Dear reader,

January will be with us very soon. It is the occasion to thank all of you to continue your subscription to our Newsletter and to wish you, your family and all the ones you love a very healthy, joyful and successful year 2011.

2011 will see several EPNOE events. I am warmly inviting you to join the International Polysaccharide Conference “Polysaccharides as source of advanced and sustainable materials” (EPNOE 2011) to be held 29 August – 2 September in Wageningen, The Netherlands. It will be a highlight of the year with its list of first-class invited lecturers and participants, its satellite events, and the usual nice atmosphere of EPNOE meetings.

Several other meetings will take place next year, one in Sophia Antipolis in February dedicated to polysaccharide industrial applications and one in Lodz (Poland) targeted at biomedical aspects of polysaccharides. EPNOE will be, as every year, involved in the scientific community, its members coordinating projects, participating to conferences and acting in various scientific societies and organisations.

This issue has a special focus on lignin. As you all know, lignin is not a polysaccharide, but it is often associated with cellulosic materials in plants and trees. Due to this close relationship, it is rare to deal with cellulose without also considering lignin. It is very common that during EPNOE meetings, lignin studies are mentioned. This pushed me to ask EPNOE partners to write a short article about their current research with lignin. As you will see, research on lignin is active among EPNOE partners.

I send you my best wishes for 2011.

Dr. Patrick Navard
Coordinator of EPNOE
Centre for Material Forming
Sophia-Antipolis
(France)
Zoom on EPNOE partner's research

New nanostructured carbons for electrochemical applications

New nanostructured and porous carbon materials were recently developed in CEMEF/Mines ParisTech in a close collaboration with CEP/Mines ParisTech. They were successfully tested for electrochemical applications as electrodes in Li/SOCl2 batteries by SAFT and in PEM fuel cell (1) by Lepmi/ CNRS and PAXITECH.

Carbons were prepared from pyrolysed Aerocellulose, a highly porous and light cellulose made via cellulose dissolution, regeneration and drying under CO2 supercritical conditions.

By varying cellulose concentration, regeneration conditions and pyrolysis parameters, monolith carbons with controlled shape and porosity were obtained (see Figure 1). The volume of mesopores (50-100 nm) is from 2 to 4 cm3/g and the density is 0.2-0.4 cm3/g. The capacity tested in button cell batteries is 30-50% higher than the one used as an industrial reference, as measured by SAFT. In single PEM fuel cell test bench, the texture of the new carbon allowed improving mass transfer at the cathode.

The results were obtained in the frame of ANR project «Carbocell » 06 MAPR 0004 and labelled by the competitiveness cluster «Capenergies».


Figure 1. Aerocellulose and its carbon

Tatiana Budtova
Center for Material Forming (CEMEF), MINES ParisTech / CNRS, Sophia-Antipolis, France

news (continued)

Members' info

PhD defences

The following PhD defences took place in Cemef (Centre for Material Forming - MINES PARISTech, Sophia-Antipolis, France):

- Romain Sesouesse defended his PhD on November 26, 2010. Title: new ultra- porous cellulosic materials and carbons prepared with green solvents. PhD director: Tatiana Budtova.

- Florian Démé defended his PhD on December 13, 2010. Title: Extrusion of flour-polyester blends for packaging applications. PhD directors: Bruno Vergnes and Edith Peuvrel-Disdier.

- Monica Spinu defended her PhD on December 21, 2010. Title: On some physical and physico-chemical aspects of cellulose accessibility. PhD director: Patrick Navard

Forthcoming articles

Electrochemical characterisation and dyeing properties of selected 9,10-anthraquinones as mediators for indirect cathodic reduction of dyes, T. Bechtold, C. Fitz-Binder, A. Turcanu - Dyes and Pigments


Swelling and dissolution mechanism of regenerated cellulose fibers in aqueous alkaline solution containing ferric tartaric acid complex - part 1. Viscose fibers, H. Vu-Manh, H.B. Öztürk, T. Bechtold - Carbohydrate Polymers

Swelling and dissolution mechanism of regenerated cellulose fibers in aqueous alkaline solution containing ferric tartaric acid complex - part II. Modal fibers, H. Vu-Manh, H.B. Öztürk, T. Bechtold - Carbohydrate Polymers

Non-alkali swelling solutions for regenerated cellulose, I. Tatarova, A.P. Manian, B. Siroka, T. Bechtold - Cellulose

Thermische Verformung von Cellulose, L. Vo Thi To, I. Tatarova, A.P. Manian, B. Siroka, T. Bechtold - Patentanmeldung
Special focus on lignin

Lignin is recalcitrant against enzymic degradation. In nature, white rot fungi seem to be the only microbes capable of efficient depolymerization of lignin. The best-studied organism is Phanerochaete chrysosporium, the genome sequence of which was established in 2004. This fungus secretes an array of oxidative enzymes, including the 4 main groups of lignin-degrading enzymes, e.g. lignin peroxidase (LiP), manganese peroxidase (MnP), versatile peroxidase (VP) and laccase (Lac), and accessory enzymes (glyoxal oxidase, aryl alcohol oxidase, etc.).

