Nordic Wood Biorefinery Conference – NWBC 2014

Lignin-coated nanocellulose from the super-biorefinery

The ultimate wood biorefinery combines its outputs into a super-bioproduct. Coat your nanocellulose with lignin for the biocomposites of the future, or integrate the barrier-plastics production into your board mill.

RESEARCH

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The fifth edition of Nordic Wood Biorefinery Conference (NWBC) gathered 240 delegates from 26 countries to Stockholm in March 2014. Besides a visit to Innventia´s research facilities, and a site visit to the LignoBoost demo plant for lignin production, a new side event was offered: a professional development course called ”Designing the Forest Biorefinery” including industrial case-studies. 18 lecturers and 21 course participants shared their experience during three days.

Since the first conference in 2008, the development within wood-based biorefining has flourished and many companies world-wide are directing towards the emerging opportunities. Rethinking of the market positioning was the subject for the opening speech by Mikael Hannus, Stora Enso. The travel from traditional pulp and paper production into new biobased markets will ask for transformation from product push to market pull and differentiated customer solutions instead of ”tonnes”. The industry has a responsibility to contribute with input regarding market needs to the research and development at institutes and universities. Actually, the co-operation between these actors in the biorefinery product development chain is reflected in the composition of NWBC 2014 delegates: 81 from industry, 68 from institutes, 68 from universities and 23 ”other”.

The biorefining business is still in its infancy, though, concludes Peter Flippo, Arizona Chemical. The barriers for commercial success are huge and today only 1/3 of the forest/agro biorefinery ventures are actually generating revenues. Low resource efficiency and too much commodity product focus are common problems.

Lignin processes and products

The subject that generated the most animated discussions was methodology for extracting lignin from alkaline cooking liquors, the titleist LignoBoost in one corner and the challenger SLRP (Sequential Liquid-Lignin Recovery & Purification) in the other. Martin Wimby, Valmet presented experience from the first commercial LignoBoost plant starting up at a Domtar mill in USA 2013 and the planning of the second plant at a Stora Enso mill in Finland 2015. The process, based on precipitating lignin with carbon dioxide, works as expected in the running facility. The two plants ”scratch the surface”, representing only 0.2% of the potential kraft lignin extraction market. The solid-biofuel value of the lignin does not alone pay a LignoBoost plant today, though. A debottlenecking of the recovery boiler, or a higher value of the lignin is still needed to motivate lignin extraction economically. The competing SLRP process, presented by Michael Lake, Liquid Lignin Company features an initial pressurised carbonation pretreatment from which a liquid lignin phase can be separated after settling. Solid lignin is thereafter precipitated from the concentrated lignin stream with sulphuric acid. The process is on a pilot scale stage and it will be interesting to follow its further adventures.

Mikael Hannus, Stora Enso and Peter Axegård, Innventia opened the conference. Photo: Johan Olsson

Lignin from black liquors entrains inorganics and carbohydrates which might need to be removed for certain future product applications. Rufus Ziesig, Innventia showed how the content of impurities can be significantly reduced by removing the most high-molecular lignin by ultrafiltration of the black liquor.

Another method for lignin fractionation has been studied by Dimitris Argyropoulos, NC State University, Raleigh addressing lignin inhomogeneity which is a general problem in the development of lignin products. He has produced lignin fractions with fairly narrow MW distributions through sequential precipitation with a non-polar solvent (hexane) of lignin dissolved in a polar solution (acetone).

But maybe high-molecular lignin is an illusion? Understanding the che-

240 delegates from 26 countries discussed biorefining at Stockholm Waterfront Congress Centre in the 2014 edition of Nordic Wood Biorefinery Conference. Photo: Johan Olsson

mical stucture of lignin is a basis for developing the material into value-added products. Claudia Crestini, Tor Vergata University has scrutinized the present lignin models with modern NMR tools. She concludes that there are large structural differences between milled wood lignin and kraft lignin and that kraft lignins are, as opposed to the existing paradigm, best described by C8 units rather than C9 units. In addition, kraft lignin is concluded to be of low molecular weight. The apparent high molecular weights typically measured are explained by the fact that the commonly used analytical methods detect aggregates rather than single lignin chains.

Another lignin challenge is to increase lignin reactivity. Gibson Nyanhongo, BOKU showed that the reactivity of lignosulphonate from sulphite cooking can be improved with laccase, enzymes that oxidise aromatic compounds, thereby making them more reactive. This was applied by producing lignosulphonate-siloxane co-polymers that might be interesting as e.g. adhesives.

Broken down to mono- and diphenols, lignin could be converted to useful chemicals or liquid fuel. Tallal Belkheiri, Chalmers University of Technology, has depolymerised kraft lignin in near-critical water with a catalyst. Methanol was used as co-solvent and hydrogen donor and phenol to suppress char formation. 70% of the lignin was converted to bio-oil with 10% water solubles and 20 % char as (unwanted) by-products. Another recipe at increased temperature and pressure was presented by Tanja Barth, University of Bergen. Water or ethanol as used with formic acid as hydrogen donor. 60 % bio-oil yield and 14% tar have been obtained.

