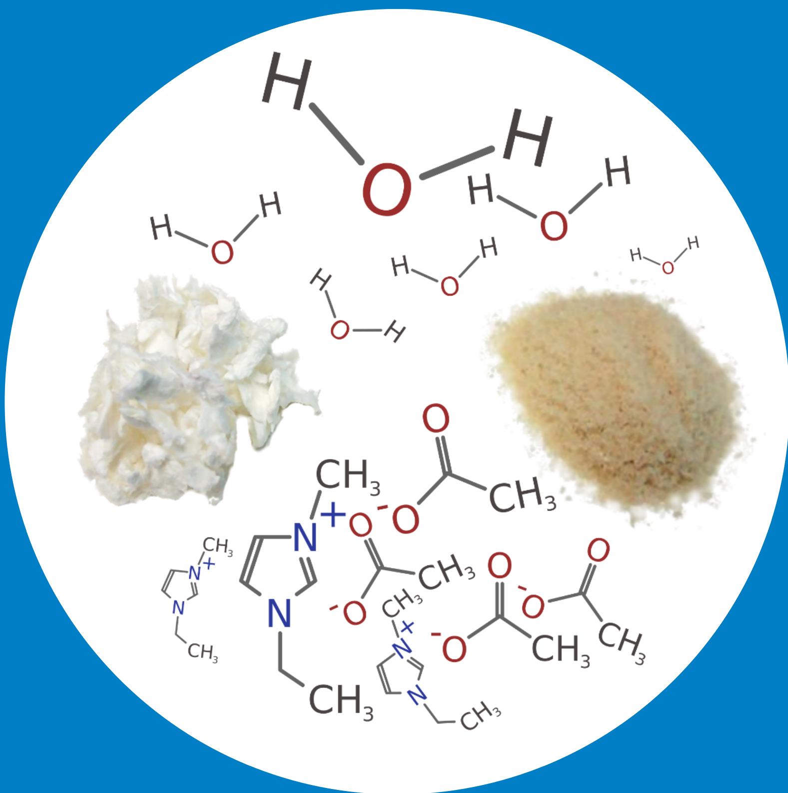
Department of Bioproducts and Biosystems

Extraction of Hemicelluloses from a Kraft Paper Pulp with an Ionic Liquid water Mixture

Annariikka Roselli



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Extraction of Hemicelluloses from a Kraft Paper Pulp with an Ionic Liquid water Mixture

Annariikka Roselli

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Abstract

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Abstract

This study introduces the IONCELL-P(ulp) process, which refines hemicellulose-rich bleached paper grade pulp to high purity dissolving pulp and polymeric hemicelluloses without yield losses or polymer degradation. Both fractions, the cellulose and dissolved hemicellulose, can be recovered quantitatively, providing a basis for a new stream of hemicellulose products and dissolving pulp production.

In order to provide valuable information for the process up-scaling, the features that affect the extraction (solvent and substrate properties, reaction conditions) and equipment requirements were studied profoundly. The studies progressed by examining the usability of the separated polymer fractions, by investigating the purity, reactivity and integrity of the polymers.

The results revealed that the solvation selectivity towards hemicelluloses was governed by the molecule size of the carbohydrate polymers. Short hemicelluloses dissolve more readily in aqueous ionic liquids, while the cellulose fraction remains intact. Thus, the molar mass distribution (MMD) of the pulp is a decisive feature regarding the suitability of this pulp for the IONCELL-P process.

A distinct difference in the size of hemicelluloses and cellulose allows for a more accurate tuning of the solvent-water mixture for the selective and efficient extraction of hemicelluloses.

A selection of different cellulose dissolving ionic liquids were tested in the process and a joint behaviour of the solvent mixtures was found, when the β-value, describing the anion's ability to accept hydrogen bonds, was divided with the water molar fraction of the solvent system. The resulting $\beta/\chi(H2O)$-value gives an approximation of the relative strength of the solvent, which is needed for maximal hemicellulose solvation, but it does not describe the limit, where a certain solvent mixture loses its selectivity towards hemicelluloses and begins to dissolve increasing amounts of cellulose. The selectivity of the solvent system was also investigated in the terms of pH. Low pH ionic liquids demanded less water to render them to hemicellulose solvents and they were less inclined to swell and dissolve cellulose. Combining these findings, the IONCELL-P process is most efficient when using a pulp with a distinct difference in the MMD between the cellulose and hemicellulose fractions and an ionic liquid with low pH and relatively high β-value. The IONCELLP purified pulp is highly reactive and suitable for various applications such as cellulose acetate production. The process preserves the cellulose I crystalline structure and neither of the fractions, cellulose or hemicellulose, undergoes degradation reactions.

Keywords	IONCELL-P, dissolving pulp, hemicellulose extraction, ionic liquids				
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Tiivistelmä

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Tekijä
Annariikka Roselli

Väitöskirjan nimi
Ionisiin nesteisiin perustuva hemiselluloosien eristys Kraft sellumassasta.

Julkaisija Kemian tekniikan korkeakoulu

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Tiivistelmä

Tämä väitöskirja käsittelee IONCELL-P(ulp)-prosessia, jonka avulla jalostetaan hemiselluloosapitoisesta paperisellusta puhdasta liukosellua ja polymeeristä hemiselluloosaa. Erotetut fraktiot (selluloosa ja hemiselluloosa) voidaan kerätä ilman saantohävikkiä tai polymeerien hajoamista, ja lisäksi prosessi säilyttää selluloosan luontaisen kiderakenteen. Täten prosessi tarjoaa korkeasaantoisen liukosellun tuotannon rinnalle perustan hemiselluloosa pohjaisille tuotteille. Työssä on tutkittu eristyksen tehokkuuteen vaikuttavia tekijöitä (liuottimen ja raaka-aineen ominaisuudet sekä reaktio-olosuhteet) ja laitteistolle välttämättömiä ominaisuuksia prosessin kapasiteetin nostoa varten. Eristettyjen fraktioiden käytettävyyttä arvioitiin analysoimalla niiden puhtautta, reaktiivisuutta ja muuttumattomuutta.

