering (Kemisk-tekniska fakulteten, KTF) was founded.

Actually, we can trace our roots even more far back, to the 18th century. In the former Royal Academy in Turku/Åbo chemistry was established as a scientific discipline in the middle of the century. A chemical laboratory was built in the early 1760´s, in the same quarters close to the cathedral where we are situated still today. The first professor of chemistry, Pehr Adrian Gadd, held his inauguration speech for the new laboratory in 1764. There, he emphasized the urgent need of applied chemistry for the benefit and welfare of society. In his speech at the doctoral conferral ceremony in 1968 professor Anders Ringbom stated that the programme declaration of Gadd, more than 200 years earlier, was still fully acceptable for a modern department of chemical engineering. Gadd and his successor Johan Gadolin developed chemistry in this applied direction achieving wide international recognition. Then in 1827, the big fire destroyed Turku and the university was moved to Helsinki the year after. Gadd´s laboratory building was demolished in the 1790´s. Then, Gadolin built a new laboratory with own funding, and that building is still standing on the Kaskis Hill.

The chemistry traditions from the Royal Academy were still deep in the minds of many persons during the years 1917–1918 when the new Åbo Akademi University (ÅA) evolved. There was a kind of tug-of-war between different disciplines for securing a place in the new academy. On one side there were the "soft sciences" with philosophy, history and social sciences, and on the other side the "hard sciences" represented by mathematics, physics and chemistry. It was especially difficult for the representatives of the soft sciences to accept the proposal for a technical faculty that was brought up by influential persons close to the industry. The idea of a technical educational programme in a university had not at that time been heard of in the Nordic countries. The technical faculty, however, got a strong and eloquent supporter in the becoming professor of mathematics, Severin Johansson, who also in 1921 became the Rector of ÅA.
Thanks to large donations received in 1918, planning of the new department (faculty) could proceed. A planning committee was appointed in 1918. Members were the four professors in the Faculty of Mathematics and Natural Sciences (MNF) and six persons with knowledge and experience of technology and industry. In addition, a special advisory board of five distinguished scientists from Sweden, Norway and Finland, among them even the Noble laureate Svante Arrhenius, was appointed to comment on the proposed plan. The plan presented in July 1919 stated that the main task of the new department (faculty) was to: "educate technical chemists devoted in particular to work in and develop chemical industrial enterprises for which there are (in Finland) good business opportunities due to the supply of raw materials and hydro power". In the plan it was further stated that the educational and research activities should be focused on those

parts of the theoretical and the technical chemistry which are important especially for the utilization of forest products and the use of hydro power. This plan, 100 years ago, had thus much in common with the thoughts we had when creating ***PCC***.

*The Centre was named Process Chemistry Group (PCG) 2000-2002 and ***PCC*** onwards

According to the plan, the two first professors appointed in the new Faculty were in General Chemical Technology and Forest Products Chemistry and Technology. Erik Hägglund from Sweden was invited to hold the chair of Forest Products Chemistry and Technology 1921–1930. He was an internationally recognised scientist already when he came, and during his ten years at ÅA he developed his laboratory to a world-leading institution. Walter Qvist was appointed to the professorship in General Chemical Technology in 1922 and held it until his retirement in 1960. He was a born administrator, being Dean of the faculty 1927–1960, and furthermore being Rector of the School of Economics at ÅA during 28 years. The third professor Jarl Salin held the professorship in Machine Construction from 1933 to 1966. He was a born educator and laid a new ground for the education of process engineers which is relevant and valid still today. The fourth professor, Anders Ringbom, was appointed to a new chair in Analytical and Inorganic Chemistry in 1943. However, he commenced his studies at KTF already in 1921 and got his engineer´s degree in 1925. First he worked as assistant to Erik Hägglund. Later he found his own line, analytical chemistry, and got his PhD in 1936. He held the chair until his retirement in 1968. He was a born scientist devoting all his life to develope analytical chemistry as a distinct and significant discipline in chemical engineering.

These four professors devoted most of their lives to the development of chemical engineering at ÅA. They can be said to have built up also the scientific base for all us four. Certainly, also their later predecessors made significant contributions to the development of our scientific platforms. We are deeply grateful to our excellent teachers and mentors: Henrik Bruun (Wood and Paper Chemistry), Erkki Wänninen (Process Analytical Chemistry), Kaj Karlsson (Combustion and Material Chemistry), and Leif Hummelstedt and Lars-Erik Lindfors (Catalysis and Reaction Engineering). The support of many professors in MNF should also be acknowledged.

The creation and development of *PCC*

In 1997 the Academy of Finland (AoF) announced that research groups could apply for funding as "Centres of Excellence" (CoE) in an open competition. First, it was discussed if the whole chemical engineering department, KTF, would apply. That, however, was found to be a too broad and heterogeneous group. Then, we four happened to meet. We laid out a new joint concept with the aim to understand and develop industrial processes and products at a deeper chemical level, at the molecular level. We branded the concept "*Molecular Process Technology"* in parallel to other molecular sciences and named the coming centre "*Process Chemistry Group"* (PCG). We were successful in the tough competition and received funding for six years, 2000–2005.

*The four founders of PCG/**PCC**:*
Ari Ivaska, Mikko Hupa (Chairman) Tapio Salmi, and Bjarne Holmbom in 1999.

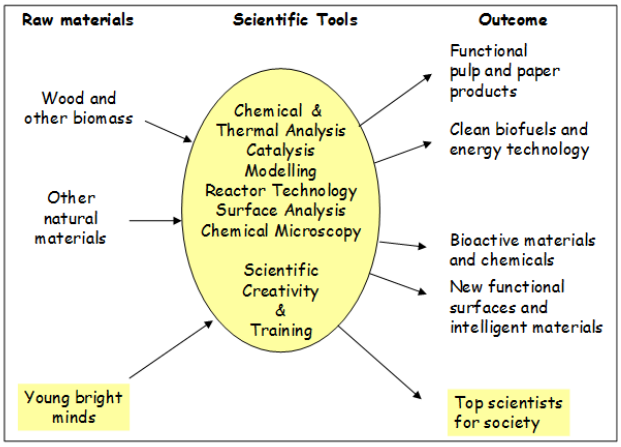
Already in the early stage of the activity of the Centre the following statement was formulated as the Mission for PCG/***PCC***: "Detailed understanding of physico-chemical processes in environments of industrial importance in order to meet the needs of tomorrow's process and product development". Our definition of Molecular Process Technology includes the study of chemical phenomena and mechanisms at the molecular level of reactions of industrial relevance as well as process models based on detailed physico-chemical understanding. Development of relevant molecular structures for industrial products and environmentally significant components discharged from processes are also included in the scope of the ***PCC*** activity.

In the beginning the synergy in the Group was not fully developed, a fact that was also pointed out by our first Scientific Advisory Board (SAB), appointed by the AoF to follow our activities and to give relevant advices. During the first period as CoE our SAB included the following professors: Thomas W. Joyce, Western Michigan University, USA, J.W. Niemantsverdriet, Eindhoven University of Technology, The Netherlands and Albert Renken, Swiss Federal Institute of Technology, Switzerland. In 2002, after three years of work, they stated that "*PCG has matured into a true Centre of Excellence. We are gratified that our concerns have been addressed by the PCG, and that we have played a small role in the progress of this Centre of Excellence into an internationally recognized research force".* In their report to the AoF they concluded that "*We urge that all due regard be given to the Centre´s funding request. This Centre can make a difference to the economic development of Finland and be internationally recognized as a source of creative research. It will truly be a source of pride for the Academy of Finland".*

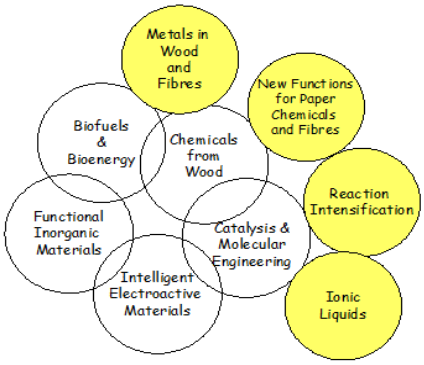
By our own initiative we appointed also an "Industrial Advisory Board", IAB, inviting research leaders from Finnish industrial companies active in the field of our scientific activity.

AoF requested new openings in the application for the second period as CoE with a well-defined research strategy. The mission as defined in the first period was further developed in the application for the second period as CoE, 2006-2011: "Sustainable Chemistry in Production of Pulp and Paper, Fuels and Energy, and Functional Materials". The program is outlined in the scheme below with the new openings as the main research areas. The selection process was very competitive including a site visit which was crucially important for the positive decision by AoF. During this second period the SAB consisted of the following professors: Jean-Claude Charpentier, CNSR, Lyon, France, Jiri Janata, Georgia Institute of Science and Technology, Atlanta, USA and Douglas Reeve,

University of Toronto, Canada. In addition the SAB had also representatives from the AoF and TEKES. In parallel to the main research program of the second period, ***PCC*** had also a special project: "Chemistry in Forest Biorefineries", supported by TEKES (National Centre of Technology and Innovations).



PCC master plan



The research areas

The European Union granted to ***PCC*** the status as "Marie Curie Training Site" for the period 2002-2006 to give Marie Curie Fellowships to students from other EU countries. The students were selected based on their applications and they spent 3-12 months in one of the research teams in ***PCC***. The program was very popular and was continued as the "Johan Gadolin Scholarship" program funded by the Åbo Akademi University Foundation. It was then also extended to students and post docs from all over the world. The visits resulted often in high quality research papers and cooperation with the home university of the student. Several of the Marie Curie and Johan Gadolin students also returned back to ***PCC*** as post doc researchers. Through both programs ***PCC*** increased its international activity and visibility and received highly motivated students and post docs.

The "Distinguished Lecturer Series" was initiated in order to invite distinguished scientists to give presentations of their research to ***PCC*** personnel and to inspire new research openings. Many top researchers participated in the program and contributed to promote ***PCC*** and its scientific profile. Every year ***PCC*** organized an Annual Seminar where the members of SAB and IAB participated. The program consisted of presentation of the activities of ***PCC*** by senior members and students. Both SAB and IAB had also their contributions. The feedback from SAB and IAB was always most valuable when planning both short- and long-term research strategies. Especially in writing new applications to AoF the proposals from SAB and IAB were found to be useful. ***PCC*** also organized internal workshops on special topics and winter colloquia with more general program. We are also grateful to the Editorial Team that through the years have edited the Annual Report and organized the Annual Seminar. Special thanks here go to Päivi Mäki-Arvela and Anna Sundberg who both have served on this team all since 1999.

PCC participated also actively in the Graduate School program of the Finnish Ministry of Education both in coordinating some of the schools and being members of the leading group of the schools.

The leading idea of the research strategy of ***PCC*** was to have common research projects between the participating teams and common supervision of the students. This was found to be most useful

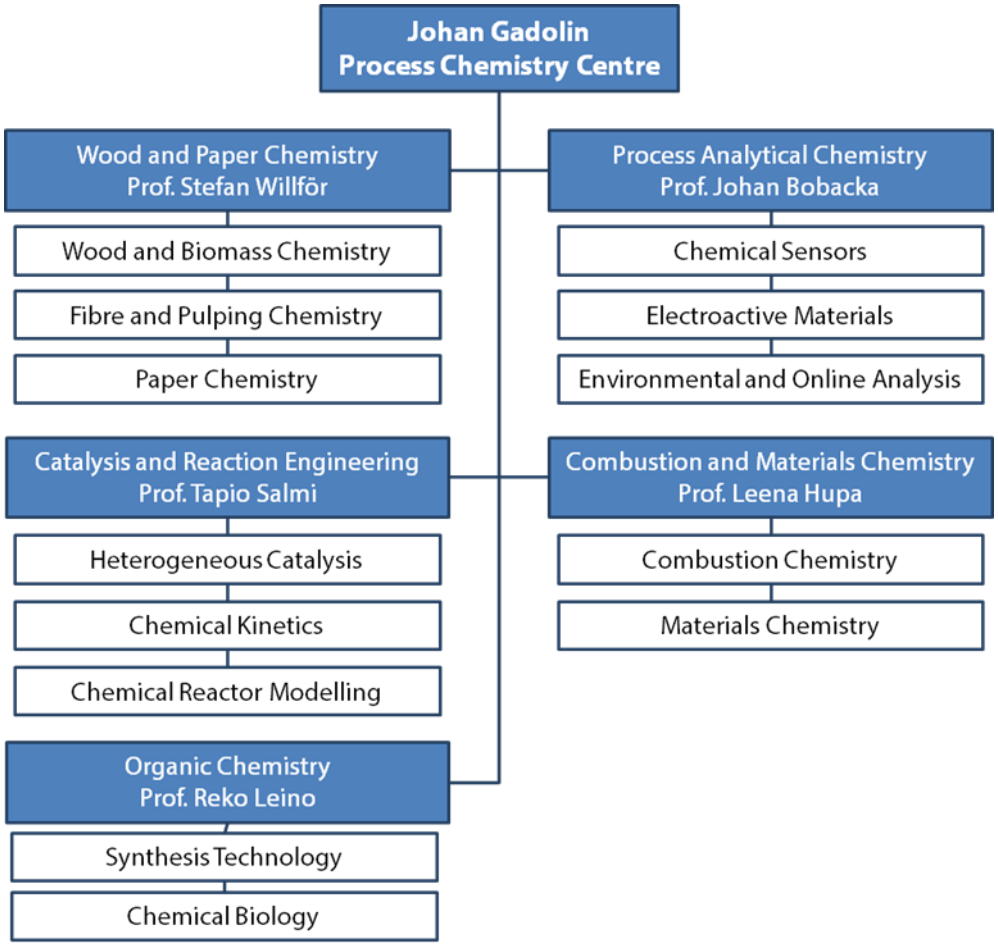
and productive which especially can be seen in the increased scientific activity of ***PCC*** as whole. As an illustrative example is the increasing number of PhD thesis and peer-review papers (page 8). Other examples are the nomination of Prof. Tapio Salmi twice to the distinguished position as Academy Professor and the scientific prizes the ***PCC*** senior researchers have received, among them: The Finnish Science Prize, The Marcus Wallenberg Prize, The Magnus Ehrnrooth Foundation Prize, The Fortum Foundation Prize, The ÅA Chancellor´s Prize and Inductee at The Paper Industry International Hall of Fame. Many junior ***PCC*** researchers and students have also been awarded different prizes, both based on their scientific contributions in general and conference contributions. The senior researchers have also been invited to several scientific societies, both national and international. Many members are also in the editorial and advisory boards of international journals. ***PCC*** personal have also been active in organizing scientific conferences both in Finland and abroad. All these scientific appreciations can be regarded as results of the ***PCC*** activity as a whole.

After the 12-year period as CoE of AoF, ***PCC*** received financial support from ÅA 2012-2014 for the programme: "Sustainable technology for green products" and was appointed as ÅA internal CoE for the period 2015-2018. Bjarne Holmbom and Ari Ivaska retired and were replaced on the ***PCC*** Executive Board by the new professors, Stefan Willför and Johan Bobacka. Mikko Hupa became Rector of ÅA in 2105 and was replaced on the ***PCC*** Board by Leena Hupa. A significant strengthening of ***PCC*** came with the merge of Organic Chemistry in 2015. Organic chemistry has been a very valuable partner in many ***PCC*** projects through the years and therefore this merge was very natural. Professor Reko Leino from Organic Chemistry is now the fifth member of the ***PCC*** Board. Stefan Willför has since 2015 been the Chairman of the Board of ***PCC***.

To conclude, in ***PCC*** four relatively small but strong research groups were joined, a new scientific concept was identified, a clear mission was formulated, and intensive work was started with the aim to create a large and internationally recognized scientific centre. Keys to success were trustful cooperation between the four leaders and their team members. Synergy between the teams was systematically developed. As a result, we can say that four times one became much larger than four (4x1 >>4). Important has also been that we developed a light and creative internal administration, and that we received valuable advice from our scientific and industrial advisory boards. The support of the administration of ÅA and the Foundation of ÅA has also been important to our success. Altogether, the creation and further development of ***PCC*** has shown that it is possible to grow big and strong in a certain scientific field through trustful and systematic internal and external cooperation even and especially in a small university such as ÅA.

3. Organization and personnel

3.1 Organization of *PCC*



Executive Board

- Professor Stefan Willför (chairman)
- Professor Johan Bobacka (vice chairman)
- Professor Leena Hupa
- Professor Reko Leino
- Professor Tapio Salmi

Coordinators

- Dr. Otto Långvik
- Dr. Markus Engblom

Scientific Advisory Board (SAB)

- Professor Raimo Alén, University of Jyväskylä
- Professor Jan-Erling Bäckvall, Stockholm University
- Professor Jiri Janata, Georgia Institute of Technology
- Professor Lars J Pettersson, KTH
- Professor Andreas Seidel-Morgenstern, Max Planck Institute Magdeburg

Forum for society (FS)

- Lars Gädda, FS Chairperson
- Örjan Andersson, Novia
- Ilmo Aronen, Raisio
- Stig-Erik Bruun, Chemigate
- Kenneth Ekman, Crisolteq
- Heidi Fagerholm, Kemira
- Linda Fröberg-Niemi, Turku Science Park
- Christine Hagström-Näsi, CLIC Innovation
- Patrik Holm, Orion Pharma
- Bertel Karlstedt, Valmet
- Kari Kovasin, Metsä Fibre
- Björn Lax, Chemec
- Timo Leppä, Chemical Industry Federation of Finland
- Lars Peter Lindfors, Neste
- Pia Nilsson, UPM-Kymmene
- Karri Mikkonen, Turku Future Technologies
- Leena Paavilainen, Luke
- Jarkko Partinen, Outotec
- Leena Sarvaranta, VTT
- Mathias Snåre, Nordkalk
- Kenneth Sundberg, Tikkurila
- Kari Toivonen, Elomatic
- Petri Vasara, Pöyry
- Stefan Wallin, Member of Parliament

3.2 Wood and Paper Chemistry

The mission of our laboratory is to *promote sustainable and multipurpose use of wood for high-value biomaterials and biochemicals and for fibre products*. We strive towards creating and publishing novel and significant scientific findings and to educate students and scientists with excellent skills and creative problem-solving ability for the needs of industry and the society.

Our research is directed towards promoting sustainable, resource efficient, and multipurpose use of wood and other renewable raw materials in products including pulp, paper, fibre, and wood products, but also for novel biomaterials, biocomposites, biochemicals, and bioenergy. Advanced analytical techniques are our tools to obtain knowledge at the molecular level on the various components of different natural raw materials and their reactions, interactions, and functions in different processes and products. Our biorefining approach aims at utilizing forest or other renewable resources as wide-ranging as possible, thus minimizing the amount of waste in the end. For example, selective extraction and recovery of hemicelluloses, cellulose, lignin, or polyphenols from wood, bark, or process waters is followed by functionalization and utilization in different value-added end-uses. A strong research approach is the utilization of nanocellulose, modified hemicelluloses, and lignin for hydrogels and materials in biomedical applications, especially through 3D bioprinting. We also work on understanding the fibre-fibre joint structure and molecular level interactions between fibre surfaces to obtain high extensibility of the fibre networks for novel mouldable packaging. Furthermore, we provide analytical services and support in process problem solving to the industry in the forest and bioeconomy sectors.

External research support 2017-2018 was obtained mainly from Academy of Finland and the industry, and from the China Research Council in form of grants for PhD students. We also have close cooperation with e.g. KTH in Sweden, University of Wollongong in Australia, and BOKU in Austria with researcher exchange and joint research and teaching. Other active partners are University of Helsinki, LUKE, and groups affiliated to the Turku Centre for Biotechnology in Finland.

Personnel of the Laboratory of Wood and Paper Chemistry in September 2018

Personnel

Professors

Stefan Willför
Bjarne Holmbom (Emeritus)

Docents

Andrey Pranovich
Annika Smeds
Anna Sundberg

Researchers

Jarl Hemming
Ekaterina Korotkova
Sebastian von Schoultz
Xiaoju Wang
Huanfei Xu (Johan Gadolin Scholar)

Early-stage researchers

Wenyang Xu
Luyao Wang
Qingbo Wang
Yongchao Zhang
Weihua Zhang

Secretary

Marika Ginman

Links

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

3.3 Process Analytical Chemistry

Our main expertise in Analytical Chemistry is in the areas of chemical sensors, electroactive materials and electrochemistry. Our research is focusing primarily on the development of novel electrochemical sensors based on advanced functional materials, new receptor molecules and new signal transduction methods. This involves basic research on new materials as well as engineering of sensor devices. Our know-how in electrochemistry is essential to our research, because the majority of all chemical sensors used today are based on electrochemical transduction.

Continuous (on-line, in-line, non-invasive) chemical analysis is well established in the process industry and is becoming more common also in environmental monitoring and health diagnostics. All these analytical applications would benefit greatly from calibration-free and maintenance-free chemical sensors. This is a major driving force for our research today. Our solid-contact ion-selective electrodes and solid-state reference electrode represent two important steps towards maintenance-free ion sensors, while our on-going work aims at eliminating the need for calibration of these sensors.

Our electrochemical studies of conducting polymers has recently resulted in a new method to amplify the analytical signal of ion sensors. This new transduction method will be investigated intensively in the next four years. Anion sensors based on new receptor molecules are in progress. Some unique features of conducting polymers are utilized for the development of electrochemical sensors for detection of DNA hybridization. Furthermore, our research on carbon nanomaterials, such as graphene, strongly support the development of new chemical sensors. Other project activities include the development of Ag^+ sensors to monitor the dissolution of Ag^+ ions from silver nanoparticles, dynamic extraction of heavy metals from soil and electrocatalytic reduction of CO_2. In a wider perspective, our knowledge in electroactive materials and electrochemistry is relevant for the development of batteries and supercapacitors that will support the move towards utilization of solar energy and electrical vehicles.

External research funding during 2017-2018 was obtained from the Academy of Finland, Business Finland, industrial partners and foundations. We perform our research in close collaboration with national and international partners from academia and industry. Our participation in the *Erasmus Mundus* joint master degree program *Excellence in Analytical Chemistry* (EACH), supported by EU, has dramatically increased the number of MSc theses in analytical chemistry from our group.

Personnel of the Laboratory of Analytical Chemistry in 2018

Personnel

Professors

Johan Bobacka
Tom Lindfors, associate professor
Ari Ivaska (Emeritus)
Andrzej Lewenstam (Emeritus)

Docents

Leo Harju
Rose-Marie Latonen
Li Niu
Di Wei
Carita Kvarnström
Tomasz Sokalski
Anna Österholm

Senior researchers

Zhanna Boeva
Ning He
Maria Khaydukova
Zekra Mousavi
Kim Granholm
Jussi Kauppila
Gregorz Lisak
Ulriika Mattinen

Laboratory manager

Tor Laurén

Doctoral students and researchers

Jesus Arroyo
Narender Joon
Jay Pee Oña
Tingting Han
Sara Lund
Ville Yrjänä

Secretary and coordinator

Mia Mäkinen
Britt-Marie Haahti

Technician

Sten Lindholm

Computer support

Peter Ekholm

3.4 Organic Chemistry

The Laboratory of Organic Chemistry strives for excellence in research and education, training students and researchers on all levels for successful careers in industry and academia.

The laboratory operates in two of the main research profiling areas of Åbo Akademi University: Molecular Process and Materials Technology; and Drug Development and Diagnostics. Within these areas, the main research efforts of the laboratory are focused on 1) Development of sustainable chemical synthesis technologies using both homogeneous and heterogeneous transition metal catalysts, organocatalysts and biocatalysts with special emphasis on understanding of reaction mechanisms and kinetics; 2) Synthetic carbohydrate chemistry and glycobiology; 3) Natural product chemistry, with particular focus on wood extractives such as lignans and hemicelluloses and lignin. All these key research areas rely heavily on utilization and understanding of advanced NMR spectroscopic techniques.

Other research activities of the laboratory range from energy research to environmental organic chemistry including studies on the environmental fate of pharmaceuticals, antibiotics and endocrine disruptors.

External research support during 2017-2018 was obtained from Business Finland, the Academy of Finland, industrial partners and foundations. The laboratory closely collaborates with several national and international partners and actively participates in research networks.

Personnel of the Laboratory of Organic Chemistry in September 2018

Link

http://www.abo.fi/organiskkemi

Personnel

Professors

Reko Leino
Jorma Mattinen (EMERITUS)

Docents

Patrik Eklund
Tiina Saloranta-Simell
Leif Kronberg
Annika Smeds
Filip Ekholm (University of Helsinki)

Experienced researchers

Jan-Erik Lönnqvist
Risto Savela
Ruzal Sitdikov
Carolina Mendez
Jani Rahkila (Instrument Centre)

Early stage researchers

Ewelina Kortesmäki
Matilda Kråkström
Lucas Lagerquist
Robert Lassfolk
Ida Mattsson
Sabine Rendon
Patrik Runeberg

Laboratory engineer

Teija Tirri

Secretary

Mia Mäkinen

Economy secretary

Britt-Marie Haahti

3.5 Combustion and Materials Chemistry

Our research strategy is to provide expertise on the detailed knowledge of chemistry in high-temperature processes and properties of high-temperature-made materials. Our main research endeavours are foremost in bioenergy and biomedicine, with a wider outreach to clean-tech and circular economy. Management of material streams and emissions, treatment and recycling of different waste streams that contain inorganic materials in energy efficient and environmentally friendly manner are essential topics in our research.

Within the bioenergy field, our research includes characterising the composition and behaviour of different biomasses and waste-derived fuels, modelling of combustion processes, measurement of emissions to the atmosphere, and development of a generic understanding of the interactions between the materials in the combustion devices, the fuels and their ashes.

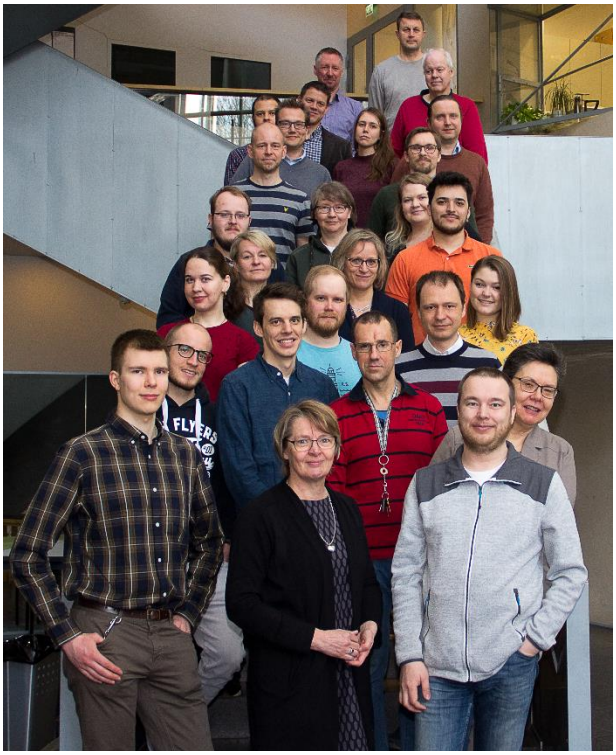
Within the biomedical field, development of composites containing bioactive glasses for wound healing and tissue engineering scaffolds are our main research focuses. Over the years, our strategy has been to understand thoroughly the influence of the oxide composition of the bioactive glasses on various cellular responses. One key goal is to develop detailed knowledge of the reaction and dissolution kinetics of the bioactive glasses when they are used in various biomimetic devices in hard and soft tissue regeneration applications.

We utilise thermodynamic equilibrium calculations to describe high-temperature processes, especially in various ash, slag and glass forming systems. For this, we develop thermodynamic databases of the high-temperature systems through thermal analysis in ambient and pressurised atmospheres containing different gases.

We use several experimental tools (single-particle reactor, thermogravimetric analyser/differential scanning calorimeter, lab-scale fluidised bed, heat microscope, scanning electron microscope and x-ray diffraction) to study the high-temperature chemistry of different fuels, ashes and materials.

We also develop sub-models to describe the chemistry in high-temperature processes, such as NOx-formation reactions in various fuels to be adapted to the modelling of combustion-related processes with computational fluid dynamics. One distinctive attribute of our research activities is the development of cleaner and more efficient combustion technologies using fuels that are "difficult".

The research is not only in laboratory scale but also includes measurements and sampling campaigns in full-scale combustion processes. Some of our core competence areas are exploring the high-temperature corrosion and erosion mechanisms of steam tubes and ceramic refractories induced by bed materials and various ashes that contain alkalis, chlorides, bromides, fluorides, etc. Recently, we have developed new techniques to accurately measure and understand the corrosion and reaction mechanisms of



Personnel of the Laboratory of Inorganic Chemistry in April 2018

the materials in their target environments.
Our research is in collaboration with groups and people from many different universities, companies and research centres. It is financed by Åbo Akademi, Tekes, Academy of Finland, the EU, NordForsk, industry and small to medium-sized enterprises. In addition to novel generic knowledge and competence, our research gives the industry partners new strategic scientific information and tools for innovations, new products and business concepts for the global market.

Personnel

Professors

Leena Hupa
Mikko Hupa (Rector of Åbo Akademi 2015-2019)

Docents

Rainer Backman
Anders Brink
Daniel Lindberg
Christian Mueller
Laeticia Petit
Bengt-Johan Skrifvars
Patrik Yrjas
Maria Zevenhoven

Laboratory manager

Tor Laurén

Secretary

Maria Lastuniemi
Mia Mäkinen

Senior researchers

Markus Engblom
Oskar Karlström
Xiwei Ke
Tooran Khazraie
Juho Lehmusto
Na Li
Mykola Moroz
Fiseha Tesfaye
Emil Vainio
Johan Werkelin

Doctoral students and researchers

Laura Aalto-Setälä
Marcela Arango Ospina
Roland Balint
Nina Bruun
Jan-Erik Eriksson
Elisa Hupa
Meheretu Jaleta Dirbeba
Xiwei Ke
Hanna Kinnunen
Thomas Kronberg
Christian Lindfors
Jonne Niemi
Paulo Santochi Pereira da Silva
Daniel Schmid
Christoffer Sevonius
Polina Sinitsyna
Jingxin Sui

Laboratory technicians

Peter Backman
Luis Bezerra
Jaana Paananen
Linus Silvander

3.6 Industrial Chemistry and Reaction Engineering

The core competence of Industrial Chemistry and Reaction Engineering is in catalysis, kinetics, chemical reactor technology as well as exploring new reaction environments and development of green process technology. Process intensification is a vital part of our research effort. Our approach is strongly methodological, but the main application area is the transformation of biomass, particularly forest biomass, to valuable chemical components. Our know-how is continuously developed on catalyst preparation, characterization and screening as well as in new approaches to chemical kinetics and reactors.

