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Kristina Elg Christoffersson, Domsjö Fabriker AB, Sweden

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Invited speaker: Thomas Rosenaau,
University of Natural Resources and Life Sciences (BOKU), Austria

Session 1:  Cellulose dissolution
Moderator: Thomas Heinze, Friedrich Schiller University of Jena, Germany
09:40-10:00  Dissolution mechanism of cellulose in tetrabutylammonium acetate/dimethyl sulfoxide
Presentation 1
Tobias Köhnke, Swerea IVF, Sweden

10:00-10:20  Impact of non-solvents in the tetrabutylammonium acetate: dimethyl sulfoxide-cellulose system
Presentation 2
Jenny Bengtsson, Swerea IVF, Sweden

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Session 2:  Cellulose chemistry and derivatives
Moderator: Patrick Navard, MINES ParisTech, PSL Research University, France
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Presentation 3
Christian Achtel, Friedrich Schiller University of Jena, Germany

11:40-11:50  Cellulose Carbonates: A Platform for Promising Biopolymer Derivatives with Multifunctional Capabilities
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Thomas Heinze, Friedrich Schiller University of Jena, Germany

11:50-12:10  Cellulose derivatisation – tuning and analysing the degree of substitution
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Ute Henniges, University of Natural Resources and Life Sciences Vienna (BOKU), Austria

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Diana Carolina Albán Reyes, Umeå University, Sweden

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Marianna Vehviläinen, VTT, Finland

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Presentation 8
Pernilla Karlsson, Royal Institute of Technology, Sweden

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Presentation 9
Tomas Larsson, Innventia AB, Sweden

14:30-15:50  Posters + coffee

15:00-16:00  All-cellulose composites via short-fibre dispersion approach
Presentation 10
Tatiana Budtova, MINES ParisTech, PSL Research University, France

16:10-16:30  The supramolecular structure of cellulose-rich wood and wheat straw pulps can be a determinative factor for enzymatic hydrolysability
Presentation 11
Fredrik Aldaeus, Innventia AB, Sweden

16:30-16:50  Influence of the amount and position of cellulose in plant stems on the behavior of plant stem reinforced-polymer composites
Presentation 12
Patrick Navard, MINES ParisTech, PSL Research University, France

16:50-17:10  Production of plasticised fibre composites (PLAFCO) with a paper machine via partial dissolution of paper
Presentation 13
Nils C. Hildebrandt, Oulu University/Baden Württemberg Cooperative State University, Finland/Germany

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18:30  Buss to “Hampnäs”
19:00 - 22:30  Dinner at “Hampnäs”
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<td>Coagulation of cellulose-EmimAc-DMSO solutions studied in order to</td>
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<td>control properties of wet-spun cellulose fibers</td>
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<td>Moderator: Thomas Rosenau, University of Natural Resources and Life Sciences (BOKU), Vienna, Austria</td>
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<td>10:55-11:00</td>
<td>Deep eutectic solvents in nanocellulose production and functionalization</td>
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<td>Henrikki Limatainen, Oulu University, Finland</td>
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<td>Production of Bacterial Nanocellulose in Submerged Cultivations</td>
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<td>Using Forest-Industrial Residues</td>
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<td>Genqiang Chen/Guochao Wu, Donghua University/Umeå University, China/Sweden</td>
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<td>Single-filament fibers of cellulose nanofibers prepared by dry spinning: Influence of binder and cold-drawing on orientation and mechanical properties</td>
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<td>11:50-12:10</td>
<td>Europe’s first pilot plant for cellulose nanocrystals production</td>
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<td>Martin Eskilsson, Holmen AB, Sweden</td>
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<td>Borregaard – a modern Biorefinery</td>
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<td>Lignin carbohydrate complexes in sodium sulfite dissolving pulps</td>
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<td>as a function of the pulping conditions used</td>
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**Workshop programme**

**Wednesday 16 November**

Ola Sundman, Umeå University, Sweden
Professor Thomas Rosenau
University of Natural Resources and Life Sciences Department of Chemistry Division of Chemistry of Renewables, Vienna, Austria

Professor Thomas Rosenau is head of the Division of Chemistry of Renewables at the Department of Chemistry, holding the Chair of Wood, Pulp and Fiber Chemistry, co-director of the Christian Doppler laboratory “Advanced Cellulose Chemistry and Analytics”, and adjunct professor of fiber chemistry at Shinshu University, Japan. Research focuses on chemical and structural aspects of celluloses and lignin, cellulose and lignin modification, cellulose aging, cellulose solvents, novel biomaterials, antioxidant chemistry, paper and fiber chemistry, as well as green chemistry approaches.

Denis SENS
Head of Tembec Innovation, Bordeaux, France

Chemical Engineer by training specialized in agro-based chemistry, with more than 28 years in R&D for the pulp and paper Industry. Working for Tembec since 1994.

Key achievements:
Took active part to the transformation of a Commodity Sulfite Fluff pulp mill (France) into a state of the art Specialty Cellulose Biorefinery.
Designed and developed high performance Specialty Cellulose grades for the Cellulose derivatives industry (esters and ethers)
Expertise in Cellulose purification and Cellulose viscosity control
Currently R&D Director for Tembec Specialty Cellulose and Lignin businesses with operations in Canada and France.
Umeå University was founded in 1965 and is Sweden’s fifth oldest university. Today, we have a strong international presence with students, teachers and researchers from all over the world. As one of the leading comprehensive universities in the nation, we are alive with enthusiasm, innovation, creativity and fresh ideas.

We have developed interaction between research, education, collaboration and innovation that challenges boundaries and plays a crucial role in the region’s development.

The University is a dynamic meeting place where interdisciplinary knowledge is generated and disseminated. Creative environments attract students, researchers, teachers and collaborating partners nationally and globally.

In 2015 the University had about 31,000 enrolled students and about 4,200 employees.

www.umu.se

Karlstad University was founded in 1999. Our ambition is to be an active and important link in the Swedish system of higher education and, at the same time, maintain our strong regional basis and international outlook.

As regards internationalisation, Karlstad University has set its targets very high, aiming to provide good opportunities for students to spend part of their study period at universities outside Sweden, and also to attract international students to Karlstad for a semester or a year. With this in mind, the University is offering an increasing number of courses and programmes in English. Doctoral students also have the opportunity to spend time at a foreign university as part of their education. Both teaching assignments abroad and staff exchange are important and common features at the university.

We have well developed cooperation with about 200 universities around the world, for instance in Germany, France, USA, Canada, Australia, New Zealand, South Africa, India, China, Korea and Japan.

In 2015 Karlstad University had about 16,300 students and about 1,200 employees.

www.kau.se
Bio4Energy
The research environment Bio4Energy aims to create highly efficient and environmentally-sound biorefinery processes – including methods and tools for making products such as biofuels, “green” chemicals and new bio-based materials – which draw on biomass sourced from forests or organic waste as a raw material. At the core of Bio4Energy are two process platforms; Bio4Energy Thermochemical Conversion Technologies and Bio4Energy Bio-polymer and Biochemical Conversion Technologies.
www.bio4energy.se

Borregaard
By using natural, sustainable raw materials, Borregaard produces advanced and environmentally friendly biochemicals that can replace oil-based products. Borregaard also holds strong positions within ingredients and fine chemicals. Borregaard has 1080 employees in plants and sales offices in 16 countries throughout Europe, Americas, Asia and Africa.
www.borregaard.com

Cleaner Growth
Is a unique long-term investment in northern Sweden - Västerbotten and Örnsköldsvik - that supports business development of companies in the clean-tech area, and drives cleaner growth and reduction of climate change. Our long term ambition is to position the region and North Sweden nationally and internationally as an attractive place to establish and grow; increase equality between women and men; develop more commercially viable products; strengthen the development of innovative and sustainable growth; provide services with environmental relevance and strengthen the collaboration between academia, municipality/region and industry within the cleantech field.
www.cleanergrowth.se

Domsjö Fabriker
The biorefinery Domsjö Fabriker is located close to the High Coast world heritage. Customer support, quality and sustainability are very important for us. Our development is based on the world's increasing demand for sustainable products. Domsjö Fabriker's main products are cellulose, lignin and bioethanol, all with an origin in sustainable Swedish forestry. The revenue is ca. 1.6 billion SEK and the company employs around 400 people at the production unit in Domsjö. Domsjö Fabriker is part of the Indian Aditya Birla Group.
www.domsjo.adityabirla.com

Holmen – a forest industry group
Holmen is a forest industry group that manufactures paperboard, printing paper and sawn timber and runs forestry and energy production operations. The company's extensive forest holdings and its high proportion of energy production are strategically important resources for its future growth. The average number of employees during 2015 was 3 315.
www.holmen.com

MoRe Research
MoRe Research Ornsköldsvik AB is a neutral and independent research and development company in the field of products and processes for e.g. the forest industry. Our company used to be a part of the MoDo group, which was founded more than one hundred years ago. The focus areas are All the way (Hela vägen®), Analytical services, Biorefinery, Process Emergency and Education.
www.more.se

SP Processum
SP Processum supports and initiates research and development within biorefinery. Together with other biorefinery initiatives, our cluster with partners from industry and academy constitutes an important hub for development of new products, processes and energy solutions from wood raw material and residual streams from the process industry. We cooperate with national as well as international partners. SP Processum AB is owned by RISE Research institutes of Sweden (60 %) and Processum Interest Association (40 %), and is thus a subsidiary of the RISE group.
www.processum.se
Invited Speaker-presentation

Celluloses I and II. Some news from an old polymer

Thomas Rosenau
Corresponding author: thomas.rosenau@boku.ac.at

BOKU University Vienna, Department of Chemistry, Division of Chemistry of Renewables,
Muthgasse 18, A – 1190 Vienna, AUSTRIA.

The allomorphism of cellulose is well established. Cellulose I and cellulose II are the most important allomorphs, the former term describing 'native' cellulose, the latter being cellulose that has either been regenerated from cellulose solutions or obtained by mercerization with concentrated lye. It is commonly accepted that in cellulose I the chains are in parallel arrangement, while cellulose II has an antiparallel chain orientation. The transition from parallel cellulose I to antiparallel cellulose II can be easily understood if the 'detour' via completely dissolved cellulose is involved: the cellulose chains are separated in solution and will re-aggregate as the thermodynamically most stable allomorph, which is cellulose II. However, how the parallel-to-antiparallel transition in solid state (during mercerization) can be imagined is still a mystery and one of the oldest riddles in cellulose science.

In our presentation, we will add some pieces to the jigsaw puzzle of the solid-state cellulose I to cellulose II transition (evidently without being able to arrange those pieces into a final, nicely ordered picture), in particular addressing the axioms that always cellulose II is regenerated from cellulose solutions and that the transition cellulose I → II is irreversible. It will be demonstrated that special regeneration conditions that align the reducing ends to one side through temporary derivative formation allow reprecipitating cellulose I from solution, independent of whether a cellulose I substrate (such as a cellulosic pulp or cotton linters) or a cellulose II substrate (such as viscose fibers) had been dissolved. The latter case represents something like a 'reverse mercerization' with regard to the allomorph change. The experiments involve different cellulosic substrates, and the transitions are studied by means of solution and solid-state NMR, light scattering as well as X-ray diffraction experiments.
Invited Speaker-presentation

Cellulose: The chemical that grows

Denis Sens, R&D Director

Corresponding author: denis.sens@tembec.com

Tembec

This presentation will provide some selected updated information about past present and future for the High Purity Cellulose Industry and its related markets:

- Tribute to some of the cellulose and cellulose derivatives pioneers
- Dissolving Pulp and Specialty cellulose markets
  - Definitions
  - Raw materials, manufacturing processes and products
  - Market size
  - Market dynamics
- Regenerated Cellulose and Cellulose derivatives markets
  - Products
  - Market size
  - Market dynamics
- Key challenges for the future from a leading Specialty Cellulose producer perspective
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Summary

The dissolution of cellulose in tetrabutylammonium acetate (TBAAc)/dimethyl sulfoxide (DMSO) was studied combining experimental and simulation techniques. It was found that the dissolution limit at 40 °C corresponded to a molar ratio close to one acetate per cellulose anhydroglucose units. MD simulations suggested that the acetate ions bind to cellulose by dual hydrogen bonds. This effectively turns cellulose into a polyelectrolyte, attracting the bulky tetrabutylammonium (TBA+) counter ions, which prevent close contact between chains in the dissolved state. This hypothesis was tested by 1H- and 13C-NMR spectroscopy, which confirmed that acetate forms hydrogen bonds to cellulose, and by diffusion NMR spectroscopy, which demonstrated a strong dynamic correlation between bound acetate and tetrabutylammonium in near-quantitative agreement with simulation. The present results suggest that offering hydrogen bonding to the acetate ions is the main driving force for dissolving cellulose and that the TBA+ counter ions form a diffuse layer around the acetate-decorated cellulose chains.

Introduction

Cellulose is the most abundant natural polymer on earth and is an important raw material in a bio-based economy. Dissolution and processing of cellulose has attracted much attention in past and present research. As cellulose cannot be melted without chemical derivatization, it needs to be dissolved in order to be shaped into new forms, such as fibers, films, or foams. Cellulose is insoluble in water and most organic solvents. Over the years, however, several classes of efficient cellulose solvents from widely different chemical families have been discovered. A class of solvents that have attracted much interest during recent years is ionic liquids (IL). Some IL can dissolve technically relevant amounts of cellulose, and have also been used successfully in wood component separation (Kilpeläinen, Xie, King, Granstrom, Heikkinen & Argyropoulos, 2007), chemical derivatization of cellulose (Heinze & Gericke, 2014), or in regeneration and cellulose fiber spinning (Sixta et al., 2015). Several of the most used IL do however show tendencies to degrade or modify the cellulose chains (Clough, Geyer, Hunt, Son, Vagt & Welton, 2015) or to be chemically labile themselves, especially at elevated temperatures. However, due to the fact that several different classes of cations as well as several different anions have been shown to be useful in cellulose dissolution, there is a vast number of possible combinations left to explore, and hence new cellulose dissolving IL are continuously being discovered. Recently, a new class of alkylammonium type IL has shown good potential in terms of cellulose dissolution capacity, stability and recyclability. Among these, TBAAc in DMSO has been
shown to dissolve cellulose of high degree of polymerization (DP) in concentrations suitable for fiber spinning (Miao, Sun, Yu, Song & Zhang, 2014).

In this study, the dissolution of cellulose in TBAAc and DMSO at different ratios was investigated by experimental and simulation techniques. Microcrystalline cellulose (MCC) was dissolved and the solutions were studied using light microscopy, turbidity, and SAXS, as well as $^1H$, $^{13}C$, and diffusion NMR spectroscopy. Results were analyzed with support from MD simulations and DFT calculations.

**Experimental**

Three solvents with different TBAAc/DMSO ratios were prepared; 1:8, 2:7, and 3:6 TBAAc/DMSO, and light microscopy was used to determine the dissolution limit of the different solvent systems. For the 1:8 solvent, undissolved cellulose could be seen between crossed polarizers around 6 wt% MCC, for the 2:7 solvent undissolved material appeared around 10 wt% MCC, and for the 3:6 solvent undissolved material appeared around 15 wt% MCC. Calculating the molar ratios, it can be seen that, for all three solvents, at 1:1 TBAAc/AGU molar ratio there seem to be a dissolution threshold. Above 1:1 TBAAc/AGU the cellulose seems to be well dissolved, around 1:1 TBAAc/AGU some undissolved material can be seen, and below 1:1 TBAAc/AGU a significant amount of undissolved material can be seen.