Other aromatic polymers than lignin can be found in bark. Spruce bark is an industry-relevant raw material for tannin production, concluded Katariina Kemppainen, VTT. The bark of Norwegian spruce contains ca 11 % tannins, polyphenolic macromolecules that are used e.g. in leather processing and animal nutrition. The market today is limited by raw material (acacia and chestnut bark) availability. Biobased insulating foams were successfully produced from mixtures of furfuryl alcohol and crude tannin, extracted with hot water from spruce bark.

Hemicellulose processes and products

The trend of converting kraft mills into dissolving pulp production opens up possibilities to utilise the carbohydrates in the pre-hydrolysate. Olumoje Ajao, Polytechnique Montreal has aimed at separating and concentrating all hemicelluloses and sugars in the pre-hydrolysate for further conversion into furfural. Nanofiltering (with a molecular weight cut-off of 200 g/mol) turned out to work well for this purpose, retaining 99% of the sugars and increasing the carbohydrate concentration fourfold.

Going one step forward in the fibre line, the separation of xylan from black liquor with ultrafiltration has been studied for some years. A drawback with this approach is the low product purity. Sverker Danielsson, Innventia, presented a new method for recovery of xylan. Black liquor xylan is sorbed onto bleached pulp that is subsequently desorbed and reused as sorption medium, Figure 1. The method gives xylan with high purity but is at an early development stage.

Even further forward – at the very end of the fibre line – Antero Varhimo, VTT has extracted hemicellulose from bleached pulp. Most of the xylan in bleached hardwood pulp can be extracted with alkali. This method does also give a very pure xylan, but the xylan-depleted pulp would need to be upgraded to a product with higher value than market pulp.

Looking for a high value from the hemicellulose product? Hydrogel products are a good choice then, revealed Anna Suurnäkki, VTT. Soil improvement and microencapsulation are examples of such applications. If the size of the market is the most important, turn your hemicellulose into packaging film!

Most studies of hemicellulose products are based on applications for non-degraded xylan. But hemicellulose sugars could also be refined into products. The challenge is to economically recover and separate the sugar acids. Crystallisation, electrodialysis or ion exchange chromatography are examples of methods that have been tried earlier. Tuomo Sainio, Lappeenranta University of Technology, is developing a method based on size exclusion chromatography of black liquor that has first been ultrafiltered to remove lignin. The recovered mixture of hydroxy acids could be used as raw material for biopolymers.

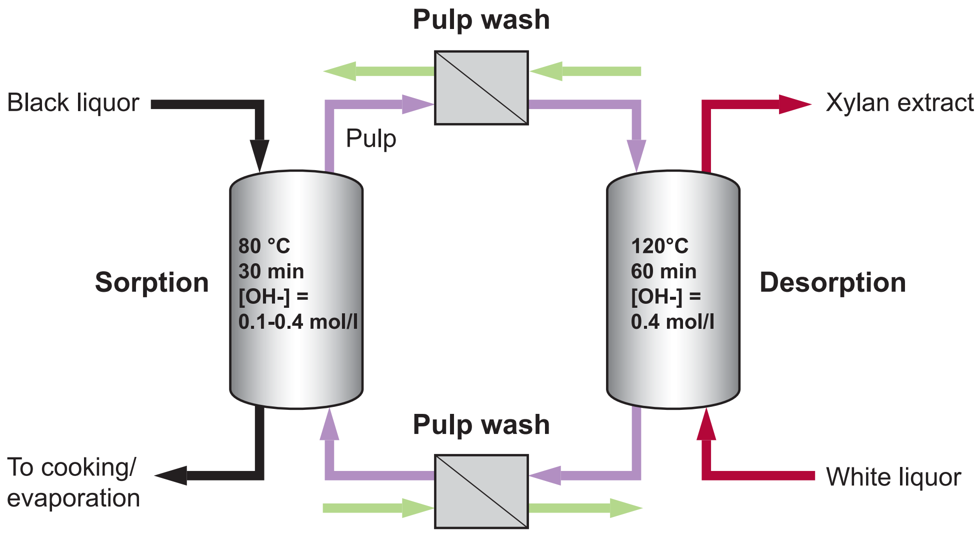

Figure 1. A new method for separating xylan from black liquor uses bleached pulp as a rechargeable sorption medium. (Sverker Danielsson, innventia)

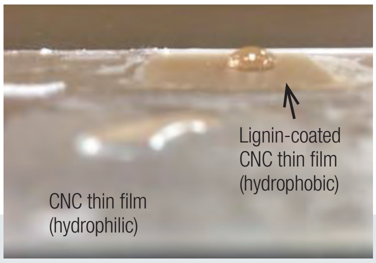

Figure 2. Coated with a thin layer of lignin, cellulose nanocrystals (CNC) become water-repellent and more compatible with many polymer materials. (Kim Nelson, American Process)

New cellulose products

A sulphur-free method to produce very pure cellulose in three steps was presented by Katarina Karlström, Innventia. A severe pre-hydrolysis of Eucalyptus globulus, followed by soda cooking and oxygen delignification, yields a >98% cellulose, i.e. purer than dissolving grades. This material is of high enough quality to be used for e.g. production of LCD screens via triacetylation. Today, such materials are produced from a limited supply of cotton linters.