Although the action of the various enzymes is reasonably well-established on relatively simple model substrates, the actual degradation of the natural lignin polymer is poorly understood. The various main enzymes act through the formation of radicals, which can either be neutralized thereby forming smaller molecules (cleavage / degradation mode), or react mutually leading to larger products (polymerization mode). By carefully controlling the reaction conditions (concentration of lignin and H2O2, presence of co-solvents, PO2, addition of co-substrates), one might be able to switch between these two modes.

Understanding of the degradation of natural lignin has been hampered by difficulties in isolating the native polymers and in analytical protocols to reliably monitor degradation in samples of such high complexity. The resolution of chromatographic equipment was insufficient to cope with the heterogeneity of the samples, and mass spectrometric techniques were inadequate to cover the high-molecular mass compounds. So far, alternative (natural) substrates, holding an intermediate position between simple model substrates and lignin with respect to molecular mass (e.g. lignan macromolecule and proanthocyanidins), have not been considered. In these substrates, the lignan and flavan-3-ol subunits, respectively, are also connected by C-C and C-O-C bonds, just like the monolignol subunits in lignin. The advantage of these oligomeric substrates is that they fall within the analytical range of our equipment. The study of such substrates with the main lignin-degrading enzymes might offer opportunities for better controlling their degradation mode.

Jean-Paul Vincken, Henk A. Schols, Harry Gruppen
Laboratory of Food Chemistry, Wageningen University,
The Netherlands.
Special focus on lignin
Lenzing’s Wood Refinery- a cooperation with Kompetenzzentrum Holz GmbH

The most efficient use of our natural resources demands a better knowledge of refinery processes. One type of a wood refinery is the classical pulping process. The lignin is one of the major components of wood and its characterization is still a challenge. A better knowledge of the lignin structure will enable the optimization of the pulping conditions and improve the specific degradation of lignin to generate wood pulp. Residual lignin in pulp influences its properties with respect to the bleaching behaviour and the reactivity. Lenzing is engaged in this research field together with the Kompetenzzentrum Holz GmbH. In this cooperation a new lignin isolation method for the characterization of residual lignin was developed. The Wood Analytical Center in Lenzing is equipped with a Bruker Avance DPX300 NMR spectrometer and therefore 1D and 2D NMR techniques are used to identify lignin moieties. Classical wet chemical methods (methoxyl group determination, phenolic hydroxyl group determination, …) serve as a supplement for modern analytics. Nano- and ultrafiltration on a laboratory scale is used to develop separation and purification strategies. Additionally Lenzing’s research lab comprises advanced analytical experience in wet and organic SEC and HPLC for carbohydrate analysis.

Figure 1: Food items (potatoes)

Figure 2: Compostable bag for organic household waste

2D HSQC spectrum of lignin.

Andrea Borgards
Lenzing, Austria

Forthcoming articles
Open access article:
Degradation of cellulose acetate-based materials: A review by Juergen Puls (Partner vTI), Steven A. Wilson (Eastman Chemical Company), and Dirk Höltter (Rhodia Acetow), published in J. Polym. Environ. It may be distributed and reproduced provided the authors and source are credited.
http://www.springerlink.com/content/m445505624825687/

Members’ info
New PhD students
- Yang Fu joined Cemef (Centre for Material Forming - MINES PARISTech, Sophia-Antipolis, France) in October 2010 to study porous cellulose materials for thermal insulation.
- Daniel Dax joined Åbo Akademi to study design of hemicellulose block copolymers in order to modify paper properties, supervisor: Prof. Stefan Willför

New post-doctoral scientist
Nicolas Delpouve joined Cemef (Centre for Material Forming - MINES PARISTech, Sophia-Antipolis, France) in October 2010 to study lignin foaming.

New MSc student:
Haolin Lu, Åbo Akademi, Supervisor Prof. Stefan Willför and Ann-Sofie Leppänen, Oxidised GGM and other hemicelluloses in papermaking

Mobility
Ron Janzon from vTI Hamburg (included in EPNOE) received a Johan Gadolin scholarship and will stay at Åbo Akademi for 6 months during 2011.