Tulokset osoittivat, että liuotuksen selektiivisyys hemiselluloosia kohtaan perustuu hemiselluloosien pienempään molekyylikokoon. Lyhyet hemiselluloosamolekyylit liukenevat suotuisammin ionisen nesteen vesiliuokseen selluloosan jäädessä kiinteään muotoon. Tämän takia sellumassan polymeerien moolimassajakauma on tärkeä ominaisuus arvioitaessa massan soveltuvuutta IONCELL-P-prosessiin. Mitä selkeämpi ero selluloosan ja hemiselluloosan molekyylikoissa on, sen paremmin on mahdollista optimoida veden määrä ionisessa nesteessä, vaikuttamaan vain hemiselluloosiin.

Valikoima selluloosaa liuottavia ionisia nesteitä testattiin prosessissa ja niistä löytyi yhteinen käyttäytymismalli. $\beta/\chi(H_2O)$-arvo muodostuu, kun liuotinseoksen β-arvo, joka kuvaa anionin kykyä vastaanottaa vetysidoksia, jaetaan veden moolifraktiolla. Tämä arvo antaa arvion seoksen liuotinvahvuudesta, joka tarvitaan hemiselluloosien eristämiseen, mutta ei kuvaa sitä rajaa, missä liuotinseos menettää selektiivisyytensä ja alkaa liuottaa myös selluloosaa. Tämän vuoksi systeemin selektiivisyyttä tutkittiin myös pH:n funktiona. Tuloksista ilmeni, että matalan pH:n ioniset nesteet vaativat vähemmän vettä selektiiviseen hemiselluloosien liuotukseen. Tämän lisäksi matalan pH:n ioniset nesteet olivat vähemmän taipuvaisia turvottamaan ja liuottamaan selluloosaa. Nämä löydökset yhdistämällä voidaan päätellä, että IONCELL-P-prosessiin soveltuu parhaiten massa, jonka selluloosa- ja hemiselluloosafraktioilla on selkeä kokoero, sekä ioninen neste, jolla on matala pH ja suhteellisen korkea β-arvo.

Avainsanat IONCELL-P, liukosellu, hemicelluloosaeristys, ioniset nesteet

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First I want to thank my professor, Herbert Sixta, for giving me the opportunity to prove that a peculiar girl from biomedicine can make pulp and later take up the challenge of making a PhD. I always valued the high interest you had towards the work and progress of your students. This is a demanding team, but you do get us to exceed ourselves over and over again. It has been an honour to work with you and I have learned so much on this journey. Thank you! Dr Michael Hummel, you are an amazing person to work with. I have never met anyone this passionate about science. Your support and willingness to lend me your brain have meant the world to me. You have also been a true friend, with an endless supply of hugs and chocolate to navigate through the ups and downs of these years. You inspire me!

There is a saying that it takes a village to raise a child, but I would say that this also applies to writing a PhD. I want to express my gratitude to my co-authors, colleagues, family and friends. Out of the co-authors, I want to thank Prof. Herbert Sixta, Dr Michael Hummel and Dr Agnes Stepan for refining my texts and providing valuable discussion about the results. Carmen Forschauer is deeply thanked for her ground-breaking finding that evolved to IONCELL-P and Paper I. Niklas von Weymarn and Kari Kovasin, I want to thank for your support, from the early days of my master's thesis through my PhD to this day. We have had many joint projects, and I treasure these experiences and your enthusiasm towards science! Prof. Ilkka Kilpeläinen, Docent Alistair King and Arno Parviainen are warmly thanked for the exceptional collaboration that our groups have achieved together. I think we constitute a perfect example about how we can reach fantastic goals in a small country by working together. Dr Paavo Penttilä, Prof. Thaddeus Maloney and Leena Nolvi are warmly thanked for their work with Paper II. Ossi Turunen, Yawei Wang, Hairong Xiong and Sari Asikainen are thanked for their input in Paper III. I especially want to thank Alireza Monshizadeh and Jaakko Vartiainen for their devoted work. You both produced important, high-quality data. Without your help, important aspects would have

been left out of this thesis. I have said it many times, but I will say it again: Great job!

I have always been amazed about the good team spirit we have at Puu. Whatever the problem, at Puu you will always get help when you need it. The work can sometimes be challenging, but you will not be facing it alone. It is the people who make it a joy to come to work, no matter what is the situation with your experiments in the lab. Dr Lidia Testova, I was so lucky to have you as my first contact at Puu. I have learned so much from you, but you are also a dear friend. You are smart, funny and kind! Always remember that! Dr Lauri Hauru is thanked for the many discussions and for teaching me how to measure the Kamlet Taft parameters. Dr Kaarlo Nieminen, you are so intelligent and so helpful! Thank you for fitting the $\beta/\chi(H2O)$ curve in Paper IV! Dr Anne Michud, Yibo Ma and Shirin Asaadi are most warmly thanked for teaching me to spin and helping me with my spinning project. You guys are the best! Anne, I also want to thank you for teaching us French ways, especially the eating well part. We have had so many wonderful dinners at your place, and the thought about I and Agi overeating still makes me smile. Rita Hatakka and Seppo Jääskeläinen are most warmly thanked for their help with everything that can go wrong in the lab. You two are amazing people, and without you this book would not be here. You two are so dedicated and so good at what you are doing. It has been a joy to work with you both!

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Espoo, 24th of August 2017
Annariikka Roselli

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List of Abbreviations and Symbols

A	acid treatment
ASA	accessible surface area
CCE	cold caustic extraction
DENA	*N,N*-diethyl-4-nitronaniline
DMAc	*N,N*-dimethylacetamide
EK	eucalyptus Kraft pulp
EPHK	eucalyptus prehydrolysis Kraft pulp
FSP	fiber saturation point
GPC	gel permeability chromatography
HW	hard wood
I	ionic liquid extraction
IL	ionic liquid
KT-parameters	Kamlet Taft parameters
MMD	molar mass distribution
NA	4-nitroaniline
OH-group	hydroxyl group
RD	Reichardt's dye
RT	room temperature
SW	soft wood
WAXS	wide angle x-ray scattering
WB	2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio) phenolate
wt %	weight percent
X	enzymatic treatment

[DBNH][EtCOO]	1,5-diazabicyclo[4.3.0]non-5-enium propionate
[DBNH][OAc]	1,5-diazabicyclo[4.3.0]non-5-enium acetate
[emim] Cl	1-ethyl-3-methylimidazolium chloride
[emim][DMP]	1-ethyl-3-methylimidazolium dimethylphosphate
[emim][OAc]	1-ethyl-3-methylimidazolium acetate
[mDBN][DMP]	1-methyl-1,5-diazabicyclo[4.3.0]non-5-enium dimethylphosphate
NMMO	*N*-methyl-morpholine *N*-oxide

α	Kamlet Taft acidity / ability to donate hydrogen bonds
β	Kamlet Taft bacisity / ability to accept hydrogen bonds
π^*	solvent dipolarity / polarizability
χ	molar fraction

List of Publications

This doctoral dissertation consists of a summary and the following publications, which are referred to in the text by their numerals.