Nanocellulose is an exciting research area with many potential future applications within and outside papermaking. Fredrik Lundell, Royal Institute of Technology, Stockholm concludes that the full potential of cellulose nanofibrils (CNF) has not been reached yet. CNF with considerably higher strength than earlier reported was produced via flow-induced alignment of the nanofibrils before locking the structure via gelling. The gel can be extruded into a smooth and homogeneous filament with excellent mechanical properties.

And why not coat your nanocellulose with lignin? This is one option Kim Nelson, American Process sees in the AVAP process that converts biomass with SO2 and ethanol into CNF with moderate need of chemicals and mechanical energy. Coating the nanofibrils with a thin lignin film improves their hydrophobicity (Figure 2) and compatibility with many matrix materials, opening up possibilities for very strong composite materials. More ”biorefinery composites”: Markku Leskelä, FIBIC suggests blending ”ordinary” cellulose with plasticised lignin into a moldable material. Monica Ek, Royal Institute of Technology uses the natural polyester suberin – abundant in birch bark – for molding hydrophobic cellulose materials.

Biochemical routes for biomass

At NWBC 2012 Domsjö reported from an investigation of using the pulp mill´s residual heat and water treatment capacity for fish farming. This time, Björn Alriksson, SP Processum showed how to feed the fish. Residual biorefinery streams – fibre sludge, spent sulphite liquor, ethanol stillage and hydrolysate – turned out to be excellent food for (obviously non-fussy) protein-rich microorganisms that were tested as fish feed. Trials in lab, pilot and demo scale with tilapia fish showed better fish growth when 68 % of the fish meal reference was replaced with the ”biorefinery feed”.

PLA is an important bioplastic today, produced from starch- or sugarcane-based lactic acid. David Sanchez-Garcia, Corbion-Purac showed a possible way for commercial production of lactic acid from hardwood. The challenge with wood lignocellulose is to convert it into fermentable sugars. The route proposed here uses alkaline pretreatment followed by enzymatic hydrolysis with an enzyme cocktail including hemicellulase activity.

Alkaline pretreatment is the basis for the Polynol process as well. Niklas Berglin, Innventia, gave a status report from the large Swedish-Brazilian cooperation. The process aims at bioconverting bagasse or forest residues into lactic acid or ethanol with lignin as an important by-product. The process is integrated with the chemical and energy recovery of a kraft or soda pulp mill for efficient lignin separation. The project is presently running its first phase: lab scale and preparing for upscaling. The goal is a ”super-biorefinery” for biobased packaging materials from board and bioplastics.

NWBC is a cooperation between Innventia in Sweden and VTT in Finland. This time Innventia organized the event. The 6th Nordic Wood Biorefinery Conference will take place in Helsinki 20-22 October, 2015 at Marina Congress Center with VTT as organizer.

Junyong Zhu, USDA forest products Laboratory, has another formula for preparing wood for bioconversion: acidic sulfite treatment. The so called SPORL method has now been run in pilot scale, producing ethanol from softwood (Douglas fir) forest residues in good yield. The lignosulphonate by-product is highly sulphonated, making it suitable for e.g. dispersant applications. The process is suitable for integration with sulphite pulp production.

Thermochemical routes for biomass

As a biomass conversion method, gasification has the advantage of giving a product – synthesis gas – that is straightforward to convert to pure chemicals or fuels. Black liquor as well as forest residues have been the objects for extensive gasification studies. Jim Andersson, Luleå University of Technology discussed co-gasification of black liquor with pyrolysis oil as a means to increase syngas production and plant flexibility. It was concluded that the solution is economically beneficial compared to gasifying either of the raw materials alone, one factor being that the alkali metals in the black liquor catalyse the gasification of the pyrolysis oil.

Michael Renz, Instituto de Tecnología Química Valencia, showed how biomass can be carbonised without drying. The so-called HTC process is a ”wet pyrolysis” method, dehydrating biomass in the precence of water into an oxygen-depleted peat-like solid, suitable as solid biofuel. The process is especially interesting for smaller-scale local biorefineries and is being tested with different biomass materials in continous 2t/d scale in an EU project. ■