The progress of green process technology is visible in many fields, particularly in the development of new continuous processes for sophisticated chemicals, such as bio-degradable surfactants, platform chemicals, bio-lubricants and chemical intermediates. This is in many cases done in micro- and milliscale reactors, which provide a real technology jump; we use them for catalyst development, kinetic screening and continuous production of chemicals in gas and liquid phases. All the experimental efforts are coupled to advanced mathematical modelling of chemical phenomena in batch, semibatch and continuous systems. Several processes based on molecules originating from biomass are under investigation, for example amination reaction and epoxidation of fatty acids, oxidation of sugars and betulinol as well as catalytic transformation of furfural. Molecularly oriented kinetic studies are conducted in several applications, particularly in the homogeneously and heterogeneously catalyzed hydrolysis of hemicelluloses and inulin as well as hydrogenation and oxidation of mono- and disaccharides, preparation of epoxidized vegetable oils. Microwave technology is used to enhance the epoxidation fatty acids and carbonation of fatty acid epoxides.
A new research effort is in progress in catalytic destruction of pharmaceuticals in wastewaters by using ozone as the oxidation agent. New, intensified catalyst structures, such as solid foams are under investigation.

National and international collaboration is flourishing with several universities and research centra. The main financers of our research are Academy of Finland, Business Finland EU and several domestic foundations. In the beginning of 2019, an Academy Professor (T.Salmi) starts a 5-year intensive research period and in autumn 2019 we have the pleasure to host the 5th International conference in Catalysis for Biorefineries (www.catbior2019.fi) – cordially welcome!

Personnel of the Laboratory of Industrial Chemistry and Reaction Engineering in May 2018

Personnel

Professors

Tapio Salmi (Academy professor 1.1.2019-31.12.2023)
Dmitry Murzin
Johan Wärnå
Jyri-Pekka Mikkola (joint professor with Umeå University)
Päivi Mäki-Arvela, associate professor
Henrik Grénman (tenure track), associate professor

Docents

Atte Aho
Kalle Arve
Narendra Kumar
Fredrik Sandelin
Pasi Virtanen
Ikenna Anugwom
Matias Kangas
Sébastien Leveneur
Esa Toukoniitty

Laboratory manager

Kari Eränen

Senior researchers

Cesar de Araujo Filho
Javier Ibanez
Alexey Kirilin
Jussi Rissanen
Juan Garcia Serna
Pasi Tolvanen
Liu Wei
Sigmund Fugleberg
Teuvo Kilpiö
Arto Laari
Ayar Nuri
Vincenzo Russo
Anton Tokarev
Zusana Vajglova

Doctoral students and researchers

Shekoufen Adhami
Steliana Aldea
Leolincoln Correia da Silva
Adriana Freites Aguilero
Imane Hachemi
Thomas Hornbogen
Taimoor Kaka khel
Christoffer Lindfors
Ali Najarnezhadmashhadi
Ricardo Pezoa Conte
Maria Pinilla de Dios
Farhan Saleem
Jonah Schaaf
Frans Storgårds
Sebastiano Tieuli
Moldir Alda-Onggar
Erfan Behvaresh
Yiran Chen
Lidia Godina
Shuayna Heredia
Ramakrishna Jogi
Ekaterina Kholkina
Luis Sans Moral
Jay Pee Oña
Andrea Perez Nebreda
Soudabeh Saeid
Jose Luis Santos
Vladimir Shumilov
Alexandrina Sulman
Nemanja Vucetic

Technician

Elena Murzina

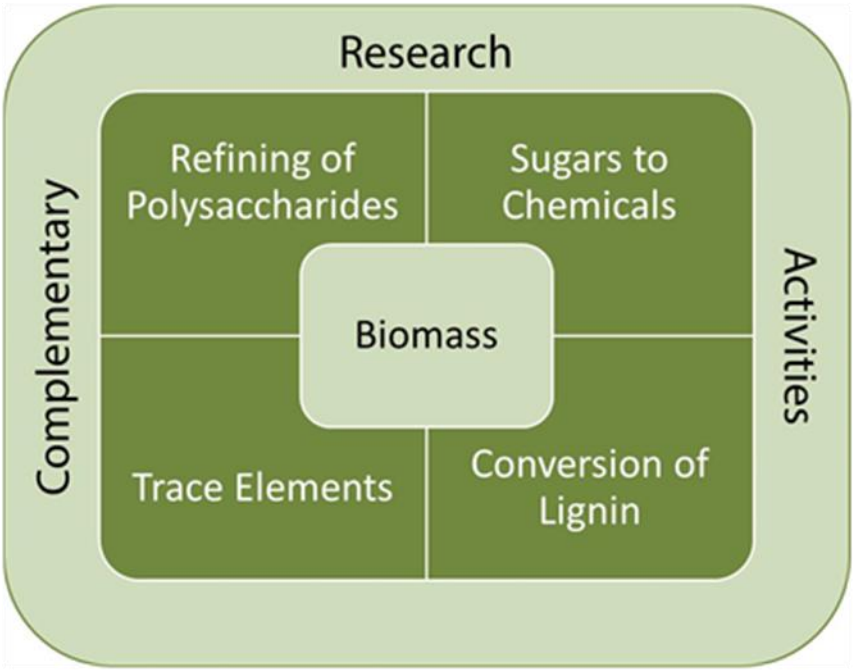
Links

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

4. Research

Our research plan "***PCC*** – Future Refining of Forest Biomass" is in the core of the Finnish Bioeconomy, Circular Economy, and Cleantech areas. Finland can become one of the pioneers in a global perspective in the evolutionary development of forest biomass, because 70% of our territory consists of forest, which is rich in lignocellulosic biomass. Finland actually has the largest amount of forest per capita in the whole of Europe and this biomass has a yearly growth that is larger than what we utilize. Forest biomass is potentially a very rich source of molecules, which can be further refined to new materials, chemicals and fuel components. The challenge is big, because the molecules appearing in biomass deviate substantially from those in fossil sources. Molecules from biomass have a high degree of functionality and high oxygen content compared to the molecules appearing in fossil sources. This implies that many of the current technology solutions cannot be applied directly to molecules originating from biomass and therefore new chemical technology is needed.

The development of new technologies should be based on a very deep-going understanding of the underlying chemical and physical processes, which we call Molecular Process Technology. ***PCC*** merges chemistry and chemical engineering to provide industrially relevant solutions for the future. The goal is to develop new, sustainable technologies for making selected platform chemicals, fine and specialty chemicals, as well as health promoting materials and chemicals. The research is mainly focused on two important types of molecules appearing in forest biomass, namely polysaccharides (hemicelluloses and cellulose) and lignin. The research programme is materialized in five work packages (WP): Refining and utilization of polysaccharides (WP1), Conversion of sugars and sugar derivatives to chemicals (WP2), Refining options of lignin (WP3), Trace elements in refining of biomass (WP4), and Complementary research activities (WP5).



PCC *research areas.*

4.1 WP1 - Refining and utilization of polysaccharides

Polysaccharides are found in many different forms in nature, much depending on the species. Forest and agricultural resources are rich in cellulose and hemicelluloses, while marine based carbohydrates are mostly various hemicelluloses. In most of the current and foreseen applications, the cellulose and hemicelluloses should be separated from each other, as well as from the lignin often present in the material. Controlled fractionation remains as an essential part of the research and understanding in biomass valorization. One of the solutions is a novel extraction and fractionation process for pure hemicelluloses (pat. appl. WO2014009604 (A1)), which is in the course of being commercialized, presents ***PCC*** with a unique availability and possibility to perform application research and develop new applications based on pure hemicelluloses. The resulted cellulose can be used to prepare high quality cellulose products and nanocellulose.
Our current research interests are on utilizing the fractionated polysaccharides for the development of high-performance products. For example, polysaccharides can be combined with conducting polymers and graphene or other compounds, such as bioactive glass for different high-value products. These materials can be utilized in applications such as water purification, chemical sensors, 3D-printed electronics and scaffolds for biomedical applications, biomedical treatment, functional barriers in packaging and films, and in biocomposites and specially designed papers for various applications including but not limited to novel packaging materials. Detailed tailoring of the polysaccharide and additive properties combined with the processing technology are key aspects in the successful development of novel products.
Polysaccharides, especially hemicelluloses, are also an excellent sources of various monosaccharides, as well as oligosaccharides, for further valorization (WP 2). The efficient, controlled and selective depolymerization of these heterogeneous polymers is an essential step in their further processing and a natural part of our research.
The ultimate goal of WP1 is to develop novel technology platforms for high value applications of polysaccharides. More specifically, the objectives are:

- To efficiently isolate hemicelluloses of high purity, which will then be used in WP1 and to selectively hydrolyze the polysaccharides to monosaccharides, which can be utilized in WP2;
- To prepare hemicellulose-based adsorbents for removal or inactivation of dissolved hazardous compounds;
- To investigate the capability of hemicelluloses as stabilizers in technical emulsions; and
- To tailor polysaccharide-based structural composites. The composites can be novel bio-based fiber-based materials for packaging. Moreover, by incorporating other composite component such as conducting polymer or other carbon material (e.g. graphene), applications in (bio)sensors and wound healing promotion are aimed for. Another option of other composite component is bioactive glass aiming at the application as scaffolds in tissue engineering.
- 3D printing technology has increasingly been developed for a variety of applications.

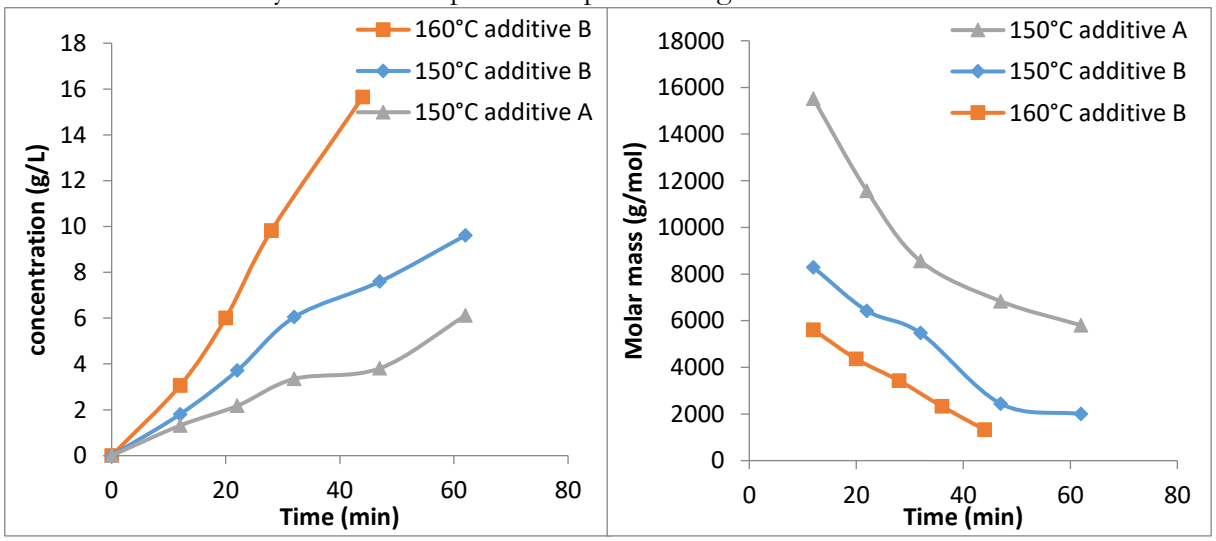
Cooperation: University of Wollongong, **Australia**, University of Natural Resources and Life Sciences, Vienna, **Austria**, University of Turku, VTT, CH-Bioforce, University of Oulu, University of Helsinki, **Finland**, University of Naples "Federico II", Naples, **Italy**, University of Valladolid, **Spain**, Friedrich-Schiller University Jena, University Erlangen-Nuremberg, Technical University of Dresden, **Germany**, Rise, **Sweden**, INSA Rouen, Institut national des sciences appliquées de Rouen, **France**

Intensified extraction and hydrolysis of hemicelluloses

Main funding: Academy of Finland, Raisio Research Foundation, Erasmus Mundus Programme

Andrea Pérez Nebreda, Jussi Rissanen, Vincenzo Russo, Kari Eränen, Wenyuang Xu, Gerd Hilpmann, Tomas Hornbogen, Jonah Schaaf, Kirsi Mikkonen, Lucas Lagerquist, Jarl Hemming, Patrik Eklund, Martino di Serio, Rüdiger Lange, *Stefan Willför, Dmitry Murzin, Tapio Salmi, Henrik Grénman*

One of the focus areas of the work is in the intensification of the extraction kinetics of hemicelluloses from wood. In addition, the possibility to influence the properties of the extracted carbohydrates in a controlled way is of great interest. The extraction was studied in the temperature interval 120 °C – 170 °C in a batch and semi-continuous reactor system using different wood species and varying pretreatment methods and particle sizes. Selected additives were used to accelerate the extraction rate and the extraction kinetics was precisely determined quantitatively. The results demonstrate that the fractionation can be considerably enhanced with the use of selected additives compared to traditional pressurized hot water extraction and that the properties of the extract can be adjusted in the process. The processing conditions influence the chemical structure, molar mass and stability of the hemicelluloses. Moreover, the separation of the utilized additive was studied and it was concluded to be easily separable from the reaction mixture.
This work contributes significantly to understanding the mechanisms involved in the extraction of hemicelluloses and the influence of the extraction parameters, especially the concentration of the additives, on the process. This enables tuning the properties of the extracts for the desired applications. Overall, when optimized properly, pressurized hot water extraction of hemicelluloses can give very good results, but the process can be even further advanced with applying selected additives. The influence of two different additives and temperature on the extraction kinetics and molar mass of carbohydrates from spruce is depicted in figure below.

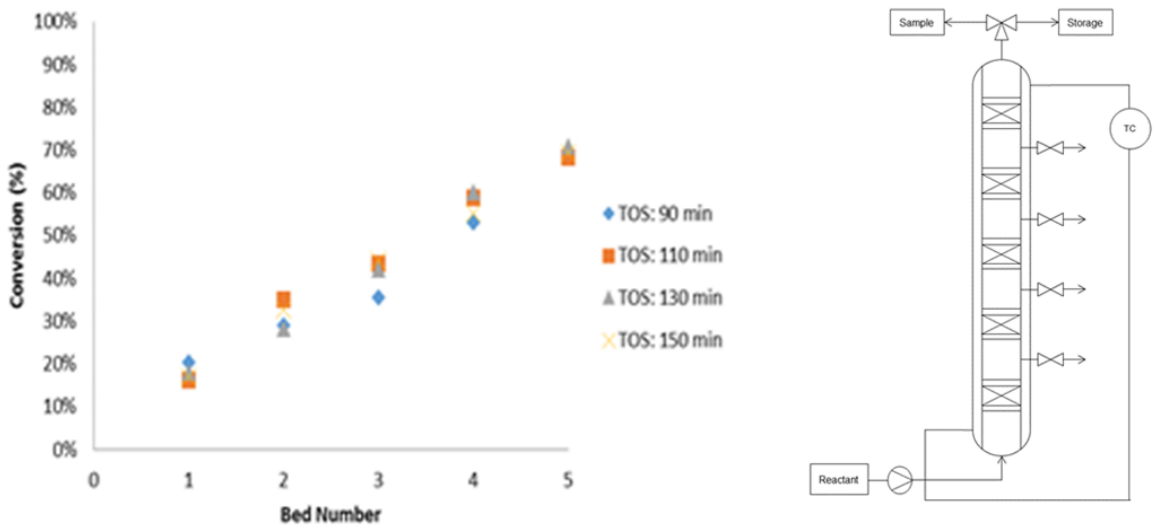


The liquid phase concentration (left) and molar mass (right) of carbohydrates as a function of time with different additives and temperatures.

After the extraction of hemicelluloses from biomass, they need to be hydrolyzed to monosaccharides or short oligosaccharides if the strive is to valorize them to value added chemicals. The current work focuses on bridging the extraction of hemicelluloses and the conversion of sugars to chemicals, which is the main focus in WP2. The aim is to be able to

sufficiently convert the hemicelluloses extracted from wood and agricultural biomass to sugar monomers and short oligomers employing model compound and moving to actual extracts, in order to complete the production chain from biomass to chemicals. The final goal is to be able to utilize heterogeneous catalysis combined with continuous reactor technology for enabling the elegant conversion and integration of the hydrolysis step into the overall production scheme without the need for excessive purification steps. Moreover, low temperatures and pressures are strived for in order to reduce the investment and production costs.

The present work focuses on the efficient production of high purity fructose by hydrolysis of inulin, which is readily available on the world market, and high purity xylose from an industrially developed high purity xylan extract. The process was carried out utilizing a heterogeneous catalyst first in a batch reactor and then in a continuous reactor. An autocatalytic end-biting mechanism was observed, for which the kinetics was studied in a batch reactor and modeled taking into account the reaction mechanism. A tailor made multi-bed reactor was constructed for studying the feasibility of continuous operation. The reactor system incorporates five catalyst beds with the possibility of taking samples after each bed (Figure below). The residence time distribution of the continuous reactor system was carefully studied employing advanced techniques and the results were utilized in modeling and optimization of the reactor performance in combination with the reaction kinetics.



Conversion to monomeric fructose after each catalyst bed at 95°C (left) and schematic representation of the reactor system (right).

The chosen heterogeneous catalyst Smopex 101 was successfully employed in a continuous reactor system leading to high purity fructose monomers with almost 100% yield. The catalyst displayed good stability under mild reaction conditions. Two heterogeneous catalysts, Smopex 101 and Amberlite 120, performed well in the hydrolysis of the industrial high purity xylan extract in a batch reactor setup. However, the reaction kinetics were concluded to be significantly slower compare to the inulin hydrolysis. Hydrolysis of the xylan was also carried out in the continuous reactor. The results showed that longer residence times and careful optimization of the reaction conditions are needed for obtaining close to complete yields. Moreover, a clear difference was observed in the hydrolysis rate of industrial xylan and purified beech xylan. Overall, the results demonstrate that the continuous hydrolysis of hemicellulosic polysaccharides utilizing heterogeneous catalysts is feasible if the catalysts and process conditions are optimized. This enables the further development of efficient biomass processing technologies.

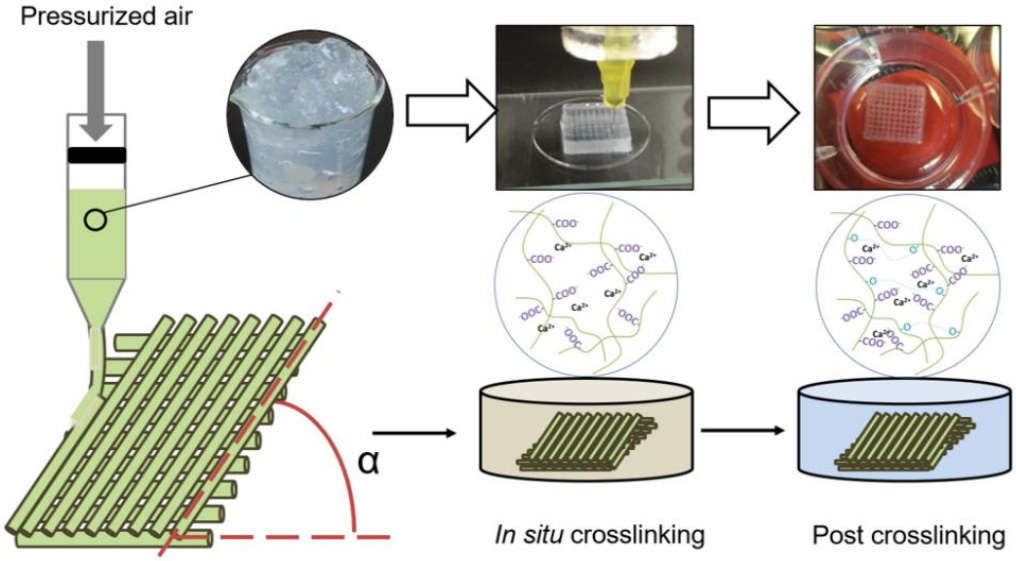
3D printing hydrogel scaffolds of woody biopolymers with tunable mechanical strength towards biomedical applications

Main funding: Johan Gadolin Process Chemistry Centre (***PCC***), Academy of Finland

Chunlin Xu, Wenyang Xu, Xiaoju Wang, Stefan Willför

Tissue engineering has become one of the most promising solutions for medical treatments, particularly for healing of chronic wounds. The building blocks of engineered wound healing platforms are usually scaffold materials embodied with cells and mechanical, electrical, or biochemical cues. Both natural and synthetic polymers have been used to mimic the structures of the extracellular matrices (ECM) in native tissues, allowing cells to adhere, proliferate, differentiate, and survive. 3D-Printing enables the creation of individual, tailor-made scaffolds to provide desired architectures, and furthermore, integration with biological cues to target cell proliferation in a controlled manner. Among versatile natural biopolymers, nanocelluloses stand out in the field of bioink formulation serving as platform biomaterial owing to their high mechanical strength as well as the structural similarity mimicking natural ECM.

The first study in this project was to develop an approach to 3D-printing of nanocellulose hydrogels with good mechanical properties and wet-stability. A double cross-linking strategy was applied: cellulose nanofibrils (CNFs) were crosslinked during printing by addition of an aqueous Ca^{2+} solution, followed by a post-printing chemical crosslinking with 1, 4-butanediol diglycidyl ether (BDDE). With further tuning with the crosslinking parameters, the mechanical strength (compressive Young's modulus) of the printed CNF scaffolds was achieved in the range of 3 to 8 kPa. Cell tests confirmed that the fabricated scaffolds are non-toxic to fibroblasts. The rigidity of the scaffolds has a clear impact on cell proliferation - the proliferation of fibroblast is promoted when the rigidity is increased within the tunable range of 3-8 kPa. This correlation is, for the first time, demonstrated by 3D-printed nanocellulose hydrogels



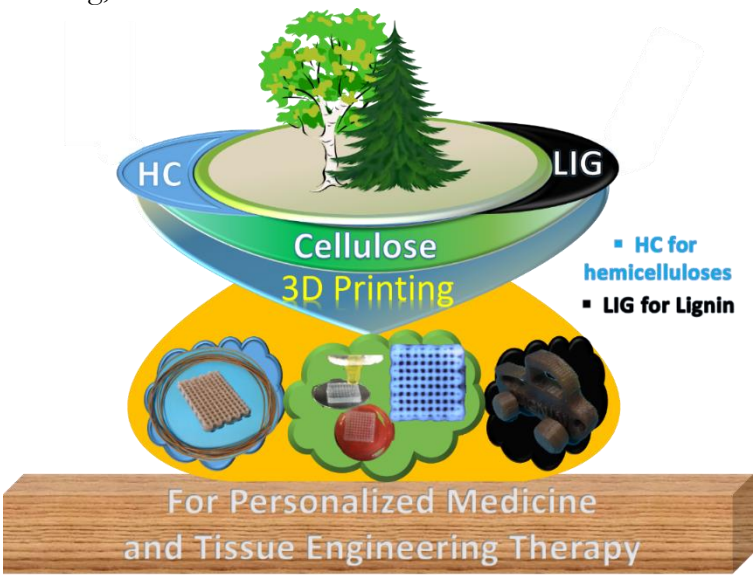
Schematic illustration of printing process and the two-step crosslinking strategy

The printed 3D scaffolds of CNF were proved to support improved cell spreading and migration. Yet, the matter loading of TEMPO-oxidized CNF constrained the tunable material stiffness within a narrow range. Meanwhile, there is a need for the approach development to control the stiffness of printed CNF hydrogels in order to proliferate the application potential of such materials in a

broad-spectrum of tissue mimics through bioprinting. To tap this challenge, our project further made efforts on developing UV-crosslinkable biopolymers as the auxiliary material for the TEMPO-mediated oxidized CNFs-based bioink. Inks with methacrylated gelatin and galactoglucomannan (GGM), respectively, were successfully prepared for printing of hydrogel scaffolds with mechanical strength in a broad range.

Gelatin, a derivative of collagen, resembles the biological structure of collagen in the native ECM tissues. Gelatin methacrylate (GelMA) with favorable thermal sensitivity and photo-crosslinking ability has been broadly evaluated in different bioink formulations. We have developed a novel low-concentration ink formulation based on 1 w/v% TEMPO-oxidized CNF and up to 1 w/v% of GelMA for extrusion-based 3D printing of nanocellulose hydrogel scaffolds. By direct ink writing technique assisted by UV post curing, high-resolution scaffolds of CNF/GelMA were successfully printed and these scaffolds demonstrated high fidelity and stability. By tuning the compositional ratio between CNF and GelMA, the compressive Young's modulus and local surface stiffness could be well tuned. The developed ink formulations are non-cytotoxic and biocompatible as confirmed by the viability assay in the culture of 3T3 fibroblasts.

Hemicelluloses, the second most abundant renewable material after cellulose, are non-toxic, biocompatible, and biodegradable. Inspired by the biomimetic perspective, i.e. the integrity of the plant cell wall structure, where the intrinsic affinity of heteropolysaccharides to cellulose provides the cell wall with a composite structure conferring both strength and flexibility, hemicelluloses or their derivatives are expected to be promising candidates for a reinforcing cross-linker in nanocellulose-based ink formulation. Methacrylate (GGMMA) of GGM, the major hemicellulose type in softwood, was synthesized by a facile approach for the use as an auxiliary component with TEMPO-oxidized CNFs in the ink formulations. By tuning the DS of GGMMA and compositional ratio between CNF and GGGMMA, the compressive Young's moduli of the formulated inks after cross-linking presented a tunable wide spectrum from 2.5 kPa to 22.5 kPa. By extrusion-based 3D printing technique, scaffolds and intricate objects were successfully printed with high resolution and good shape-fidelity. The developed low-concentration ink formulations of CNF/GGMMA present a facile yet effective approach to fabricate light-weight hydrogel with a wide spectrum of mechanical properties, which potentially meets the requirements for a variety of in vitro cell-matrix and cell-cell interaction studies in the context of tissue engineering, cancer cell research, and high-throughput drug screening, etc.



Conceptual overview of applying 3D printing of woody biopolymers in regenerative medicine fields

Conducting ink based on cellulose nanocrystals and polyaniline for flexographical printing

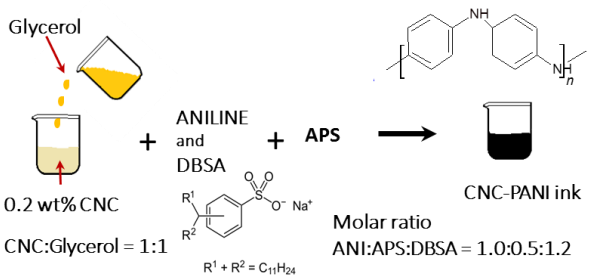
Main funding: Academy of Finland

Rose-Marie Latonen, Wenyang Xu, Chunlin Xu, Xiaoju Wang

Nanocellulose is a strong candidate for a wide range of high and low volume applications. It is especially suitable for forming both free-standing and biodegradable substrates and ink formulations due to its nanoscale dimensions, high surface area, outstanding mechanical properties, low density and suspension stabilizing and binding abilities. In e.g. printed electronics, sensor development and drug delivery applications composites of nanocellulose with electrically conducting materials are needed. In this project electrically conducting composites of nanocellulose, both cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC), with conducting polymers have been developed.

In this project, the application of a water-based environmentally friendly and highly conducting ink suitable for flexographical printing is highlighted. The ink is composed of CNC and polyaniline (PANI), an electrically conducting polymer, and glycerol has been used to assist synthesis of spherical nanosized PANI particles and to act as a further stabilizer hindering precipitation of the particles. Aniline was chemically polymerized in a micellar solution of dodecylbenzenesulfonic acid (DBSA) in presence of CNC and glycerol. The properties of the CNC-PANI ink were compared with the properties of a PANI ink without CNC. Both inks were printed with the flexographical printing method offering high-volume and low-cost characteristics on a curtain coated paper substrate.

The developed CNC-PANI and PANI inks showed conducting properties and had suitable viscosities for the chosen printing method after optimization of the synthesis parameters. Optical and atomic force microscopy methods confirmed that after 10 print layers a rather full coverage of the rough paper substrate was obtained besides some variations in local thickness or density were observed. The relative surface coverage of the CNC-PANI ink increased faster compared to the PANI ink due to higher affinity of the CNC-based ink to the cellulose-based surface of the paper substrate. Cyclic voltammetric characterization of the prints showed high electroactivity and stable current responses of the printed layers, however, being higher for the CNC-PANI prints than for the PANI prints. The effective electrical conductivity of the CNC-PANI prints was also found to be an order of magnitude higher than that of the corresponding prints without CNC. This higher electroactivity and conductivity could be due to the negative charge of the CNC crystals serving as couterions for some part of the synthesized PANI surrounded by the PANI(DBSA) nanospheres. This phenomenon increased the dispersability of the particles and therefore the conducting network is expected to be longer.



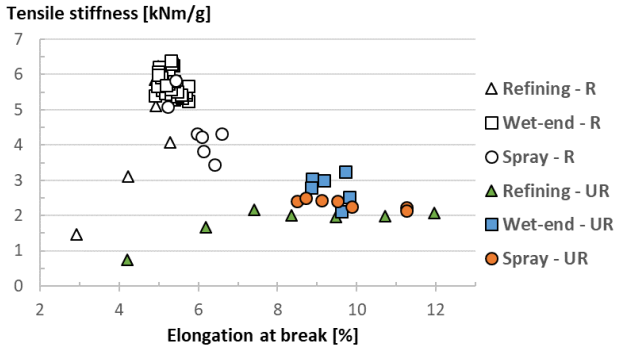
Preparation procedure of a highly electrically conducting water based ink composed of CNC and PANI.

Tailored fibre-fibre interactions for boosted extensibility of bio-based fibre networks - ExtBioNet

Main funding: Academy of Finland

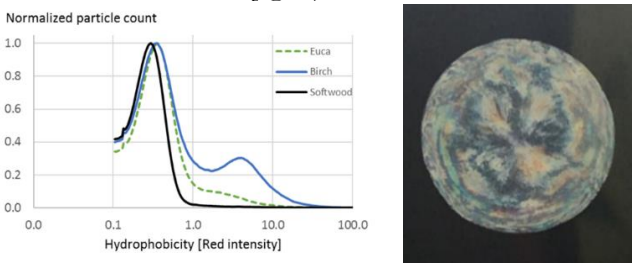
Anders Strand, Anna Sundberg

This project is targeted towards the development of new types of renewable fiber-based paper with high deformation potential, which is needed to obtain novel, bio-based packaging material for the use in forming processes. Fiber network with high elongation at break and sufficiently high stiffness may be the key for packaging applications of the future.
Refining, wet-end additions of bio-based additives, or spray addition of polysaccharides did increase the tensile stiffness if the papers were dried under restraint, but the elongation of break was limited to about 6% (*figure*). The same treatments resulted in papers with high elongation (12%) but limited stiffness if the papers were dried unrestrained. The same pulp treatment/additives will cause either stiffness or stretch depending on drying technique, even if treatments could mitigate some of the changes.