Paper I

Carmen Froschauer, Michael Hummel, Mikhail Iakovlev, Annariikka Roselli, Herwig Schottenberger, and Herbert Sixta. 2013. Separation of Hemicellulose and Cellulose from Wood Pulp by Means of Ionic Liquid/Cosolvent Systems. Biomacromolecules. 14 (6), 1741-1750.

Paper II

Annariikka Roselli, Michael Hummel, Alireza Monshizadeh, Thaddeus Maloney and Herbert Sixta. Ionic liquid extraction method for upgrading eucalyptus Kraft pulp to high purity dissolving pulp. 2014. Cellulose. 21 (5), 3655-3666.

Paper III

Annariikka Roselli, Sari Asikainen, Agnes Stepan, Alireza Monshizadeh, Niklas von Weymarn, Kari Kovasin, Yawei Wang, Hairong Xiong, Ossi Turunen, Michael Hummel, Herbert Sixta. Comparison of pulp species in IONCELL-P: selective hemicellulose extraction method with ionic liquids. 2015. Holzforschung. 70 (4), 291-296.

Paper IV

Annariikka Roselli, Michael Hummel, Jaakko Vartiainen, Kaarlo Nieminen, Herbert Sixta. Understanding the role of water in the interaction of ionic liquids with wood polymers. Carbohydrate Polymers. 168 (15), 121-128.

Author's Contribution

Paper I: Separation of Hemicellulose and Cellulose from Wood Pulp by Means of Ionic Liquid/Cosolvent Systems.

Annariikka Roselli was responsible for the experimental part of NMMO, including tests and analysis. The results were then compared to the [emim][OAc] data, performed by the first author of the paper.

Paper II: Ionic liquid extraction method for upgrading eucalyptus Kraft pulp to high purity dissolving pulp.

Annariikka Roselli was responsible for the experimental design, performed the major part of the experimental work and analysis, and wrote the manuscript as the principal author. Porosity measurements were performed in prof. Maloney's group and WAXS analysis at the University of Helsinki by Paavo Penttilä.

Paper III: Comparison of pulp species in IONCELL-P: selective hemicellulose extraction method with ionic liquids.
Annariikka Roselli was the responsible researcher for the experimental part and writing of this paper, excluding the endoglucanase treatments, which were performed by VTT under the supervision of Sari Asikainen. The mannanase enzyme was received from co-authors Yawei Wang, Hairong Xiong and Ossi Turunen. Laboratory assistance was performed by Alireza Monshizadeh.

Paper IV: Understanding the role of water in the interaction of ionic liquids with wood polymers.

Annariikka Roselli was the responsible author of the experimental work and writing. Kaarlo Nieminen created the mathematical model of the xylan dissolution. Laboratory assistance was performed by Jaakko Vartiainen.

1. Introduction

The world population and the amount of needed consuming goods are growing at an increasing rate. Growth rate is accelerated by the rising economies of developing countries, triggered by products and items that are made for a short life cycle. The clothing industry is a perfect example of this phenomenon. However, environmental awareness is growing and fossil resources are diminishing, bringing new requirements for production chains. In order to answer these challenges and customer demands, the industry needs to adopt renewable raw materials, increase material efficiency, and minimize the amount of wastes and emissions by changing to sustainable and greener technologies.
Cellulose is gaining an increasing interest as a renewable raw material since it is the world's most abundant biopolymer. There are already number of consumables that are made from cellulose and lignocellulose. From these, the paper and packaging products are the most commonly known, but there are also many special applications for hemicellulose free pulps, better known as dissolving pulps. Typical products from dissolving pulps are plastics, films, and textile fibers. The production of high purity dissolving pulps is currently dominated by combined prehydrolysis Kraft and cold caustic extraction processes. The major drawbacks of these processes are yield losses and polymer degradation. These problems are amplified if a high cellulose purity is demanded. In addition, these process remove hemicelluloses in a degraded form, which makes their further use difficult and economically challenging.

This thesis report is about the development of the IONCELL-P(ulp) process, which refines hemicellulose-rich bleached paper grade pulp to high purity dissolving pulp and polymeric hemicelluloses without yield losses or polymer degradation. Both fractions, the cellulose and dissolved hemicellulose, can be recovered quantitatively, providing a basis for a new stream of hemicellulose products. In order to provide valuable information for the process up-scaling, the features that affect the extraction: solvent and substrate properties, reaction conditions and equipment requirements are studied profoundly. The studies are continued by examining the usability of the separated polymer fractions. The purity, reactivity and unaffectedness of the polymers are investigated.

In Paper I the fundamental principle, that an [emim][OAc]-water mixture is able to dissolve hemicelluloses selectively is introduced and that this selective extraction performance could also be achieved with an NMMO-water mixture. The main focus was put on a complete mass balance, revealing the purity of the cellulose fraction and the absence of any degradation of the separated polymers.

Furthermore, it was proven, that the IONCELL-P extraction is so gentle treatment, that it preserves the cellulose I crystal structure of the purified cellulose fraction.

In paper II, *Eucalyptus globulus* paper pulp was converted to a high purity, acetate-grade dissolving pulp by means of extraction with an [emim][DMP]-water mixture. The overall yield, properties and applicability to triacetate production of the produced pulps were compared to those prepared by cold caustic extraction (CCE), which constitutes the conventional way of extracting hemicelluloses from hard wood paper pulp. A commercial acetate-grade pulp was used as a benchmark in testing the triacetate properties. The study proved that the IONCELL-P produces high purity cellulose with good reactivity, which is well comparable with commercial acetate grade pulp and superior to CCE pulp. In this comparison, the purity and good porosity were not the only advantages in the IONCELL-P process, but also the superior overall yield of the process, which was further improved by the extracted polymeric hemicellulose fraction. In this paper it was also shown that the hemicellulose removal could be enhanced by an enzymatic pre-treatment with hemicelluloses degrading enzymes.