**Results**

The $^1H$ NMR chemical shift changes obtained when increasing the cellulose concentration can be seen in Figure 1, for all used solvents. The chemical shift differences are normalized to the average of the three least changing signals, the three TBA-signals I, II, and III. In the figure all three different solvent 1:8, 2:7, and 3:6 TBAAc/DMSO are overlaid.

![Figure 1](image-url)

**Figure 1.** $^1H$ NMR chemical shift changes with increasing MCC concentration, for all used solvents. Lines are added to guide the eye. Molecular structures of all components used can be seen with positions denoted with Roman numbers.

The chemical shift changes are here related to the shifts of each neat solvent, with no added cellulose. An inset with molecular structures of all components can also be seen in the figure with positions denoted with Roman numbers. An increase of the chemical shift of the acetate ion could be seen with increasing amount of added cellulose. For the EMIMAc system, this effect has previously been explained by increasing amount of hydrogen bonds between cellulose and the acetate ion, with increasing cellulose content (Ries, Radhi, Keating, Parker & Budtova, 2014). A corresponding
decrease in the chemical shift of the hydrogen closest to the nitrogen in the TBA⁺ could also be seen. From DFT calculations similar trends in the chemical shift changes could be seen. This effect could be explained by a two-state model of the acetate; either hydrogen bonded to cellulose, or free in the bulk.

From the chemical shift changes above it could be noted that the acetate show effect of hydrogen bonding to the cellulose. No such effects could be seen for the TBA⁺. Using diffusion NMR both TBA⁺ and acetate decrease to the same diffusion rate at high cellulose concentration, as seen in Figure 2. This phenomenon could be explained by a model where the TBA⁺ is electrostatically bound to the acetate, hence being affected by the decreased diffusion rate of the molecule.

**Figure 2.** Decrease of absolute diffusion rates of TBAAc and DMSO with increasing MCC concentration, in the 2:7 solvent. Full symbols are experimental data, empty symbols are from simulations.

It can also be seen that the diffusion rate of DMSO is decreasing with increased cellulose concentration. Although this effect is less pronounced that the effects seen for the TBA⁺ and acetate it could not be explained solely as a viscosity or obstruction effect. Proposing a model where some of the DMSO solvated the TBA⁺, could explain this behavior. Whereas this would only have a minor impact on the chemical shift, due to a wide line of possible TBA⁺/DMSO configurations, the diffusion rates should be visibly affected. Diffusion rates extracted from the MD simulations yielded similar results advocating the proposed theory.

**Conclusions**

In this work, the dissolution of cellulose in TBAAc in DMSO was investigated, using a combination of experimental and modeling techniques. Light microscopy and turbidity measurements showed that the dissolution limit of cellulose, for all solvents used, was around the molar ratio 1:1 TBAAc:AGU. MD simulations suggested that acetate preferentially binds to cellulose by dual hydrogen bonds. This effectively turns cellulose into a polyelectrolyte, attracting the bulky tetrabutylammonium counter ions, which prevent close contact between chains in the dissolved state. Clear effects of hydrogen bonding between the acetate and cellulose could be seen using ¹H- and ¹³C-NMR spectroscopy. A decrease of the diffusion rate also for the TBA⁺ ion is consistent with the polyelectrolyte picture. The chemical shift changes, diffusion rates found from the experimental results, verified that the model used in this work for the simulations described the real system well.

The present results suggest that offering hydrogen bonding to the acetate ions is the main driving force for dissolving cellulose in the present solvent mixture. Strong hydrogen bonding to the acetate anion is a feature that is well-known from neat IL cellulose solvent systems and does not appear to be changed dramatically by the presence of DMSO. However, DMSO weakens the electrostatic coupling...
between anions and cations to such an extent that the TBA⁺ ions can form a diffuse layer around the acetate-decorated cellulose chains, as opposed to the discrete solvent shell expected in neat IL. This is beneficial for dissolution as the steric repulsion between the TBA⁺ counter ions presents a barrier for aggregation in the solutions.

Acknowledgements
This research was performed with financial support from The Swedish Research Council Formas, in collaboration with the research cluster Avancell – Centre for Fibre Engineering.

Literature


Impact of non-solvents in the tetrabutylammonium acetate:dimethyl sulfoxide-cellulose system

Jenny Bengtsson1, Carina Olsson1, Alexander Idström1 and Tobias Köhnke1

Corresponding author: jenny.bengtsson@swerea.se

1Bio-based fibres, Swerea IVF, Mölndal - Sweden.

Abstract
This work examines the potential of tetrabutylammonium acetate: dimethyl sulfoxide (TBAAc:DMSO) as a solvent used in a process for producing man-made cellulose fibers. The tolerance towards non-solvents is an important step to evaluate the recyclability of the solvent. TBAAc:DMSO was in this work further confirmed to be an efficient solvent for cellulose. Non-solvent tolerance depended on cellulose concentration, TBAAc:DMSO ratio and type of non-solvent. There was no significant change in mechanical properties for filaments regenerated from solutions containing 2 wt% non-solvent compared to those spun from virgin solvent. With 4 wt% ethanol present in solution very brittle filaments were produced, not suitable for use as textile fibers.

Introduction
The world’s total textile fiber consumption is increasing as a consequence of the growing population and rising prosperity. In a future scenario arable land will be needed for food, hence the cotton production most probably won’t be able to meet the future cellulosic fiber demand (Eichinger 2012). To fill this predicted “cellulose gap” a realistic solution is an increase in production of regenerated cellulose fibers (Hämmerle 2011). Regenerated cellulose fibers are mainly produced from wood-based pulp, which requires dissolution and thereafter regeneration or reshaping into cellulose filaments. The gained market motivates development of new efficient methods for production of regenerated cellulose fibers, which is further supported by the fact that today’s commercially available processes are either using harmful chemicals or being very energy intensive (Klemm et al 2005; Liebert 2010).

An important issue when developing a new system for dissolution and precipitation of cellulose is to evaluate the possibility of efficient recycling of the solvent. Ionic liquids have demonstrated many favorable properties when it comes to dissolving cellulose. They are thermally stable, can dissolve cellulose at low temperatures and relatively low viscosity. Nevertheless there is still debate whether or not it would be efficient to recycle ionic liquids. Complete separation of a hygroscopic ionic liquid and coagulation medium is most probably not realistic to achieve in an industrial scale, as it would be too energy intensive. Further there will always be some water entering the system, since fully dried cellulose is impossible to accomplish. Understanding the impact of non-solvents, during dissolution and regeneration is therefore a crucial part of evaluating a new potential solvent for cellulose fibers. According to previous studies with other ionic liquids it has been found that their tolerance towards non-solvents is difficult to predict, why so far experimental work is necessary for each interesting IL (Le et al. 2014; Wawro et al. 2015).
In present work a newly developed solvent for cellulose is investigated: Tetrabutylammonium acetate together with dimethyl sulfoxide as co-solvent (Miao et al. 2014). Water and ethanol were chosen to evaluate the impact of non-solvents in the system.

**Experimental**

Dissolving pulp ($M_w = 162300$, $M_n = 518009$) was provided by Södra Cell, Mörrum – Sweden. TBAAc (≥97 %) was purchased from Sigma Aldrich and DMSO (99.7%) was bought from Fischer Scientific, both used as received. The solvents were prepared by dissolving TBAAc in DMSO by stirring at 40°C until clear. A certain amount of deionized water or ethanol (99.6%) was thereafter added to the TBAAc:DMSO solution. 5 % of cellulose was added by dry weight (held in the range of 94-96% from drying over night in 40°C) and dissolved by stirring for 1 h at 60°C in a closed container.

Solutions were thereafter observed through Nikon SMZ 1500 light microscopy with crossed polarizes to detect presence of any non-dissolved fibers. The turbidity of the solutions was calculated from measured absorbance at 800, 825 and 850 nm, conducted on a Specorde 200 Plus, Analytic Jena, UV/Vis spectrometer. Finally viscoelastic data were obtained through a Bohlin Instruments CS Rheometer equipped with a 25 mm/5° cone and plate measuring system. To estimate if any cellulose degradation occurred during dissolution the intrinsic viscosity was measured for both pulp and filaments according to ISO 5351:2010.

After filtration through 20 µm sintered metal fleece filter, films and filaments were prepared from the solutions. Films were pressed by allowing solution to coagulate between two flat, circular surfaces. Filaments were spun on a customized laboratory equipment with a piston spinning unit using a spinneret with 64 holes and capillary diameter of 100 µm. Solution and coagulation baths were both kept at room temperature for all spinning trials.

Films and filaments were analyzed through solid state NMR spectroscopy to receive information regarding the inner structure, such as crystallinity, using a Varian Inova-600 following method explained elsewhere (Olsson et al. 2014). In addition mechanical properties of filaments were measured using Vibroskop and Vibrodyn, Lenzing Instruments, in 21.5°C and 65% RH. The average orientation of the crystalline and amorphous phase, birefringence, was measured with Nikon Eclipse Ci POL, polarized light microscope equipped with a 3A Berek compensator. The birefringence was given by the retardation of the polarized light divided by the filament diameter, calculated from titer using a cellulose density of 1.5 g/cm³. The surface of spun filaments was observed in a SEM of type JEOL JSM-6610LV.

**Results and Discussion**

Turbidity measurements concluded that cellulose can be dissolved in pure TBAAc:DMSO up to a molar ratio of 1:1 AGU:TBAAc, which makes TBAAc efficient compared to other ionic liquids (Le et al. 2014). The intrinsic viscosity was not altered between pulp and filaments, indicating no degradation of cellulose during dissolution, in line with previous work (Miao et al. 2014).

Observations in light microscope showed that more ethanol than water, expressed as wt%, was tolerated, summarized in Figure 1. However, if the concentrations are expressed in molar fractions the relation is reversed. It was also found that if the TBAAc concentration of the solvent was increased, the solutions could tolerate a higher concentration of non-solvent.
Figure 1. Phase diagram of cellulose in 2:7 TBAAc:DMSO-water (left) 2:7 TBAAc:DMSO-ethanol (right) obtained by light microscopy. Circles correspond to clear solutions, for crosses non-dissolved fibers were visible.

From NMR measurements on films, non-dissolved fibers could once again be confirmed by presence of cellulose I for higher non-solvent concentrations. For spun filaments the inner structure was, in addition to solvent composition, also dependent on coagulation medium. Filaments coagulated in water were partly crystalline, displaying signals characteristic to cellulose II (around 108 and 88 ppm), as visible in Figure 2. The mechanical properties of the spun filaments are shown in Table 1. With up to 2 wt% of non-solvent in the solution there was little or no change in filament properties. Neither did the viscoelastic behavior of these solutions differ much from that of solutions with no added non-solvent. Changes in mechanical properties started to appear with 3 wt% non-solvent in solution and were clear with a concentration of 4 wt% ethanol, when the filaments proved to be very brittle.

Figure 2. NMR spectra for filaments coagulated in water and ethanol respectively. Spun from solutions containing 5 wt% cellulose, no added non-solvent and with a draw ratio of 1.

Table 1. Mechanical properties of filaments.

<table>
<thead>
<tr>
<th>Non-solvent</th>
<th>Concentration</th>
<th>DR</th>
<th>Tenacity (cN/tex) ±</th>
<th>Elongation, % ±</th>
<th>Elastic modulus 1% (cN/tex) ±</th>
<th>Birefringence Δn * 10^2 ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>No added water</td>
<td>1</td>
<td>15.9 0.4</td>
<td>16.9 1.9</td>
<td>594.2 26.0</td>
<td>2.43 0.07</td>
</tr>
<tr>
<td>Water</td>
<td>2 wt%</td>
<td>1</td>
<td>15.3 0.4</td>
<td>18.9 1.5</td>
<td>576.9 20.6</td>
<td>2.43 0.14</td>
</tr>
<tr>
<td>Water</td>
<td>3 wt%</td>
<td>1</td>
<td>14.4 1.0</td>
<td>5.8 0.9</td>
<td>743.3 27.6</td>
<td>2.66 0.33</td>
</tr>
<tr>
<td>Ethanol</td>
<td>No added ethanol</td>
<td>1</td>
<td>11.3 0.5</td>
<td>15.3 1.9</td>
<td>476.4 18.6</td>
<td>2.26 0.16</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2 wt%</td>
<td>1</td>
<td>11.3 0.4</td>
<td>18.5 1.7</td>
<td>476.8 28.5</td>
<td>2.10 0.14</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3 wt%</td>
<td>1</td>
<td>13.0 0.3</td>
<td>12.8 0.9</td>
<td>577.1 31.2</td>
<td>2.50 0.11</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4 wt%</td>
<td>1</td>
<td>12.7 1.0</td>
<td>4.9 1.3</td>
<td>684.4 55.4</td>
<td>2.52 0.23</td>
</tr>
<tr>
<td>Ethanol</td>
<td>5 wt%</td>
<td>1</td>
<td>5.6 0.6</td>
<td>1.9 0.5</td>
<td>410.8 25.0</td>
<td>-</td>
</tr>
</tbody>
</table>
Summary and Outlook

The combination of TBAAc:DMSO proved to be an efficient and non-degrading solvent for cellulose, in line with results reported by Miao et al. (2015). The system’s ability to tolerate non-solvent depended on cellulose concentration, TBAAc:DMSO ratio and type of non-solvent. Solutions with a non-solvent concentration above the dissolution limit, confirmed by non-dissolved fibers, appeared gel-like. It was expected to find a difference between the impact and tolerance of ethanol and water content, but the difference is surprisingly small. Computational modelling will be used to further study this system and give information regarding the molecular interactions.

For spun filaments the mechanical properties were not altered with up to 2 wt% water or ethanol in solvent. With increased amount of ethanol in solution the maximum elongation possible was significantly lowered, with 4 wt% ethanol the filaments became very brittle and are no longer suitable as textile fibers. This shows that properties are preserved only up to fairly low non-solvent concentrations, but this limit can most probably be elevated by an increase of TBAAc in solvent.

Interesting properties indeed arose with higher non-solvent concentration in solution. Filaments spun from a solution with 4wt% of ethanol show a higher elastic modulus than filaments from solution with none or lower ethanol concentration, this suggests a change in inner structure of the filaments as a result of solution composition. The inner structure of the filaments will be further investigated, especially through solid-state NMR.

Acknowledgements

This work was funded by The Swedish Research Council Formas. NMR measurements were carried out at the Swedish NMR Centre, Göteborg, Sweden.

Litterature


Presentation 3
Homogenous modification of cellulose in the new solvent triethyloctylammonium chloride in combination with organic liquids

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Recently, it has been demonstrated that triethyloctylammonium chloride (N2228Cl) bears great properties as cellulose solvent both as melt and in combination with organic solvents (Kostag et al. 2013; Kostag et al. 2014). On one hand, N2228Cl and N,N-dimethylacetamide (DMAc) dissolve cellulose within 2 h without prior activation of the polysaccharide. On the other, N2228Cl unexpectedly dissolves cellulose in the presence of acetone, which typically is known as precipitation agent for cellulose. On very recent studies, the novel solvent was applied for tosylation, acetylation and silylation of cellulose (Achtel 2016). These types of reactions were chosen, because tosylcellulose is an important intermediate for nucleophilic displacement reaction with cellulose, cellulose acetates are of industrial interest, and silylation of cellulose is commonly used to achieve products that form ultrathin films by spin-coating useful as model surface. The reactions were studied under different conditions and the resulted degree of substitutions (DS) were compared with values obtained in common cellulose solvents (LiCl/DMAc, DMSO/TBAF or ionic liquids).

Figure 1.