The drying procedure have a large impact on paper properties. If the papers are dried under restraint (R), refining, wet-end addition of chemicals, or spray addition of polysaccharides on top of wet papers results in papers with high stiffness. The same treatments will result in paper with high elongation at break if the papers are dried freely (unrestrained, UR).

Polyelectrolyte complexes (PECs) can be formed from two or more opposite charged polyelectrolytes. Flow cytometry were used to study PECs *in situ* from papermaking additives, prepared at different cation/anion ratios. The behavior of a coagulating PEC mixture as a function of contact time could be studied. The ratio of the light scattering properties in side direction (SSC) and forward direction (FSC) were shown to be connected to the structural density of the particles. The hydrophobicities of the PECs were lowest around the theoretical point of neutralization for the polyelectrolytes. FCM was also used to study the hydrophobicity of cellulose nanocrystals (CNCs), and it was clearly seen that CNCs prepared from birch contained significantly more hydrophobic particles than CNCs prepared from softwoods (*figure*). A methodology for preparation of high-yield CNCs, with similar properties to commercial CNCs, were also generated. Film casted from the CNCs had chiral nematic structure (*figure*).

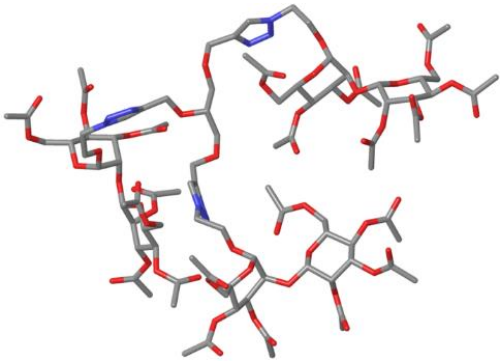


Flow cytometry can be used to study polyelectrolyte complexes or cellulose nanocrystals (CNCs) in situ. It was shown that CNCs from birch contain more hydrophobic particles than CNCs from softwood (Left). Polarized light image (transmission, between crossed polar) of film cast from high-yield CNC (right).

4.2 WP2 - Conversion of sugars and sugar derivatives to chemicals

The research in WP2 is inducted by the general interest on chemicals produced from bio-based raw-material instead of fossil resources. More precisely, WP2 focuses on one hand on the chemistry and technology needed in biorefinery concept for preparation of high value chemicals from monomeric sugars obtained by carefully controlled hydrolysis of hemicelluloses and cellulose and on the other hand on synthesis and studying of specialty chemicals and functionalized materials utilizing carbohydrate derivatives. Recent research by us and other groups has shown that rare monomer sugars can be obtained in high yields from hemicelluloses. Furthermore, platform, fine and specialty chemicals can be obtained from the monomers of hemicelluloses and cellulose. WP2 combines different research areas, such as, organic chemistry, catalyst preparation, characterization, kinetic and mass transfer studies, continuous reactor technology and process intensification. The group has experts on catalysis, chemistry and analysis of biomass, as well as on chemical kinetics and reaction engineering. Advanced catalyst characterization and reactor equipment as well as various analytical chemistry tools are at our disposal (batch autoclaves, parallel screening reactors, SEM, TEM, XRD, XPS, FT-IR, NMR). Many of the projects include also national as well as international collaboration between different universities and companies in all over Europe.
The main targets of the research in WP2 are to develop applications to prepare high value chemicals from cheap renewable sugars. More precisely we are focused on:

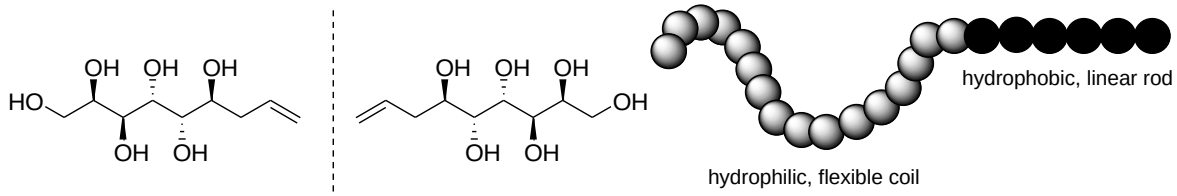
- Studying of immunostimulatory glycocluster adjuvants in allergy treatment, where inspired by the cell surface oligosaccharides of *Candida albicans*, we have developed and discovered first-in-kind, β-(1→2)-mannobiose derived trivalent glycoclusters, showing unusually high activity as novel immunostimulants. A proof-of-concept study in an in vivo, timothy induced chronic allergic inflammation model demonstrated almost complete inhibition of the development of eosinophilic inflammation of respiratory tract in mice treated with the glycocluster lead compound.



- Investigating the Binding of Mannans to Galectin-3. To investigate this, we have designed and prepared polysaccharides that mimic the *C. albicans* cell wall by attaching β-(1→2)-linked mannobioses to a dextran-based backbone. To further assess the possibilities of using polysaccharides as scaffolds for biomolecular probes we are also investigating lactose and maltose analogues of the dextran polymer.
- Developing new catalytic materials and reactor technology as well as kinetic model for production of high value chemicals from monomeric sugars in different reactions. Studies of interconversion of aldoses to ketoses showed that the sugar structure did not influence the catalytic properties, when range of base catalysts including magnesia, hydrotalcites, magnesium aluminates and mixed oxides of magnesia and alumina were applied. Also, oxidation of furfural in aqueous phase with hydrogen peroxide as an oxidant has been studied. The aim was to improve the yield of succinic acid in furfural oxidation. Succinic acid is considered as a replacement for a large number of intermediates that are currently derived from fossil resources. It turned out that Smopex -101, a fibrous non-porous

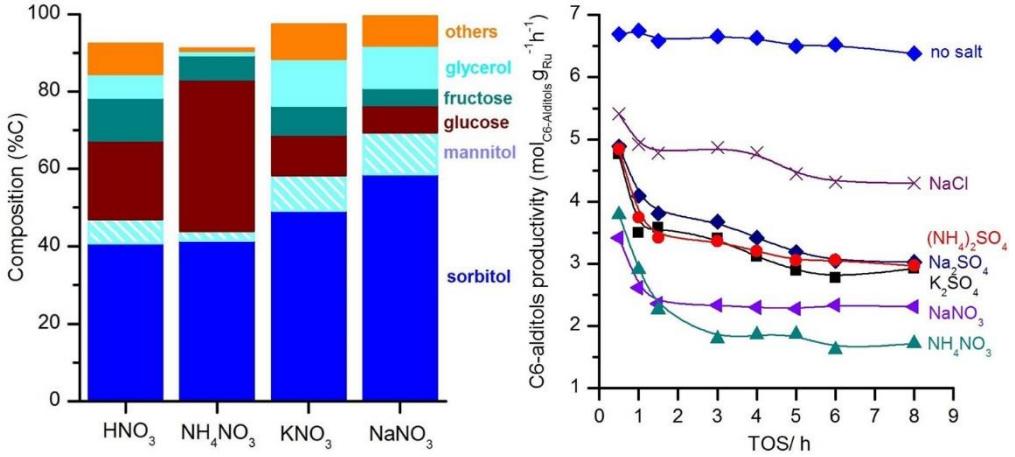
material with sulphonic acid functional groups grafted on poly(ethylene-graft-polystyrene) is a very promising catalyst for this reaction.

- Synthesizing of functional materials by utilizing carbohydrate derivatives, such as allylation of mannoses and investigating their self-assembling behavior as well as coupling them to various polymers and surfaces. A representative example of a reaction selectively targeting the aldehyde functionality is the metal (typically In or Sn) mediated allylation of unprotected monosaccharides, efficiently yielding alkene-terminated chiral polyols.



Chemical structures of allylated D-mannose (left) and L-mannose (middle). Schematic presentation of rod-coil copolymers (right).

- Developing mild, selective and environmentally benign oxidation methods for wood-based compounds.
- Studying hydrogenation of sugars in various conditions such as how neutralization salts effect the hydrogenation selectivity and activity as shown in figures below.



- Investigation of β-(1→4)-linked mannan model compounds by NMR spectroscopy has revealed that one acetyl group of the trisaccharide migrates towards the reducing end of the molecule, more precisely to the O6 position of the first monosaccharide unit. In nature, acetyl groups may be involved in activation and deactivation of various substrates, suggesting that acetyl group migration in polysaccharides could also have implications for the biological activity of the polysaccharides.

Cooperation:

Johnson Matthey; Federal University of Rio de Janeiro, **Brazil**; University of **Chile;** Imperial College of London, **England;** Aalto University, University of Helsinki, University of Jyväskylä, University of Oulu, University of Turku, **Finland;** Institute Universitaire de Technologie Paul Sabatier, **France;** Bayer AG, Friedrich-Alexander-University, Erlangen-Nürnberg, FutureCarbon GmbH, Ludwig Maximilian University of Munich, Max-Plank-Institut für Kohlenforschung (Mülheim), Technische Universität Darmstadt, **Germany;** Università di Palermo, **Italy;** Biomass Technology Group, University of Twente, **the Netherlands;** Boreskov Institute of Catalysis, Novosibirsk, St. Petersburg State Institute of Technology, **Russia;** CIC bioGUNE, Bilbao, Universidad Autonoma de Madrid, **Spain**.

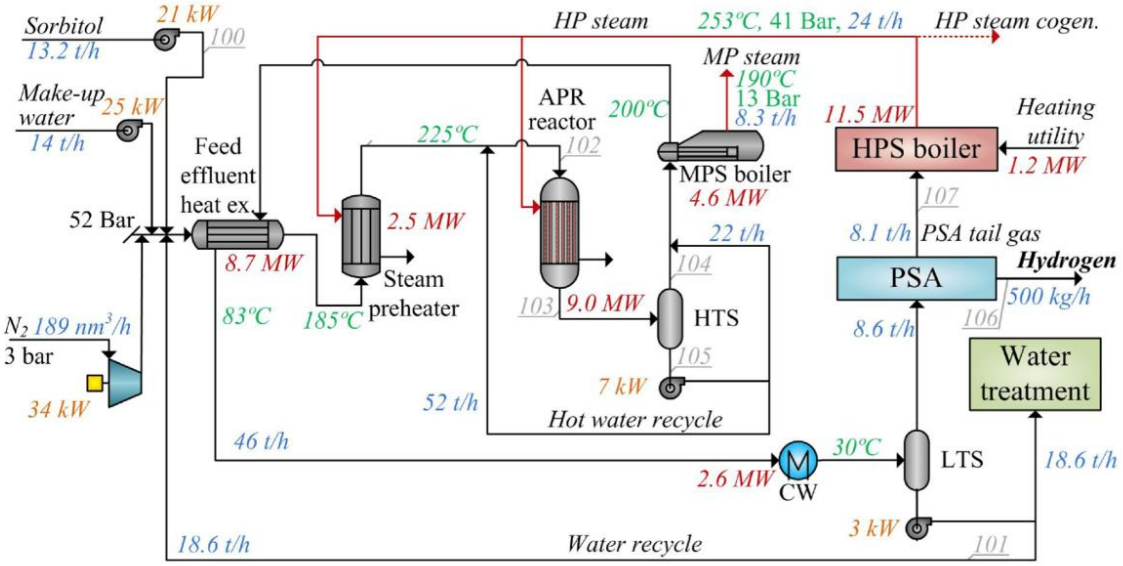
Process design of polyols aqueous phase reforming to hydrogen and alkanes

Lidia Godina, Anton Tokarev, Teuvo Kilpiö, Vincenzo Russo, Johan Wärnå, Dmitry Sladkovskiy, Kirill Semikin, Dmitry Murzin

Carbohydrates can be utilized in various processes of biomass conversion to commodity products. One of them is aqueous-phase reforming (APR), allowing production of hydrogen and alkanes at relatively low temperatures and pressures. Conversion of a liquid aqueous solution of a certain substrate is performed over a heterogeneous catalyst at 463-523 K and low pressures to keep the substrate in the liquid phase. Various transition metals are active in APR, and different support have been applied. APR requires catalysts with high hydrothermal stability and resistance to impurities potentially presented in the feedstock

A key advantage of APR is that it enables flexibility in choosing the source of hydrogen supplied to the plant. The method allows utilization of a wide range of substrates: alcohols and polyols, including, for example, methanol, ethanol, propanol, ethylene glycol, glycerol, xylitol, mannitol, galactitol and sorbitol. It is advantageous for an industrial process, where the feedstock can be a mixture of various compounds. APR is also considered as a method of in-situ hydrogen formation in complex biomass to fuel processing.

Literature on APR typically does not details on energy consumption, process optimization and design. The present work is aimed to fill this gap by determining process and economic parameters, influencing hydrogen costs. The sorbitol syrup was selected as a feedstock for production of 500 kg/h of hydrogen. The capacity was selected based on an estimated amount needed for 100 000 tones of green diesel annual production from tall oil. A detailed simulation was done using Aspen HYSYS. A new feature in the simulations was consideration of in-situ phase equilibrium for the reactor heat demand calculations not previously described in connection with APR. The process optimization included several conceptual improvements (*i.e.* middle pressure steam co-generation and hot water recycle), which can significantly decrease the operation costs. The optimized process is shown below.



APR process design.

A mixture of the sorbitol syrup, make-up and recycling water, and the sweep gas (nitrogen) is preheated to a 210°C in a feed-effluent heat exchanger. The inlet sorbitol concentration is 10 wt-%. Nitrogen co-feeding ratio was selected as 2 nm^3 N_2 /m^3 liquid at the reactor inlet. High pressure steam (HPS) boiler is applied to subsequent input stream heating to the reaction temperature (225°C) due to precise temperature control. The reaction takes place in a downflow plug flow multitubular reactor, which is supplied with HP steam to sustain the isothermal conditions. Reactor pressure is 50 bar.

The product stream contains both aqueous and gas phases. A hot temperature separator (HTS) or a special reactor design with a separation zone can be applied. For optimization purpose unreacted hot water could be separated before cooling and recycled back to the reactor inlet. As a result, a flowrate and corresponding duties of the preheater and the effluent heat exchanger can be decreased. Another way of optimization is to use the hot reactor effluent as a heat source for medium pressure (MP) steam generation.

Afterwards, the product stream is cooled down to 30C in the feed-effluent heat exchanger and water cooler for separation the gaseous product and to direct it to pressure swing adsorption (PSA) unit. The (PSA) unit with 85% H_2 recovery was selected for separation of gas phase products from carbon dioxide. The PSA tail gas with pressure below 3 bar is combusted in the boiler to generate HP steam which is then supplied to the reactor and preheater. The excess of HP steam can provide extra income. In cases of a highly diluted feed the amount of tail gas is not enough to cover the reactor heat duty, therefore an external heating utility is required. A fraction of the recycled water can be drawn to waste water treatment in order to prevent accumulation of relatively stable liquid components in the recycle such as acids and furans.

The design option which have been considered in this work were modeled using Aspen HYSYS and simulation data further utilized for approximate equipment sizing and cost calculations. The methods used in the current work are conventionally applied in costs calculations giving typically errors of ca. within ±20–30%. The major contribution to the operating costs and the corresponding specific hydrogen cost is the feedstock cost (91.8%). Other operating costs (electricity and water treatment) are partially covered by the revenue of steam cogeneration. Optimal reaction conditions were determined on the basis of water evaporation and the reactor heat duty. Utilization of pressures above 40 bars is reducing the heat duty of the reactor and can provide a cost-efficient operation with the diluted feed. The process optimization determines that the medium pressure steam co-generation and hot water recycle can significantly decrease the operation costs.

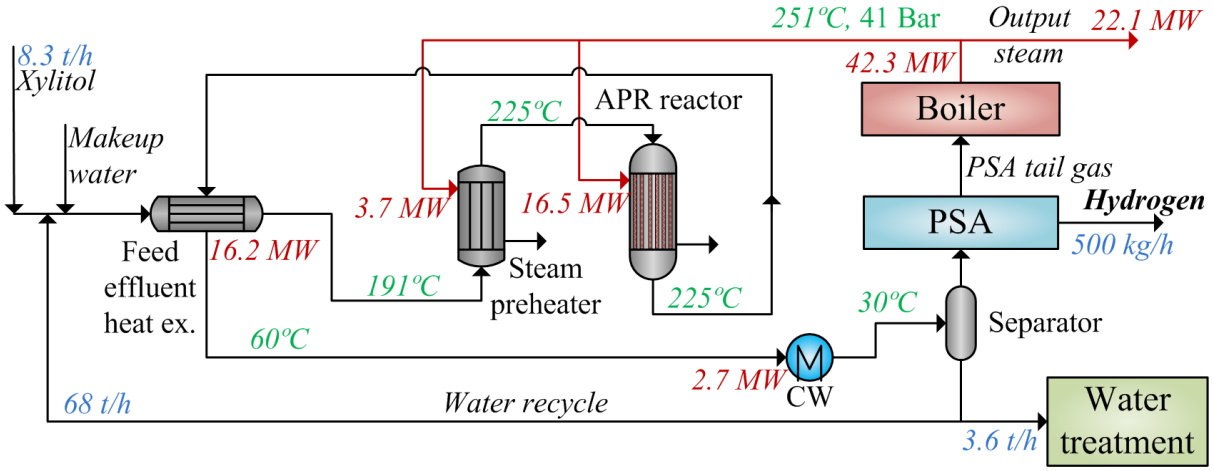
Considering concentrations of sorbitol applied in the range of 5–30 wt %, the costs of hydrogen do not change significantly in the range of 12.94–13.58 $/kg, while the operating costs vary to a larger extent. The optimized design has lower capital costs due to a decrease of heating/cooling equipment duty and also a lower hydrogen price because of revenues from stream cogeneration.

The cost of hydrogen produced by an alternative method of methane steam reforming is approximately 1.8 $/kg (not including the catalyst costs and capital charge). To reach similar product costs the sorbitol price for APR process should be lower than 150 $/t. Such low feedstock price of 150–300 $/t is achievable only if sorbitol would be efficiently produced from cellulosic biomass.

Dynamic model simulation of reactor performance was done to explore the influence of various parameters on APR of another polyol- xylitol. The effect of the fluid−solid mass transfer coefficient on the concentration of reactants vs time was studied. As a next step, it was tempting to make the simulations for a larger scale unit. The model for flow-sheeting was based on the reactor simulation data.

Unit capacity was specifically selected for the production of 500 kg/h of H_2 from xylitol feedstock. The Aspen HYSYS with Peng−Robinson thermodynamic package was used to simulate such

processes as heating, cooling, recycling, and separation. The process flow diagram is displayed below, which also contains simulation data.



Xylitol APR process flow diagram.

A mixture of the feedstock, makeup, and recycling water is heated to a near-reaction temperature in a feed-effluent heat exchanger, then heated up to a reaction temperature of 225 °C by high pressure steam (41 bar, 251 °C) and directed to the APR tubular reactor. The reactor size estimation is the following: tube bundle diameter, 1.9 m; tube length = 3.0 m; dt = 25.4 mm (ID), tubes number, −2650,; heat transfer surface, 714 m2; catalyst loading, 3.5 t (4.0 m3). The size of the catalyst particles was supposed to be 750 μm (egg-shell type of catalyst, ensuring negligible impact of mass transfer limitations). The reactor is also supplied by high pressure steam (HP) to sustain the isothermal conditions. The reactor product stream consisting of aqueous and gas phases is cooled in the feed-effluent heat exchanger and water cooler down to 30 °C to separate the gaseous product and to direct it to the pressure swing adsorption unit (PSA) for hydrogen separation. A PSA unit was modeled with a hydrogen recovery rate of 85%. Such a recovery level is rather typical for 4−6 bed adsorption. Higher values, corresponding to 90−95% hydrogen retrieval, are achieved with 10 bed units. This can be, however, recommended to be used only for units with a capacity exceeding 5000 kg/h. The PSA tail gas comprised from H_2, CO_2, and alkanes is combusted in the boiler to generate HP steam which is supplied to the reactor and preheater. Boiler fuel efficiency was selected as 90%. The generated heat of 42.3 MW supplies the reactor (16.5 MW) and preheater (3.7 MW). The rest of the energy, 22.1 MW, can provide extra income from the process, decreasing thereby hydrogen production costs. A fraction of the recycled water can be drawn to wastewater treatment to prevent accumulation of relatively stable liquid components in the recycle such as acids and furans.

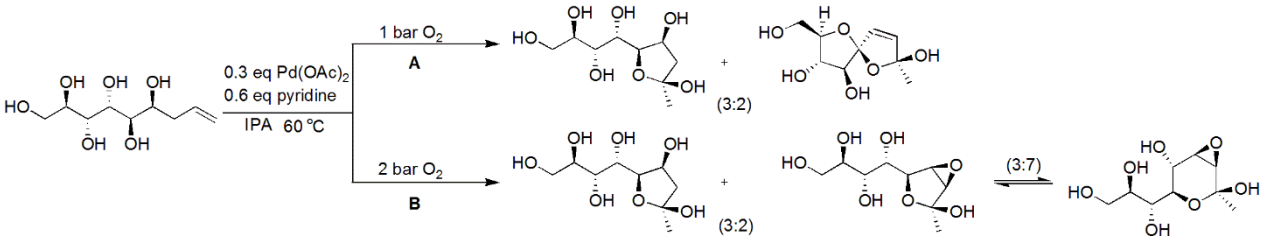
Overall, it can be summarized that the process design does not require any external heat source due to utilization of process byproducts - alkanes C1−C5. These calculations demonstrate that the catalyst for hydrogen production should not be too selective toward hydrogen and CO2 but from the process optimization viewpoint should also generate alkanes as byproducts. In fact, 159 MJ (44 kW·h) per kilogram of hydrogen of heat can be produced for the designed hydrogen capacity of 500 kg/h. Such scale can be required for stand-alone green diesel production plants located close to pulp mills, where hydrogen is not readily available, and instalment of a small-scale methane steam reformer can be economically unattractive.

Selective oxidation of unprotected carbohydrates, polyols and phenolic structures from the biorefinery feedstock

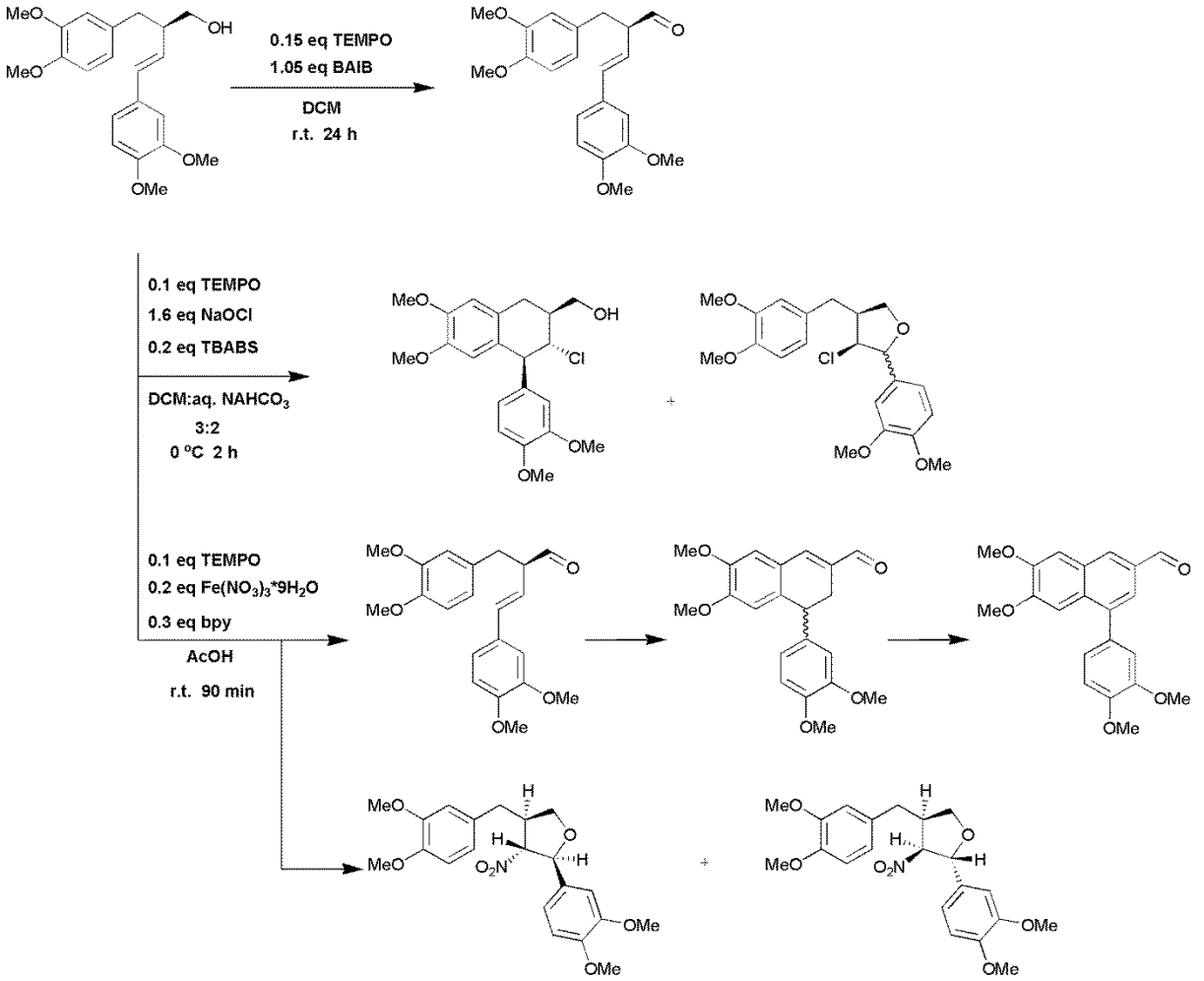
Main funding: Academy of Finland, Raision Säätiö

Patrik Eklund, Patrik Runeberg, Stefan Willför, Dominique Agustin

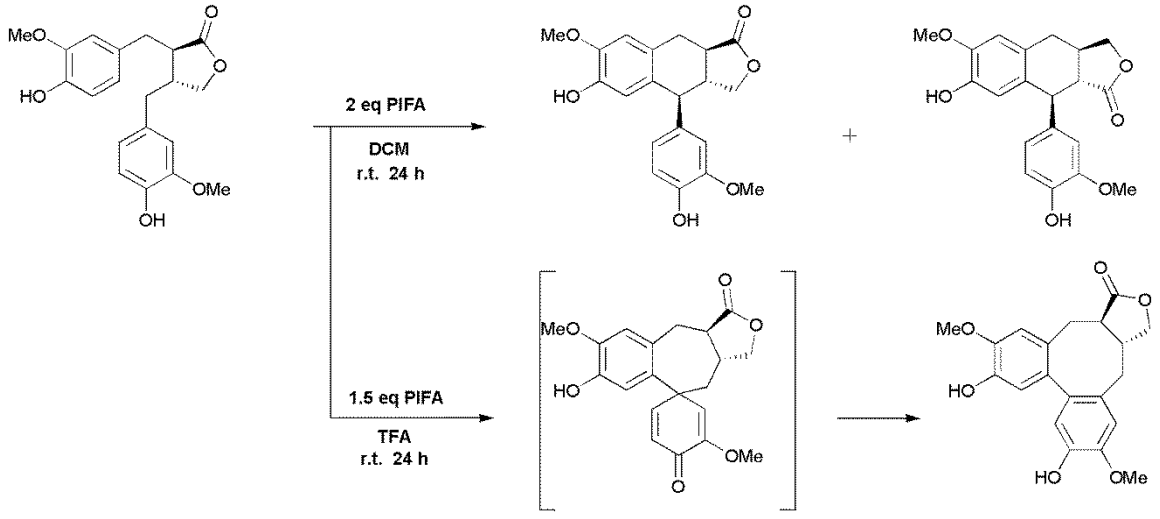
In recent years, the use of wood in lignocellulose-feedstock based biorefineries has become more and more important. Still much attention is focused on the use of lignin and cellulose for production of fuels and materials. However, more sophisticated methods for isolation, and purification of single compounds, or mixture of specific compounds, have emerged. In many cases, wood-based compounds may need further chemical modification to meet the requirements of different applications. Oxidation is one of the most important and frequently used reactions in this context. However, selective oxidation of complex wood-based compounds from the biorefinery feedstock are much more difficult compared to oxidation of hydrocarbons from the petrochemical feedstock. Often, modern catalytic transition metal-based oxidation reactions are not compatible with, for example, polyolic structures of unprotected carbohydrates and phenols.
The objective of this research was to find and develop new mild, selective, and environmentally benign oxidation methods for wood-based compounds. The oxidations were based on catalytic methods, oxidation by molecular oxygen, oxidation by oxo-molybdenum catalysts and UV mediated oxidations. Due to our previous research in this field, lignans, norlignans, stilbens and carbohydrates from the biorefinery feedstock, were used as model substrates for the oxidations.
Results of the studies showed that selective oxidation of different biorefinery based substrates can be achieved by for example Pd-catalysts in aerobic conditions, TEMPO-mediated oxidations, and hypervalent iodine reagents. Also, molybdenum complexes with Shiff base ONO- or ONS-tridentate ligands catalyzed selectivity oxidation of olefinic lignans.



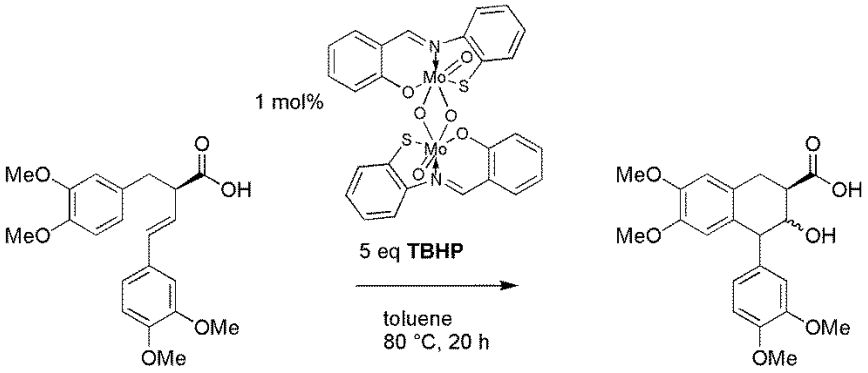
Palladium-catalyzed aerobic oxidation of unprotected polyol, in this example allylated D-mannose.