[Emim][OAc] and [emim][DMP] solutions have been studied in detail in Paper III as selective hemicellulose solvents. Different pulp species were tested for the IONCELL-P process with these ionic liquid-water mixtures. The results showed that the selectivity of the IONCELL-P was not pulp species dependent, but connected to the molar mass distribution of the polymers of the pulp. Here, we introduced the hypothesis that the hemicelluloses can be more quantitatively and selectively removed the less their molar mass distributions are overlapping with those of the cellulose fraction. In continuation to Paper II, this was shown by the treatment of a paper pulp with hemicellulases, especially mannanases in the case of softwood pulps, prior to the solvent extraction where the molar mass distributions of the hemicelluloses were shifted to lower values. Paper III also motivated a separate study by Laine et al., in which 400g of the pine pulp was extracted according to the conditions optimized in Paper III. The study of Laine et al. proved that the IONCELL-P process is scalable and that the dissolved hemicellulose fraction can be utilized for film production.

Other cellulose dissolving ionic liquids were investigated for the IONCELL-P process, and the respective results were published in Paper IV with extensive investigations of the ionic liquid properties that affect the process. Kamlet Taft parameters of the solvent mixtures and their link to hemicellulose removal efficiency were investigated along with viscosity, pH, and ability tolerate high pulp consistencies. A high Kalmet-Taft β-value has been connected to ionic liquids' ability to dissolve cellulose, but the correlation was not found, when operating with ionic liquid-water mixtures and aiming for selective hemicellulose solvation. In Paper IV, we discovered that the β-value needs to be divided with the water molar fraction of the solvent mixture in order to describe the polymer dissolution power. This is because the added water does not only decline the overall hydrogen accepting potential of the solvent, but also competes for the hydrogen bonds with the substrate. A second important finding in Paper IV, was that the pH of the solvent system seems to influence the selectivity of the solvent system.

High pH ionic liquids seem to swell and dissolve cellulose easier than low pH ones. This is why high pH ILs demand higher water contents for the solvent system to maintain the selectivity towards hemicelluloses. High water content diminished the dissolution power and lead to higher residual hemicellulose contents. This means that the most suitable ionic liquid would have a low pH and relatively high Kalmet-Taft β-value.

Figure 1 reveals a simplified flow scheme of the IONCELL-P process and highlights the most important analysis applied for the characterization of the efficiency and selectivity of the process.

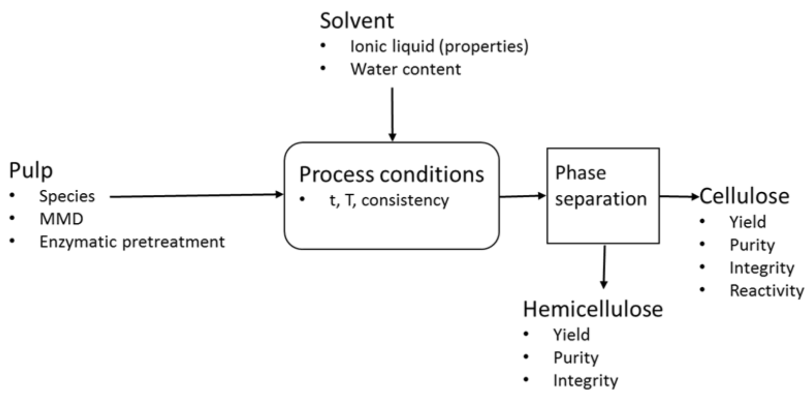

Figure 1. Simplified flow scheme of the IONCELL-P process highlighting the experimental key parameters of this thesis.

Figure 2 presents the publications related to the IONCELL-P process. This includes the original patent, four publications that are part of this thesis, three collaboration papers and two master's thesis. In addition, the work has been presented in several conferences and professional venues.

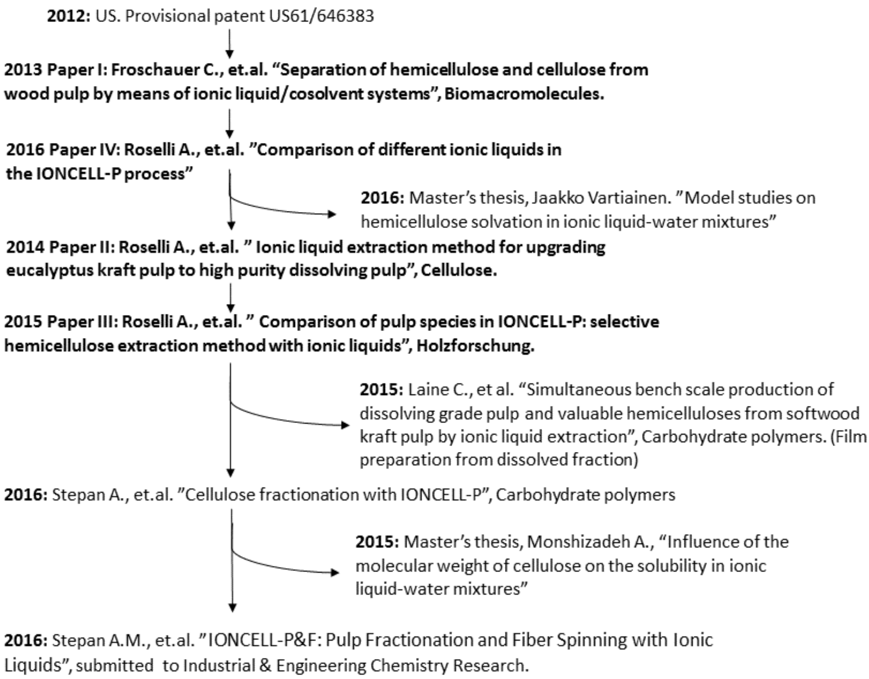

Figure 2. Published work connected to the IONCELL-P process.

2. Research questions

This work started in 2012. The purpose was to answer the many questions that arose from the initial findings published in the article of Carmen Froschauer et al., where the selective dissolution of pulp hemicelluloses in an ionic liquid – water mixture was described. The goal of this thesis work was to provide systematic information about the IONCELL-P(ulp) process and provide tools for up-scaling. The following questions were investigated in order to deliver the needed information:

- What kind of equipment would serve best the small scale screening tests and larger extraction experiments? What are the limitations and bottlenecks of the system? (This was a required step for further studies, after the initial discovery with [emim][OAc]).