Presentation 4

Cellulose Carbonates: A Platform for Promising Biopolymer Derivatives with Multifunctional Capabilities

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In addition to cellulose tosylates (Heinze et al 2016), cellulose carbonates represent a new type of platform compounds that open new possibilities for the design of advanced materials based on the most important renewable resource cellulose. In addition, the synthesis concept can be used for polysaccharides in general that could be proofed for starch and dextran carbonates. In the presentation, the efficient preparation of well-soluble cellulose carbonates is discussed based on own research program about organo-soluble and reactive polysaccharide derivatives. Homogeneous procedures are most efficient applying typical cellulose solvents including N,N-dimethylacetamide (DMAc)/LiCl and ionic liquids (IL) in combination with organic solvents like pyridine. Even products with complete functionalization of all hydroxyl groups are available (degree of substitution, DS 3). The cellulose carbonates are commercially available from a start-up company and are well suitable for homogeneous conversion with nucleophilic compounds in particular with amines. They are easily soluble in organic solvents; thus, the time-consuming and tricky dissolution of cellulose in complex solvents can be omitted. The synthesis and aminolysis of cellulose carbonates with low, intermediate, and high DS and the evaluation of this chemistry with respect to specific challenges will be exemplarily discussed. Functional cellulose carbamates, obtained from cellulose phenyl carbonate by aminolysis, show the potential use of this class of celluloses. Immunoassays, zwitterionic polymers, products for laundry applications are included as representative examples regarding properties and application of the new cellulose-based products (Elschner and Heinze 2015)

![Figure 1](image)

Figure 1.

Literature


Presentation 5
Cellulose derivatisation – tuning and analysing the degree of substitution

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Pulp fibres are negatively charged by nature, but the resulting electrostatic repulsion can be changed by cationisation. This rather straightforward chemical modification will considerably broaden the application range of lignocellulosic materials, such as wood pulp fibres. The pulp fibres can be covalently modified with the same reagent that is widely used for the cationisation of starch, 2,3 epoxypropyltrimethylammonium chloride. In general, one option for the hydroxyalkylation of cellulose is in slurry processes with organic diluents.

Using different organic solvents, the cationisation efficiency as well as on the properties of pulp can be influenced easily. In the presented study, a bleached softwood Kraft pulp was cationised in alkaline mixtures of water with dimethyl sulfoxide (DMSO), isopropanol, and tetrahydrofuran (THF). Of the systems studied, THF offered the highest reaction efficiency with respect to the achieved degree of substitution (DS). The system with DMSO was the only one that considerably decreased the molar mass of the material; the reaction efficiency was similar to a purely aqueous system. Alkaline isopropanol had the greatest impact on crystallinity and while this system increased the reaction efficiency, it was still less effective than THF. Replacing 90% of the water with THF yielded a significantly higher DS. The DS linearly depended on the concentration of reagent in respect to the present water; this was observed not only for purely aqueous systems but also for systems that contained THF. This correlation may be deployed to plan and control laboratory-scale cationisation assays.

Tuning the DS as described above also calls for reliable analytical techniques for DS determination. The resulting materials with different DS were analysed by titration, infrared spectroscopy (IR), elemental analysis, and thermogravimetry. All the methods tested have their merits. While titration and elemental analysis are well-established reference methods with many published data, they require time-consuming pre-treatments. This can be avoided by fast and simple IR spectroscopy. However, IR spectroscopy relies on a reference method to quantify the DS. Another option explored in this work is thermogravimetry that yields additional information on water content and purity of the sample. This method, too, requires a reference method to evaluate the impact of the DS on the changed thermograms.
Presentation 6
Activation of dissolving cellulosics pulp for viscose and cellulose ether production

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Mercerisation of cellulose by alkali treatment is the most common procedure used to activate natural cellulose fibres into many commercial cellulosic materials. During mercerisation, the NaOH solution enters the cellulose fibres, transforming them into a swollen and a highly reactive material called alkali cellulose (Na-Cell). In case NaOH is completely washed out of the cellulose structure, Na-Cell turns into Cellulose II upon drying.

Traditionally the cellulose is mercerised by suspending it in a 15-20% NaOH solution. The result is a high (15-25 mol/mol) NaOH: Anhydroglucose molar ratio (r) and mercerisation in these conditions have been extensively studied. However, in modern production of cellulose ethers, the mercerisation conditions are often very different. The main reason is that any excess of water and OH-ions used during the mercerisation can later react with different chemicals in the process, thus forming unwanted by-products e.g. methanol. One way to avoid this kind of side reaction is by using low-water-content mercerisation conditions, i.e. low (r) = 0.8-1.8 mol/mol and high NaOH concentration (45-55% w/w). The traditional mercerisation is a suspension process while the cellulose during the latter process, i.e low-water-content mercerisation conditions, remains quite “dry”. Thus, although the chemical reaction principles of activation of cellulose for both viscose and cellulose ethers processes are the same, the activation conditions used are often very different. Therefore, the different dependencies of process parameters as well as any similarities between the processes are interesting.

The presentation summarises the findings presented in two papers which described the influence of the different parameters on the mercerisation/activation of softwood Sulphite dissolving pulp in viscose production conditions (Albán Reyes et al. 2016) and cellulose derivatives production conditions (Albán Reyes et al.) respectively. In the individual studies this has been done by analysing the degree of transformation (DoT) of dissolving pulp to Na-cellulose (or more correctly cellulose II after washing and upon drying) as a function of simultaneous variation of [NaOH], temperature, and reaction time varied using design of experiment. Also the (r) was varied for samples mercerised at dry conditions. A combination of Raman imaging and multivariate data analysis have been used to study the DoT to Cellulose II.
It was found that the mercerisation under the different conditions was dependent on different parameters. For traditional mercerisation, on the one hand, the temperature was shown to be important for the DoT and showed negative correlation with the data, while [NaOH] showed a positive correlation. On the other hand, at low-water-content mercerisation conditions the (r) was overall most important while the temperature showed no statistical importance in a Partial least squares analysis. Traditional mercerisation gave much higher DoT than the low-water-content mercerisation. Thus, the data for low-water-content mercerisation was further examined at the different (r). The same chemistry is always expected and the different influences of the parameters seen is understood and discussed in terms of the different physical reaction mechanisms.

**Literature**


Albán Reyes DC, Stridh K, de Wit P, Sundman O In preparation.
Presentation 7
Novel cellulose based fibre and fibril yarns

Ali Harlin1, Hannes Orelma1 and Herbert Sixta2
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There is continuous need for performance materials and cellulose provides more sustainable way to added value products. In Finland we have developed novel cellulose based filaments based on pulp fibres and nano fibril. Actually they are yarns. In order to form the cellulose I yarns there has been developed multiple continuous production technologies based on both wet and dry spinning processes. There are applied several binding methods and one exciting developments has been based on the use of deep eutectic solvents.

Further we have developed and demonstrated regenerated textile fibres from recycled cellulose like paper, board and cotton cloths. Novel recycled fibres materials increase the sustainability as well as the raw material independency of fashion and hygienic products. There are also quite unique developments on cellulose II fibre raw materials including lignin containing and recycled alternatives.

The developments are made in several research programs and projects and now they are approaching piloting stage. Recently it seems also that the developments have arising industrial interest, because there are several start-ups coming up. This presentation will give you an overview of the resent developments. In this presentation are highlighted the resent achievements accordingly.
In order to develop new cellulose-based materials and optimize their production processes, a fundamental knowledge of the interactions between cellulose and other substances is crucial. Exposure to various environmental conditions is expected and there is hence a need to develop a model cellulose material that can be used to characterize moisture adsorption, condensed water adsorption, polymer adsorption, adhesion between cellulose and other materials etc.

To meet these demands we have developed a new type of cellulose hydrogel beads with macroscopic dimensions (1-3 mm) and controlled chemical composition. This was achieved by dissolving cellulose in LiCl/DMAC and a controlled regeneration of the cellulose into smooth beads with a special precipitation procedure (Carrick, Ruda et al. 2013). The cellulose beads possess a spherical geometry that is preserved when subjected to various water based solutions and upon drying (see Figure 1.). Initially we have used these beads in studies aimed at clarifying the fundamentals behind swelling of cellulose hydrogels. The focus in the present work is on using the beads to establish the fundamental factors controlling the swelling of cellulose rich fibres. Despite considerable work on clarifying the ion-induced swelling of cellulose hydrogels (Grignon and Scallan 1980, Lindström and Carlsson 1982), there is still a very limited knowledge about the factors controlling the non-ionic swelling of the hydrogels which in fact is the dominating factor controlling fibre swelling.

The cellulose beads used in our current investigation have been made with different amount of carboxyl groups to be able to mimic the polyelectrolytic behavior of a fibre wall and to quantify the relative significance to the overall swelling of the cellulose hydrogel beads. It has been shown that the cellulose beads follow the similar trends shown in literature regarding the swelling due to changes in pH and ionic strength (Racz and Borsa 1997, Fält, Wågberg et al. 2003). The cellulose beads have a wet modulus which varies with the amount of carboxyl groups in the cellulose beads going from approx. 32 down to
10 kPa with increasing amount of carboxyl groups. This trend has been reported previously when studying the modulus of pulp samples (Scallan and Tigerström 1992).

Significant efforts have also been conducted to describe the internal structure of the cellulose beads. Possible crystalline domains in the cellulose beads were investigated using solid state CP/MAS $^{13}$C NMR and Small Angle X-ray Scattering was performed to reveal internal repeating scattering objects in the nano-scale range. These results lead to the interpretation of the cellulose beads being a molecularly dispersed gel with no crystalline domains containing polymer coils with a radius of gyration of approx. 25nm.

By changing the solution composition outside the hydrogel we have also been able to characterize how osmotic stress will alter the swelling of the hydrogel and how this compares with conventional superabsorbent polymers.

All of our results indicate that we have developed a new interesting material that can be used to mimic the behavior of the delignified wood fibre wall regarding water adsorption and absorption. These probes are also expected to be of valuable use for fundamental research on cellulose in other areas such as polymer adsorption and adhesion.

Literature


Controversies still remain regarding the supra-molecular structure of cellulose I isolated from plants such as wood. Emphasis is here made on the concept of isolated cellulose meaning a cellulose rich, typically above 95 % to 96 % glucose, cellulose I material with a low content of charged groups, typically below 30 micromoles per gram. Cellulose I isolated in the form of cellulose rich pulp fibres can be used as the starting material for chemical modifications, for example TEMPO-oxidation.

Although there are several models used for describing the supra-molecular structure of the smallest cellulose I building-block, here called a fibril, common to all is the limited lateral dimension of the fibril. Cellulose fibrils isolated from wood typically have lateral dimensions in the range of 3 nm to 5 nm. These fibrils contain a core, normally considered as crystalline, surrounded by surface polymers possibly of a lesser degree of order. With an estimated crystalline density of 1500 kg/m3 to 1600 kg/m3 the interior part of fibrils are considered dense enough to be impenetrable to most molecules, e.g. water.

During heterogeneous reactions, chemical modification of cellulose is a process initially occurring at the fibril surface. Depending on the chemistry involved, fibril surfaces can be more or less accessible depending on how the fibrils are packed together, aggregated, one aspect of the complex supra-molecular structure.

In this work the focus was on the fate of the cellulose supra-molecular structure during the initial phase of TEMPO-oxidation. When combining existing results from solid state NMR (CP/MAS 13C-NMR), atomistic molecular dynamics simulations and x-ray diffraction (XRD) (Su et al. 2015), a coherent picture was found. The consistency between the experimental and computational results adds further support to a fibril model in which fibril surfaces are parallel to the (1,1,0) and (1,-1,0) crystallographic planes.

Litterature

Presentation 10
All-cellulose composites via short-fibre dispersion approach

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Polymer composites with improved mechanical properties are typically reinforced with dispersed glass or carbon fibres; recently, natural fibres have been considered as promising reinforcing materials. However, the poor interface between the fibres and the matrix made of chemically different materials is causing bad stress transfer and thus insufficient mechanical properties. These drawbacks have been overcome by making “self-reinforced” composites (for example, a polypropylene matrix reinforced with polypropylene fibres). The adhesion between the fibres and matrix is then practically perfect. Such “one-polymer” composites exhibit significantly enhanced mechanical properties and greatly simplifies recycling.

This “self-reinforced” idea can also be applicable to cellulose and natural fibres for making all-cellulose composites. With cellulose fibres embedded into a cellulosic matrix, these strong self-reinforced cellulose composites will be fully bio-based, biocompatible and biodegradable.

In our work we used “short fibre dispersion” approach mimicking the preparation of polymer-short fibre composites. 8wt%NaOH-water was used for dissolving cellulose pulp for making a matrix and soft wood kraft pulp was used as reinforcing fibres. The evolution of fibre size and dissolution during mixing was monitored. The mechanical properties of composites were controlled by the concentration of the reinforcing fibres and DP of dissolving pulp. Composite structure-properties relationships will be presented and discussed.

Acknowledgements
The work was performed in the frame of “ALL-CELL” project financed by TEKES (Finland) and supported by Stora Enso, UPM, Fibertus and Separation Research.
The supramolecular structure of cellulose-rich wood and wheat straw pulps can be a determinative factor for enzymatic hydrolysability

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Conversion of biomass to biofuels and other products is a research area that is currently attracting a great amount of interest, particularly because such production may be envisaged as a key part of any bio-based economy. Lignocellulosic biomass is abundant and sustainable, and can therefore potentially support large-scale production of biofuel as an alternative to petroleum-based fuel.

The enzymatic hydrolysability of three industrial pulps, five lab made pulps, and one microcrystalline cellulose powder was assessed using commercial cellulolytic enzymes. To gain insight into the factors that influence the hydrolysability, a thorough characterization of the samples was done, including their chemical properties (cellulose content, hemicellulose content, lignin content, and kappa number), their macromolecular properties (peak molar mass, number-average molar mass, weight-average molar mass, polydispersity, and limiting viscosity) and their supramolecular properties (fibre saturation point, specific surface area, average pore size, and crystallinity). The hydrolysability was assessed by determination of initial conversion rate and final conversion yield, with conversion yield defined as the amount of glucose in solution per unit of glucose in the substrate. Multivariate data analysis revealed that for the investigated samples the conversion of cellulose to glucose was mainly dependent on the supramolecular properties, such as specific surface area and average pore size. The molar mass distribution, the crystallinity, and the lignin content of the pulps had no significant effect on the hydrolysability of the investigated samples.

In addition, experiments were carried out aiming at identifying suitable conditions for pre-treatment of wheat straw, for the purpose of making cellulose rich pulps with improved enzymatic reactivity. Two sets of conditions for pre-treatment of wheat straw were identified; a combination of low temperature alkaline washing and acid pre-hydrolysis, or high temperature acid pre-hydrolysis. Both bleached wheat straw pulps showed similar enzymatic reactivity. However, the enzymatic reactivity of both bleached wheat straw pulps was found to be significantly less than what has been achieved for wood pulps. A probable explanation for the low enzymatic reactivity of the bleached wheat straw pulp can be the small pore size, limiting the access for enzymes to the cellulose surfaces in the fibre wall interior.

Text, figures and tables in an extended abstract (< 4 pages with title and references).
Presentation 12

Influence of the amount and position of cellulose in plant stems on the behaviour of plant stem reinforced-polymer composites

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Polymer composites prepared with a polymer matrix reinforced by elongated, broken fragments of plant stems can in some cases favourably compete with the same composite reinforced by glass fibres. However, the mechanical properties of the final composite are directly related to the properties of the stem fragments. Cellulose is the main polymer controlling the mechanical strength of these fragments. Two plants will be studied, miscanthus and sorghum.