Examples of 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO)-catalyzed oxidations, here on the norlignan dimethyl-imperanene.

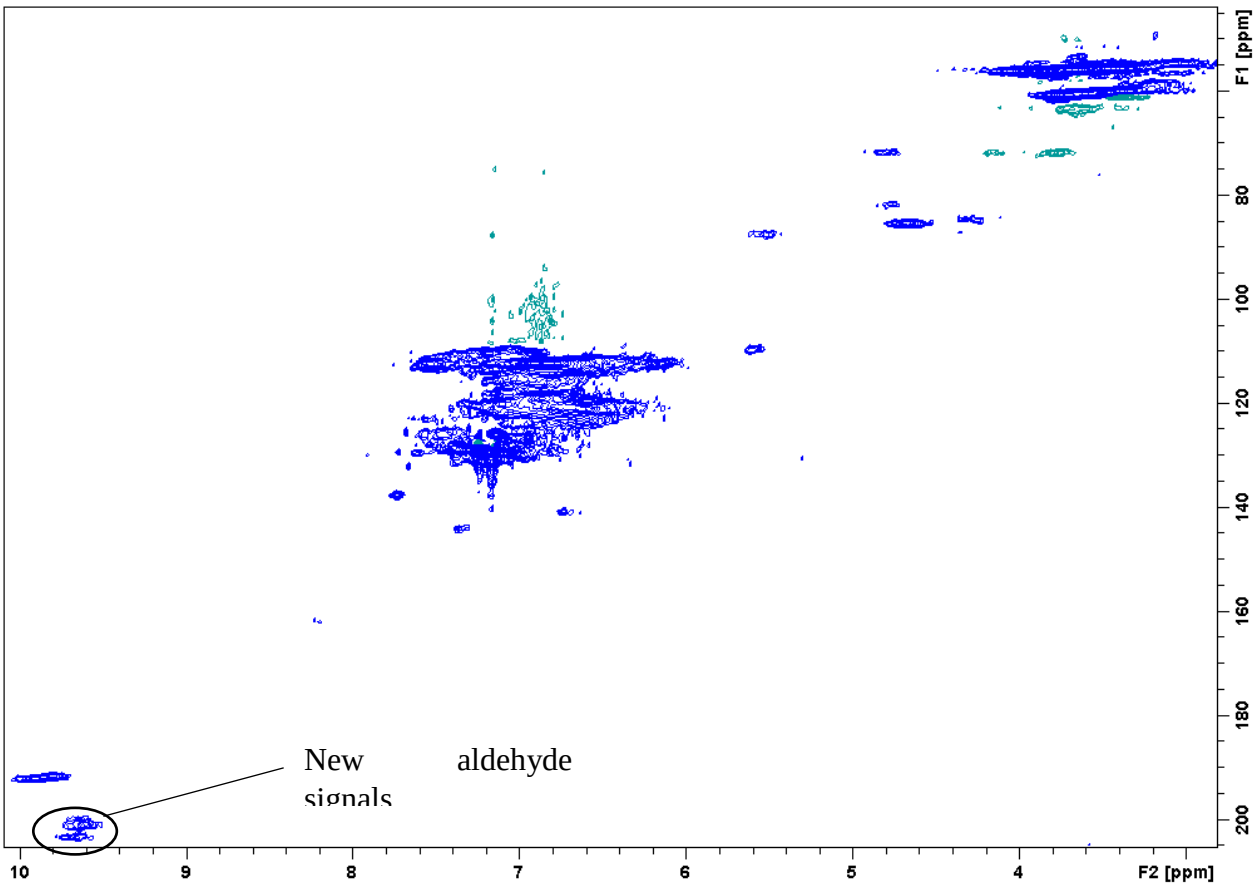


Oxidation of the lignan matairesinol by the hypervalent iodine reagent [Bis(trifluoroacetoxy)iodo]benzene (PIFA).



Molybdenum-catalyzed oxidation of the lignan imperaneic acid.

Also, oxidation of soda-type technical lignin from softwood was studies. It was shown that TEMPO catalyzed the oxidation of primary hydroxyls to aldehydes in these lignin structures, without oxidative depolymerization.



HSQC 2D NMR spectrum of TEMPO and BAIB oxidized soda-type lignin of pine. New aldehyde signals can be seen, and the primary hydroxyl signals have disappeared.

4.3 WP3 - Refining options for lignin

1. Fractionation, purification and characterization of lignin(s).

The valorisation of lignin from various biorefinery processes, including traditional pulping, for something else than simple burning is a continuous challenge. The increased interest in producing liquid transportation fuels and or platform chemicals from cellulosic biomass, together with bioengineering efforts, has also increased the potential lignin reserves outside the common Kraft and sulphite lignin currently available. Potential value-added products include carbon fibres, plastics, thermoplastic elastomers, foams, and membranes and naturally a multitude of biochemicals that all could replace part of the current oil-based products used. It is also evident that other lignin sources than the above-mentioned are emerging. So-called organosolv and steam explosion lignins are examples of such. Lignins from various sources and processes have distinct characteristics that may render them useful for different applications. However, in most cases some chemical or enzymatic modification is needed to achieve the functional design appropriate for a certain product. At the ***PCC*** we have focused on a soda type water-soluble sulphur-free lignin, which can be obtained by isolation from process waters from thermomechanical pulp production (TMP) or by a novel method using extraction of wood with pressurized hot water (PHWE). PHWE lignin(s) have been thoroughly studied at our centre and a specific soda-type lignin (BLN-lignin) is today produced by a local company, CH-Bioforce Oy. In the separation process, the lignin is sequentially removed from the fibre fraction using a milder alkaline process in comparison to traditional Kraft pulping. This approach also processes the biomass at lower temperatures (< 150°C) than in traditional pulping, which seem to result in a scarce introduction of LCC. Lignins obtained from different extraction conditions have been carefully characterized with for example size-exclusion chromatography, NMR-spectroscopy, IR, TGA, DSC, Pyrolysis GC-MS, and THM-GC-MS. Furthermore, lignin has been fractionated and purified according to molar mass and solubility. The technical soda lignin can be fractionated into high-molecular weight, medium-molecular weight and low-molecular weight fractions. Also other types of lignin such as kraft lignins, hydrolysis lignins, organosolv lignins and milled-wood lignins have been studied and compared to the soda lignin.

2. Chemical properties, reactivity, derivatization and chemical modifications

Valorization of lignin often require chemical modification in various ways and in order to explore the possibility for further modifications of the above mentioned soda lignin its chemical properties have been studied by multiple chemical conversions. Oxidations reactions have been performed with TEMPO, BAIB and PIFA. Pulsed corona discharge oxidation and ozonolysis have been studied for oxidative deconstruction of lignin. Also, catalytic reduction has been studied at different conditions. Further, numerous esterifications and etherifications have been performed to study the reactivity and amounts of free OH-groups. Allylations, propargylations and Mannich-reactions have also been performed as part of the reactivity studies as well as for further derivatization and valorization. For technical use (in 3D printing) methods for the preparation of fatty acid ester have been developed. We have also investigated the electrochemical properties of the BLN-lignin as well as modified lignins by cyclic voltametry. The preliminary results show that the electrochemical properties are influenced by the amounts of hydroxyl and carboxylic acid groups.

3. Novel applications, adhesives, biocomposites and barrier material from lignin.
Isolated mild alkali-extracted lignin can be used as novel eco-friendly adhesives and as a part of biocomposites which may solve typical problems such as moisture stability or decrease the extensive use of phenol formaldehyde resins. The usability of the composites for adhesives, wood protection applications, insulation materials for buildings, and as specialty chemicals have been evaluated. The use of BLN-lignin as a phenol source in phenol formaldehyde resins have been studied in collaboration with CH-Bioforce Oy.

Within the ***PCC*** activities the use of spruce lignin as a plant growth regulator has also been investigated. The germination of *Linum usitatissimum L.* was studied using two different molecular mass fractions of lignin as a plant regulator. The lignin improved the growth at 0,0001% concentration.

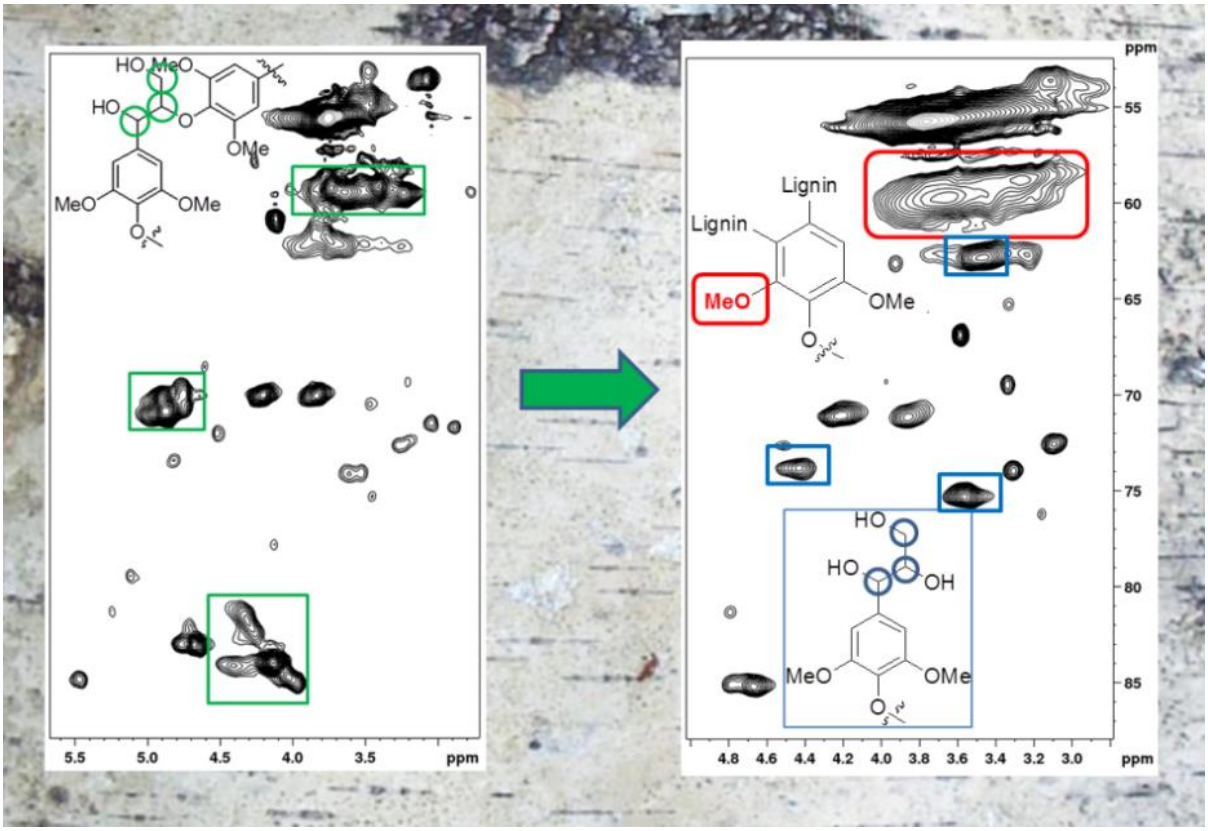
Preparation of biocomposites for 3D printing have in addition to lignin characterization been the core activities of WP3 which is presented as selected project presentations below.

Cooperation:
VTT technical research Centre of Finland, University of Helsinki, CH-Bioforce Oy, University of Lappenranta, Mirka Ab, Tikkurila Oyj, CH-polymers, St1 Oy, Fortum Oyj, Forchem Oyj, Aalto University.

Exploring the structure and reactivity of a novel type of mild alkali pressurized hot-water extracted lignin

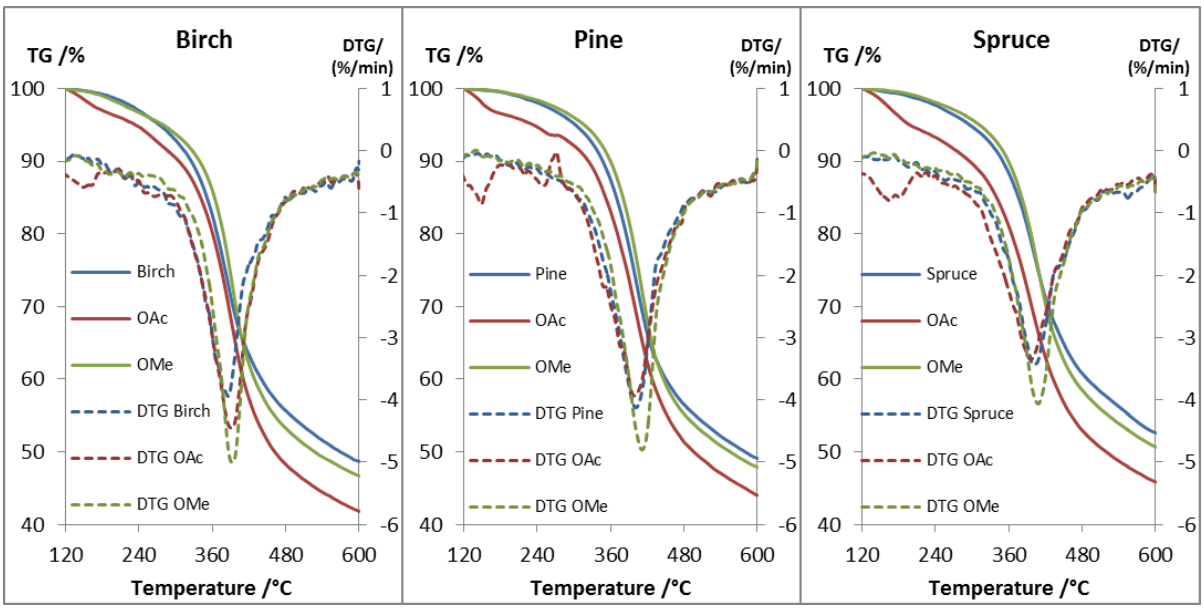
Main funding: Suomen Luonnonvarain Tutkimussäätiö, Fortumin Säätiö
Lucas Lagerquist, Andrey Pranovich, Rasmus Kempe, Wolter Rautelin, Annika Smeds, Jani Rahkila, Stefan Willför, Patrik Eklund

In this project we have worked with lignin obtained from a novel bio-refinery process. The process, developed by CH-Bioforce Oy, separates the hemicelluloses from the biomass by pressurized hot-water extraction, followed by separation of the cellulose from the remaining fibers by mild alkali pulping. Both steps are conducted in oxygen starved conditions. As both of the carbohydrate fractions are isolated in both high purity and yields it is of importance to determine the condition of the lignin fraction for possible future utilization. The process is currently being up-scaled to a facility being able to process up to 100 k ton biomass annually. Initial studies were focused on developing a practical method of obtaining the lignin from the black liquor. During the development of precipitation and purification methods of the lignin also different solvent fractionation strategies were studied. After the initial studies a proper structural characterization was performed on birch lignin (and later on pine and spruce lignin) from the process. The lignin was analyzed with the spectroscopic methods ^{13}C NMR, ^{13}C DEPT experiments, ^{31}P NMR, 2D HSQC, and FTIR as well as methods such as size exclusion chromatography (SEC), elemental analysis, pyrolysis-gas chromatography-mass spectrometry (*py*-GC-MS), methoxy group determination and carbohydrate determination after methanolysis. The lignin was compared to structurally intact milled wood lignin (MWL) that was supplied by collaborators. Degradation and condensation could be observed in all lignins, even though the structure and reactivity of softwood was different compared to hardwood. The study on the softwoods also focused on the thermal properties of the lignin, as well as chemically modified derivatives. The modifications were performed to see if the thermal stability could be increased by simple derivatization.



Degradation of traditionally occurring lignin linkages and formation of new structures illustrated by the 2D NMR spectroscopy

It was concluded that the isolated BLN-lignin had relatively few of the traditionally occurring alkyl-aryl ether linkages remaining, that the lignin was fragmented during the process and that re-condensation is also occurred. We also identified multiple structural anomalies caused to the lignin by the process. The sulfur-free BLN lignin contained proportionately high amounts of phenolic hydroxyl groups, which can be utilized for functionalization of the lignin. In addition, the uncommon arylglycerol end group linkages, as well as two new peaks, which seemed to originate from condensed syringyl structures, were identified in the BLN birch lignin. This also strengthen the hypothesis of C2/C6 condensation of hardwood lignins under certain pretreatment conditions of biomass and that the condensation seems to be more commonly occurring phenomena in weakly acidic pretreatments. We utilized multiple different analysis techniques for S/G determination and concluded that, while differences in the values showed an increase in the ratio. This seems contradictory to the fact that the total amount OMe was decreased, however, the ratio should most likely be higher due to the fact that some condensed G-units might not be included in the S/G determinations. Comparing the S/G ratio of MWL to technical lignin might be misleading, as the amount of S-units and G-units cannot be unambiguously determined due to the fact that the methods are not completely quantitative and the by the fact that presence of condensation affects the analysis. Softwood lignin was degraded in a similar fashion; however, the C2/C6 condensation could not be unambiguously determined since softwoods lack the syringyl unit and thereby no separate signal can be observed in the NMR spectra. The thermal analyses showed that lignins were stable up to 270-300 °C, varying on tree species, and had considerable char residue left at 600 °C. The thermal properties could also be tailored by simple chemical reactions, such as acetylation and methylation, were the acetylated lignin showed reduced the stability and methylated increased stability.



Thermal stability of the different tree species as well as their chemical analogues

As the process cause fragmentation of the native lignin and an enrichment of carbon via condensation reactions, the lignin is more suitable to be used in applications in its polymeric form instead of degradative valorization, as degradative methods often rely on the cleavage of the alkyl-aryl ether bonds. Applications areas for this lignin could for example be as a copolymer, in blends or in composites, either to reduce the price of expensive polymers or to change the material properties. The high amount of free phenolic hydroxyl groups allows for easy chemical modification that can be used to further modify the material properties. The reactivity of the lignin was studied by various chemical modifications, such as mild hydrogenation, ozonation, oxidations and simple chemical modifications. The mild hydrogenations were performed using catalytic amount of Pd/C at relatively low temperatures and hydrogen pressure. The intent of the study was to study the structural changes to the lignin without completely degrading it, however, the lignin was shown to be stable under these conditions without any noticeable changes. Multiple oxidation methods were performed on the lignin. For example, pulsed corona discharge (PCD) oxidation method that was tested in cooperation with Lappenranta University of Technology. This method modified the lignin into highly oxidized structures, containing large amounts of carbonyl functions and carboxylic acid salts. Based on the knowledge from the PCD oxidations some initial ozonation oxidation were also performed on the lignin to yield highly oxidized structures, but also more selective methods using PIFA, BAIB and TEMPO have been explored in cooperation with other projects. In an effort to valorize the lignin, different chemical derivatizations were also studied. One such method is the allylation or propargylation followed by Claisen rearrangement, to introduce reactive double or triple bonds that could be further polymerized into new materials.

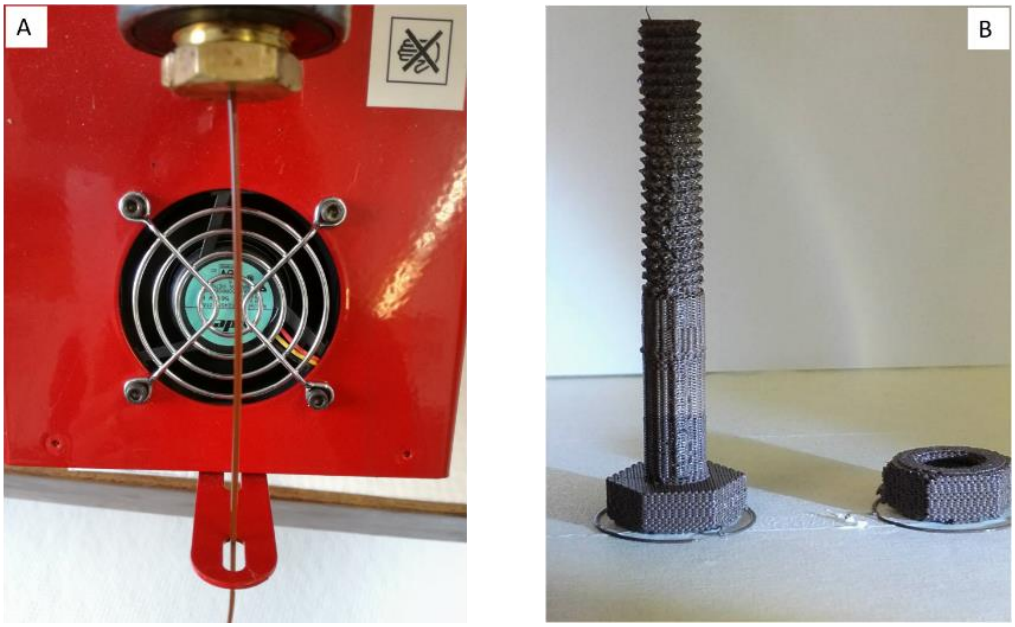
Lignin/polylactic acid (PLA) composites as 3D printer feedstock materials: adapt lignin modification with fatty acid to improve the miscibility with PLA

Main funding: ***PCC***, Fortum Foundation

Xiaoju, Wang, Lucas Lagerquist, Yongchao Zhang, Wenyang Xu, Andrey Pranovich, Patrik Eklund, Stefan Willför

Additive manufacture (AM), also known as three-dimensional (3D) printing, offers rapid prototyping capability and precise control over the complex geometry and fine feature resolution for the fabricated objects with the aid of computer-aided design (CAD) model and computer-controlled software. In AM technology family, fused deposition modeling (FDM) has shown greatest versatility by nozzle-deposition-based extrusion with the utilization of a variety of biodegradable polymers. Polylactic acid (PLA) is one of the main desktop 3D printer feedstock materials, owing to its favorable mechanical properties and thermoplastic processability, as well as the green feature of its synthesis routes from renewable resources. More recently, as one of the wood biorefinery side and waste-stream product, lignin has showed great potentials in preparing composites as 3D printing feedstock materials, which shows money being made out of lignin. In our project, we have investigated whether the fatty acid (FA)-modified lignin can have improved miscibility with PLA in formation of the composite, as that was the problem accounting for the brittleness in PLA when we previously blended unmodified lignin with PLA with a solution casting method to obtain filaments of lignin/PLA via hot melt extrusion (HME).

The esterification to the refined lignin fractionated from a pine resource with a series of FAs with varied aliphatic chain length was carried out. The influence of the aliphatic chain length in fatty acid on the thermal properties of the FA-modified lignins is under investigation. Also, the miscibility of FA-modified lignins with PLA in the composite preparation and the consequent impact on the mechanical properties of obtained composite with PLA are also the main focuses of the ongoing project. The obtained composites of FA-modified lignin/PLA composite are extrudable (as seen in Figure 1A below) and FDM 3D printing has successfully employed the extruded filament to print objects such as screw species (as showed in Figure B, below).



(A) The FA-modified lignin/PLA filament which was extruded by HME; and (B) Screw objects fabricated by FDM 3D printing with the FA-modified lignin/PLA filament as the feedstock material.

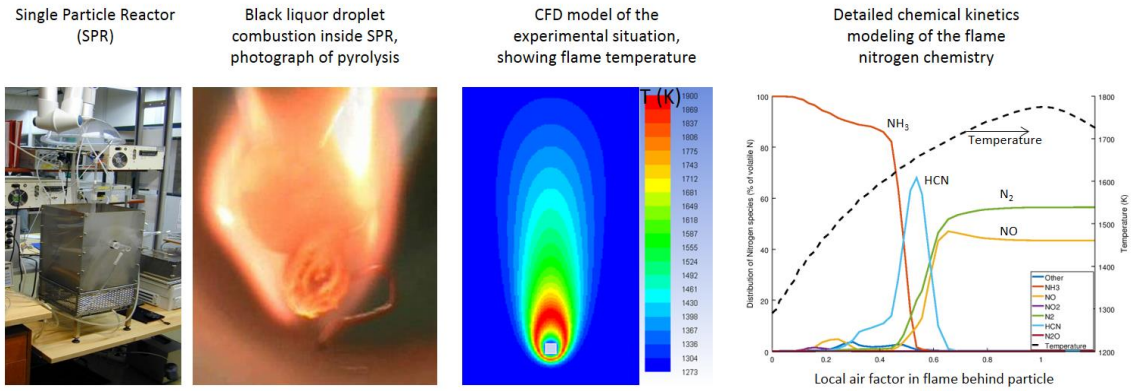
4.4 WP4 - Trace elements in refining of biomass

Inorganics invariably play a role in the refining and processing of biomass and biomass residues. They enter the process with the biomass and may also be added to aid in the fractionation of biomass as is done in chemical pulping. Until relatively recently, these inorganic elements have been primarily seen as a source of problems. The inorganic elements in the biomass can create challenges for industry such as emissions, scaling and corrosion. As more biomass is utilized, there is increased interest also in the recovery of key elements so that they can be returned to the land as fertilizer or utilized in other ways rather than being landfilled.

Within this work package, we have three areas of focus:

- Selective leaching analysis
- Anionic species
- Modelling of the fate of metals

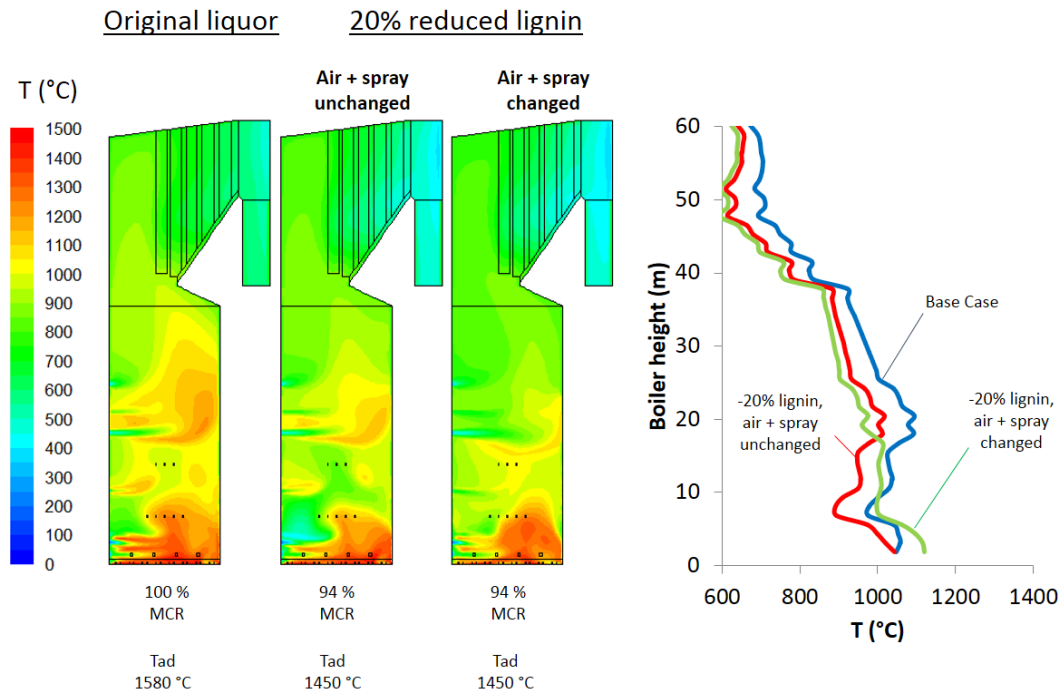
Selective leaching is the step-wise leaching of biomass with water, ammonium acetate, and acid to remove water soluble salts, organically bound metals and acid soluble salts respectively. This provides a basic understanding of the distribution of the inorganic elements in different biomass samples. This in turn gives some preliminary information of how the elements will partition in the processing of biomass. Anionic species in biomass includes both the anions in salts, organic anions such as oxalate and anionic sites such as carboxylic and phenolic groups in biomass. These groups not only enter the process with the biomass, but they also can be formed during the processing. An example of this is oxalate formation during chemical pulping from the degradation of organics. The concentration and form of anionic species, combined with solution pH in the processing of biomass influences how the cationic species are distributed during the refining of biomass. Modeling of the distribution of inorganics in the refining of biomass is a useful tool in helping industry realize new refining technologies. A core element of this work is to incorporate the experimental knowledge within the Johan Gadolin Process Chemistry Centre into predictive models. Mathematical modeling is also utilized in combination with experimental techniques in the laboratory for a better understanding of the biomass trace element chemistry. Examples of experimental and modeling tools are shown in figure below.



Experimental and modeling tools for understanding chemistry of trace element in biomass

The understanding gained from detailed studies into the trace element chemistry is also utilized in the development of models based on Computational Fluid Dynamics (CFD) for simulation of

large-scale industrial processes. The figure below shows examples of CFD simulation of a black liquor recovery boiler.



Computational Fluid Dynamics model of a black liquor recovery boiler; simulation of how boiler air distribution and liquor spraying temperature should be changed to accommodate for changed liquor characteristics due lignin removal

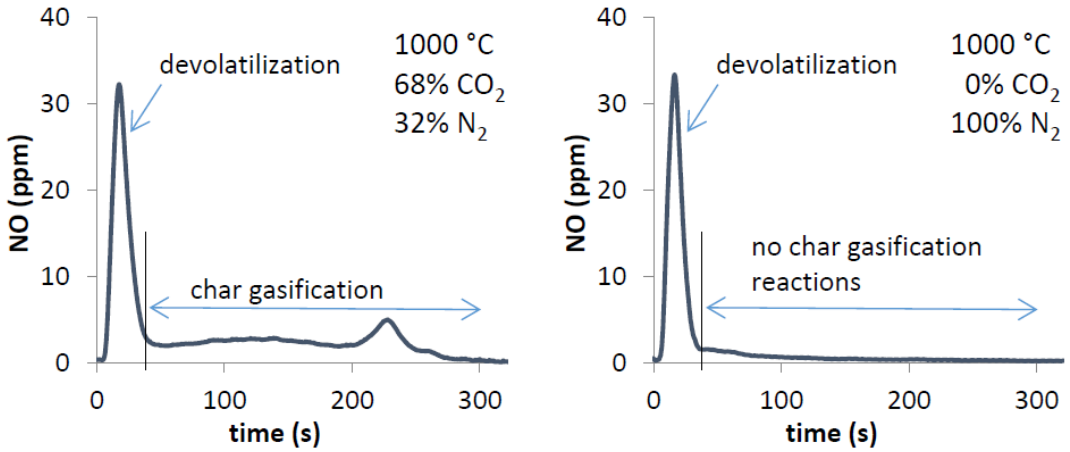
Trace elements in biomass contribute to problems such as scaling and corrosion. Future thermal conversion processes utilizing biomass can be expected to face similar challenges as the processes of today. Understanding the details of the chemistry involved will benefit current and future biomass-based industry. Selected projects are presented below to highlight the activities focusing on NOx emission formation, low-temperature corrosion due to hygroscopic salts, and development of thermodynamic modeling databases relevant to circular economy.