- What are the common features that specify a suitable solvent for the process? How do the empirical Kamlet-Taft parameters represent the suitability and effectiveness of the solvent system? Does the pH of the solvent system affect the dissolution selectivity?

- How do different pulp species behave in the process? What are the substrate properties that influence the process (with an emphasis on the differences in carbohydrate composition and molar mass distribution of the pulps)?

- What are the properties of the extracted fractions, e.g. carbohydrate composition and molar mass distribution? Is the quality and reactivity of the purified cellulose suitable for cellulose triacetate production?

- What are the features that determine the optimum conditions for the IONCELL-P extraction such as limit of the extraction temperature, pulp consistency, and water content of the solvent system?

3. Background

3.1 Lignocellulosic plant material

Lignocellulosic plants as a petroleum replacing raw material for consumables have become the focus of a wide spectrum of research activities in order to maintain global sustainability. Lignocellulosic plants are not only a renewable raw material, but also the products are in many cases biodegradable. Petrochemical products often turn into slowly degrading microplastics, which especially burden the water ecosystems. Biopolymers have the potential to become the green alternative for many currently oil-based products. However, first the biopolymers need to be isolated and purified from the plant's structural matrix.

Wood and other lignocellulosic plants contain three basic polymer types: cellulose, hemicellulose and lignin. A plant's lignin is a heterogeneous network, which keeps the wood matrix together and is mostly removed during Kraft pulping, freeing the cellulose fibers. Cellulose is a linear high molar mass polymer, made from glucose monomers. The degree of polymerization of cellulose is approximately 10 000 units. The cellulose polymers form bundles called microfibrils. Microfibrils construct macrofibrils, from which the wood fibres are then built. In the cell wall, the cellulose microfibrils are organized into rigid crystals, with amorphous regions between them. The highly organized crystalline structure is held together by intra- an intermolecular hydrogen bonds between cellulose polymers, hydrophobic stacking between cellulose polymer layers, and inter-layer hydrogen bonds. These interactions give cellulose recalcitrance towards solvation processes. (Jääskeläinen 2007, pp. 65-82; Rojas 2015)

Hemicellulose is a complex, branched and heterogeneous biopolymer group. The degree of polymerization is around 100 units, making the hemicelluloses rather short polymers, when compared to cellulose. The hemicelluloses are constructed from pentoses (xylose and arabinose) and hexoses (galactose, glucose, and mannose). Mannan is present mainly in soft woods, while xylan is the major hemicellulose type in hard woods. Hemicelluloses supposedly connect the lignin and cellulose domains in the cell wall. Xylan and mannan polymers are illustrated in **Figure 3** where the heterogeneous, branched nature of the polymers can be seen along with some acetylated OH-groups. Unlike lignin, the hemicelluloses are wished to be preserved in the paper grade pulp. This is because the hemicelluloses increase the fiber binding capability and the pulp yield. Typical hemicellulose content of a bleached paper pulp is approximately one quarter of the total mass. An example of the changes in softwood and hardwood hemicellulose contents after Kraft cooking are presented in **Table 1**. (Jääskeläinen 2007, pp. 65-82)

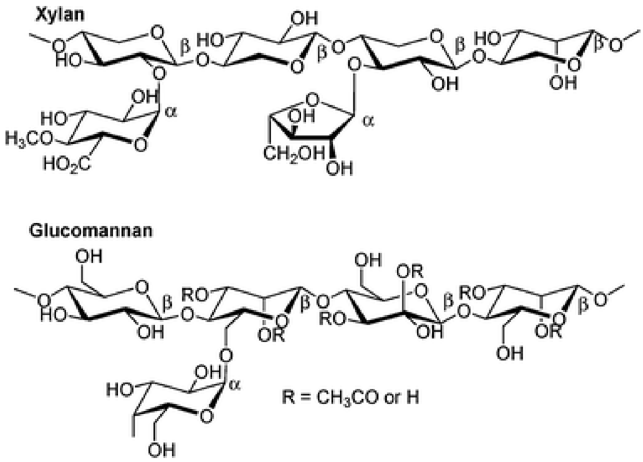

Figure 3. Structure of xylan and glucomannan polymers.

Table 1. Hemicellulose content in softwood and hardwood before and after Kraft cooking. Table adapted from (Gullichsen 2000, p.A28).

Hemicellulose	Wood		Kraft pulp	
	Pine	Birch	Pine	Birch
Xylan	7-10	25-30	5	16
Glucomannan	15-20	2-5	5	1

As mentioned above, the hardwoods and softwoods contain different amounts of xylan and mannan. These hemicelluloses are also present in different variants, depending on the wood type. The major hemicelluloses in softwoods are galactoglucomannan (GGM), glucomannan (GM) and arabinoglucuronoxylan (AX). The difference between GGM and GM is that GGM has higher amount of galactose side chains. In AX there is a L-arabinose unit attached to every 5-12 xylose unit and there is no acetylation of the side groups. Hardwoods express mainly xylan (GX, O-acetyl-4-O-methylglucurono-ß-D-xylan), that contains acetyl side groups, and approximately every 10th xylose unit is substituted with methylglucuronic acid residue. In addition to GX, hardwoods contain small amounts of GM. The degree of polymerisation (DP) of hardwood GX is the highest (approx. 170 units, depending on the source), while the DP of pine xylan is only 80. The DP of softwood mannan is approximately 100 units. Xylan is preserved most efficiently during Kraft cooking as mannan is more inclined to alkaline peeling reactions. (Jääskeläinen 2007, pp.73-83.)