We will show that amount of cellulose in the stem fragments depends on the preparation methods of these fragments. We will report the correlations which exists between the amount of cellulose and its location within the different tissues of the stem and the mechanical properties of the final composite product.
1. Introduction

Growing environmental awareness and increasing interest in sustainable material concepts have led to the development of biocomposites for structural material applications. All-cellulose composites (ACCs) are a subtype of biocomposites which are single-polymer composites where both the matrix and reinforcement are based on non-derivatized cellulose (Nishino et al. 2004). In addition to their biodegradability, the benefit of ACCs is the chemical similarity of the matrix and the reinforcing phase, whereby they are able to overcome the problem of poor fibre-matrix adhesion which is common in biocomposites (Huber et al. 2012; Kalka et al. 2014).

ACCs can be prepared using one of two routes: Cellulose reinforcement fibres are mixed with a pre-dissolved cellulose solution that forms the matrix (Nishino et al. 2004) or cellulose fibres are brought into contact with a solvent to partially dissolve the fibre surface, thereby creating a cellulose matrix in situ (Nishino and Arimoto 2007). Both routes require a solvent for non-derivatized cellulose.

NaOH-based aqueous solutions as cellulose solvents are a group that has a low environmental impact. The use of aqueous NaOH as a cellulose solvent was discovered in the 1930s by Davidson (Davidson 1934; Davidson 1936). However, the dissolution of most untreated cellulose samples was found to be only partial. Davidson also showed that a decrease in temperature improves cellulose dissolution. Later, the use of additives such as urea (Cai and Zhang 2005; Cai et al. 2007; Yang et al. 2011; Xiong et al. 2014; Shi et al. 2015), thiourea (Zhang et al. 2002) and ZnO (Kihlman et al. 2012) was found to increase the solubility of cellulose and the stability of the solution.

The most used solvent contains 7 wt% NaOH and 12 wt% urea in destilled water, which is also used for the production of the plasticised fibre composite presented in this work.

2. Experiments

Laboratory sheets made from high dissolving pulp with an initial grammage of 100 g/m² (oven dried) were dipped into the NaOH/urea solvent and then placed into a cooled glass vessel for 2, 30, 60, 120 and 240 seconds before washing with tap water to regenerate the dissolved cellulose. The obtained material, called plasticized fibre composite (PLAFCO), was characterized via FESEM, Wide-Angle X-Ray diffraction (WAXS) and mechanical tests.
XRD patterns were simulated for crystalline cellulose I, II and amorphous cellulose using .cif files and fitted to the measured ones. This gave the relative amounts of each crystal structure contained in the ACCs.

The process was also adapted to a running pilot paper machine. For this the preformed and dried paper was drawn through a size press that was filled with cooled NaOH/urea solvent, subsequently washed with water by hand and again dried to verify the possibility of producing PLAFCO in industrial scale.

3. Results

SEM images at 1000x magnification are provided in Figure 1, which shows the morphological development of cross-sectional surfaces of the ACC produced with different dissolution times. The untreated cellulose sheet is presented in Figure 1a, clearly showing the fibrous structure of the starting material. After a treatment time of 2 s, the fibre structure was still clearly visible, which indicates that the formation of the matrix phase did not effectively occur during the first 2 s of dissolution.

After 30 s of dissolution, the visible fibre structure had completely disappeared and distinctive matrix and reinforcing fibre phases could not be seen.

![Figure 1](image)

Table 1 shows the relative amounts of cellulose I, cellulose II and amorphous cellulose as obtained from fitting the XRD patterns. The fitting gives a value of 91% cellulose I for the untreated sheet, which is in total accordance with the material data sheet. As it can be seen, the amount of cellulose I decreased within the first 30 s of treatment from 91% to 58% and after this just slightly, while the amount of amorphous cellulose increased just within the first 30 s. This behaviour indicates that the dissolution of cellulose fibres progressed effectively over the first 30 s, but afterwards the dissolution was much slower or stopped.

Table 1. Relative amounts of cellulose I, cellulose II and amorphous cellulose obtained from fitting

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amorphous</th>
<th>Cellulose</th>
<th>Cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>7.2 ± 0.2</td>
<td>91.3 ± 0.3</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>
The averaged stress–strain curves for untreated dissolving the wood pulp sheet and ACCs are presented in Figure 2.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 s</td>
<td>10.5 ± 0.2</td>
<td>77.1 ± 0.3</td>
<td>12.4 ± 0.2</td>
</tr>
<tr>
<td>30 s</td>
<td>13.8 ± 0.2</td>
<td>58.4 ± 0.3</td>
<td>27.8 ± 0.3</td>
</tr>
<tr>
<td>60 s</td>
<td>15.8 ± 0.2</td>
<td>57.7 ± 0.3</td>
<td>26.5 ± 0.2</td>
</tr>
<tr>
<td>120 s</td>
<td>14.4 ± 0.2</td>
<td>57.6 ± 0.3</td>
<td>28.0 ± 0.3</td>
</tr>
<tr>
<td>240 s</td>
<td>15.2 ± 0.2</td>
<td>52.9 ± 0.4</td>
<td>31.9 ± 0.3</td>
</tr>
</tbody>
</table>

Figure 2. Averaged stress-strain curves

Tensile strength at break increased at dissolution times of 2 to 30 s rapidly from 3 MPa to 49 MPa, and longer dissolution times did not have an effect on strength. This is analogous to earlier findings from XRD and FESEM.

4. Conclusion

ACCs were successfully prepared using NaOH/urea solvent from dissolving cellulose pulp raw material. Reasonable amount of cellulose can be dissolved and thereby a remarkable increase in ACC tensile properties is obtained within a short (30 s) treatment time. FESEM images showed that the fibre network becomes invisible with increasing treatment time while the XRD results indicated that the fibres are just partially dissolved and therefore lead to the conclusion that the fibre network was still present in the composite.

Tensile strength increased more than ten times with a short solvent treatment. Strain at break increased only slightly, and the reason for this might have been the restrained shrinkage in the planar direction during drying in the Rapid-Köthen former. Short processing times and the use of green chemicals suggest that this process has potential to be used in a large-scale industrial all-cellulose composite production.
5. Literature


Note: The above references are extracted from the text. Additional information or context may be necessary to fully understand the content.
Presentation 14
Cellulose II nano- and microparticles through a heterogeneous approach

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A side-product of the TENCEL®¹ fiber production was used as a raw material for preparation of cellulose II nanoparticles and nanostructured gels. The gels were generated by enzymatic pre-treatment and a single cycle in a high-pressure homogenizer. Their microhierarchies were revealed to originate from individual particles that aggregated and formed a suspension with rheological properties of a soft solid (Beaumont et al. 2016 a). The gels were characterized comprehensively by light-microscopy (structure), rheology, GPC, solid-state NMR and x-ray scattering. The gel was implemented for two applications: to produce porous nanostructures and as precursor for nanoparticles.

![Cellulose II gel](image1.png)

**Figure 1.** Fluorescence microscope image of cellulose II gel after staining with calcofluor-white (A) and SEM micrograph of the cellulose II cryogel after freeze-drying. The TEM micrographs (C, D) show the spherical nanoparticles, which are obtained from the gel after carboxymethylation and subsequent mechanical shearing.

¹ TENCEL® is a trademark of Lenzing AG.
Quite remarkably, freeze-drying of the gel with a prior solvent-exchange to tert-butanol resulted in formation of a porous aerogel with a surface area of 298 m²/g consisting of particles with a fibrillar nanostructure (Figure 1B). The porosity of the gel was investigated by thermoporosimetry and nitrogen sorption and showed that the cryogel is micro-, meso- and macroporous with a mean pore size of 52 nm (Beaumont et al. 2016b). Further analysis of this porous material with inverse gas chromatography showed that the sample is energetically heterogeneous and has a total surface energy of 59 mJ/m².

In addition to that, chemical modification of the particles by carboxymethylation was employed to introduce repulsive charges onto the cellulose surface, causing spherical nanoparticles to form (Beaumont et al. 2016c). Dependent on the degree of substitution, the size of these nanocolloids was tailored from a mean size of 73 nm to 129 nm (Figure 1 C, D). After drying, the nanoparticles could be easily redispersed in water just by magnetic stirring.

The economic and straight-forward production of this gel and the possibility to tune the particle size render it a promising contribution to the family of nanocelluloses.

**Literature**


Shaping of cellulose into films or fibers is possible by dissolution and precipitation from a solvent, such as N-Methyl-Morpholine-Oxide and more recently from ionic liquids (ILs). A range of questions remain before large scale plants can be built based on any of this group of newer solvents (ILs). One such issue is to control material properties, so as to generate high added values in such production plants. In order to better understand the dependencies of structural, micro- and macro properties on process parameters a PhD-project was initiated in 2013 by Södra Innovation in cooperation with Swerea IVF, Lund University of Technology and Chalmers University of Engineering, as part of a 3rd generation within the long term Avancell project. In this project a range of aspects of coagulation have been investigated on a rather fundamental level, such as: critical concentrations of non-solvent for coagulation, rates of mass-transport for the multiple species exchanged with the coagulating fiber and the structures regenerated as a function of the coagulation conditions. These have not been very closely studied before and several new methods were developed to do so. As a consequence there is now a rather wide phenomenological understanding of the different sub-processes involved as cellulose solutions go from liquid to solid. E.g. it appears that several of the interpretations made and beliefs held by some previous researchers must be revised. Due to the relative completeness of data around a single ionic liquid (IL) based system (1-Ethyl-3-Methyl-Imidazolium Acetate, EmimAc, and DMSO coagulated in alcohols or water) the understanding obtained becomes more general and in many respects translatable also to other ILs.

Coagulation values

In this project a first question was how much non-solvent is required to induce phase separation in the solutions used for fiber spinning. For this purpose a method was developed in which opacity is measured as a function of the weight of non-solvent absorbed from a vapor in the apparatus in Figure 1, left. To the left, is a typical such curve from a measurement with the coagulation value pointed out. With this method we found clear differences between the three non-solvents tested: CV<sub>water</sub>< CV<sub>EtOH</sub>< CV<sub>2PrOH</sub> (if expressed in weight) or CV<sub>water</sub>< CV<sub>EtOH</sub>< CV<sub>2PrOH</sub> (if expressed in moles). There were also strong trends from the cellulose concentration of the solution and the amount of co-solvent, DMSO, included in some of the solutions. By applying linear fits, which functioned well, to this data we could also parameterize these dependencies (parameters in Table 1), seen in Figure 2, by an equation which describes a molar balance between solvent, non-solvent and cellulose (nAGU) for the limit of precipitation:

\[
n_{\text{EmimAc}} = A \cdot n_{\text{AGU}} + B \cdot n_{\text{H2O}} + C \cdot n_{\text{EtOH}} + D \cdot n_{\text{2PrOH}}
\]
Figure 1. Left: Cross section of the setup used for measurements. Scale (1), enclosure or chamber (2), wire mesh (3), light meter (4), enclosing beaker (5), beaker with non-solvent (6), heating element with PT-100 sensor and regulator (7), vapors pass through wire mesh (8), tube infusing N₂ (9), HDPE pipe transmitting force to scale (10), light source (9 LEDs) (11) and glass plate with polymer solution coating (12).

Right: evaluation of coagulation value, CV, from opacity measurement curve marked by steepest slope (red arrow).

Figure 2. Molar CV data for different solutions and non-solvents.

Table 1. Parameters for linear fits of CVs, to describe dependencies on cellulose concentrations

<table>
<thead>
<tr>
<th>Solvent (wt:wt) EmimAc:DMSO</th>
<th>n(nEmimAc/nAGU)</th>
<th>n(nEmimAc/nH₂O)</th>
<th>n(nEmimAc/nEtOH)</th>
<th>n(nEmimAc/n2PrOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>2.303</td>
<td>0.373</td>
<td>0.617</td>
<td>0.749</td>
</tr>
<tr>
<td>75:25 (58:42)</td>
<td>1.880</td>
<td>0.273</td>
<td>0.509</td>
<td>0.621</td>
</tr>
<tr>
<td>50:50 (68.5:31.5)</td>
<td>1.395</td>
<td>0.198</td>
<td>0.476</td>
<td>0.497</td>
</tr>
</tbody>
</table>

To conclude on this part of our work it may be stated, that although precipitation is not as sensitive to non-solvents as the dissolution process, the amounts required to induce phase separation in solutions which would be used in fiber spinning are still small (~10wt% on the solution). In addition there are also rheological (gel-like) changes induced even at concentrations below those observed optically in our study.
Structures of coagulated never dried cellulose

In order to understand what kind of cellulose structures are present in the coagulated material, we coagulated a range of cellulose solutions in H₂O and 2PrOH. The material was then washed and solvent exchanged in several steps, so that the final drying would be from cyclohexane, which preserves the originally coagulated structure much better than if a more polar solvent is removed by evaporation. The resulting material was observed in SEM and several additional measurements were performed: crystallinity index by solid state NMR, specific surface are by BET and other methods. The results showed that the structures are heterogeneous with a continuous pore system surrounding a fibrillar network of cellulose. Also the very large specific surface areas (up to ~380m²/g) disclose very small fibril dimensions. The crystalline index may also be interpreted in terms of crystalline dimensions if it is supposed that crystal interiors give a crystalline signal in solid state NMR, while its surfaces do not. To compare these two measures of fibril and crystallite dimensions is another interesting aspect of these results. Further, water as non-solvent generally gave higher crystalline indexes and BET-surface areas, compared to 2PrOH, in which the crystalline index becomes almost negligible. When water is the coagulant an increased cellulose concentration will reduce the crystalline index but increase the specific surface area.

Figure 3. Cellulose coagulated in water from 25wt% cellulose solution (left) and 14.3wt% solution (right).

Mass-transport during coagulation

During coagulation of cellulose, multiple diffusive fluxes add up to a total gain or loss of mass and volume. This is an important parameter as dilution of polymers typically affects their entanglement density and consequently the structural properties of the material produced from it. The general rates are also of importance. Thus an experimental method was developed whereby both the concentration of solvent in the coagulation liquid and the solution mass could be tracked as a function of time (example in Figure 4, left). Apparent diffusion coefficients (D) could be calculated from this data. An apparent D represents a “mean, effective” diffusion coefficient for the process as a whole, even though the real D is a function of concentrations which will vary in both space and time dimensions. When comparing such apparent Ds to corresponding self Ds, from diffusion NMR experiments, they are not as different as might be expected based on their high cellulose concentrations which could inhibit diffusion. There was neither any general trend in apparent D due to cellulose concentration. The reason for this independency with regard to cellulose concentration was also observed in the structural study above: the open continuous porous structure of coagulated cellulose, which only constitutes a minor volume fraction, does not interact significantly with the diffusing species. That cellulose did not have a very important effect, has many important implications, of which one is the ability to model diffusion in
coagulation processes numerically, with much less effort than if cellulose was having a large effect on mass transport. This was also verified by a very simplistic attempt to generate a concentration distribution inside the coagulating material of non-solvent and solvent by such a numerical model, of which the results are found in Figure 4, right.

![Figure 4](image)

**Figure 4.** Diffusive fluxes' propagation in time, left (measurements), and in space, right (numerically modelled).

**Outlook**
The new methods and understanding adds to Swerea IVF’s abilities as developers of fiber spinning processes, for which it was already well equipped in terms of experienced staff and equipment for dissolution, fiber spinning and analysis. The general picture of cellulose coagulation processes is a central piece of the puzzle to control fiber properties in these processes. This piece, we are happy to contribute to future R&D projects and share with industrial partners.