Cooperation:
ANDRITZ, Fortum, International Paper, UPM-Kymmene Corporation, Valmet Technologies Oy, Aalto University, Tampere Technical University, Lappeenranta University of Technology, **Finland**, University of Toronto, **Canada**, Seoul National University, **South Korea**, Stellenbosch University, **South Africa**, Chalmers University of Technology, Lund University, Umeå University, **Sweden**,

Fate of fuel bound nitrogen

Main funding: Academy of Finland, ***PCC***
Oskar Karlström, Markus Engblom, Anders Brink, Daniel Schmid, Paulo Santochi

While in the past decades, large reductions in nitrogen oxide emissions from combustion have been achieved through a better understanding of nitrogen chemistry, particularly the gaseous NO chemistry. Gasification of biomass is a technology that is increasingly being applied as a means of reducing fossil fuel utilization, such as the gasification of bark to replace natural gas or fuel oil in lime kilns in pulp mills. For biomasses with high nitrogen contents, such as annual crops, high nitrogen emissions may become an issue. In biomass gasification, the formation of harmful nitrogen emissions originates from the fuel bound nitrogen (fuel-N). Around 70-90% of the fuel-N is released during devolatilization with the remaining part, around 10-30%, remaining in the char (char-N). During devolatilization, the nitrogen is released as e.g. NH_3, HCN, HNCO, NO, N_2O, N_2 and tar-N. The product distribution depends on the nitrogen content of the fuel, volatile matter, heating rate, final temperature, and surrounding gas atmosphere. Based on a review of the literature, the conversion of biochar-N has not been investigated before under gasification conditions.



Measured concentration of NO from a 6 mm straw particle experiment at 1000 °C either in a CO_2-rich atmosphere or in 100 % N_2.

The figure above shows NO emissions from a biomass pellet gasified in CO_2/N_2 and in N_2. The figure shows for the first time that NO is a reaction product from biomass char gasification by CO_2. This surprising observation is important in understanding the formation of nitrogen emissions in thermal gasification of biomass. For comparison, char nitrogen will form cyanate during CO_2 gasification if the char contains potassium carbonate. Most biomasses do not contain high amounts of potassium carbonate, but black liquor char does. Different types of biomass chars, as well as chars from demineralized biomass, have also been studied in different gas atmospheres (mixtures of CO_2, H_2O, O_2) to understand the role of inorganics and gas composition. For example, nitrogen forms NH_3 during H_2O gasification.
The project lead to nine scientific publications and with the novel measurement methods we showed that the primary nitrogen compound products strongly depend on the gasification atmosphere. This information is needed to implement optimal cleaning strategies in future gasification systems in order to recover and recycle more critical elements from biomass.

Low-temperature corrosion in combustion – old problem, new approaches

Main funding: Academy of Finland
Emil Vainio, Juho Lehmusto

Clean and efficient utilization of biomass and waste fuels as energy sources for the production of heat and electricity is of great importance. The qualities and properties of different biomasses vary a lot, and the ash forming elements may lead to several challenges in their use (Figure 1). Furthermore, additives used to mitigate emissions greatly impact the ash and deposit chemistry. Ash forming elements may cause problems with deposit build-up and corrosion. Low-temperature corrosion is an old problem in combustion of fossil fuels with high sulfur content. The limiting factor in lowering the flue gas temperature is the sulfuric acid dew point. The cause of low temperature corrosion in biomass combustion appears to be dramatically different. The old experiences and rules of thumb seem to be completely invalid in biomass combustion. This lies in key factors of biomass combustion, such as different combustion technology, lower sulfur content, and ash composition. The objective of this research is to better understand the causes of low temperature corrosion in combustion of various biomass fuels by using new analysis and sampling techniques, and in this way pave the road for new solutions to avoid corrosion and improve energy efficiency utilizing sustainable fuels.

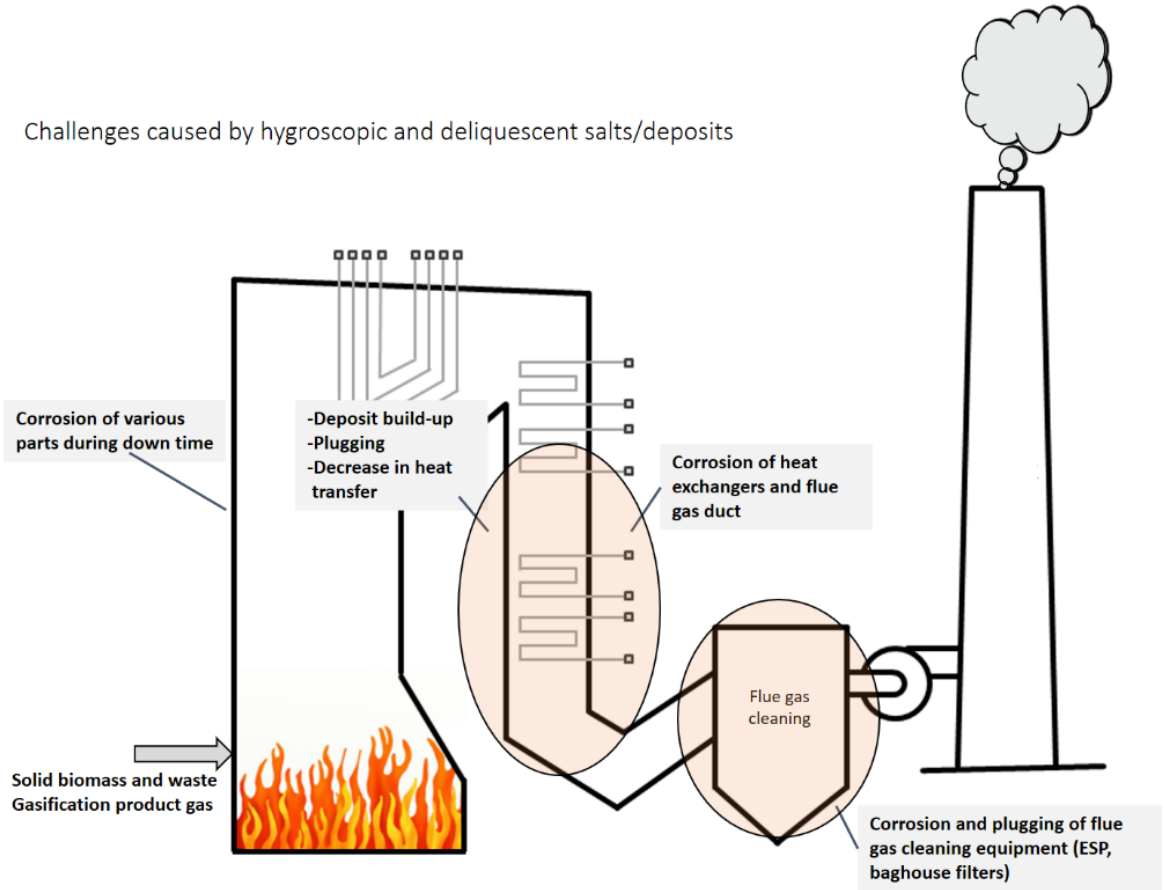


Figure 1. Challenges caused by hygroscopic and deliquescent salts/deposits in energy production.

The main findings:

- Deliquescent deposits turned out to be the main cause of low-temperature corrosion in biomass combustion.
- Deliquescence is the phenomena when a salt absorbs water vapor to fully dissolve in the water (Figure 2).
- For many salts deliquescence occurs above 100°C, *e.g.*, $CaCl_2$, K_2CO_3, $ZnCl_2$
- If deliquescence of, e.g., $CaCl_2$ occurs on steel surfaces it may lead to severe corrosion.
- Hygroscopic and deliquescent salts formed in biomass and waste conversion cause several operational issues in the cold end of boilers (70-200°C): deposit-build-up, decrease in heat transfer, corrosion in various parts, and plugging of flue gas cleaning equipment (Figure 1).
- Virtually no sulfuric acid in flue gases in biomass combustion, this is mainly due to the lower furnace temperatures use in biomass combustion compared to fossil fuel combustion, and ash chemistry. Alkaline ash effectively captures SO_3, the precursor to sulfuric acid.
- One of the important properties of deliquescent salts is the recrystallization. Many salts show a hysteresis effect upon drying, *i.e.*, much higher temperature is needed for the salt to dry again or the humidity needs to be considerably lowered. This has important implications on boiler operation.
- Electrochemical methods were developed to study hygroscopic properties of salts.
- The hysteresis effect was studied by measuring the salts conductivity at different conditions. An example of a measurement is shown in Figure 3. $CaCl_2$ clearly shows a hysteresis effect. As the temperature is increased to 118°C and kept stable for 10h, the salt is still wet and the conductivity increases do to a higher ion concentration of the solution. The salt fully dries when increasing the temperature from 140 to 150°C.

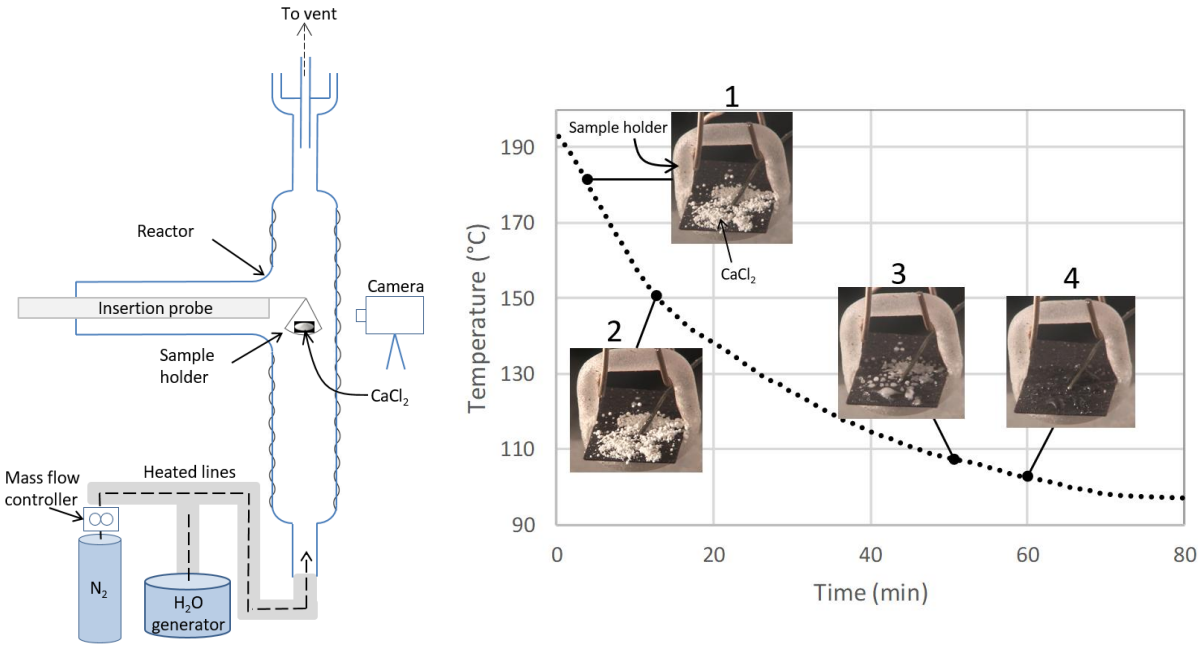


Figure 2. a) Schematic of the reactor used to study the deliquescent behavior of $CaCl_2$.b) Typical temperature profile in the reactor and pictures of the sample holder from a test with 25 vol% H_2O. 1) Dry anhydrous $CaCl_2$, 2) Swelling of the salt due to formation of hydrates, 3) Deliquescence at 108°C 4) Salt fully dissolved.

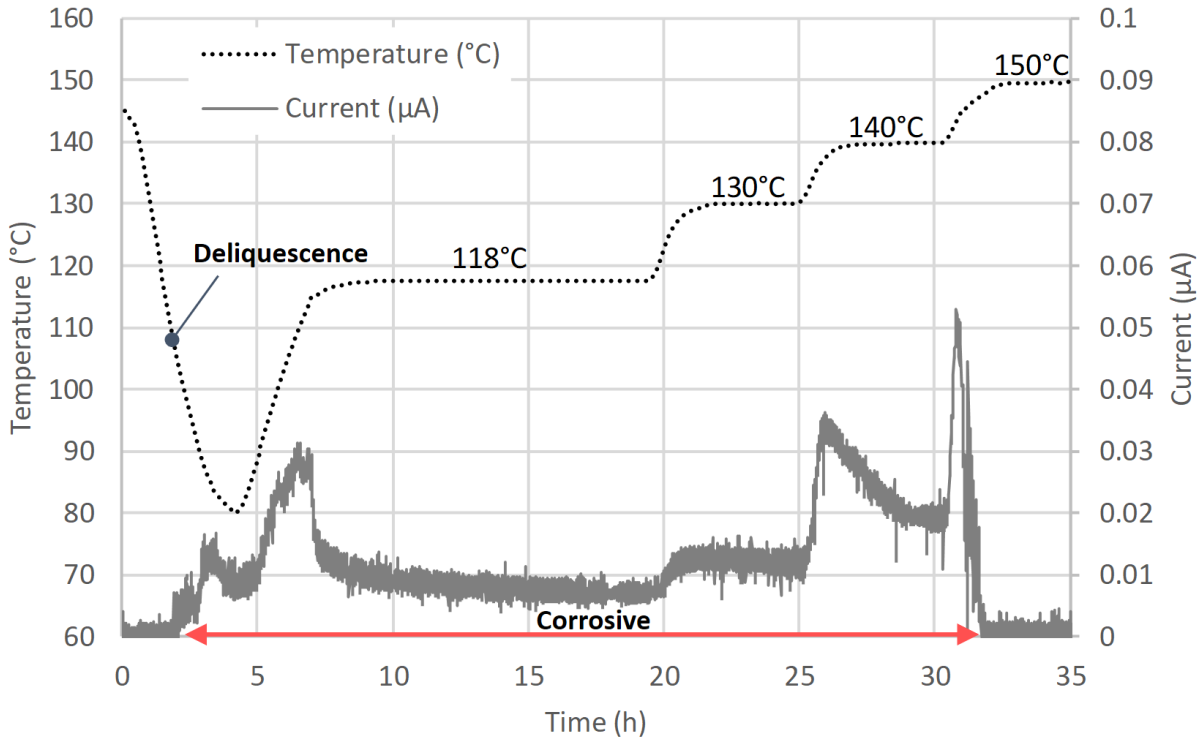


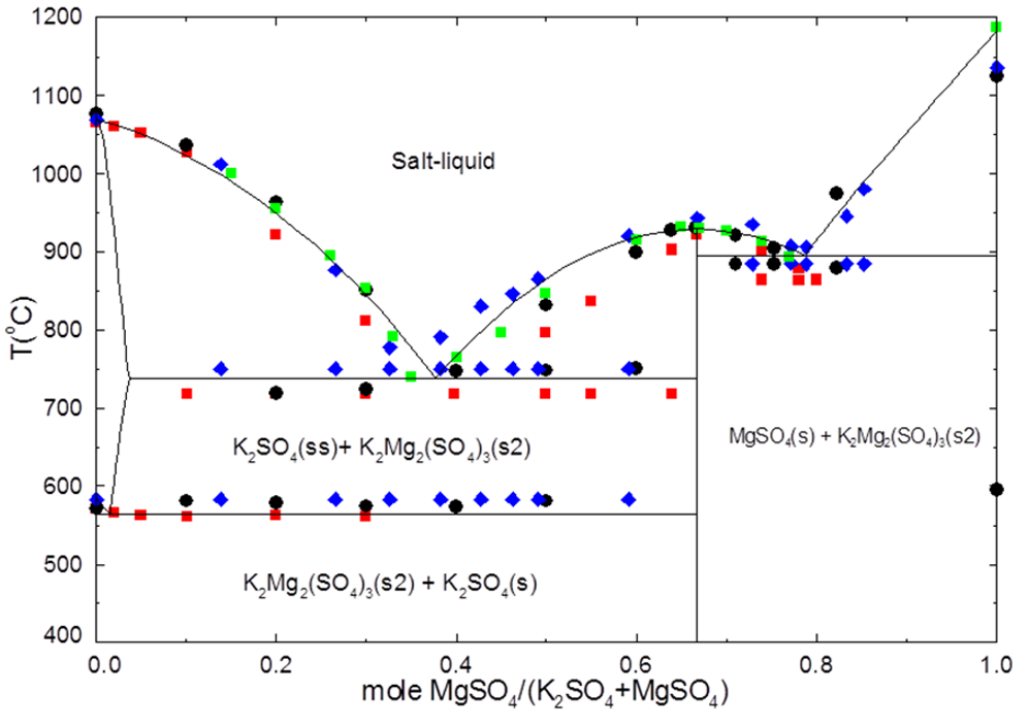
Figure 3. Conductivity of $CaCl_2$ at 25 vol% H_2O. Deliquescence at 108°C and clear hysteresis effect when heating the salt, recrystallizes when temperature increased from 140 to 150°C.

Thermodynamic investigation of complex inorganic material systems for improved renewable energy and metals

Main funding: Academy of Finland
Fiseha Tesfaye, Daniel Lindberg

By 2020 Finland targets to obtain at least 38% of its energy from renewable sources. Solid biomass is one of the most important energy sources for meeting these targets. However, fouling, slagging and corrosion threaten long-term operation availability and costs of biomass power plants. A high concentration of potassium in biomass fuel tends to result in the formation of compounds with low melting points. Significant amounts of highly corrosive alkali chloride in the flue gases emanate through these processes. Slags on superheaters often constitute a considerable percentage of the complex inorganic phases. However, thermodynamic properties of the complex inorganic compounds and their combined effect with the chlorides have been either poorly studied or not available.

The main objective of this project is to promote a better understanding and control of the properties, behavior and role of complex inorganic phases in the high-temperature industrial processes. The current project will give new information concerning properties of the metallic sulfates, chlorides and their phase mixtures, which will help to solve slagging and high temperature corrosion related problems. Databases that are developed in this project will contribute to the control of slagging and high-temperature corrosion related problems and develop sustainable methods for ash treatments, as well as improve chemical and energy recoveries from waste streams. It will also optimize economically sound and environmentally friendly energy and metals production processes with reduced frequencies in plant shut downs and boiler tube changes.



Optimized phase diagram of the K_2SO_4-Mg_2SO_4 system

4.5 WP5 – Complementary research activities

This work package combines the research activities in various cutting-edge research fields ranging from *e.g.* electrochemical sensors, materials science, catalysis, energy, combustion chemistry, bioactive glass, fine chemicals to removal of pharmaceuticals from wastewater, as highlighted below. The work package has an extensive national and international collaboration with academia and industry.

In electrochemical sensors, we have developed a new method for signal transduction in solid-contact ion-selective electrodes. This project (PRECISE) was recently granted four years (2018-2022) funding from the Academy of Finland. The objective is to amplify the analytical signal in order to improve the precision of ion sensing. This research is particularly relevant for applications where small changes in concentrations are of interest, such as in clinical analysis. The ***PCC*** hosts also two other big electrochemical sensor projects. The CaMaFree project focusing on calibration- and maintenance-free multi-sensor probes suitable for wireless monitoring have received a funding from Business Finland (2015-2018). Jane and Aatos Erkko Foundation has granted funding for a project dealing with new electrochemical sensing platforms for health diagnostics (2016-2018). It utilizes conducting polymers for an easy-to-use mutational analysis of DNA sequences for clinical diagnostics and personalized medicine. Both projects are highlighted more thoroughly below. A related health diagnostic project in ***PCC*** uses functionalized polythiophene nanocomposites in the fabrication of genosensors for the detection of mismatches in DNA.

The electrochemical sensor research at ***PCC*** is very vital and on the absolute international forefront. We are paying special attention to potentiometric solid-contact electrodes with reproducible standard potential that would pave the way for the commercialization of calibration-free solid-state ion-selective electrodes. We are using different approaches to receive this goal either by pre- or post-adjusting the potential of the electrodes, which can be prepared on flexible substrates, such as paper and graphene, thus facilitating their use in wearable devices. Together with our collaborators at the Budapest University of Technology and Economics (Hungary) where we are currently identifying the reasons for the irreproducibility of the standard potential. We have also integrated graphene-based barrier layers in the ion-selective membranes to prevent the diffusion of water, carbon dioxide and oxygen to the electrode substrate that will cause response instability (potential drift) of the solid-contact ion-selective electrodes. Studies on preventing biofouling of solid-contact electrodes are also carried out at the centre.

In collaboration with researchers from the University of Tartu (Estonia), we are using novel ionophores for bicarbonate, phosphate, and glyphosate in solid-contact ion-selective electrodes with potential application areas within clinical and environmental analysis. In the case of glyphosate, we note that it is especially crucial for food and environmental safety to develop affordable and portable sensors for detection of hazardous substances. ***PCC*** develops also robust Ag^+-selective electrodes with mesoporous carbon as solid contact. The objective of this project is dynamical monitoring of the nanoparticles dissolution and the sensors will be used to access the toxicity of the nanoparticles.

European Commission has listed natural graphite as one of 20 critical raw materials in Europe. In the multi-disciplinary FennoFlakes project funded mainly by the Academy of Finland, we are therefore identifying new flake graphite ores in Finland with Geology and Mineralogy (ÅAU) and industrial partners. We will use the defect-free and high-quality Finnish graphene for high-end proof-of-concept applications in collaboration with the Laboratory of Physical Chemistry (FUNMAT-ÅAU). We expect that the FennoFlakes project will contribute to increase the

competitiveness of Finland as a future producer of high-quality flake graphite and make it a key player in graphene research.

PCC develops also on-line column-based dynamic leaching methods for the investigation of chemical remediation procedures for environmental solid samples. The project dealing with this focuses on the development of novel methods for the determination and removal of toxic metal ions from environmental samples. In addition, the work package deals with the electrocatalytic reduction of CO_2 to CO with gold nanoparticles.

In catalysis, the ***PCC*** group has studied hydrodeoxygenation of phenolic lignin-derived model compounds for the production of fuels using different model compounds with Pd, Pt, Ru, Ir and Ir-Re supported catalysts. The project focuses on understanding the reaction network and maximizing the yield of the liquid hydrocarbon products, which is crucial for their use in jet fuels. Also in developing heterogeneous catalysts for synthesis of fine chemicals several reactions have been investigated including oxidation of sugars on Au catalysts, oxidation of betulin on Ru, Ag and Au supported catalysts, Guerbet reaction using Ni supported basic catalysts for synthesis of lubricants, Prins cyclisation, α-pinene oxide isomerization and valeraldehyde cross condensation with cyclopentanone over tailored acid-base catalysts giving compounds, which we expect can be used in pharmaceuticals and perfumes. Development of a new supported ionic liquid catalyst for the Heck reaction has made a breakthrough.

We have developed synthesis methods of spatially controlled catalysts with superior performance. The starting point for the project was the large zeolite pellets that have been used for decades in industry for production of fuels and various chemicals. However, this field lacks fundamental knowledge on how the conditions of the catalyst synthesis, acidity and structure influence the catalyst shaping by extrusion and its performance. We have therefore conducted a systematic study on the preparation of zeolite-binder composites by different methods. The characterization of the composites and the catalytic testing have been carried out with the aim to reveal the interactions between the catalyst binder and zeolite, investigate rheological properties of the composites and evaluate their catalytic behavior.

Slip of pharmaceuticals from waste waters to rivers, lakes and seas is a serious environmental issue. Therefore, a new project based on the combination of ozonation and heterogeneous catalyst was commenced. Several metal catalysts, such as Cu, Pt and Pd were screened and the results revealed that the destruction rate of pharmaceuticals can be enhanced by coupling ozonation and heterogeneous catalysts. Moreover, the concentrations of partially oxygenated intermediates were considerably suppressed by incorporating catalytic metals.

New reactor technology is actively developed with the focus being in the development of microreactor technologies, solid catalyst foams and innovative reactor structures. Microreactor technology has been successfully applied on the preparation of chemical intermediates and very precise kinetic measurements. The main application has been the hydrochlorination and oxidation of alcohols on gold catalysts. In the alcohol oxidation, the metal particle size and the influence of the support material as well as the coating technology was studied in order to find optimal reaction conditions. The skills in the preparation solid foam catalysts for process intensification have been improved and the foam catalysts have been investigated by traditional methods and X-ray tomography. CFD-modelling of solid foams is an ongoing sub-project. Combined microwave and solid catalyst technologies have been successfully implemented in the epoxidation and carbonation of vegetable oils in order to obtain bio-lubricants and valuable intermediates. A new variable-diameter column reactor was used in gas-liquid reactor technology. All the reactor technology development was strongly coupled to mathematical modelling.

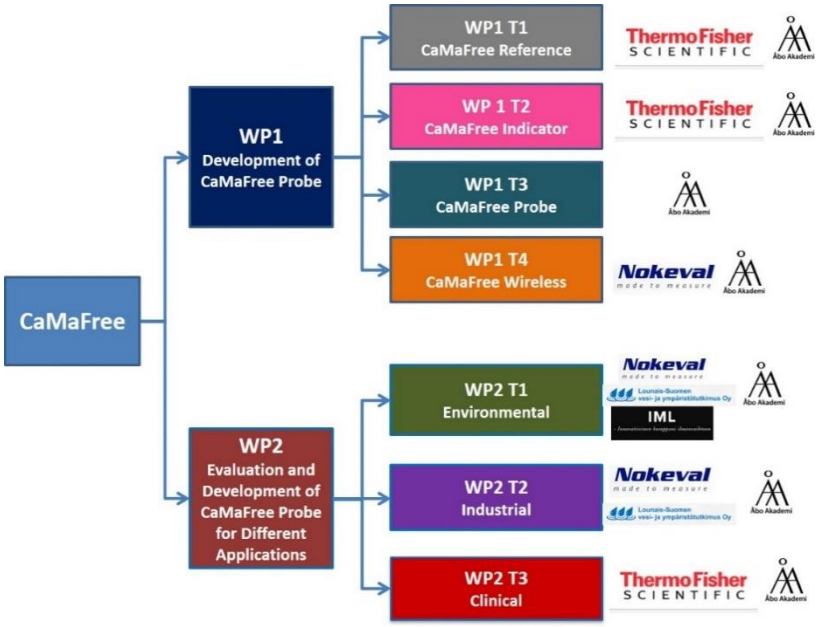
Our research in high temperature processes and combustion, as well as in tissue engineering scaffolds made of bioactive glasses is nicely summarized in the two projects highlighted in the end of the WP5 text.

Cooperation:
University of Wollongong, **Australia**, Engie Laborelec, **Belgium**; University of Toronto, University of British Columbia, **Canada**; Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences (CAS), Nanjing University, **China**; Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Tomas Bata University in Zlín, **Czech Republic**; Technical University of Denmark, Ørsted, **Denmark**; University of Tartu, **Estonia**; Mitsubishi Hitachi Power Systems **Europe** GmbH; Aalto University, ANDRITZ, Boliden Harjavalta, Bonalive Biomaterials Ltd, Defour, Fennoscandian Resources, Finnish Environment Institute, Fortum, FUNMAT-ÅAU, Geological Survey of Finland, Geology and Mineralogy (ÅAU), Ilmastointimittaus Lind Oy (IML), Lappeenranta University of Technology, Lounais-Suomen vesi- ja ympäristötutkimus Oy (LSVSY), Metsä Fibre, Nokeval, Oulu University of Applied Science, Outotec, Sumitomo SHI FW Energia Oy, Tampere University, Tampere University of Technology, Thermo Fisher Scientific, Turku Science Park, Turku University of Applied Science, University of Helsinki, University of Turku, UPM-Kymmene Corporation, Valmet Technologies Oy, VTT Technical Centre of Finland Ltd, **Finland**; Université de Normandie-INSA Rouen, **France**; Karlsruhe Institute of Technology (KIT), Technical University of Munich, TU Dresden, Helmholtz-Zentrum Dresden Rossendorf, University Koblenz-Landau, University of Erlangen-Nüremberg, University of Jena, University of Ulm, **Germany**; National University of Athens, **Greece**; Budapest University of Technology and Economics, **Hungary**; Università di Napoli, University of Messina, **Italy**; Osaka University, **Japan**; NO, **Netherlands**; Otago University, **New Zealand**; The Bellona Foundation, Norwegian University of Science and Technology, SINTEF, **Norway**; AGH-University of Science and Technology, Warsaw University, **Poland**; M.V. Lomonosov Moscow State University, Saint-Petersburg State University, University of Tver, **Russia**; Nanyang Universidade de Lisboa **Portugal**; Technological University, Nanyang Environment and Water Research Institute, **Singapore**; POLYMAT University of the Basque Country UPV/EHU, Universidad de Valladolid, University of the Balearic Islands, **Spain**; Chalmers University of Technology, Lund University, Malmö University, Sibelco Nordic AB, University of Borås, University of Umeå, Uppsala University, **Sweden**; University of Geneva, **Switzerland**; Ivan Franko National University of Lviv, **Ukraine**; Beowulf Mining, **United Kingdom**; Georgia Institute of Technology, International Paper, Oak Ridge National Laboratory, New York University, University of Memphis, **United States**.

Calibration- and maintenance-free multi-sensor probe for wireless monitoring (CaMaFree)

Main funding: Business Finland (former Tekes) Challenge Finland
Tomasz Sokalski, Zekra Mousavi and Kim Granholm

Chemical analysis in industrial processes and environmental monitoring is mainly done by manual sampling and subsequent determination in the laboratory. The main reason for this approach is that most measuring equipment needs maintenance and frequent calibration. Such an approach (sampling and laboratory analysis) is labor-intensive, expensive, time-consuming, and does not give real-time information. As a result, important trends or short-time changes of the measurement parameters will go unnoticed. A simple, reliable, real-time monitoring system with wireless transmission which does not need calibration or other maintenance, and which can be used on-site, would therefore fill a big gap in the market.



Work packages, tasks, and companies in the CaMaFree project.