3.2 Dissolving pulp

Dissolving pulps differ from paper grade pulps by their low hemicellulose content. These hemicellulose lean pulps are used as an oil replacing raw material for many high value consumables, but the majority is used for different cellulosic fibers for textile and non-woven products. Typical applications are viscose fibers (and related products such as Modal or tirecord fibers), TENCEL® fibers and cupro filaments. In addition, some high quality products like films (e.g. cellophane or cellulose (tri-)acetate), nitrocellulose and microcrystalline cellulose can be produced from purified cellulose pulp. (FibreYear 2016)
Although the textile market is dominated by synthetic polyester fibers, natural fibers are often preferred due to their nice hand feel and moisture handling abilities. Furthermore, consumers have started to demand sustainability from the products they buy. Cotton is the main alternative for polyester, but man-made cellulosic fibers are an increasing industry, filling the gap between the need and production of cotton. In addition, the man-made fibers are seen as the more ecological alternative than cultivated cotton, which demands a lot of agricultural land, irrigation water, pesticides and fertilizers. Man-made cellulosic fibers are mostly produced from wood based dissolving pulp. This makes the feedstock reliable and independent from the fluctuations of the annual crop, which, in the case of cotton, is often influenced by the rainfall. The reliability of the feedstock also means that the production of the man-made fibers can be adjusted to the current market demand. (FibreYear 2016)

The alpha cellulose content of dissolving pulps varies from 90-99 %. A commonly defined limit for residual hemicellulose content of dissolving pulp is 5 wt %. This type of pulp can be used in robust applications like viscose fiber production, but the more delicate the end product is, the higher pulp purity is required. Transparent plastics and cellulose triacetate products, where the degree of substitution is quickly diminished by hemicellulose, can tolerate only very low amounts of impurities within the cellulose. In acetylation the hemicelluloses block the OH-groups of the cellulose and compete for the reaction chemicals. This causes defects in the end product and can lead to, for example, haze formation in the plastic. The most common production paths of dissolving pulp are prehydrolysis Kraft or sulphite process combined with cold caustic extraction (CCE). Yield losses and polymer degradation are limiting the purification intensity in these processes and increasing the production costs, when a high purity cellulose is manufactured. (Gardner and Chang 1974; Sixta 2006, pp.933-1023)

As stated, the hemicelluloses correspond roughly to 25 % of the wood material. The hemicelluloses that are removed during pulping, are often burned, but their low heat value makes it unprofitable. A lot of research is devoted to the use of hemicelluloses as a raw material for side products of the pulping industry in order to increase the material efficiency. Polymeric xylan has a good affinity with cellulose, making it a suitable strengthening agent in paper or in bio-composites. Xylan can be modified to bring new material properties, such as hydrophobicity and thermal formability. The extracted xylan can also be degraded to xylose, which could be converted to for example ethanol, xylitol or lactic acid and other valuable products by pentose fermenting microbes. Softwood glucomannan has functional film-forming properties. Glucomannan containing films have demonstrated good gas barrier properties, and therefore it is an interesting material for food packaging. Cross-linked glucomannan has good water absorption properties and could be a potential alternative as an environmentally friendly liquid absorbent, for instance in the form of a hydro gel. However, the hemicelluloses are typically degraded in the extraction processes and distributed into the liquid phase, from where they are difficult to collect and purify economically. (Hartman et al. 2006; Saadatmand et al. 2012; Li et al. 2013; Alekhina et al. 2014; Laine et al. 2016)

3.2.1 Prehydrolysis Kraft pulping

Prehydrolysis Kraft process is the most commonly used method to produce hemicellulose lean pulp. An autohydrolysis or acid catalysed hemicelluloses degrading step is added to the pulping process before the lignin removing Kraft cooking. The remaining hemicellulose content is reduced effectively during the delignification step, because the prehydrolysis has increased the amount of reducing ends for peeling reactions. Unfortunately, this applies also to the cellulose, which leads to yield losses. For example, a single step Kraft cooking of soft wood can increase the pulp alpha cellulose content to 88 % with yields of 42-46 % on raw wood. Prehydrolysis can increase the alpha cellulose content up to 96 %, but this reduces the yield down to 35 % on raw wood and has an influence on the intrinsic viscosity of the pulp. 2.5-5 % hemicellulose content can be obtained by rather mild prehydrolysis conditions and by relatively low yield losses, depending on the wood species. For example, xylan from certain Eucalyptus species is removed more efficiently than birch xylan in identical conditions (Sixta 2006 pp.325-365). In order to reach acetate grade pulp (< 2% hemicellulose content), the P-factor of the prehydrolysis, which describes the temperature and time profile of the reaction, needs to be increased from 300 to at least 600 and even so the reduction of hemicellulose is moderate when compared to the yield losses and polymer degradation. A possible explanation for this stern resistance of the final hemicelluloses could be that some of the hemicelluloses are chemically bond to lignin by glycoside linkages. These linkages are then transferred to cellulose by transglycosidation reactions during Kraft cooking, maintaining the resistance of the hemicelluloses. (Rydholm 1965, pp.649-672; Stephenson 1989; Sixta 2006, pp.325-365; Chirat et al. 2012)

In prehydrolysis especially the pentosans are degraded to oligosaccharides. The process is mainly driven by acid catalysed cleavage of glycosidic bonds. In autohydrolysis the wood chips are treated only with steam or water, and the released acetic acid from the wood promotes the hydrolysis reactions. As a drawback, the autohydrolysis demands higher temperatures than acid catalysed hydrolysis. Applying steam instead of water reduces the amount of liquid in the hydrolysate, which facilitates its combustion in the recovery boiler. However, steam also provokes condensation reactions of lignin, hindering the lignin removal and pulp reactivity during pulping. Water prehydrolysis is also inclined to condensation reactions, and a sticky pitch like material is formed, staining surfaces and the wood chips. In addition, the material losses are more extensive in high liquid to wood ratios. Acid catalysed prehydrolysis is more energy efficient as the sulphuric acid catalyst decreases the heat demand, but the problems there are the reduced recyclability of the chemicals and corrosion. (Rydholm 1965, pp.649-672; Sixta 2006, pp.325-365)

The prehydrolysis step is stopped by adding alkali to the hydrolysate without pressure drop. This neutralizes the reactive hydrolysis products (organic acids) and fragments oligosaccharides, causing the major part of the hemicellulose removal in the process. Neutralized hydrolysate is displaced prior to the cooking stage. These advanced procedures are preventing condensation reactions and staining, and are referred to as the Visbatch® process. (Sixta 2006, pp.325-365)