**The 7th Workshop on Cellulose**
Regenerated Cellulose and Cellulose Derivates

**15-16 November 2016**
Örnsköldsvik, Sweden

**Literature**

Introduction

Deep eutectic solvents (DES) are a promising and versatile class of chemicals that can function as solvents, reagents, and catalysts in many applications (Zhang et al. 2012). They are readily available, have low toxicity, are in many cases biodegradable, and exhibit negligible vapor pressure, which reduces their volatile organic compound (VOC) emissions (Singh et al. 2011). DESs are typically synthesized by complexation of a halide salt of quaternary ammonium or phosphonium cation as the hydrogen bond acceptor (HBA) along with a hydrogen bond donor (HBD) (e.g. urea, glycerol or ethylene glycol) to form a mixture that exhibits a notable lower melting point compared to either HBA or HBD. The strong hydrogen bonding prevents the parent components from crystallizing (Wagle et al. 2014). DESs are often classified as ionic liquids, although they can also be obtained from nonionic species. Compared to ionic liquids, DES exhibit certain advantages, including easy preparation from two or more components without the need for separate purification steps (Smith et al. 2014). Consequently, these properties make DES one of the most promising solvents and chemicals for sustainable material production.

Recently DESs use in biomass conversion has increasingly been reported (Xia et al. 2014; Kumar et al. 2016), but only few studies on the use of DES solvent systems for the fabrication of nanocelluloses have been published so far. In this work we report potential DES systems for the production of cellulose nanofibrils (CNF) and nanocrystals (CNC) and DES use in nanocellulose functionalization. Moreover, examples of DES-nanocellulose use as oil in water emulsion stabilizers are presented.

Non-derivatizing deep eutectic solvents as pre-treatments for nanofibrillation of cellulose fibers

Various chemical and enzymatic pre-treatments have been used for loosening the strong, hydrogen bonded structure of cellulose fibers and promoting their nanofibrillation. We investigated the potential of non-hydrolytic urea-based DES systems as novel pre-treatments for cellulose nanofibril production (Sirviö et al. 2015). In the experiments, deep eutectic systems containing urea and choline chloride, ammonium thiocyanate or guanidine hydrochloride as a second component were formed at 100 °C and then applied for pre-treatment of hardwood cellulose fibers. All DES systems were able to loosen and swell the cellulose fiber structure as indicated by the increase in the lateral dimension of fibers. After mechanical disintegration with a microfluidizer, individual cellulose nanofibrils with widths of 2–5 nm and larger nanofibril bundles with widths ranging from 15 to 200 nm were observed (Fig. 1a). Wide-angle X-ray diffraction (WAXD) and degree of polymerization analysis using the limiting viscosity method revealed that both the cellulose crystalline structure and the degree of polymerization of the cellulose remained intact after pre-treatment with DESs. Solvent casting was used to produce translucent films from the DES-nanofibrils. They exhibited good thermal stability and mechanical properties, with tensile strengths of approximately 135 to 189 MPa and elastic modulus of 6.4 – 7.7 GPa.
We also examined the potential of urea-choline chloride based DES in the production of nanofibrils directly from different secondary fiber sources without any other chemical treatments. Cellulose board grades including waste board (B), fluting (F) and waste milk container board (MCB) were pre-treated with urea-choline chloride and nanofibrillated using Masuko grinder. The fabricated nanofibril suspension obtained from DES pre-treatment had a viscous gel-like appearance with typical shear thinning behaviour. The nanofibrils showed a well individualized structure without significant loss in their crystallinity (Fig. 1b). Consequently, DES chemical pre-treatment showed to be a promising route to obtain cellulose nanofibrils directly from waste board and papers.

![Figure 1](image)

**Figure 1.** Cellulose nanofibrils obtained from a) hardwood pulp b) waste board using urea-choline chloride pre-treatments.

**Anionic cellulose nanofibrils functionalized in deep eutectic solvent**

Deep eutectic solvents represents a green medium for traditional solvents or ionic liquids for chemical modification of cellulose. We demonstrated urea-LiCl based DES as a successful reaction medium in the anionic functionalization of softwood cellulose with succinic anhydride (Fig. 2a) (Selkälä et al.). Based on the degree of polymerization and crystallinity analyses the urea-LiCl was found to provide a non-degrading and non-dissolving conditions for the functionalization. After succinylation reaction, the fibers having the carboxyl contents above 0.57 mmol/g were further nanofibrillated using a microfluidizer to anionic nanofibrils having diameters of 2-7 nm observed via atomic force microscopy (Fig 2b). Samples treated at 70-80 °C for 2 h gave the best outcome, resulting in highly viscose and transparent gels. The sample treated at 90 °C contained bigger nanoparticles and larger aggregates due to the occurrence of possible side reactions but resulted in better thermal stability than the samples treated at lower temperatures.
Production of cellulose nanocrystals using hydrolytic deep eutectic solvents

Acidic hydrolysis using aqueous mineral acids, such as sulfuric, hydrochloric, or phosphoric acids (Camarero Espinosa et al. 2013) has been the most common method to dissolve the non-crystalline regions of cellulose to produce CNCs. Acidic DES systems provide green alternatives for CNC production. For this purpose, we studied several choline chloride and organic acids DES systems including oxalic acid (anhydrous and dihydrate), p-toluene sulfonic acid monohydrate, and levulinic acid as acid components (Sirviö et al. 2016). All the DES treatments enhanced the degradation of wood fibers into micro-sized fibers and after mechanical disintegration, CNCs were successfully obtained from choline chloride-oxalic acid dihydrate-treated fibers, whereas no liberation of CNCs was observed with other DESs. The DES-produced CNCs had a width and length of 9–17 and 310–410 nm, respectively (Fig. 3). The crystallinity indexes (CrIs) and carboxylic acid content of the CNCs were 66–71% and 0.20–0.28 mmol/g, respectively. CNCs exhibited also good thermal stabilities (the onset thermal degradation temperatures ranged from 275–293 °C).

Cellulose nanocrystals from deep eutectic solvent as oil in water emulsification agents

Colloidal particles ranging from micro to nano-size can be used for stabilization of o/w emulsions to form so-called Pickering emulsions (Ojala et al. 2016). These particles provide also attractive alternatives for soluble polymeric dispersant in oil spill remediation in which the colloids can be used to disperse the oil slicks to smaller droplets and promote inherent biodegradability of oil by marine microbes. We investigated cellulose nanocrystals synthesized using choline chloride-oxalic acid dihydrate based DES and two commercially available cellulose nanocrystals (CNC-Ref) as marine diesel oil-water Pickering emulsion stabilizers (Fig. 4). Especially, oil in water (o/w) emulsion formation and stability of emulsified oil during storing were addressed. The results showed that CNCs were effective emulsifying agents for the marine diesel oil-water system by preventing the oil droplet coalescence and resulting in stable creaming layer. The CNCs prepared using green DES systems had performance comparable to that of commercial CNCs showing effectiveness already at 0.1% dispersant dosage.
Figure 4. Stabilization of o/w emulsions by cellulose nanocrystals obtained from DES.

Literature


Production of Bacterial Nanocellulose in Submerged Cultivations Using Forest-Industrial Residues

Genqiang Chen¹, Guochao Wu², Björn Alriksson³, Feng F. Hong¹ and Leif J. Jönsson²

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Our investigation points towards the opportunity to upgrade low-quality residual streams from pulp mills and biorefineries to high value-added BNC (bacterial nanocellulose) for advanced material applications (Fig. 1).

Bacterial nanocellulose (BNC), also known as bacterial cellulose and microbial cellulose, is a biodegradable extracellular macromolecule mainly synthesised by acetic acid bacteria. Since reported for the first time in 1886 (Brown 1886), BNC has drawn increasing attention due to its versatile properties (Gama et al. 2012; Lin et al. 2013). As plant cellulose, BNC is an unbranched polymer composed of beta-1,4-linked glucopyranose residues. However, its macromolecular structure and
properties are different from those of plant cellulose. BNC has much higher crystallinity and higher degree of polymerization than plant cellulose. The diameter of the BNC fibre, ranging from 20 to 80 nm, is also smaller than that of other natural or synthetic nanofibres. Besides, BNC features many other important unique properties, including high purity, high tensile strength, high Young’s modulus, large water-holding capacity, good shape maintenance, excellent biocompatibility, structure controllability during biosynthesis, and good controlled-release ability. These properties endow BNC with great potential in the areas textile manufacturing, fibre-based paper and packaging products, food industry, biomedical materials, and advanced functional bionanocomposites (Gama et al. 2013; Mohite and Patil 2014). However, these applications of BNC are restricted by its relatively high price. The high price is due to the high cost of the culture medium and the low yield of cellulose obtained in slow-growing stationary bacterial cultures.

We compared four bacterial strains with regard to their ability to produce BNC. The strains were compared using both stationary cultivation and shaking cultivation and at pH 4.0, pH 5.0 and pH 6.0. The yields of BNC on basis of initial and consumed sugar were investigated. The properties of the BNC from the four strains were also investigated and compared. Scanning electron microscopy was used to study surface morphology and distribution of the fibre diameter. Viscometry was employed to determine the degree of polymerization. FTIR and X-ray diffraction spectroscopy were used to study the chemical structure and the crystallinity. Using paper sheets made of BNC, the tear resistance and the tensile strength were measured.

Additionally, we investigated the possibility to utilize a low-value culture medium, viz. enzymatically hydrolyzed fibre sludge. Fibre sludge is a residual material obtained from pulp mills and biorefineries. It is usually relatively easy to hydrolyse fibre sludge enzymatically without prior thermochemical pretreatment, which is advantageous since pretreatment usually results in formation of substances that inhibit the bacterium. Commonly used bacteria are sensitive to inhibitory compounds except aliphatic carboxylic acids (Zhang et al. 2014a; 2014b). In a previous investigation (Cavka et al. 2013) production of BNC from waste fibre sludge by the commonly used strain Gluconacetobacter xylinus ATCC 23770 was assessed. It was reported that the productivity of BNC in a medium based on fibre sludge could even be higher than that in a medium based on glucose (Cavka et al. 2013). However, G. xylinus ATCC 23770 offers relatively low productivity of BNC. Furthermore, Cavka et al. (2013) studied only stationary cultivation and did not attempt to do up-scaling. By contrast, in the current study the feasibility of using a medium based on hydrolysed fibre sludge was studied using shaking cultivation with the strain that had the highest productivity of BNC.

Up-scaling of BNC production using a stirred-tank pilot bioreactor was investigated to assess the possibility to improve BNC production. Up-scaling was studied using the bacterial strain that exhibited the highest BNC yield. Downstream processing of the BNC from the stirred-tank bioreactor was studied by comparing different harvesting methods. The methods studied included using a washing centrifuge, a high-speed centrifuge, a filter press, and multilayer gauze. The washing method was optimized to improve the yield of purified BNC.

References


In this study, two different types of dry-spun single-filament fibers were prepared by spinning of concentrated aqueous suspension of cellulose nanofibers (CNF) as well as CNF suspension mixed with hydroxyethyl cellulose (HEC). To reduce the spinnable concentration of the suspension, which is supposed to increase the orientation of the CNF along filament axis, and subsequently improve the mechanical properties of the filament, HEC, which is a water-soluble cellulose-based polymer, as a binder was mixed with CNF prior to the spinning. The filaments were prepared using a capillary rheometer with a single-hole die and were collected on glass sheets. Addition of HEC improved the processability and lowered the spinnable concentration of the suspension by ≈ 40% from 7 wt% for solely CNF to 4.3 wt% for CNF-HEC. Moreover, the nanofibers were further aligned by stretching the semi-dried filaments using a tensile-testing machine. The orientation index of the drawn CNF-HEC filament compared to as-spun CNF filament increased by 43%, which resulted in improvements of 76% and 73% in modulus and strength respectively, being 15.0 GPa and 260 MPa. We believed the process used in this study has good potential for upscaling for use in fiber-reinforced composites; however, more improvements on processing set-up are required to improve the processability and drawability of the filaments.

**Presentation 18**

Single-filament fibers of cellulose nanofibers prepared by dry spinning: Influence of binder and cold-drawing on orientation and mechanical properties

Saleh Hooshmand, Yvonne Aitomäki and Kristiina Oksman

Division of Materials Science, Composite Center Sweden, Luleå University of Technology, Luleå, Sweden.

In this study, two different types of dry-spun single-filament fibers were prepared by spinning of concentrated aqueous suspension of cellulose nanofibers (CNF) as well as CNF suspension mixed with hydroxyethyl cellulose (HEC). To reduce the spinnable concentration of the suspension, which is supposed to increase the orientation of the CNF along filament axis, and subsequently improve the mechanical properties of the filament, HEC, which is a water-soluble cellulose-based polymer, as a binder was mixed with CNF prior to the spinning. The filaments were prepared using a capillary rheometer with a single-hole die and were collected on glass sheets. Addition of HEC improved the processability and lowered the spinnable concentration of the suspension by ≈ 40% from 7 wt% for solely CNF to 4.3 wt% for CNF-HEC. Moreover, the nanofibers were further aligned by stretching the semi-dried filaments using a tensile-testing machine. The orientation index of the drawn CNF-HEC filament compared to as-spun CNF filament increased by 43%, which resulted in improvements of 76% and 73% in modulus and strength respectively, being 15.0 GPa and 260 MPa. We believed the process used in this study has good potential for upscaling for use in fiber-reinforced composites; however, more improvements on processing set-up are required to improve the processability and drawability of the filaments.
Holmen is a Swedish forest industry group with annual turnover of 16 billion SEK and 3300 employees. The group consists of five separate business areas focusing on printing paper, paperboard, sawn timber, forestry and energy.

The pulp and paper industry has, as stated numerous times before, been subject to a world in change during the beginning of the 21st century. This rapidly shifting landscape has both induced challenges, due to new ways of consuming media and increased competition from emerging markets, as well as opportunities, such as increased environmental awareness in various industries. Responding to these issues, Holmen has enhanced its focus on finding new business opportunities from forest-based raw materials. Nanocellulose has, due to its unique properties, early on been identified as one of these opportunities.

In 2012, Holmen therefore initiated a strategic collaboration with the Israeli company Melodea, which has developed a novel technology for the production of cellulose nanocrystals (CNC) from various cellulose-based raw materials, such as pulp and paper waste streams. The produced material has showed significant potential for use in various applications, such as structural foams, adhesives and concrete, but is currently only available in lab quantities. Thus, in order to evaluate and verify its full potential, access to larger volumes is needed.

To realize this, a consortium of four companies, including Holmen, Melodea, SP Processum and MoRe Research, has initiated the erection of a 100 kg per day pilot plant. The plant will be built during 2016 and placed adjacent to SP Biorefinery Demo Plant in Örnsköldsvik – An ideal location with access to existing industrial infrastructure and extensive laboratory facilities. Furthermore, this broad four-partner approach is expected to help leveraging R&D and marketing of the material, thereby accelerating the path towards commercialization.

This presentation will thus describe the current status and future possibilities of the pilot plant as well as Holmen’s view on areas in which CNC is expected to yield immediate value.
Presentation 20
Effect from activator on dissolving pulp – dosing position and hypothesis of mechanisms

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Cellulose reactivity is of significant importance when processing dissolving pulp to viscose fibre. Reactivity, accessibility or the efficiency in the reaction is influenced by many factors, both from pulp cellulose properties and process conditions. In viscose process there are three steps where reactivity and accessibility are critical; alkali swelling/formation of alkali cellulose, pre-aging/denpoymerisation to required DP and xanthation/reaction with carbon disulphide. To help increase the reactivity/accessibility in xanthation step activators can be used. Especially when the viscose process is run in a not optimal way for example when pulp alkali swelling/mercerization is performed at high temperature and short time an activator can compensate for the poor activation and help the reaction in xanthation step. The adding position for such activator has traditionally been on the pulp during drying step. Often also additional adding in the viscose process is performed. In this study the influence of the dosage position is investigated with the aim to understand where it is most efficient to add activator to get the optimal effect in the overall process from pulp to fibre. Also the mechanism for the influence from the activator in xanthation step is discussed.