1. Testing the Solid-State Composite (SSC) reference electrodes in environmental and industrial applications

Lifetime

For many environmental and industrial applications, the long lifetime of a reference electrode is of the most importance. In order to test the lifetime of the SSC reference electrodes, a flow-through system was designed and built to maximize the washing out of inorganic salts from the reference electrode (figure below). Three identical flow-through systems were filled with different solutions: distilled water, tap water, and 0.1 M NaCl solution to mimic the conditions in heat-exchanger pipes, drinking water, and sea water in the Baltic Sea, respectively. In each box, there are two SSC reference electrodes made using the chemical polymerization (CP) or injection moulding (IM) method.

The flow-through system for long-term testing.

The obtained results show that the SSC reference electrodes have over one year lifetime that makes them suitable for prolonged environmental or industrial applications.

Multi-solution protocol

The SSC reference electrodes were studied using the multi-solution protocol to evaluate the effect of the nature and concentration of the sample electrolyte on the performance of the electrodes. The potential stability of IM SSC reference electrodes in all solutions, except for 10^{-2} M HCl and 10^{-3} M KOH, was found to be fairly good (± 1mV). All CP SSC reference electrodes demonstrated excellent stability with all the tested solutions (± 2 mV)

Influence of temperature

The calibration of K-ISE was performed at 5°C, 14°C, 18°C and room temperature (22±1°C) using the IM SSC, CP SSC, or Orion reference electrodes. The change of temperature affects both the indicator and reference electrode. The slope of the K-ISE decreased with decrease in the temperature. Theoretical and experimental Nernstian ratios were found to be very comparable for all tested reference electrodes.

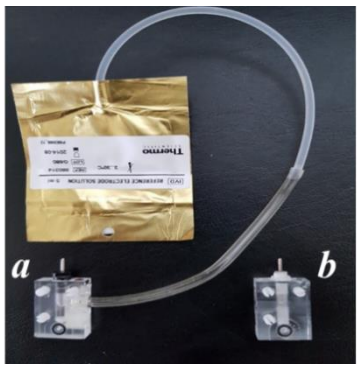
Measurements in river water samples

The SSC reference electrodes were used in measuring K, Na, Cl, Ca, and pH in river water samples. The river water samples were obtained from Halistenkoski (Aura river) and Savijoki. The results of five target ions in the samples were very comparable to those obtained by LSVSY (consortium partner).

Sampling of river water in a) Halistenkoski and b) Savijoki.

2. Testing SSC reference electrodes in clinical applications

Biological samples can contain substances such as proteins and albumins that may influence the response stability of a reference electrode. Therefore, the performance of the SSC reference electrodes was studied and compared with that of commercial reference electrodes from TFS. The Indiko TM clinical analyser with an analyser block containing chloride-, sodium-, and potassium-ISEs was used in this study.



Classical reference electrode used by Thermo Fisher (a) and the SSC reference electrode (b).

The SSC (or TFS) reference electrode was tested using standard solutions and different human sera samples. The results showed that the performance of SSC reference electrodes is comparable to the classical reference electrode while having simpler construction (as shown in the figure above), and being maintenance-free.

3. Study and improvement of the standard potential stability

Long-term stability of solid-state ion-selective electrodes (ISEs) was evaluated from the reproducibility of their standard potential (E^o) over long periods. PEDOT(PSS) and PEDOT(Cl) composites were used as solid-contacts in the fabrication of potassium (K)- and chloride (Cl)-ISEs. The effect of using different dopants for PEDOT and the deposition of silver (Ag) on the PEDOT(PSS) film towards E^o stability were assessed. Furthermore, the effect of using gold nanoparticles-modified glassy carbon (GC-AuNPs) electrode as conducting substrate on the long-term stability was also studied. The results showed that E^o stability is better for the K-ISE with PEDOT(Cl) as solid-contact than that with PEDOT(PSS).

Better E^o stability was achieved when using GC-AuNPs instead of GC as conducting substrate. Furthermore, when GC-AuNPs was used as conducting substrate, E^o stability of K-ISE with PEDOT(PSS) as solid contact was comparable to that with PEDOT(Cl) as solid contact. In the case of solid-contact Cl-ISEs (SC-Cl-ISE), the results showed that the E^o stability was higher for the SC-Cl-ISE with GC-AuNPs as the conducting substrate than that with GC as conducting substrate. On the other hand, the Ag/AgCl/Cl-ISM electrode gave a comparable E^o stability to the PEDOT-based SC-Cl-ISEs for a longer conditioning period of 103 days. The effect of silver deposition in the PEDOT(PSS) film on the potentiometric response of the GC/PEDOT(PSS) electrode was also studied. The GC/PEDOT(PSS) electrode with Ag-deposited PEDOT(PSS) film showed cationic response in $AgNO_3$, Na_2SO_4, NaF, $NaHCO_3$, $Na_2C_2O_4$, KNO_3, and $K_2Cr_2O_7$ solutions. On the other hand, anionic response was observed in KCl, KI, NaBr, NaSCN, and Na_2CO_3 solutions. The anionic response may be attributed to the presence of silver in the polymer film, which can form a salt with the anions present. Interestingly, the slopes of the calibration curves in solutions where anionic response was observed seem to correlate with the K_{sp} of the salt formed between silver and the anion present.

New electrochemical sensing platform for health diagnostics

Main funding: Jane and Aatos Erkko Foundation

Zhanna Boeva, Maria Khaydukova and Emily Kemp

The project is aimed to develop an easy-to-use technique for mutational analysis in DNA sequence for clinical diagnostics and personalized medicine.

The technique being developed during the project implementation relies on a basic principle of electrostatic interactions of a single stranded DNA with conducting polymers as a source of an analytical response. In this technique, single use inexpensive electrodes made of conducting polymer with immobilized single stranded DNA oligomers arrays are used as disposal sensing chips for analyses *in vitro*. These chips are functioning potentiometrically and require only a potentiostat as instrumentation. The conducting polymer works is an integrated part of the recognition system, having single-stranded DNA probe immobilized on its surface. The probe is capable to recognise another DNA with a sequence of nucleotides complementary to it (target). Upon the recognition the target binds to the probe and forms a double helix, which influences the electrical field at the vicinity of the conducting polymer, thus generating an ionic response which is then converted to an electrical signal with the help of the conducting polymer acting as an ion-to-electron transducer. The amplitude and time of generation of such electrochemical response depends on many factors. One is the particular counterion compensates for the positive charge of the conducting polymer backbone. Another factor is the acid used as a dopant for the synthesis of the polymer.

In order to understand if there is difference between polyaniline (PANI) prepared by using HCl and H_3PO_4 as a dopant, we compared the response of PANI-H_2PO_3 electrodes (*i.e.* sensors) with immobilized single stranded DNA probe toward its complementary counterpart. Figure 1 shows a typical example of the detection of DNA hybridization by using electrodes made of PANI fabricated in hydrochloric and phosphoric acid. In the figure, the open circuit potential (EMF) was continuously monitored during the experiment (ca. 16 h).

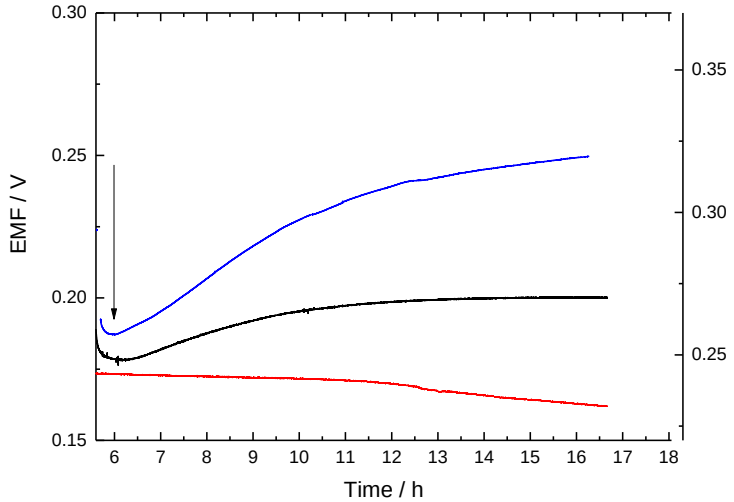


Figure 1. Typical response curves of the hybridization detection of 20-mer target (red line; right-hand axis) and 50-mer target (black line) using the PANI-Nylon electrode prepared by chemical oxidative polymerization of aniline with the use of H_3PO_4 as a dopant. The blue line shows for comparison the response of the PANI-Nylon electrode on the 50-mer hybridization, in the case when PANI was prepared in HCl and reprotonated with H_3PO_4.

At the sixth hour of the experiment, a complementary single stranded DNA of the same length was added to the film having the probe immobilized onto the surface of PANI-Nylon electrode. As can be seen in Figure 1, after the addition of the complementary strand of DNA to the solution, the potential increased for the 50-mer DNA due to the hybridization, and was slightly decreasing due to deprotonation in the case of 20-mer. The electrode made of PANI-Nylon synthesized in the presence of hydrochloric acid showed a significantly larger response to the 50-mer hybridization compared to the PANI-Nylon prepared with H_3PO_4. The difference in the sensitivity of the PANI electrodes in these two cases can be explained with the larger surface area of the electrode prepared with HCl as the dopant.

In Figure 2, we have compared the sensitivity of the PANI electrodes towards the hybridization of the probe and the target consisting of oligonucleotide sequences with different lengths.

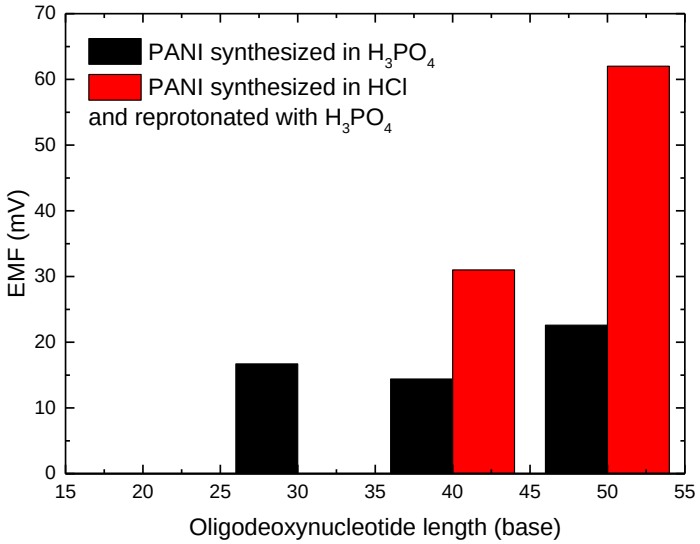


Figure 2. The hybridization response of PANI-Nylon electrodes to 20, 30, 40 and 50-mer DNA oligonucleotides. PANI-Nylon was either prepared in HCl and reprotonated with H_3PO_4 (red bars) or in H_3PO_4 without further reprotonation (black bars).

It appears that the response of PANI-Nylon electrodes made in phosphoric acid is substantially lower compared to the electrode made of reprotonated polyaniline. However, it possible to detect 30-mer oligonucleotides with PANI prepared only with H_3PO_4, whereas PANI prepared in HCl detects only 40 and 50-mers. In conclusion, we note that there are some significant benefits of using PANI prepared in H_3PO_4 without any further post-treatments: 1) There is no need for tedious deprotonation and reprotonation, 2) it is possible to detect the 30-mer hybridization and 3) the PANI electrode potentials significantly more stable compared to the electrodes exposed to reprotonation.

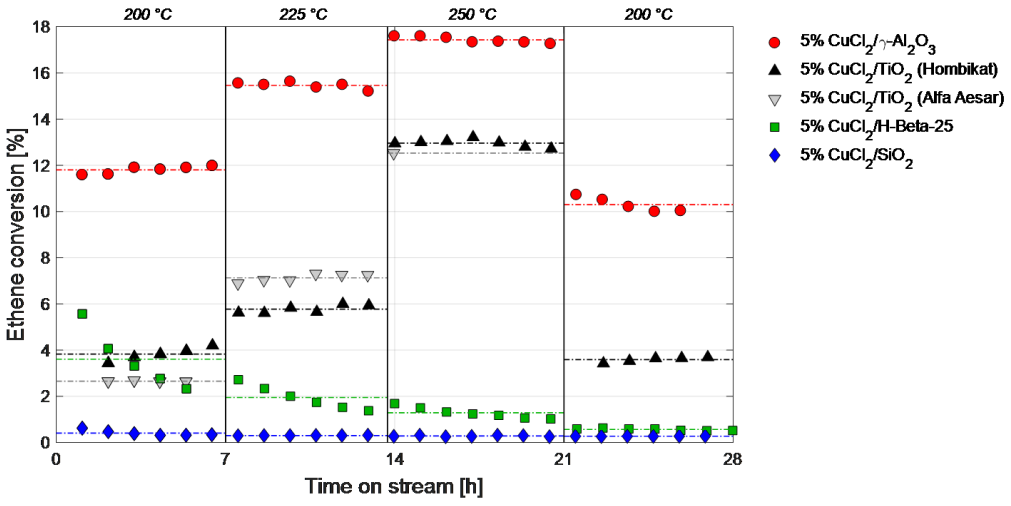
Process intensification and reactor technology

Micro- and Milliscale Reactor Technology

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

Kari Eränen, Zuzana Vajglova, Erfan Behravesh, Alberto Moro Lobo, Sabrina Schmidt, Nicola Gemo, Narendra Kumar, Teuvo Kilpiö, Vincenzo Russo, Cesar de Araujo Filho, Shuyana Heredia, Andrea Perez Nebreda, Yaseen Khan, Nemanja Vucetic, J.-P. Mikkola, Johan Wärnå, Päivi Mäki-Arvela, Dmitry Murzin and Tapio Salmi

Micro- and millireactors enable an efficient performing of chemical processes – they provide the future technology for safe on-site production of chemical intermediates. Gas-phase microreactors have been successfully implemented to prepare chemical intermediates, such as ethylene oxide, methyl chloride, ethyl chloride as well as oxochlorination processes. Silver-based microreactor combined to micro-gas chromatography gave excellent results in the preparation of ethylene oxide, while zinc doped alumina turned out to be the best catalyst for preparation of methyl and ethyl chlorides. The dramatic effect of the catalyst support on the oxychlorination of ethene was demonstrated. In general, the microreactor coating technology by using aluminium oxide as well as micro- and mesoporous materials was successfully developed; we are able to prepare catalytically active and mechanically strong coatings. Catalytic oxidation of hydroxyl and carbonyl groups in molecules from biomass using gold catalysts was performed. Gas-phase microreactors were successfully applied to analyze the very precise kinetics of ethanol oxidation. Monometallic and bimetallic gold nanoparticles have recently turned out to be most interesting catalysts in alcohol oxidation with environmentally friendly oxidizers such as molecular oxygen. A new crafted catalyst concept was developed for the Heck reaction using the concept of supported ionic liquids (SILCA). Millireactor technology was introduced to prepare epichlorohydrin from hydrochlorinated products of glycerol. The results illustrated how the kinetics of very rapid liquid-phase reactions can be very precisely measured by applying millireactor technology. A new millireactor system was also used for liquid-phase reactions and it was successfully used for the homogeneously and heterogeneously catalyzed hydrolysis of inulin and hemicelluloses.



Oxychlorination of ethene – the effect of the catalyst support on the ethane conversion.

Big steps forward in the demanding field of mathematical modelling of milli- and microscale reactors were taken by using the very advanced and user-friendly modelling software gPROMS. A generalized mathematical model was developed for catalyst layers in micro- and millireactor structures. The model describes the reaction-diffusion phenomena in the porous structure very well. Our research group won an international prize for its achievements in micro- and millireactor modelling. The prize was awarded to us because of an article in Chemical Engineering Science (Vincenzo Russo et al.): PSE Model-Base Innovation Prize Runner-Up. A new co-operation with Karlruhe Institute of Technology (KIT) was established (the research visit of Erfan Behravesh to the group of prof. R. Dittmeyer).

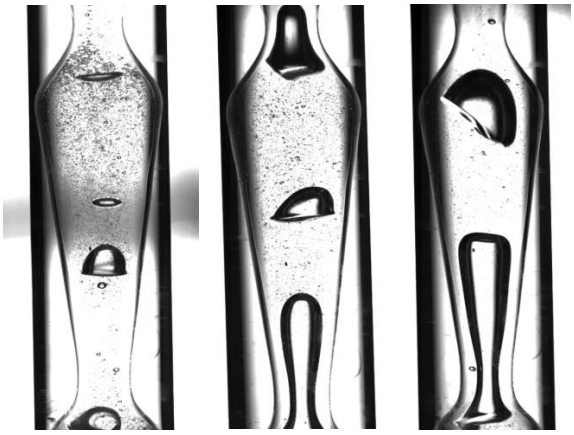
Multiphase Reactor Technology

Main funding: ***PCC***, Academy of Finland, Magnus Ehrnrooth Foundation

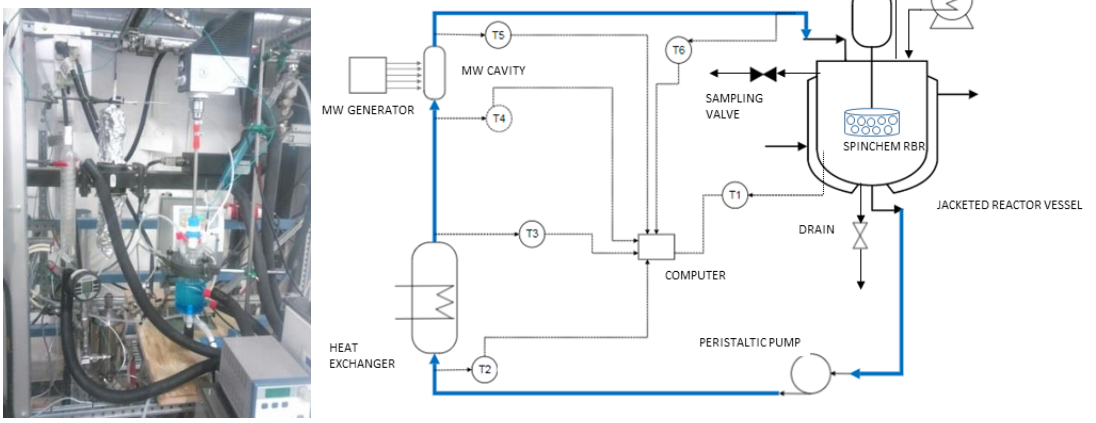
Johan Wärnå, Teuvo Kilpiö, Pasi Tolvanen, Cesar de Araujo Filho, Adriana Freites Aguilera, Tina Samson, Adrien Oger, Mapenda Cisse, Xiashuang Kai, Jun Liu Zheng, Sébastien Leveneur, Leolincoln da Silva Correia, Juan Garcia Serna, Pierdomenico Biasi, Javier Ibanez, Elise Winter, Debanga Mondal, J.-P. Mikkola, Tapio Salmi

Advanced modelling of multiphase reactors is the topic of the project, 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, and catalytic liquid-phase hydrochlorination. The feasibility of hydrogen peroxide direct synthesis in a continuous fixed bed was successfully demonstrated and modelled mathematically. The work was combined to kinetic studies carried out in a tailored batch reactor for hydrogen peroxide synthesis. Production of epoxidized vegetable oils under the presence and absence of microwaves was studied extensively and the results were astonishing: a considerable rate enhancement was achieved by applying microwave technology on the epoxidation process. A further enhancement of the epoxidation process was achieved by introducing cation-exhange catalysts and SpinChem mixing technology to improve the perhydrolysis step in the epoxidation process. The products are valuable chemical intermediates and bio-lubricants. Detailed kinetic modelling and modelling of the microwave effect was carried out in collaboration with University of Wollongong, Australia (the research visit of Adriana Freites Aguilera).

Valorization of glycerol was carried out in very successfully both in continuous reactors. A co-current bubble column and a variable-diameter bubble column were used to investigate the glycerol hydrochlorination process under continuous operation. The influence of liquid flow rate, gas flow rate, temperature and catalyst concentration on the glycerol conversion and the product distribution was studied. The fluid dynamics of the system showed a remarkable behaviour, which was carefully investigated and described. High-speed camera images and residence time distribution experiments were conducted to collect relevant information about the flow conditions inside the column reactor. A model based on the axial dispersion concept was developed and confronted with the experimental data. The kinetic and solubility parameters estimated from the semi-batch experiments were successfully used for describing the mass transfer and the fluid dynamics of the bubble column reactor. The variable diameter column reactor gave a clearly better performance than the classical bubble column, the reason being the suppression of backmixing in the liquid phase.



Flow pattern in a variable-diameter column reactor - the effect of increasing gas flow rate (from left to right). Case: hydrochlorination of glycerol.



A loop reactor system for studies of microwave effects on solid-catalyzed liquid-liquid reactions (epoxidation of fatty acids).

Development of structured catalysts

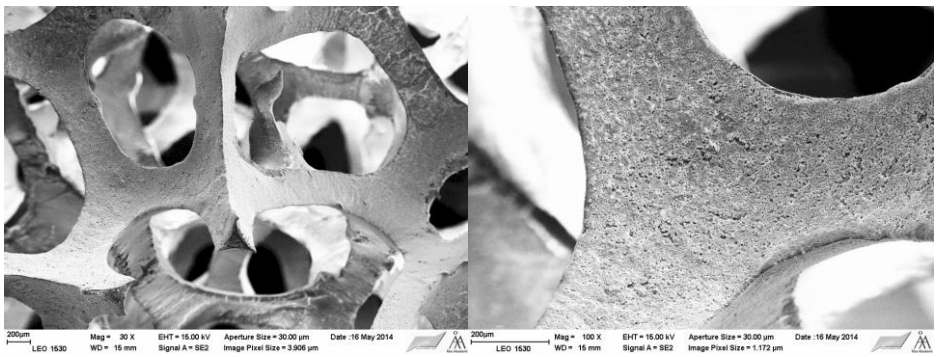
Main funding: GSCE, Fortum Foundation

Vladimir Shumilov, Ali Najarnezhadmashhadi, Kari Eränen, Leena Hupa, Johan Wärnå, Dmitry Murzin, Tapio Salmi

Structured catalysts such as open-cell foam catalysts offer new possibilities for process intensification. Open-cell foams have some excellent features such as very low pressure drop and high voidage despite of the high geometrical surface area per unit volume that favor the application as reactor packing because the foam packing increases the gas-liquid and liquid-solid interfacial area and create local turbulences by splitting and recombining the fluid that leads to enhancement of mass and heat transfer.

Ceramic foams have a wide range of potential applications in biomedicine, thermal insulation, filtration of molten metal alloys, absorption of environmental pollutants, catalyst supports, etc. Since the physical properties of the foams do not fully meet the requirements in some applications, improvement of conventional fabrication methods or totally new techniques are of interest. Procedure for manufacturing of ceramic foams via the replica technique with subsequent

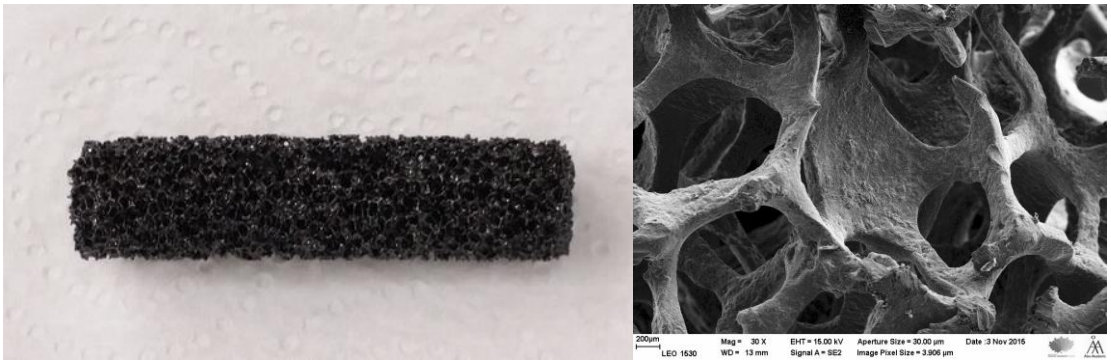
washcoating and deposition of the catalytic phase was developed. Slurries consisted of alumina powder mixed in aqueous solutions of polyvinyl alcohol (PVA) and magnesia and titania as sintering aids. The foams were produced by tuning different processing parameters to give properties suited for catalyst supports. These parameters included pore size of the polyurethane (PU) foam used as a template, parameters in the PU foam pretreatment, particle size of alumina powder in the slurry, slurry loading and drying of the green alumina coated PU foam.



SEM image of the slurry coated sponge (30x) and (100x).

Structured **catalyst supported by carbon-coated aluminum foams** were developed and tested. Foams with a pore density of 40 PPI were applied. To attain a homogeneous polymer layer on the foam and also to avoid clogging of the foam structure, a controlled polymerization of furfuryl alcohol had to be conducted. For this purpose, the foam samples were rotated with a defined stirring speed during the whole polymerization process. After the polymerization step, the sample was pyrolyzed in a tubular furnace in a nitrogen stream. To obtain a porous carbon layer, the foam samples were activated in an air stream.

Homogeneous deposition precipitation (HDP) was chosen to incorporate ruthenium into the carbon-coated foam substrates. The HDP process was carried out by putting pre-treated carbon-coated foam in beaker filled with a solution precursor and urea with a ratio of 1:5 in distilled water.



The Ru/C/Al foam catalyst in real scale and in microscale (SEM image).

The coated foams (Ru/C/Al) were used for the valorization of sugar monomers through catalytic hydrogenation of selected sugars to sugar alcohols, such as hydrogenation of glucose to sorbitol and hydrogenation of arabinose to arabitol. Moreover, it is important to investigate the hydrogenation of sugar mixtures and to determine the interaction of sugars mixtures on catalyst surfaces. Sugar alcohols are excellent sweeteners and health promoting components with anti-caries and anti-inflammatory properties.

Sugar hydrogenation can be performed over supported metals belonging to the platinum, rhodium, and ruthenium. Supported ruthenium catalysts have been found to be the most active ones.

Extensive hydrogenation of sugar and sugar mixtures experiments have been conducted and are ongoing by varying the reaction conditions. Hydrogenation was successful, the reproducibility is good, the catalyst is stable, and the selectivity is high. The influence of the sugar molar ratios on the hydrogenation kinetics of both sugars (L-arabinose and D-galactose) in the mixture have been studied, several experiments are ongoing and will be carried out at different molar ratios of D-galactose and L-arabinose (0.1-10). Kinetic modelling was successfully applied to the sugar hydrogenation data, and the CFD modelling of the randomfoam structures was initiated in collaboration with University of British Columbia, Vancouver (a research visit of Ali Najarnezhadmashhadi).

Removal of pharmaceuticals from waste waters

Main funding: Åbo Akademi University, GSCE

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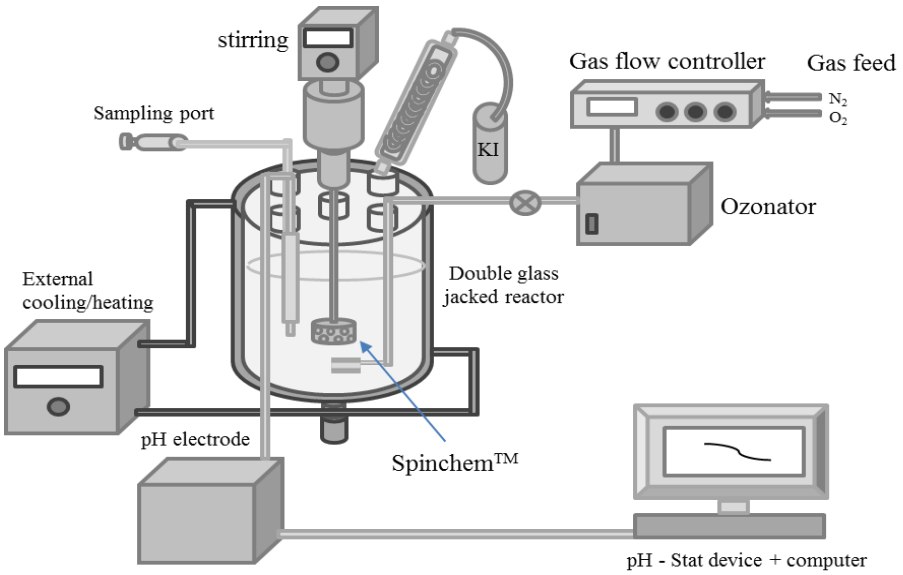
The presence of pharmaceuticals in natural water, drinking water and wastewater has attracted significant concern because of their non-biodegradability, resistance, and toxicity. Due to a globally increasing consumption of pharmaceuticals, a pharmaceutical cocktail has emerged in surface waters and effluents of communities. In the current decade, several studies have been published concerning the occurrence and ecological hazard of the pharmaceuticals and personal care products released into the environment. Some of these pharmaceuticals possess a high-risk to the aquatic life and humankind, because they interact heavily with the ecosystem. Pharmaceuticals are hardly decomposed at all by conventional water treatment technologies due to their chemical stability. For pharmaceuticals, which are resistant to biodegradation processes, an advanced oxidation process (AOP) is necessary.

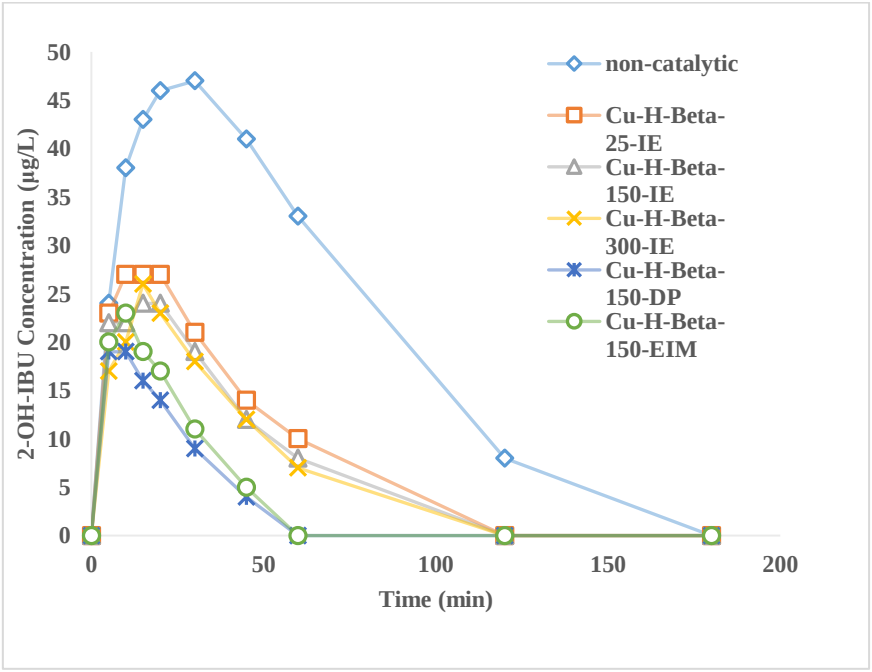
Ozone is generally employed in water treatment due to its solubility, reactivity as well as electrophilic and nucleophilic characteristics. Pharmaceutical components can be at least partially decomposed by ozone treatment. However, it is important that the destruction is complete, and no harmful partially oxidized intermediates appear in the cleaned water. A new, combined method of heterogeneous catalysis and ozonation is developed in this project. Selected, frequently appearing pharmaceutical components, such as ibuprofen are used as model components.