Network
The laboratory of Wood and Paper Chemistry at Åbo Akademi University is now part of the Nordforsk researcher network «Refining Lignocellulosics to Advanced Polymers and Fibers», which is led by Prof. Maija Tenkanen at University of Helsinki in Finland.
One of the primary research fields in lignin utilisation has been the incorporation of lignin into phenol-formaldehyde resins (LPF-resins). However, condensation reactions in lignin cannot be as effective as in synthetic PF resins, due to the complex chemical composition and the physical behaviour of lignins. That means that lignin based resins generally tend to have weaker adhesion properties and a higher degree of performance variability.

In order to improve the adhesive properties towards industrially acceptable products it is important to better understand the impact of lignin type and synthesis route on the resin quality. The wood bonding effectiveness of new thermosetting adhesives was determined by the automated bonding evaluation system (ABES) developed by Humphrey (1999) (Fig. 1). This system allows the rapid testing of the bond strength development on small veneer strips in shear mode depending on press temperature and time.

Shear strength development curves of PF and kraft lignin modified resins (LPF-resins) were obtained by the ABES-system (Fig. 2).

The initial stage shows a rapid nearly linear increase of shear strength versus pressing time. Furthermore a steadily decreasing bonding rate is obtained which reached a typical maximum shear strength level for each resin.

All resins did not show significant differences concerning reactivity at a press temperature of 105°C. In contrast, the final bond strengths indicated differences in the bonding ability.

High quality bonds were produced with the PF resin. As expected, bond strength decreased when the amount of lignin increased. It is evident that the use of methylolated kraft lignin (HyLignin) results in an LPF-resin with a higher bond quality compared to resins with unmodified lignin.

Thus, methylolation might contribute to a better incorporation of lignin into the polymer network. Further studies will focus on the reactivity of different modified and unmodified organosolv lignins from lignocellulosic biorefinery.

Dr. Ralph Lehnen
vTI-Institute for Wood Technology and Wood Biology, Hamburg, Germany
Hydrotropic lignin is obtained by the treatment of biomass with concentrated solutions of hydrotropic salts. Hydrotropic salts (typically alkaline or alkaline earth metal salts) are amphiphilic substances, which means that they have both hydrophilic and hydrophobic parts resembling in that way the structure of surfactants. However, hydrotropes have smaller hydrophobic part than surfactants (examples are sodium benzoate, sodium xylenesulphonate, sodium p-toluenesulphonate and others). The ability of hydrotropes to enhance the solubility of poorly soluble or insoluble in water compounds was discovered in 1916 by Neuberg, who had tested a number of such salts and first described the phenomenon of hydrotropy.

Hydrotropic treatment was extensively studied in 1950s-1970s as an alternative for existing pulp- ing methods. In that respect the hydrotropic pulping had some advantages over sulphite and kraft methods. Among them are the simplicity of the chemical recovery and environmental friendliness. Despite the advantages of the method, it has not been implemented in industry, mainly due to process conditions (relatively long treatment time) and not feasible pulp properties with regard to papermaking.

Nowadays the hydrotropic treatment can be reconsidered for the biorefinery concept as a means to isolate lignin from biomass, and such process can be used as a stage in a biomass processing sequence.

The main advantages offered by the hydrotropic treatment are:

- Lignin is easily recovered from the spent solution by dilution with water;
- Hydrotropic lignin unlike kraft lignin or lignosulphonates does not contain sulphur;
- The same hydrotropic solution can be used up to 6-7 times before recovering;
- Simplicity of the recovery system;
- Environmentally harmless process.

Precipitated lignin after filtering, washing and drying can be used as raw material for various applications, e.g. chemical conversion (source of phenolic substances) and thermoconversion (biofuels and gasification).

Fig. 1 Sulphur free lignin obtained after extraction using hydrotropic solution and precipitation in water. A simple and sustainable way to disassembly lignin from biomass.

Konstantin Gabov and Pedro Fardim
Åbo Akademi University, Lab. of Fibre and Cellulose Technology
Complementary to the exploitation of polysaccharides, utilization of lignin is becoming more and more an integral part of modern biorefinery concepts. One of the most promising applications of lignins - which have a close structural relationship to natural humic substances - pertains to their use as organic soil-improving and fertilizing materials. The latter are urgently required on a large scale to combat the progressive desertification which is nowadays one of the most alarming processes of environmental degradation.