Effect of dosing position
Several independent internal studies, done by Domsjö Fabriker AB together with MoRe Research, have indicated that the addition position of activator, e.g. on pulp sheet or in viscose steeping step, does not seem to influence the quality of the viscose dope. The filterability of viscose dope in terms of filter clogging value, either $K_w$ or viscosity corrected $K_r$, is commonly used to evaluate the viscose quality. Study results show that the filterability is equally improved when activator is added on one side and on both sides of a laboratory Rapid Köthen sheet as well as distributed homogenously within a Rapid Köthen sheet (figure 1a). Furthermore, addition of activator in steeping lye gives the same improvement in filterability as the different activator additions on a Rapid Köthen sheet. When testing the effect on viscose filterability of two different activators at different adding positions the results show that adding on pulp or in the steeping lye gives equally good effect for both activators (figure 1b). Addition of activator in the steeping step seems to even give slightly better filterability compared to when added on pulp.
Figure 1. The filterability ($K_r$) for two different studies; a) Effect on viscose filterability from optimal distribution of activator on pulp and addition in steep lye and b) Evaluation of two different activators at different adding positions. Addition of activator gives better filterability (i.e. lower $K_r$) than without but the adding position, e.g. on pulp or in steeping, doesn’t seem to matter.

Hypothesis of mechanisms for the influence of activator

It is probably that the used activator acts as a micellar phase transfer catalysts of non-ionic surfactant type. In the literature this mechanism is described for the chemical, Triton X-100, Dow Chemicals, which is often used for these purposes. Its structure is very similar to the activator used in the studies presented here. Triton X-100 has a hydrophilic polyethylene oxide chain and an aromatic hydrocarbon hydrophobic group. It is soluble in water. It forms micelles with the poly ethylene oxide chains directing to the aqueous phase and the aromatic hydrocarbon groups surround the water insoluble reactant. The activator has the ability to do the same with the carbon disulphide. By forming micelles and enclose the carbon disulphide during its passage in the sodium hydroxide-water phase, the activator can facilitate a rapid transport into the alkali cellulose (Starks et al. 1994).

Literature

Sustainable biochemicals from wood
Borregaard operates one of the world’s most advanced biorefineries. By using natural, sustainable raw materials, Borregaard produces advanced and environmentally friendly biochemicals and biomaterials that can replace oil-based products.

Borregaard’s bio-based products are alternatives to petrochemical-based products, thereby contributing to resolve some of the long-term global challenges associated with access to resources and the impact on the environment and climate. By using wood (Norway spruce) as a raw material Borregaard produces specialty cellulose, lignin, vanillin and bioethanol. The production process focus on an optimum use of resources, which helps limit the need for raw materials.

Figure 1. Borregaard mill in Sarpsborg.

Green products
The fibres in the spruce are converted into advanced grades of specialty cellulose for products in the construction industries, and for the production of foodstuffs, tablets, cosmetics, filters, hygiene products, paints and much more. Textiles such as viscose and rayon are wood-based and can be good alternatives to synthetic fabrics or cotton, which is often cultivated with extensive use of insecticides, fertilisers and genetically modified organisms.

The binding agent in the wood, lignin, is the raw material for additives used in e.g. concrete and building materials, textile dyes, ceramic products, batteries and agricultural and fishery products. Borregaard is a world leader in lignin-based products. The most important area of use for lignin products is as an additive in concrete. In addition to providing advantages in terms of strength and quality, the lignin also means that the water and cement content of the concrete can be reduced. This contributes to a lower energy need and not least lower CO$_2$ emissions in the production of cement.

Lignin is also the source of the flavouring agent vanillin. Vanillin is the world’s most used taste and flavouring agent. Most of the world's vanillin production is based upon petrochemical raw materials and Borregaard is the only producer in the world to make vanillin from wood.

Borregaard's ethanol is so-called second generation bioethanol and is produced through fermentation of the sugars in the wood and is used for e.g. technical purposes in the pharmaceutical industry, paints, varnishes, car care products, and as environmentally friendly fuel.

![Figure 2. Wood utilization at Borregaard](image)

**Small CO$_2$ footprints**

Borregaard, in partnership with Østfold Research, has carried out a life cycle analysis (LCA) of the products specialty cellulose, ethanol, lignin and vanillin. This analysis confirms that Borregaard’s bio-based products do well from a climate perspective when compared with petrochemical alternatives. To give an example, the CO$_2$ emissions connected with Borregaard's vanillin made from wood (EuroVanillin Supreme) are 90 percent lower than those associated with vanillin based on guaiacol (petrochemical raw material). Borregaard's bioethanol has emissions 85 per cent lower than those of diesel. If emissions from the use phase are also included, the results are even more impressive. Borregaard's wood-based bio products release no emissions since the raw materials are renewable, whereas the fossil alternatives release CO$_2$ emissions in the use phase. Borregaard has also made efforts to reduce greenhouse gas emissions in its own processes, including elimination of heavy oil consumption and increasing the amount of energy supplied from more eco-friendly energy sources.
Research and development

In line with the Borregaard strategy of specialisation and enhanced value creation, the company invests substantial resources in research, development and innovation. Borregaard has close to 100 employees in Innovation and R&D of which 34 of our scientists hold a PhD degree.

Borregaard’s research efforts are important for the company’s future. 13 percent of the Group’s sales comes from new products that they did not have five years ago. The ambition is to increase further the rate of innovation spending around 5 percent of revenues annually on research and development. This is an effort that has gained recognition and support from the European Union, Innovation Norway and the Norwegian Research Council.
International Company
Besides its advanced biorefinery, Borregaard also holds strong positions within ingredients and fine chemicals. The Group has 1080 employees in plants and sales offices in 16 countries throughout Europe, Americas, Asia and Africa.

Figure 3. Main office in Sarpsborg
Presentation 22
Lignin carbohydrate complexes (LCC) in pine sulfite dissolving pulps as a function of the pulping conditions used

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Abstract
Production of sulfite dissolving pulp using different wood raw materials is well known but how to avoid the formation of LCC (Lignin carbohydrate complexes) which hinders the delignification process is not yet fully known. A study was therefore carried out on 100 % pine heartwood to understand and verify the LCC behaviour during a sulfite pulping process. A neutral pH protocol for LCC fractionation (Giummarella et al. 2016) was used in our study to investigate in-depth the presence of lignin-carbohydrate linkages for pine heartwood pulps. The LCC analyses were carried out on pure pine heartwood, single stage acid sulfite and two-stage sulfite pulps.

Results
The chemical composition of the pine heartwood and the pulp obtained after different sulfite pulping conditions were analyzed for carbohydrate, lignin and extractives contents as shown in Table 1. The acid sulfite cook and the two-stage cook pulps were chosen as they had almost the same pulp yield. It can be seen that the lignin content was lower after two-stage cooking as compared with acid sulfite cooking at 142 °C; and there was no significant difference in cellulose and hemicelluloses content at these cooking conditions. It can also be seen that the pinosylvin content in the pulp was lower for the two-stage cook compared with single stage cooking.

Table 1: Wood and different sulfite pulps composition
The heartwood and the pulp samples were milled to a fine powder using ball milling technique. The samples obtained after ball milling were subjected to hot water treatment to fractionate the soluble lignin fractions and these were analysed using UV light absorption as shown in Figure 1. As can be seen in the figure the dissolved lignin was compared with pure sodium lignosulfonate sample. The acid sulfite and two-stage sulfite pulps showed the same behaviour as pure lignosulfonate which was used as reference sample. It can thus be concluded that the sulfonated lignin was soluble in hot water and acid sulfite pulp samples showed higher soluble lignosulfonate values compared with two stage sulfite pulp. The pine heartwood sample showed different behaviour with soluble lignin, since there was no sulfonated lignin in pure heartwood sample.

<table>
<thead>
<tr>
<th></th>
<th>Pine heartwood</th>
<th>142 °C, Acid sulfite</th>
<th>Two stage cooking</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2 h</td>
<td>60 min</td>
</tr>
<tr>
<td>Yield, %</td>
<td>100</td>
<td>65.55</td>
<td>61.5</td>
</tr>
<tr>
<td>Lignin, %</td>
<td>26.6</td>
<td>16.3</td>
<td>11.19</td>
</tr>
<tr>
<td>Cellulose, %</td>
<td>35.0</td>
<td>34.5</td>
<td>33.00</td>
</tr>
<tr>
<td>Glucomannan, %</td>
<td>12.6</td>
<td>3.0</td>
<td>3.95</td>
</tr>
<tr>
<td>Xylan, %</td>
<td>6.9</td>
<td>2</td>
<td>2.51</td>
</tr>
<tr>
<td>Acetone, %</td>
<td>11.8</td>
<td>4.7</td>
<td>3.57</td>
</tr>
<tr>
<td>Pinosylvan, mg/kg</td>
<td>2411</td>
<td>127</td>
<td>12.3</td>
</tr>
</tbody>
</table>

The heartwood and the pulp samples were milled to a fine powder using ball milling technique. The samples obtained after ball milling were subjected to hot water treatment to fractionate the soluble lignin fractions and these were analysed using UV light absorption as shown in Figure 1. As can be seen in the figure the dissolved lignin was compared with pure sodium lignosulfonate sample. The acid sulfite and two-stage sulfite pulps showed the same behaviour as pure lignosulfonate which was used as reference sample. It can thus be concluded that the sulfonated lignin was soluble in hot water and acid sulfite pulp samples showed higher soluble lignosulfonate values compared with two stage sulfite pulp. The pine heartwood sample showed different behaviour with soluble lignin, since there was no sulfonated lignin in pure heartwood sample.

Figure 1. The UV measurement of water soluble fraction of pine heartwood, acid sulfite and two-stage sulfite pulp samples being compared with pure lignosulfonate as reference sample.
The ball milled samples were also treated with Ionic liquid (1-allyl-3-methylimidazolium chloride) and DMSO (Dimethyl sulfoxide) to get a new set of LCC fractions (Giummarella et al. 2016). The LCC fractions obtained after chemical treatments were analysed with SEC (Size exclusion chromatography) and NMR (Nuclear magnetic resonance) to determine the presence of different LCC linkages.

**Discussions**

The presence of lignin-carbohydrate bonds were observed in the pulp samples and it comprised of ester and glycoside type linkages. It was also observed that residual lignin carbohydrate complexes in the pulp were significantly sulfonated. Hence it can be concluded that the sulfonation mechanism alone is not sufficient for lignin dissolution in sulfite pulping but the cleavage of LCC bonds is equally important to completely delignify the pulp. This phenomenon was found to be same for single stage acid sulfite and two-stage sulfite pulping. The analysis data indicated that some covalent bonds between lignin and hemicellulose present in wood survive the sulphite pulping conditions. However, it appeared that the α-ethers were broken in the pulp and this reaction is probably of large importance in the removal of the lignin during the sulfite pulping.

**Literature**


Evaluation of the Effects of Wood Chips Quality on Pulping and Biorefining Processes

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Conversion of wood for pulping processes and for new biorefining processes is likely to play an increasingly important role in the future for production of green chemicals, advanced biofuels, and bio-based materials. As the costs for the feedstock are generally a large part of the operating expenditures of pulp mills and biorefineries, it is critical to achieve high yields in the production of Kraft pulp, dissolving pulp, and other commodities. Regardless of whether the process is conventional pulp and paper making or if it is a biorefinery operation, one of the first steps in the conversion of wood logs is mechanical disintegration by chipping. The quality of the wood chips, for example their dimension, needs to be optimized to suite the particular type of process they will be used for. To achieve a high yield of the cellulosic product from the feedstock, the chipping needs to be designed so that the fraction of rejected chips (too small or too large wood chips) is as low as possible. The quality of the wood chips will also affect the impregnation process, the overall processability, and the quality of the cellulosic product.

Industrial wood chippers of today are typically disc chippers, which are energy-demanding and which produce wood chips of a relatively large size range as the outer and inner part of the disc have different velocity. In this project, we compare conventional disc wood chippers with a newly developed modified drum chipper designed for industrial use. The effects of wood chipping on the quality of the wood chips, on alkaline and acidic impregnation processes, on the cooking process, and on the yield of the cellulosic product will be discussed.
Poster 1  Cellulose biosynthesis in wood relies on cytosolic invertase activity
Umut Rende and Totte Niittylä

Poster 2  Combination of starch hydrolysis and dilute-sulfuric acid pretreatment for enhancing the recovery of cassava stem glucans for ethanol production
Carlos Martín

Poster 3  Novel approach for SEC analysis of poorly soluble cellulose samples
Stephan Silbermann

Poster 4  Advanced structural characterization of loncell-F fibres
Shirin Asaadi

Poster 5  Dissolution of cellulose in NaOH(aq) mediated by reversible carbonation with CO2
Maria Gunnarsson

Poster 6  Extraction and characterization of residual hemicellulose in dissolving pulp
Chaehoon Kim

Poster 7  Textile fibers production via a novel organosolv fractionation process
Huy Quang Lê
Poster 1

Cellulose biosynthesis in wood relies on cytosolic invertase activity

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In several tree species carbon for cellulose biosynthesis is derived from sucrose, but the pathway from sucrose to cellulose has not been defined in wood. We investigated the role of cytosolic invertases (CINs) during wood formation in hybrid aspen (Populus tremula x tremuloides) and identified CIN12 as a critical enzyme for cellulose biosynthesis. Reduction of CIN12 during secondary cell wall formation caused a significant decrease in crystalline cellulose and an increase in amorphous cellulose. The changes in cellulose were also reflected in reduced diameter of acid insoluble cellulose microfibrils and increased glucose release from wood upon enzymatic digestion of cellulose. Reduced CIN12 activity decreased the amount of the cellulose biosynthesis precursor UDP-glucose in wood. These results place CIN12 in an initiation position on the pathway from sucrose to cellulose, and show that cellulose biosynthesis in wood relies on a quantifiable UDP-glucose pool. This conclusion counters the prevailing cellulose biosynthesis model where sucrose synthase channels UDP-glucose directly to cellulose synthesis. Our findings establish cytosolic invertase activity as a major rate-controlling step in the cellulose biosynthesis of trees, and introduce a concept of altering cellulose microfibril properties by modifying substrate supply to cellulose biosynthesis.
Poster 2

Combination of starch hydrolysis and dilute-sulfuric acid pretreatment for enhancing the recovery of cassava stem glucans for ethanol production

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Abstract
In this work, cassava stem starch was removed by a preparatory enzymatic hydrolysis, and the starch-free material was then subjected to dilute-sulfuric acid pretreatment. The conversion of cellulose upon enzymatic hydrolysis of the pretreated stem increased with the increase of the temperature and time. A region of optimal conditions was found, and it was possible to reach enzymatic convertibilities of pretreated cellulose above 80%. The mass balance over the whole sequence revealed that around 72% of the glucan contained in the initial material was recovered as glucose in the process streams.

Introduction
Cassava (Manihot esculenta C.) is a basic food crop for millions of people (Uchechukwu-Agua et al., 2015). During the harvest, the stem is separated from the roots, and a minor part of it is used for propagation, while high amounts are burnt (Zhu et al., 2015). Due to its high carbohydrate content and availability, cassava stem is a potential feedstock for producing ethanol and other sugar-platform products within a biorefinery scenario. As a lignocellulosic material, cassava stem requires to be pretreated in order to yield fermentable sugars by enzymatic hydrolysis of cellulose. The use of dilute-sulfuric acid has received some attention for pretreating cassava stems (Han et al., 2011; Martín et al., 2007).

Cassava stem contains around 31% cellulose and 36% starch (Martín et al., submitted). While such a high glucan content is a bonus for producing sugar-based products, the risk of starch degradation represents a challenge for pretreatment and acid hydrolysis processes. Therefore, for achieving high glucose yields, starch should be hydrolyzed in a separate step before the pretreatment required for cellulose hydrolysis.