A tailored laboratory-scale equipment was designed to conduct catalyst screening and kinetic ozonation studies. The catalyst was placed in Spinchem TM rotating bed stirrer and ozone was created in situ by an ozonator. Very well reproduced kinetic results were obtained. Solid metal catalysts with various amounts of Lewis and Brønsted acid sites were screened and the the influence of metal particle sizes of Cu, Pd, Fe and Ni in ozone degradation was revealed. The catalyst characterization methods included nitrogen adsorption-desorption, scanning electron microscopy, transmission electron microscopy and Fourier-transform infrared spectroscopy. Inductive coupled plasma spectrometry was used to study potential leaching of Fe, Cu, Ni, Pd in the reaction. Liquid chromatography-mass spectrometry was used for quantification of by-products. NMR spectroscopy was used for product identification.



Scheme of the semi-batch reactor system for the evaluation of heterogeneous catalysts in the degradation of pharmaceuticals in aquatic environment.

The kinetic results revealed that pharmaceuticals can be efficiently removed by the combined treatment with ozone and heterogeneous catalyst. The catalyst metal and the support play a decisive role in the destruction process as was illustrated with the model molecule ibuprofen. By incorporating a heterogeneous catalyst, the amounts of harmful, partially oxidized intermediates can be efficiently suppressed. Detailed kinetic modelling of the ozonation process in progress.



The oxidation kinetics of ibuprofen and the partially oxidized intermediate 2-OH-IBU in the presence of copper catalysts on various supports.

Chemical details in high temperature processes and combustion

Main funding: Academy of Finland (AoF), Business Finland (BF), European Union (EU), Swedish Energy Agency (SEA), Finnish Recovery Boiler Committee (FRBC), Nordic Energy Research (NER), Enova, European Regional Development Fund (ERDF), Graduate School of Chemical Engineering (GSCE), Industrial Partners (IP), ***PCC***

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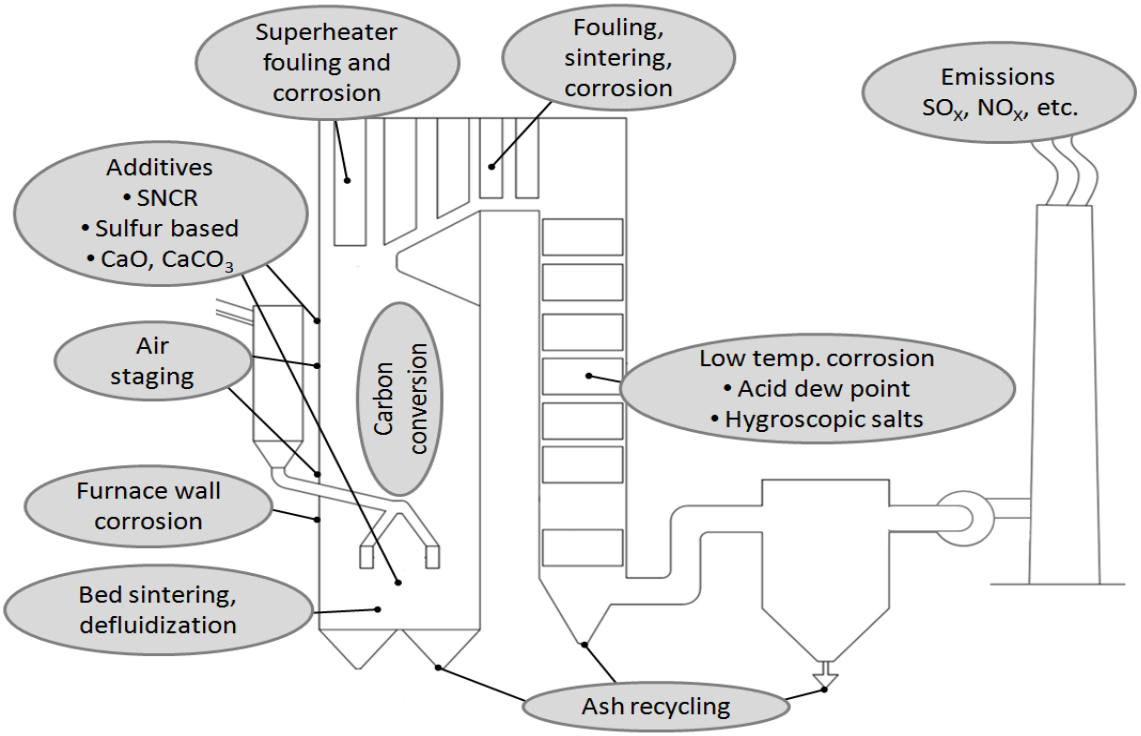
The major part of the research activities at the Combustion and Materials Research group deal with the chemical details in combustion and other high temperature processes. Molecular level understanding of these processes as well as the performance of the refractory materials used in the boilers and furnaces have been in the core of the ***PCC*** activities from the very beginning of the centre. The overall goals of the research are the development of more reliable and efficient boiler technologies as well as to minimize harmful emissions. In addition to being inexpensive energy sources, biomass-derived fuels have a low greenhouse gas footprint. The figure below summarizes our areas in the combustion research.



Chemistry related challenges in biomass combustion (Hupa, M., Karlström, O., Vainio, E., Proc. Comb. Inst. 2017).

We study the impact of low-grade fuels, such as biomasses and various waste-derived fuels on many aspects of the furnace and boiler operation. We develop and apply advanced Computational Fluid Dynamics (CFD) modelling to study the main combustion and the carbon conversion in the

furnaces under different air feed configurations and conditions (*CLUE - clean and efficient utilization of demanding fuels*, *New insight on the ignition of ultra-lean gas combustion,* IP, AoF, ***PCC***). Further, we analyse the tendency of the impurities in the fuels (ash forming matter) to interact with bed materials and to cause agglomeration and defluidization of the bed materials in fluidized bed combustion (*CLUE*, IP) and chemical looping combustion (*Negative CO_2 - Negative CO_2 Emissions with Chemical Looping Combustion of Biomass*, NER).

Some of the renewable fuels contain considerable amounts of elements such as potassium, sodium, zinc, lead, and chlorine, which are known to create fly ash with a low melting point, making the ash more likely to adhere to the heat-transfer surfaces, for instance, the superheater tubes. These ash deposits cause slagging and fouling, which may lead to corrosion of the superheater tubes and at its worst, to unscheduled shutdowns of the power plant. Therefore, more efficient ways to prevent corrosion are needed so that power plants using biomass and waste-derived fuels can operate at higher steam temperatures. From the chemical point of view, although the chloride-induced corrosion has been widely studied, the reaction mechanism is still under debate. In addition, the very onset of the corrosion reaction and the role of different combustion variables (temperature, deposit composition, atmosphere) in it have been scarcely addressed. We study the onset chemistry of the high-temperature corrosion reactions and develop innovative experimental techniques to high-temperature corrosion studies (*Novel approaches to study corrosion mechanisms in high-temperature industrial processes,* AoF*).*

We study the impact of deposit formation on the corrosion of boiler materials (*Behaviour and properties of molten ash in biomass and waste combustion, Negative CO_2, CLUE,* AoF, GSCE, NER, IP), develop predictive tools for understanding the details of the deposit chemistry and for estimating the risk of corrosion of the steels in energy and black liquor recovery boilers (*Understanding the dynamics of intradeposit chemistry and morphology for control of corrosion in high temperature processes*, *Deposits in black liquor boilers*, AoF, GSCE). Solving and understanding the ash-related problems, slagging, fouling and corrosion, is essential also when developing the next generation of biomass-fired combined heat and power plants. In addition, we explore the effect of fuel pre-treatment methods to reduce the content of the problematic inorganic elements chlorine, sulphur and alkali metal in the fuel (*Bioefficiency*, EU).

Corrosion of the boiler materials in the low-temperature range of around 100-420°C caused by chlorides and sulphates of heavy metals (e.g. Pb and Zn), sulphuric acid or by hygroscopic salts has been studied in several projects (*KME-717, Understanding Low-temperature Corrosion in Black Liquor Combustion, In-furnace measurements of deposit build-up and corrosion in a copper flash smelting heat recovery boiler*, SEA, AoF, FRBC, IP). We develop different laboratory testing methods, utilize thermodynamic equilibrium modelling and probe testing in real boiler environments to better understanding of the role of specific compounds on the low-temperature corrosion. The ultimate goal is to develop tools for process optimization and corrosion prevention (WP4).

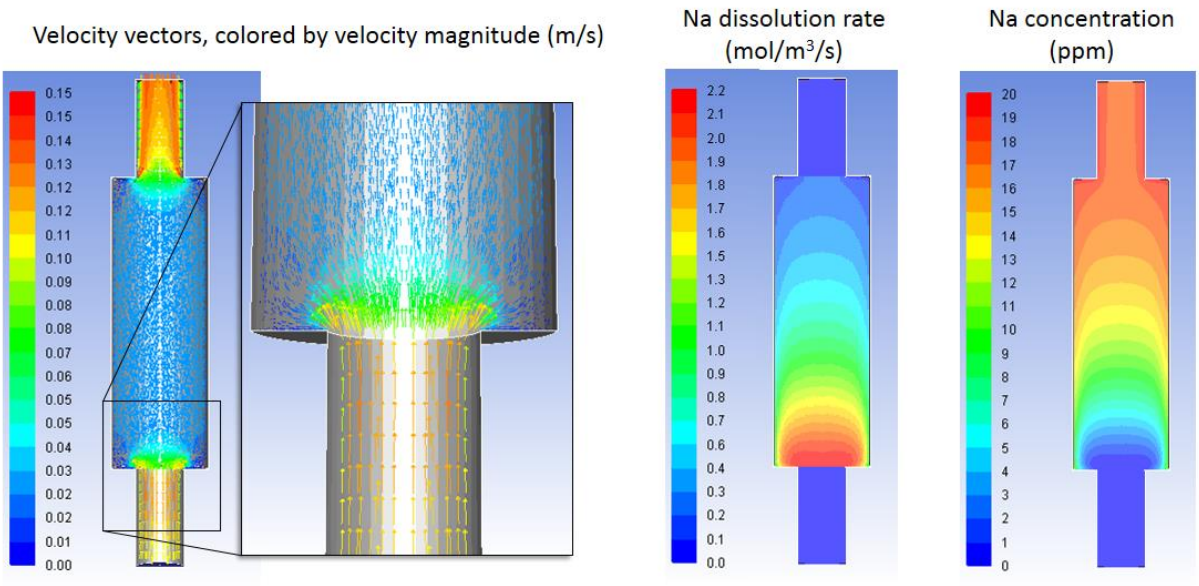
We also characterize the composition of ashes with the goal to understand their impact on the corrosion of the boiler materials and to assess their suitability as secondary raw materials in added-value products (*CircVol - Utilization of side streams and masses of soil the cities, Waste-to-Energy 2030, CLUE,* ERDF, Enova, IP, ***PCC***). In addition, we also study the potential of thermal treatments and different leaching procedures to decrease the content of harmful components in the ashes. Our approaches to study the impact of biomass composition on the emissions are presented in WP4.

Tissue engineering scaffolds based on bioactive glasses

Main funding: Doctoral Network of Materials Research, Graduate School of Chemical Engineering, Business Finland, ***PCC***

Laura Aalto-Setälä, Polina Sinitsyna, Minna Siekkinen, Peter Uppstu, Markus Engblom, Oskar Karlström, Leena Hupa

Over the years, the main goal of our bioactive glass research has been to determine the relationships between the properties and composition of the glasses. We study both the properties controlling the manufacture of the bioactive glass-based devices and the properties of these devices in conditions simulating their target use. One major challenge of the bioactive glass research today is to manufacture 3D implants, so-called tissue engineering (TE) scaffolds, of controlled and interconnected porosity that is similar to the structure of the tissue(s) in the implantation site. We measure and model the thermal properties of relevance for the scaffold manufacture such as the viscosity-temperature relationship and the crystallization kinetics of the glasses. This information is used to select the conditions for the sintering of the TE scaffold, either through simple sintering of particles in molds or through different additive manufacturing (printing) techniques. For the characterization of the in vitro bioactivity and the ion release rate from the scaffolds, we utilize a continuous flow-through reactor. Our reactor has been developed to mimic the dynamic fluid conditions in the body environment. We utilize the rector to define kinetic parameters for the release of the inorganic ions from the glasses. These ions are known to simulate the cellular processes in the regeneration of injured or diseased tissue. Bone regeneration is the best-known application of bioactive glasses. Future plans include implementation of glass dissolution kinetics into a model based on Computational Fluid Dynamics (CFD). The figure below shows conceptually the impact of local fluid flow velocity in the reactor on the concentration profile of sodium ions releasing form the bioactive glass particles in the reactor. Our collaborators carry out the cell culture and in vivo tests of the glasses and TE scaffolds.



Example of CFD simulation concept of flow reactor experiments of dissolution of bioactive glass particles; on left: intra-reactor flow profiles; on right: Na^+ release, with dissolution kinetics implemented as volumetric reaction proportional to local H^+ concentration.

5. Publications 2017 – 2018 (9)

5.1 Theses

5.1.1 Doctoral theses (10)

Brusentsev, Yury, Synthetic modifications of the natural lignan hydroxymatairesinol towards ligands for asymmetric catalysis, 17.2.2017

Hachemi, Imane, Catalytic transformation of algae, tall-oil fatty acids and triglycerides to renewable fules and chemicals, 18.6.2018

He, Ning, Application of Hydrophobic Solid Contacts in Ion-Selective Electrodes, 13.10.2017

Meierjohann, Axel, Application of LC-MS/MS for environmental analysis, 7.9.2018

Nisula, Linda, Wood extractives in conifers – A study of stemwood and knots of industrially important species, 23.2.2018

Pezoa Conte, Ricardo Miguel, Fractionation of marine algae to its constituents towards valuable chemicals and energy products, 20.11.2017

Pinilla de Dios, María, Heterogeneous catalytic copolymerization reactions of carbon dioxide and propylene oxide over polyalcohols under subcritical conditions, Double degree with University of Valladolid, 15.3.2017

Rahkila, Jani, Multivalency in Carbohydrate Chemistry: From Oligosaccharides to Oligovalency and Beyond, 16.2.2018

Russo, Vincenzo, Reactor modelling for fluid-solid systems, 13.10.2017

Yu, Kai, Synthesis, characterization and application of polypyrrole/zeolite composites, 2.6.2017

5.1.2 Master's theses (30)

Alda-Onggar, Moldir, Hydrodeoxygenation of bio-oil model compounds using alumina, zirconia and carbon supported catalysts, 2018

Arandia, Kenneth, Analysis of silicon oil in tall oil products, 2018

Blidi, Slim, Solid-state composite reference electrodes: evaluation in different applications, 2018

Gamaethiralalage, Jayaruwan Gunathilake, Determination of carbonic acid species using carbonate- and novel bicarbonate-selective electrode, 2018

Graeffe, Daniela, Studium av extraherbara näringsämnen i markprover med jonkromatografi och ICP-OES, 2017

Holmbäck, Olle, Alternative, renewable jet fuels – a literature review on their impact on emissions and development status, 2017

Isua-Ikoh, Ime Bassey, Analysis and characterization of biofuel ashes using SEM-EDX and modification for utilization as additives in cement industry – Studies of leaching kinetics, 2017

Jovanovski, Dimitar, Analysis of behavior of biofuel ashes in foaming concrete mixtures based on their composition and leaching kinetics, 2017

Kempe, Rasmus, Hydrering av BLN-lignin under milda förhållanden, 2017

Kholkina, Ekaterina, Synthesis and physico-chemical characterization of slag-based catalysts and their application in catalytic pyrolysis of sawdust, 2017

Koivunen, Niklas, The influence of potassium on the melting properties of kraft recovery boiler smelt, 2017

Lassfolk, Robert, Acetylgruppsmigrering i galaktoglukomannan: en undersökning av modellföreningar, 2017

Li, Changbai, Determination of acetate in wine: comparison between ion chromatography and ion-selective electrodes, 2018

Nylund, Pamela, Dicarbene iridium complexes for C-H activation and C-C bond formation, 2017

Nynäs, Emma, Termisk konversion och behandling av plastrester från biogasanläggningar, 2018

Oña, Jay Pee, Towards calibration-free solid-contact ion-selective electrodes: study and improvement of the standard potential stability, 2018

Rantala, Joni, Determination of bio-oil corrosion, 2018

Råberg, Mathilda, Strukturbaserad läkemedelsdesignstrategi för syntes av biologiskt aktiva stilbener, 2017

Salminen, Patrik, Interaction between potassium salts and bed materials in chemical looping combustion under oxidising conditions, 2017

Sergeeva, Anna, Preparation of iron phosphate by precipitation from pickling acid residue, 2018

Siekkinen, Minna, Effekten av jonkoncentrationen på den kemiska beständigheten på bioaktivt glas i ett kaskadreaktorsystem under kontinuerlig genomstömning, 2018

Strandberg, Mattias, Preparation and properties of cellulose nanofibrils from pulps with different lignin content, 2017

Sinitsyna, Polina, Interactions between kaolin-type minerals and potassium under conditions typical for biomass fluidized bed combustion, 2017

Sjögren, Frida, Karakterisering av CH-Bioforce dissolvingmassa, 2018

Slotte, Robert, From hemicelluloses to sugar alcohols, a process scheme involving hydrolysis of hemicellulose and hydrogenation of sugars, 2017

Storgårds, Frans, Catalytic conversion of hexanol to 2-butyl-octanol through the Guerbet reaction, 2017

Sulman Alexandrina, Hydrodeoxygenation of lignin based model compounds, 2017

Sundelin Heidi, Determination of L-cystein, 2-methyl-1,3-thiazolidine-4-carboxylic acid, acetaldehyde and ethanol in gastric juice and saliva, 2017

Vega, Pablo, Modifying nanocellulose hydrogels with O-acetyl-galactoglucomannan derivatives: tuning the surface hydrophilicity of the fiber surface, 2018

Yrjänä, *Ville*, Potentiometric sensors for the determination of glyphosate concentration, 2017

5.2 Publications 2017

5.2.1 Articles in refereed international scientific journals and series (119)

1. Abdelouahed, L., Leveneur, S., Vernieres-Hassimi, L., Balland, L., Taouk, B., **Comparative investigation for the determination of kinetic parameters for biomass pyrolysis by thermogravimetric analysis**, *Journal of Thermal Analysis and Calorimetry* 129 (2017) 1201–1213

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103. Sukhomlinov, D., Tesfaye, F., Hellsten, N., Lindberg, D., Taskinen, P., **Thermodynamic stability of solid phases in the system Cu-O-Al_2O_3 by means of the EMF and DSC-TGA technique**, *Journal of Solid State Electrochemistry* 22 (2018) 4, 959–972

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115. Wang, Y., Vernières-Hassimi, L., Casson-Moreno, V., Hébert, J.-P., Leveneur, S., **Thermal risk assessment of levulinic acid hydrogenation to γ-valerolactone**, *Organic Process Research & Development* 22 (2018) 9, 1092-1100

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121. Zheng, J. L., Tolvanen, P., Eränen, K., Taouk, B., Salmi, T., Leveneur, S., **Synthesis of carbonated vegetable oils: investigation of microwave effect in a pressurized continuous-flow recycle batch reactor**, *Chemical Engineering Research and Design* 132 (2019) 9–18

122. Zwirchmayr, N., Henniges, U., Bacher, M., Hosoya, T., Potthast, A., Elder, T., Rosenau, T., **Degradation of the cellulosic key chromophores 2,5- and 2,6-dihydroxyacetophenone by hydrogen peroxide under alkaline conditions. Chromophores in cellulosics, XVII**, *Cellulose* 25 (2018) 7, 3815–3826

5.3.2 Review articles in refereed international scientific journals and series (1)

123. Xu, W., Wang, X., Sandler, N., Willför, S., Xu, C., **Three-dimensional printing of wood-derived biopolymers: A review**, *ACS Sustainable Chem. Eng.* 6 (2018) 5, 5663-5680

5.3.3 Books and book chapters (10)

124. Ekholm, F. S., Leino, R., **Acyl Migrations in Carbohydrate Chemistry**, in: Vidal, S., Ed. *Protecting Groups: Strategies and Applications in Carbohydrate Chemistry,* Wiley-VCH: Weinheim, 2018, ISBN: 978-3-527-69701-4

125. Eriksson, J.-E., Khazraie, T., Hupa, L., **Different methods for the characterization of ash compositions in co-firing boilers**; In: Sun Z. et al. (eds) *Energy Technology 2018, Minerals, Metals & Materials Series, Part F6*, pp. 253–263

126. Hamuyuni, J., Halli, P., Tesfaye, F., Leikola, M., Lundström, M., **A sustainable methodology for recycling electric arc furnace dust**; in: Sun, Z. et al. (eds) *Energy Technology 2018, Minerals, Metals & Materials Series, Part F6*, pp. 233–240

127. Hupa, L., Wang, X., Eqtesadi, S., **Springer Handbook of Glass**; *Bioactive glasses*, (2018). Accepted for publication

128. Khokarale, S.G., Anugwom, I., Mäki-Arvela, P., Virtanen, P., Mikkola, J.-P., **Switchable Polarity Liquids**; In: Eftekhari, A. (ed.) *Polymerized Ionic Liquids in Smart Materials Series*, Chapter 5, RSC publishing 2018, print ISBN 978-1-78262-960-3, PDF eISBN 978-1-78801-053-5, EPUB eISBN 978-1-78801-221-8, ISSN 2046-0066, http://pubs.rsc.org/en/content/ebook/978-1-78262-960-3

129. Lindberg, D., Vainio, E.,Yrjas, P. (2018) **Thermal separation and leaching of valuable elements from waste-derived ashes**; In: Sun Z. et al. (eds) Energy Technology 2018, Minerals, Metals & Materials Series, Part F6, pp. 241-252

130. Liu, J., Willför, S., Xu, C., **Tuning microscopic and mechanical properties of bio-based aerogels**; In: Sabu Thomas, Laly A. Pothan, Rubie Mavelil-Sam, eds., *Biobased aerogels: Polysaccharide and Protein-based Materials*, Green Chemistry Series No. 58, Royal Society of Chemistry (2018), 201-219, eISBN: 978-1-78801-519-6, print: ISBN: 978-1-78262-765-4

131. Moroz, M., Tesfaye, F., Prokhorenko, M., Demchenko, P., Lindberg, D., Reshetnyak, O., Hupa, L. **Thermodynamic properties of magnetic semiconductors $Ag_2FeSn_3S_8$ and Ag_2FeSnS_4 determined by the EMF method**; In: Lambotte G. et al. (eds) Materials Processing Fundamentals 2018, Minerals, Metals & Materials Series, Part F2, pp. 87–98

132. Murzin, D. Yu., **Chemical Product Technology;** 269p., De Gruyter, 2018, https://www.degruyter.com/view/product/472332?format=B, ISBN 978-3-11-047531-9.

133. Tesfaye, F., Lindberg, D., Hupa, L. **The K_2SO_4-$CaSO_4$ system and its role in fouling and slagging during high-temperature processes**; In: Lambotte G. et al. (eds) Materials Processing Fundamentals 2018, Minerals, Metals & Materials Series, Part F2, pp. 133-142.

5.3.4 Articles in refereed international edited volumes and conference proceedings (8)

134. Huttula, M., Patanen, M., Piispanen, R., Ohigashi, T., Kosugi, N., Swaraj, S., Belkhou, R., Pranovich, A., Jyske, T., Kilpelainen, P., Karkonen, A., Korpinen, R., Laakso, T., Valkonen, S., Saranpää, P., **STXM chemical mapping of Norway spruce knotwood lignans**, *Microscopy and Microanalysis* (Proceedings of the 14th International Conference on X-ray Microscopy (XRM2018)) 24 (2018) S2, 482–483

135. Lindberg, D., Niemi, J., Engblom, M., Laurén, T., Yrjas, P., Hupa, M., **Experimental and modeling approaches to simulate temperature-gradient induced intradeposit chemical processes with implications for biomass boiler corrosion**, 23rd International Conference on FBC, Grand Ambassador Seoul, Seoul, South Korea, May 13 - 17, (2018) C9-1, pp. 1124–1134

136. Prestipino, M., Galvagno, A., Karlström, O., Brink, A., **Predicting reactivity and conversion profile of agro-industrial residues in steam gasification processes: A kinetic approach**, 26th European Biomass Conference and Exhibition -EUBCE 2018.

137. Strand, A., Kouko, J., Oksanen, A., Salminen, K., Ketola, A., Retulainen, E., Sundberg, A., **Boosting the elongation potential of paper by mechanical refining and additives**, PaperCon 2018, Charlotte 16-18.4.2018, ISBN: 978-1-59510-268-3

138. Tesfaye, F., Moroz, M., Lindberg, D., Hupa, L., Jung, I.-H., **Thermodynamic Investigation of Selected Metal Sulfates for Controlling Fouling and Slagging During Combustion**, 23rd International Conference on FBC, Grand Ambassador Seoul, Seoul, South Korea, May 13 - 17, (2018), C7-4, pp. 1070–1077

139. Vainio, E., Hupa, E., Engblom, M., Lehmusto, J., Lindberg, D., **A novel method to detect hydrate formation and deliquescence of salts and deposits related to low-temperature corrosion**, 23rd International Conference on FBC, Grand Ambassador Seoul, Seoul, South Korea, May 13 - 17, (2018), A8-3, pp. 310–317

140. Vainio, E., Mannisto, T., Hupa, L., Zabetta, E.C., Vänskä, K., **High-temperature erosion studies of boiler materials**, 23rd International Conference on FBC, Grand Ambassador Seoul, Seoul, South Korea, May 13 - 17, (2018), B8-3, pp. 712–721.

141. Yrjas, P., Carbo, M., Janssen, A., Abelha, P., Leino, T., Hupa, L., **Influence of fuel pre-treatments on ash-forming elements and implications on corrosion**, 23rd International Conference on FBC, Grand Ambassador Seoul, Seoul, South Korea, May 13 - 17, (2018), C9-2, pp. 1135–1143

5.4 Edited conference proceedings and reports

Grénman, H., Latonen, R-M., Mäki-Arvela, P., Saloranta-Simell, T., Sundberg, A., Werkelin, J. (eds) Åbo Akademi Johan Gadolin Process Chemistry Centre Annual Report 2016-2017, Åbo Akademi University, 2017, ISSN: 1459-8213, Painosalama, Turku, Finland, 2017

5.5 Patents and invention disclosures

5.5.1 Patents

Mavrynsky, Denys, Leino, Reko, **Method for preparation of thiomannoside derivatives**, Eur. Pat. Appl. (2017), EP 3252056 A1 20171206

Mavrynsky, Denys, Leino, Reko, **Method for preparation of thiomannoside derivatives**, PCT Int. Appl. (2017), WO 2017207542 A1 20171207

Mikkola, Jyri-Pekka, Samikannu, Ajaikumar, Vanklint, Kent, Siljebo, William, **Conversion of alcohols to hydrocarbons using a dual catalyst system comprising basic oxide on mixed oxide or mesoporous carrier and etched metal loaded zeolite catalyst**, PCT Int. Appl. (2017), WO 2017111691 A1 20170629.

Nowicki, J., Muszynski, M. Mikkola, J.-P., **Process for preparing fluorinated basic ionic liquids** PL 224608 B1 20170131.
Rahkila, Jani, Leino, Reko, Savolainen, Johannes, **Immunostimulatory adjuvants and uses thereof**, PCT Int. Appl. (2017), WO 2017109288 A1 20170629

Sokalski, Tomasz, Lewenstam, Andrzej, Mousavi, Zekra, Granholm, Kim, **A reference electrode and an arrangement for an electrochemical measurement,** Application No. 14/652,080, approved for grant in United States of America.