3.2.2 Cold caustic extraction

Sodium hydroxide is able to dissolve only short cellulose fragments and not native cellulose. Thus, cold caustic extraction removes relatively selectively alkali soluble impurities and short chain carbohydrates. The CCE causes mainly physical changes in the pulp, without chemical reactions to the polymers. The hemicellulose to cellulose hydrogen bonding is weaker than the hydrogen bond network between cellulose molecules. This way the hemicellulose hydrogen bonds can be overcome selectively with alkali concentrations that will not dissolve cellulose effectively. The CCE is often applied as an after treatment for acid sulphite process, but is also used in combination with the PHK process. The extraction is carried out in mild temperatures between 20 to 40 °C and the alkali concentration is adjusted between 5 and 12 %, these two process conditions being the main variants affecting the extraction efficiency. However, alkali concentrations above 11 % can lead to the formation of alkali cellulose, which is regenerated as cellulose II during washing. Cellulose II forms more inter and intramolecular hydrogen bonds during drying than cellulose I, leading to a decreased reactivity of the pulp. The gradual formation of alkali cellulose is described in **Figure 4** as the function of temperature and alkali concentration.
Another weakness of the CCE process are the inevitable cellulose losses, even though CCE is currently seen as the most selective way to remove hardwood xylan. (Mannan in a softwood Kraft pulp remains very resistant towards a CCE treatment.) The cellulose yield losses vary from 1.2-1.5 % per each increased % in alpha cellulose content. In addition, when a high purity cellulose is aimed for, the substrate should not contain much of high molar mass xylans, as they have the tendency to precipitate on fiber surfaces, even in high caustic concentrations. (Rydholm 1965, pp.992-1023; Sixta 2006, pp.933-965)

Despite the favourable selectiveness of the cold caustic extraction towards xylan, its implementation at a larger scale is challenging because of the high chemical demand, which limits the economy of the process. Firstly, the caustic lye is difficult to separate from swollen pulp, reducing the recyclability of the chemicals. Only a small fraction of the alkali is consumed in neutralizing the pulp originated acids, but the lye cannot be reused in the CCE process. This is because impurities cumulate into the lye, which would hamper the extraction process.

However, the CCE lye from the purification of PHK pulp can be completely re-used in Kraft cooking, if the processes can be operated in parallel. (Rydholm 1965, pp.992-1023; Sixta 2006, pp.933-965)

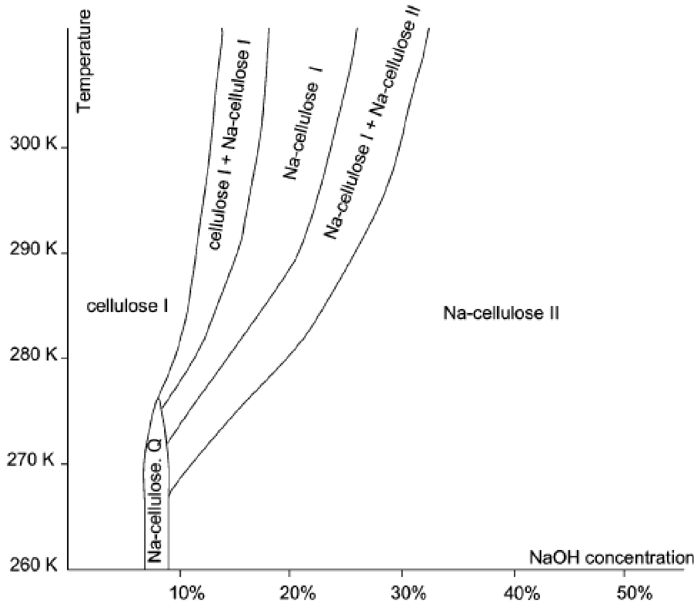

Figure 4. Phase diagram of cellulose conversion to Cellulose-Na I and cellulose-Na II as a function of temperature and alkali concentration. Reprinted with permission. (Porro et al. 2007)

3.2.3 Nitren extraction of xylan

Nitren can convert paper grade pulp to dissolving pulp when applied as aqueous solutions. Nitren is a complex of tris(2-amino-ethyl)amine and nickel (II) hydroxide (1:1 ratio) and it is selective towards pulp xylan in concentrations of 3-7 w%, but cannot influence mannan. This strongly alkaline solution (pH 13) dissolves polymers by first deprotonating the hydroxyl groups at C2 and C3 positions. The diolate moieties are then bound to the nickel atom through cis-configured hydroxyl groups by strong coordinate bonding. The xylan removal proceeds from low MM polymers to high MM polymers with increasing nitren concentration. (Janzon et al. 2006; Janzon et al. 2008)

The nitren based xylan dissolution is a mild treatment. The reaction temperature is only 20°C and the dissolution is completed in 1h. The cellulose I crystalline form is not influenced by the treatment. 96-97 % cellulose content can be obtained with 7 % nitren concentrations, but this already starts to degrade the cellulose fraction slightly. With 5 % nitren concentration, the selectivity can be maintained, but the cellulose content will remain at 94-96 %. In addition, the use on nickel is a disadvantage, and the process demands an effective and careful washing of the fractions. (Janzon et al. 2006)

3.3 General introduction to ionic liquids

Ionic liquids are salts, which are in liquid state below 100 °C. This temperature is a defined arbitrary value corresponding to the boiling point of water, which is generally considered as a limit for liquid chemistry. These molten salts are intensively studied for many applications. There are clear advantages in performing variable reactions in ionic liquids due to the improvements in process economics, reactivity, selectivity, and process yield. The interesting features of ionic liquids and their applications on different fields are presented in **Figure 5**. In addition to organic synthesis and catalysis, ionic liquids are especially regarded as promising solvents. (Welton 1999; Wasserscheid and Keim 2000; Earle and Seddon 2002; Thuy Pham et al. 2010) The unique physicochemical properties of ionic liquids comprise of a low melting point, low vapor pressure, wide liquidus range, thermal stability, a broad electrochemical window, and the ability to dissolve various organic and inorganic substances. As the variety of possible ionic liquids is immense, it is natural that not all of these properties apply unconditionally to each ionic liquid, but these are the properties that are principally looked for when a new ionic liquid is designed. (Seddon 1997; Welton 1999; Stark and Seddon 2000; Wasserscheid and Keim 2000; Mäki-Arvela et al. 2010; Wang et al. 2012; Hayes et al. 2015)

The ionic liquid characteristics, described above, derive from their unique chemical structures. Typically, the cation depicts an asymmetrical, bulky, organic moiety, which often contains one or several alkyl residues attached to the core unit. The most commonly applied cations are based on imidazolium, tetraalkylphosphonium, tetraalkylammonium or pyridinium. (Welton 1999; Pinkert et al. 2009; Hallett and Welton 2011; Ghandi 2014) The IL remains in liquid state as the degree of freedom of the flexible alkyl chains is greatly enhanced in the liquid state. Thus, the solid-liquid phase transition is connected to an entropy gain. The positive charge is often delocalized, reducing the total Coulomb energy of the ionic system. This leads to a depression of the lattice energy and a low or negative Gibbs free enthalpy of fusion at ambient temperature. Isolating the effects of cation and anion on the physical and chemical properties is difficult and usually only consistent in homologue series. However, the ability to accept hydrogen bonds, which is of particular interest in the light of this thesis, is mostly attributed to the anion. (Seddon 1997; López-Martin et al. 2007; Hayes et al. 2015)