We have previously shown that a two-fold increase of the glucan yield can be achieved if cassava stem starch is hydrolysed prior to acid pretreatment (Martín et al., submitted). However, the pretreatment conditions used in that study were far from optimal, and the achieved enzymatic convertibility of cellulose was relatively low. In the current work, a throughout investigation on dilute-sulfuric acid pretreatment of starch-depleted cassava stem was performed in order to gain more insight on the effect of pretreatment conditions on the hydrolytic conversion of cellulose.

Methodology
Enzymatic hydrolysis of starch
Eight hydrolysis batches were prepared by suspending 40 g (DM) of milled stems in water at a 9:1 liquid-to-solid ratio in a 1-L flask. The hydrolysis was performed in two steps, the first one at pH 5.8 and 85°C...
with thermostable α-amylase (Liquozyme SC4X, Novozymes), and the second one at pH 5.0 and 65°C with amyloglucosidase (Spirizyme Excel XHS, Novozymes). At the end, the slurries were filtered, and the starch-depleted cassava stem (SDCS) was washed, air dried, and stored in a plastic bag at room temperature.

**Pretreatment**

The SDCS was pretreated following a Box-Behnken experimental design with the temperature (165-195°C), pretreatment time (5-35 min) and H₂SO₄ concentration (0.2-1.0%) as independent factors (Table 1), and the enzymatic conversion of cellulose as response factor. Ten grams (DM) of stem were mixed with diluted H₂SO₄, at a liquid-to-solid ratio of 9:1, in a 250-mL stainless steel cylindrical vessel with magnetic stirring and temperature control, and heated with a heating mantle. By the end of the pretreatment, the reactor was cooled by immersion in a cool water bath. The slurry was separated by filtration, and the pretreated solids were washed with water, and air dried the dry matter content was around 90%. The pretreatment liquors were stored frozen. In a complementary experiment, SDCS was pretreated at 195°C and with 0.6% H₂SO₄ for periods lasting from 50 to 110 min.

### Table 1. Pretreatment conditions

<table>
<thead>
<tr>
<th>Exp. run</th>
<th>Pretreatment conditions</th>
<th>Temperature, °C</th>
<th>Time, min</th>
<th>H₂SO₄ conc., %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>165</td>
<td>5</td>
<td>0.6</td>
<td></td>
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<td>2</td>
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<td>0.2</td>
<td></td>
</tr>
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<td>3</td>
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<td>20</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>165</td>
<td>35</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>5</td>
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<td>5</td>
<td>0.2</td>
<td></td>
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<tr>
<td>6</td>
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<td>5</td>
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<td></td>
</tr>
<tr>
<td>7</td>
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<td>35</td>
<td>0.2</td>
<td></td>
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<tr>
<td>8</td>
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<td>1.0</td>
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<tr>
<td>15</td>
<td>195</td>
<td>35</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

**Enzymatic hydrolysis of cellulose**

Duplicate aliquots of 50 mg (DM) of pretreated material were suspended in 900 μL of 50 mM sodium citrate buffer (pH 5.2), and 50 μL of a 50:50 mixture of cellulase and β-glycosidase preparations (both supplied by Sigma-Aldrich) were added. The mixture was incubated for 72 h at 45°C and 170 rpm. At the end of hydrolysis, the hydrolysate was subjected to HPLC analysis for glucose quantification, and, based on that, the enzymatic conversion was calculated.

**Chemical analysis**

Carbohydrates and lignin in the raw and processed stem was determined by analytical acid hydrolysis (Sluiter et al., 2008), followed by quantification of the monosaccharides by high-performance anion-exchange chromatography (HPAEC). Acid-insoluble lignin was determined gravimetrically, whereas soluble lignin was determined spectrophotometrically at 240 nm. The extractive compounds were determined by sequential extraction with water and 95% ethanol, and ash content was determined by incineration at 550°C. The dry matter content was measured with a halogen moisture analyser. Starch was determined according to a protocol based on enzymatic hydrolysis (Sluiter and Sluiter, 2008), and the released glucose was analyzed by HPLC. The concentration of sugars and aliphatic acids in the pretreatment liquors was determined by HPAEC, while furan aldehydes were analyzed by HPLC.

**Results and discussion**

**Yield and composition of the pretreated materials**

The yield of pretreated solids decreased with increasing of the temperature of the acid pretreatment of the PDCS (Fig. 1). The pretreated solids were composed mainly of cellulose and lignin. The cellulose content in the pretreated solids ranged between 46 and 54%, and the recovery was close to 85–90% in most of the pretreatments, except in some of the most severe experimental conditions.
The xylan content was low and decreased remarkably with increasing the severity of the pretreatment. Around 25–38% of the initial xylan remained in the solids for some of the milder pretreatments, while it was completely solubilized in some of the most severe runs. Approximately 5–8% lignin was solubilized in the experiments performed under low temperatures and short pretreatment times. As the severity increased, lignin solubilisation was compensated by formation of pseudo-lignin. The formation of sugar-degradation products, like furan aldehydes and aliphatic acids, especially under the most severe pretreatment conditions, was detected in the pretreatments. The experiment revealed that the acid concentration exerted the strongest effect on cellulose recovery and formation of degradation products, while the time had the least significant effect.

Figure 1. Yield of solids and cellulose recovery after pretreatment of starch-depleted cassava stem. The numbers in the abscissa axis correspond to the conditions indicated in Table 3.

Enzymatic conversion of the pretreated materials

The overall conversion of cellulose during the enzymatic hydrolysis increased with the temperature and time, while it was inversely affected by the interaction between temperature and acid concentration (Fig. 2-A).

Figure 2. Pareto chart of standardized effects (A), estimated response surface (B) and contour plots (C) for the overall conversion of cellulose.

The contour graph revealed the proximity of a region of optimal conversion for 195°C, low acid concentration and pretreatment times above 35 min (Fig. 2-B). Based on that, the experiment was augmented by prolonging the time up to 110 min while holding the temperature and acid concentration at 195°C and 0.6%, respectively. The extension of the pretreatment time led to increased enzymatic convertibility of pretreated cellulose, which was above 80% starting from the experiment held at 50 min and reached almost 90% in the one performed for 80 min (Fig. 3). A different trend was observed for the overall conversion, which considers the cellulose contained in the original material. The overall conversion increased with the time only for short pretreatments, but after 50 min it decreased continuously due to the high loss of cellulose. The best overall conversion of the initial cellulose (55.5%) was achieved for the pretreatment lasting 50 min. A mass balance performed for that pretreatment showed that 72% of the initial glucan was recovered in...
all the process streams, including starch hydrolysate, pretreatment liquor and cellulose hydrolysate, while 22% of the initial glucan was lost during the pretreatment stage.

Figure 3. Effect of the pretreatment time on the enzymatic convertibility of pretreated cellulose and overall conversion of initial cellulose

Conclusions
A region of pretreatment conditions leading to high enzymatic conversion of cellulose was found for 195°C, low acid concentration and pretreatment times above 35 min. If the acid concentration is set at 0.6% the optimal conversion is achieved when the material is pretreated for 50 min.
The mass balance revealed that around 72% of the glucan contained in the initial material was recovered in the process streams, and that improving the preservation of cellulose during pretreatment is crucial for achieving higher glucan conversions.

Acknowledgments
This work was supported by the Bio4Energy research environment (www.bio4energy.se). Stefan Stagge is gratefully acknowledged for his valuable assistance with the chromatographic analyses.

Literature
Poster 3

Novel approach for SEC analysis of poorly soluble cellulose samples

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ABSTRACT

Size exclusion chromatography (SEC) is utilized to obtain information about the molar mass distribution (MMD) of natural and manmade cellulosic fibers and pulps. Therefore cellulosic materials need to be fully dissolved in the solvent system N,N-dimethylacetamide/lithium chloride (DMAc/LiCl). Although standard dissolving pulps get dissolved after known protocols some cellulose samples (e.g. regenerated cellulose fibers, softwood prehydrolysis kraft pulps and cotton lint fibers) are of poor solubility. For improving the latter, different pre-activation and activation steps have been developed. Although some of the developed methods do improve dissolution of the samples, they either have an influence on the molar mass distribution or the whole activation procedure becomes very time-consuming.

The scope of this study was to further improve established methods to a single, short and effective activation method to obtain completely soluble samples. A single activation step with dimethyl sulfoxide (DMSO) instead of DMAc increases the solubility in DMAc/LiCl and makes subsequent SEC analysis possible. For increasing the overall throughput of SEC analysis the optimum activation time was found by observing the time needed for maximum swelling applying light microscopy. By comparing the MMDs of partly soluble reference materials obtained by the conventional and the new method it could be shown that the novel approach provides comparable results.

KEYWORDS

Activation, dissolution, DMAc, DMSO, SEC

INTRODUCTION

Determination of the molar mass distribution (MMD) provides fundamental information in characterizing natural and man-made cellulosic materials. Size exclusion chromatography (SEC) combined with multi-angle light scattering (MALS) detection has been established as a valuable tool for this characterization. Although most of the standard dissolving pulps can be completely dissolved in the solvent system N,N-dimethylacetamide/lithium chloride (DMAc/LiCl), regenerated cellulose fibers (i.e. Lyocell and viscose fibers), softwood prehydrolysis kraft (PHK) pulps and cotton fibers are often insoluble or difficult to dissolve. Major reasons are the high orientation in man-made fibers, the occurring gel formation in PHK pulps and the dense cell wall structure in cotton fibers. Even though some of these fibers and pulps can be completely dissolved after several time-consuming pre-activation and activation steps, most solutions remain undissolved and thus turbid.
Different activation and dissolution methods are available in literature (Henniges et al. 2014; Schelosky et al. 1999; Siller et al. 2014). However, some of the activation steps do not improve the solubility of the cellulose samples used in this study and some have an influence on the MMD, as severe cellulose chain degradation occurs (Potthast et al. 2002). Therefore, a mild but effective method had to be developed with regard to subsequent dissolution and SEC measurement. In addition, an effective method was required with regard to the time-consuming pre-activation and activation steps. Hence, the work of Siller et al. (2014) was used as a basis, hereafter developed further and extended to a wider pool of raw materials.

RESULTS AND DISCUSSION

In order to obtain fully dissolved cellulose samples an improved pre-activation and activation procedure had to be achieved. For comparison, first trials were performed according to Siller et al. (2014) and according to the internal standard method based on Schelosky et al. (1999).

Two samples were swollen in water for several days as a pre-activation step.

After removing the water by vacuum filtration and washing with ethanol the first sample was washed and swollen in DMSO (step 1). Subsequently excess DMSO was removed by vacuum filtration and the samples was washed and swollen in DMAc (step 2). The swelling duration was one day independent of the solvent.

After removing the water and washing with ethanol the second sample was continuously washed and swollen in fresh DMAc five times with the same duration of each step.

After removing excess DMAc by filtration after the last activation step of both samples, vials were filled with obtained fibers and DMAc/LiCl (9% w/v). Subsequently vials were vortexed and placed on a rotary shaker at room temperature for dissolution.

A second trial was conducted by skipping the pre-swelling in water, the washing with ethanol and the washing and swelling in DMAc steps. Hence, a one-step activation in DMSO was conducted. After removing excess DMSO by filtration, the fibers were directly added to the solvent system DMAc/LiCl in DMSO wet condition. Sample was vortexed and dissolved at room temperature on a rotary shaker.

For further time reduction to increase the efficiency of work the swelling kinetics of the fibers was observed applying light microscopy. The time needed for reaching the maximum fiber diameter (maximum swelling) was found as optimum activation time.

In order to better understand the role of DMSO and DMAc for activation and in the solvent system with LiCl, transverse trials were investigated. Therefore, samples were activated after the standard method in DMAc and in the one-step activation in DMSO. Subsequently each sample was split in half. Vials were filled with each split sample and DMAc/LiCl and DMSO/LiCl (9% w/v), respectively.

Clear solutions were diluted 1:2.5 with DMAc and stored in a refrigerator until injection. The molar mass distribution of the cellulose samples was analyzed by SEC combined with MALS.

Results are shown exemplarily for cotton lint fibers; results for regenerated cellulose fibers as well as softwood prehydrolysis kraft pulps are congruent.
The first sample (activation in water – DMSO – DMAc) was a little soluble in DMAc/LiCl after shaking for several days; the majority of fibers remained undissolved in the solution. The five times activated sample was partly soluble in DMAc/LiCl after shaking for two weeks. The sample activated by the standard method remained undissolved independent on shaking time and hence, turbid.

Regarding the sample activated only in DMSO, almost complete dissolution in DMAc/LiCl occurred after shaking the sample for several hours, only few undissolved fibers remained in the solvent. For comparison of turbid and clear solutions, see Figure 1.

Figure 1. Cotton lint fibers activated with DMAc (left, turbid) and DMSO (right, almost clear) and dissolved in DMAc/LiCl (9 % w/v)

A significant time reduction was achieved by investigating the maximum fiber diameter applying light microscopy. Maximum fiber diameter is equated with maximum swelling. The culmination of the fiber diameter and thus maximum swelling occurred after several minutes.

In addition, the role of DMSO and DMAc for activation and in the solvent system with LiCl was investigated. It is demonstrated that the combination of activating in DMSO and dissolving in DMAc/LiCl gave clear solutions with only few undissolved fibers. When samples were activated once in DMAc and subsequently dissolved in DMAc/LiCl, solutions remained turbid. Dissolution in DMSO/LiCl was impossible independent of the activation procedure.

By comparing the MMDs of the five times activated sample in DMAc and the one-step activated in DMSO it could be shown that the new method had no influence on the results. Chain degradation as well as discrimination of the low molar mass portion did not occur, see Figure 2.
CONCLUSIONS
The simple and effective method allows for a dramatic reduction of activation and dissolution time providing a higher throughput in overall fiber analysis. Time-consuming pre-activation and activation steps were either skipped or the duration of the step was reduced to the minimum. In addition, fibers which hitherto were insoluble could be prepared for SEC analysis within hours.

It was also demonstrated that only the combination of activating in DMSO and dissolving in DMAc/LiCl gives reliable results.

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REFERENCES
Advanced structural characterization of Ioncell-F fibres

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Abstract
The ionic liquid 1,5-diazabicyclo[4.3.0]non-5-ene acetate ([DBNH]OAc) was recently identified as an excellent cellulose solvent for dry-jet wet fibre spinning. Fibres spun from cellulose-[DBNH]OAc solution have shown very high tenacities and moduli. As mechanical tests have shown, there is a significant improvement in tensile properties of the Ioncell-F fibres when increasing the draw of the filaments until a ratio of approximately 6. Further draw has only a minor effect on the development of the mechanical properties. X-ray scattering techniques (SAXS and WAXS) were applied to elucidate structural details of the Ioncell fibres.

Introduction
Recent studies on the application of ionic liquids (ILs) in cellulose chemistry have attracted a lot of commercial interest, including the production of regenerated and modified cellulose fibres. Ionic liquids have excellent solvation characteristics, low toxicity and volatility leading to facile recovery (Rein, Khalfin et al. 2014).

The ionic liquid 1,5-diazabicyclo[4.3.0]non-5-ene acetate ([DBNH]OAc) was recently identified as an excellent cellulose solvent for dry-jet wet fibre spinning. Fibres spun from cellulose-[DBNH]OAc solution have shown very high tenacities and moduli. (Hummel, Michud et al., Michud, Tanttu et al. 2015, Sixta, Michud et al. 2015) However a systematic structure analysis of the fibres is lacking.

The aim of this study is to investigate the structure of the Ioncell-F fibres utilizing X-ray diffraction techniques, (WAXS and SAXS). The results from the SAXS measurements could resolve the structural model of cellulose.