Ammonoxidation of lignins, providing “N-lignins”, has been established as a suitable chemical process for enriching lignin with nitrogen and for converting lignin into soil-improving materials which were proven to share similarities with natural humic substances. Current studies are aimed at structural elucidation of N-lignins, analytics of natural and artificial humification processes, as well as at applicability of this technical process, e.g. for valorising rice straw from the Egyptian Nile delta. The elucidation of the different types of nitrogen bonding present in natural and artificial humic substances and the investigation of the mechanisms of nitrogen fixation during humification are main subjects.

Lignin-based hydrogels are representatives of another class of materials that is currently in the spotlight of our research. Water is one of the most valuable goods on earth with many regions suffering from lacking water for drinking or irrigating farmland. The application of lignin hydrogels for soil improvement is therefore considered to be an innovative approach aiming at a retarded loss of water (precipitation, irrigation, condensation) by evaporation or gravitation. This would be mostly beneficial to arid and semiarid regions, where the climatic water balance is negative and hence water is the limiting factor for plant growth. Strongly swellable lignin hydrogels with free swelling capacities of up to 50 g H2O / g lignin were obtained by different approaches.

Reinforcement of ultra-lightweight cellulosic aerogels with lignin and subsequent pyrolysis to highly porous carbon aerogels is another target of our research in the field of lignin chemistry. Lignin aerogels and the resulting carbon aerogels are tested for gas storage (hydrogen), heterogeneous catalysis or supercapacitor applications. As porosity, pore surface area and pore size distribution are key parameters for the above-mentioned applications current studies are dedicated to the development of novel techniques for controlling these parameters.

General lignin analytics is concerned with structural changes in lignin during pulping, bleaching and processing. A focus is on structural elucidation of lignin-carbohydrate complexes. Analysis is based on NMR techniques (solid, gel and liquid state), pyrolysis-GC/MS and gel permeation chromatography (GPC).

Contact: thomas.rosenau@boku.ac.at or falk.liebner@boku.ac.at
Nature makes polysaccharides, EPNOE turns them into products

Lignin-natural fiber composites
Lignosulfonates, a low cost and abundant source of materials, are added to several natural fibers in order to produce a fully bio-based and renewable composite prepared by compression molding. Process conditions are 130-160°C at 50-100 bars, with a fiber content up to 70%. A three-point bending test is carried out to assess mechanical properties of the composite. Botanical origin of the fibers, type of lignosulfonates, processing conditions and ways to treat fiber surface are strongly influencing the composite properties.

Lignin-cellulose interactions and preparation of highly porous materials
Mixtures of microcrystalline cellulose and organosolv lignin (kindly provided by vTI, Hambourg) in a common solvent 8%NaOH-water were studied with the objective to understand the influence of lignin on the properties of cellulose solutions and on the morphology of dry porous materials. Cellulose-lignin solutions were gelled, coagulated in aqueous acid baths and dried under supercritical CO2 to obtain Aerocellulose, an aerogel-like material (Figure a).

The presence of lignin accelerates cellulose gelation which was hypothesised to be due to the formation of cellulose rich domains. During regeneration part of lignin was washed out. This created large pores and channels in the dry materials. The overall results obtained showed that cellulose and lignin are not compatible in the solvent used (1).

The results were obtained in a close collaboration with CEP/Mines ParisTech in the frame of ANR project « Carbocell » 06 MAPR 0004 and labelled by the competitiveness cluster «Capenergies».

Lignin is the most abundant renewable resource available on earth containing aromatic ring structures. As lignin is extracted in the pulp & paper industry and remains as the non-converted fraction in many biorefinery processes, huge quantities of lignin will be produced annually. Finding value added applications for this fraction is a necessity to develop economically feasible biorefinery concepts.

At Wageningen UR Food & Biobased Research (FBR) more than a decade of R&D work has been devoted developing value added applications using the lignin fraction obtained from the pulp & paper and biorefinery industry. FBR coordinated several European projects and a lignin network (EUROLIGNIN) to increase the use of lignin and the critical mass necessary to establish these developments. This has lead to the following propositions at FBR:

- Biomass fractionation to obtain high quality (hemi)cellulose and lignin using chemical and biochemical approaches
- Developed advanced analytical techniques to characterize lignin, fractions, intermediates and products
- Lignin fractionation to tailor the properties for applications like binders, polyols for polyesters and polyurethanes, conversion to aromatics
- Lignin as a binder after chemical activation
- Lignin as UV stabilizer for (bio)polymers
- Coatings based on lignin
- Catalytic thermal conversion of lignin by ether cleavage, decarboxylation and demethoxylation to produce phenolic oil and chemicals
- Key player in lignin research

Recently, within Wageningen UR all groups working on lignin related activities have combined their forces to cover the whole R&D chain from lignocellulosic biomass, biomass fractionation, cellulose and lignin conversion to value added biobased products (Figure 1). Together with industrial partners Wageningen UR will use this strength to develop key know-how and value added applications for this challenging biopolymer.