5.5.2 Inventions disclosures

Mikkonen, K., Tenkanen, M., Xu, C., Willför, S., BITE-project, **Use of non-starch, non-cellulosic plant polysaccharide-rich extracts to stabilize alkyd oil emulsion in paint formulation**

5.6 Awards granted

Aalto-Setälä, Laura and Uppstu, Peter
"Bone savers – Enhanced treatment of large bone defect", first prize in the Åbo Akademi Innovation Catalyst innovation competition, 2018

Aalto-Setälä, Laura
Winner of the writing competition of scientific and research articles to the magazine "Tiede": Biolasi muuttuu luuksi ja taistelee superbakteereja vastaan (Bioactive glass transforms into bone and battles against bacteria), 2018

Hupa, Leena and Lindberg, Daniel
Members of the team HeatStock (New materials for long-term heat storage), shared 1st place in the Helsinki Challenge competition, 2017

Korotkova, Ekaterina,
Best oral presentation award, Renewable plant resources: chemistry, technology, medicine 2017, St. Petersburg, Russia

Pranovich, Andrey,
Elected as Fellow of the International Academy of Wood Science / IAWS, 2017

Salmi Tapio, Shumilov, Vladimir, Eränen, Kari, Kumar, Narendra, Hupa, Leena, Murzin, Dmitry, Boden, Stefan, Schubert, Markus, Hampel, Ulrich, Sulman, E.,
Excellent Poster Award, CAMURE-10 & ISMR-9, Qingdao, P.R. China, July 2017

Werkelin, Johan,
Best Poster Award, Keramiktillverkning i vedeldad brännugn (Ceramics in a wood-fired Kiln), Finlandssvenska Fysik- och Kemidagarna 2017, Helsinki, Finland

Zhang, Yongchao,
China Scholarship Council 09. 2017-08. 2018 (24 months), GSCE Funding 09.2016-05.2017

Xu, Wenyang,
Best oral award on 15th European Workshop on Lignocellulosics and Pulp (EWLP), Aveiro, Portugal

6. External interactions

6.1 Organization of conferences/courses/meetings

Industrial lignin seminar: ”You can make anything out of lignin – also money”, 4.5.2017, Åbo Akademi University

Modern Analytical Tools for Pulp and Paper, Dec 2017, Åbo Akademi University

6.2 Visitors and visits

Visitors

Abad, Javier-Ibánez, Université de Lille 1, France, 1.4-31.8.2018, 5 months, **Johan Gadolin Scholarship**

Adhami, Shekoufeh, Islahan University, Teheran, Iran, 1.1-1.7. 2017, 28 weeks, **Johan Gadolin Scholarship**

Akhmetzyanova Uliana, Unipetrol Centre for Research and Education, Czech Republic, 1.1-28.2.2017, 8 weeks

Alexis Lebeau, Rouen France, Erasmus student (6 months), 15.5-15.11.2018

Attah-Kyei, Desmond, Stellenbosch University, South Africa, April – May 2018

Balint, Roland, Technische Universität München, Germany, October 2017 – March 2018

Bembaron, Julia, INSA Rouen, France, 11-6-17.8.2018, 3 months

Benabidi, Bilal, Institute of Technology, St. Petersburg, Russia, August 2017, 3 weeks

Benouadah, Nacéra, M'Hamed Bougara University, Boumerdesm, Algeria, October 2016 - June 2017, **Johan Gadolin Scholarship**

Bomont, Louis, ENSACAEN, France, 3.4-21.7. 2017, 15 weeks

Bollella, Paolo, University of Rome “La Sapienza”, Italy, August-September 2018, **Johan Gadolin Scholarship**

Cai, Xiaoshuang, Institut National des Sciences Appliquées (INSA) Rouen, France, 01.10.18-28.02.19, **Johan Gadolin Scholarship**

Corcoran, Angelica, Chalmers University of Technology, Sweden, August 2017

Chaperon, Sarah, École Nationale Supérieure de Chimie de Rennes, France, 2018, 3 months

Cisse, Maperda, INSA Rouen, France, 11.6-31.8.2018, 3 months

Coudoz, Antoine, INSA, Rouen, France, 12.6.-5.9. 2017, 11 weeks

Daigue, Emilieu, INSA, Rouen, France, 15.11. 2017-15.5. 2018, 6 months

Diamond, Dermot, Dublin City University, Ireland, May 2017

Dorofeeva, Liza, St. Petersburg University of Technology, Russia, 22.11-20.12. 2017, 4 weeks

Eliason, Felicia, Chalmers University of Technology, Sweden, February – May 2018

Fernanda Gutierrez Sanchez, Maria, Universidad Nacional, Bogota, Columbia 19.9.-31.12. 2017, 14 weeks

Fedorov, Vyacheslav, St. Petersburg University of Technology, Russia, 20.7.-25.8. 2017, 3 weeks

Galasheva, Sofia, St. Petersburg University, Russia, August 2017

Godino, Andres Morato, University Carlos III of Madrid, Spain, October 2017 – January 2018 and August – September 2018

Gonzalez Carlos Rosales, University of Vallidolid, Spain, 25.8.2017.-31.5. 2018,9 months

Hemery, Remi, INSA Rouen, France, 9.6-31.8.2018, 3 months

Hildor, Fredrik, Chalmers University of Technology, Sweden, January-May 2017

Hornbogen, Thomas, Technical University of Dresden, Germany, 1.4-31.8. 2017, 20 weeks

Ho-Wen-Tsa, *Anrnung*, INSA Rouen, France, 11-6-31.8.2018, 3 months

Itterheimová, Petra, Masaryk University, Czech Republic, January-June 2018

Ke, Xiwei, Tsinghua University, China, 13.08.2018-16.12.2018*,* **Johan Gadolin Scholarship**

Khaydukova, Maria, Saint-Petersburg State University, Russia, August 2017 – October 2018, **Johan Gadolin Scholarship**

Kolobova, Ekaterina, Tomsk Polytechnic University, Russia, November 2017, 4 weeks

Kovács, *Barbara,* University of Szeged, Hungary, 2017, **Johan Gadolin Scholarship**

Krauß, Annabelle, University of Stuttgart, Germany, 2018

Lecomte, Correntin, INSA, Rouen, France, 12.6-5.9. 2017, 11 weeks

Le Guillant, *Amadelie*, INSA Rouen, France, 11.6-31.8.2018, 3 months

Link, Siim, Tallinn University of Technology, Estonia, January – September 2017

Lozachmeur, Chlóe, INSA Rouen, France, 11.6-18.8.2018

Mael, Laurent, INSA, Rouen, France, 12.6-5.9. 2017, 11 weeks

Maráková, Nela, Tomas Bata University, Czech Republic, February-March 2017

Marchetti, Jorge Marchetti, Associate Professor at NMBU - Norwegian University of Life Sciences, Norway, February 2017

Martin, Kerli, University of Tartu, Estonia, April-September 2017, **Johan Gadolin Scholarship**

Matveeva, Anna, St. Petersburg University of technology, Russia, 22.11-20.12. 2017, 4 weeks

Mendez, Carolina, Universidad de Chile, Chile, 01.04.2018-30.11.2018, **Johan Gadolin Scholarship**

Miró, Manuel, University of the Balearic Islands, Spain, May 2017

Moro Lobo, Alberto, University of Vallidolid, Spain, 6.9.2107-30.6.2018, 10 months

Moroz, Mykola, National University of Water and Environmental Engineering, Ukraine, 01.05.2017-31.10.2017, **Johan Gadolin Scholarship**

Nuri, Ayat, University of Mohaghegh Ardabili, Iran, 15.2-15.10.2018, 8 months

Näykki, Teemu, Finnish Environment Institute (SYKE), Finland, May 2018

Ocaña, Cristina, Autonomous University of Barcelona (UAB), Spain, January-March 2017

Oger, Adrien, INSA, Rouen, France, 12.6–5.9. 2017, 11 weeks

Ospina, Marcela Arango, Institute of Biomaterials, Friedrich Alexander Universität Erlangen-Nuremberg, Germany, 01.08.2018-31.10.2018*,* **Johan Gadolin Scholarship**

Ozanne Sophie, INSA, Rouen, France, 7.5-16.8.2018, 3 months

Papp, Soma, Budapest University of Technology and Economics, Hungary, August-November 2018, **Johan Gadolin Scholarship**

Park, Kyoungil, Korea Electric Power Corporation, Seoul, South Korea, May 2017

Prestipino, Mauro, University of Messina, Italy, 08.08.2017-31.10.2017, **Johan Gadolin Scholarship**

Riabukhin, Dmitry, Saint-Petersburg State Forest Technical University, Russia, June 2017- February 2018, **Johan Gadolin Scholarship**

Rossello, Teresa Marti, University of Strathclyde, Glasgow, United Kingdom, May – June 2018

Santos Munoz, Jose Luis, University of Sevilla, Spain, 5.8.-10.11. 2017, 12 weeks

Salazar, Dahiana Andrea Avila, Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Germany, 01.08.2017-30.11.2017, **Johan Gadolin Scholarship**

Sanz Moral, Lius Miguel, Vallidolid, Spain, 1.4-30.9. 2017, 24 weeks, **Johan Gadolin Scholarship**

Schaaf, Jonah, Technical University of Dresden, Germany, 1.4-31.8. 2017, 20 weeks

Schuhladen, Katharina, Institute of Biomaterials, University of Erlangen-Nuremberg, Germany, 01.08.2017-15.12.2017, **Johan Gadolin Scholarship**

Schwarzer, Lars, Technical University of Denmark, August – December 2017

Seumo, Patrick, University of Yaounde I, Cameroon, September-December 2017, **Johan Gadolin Scholarship**

Shcherban, *Nataliya*, L. V. Pisarzhevsky Institute of Physical Chemistry, National Academy of Sciences, Ukraine, 1.5.-30.7. 2017, 12 weeks, **Johan Gadolin Scholarship**

Shchukina, Anastasia, St. Petersburg University, Russia, August-September 2018

Sitdikov, Ruzal, Kazan Federal University, Russia, 01.08.2017-30.04.2018, **Johan Gadolin Scholarship**

Stiller, Adrian, University of Ulm, Germany, January – May 2018

Supala, Eszter, Budapest University of Technology and Economics, Hungary, August-September 2017

Tieuli, Sebastiano, Ca'Foscaro, Venezia, Italy, 4.12.2017-7.3.2018, 3 months

Torres, Gaetan, INSA Rouen, France, 19.2-27.4.2018, 2 months

Truffier-Blanc, Julius, INSA Rouen, France, 11.6-31.8.2018

Wagner, Karin, Salzburg University of Applied Sciences/Salzburg University, Austria, August - September 2017

Vajglova, Zuzana, Institute of Chemical Process Fundamentals of the ASCR, Czech Republic, 01.04.2017-30.06.2017, **Johan Gadolin Scholarship**

Wei, Lingyuan, Delft University of Technology, the Netherlands, 3-7/2018, 5 months

Winter, Elise, INSA, Rouen, France, 12.6-5.9.2017, 11 weeks

Xu, Huanfei, Quingdao University of Science and Technology, China, 01.09.2018-28.02.2019, **Johan Gadolin Scholarship**

Yin, Tanji, Yantai Institute of Coastal Zone Research, China, August-November 2018, **Johan Gadolin Scholarship**

Zergane, Hichem, University of Science and Technology Houari Boumadiene (USTHB), Algeria, September-November 2018

Visits

Boeva, Zhanna, Budapest University of Technology and Economics, Hungary, June 2017 and June 2018

Boeva, Zhanna, New York University, Tandon School of Engineering, USA, March-May 2017

Boeva, Zhanna, Georgia Institute of Technology, USA, September-October 2018

Grenman Henrik, visiting researcher, Delft University of Technology, Process and Energy, The Netherlands, 7/2017-1/2018

Joon, Narender Kumar, Delhi Technological University, India, March 2017

Joon, Narender Kumar, Nanyang Technological University, Singapore, April 2017

Joon, Narender Kumar, Malmö University, Sweden, August-September 2017

Karlström, Oskar, Technical University of Denmark, March – July 2017

Korotkova, Ekaterina, Tver State Technical University, Russia, 18.04.2017-28.04.2017 and 25.09.2017-29.09.2017

Lehmusto, Juho, Oak Ridge National Laboratory, Tennessee, USA, July – December 2018

Lindberg, Daniel, Polytechnique Montréal, Montreal, Canada, October – December 2017

Lindfors, Tom, Budapest University of Technology and Economics, Hungary, June 2017

Lindfors, Tom, Budapest University of Technology and Economics, Hungary, May-June 2018

Pranovich, Andrey, St. Petersburg Forest Technical University, Faculty of Chemical Technology and Biotechnology, Russia, April 2017 and April 2018

Rahkila, Jani, Cic BioGune, Bilbao, Spain, February 2017

Runeberg, Patrik, CNRS, Laboratoire de Chimie de Coordination (LCC), Institut Universitaire de Technologie, Paul Sabatier, Castres, France, April 2017

Savela, Risto, Technical University of Dortmund, Germany, April-June 2018

Sundberg, Anna and Willför, Stefan, University of Natural Resources and Life Sciences (BOKU), Vienna, Austria, November 2017

Sundberg, Anna, RISE, Sweden, August 2018

Tesfaye, Fiseha, Seoul National University, South Korea, March – August 2018

Vainio, Emil, University of Borås, Sweden, August – December 2017

Wang, Xioaju, University of Wollongong, New South Wales, Australia, January – May 2017

Xu, Chunlin, University of Wollongong, New South Wales, Australia, January – May 2017

Xu, Wenyang, University of Wollongong, New South Wales, Australia, July - November 2017

Zhang, Yongchao, Lakehead University, Canada, January – July 2018

6.3 External evaluations and reviews

External evaluations

Evaluator of research proposals/member of evaluation panels for FCT Fundacao para a Ciencia e a Tecnologia (Portugal), ARRS Slovenian Research Agency, Latvian Council of Science, European Research Council (ERC), Belgian Fund for Scientific Research (FNRS), *Reko Leino*

Vice-chair of H2020-MSCA-ITN-2017, H2020-MSCA-ITN-2018 and H2020-MSCA-IF-2017 evaluation panels and final evaluation of two FP7-MC-ITN projects for EU Research Executive Agency (REA), *Reko Leino*

Evaluation of proposals in the EU H2020 Marie-Skłodowska-Curie Actions-IF-ST-CHE, vice chair, 2017, Brussels, *Päivi Mäki-Arvela*

Evaluation of proposal in Norwegian Research Council, October, 2017, *Päivi Mäki-Arvela*

Evaluation of proposals in the EU H2020, 2017, 2018, vice chair, *Päivi Mäki-Arvela*

Evaluation of European Synchrotron Radiation Facility Application, May 2017, *Päivi Mäki-Arvela*

Evaluation of Haldor Topsoe PhD scholarship program, 2017, 2018, *Dmitry Murzi*n

Evaluation of Applications in French National Agency of Science, *Dmitry Murzi*n

Evaluation of Applications in Danish Science Foundation, *Dmitry Murzin*

Evaluation of Applications in UK Science Foundation, *Dmitry Murzin*

Evaluation of Applications in Kazakhstan Science Foundation, *Dmitry Murzin*

Referee, ERC Starting Grant, *Dmitry Murzin*

Evaluation of proposal, FONDECYT, Research council in Chile, July, 2018, *Päivi Mäki-Arvela*

Evaluation of ISCRE conference abstracts, *Henrik Grénman*

Evaluation of proposals in the EU H2020 Marie-Skłodowska-Curie Actions-IF-2017, *Z. Boeva*

Doctoral thesis evaluations

Almanasrah, Mohammad, Lappeenranta University of Technology, Finland, reviewer and opponent, *Stefan Willför*, 2017

Bicheng Zhu, the University of Auckland, New Zealand, external reviewer, Tom Lindfors, 2017

Camacho, A. R., University of Valladolid, evaluator of doctoral thesis, *Dmitry Murzin*

da Costa Lopes André Miguel, Faculdade de Ciências e Tecnologia da U.N.L., Lissabon, opponent, Jyri-*Pekka Mikkola*, 2017

Dong Yue, University of Oulu, evaluator *Päivi Mäki-Arvela*, 2017

Gallina, S. Gianluca, Universidad de Valladolid, tribunal member, Jyri-*Pekka Mikkola,* 2018

Hantzlik Anne, Technische Universiteät Dresden, opponent, *Tapio Salmi*

Huiran Lu, KTH Royal Institute of Technology, Sweden, evaluation committee member, *Tom Lindfors, 2017*

Ibanez Abad, J., University of Lille, referee of doctoral thesis, *Dmitry Murzin*

Jennifer Jarvis, University of Memphis USA, Opponent for the doctoral thesis*, Johan Bobacka, 2018*

Keskiväli, Juha, University of Helsinki, opponent, *Leino Reko*, 2018

Lauberts, Māris University of Latvia, Latvia, official opponent/reviewer, *Andrey Pranovich*

Li Yunxiang, Stockholm University, opponent, *N. Kumar*, 2017

Lin Rongzhou, Nanyang Technological University, Singapore, Examiner of the doctoral thesis, Johan Bobacka2017

Montecchio Francesco, KTH Royal Institute of Technology, Sweden, evaluation committee member, *Henrik Grénman*, 2018

Nissinen, Ville, University of Eastern Finland (Joensuu), opponent, *Reko Leino* 2017

Ocwelwang, Atsile Rosy, University of Kwazulu-Natal, South Africa, reviewer, *Stefan Willför* , 2017

Paunovic Vladimir, ETH Zurich*, Dmitry Murzin, 2018*

Pinilla De Dios Maria, Universidad de Valladolid, opponent, *N. Kumar,* 2017

Quesada Sanchez Jorge, Univerity of Oviedo*, Dmitry Murzin, 2018*

Ramnath, Lucretia, University of Kwa-Zulu-Natal, South Africa, external evaluation, *Anna Sundberg*, 2017

Sanchez Álvaro Cabeza, Universidad de Vallidolid, Dmitry Murzin, 2018

Schedl, Andreas, University of Natural Resources and Life Sciences (BOKU), Vienna, Austria, reviewer, *Stefan Willför*, 2017

Schneider, Laura, University of Oulu, opponent, *Päivi Mäki-Arvela*, 2017

Terrades Llorenc Gavila, Universitat Rovira i Virgili, Tarragona, Spain, opponent, *J.-P. Mikkola,* 2017

Wirtanen Tom, University of Helsinki, evaluator, *Päivi Mäki-Arvela*, 2017

Xiao Huang, Uppsala University, Sweden, evaluation committee member, *Tom Lindfors, 2018*

Zdeňka Jarolímová, University of Geneva, Switzerland, Opponent for the doctoral thesis*, Johan Bobacka, 2017*

Evaluation of candidates

Stephen Ralph, University of Wollongong, External assessor for academic promotion of Associate Professor to Professor (Level E)*, Johan Bobacka, 2017*

Editorial boards

Catalysis today, editorial board member, *Dmitry Murzin*

Catalysis for Sustainable Energy, editorial board member, *Dmitry Murzin*

Chemistry of Plant Raw Material (KHIMIIA RASTITEL'NOGO SYR'IA), editorial board member, *Andrey Pranovich, Bjarne Holmbom*

Bulletin of Chemical Reaction Engineering and Catalysis, regional editor for Europe, *Dmitry Murzin*

Bulletin of St. Petersburg State Institute of Technology, editorial board member, *Dmitry Murzin*

Catalysis in Industry, Associate editor and editorial board member, *Dmitry Murzin*

Catalysis Letters, scientific advisory board, editorial board member, *Dmitry Murzin*

Cellulose Chemistry and Technology, editorial board member, *Bjarne Holmbom, Stefan Willför*

Chemosensors (MDPI), Editorial Board member, *Johan Bobacka*

Current Catalysis, editorial board member, *Dmitry Murzi*n

Current topics in electrochemistry (Research Trends), Editorial Board member, *Johan Bobacka*

Electrochimica Acta (Elsevier), Editorial Advisory Board member, *Johan Bobacka*

Frontiers in Chemistry, Green and Environmental Chemistry, editorial board member, *J.-P. Mikkola*

Holzforschung, editorial board member, *Bjarne Holmbom, Stefan Willför*

International Journal of Chemical Engineering, editorial board member, *Dmitry Murzin*

Izvestija Sankt-Peterburgskoj Lesotehnicheskoj Akademii, editorial board member, *Andrey Pranovich*

Jacobs Journal of Materials Science, editorial board member, *Andrey Pranovic*h

Journal of Engineering, editorial board member, editorial board member, *Dmitry Murzin*

Journal of Wood Chemistry and Technology, editorial board member, *Stefan Willför*

Kinetics and Catalysis, editorial board member, *Dmitry Murzin*

Nordic Pulp and Paper Research Journal, member of editorial board, *Anna Sundberg,* member of scientific advisory board*, Stefan Willför*

O´Papel, editorial board member, *Bjarne Holmbom*

Progress in Industrial Ecology, editorial board member, *J.-P. Mikkola*

Russian Journal of Chemical Industry, editorial board member, *Dmitry Murzin*

Sensing and Bio-Sensing Research (SBSR), editorial advisory board member, *Tom Lindfors*

Sensors and Actuators B: Chemical (Elsevier), Editor, *Johan Bobacka*

The Open Catalysis Journal, *Dmitry Murzin*

Topics in Catalysis, scientific advisory board, *Dmitry Murzin*

Wood Science and Technology, editorial board member, *Bjarne Holmbom*

Member of scientific committees and boards

International Symposium on Chemical reaction Engineering, ISCRE2018, Firenze, *Tapio Salmi*
CHISA 2018, *Tapio Salmi*

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

Delft Process Technology Institute (DPTI), TU Delft, member of international advisory board, *Tapio Salmi*

25th International Symposium of Chemical Reaction Engineering (ISCRE), reviewer, *Henrik Grenman*

Bio4Energy research programme (Swedish government) 2009- (www.bio4energy.se), Steering Group member *J.-P. Mikkola*

Biocity Turku SmartBio research program "Advanced Bioresources and Smart Bioproducts – Towards Sustainable Bioeconomy", Vice-chair, *Stefan Willför*

Biofuel Technology Center (www.btk.slu.se), SLU, (Sweden), scientific advisory board member, *J.-P. Mikkola*

Biorefinery of the Future 2008- (www.bioraffinaderi.se). RISE PROCESSUM AB, Member of the Research & Development Council, *J.-P. Mikkola*

Chemical Industry, "Kemianteollisuuden tieteellinen neuvottelukunta, Kemianteollisuus ry, scientific advisory board member, S*tefan Willför*

CATBIOR 2017, Lyon, France, Member of the scientific committee, *Dmitry Murzin*

CatBior 2019, Åbo-Turku, Finland, Member of the scientific committee, *J.-P. Mikkola*

ERC Consolidator Grant, panel member, *Dmitry Murzin*

EU COST action FP1306, Deputy member of the Management Committee, *Stefan Willför*

Industrial Biotechnology Cluster Finland (IBC Finland), board member, *Stefan Willför*

Institute of Human Rights, ÅAU, board member, *Stefan Willför*

International Conference of Chemical Technology 2016, Member of the scientific committee, Mikulov, Czech Republic, *Dmitry Murzi*n

National Bioeconomy, Panel member appointed by the Ministry of Employment and the Economy, *Stefan Willför*

Research Ethics of ÅAU, board member, *Stefan Willför*

Renewable Resources: Chemistry, Technology, Medicine, International conference in St. Petersburg Russia, scientific advisory board member, *Stefan Willför*, co-chairman and co-organizer, *Andrey Pranovich*

Russian Congress on Catalysis, Nizhnii, Novgorod, Russia, Session chairman, *Dmitry Murzin*
Shareholder Forum and in the Bioeconomy task force for Clic Innovation Ltd, ÅAU representative, *Stefan Willför*

SpinChem AB, Scientific advisory board, *J.-P. Mikkola*

The Vasa Ship Preservation, member of council, Sweden, *Bjarne Holmbom*

Biocity Turku Research Programme: Diagnostics Technologies and Applications Programme, Board member (vice director), 2018- *Johan Bobacka*

Member of the Publication Forum (JUFO) Panel *4 (Chemistry),* 2014-2017 *Anna Sundberg*, 2018- *Johan Bobacka*

Academic board member of the Erasmus Mundus Joint Master Degree Programme "EACH – Excellence in Analytical Chemistry", *Johan Bobacka*

Board member, scientific advisor and co-founder of the start-up company GlucoModicum Oy, *Johan Bobacka*

President of the Chemistry Club "Kemistklubben vid Åbo Akademi r.f.", *Johan Bobacka*

Academy of Finland, Research Council for Natural Sciences and Engineering (2016-18), *Reko Leino*

National Research Infrastructure Committee (TIK) (2018), *Reko Leino*

Board member, Walter Ahlströms foundation, 2018-*, Anna Sundberg*

7. Doctoral theses in progress at *PCC*

Aalto-Setälä, Laura (MSc 2014, University of Helsinki): *Gradient-Structured Bio-Engineered Implant Surfaces*

Ahamed, Ashiq (MSc 2012, Nanyang Technological University): *Material Characterization and Ecotoxicity Assessment of Spent Nanomaterial in Marine Ecosystem*

Akhmetzyanova, Uliana (MSc 2013, Tver Technical University, MSc 2015, Åbo Akademi University): *Hydroconversion of Biomass Derivatives over Heterogeneous Catalytic Systems Based on Transition Metal Carbides, Nitrides, and Phosphides*

Arroyo Condori, Jesús (MSc 2011, Åbo Akademi University): *Electrochemically Controlled Chromatographic Separations*

Balint, Roland (MSc 2018, Technical University of Munich): *Boiler Deposit Aging – the Influence of Temperature Gradient on Intra-Deposit Transport Phenomena*

Behravesh, Erfan (MSc 2014, Åbo Akademi University): *Millistructured Flow Chemistry for Oxidation Processes of Molecules from Biomass*

Björkvik, Leena (MSc 2011 Åbo Akademi University): *Bioactive Glass Composites*

Bruun, Nina (MSc 1984, Åbo Akademi University): *Challenge of Bio-Oil in Marine Engines*

Dirbeba, Meheretu Jaleta (MSc 2013, Addis Ababa University): *Characterization of Biomass-Containing Industrial Byproducts for Thermochemical Conversion*

Freites, Asdriana (MSc 2015, University of Simon Bolivar): *Epoxidation of Vegetable Oils under Microwave Irradiation, Process Intensification for Biomass Conversion*

Godina, Lidia (MSc 2012, Mendeleyev University of Chemical Technology): *Understanding Catalysis and Hydrothermal Stability of Carbon Supported Noble Metals for Sustainable Fuel Production by Aqueous Phase Reforming*

Han, Tingting (MSc 2008, Åbo Akademi University): *Novel Signal Readout Principle for Solid-Contact Ion-Selective Electrodes*

Hupa, Elisa (MSc Åbo Akademi University): *New Approach to Determine Initial Melting of Corrosive Deposits*

Jogi, Ramakrishna (MSc, 2010, Gitam University, India): *An integrated process for the production of green aviation fuel range cycloalkanes through hydrothermal liquefaction of lignocellulosic biomass*

Joon, Narender (MSc 2016, Åbo Akademi University): *Continuous Dynamic Extraction and On-Line Determination of Metals from Solid Environmental Samples*

Kholkina, Jekaterina, MSc 2017, Åbo Akademi University): *Synthesis of value-added products from residual materials: a green approach for the sustainable development of novel catalytic materials for biomass valorization*

Kinnunen, Hanna (MSc 2009, Tampere University of Technology): *Influence of Lead and Zink Compounds on Superheater Corrosion in Fluidized Beds Firing Demolition Wood*

Kråkström, Matilda (MSc 2015, Åbo Akademi University): *Evaluation of Advanced Oxidation Processes for Removal of Antibiotics in Wastewater Treatment Plants*

Korotkova, Ekaterina (MSc 2011, Åbo Akademi University): *Mild-Alkaline Extraction of Spruce Lignin and its Applications*

Kortesmäki, Ewelina (MSc 2013, University of Gdansk): *Occurrence and Fate of Antibiotics in Wastewater, Wastewater Treatment Plants and Recipient Waters*

Lagerquist, Lucas (MSc 2011, Åbo Akademi University): *Exploring the Structure and Reactivity of a Novel Type of Pressurized Hot Water Extracted Lignin*

Lassfolk, Robert (MSc 2018, Åbo Akademi University)*: Acyl Migration in mono-, oligo- and polysaccharides*

Li, Na (MSc 2007, Åbo Akademi University): *High-Temperature Corrosion of Ceramics in Biomass Combustion*

Lindfors, Christian (MSc 2008, Helsinki University of Technology): *Quality Improvement of Biomass Pyrolysis Bio-Oil by Additives or Organic Catalysts*

Lund, Sara (MSc 2013 Åbo Akademi University) *Liquid-Phase Exfoliation of Finnish Flake Graphite in Cellulose Nanocrystals and Preparation of Electrically Conducting Composite Films for Sensor Applications*

Mattsson, Ida (MSc 2015, Åbo Akademi University): *Smart Materials from Sweet Molecules: Self-Assembling Polyols Derived from Mannose*

Najarnezhasmashbadi, Ali (MSc 2015, Åbo Akademi University*)*: *Development of New Structured Catalyst and Reactor Technologies for Biomass Conversion*

Niemi, Jonne (MSc 2014, Åbo Akademi University): *The Role of Temperature Gradient in Ash-Deposit Chemistry and Superheater Corrosion*

Oña, Jay Pee (MSc 2018, Åbo Akademi University): *From fossil to biohydrogen in Finnish (bio)industry - utilizing electrocatalysis in Aqueous Phase Reforming of hemicelluloses*

Pérez Nebreda, Andrea (MSc 2013, Universidad de Cantabria): *Valuable Monomers and Oligomers from Hemicelluloses*

Rai, Varun (MSc 2015, Åbo Akademi University): *High-Temperature Erosion of Boiler Materials*

Rendon, Sabine (MSc 2011, Åbo Akademi University): *Dyes in Dye-Sensitized Solar Cells*

Runeberg, Patrik (MSc 2014, Åbo Akademi University): *Selective Oxidation of Unprotected Carbohydrates, Polyols and Phenolic Compounds from the Biorefinery Feedstock*

Saeid, Soudabeh (MSc 2015, Islamic Azad University Tabriz): *Elimination of Pharmaceutical Products from Waste Water by Ozonation and Heterogeneous Catalysis - a Systematic Kinetic and Reaction Engineering Approach towards New Technology*

Saleem, Farhan (MSc 2013, Åbo Akademi University): *Furfural Valorization by H_2O_2: Synthesis of Green Dicarboxylic Acids*

Santochi, Paulo (MSc 2012, Åbo Akademi University): *Mathematical modelling of nitrogen oxide formation in black liquor combustion*

Sevonius, Christoffer (MSc 2012, Åbo Akademi University) *Agglomeration Studies in a Laboratory Bubbling Fluidized Bed in Conditions Typical for Biomass and Agrofuel Firing*

Shumilov, Vladimir (MSc 2014, Åbo Akademi University and Tver State Technical Univeristy): *Development of Structured Reactors for Transformation of Biomass Components to High-Value Products: Green Process Intensification*

Da Silva Correia, Leolincoln (MSc 2016, IFP School, France): *Health-promoting components and food additives from biomass - an intensified chemical engineering approach*

Jingxin, Sui (MSc 2011, Åbo Akademi University): *An Electrochemical Approach to High-Temperature Corrosion*

Sundqvist, Maria (MSc 2015, Åbo Akademi University): *Refining of Industrial-Based Wastes to High-Value Products*

Vucetic, Nemanja (MSc 2013, Belgrade University): *Preparation of Valuable Organic Chemicals from Homogeneous Catalysis to SILCA and Batch to Continuous Technology*

Wang, Luyao (MSc 2018, Qingdao Institute of Bioprocess and Bioenergy Technology, Chines Academy of Science, China): *Characterization and modification of technical lignin for sustainable lignin-based wood adhesive synthesize*

Wang, Qingbo (MSc 2018, Kunming University of Science and Technology, China): *3D bioprinting of lignocellulosic nanomaterials and wood polysaccharides in biomedical application*s

Xu, Wenyang (MSc 2015, Åbo Akademi University): *Three Dimensional Printing of Wood-Based Biopolymer for Biomedical Application*

Yrjänä, Ville (MSc 2018, Åbo Akademi University): *Developing Potentiometric Ion-Selective Electrodes for Anions*

Zhang, Yongchao (MSc 2015, Qilu University of Technology): *Development of a Novel Biomass Fractionation Approach Using Performic Acid Hydrolysis towards Integrated Lignocellulosic Biorefinery*

Zhang, Weihua (MSc 2017, Ocean University of China): *Constructing nanocellulose-based advanced functional materials for pollutant removal in industrial waste waters*