Material
Enocell birch pre-hydrolyzed kraft pulp 476 ml.g-1 (Mw = 274.3 kg.mol-1, Mn = 68.2 kg.mol-1, D = 4 from Stora Enso, Finland) was used as a cellulose solute. [DBNH]OAc ionic liquid was synthesized and used as solvent to prepare the 13% cellulose spinning solution. The pulp has been dissolved in the ionic liquid and spun by dry jet wet spinning.

Fibre analysis
Fibres linear density determination and tensile testing has been carried out with vibroskop and vibrodyn system (Lenzing instrument GmbH & CoKG, Austria).
Fibres birefringence has been determined with Zeiss Axio Scope A1 microscope and a Leica B 5λ-Berek tilting compensator. Birefringence is the optical retardation divided by the diameter.

Wide and small angle diffraction experiments were carried out at laboratory scale x-ray instrument with λ= 0.154 nm for dry and swollen fibres. A bundle of cellulose fibre were mounted on the sample holder with the fibre direction perpendicular to the X-ray beam for dry fibres. Swollen fibres have been inserted into capillaries filled with water and sealed. A typical acquisition time for WAXS experiment were 300s and for the SAXS 2700 s.

The average crystallite size \( L_{hkl} \) perpendicular to the reflection planes \( (h k l) \) was determined according to the Scherer equation.

\[
D(hkl) = \frac{0.9\lambda}{(\beta \cos \theta)}
\]

where \( \lambda \) is the wavelength of the X-ray, \( \beta \) is the FWHM (full width at half maximum) of the reflection plane \( (h k l) \) and \( \theta \) is the half of diffraction angle \( (2\theta) \). The crystal orientation factor along the fibre axis was calculated from WAXS pattern by Herman’s orientation parameter \( (f_c) \).

\[
f_c = \frac{(3\cos^2 \varphi - 1)}{2}
\]

Where \( \cos^2 \varphi \) is the orientation parameter and is determined from azimuthal angle and intensity along the \( (110)/ (020) \) reflection. (Alexander 1969)

RESULTS AND DISCUSSION

Tensile strength, linear density and birefringence

Figure 1 shows the tenacity of the Ioncell-F fibres, their linear density and total orientation vs. draw ratio. By increasing the draw ratio the linear density is decreasing while the tenacity and total orientation is increasing. These changes in fibre properties are very significant until a draw ratio of approximately 7. A further increase in the draw ratio results only in a slight increase in tenacity.

![Figure 1. Tensile strength, linear density and total orientation vs. draw ratio Ioncell-F](image)

SAXS and WAXS

Figure 2 shows the 2D WAXS and SAXS pattern and the SAXS scattering curve of the Ioncell fibres from lowest to highest draw ratios. The 2D-SAXS pattern of the fiber with a draw ratio of 0.5 is showing meridional broadening while the fibers with the highest draw ratio of 15 reveal an elongated sharp streak along the equator which implies an increase of disorientation at a draw ratio 0.5 and oriented pores at a draw ratio 15, respectively. The slope of the SAXS scattering curve (dry) is
proportional to $q^{-4}$ according to Porod’s law, the particles are larger than the resolution limit and the scattering originates from the surface.

The crystallite width of different draw ratios has been calculated according to the Scherrer equation from the (002) reflection. It increases with increasing draw ratios from 8 to 16 nm at a draw ratio of 10. Table 1 shows the orientation factor of the crystallites and the total orientation factor (from birefringence) of fibres with different draw ratios. The amorphous orientation is increasing by an increase of the draw ratio while the crystalline orientation does not show much variation as a function of the draw ratio.

Table 1. Crystalline and total orientation of different draw ratios

<table>
<thead>
<tr>
<th>DR</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>10</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{cr}$</td>
<td>0.85</td>
<td>0.85</td>
<td>0.88</td>
<td>0.88</td>
<td>0.88</td>
<td>0.89</td>
<td>0.88</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>$f_t$</td>
<td>0.53</td>
<td>0.63</td>
<td>0.66</td>
<td>0.69</td>
<td>0.72</td>
<td>0.67</td>
<td>0.72</td>
<td>0.78</td>
<td>0.70</td>
</tr>
</tbody>
</table>

CONCLUSIONS

1. WAXS pattern of the Ioncell fibres reveals the prominent lattices of the cellulose II structure. The crystallite size increases with an increase of the draw ratio. High crystalline orientation has been observed already for low draw ratios but it is further increasing moderately further with increasing draw ratios.

2. The SAXS scattering curves show enhanced reflections from swollen fibres, indicating an evidence for long periods, which, however, this needs, further studies. Complementary measurements such as TEM, solid state NMR, dynamic moduli analysis and water retention are necessary to reveal the structure of the ioncell fibres.

Figure 2. a) 2D-WAXS (top figures) and 2D-SAXS (bottom) of draw ratio 0.5(left) and 15 (right) Ioncell-F b)SAXS scattering curve of dry and swollen fibres of draw ratio 0.5 and 15

Literature


Given the unsustainable character of cotton cultivation, there is an urge to meet the increased textile consumption by wood cellulose based textiles, capable of gradually replacing the less sustainable fibers. This undoubtedly implies a strong need to search for new solvent systems for cellulose. Today there are only few solvents capable of dissolving the intricate cellulose structure while being environmentally friendly and industrially viable. One of them, experiencing a renewed interest and intense research efforts is undoubtedly cold NaOH(aq). It employs benign and easily available components and is as such a very plausible alternative to the existing concepts. However, due to specific requirement on the hydration level of the NaOH along with the long range organization of cellulose chains, favorable interactions in this system are restricted to a very narrow window, implying need for either appropriate additives or modifications of cellulose structure in order to promote the dissolution process.

In this work a reversible carbonation of cellulose as a means of facilitating dissolution in cold NaOH(aq) has been investigated. Carbon dioxide has been employed as a carbonating agent in the presence of selected tertiary amines as catalysts. Formation of cellulose carbonate was studied as a function of reaction parameters by FTIR and NMR spectroscopy, including mechanistic investigations on low molecular model compounds. The effect of this chemical conversion on cellulose dissolution in cold alkali was evaluated in terms of solubility, solution stability and chemical stability of the produced cellulose carbonate under different dissolution conditions using gravimetric and spectroscopic methods, as well as and microscopy studies. Possibilities of governing dissolution conditions by choosing appropriate carbonation parameters have been investigated. Furthermore, the appealing idea of utilizing the reversibility of the carbonation reaction to control the regeneration process has been explored.

References:


For the production of cellulose derivatives, dissolving pulp with high cellulose purity is required as a raw material. In order to minimize the hemicellulose and lignin content, dissolving pulp is produced by acid sulfite or prehydrolysis kraft pulping process. As the pulping process is operated at a severe condition, the cellulose purity is increased but it might lead to a decrease in cellulose yield and reactivity, and an increase in operational and environmental cost. Therefore, typical dissolving pulp contains up to 5% hemicellulose and its cellulose purity can be adjusted based on the final product application.

Hemicellulose is known as the main reason for the deterioration of final product quality and processability problems such as poor filterability, increased viscosity, and discoloration. For the cellulose acetate process, the amount of residual hemicellulose with less than 1.5% can cause the haze and color formation of cellulose acetates solution. However, deteriorating issue due to residual hemicellulose is only known by practical experience.

In this work, residual hemicellulose was extracted from dissolving pulp by two-stage alkaline extraction and its chemical and structural characteristics were analyzed. It was found that refining treatment and cold temperature extraction enhanced hemicellulose extraction. Compared to the extraction from unrefined dissolving pulp at a room temperature, hemicellulose extraction yield was improved up to four times. Also their effects on the carbohydrate composition and molecular weight of extracted hemicellulose also were studied. The correlation between chemical structure of residual hemicellulose and reactivity of dissolving pulp was investigated in detail. The findings from the study will provide useful information not only for the dissolving pulp industry also for all over the field of biomass utilization.
A novel biorefinery concept based on the fractionation of woody biomass in a γ-valerolactone (GVL)/water binary mixture is introduced. Under optimal GVL/water ratio, Eucalyptus globulus wood was effectively fractionated in a single step into its principal components. The pulp fraction, characterized by high yield, high cellulose purity and high bleachability, was directly spun to produce regenerated cellulosic fibers with mechanical properties comparable to the best man-made fibers currently available in the market.

INTRODUCTION

Dissolving pulp is relatively pure reactive cellulose, characterized by high cellulose content (>90%), high brightness and low macromolecular polydispersity, which is employed in the production of regenerated fibers and cellulose derivatives. Global dissolving pulp production is currently small (about 6.4 million tons in 2013 (Young 2014), i.e. less than 4% of that of paper-making pulp), however, the demand for dissolving pulp is significantly increasing due to a persistent growth of the cellulosic textile fiber consumption during the coming years (The Fiber Year 2016). To meet this increasing demand, global production of dissolving pulp is expected to double in the next two decades (Hämmerle 2011). Currently, dissolving pulp is commercially produced from wood, by either the acid sulfite or the prehydrolysis kraft (PHK) pulping process, or from cotton linters by refining, with a production share of 50, 35 and 15 %, respectively (Sixta 2006). However, these methods encounter inherent drawbacks, mainly related to environmental issues. Therefore, environmentally benign fractionation methods for dissolving pulp production have been intensively investigated, including various organosolv and ionosolv processes.

Recently, gamma-valerolactone (GVL) has also been identified as a promising green organic solvent for biomass conversion (Fang and Sixta 2015, Horvath et al. 2008, Luterbacher et al. 2014). Inspired by the pioneer work on GVL, we hereby suggest a biorefinery concept based on GVL/water fractionation of eucalyptus wood chips where the cellulose fraction is converted to dissolving pulp, and subsequently, to textile fibers. The hemicelluloses fraction in the spent liquor is then characterized and discussed in relation to its valorization pathways to furanic platform chemicals and to GVL. Finally, the lignin fraction is precipitated and characterized, and based on the lignin properties possible applications are evaluated. This writing mainly reports the valorization pathway for the cellulose fraction; that for hemicellulose and lignin will not be discussed. More detailed information on the characterization and valorization of the cellulose, hemicellulose and lignin fractions can be found in the work of Le et al. (2016).

MATERIAL AND METHODS
Eucalyptus globulus wood was fractionated in a binary mixture of GVL/H2O. No catalyst or additives were added. Small scale trials with sawdust (particle size < 125µm) were conducted in 30mL vials heated in a microwave reactor (Anton Paar Monowave 300). Reaction temperature, time and liquor-to-wood ratio (L:W) were 180°C, 120 minutes and 10 L/kg, respectively. The GVL content in the fractionation liquor ranged from 0 – 98 wt%. The fractionation of wood chips was done in 225 mL bombs heated in a silicon oil-bath reactor (Haato-tuote 43427) or in 2.5 L bombs heated in an air-bath reactor (Haato Oy 16140-538). The reaction temperature was 180°C, the GVL content in the liquor was 50 and 60 wt%, L:W ranged from 2 to 10 L/kg, and the fractionation time (retention time at 180°C) ranged from 60 to 180 minutes. For wood chips, an impregnation time of 60 minutes at 120°C was employed. The pulp was separated from the spent liquor by filtration, followed by washing. Yield was determined gravimetrically, and the pulp was analyzed for carbohydrate, lignin and hexenuronic acid (HexA) content, molar mass distribution (by Gel Permeation Chromatography) and intrinsic viscosity (only for pulps produced from wood chips). Spent liquor was analyzed for the content of carbohydrate, furanics, organic acids and dissolved lignin. Washing liquid was analyzed for dissolved lignin content.

A selected pulp sample from a GVL/water fractionation was bleached using an ECF (Elemental-Chlorine-Free) sequence of D0-Ep-P. The bleaching was done in plastic bags, heated by steam in a water bath. The conditions for each bleaching stage were: D0: 50°C, 60 minutes, 10% consistency, active chlorine charge according to a Kappa factor of 0.25; Ep: 70°C, 60 minutes, 10% consistency, 1.5% NaOH, 0.5% H2O2; P: 70°C, 120 minutes, 10% consistency, 0.6% NaOH, 0.5% H2O2.

Selected bleached and unbleached pulps produced from wood chips were spun to regenerated cellulose fibers by the IONCELL-F process developed by Sixta et al. (2015). IONCELL-F is a dry-jet wet spinning process utilizing ionic liquids (in this case [DBNH][OAc]) to dissolve the pulp and to produce the spinning dope. Mechanical properties of the fibers (linear density, tenacity and elastic modulus) were determined.

RESULTS AND DISCUSSION

Eucalyptus wood fractionation

Small scale fractionation trials using sawdust were first conducted to determine the optimum GVL/H2O ratio for delignification. The behavior of the wood main components, namely cellulose, hemicelluloses and lignin, in GVL/H2O fractionation is showed in Figure 1. The results indicate that the cellulose fraction was recovered almost quantitatively at any GVL/H2O content, while delignification reached a maximum when fractionation liquor contained about 50 – 60 wt% GVL. Hemicellulose removal increased with increasing the water content due to enhanced hydrolytic degradation.
Figure 1. Effect of GVL content in fractionation liquor on the separation of eucalyptus sawdust main components. (odw: oven-dried wood).

The high cellulose content in the pulps produced in 50% and 60% GVL liquors, coupled with the relatively low hemicellulose and lignin content suggests the potential to convert GVL/water pulp to dissolving pulp of viscose grade after bleaching. This was further investigated by the fractionation of wood chips in 50 and 60 wt% GVL solutions. In comparison to fractionation with 60 wt% GVL, employing 50 wt% GVL liquor gave a slight advantage on delignification and hemicellulose removal at the expense of pulp viscosity.

The removal of wood components and the viscosity of the pulps along the course of fractionation in 50 wt% GVL are shown in Figure 2. Wood defibrillation took place in the early stages of fractionation, with almost no rejects detected after 60 minutes of reaction. Extending the reaction time beyond 60 min slightly increased the removal of wood components, but the intrinsic viscosity decreased considerably. In all cases, wood chips were effectively converted into pulps with high cellulose yield and purity. Reduction of L:W did not impair the extent of delignification and hemicellulose removal but the degree of polymerization of cellulose was significantly affected.

![Figure 2](image)

Figure 2. Effect of time in oil-bath digester (left) and liquor-to-wood ratio in air-bath digester (right) on wood component removal during fractionation of wood chips with 50 wt% GVL liquor. (odw: oven-dried wood).

Production of textile fibers

The pulps produced with 50 wt% GVL/H$_2$O at L:W=10 L/kg were selected for their conversion into regenerated cellulose fibers. The pulp obtained after 180 minutes of fractionation was spun directly without bleaching. The pulp produced after 150 min fractionation time was bleached with a short ECF sequence prior to spinning. A commercial bleached acid sulfite pulp from hardwood, with similar molecular mass distribution as the GVL pulps (Table 3 and Figure 3), was selected as reference and spun to regenerated cellulose fibers with the same procedure.

Table 3. Properties of selected pulp samples employed in spinning trials. (odp: oven-dried pulp).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition [%odp]</th>
<th>ISO brightness</th>
<th>Viscosity mL/g</th>
<th>$M_w$ (a) KDa</th>
<th>PDI (b)</th>
<th>DP&gt;2000 (c) wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-GVL (d)</td>
<td>92.7</td>
<td>5.2</td>
<td>2.1</td>
<td>-</td>
<td>456</td>
<td>352</td>
</tr>
</tbody>
</table>
### CONCLUSION

GVL/H₂O mixtures enable a quantitative and selective fractionation of all lignocellulosic components in just one single step. The cellulose fraction can be converted to dissolving pulp, then successfully spun into regenerated cellulose fibers with mechanical properties comparable to those of the best man-made fibers existing in the market.

### LITERATURE


We thank our sponsors for their valuable contributions