If you are interested to know more about these activities at Wageningen UR FBR please contact Mr. Richard Gosselink, Richard.gosselink@wur.nl.

More information can be found at:
www.fbr.wur.nl
www.lignovalue.nl
www.biosynergy.eu
www.vpp.wur.nl/UK/Research/Projects

Wageningen University, The Netherlands
We warmly welcome scientists from industry, academia and research institutions across Europe and from around the world to Wageningen, the Netherlands, for the second international polysaccharide conference organized by The European Network of Excellence (EPNOE), the Wageningen University and Research Centre (WUR) and the Graduate School VLAG.

The conference aims to develop strong links between academic and institutional research scientists and industry and to create a forum for exchange of information and the initiation of new collaborations.

The conference program will feature review lectures by expert speakers from throughout the world, one session will be dedicated to innovation with active participation of the industry. Short lectures will be given based on submitted abstracts of the participants and there will be a poster session.

The sessions will cover following topics:
- Sources of functional polysaccharides
- Biosynthesis, enzymatic degradation and modification of polysaccharides
- Physical, chemical and structural characterization of polysaccharides
- Properties & functionality of polysaccharides
- Design & manufacture of polysaccharides and derived structures
- Advanced applications of polysaccharides and their derivatives:
  o Food and feed applications of polysaccharides
  o Polysaccharides in cosmetic, pharmaceutical and medical applications
  o Polysaccharides for materials and processing additives
  o Polysaccharides for biofuels and value chemicals

A course “Tools in Polysaccharide Engineering” for young researchers and professionals from industry will be offered on 28 August 2011. Participation in this course and the conference with a poster will be awarded with 3 ECTS.

Important dates:
- January 1, 2011: Opening conference registration and abstract submission
- April 15, 2011: Deadline for submission of abstracts
- July 1, 2011: Deadline early registration

Conference venue: Hof van Wageningen, Wageningen, The Netherlands

Conference secretariat:
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“Nature makes polysaccharides, EPNOE turns them into products”

Technology Offer
Process For Thermal Treatment To Form Cellulose Carbamate

Scientists from Innsbruck University, Austria succeeded in identifying a new non-toxic and highly efficient method for introducing carbamate groups to cellulosic materials.

BACKGROUND
Cellulose carbamate (CC), an ester of cellulose and carbamic acid is conventionally produced by heating, cellulose at high temperatures in the presence of ammonia derivatives, such as urea, thus forming the alkali-soluble CC. The substance, an interesting alternative to petroleum-based polymers can be processed to form fibres, foils, sponges, membranes, and other products. In conventional processes, CC is produced by reaction of cellulose with urea in alkali, organic solvents or liquid ammonia with or without the presence of catalysts. Alternative production technologies are known where the reaction requires microwave treatment, electron radiation, or supercritical carbon dioxide. These processes, however, are time intensive and require a high consumption of chemicals.

TECHNOLOGY
The novel technology allows for a solvent – and radiation-free production of CC. Carbamate groups are introduced to cellulosic materials by using only non-toxic and environmentally friendly chemicals. The total processing time is reduced by 50 – 90%, thus, increasing the process efficiency. All residues can be removed easily.

BENEFITS
- Solvent-free and no radiation required
- No environmental (air and water) pollution
- Reduced chemicals and time consumption
- Easy and flexible production - can be applied on all types of raw materials (pulp, fibres, films, paper, fabrics)
- Benefits of biodegradation, built-in antimicrobial activity, and high water absorbance properties of cellulose carbamate

STATUS OF THE TECHNOLOGY
Early stage of development

APPLICATION
- Fibre/ film/ membrane/ sponge or related industry
- Paper converter industry
- Nonwoven industry

INVENTORS
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Dr. Barbora Siroka

IP POSITION
Patent pending in AT; A 464/2010
Priority date: 23.03.2010
Owner: University of Innsbruck
Our Reference: H090301

LICENSING CONDITIONS
Application specific exclusive or non-exclusive license

COOPERATION OPTIONS
Development cooperation

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