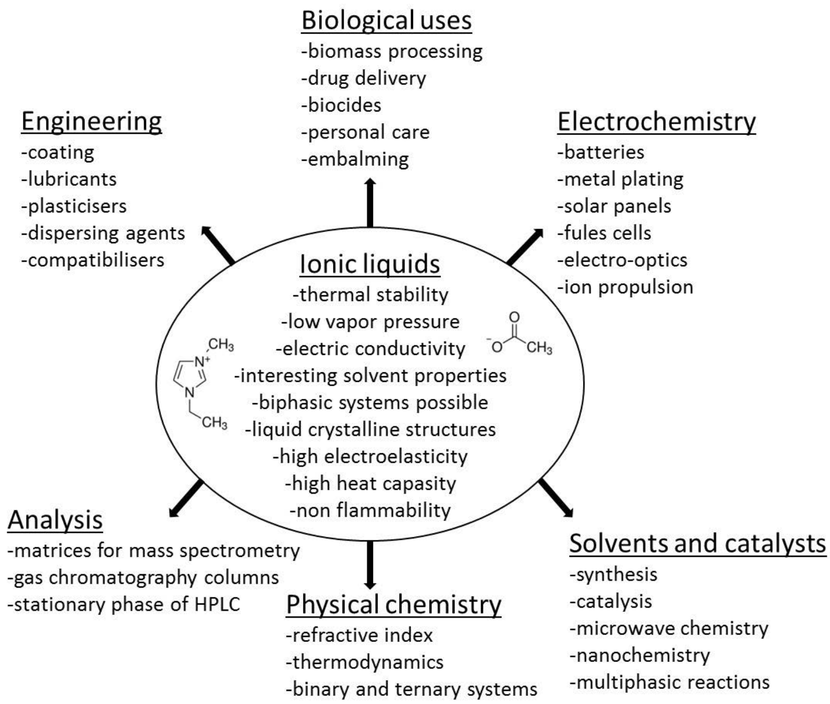

Figure 5. Ionic liquid properties and applications of different fields.

3.4 *N*-methylmorpholine *N*-oxide (NMMO)

N-methylmorpholine *N*-oxide (NMMO) monohydrate is an ionic liquid like, direct cellulose solvent. NMMO is used on an industrial scale in the so-called Lyocell process for the production of man-made textile staple fibers. NMMO is a molecule with a strong dipole moment, which allows it to interact with cellulose through the formation of hydrogen bonds. It is notable that neat, water-free NMMO is not able to dissolve cellulose, but requires one mole-equivalent of water to act as a cellulose solvent. The structure of the NMMO monohydrate is illustrated in **Figure 6**. (Rosenau et al. 2001; Rosenau et al. 2002)

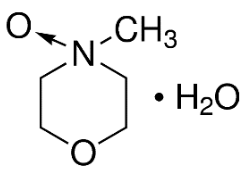

Figure 6. Structure of *N*-methylmorpholine *N*-oxide monohydrate.

The problems associated with the large-scale use of NMMO are the high melting point (Lyocell process operates in 90-120 °C), its corrosive nature, and a distinct thermal instability of the solvent. The instability of NMMO can lead to multiple radical side and degradation reactions, which can accelerate the degradation of NMMO and cellulose even further and cause decolourization of the spun fibers. Stabilisers, like propyl gallate, are added to scavenge radicals and stop unwanted side-reactions, which can be highly exothermic events. Spontaneous runaway reactions (explosions) have occurred in the past when appropriate counter-measures were missing. On the other hand, NMMO is a low-toxic and biodegradable cellulose solvent, and the Lyocell process is much simpler and more ecologically friendly than the viscose process. (Rosenau et al. 2001; Rosenau et al. 2002)

3.5 Kamlet-Taft parameters

Kamlet-Taft parameters are empirically determined solvatochromic solvent descriptors, and they have become an important tool in describing and understanding the performance of solvents. The solvatochromic Kamlet-Taft parameters are composed of α, β, and π*values. The hydrogen-bond acidity α represents the solvent's ability to donate a proton in forming hydrogen bonds, while β quantifies the capability to accept the proton (donate an electron pair) in hydrogen bonds. π* stands for dipolarity/polarizability ratio and is related to the solvents ability to develop a dipole moment in response to an external field. This is illustrated in **Figure 7**, with an example of solvatochromic probe. Examples of Kamlet-Taft parameters of water, toluene, and [emim][OAc] are given in **Table 2**. The selection grants a basic overview of typical solvent types. (Kamlet and Taft 1976; Taft and Kamlet 1976; Kamlet et al. 1977; Kamlet et al. 1983; Doherty et al. 2010)

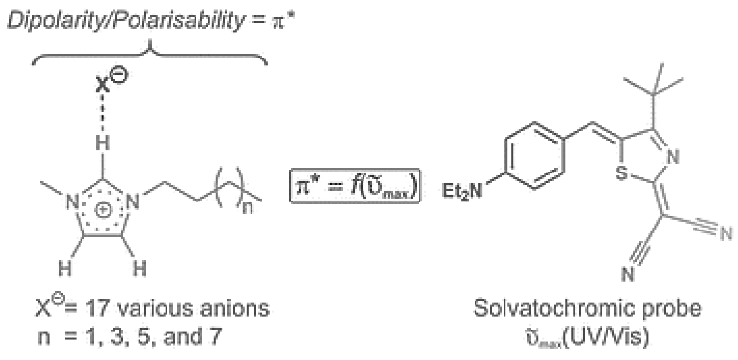

Figure 7. Dipolarity/Polarisability can be measured with a solvatochromic dyes. Repreinted with permission (Lungwitz et al. 2010).

Table 2. Example values for Kamlet-Taft solvent parameters.

Solvent	α	β	π
Water	1.17	0.47	1.09
Toluene	0.00	0.11	0.54
[emim][OAc]	0.50	1.09	1.01

The Kamlet-Taft parameters are of significance for this thesis study mostly in terms of the β-value, which has been proposed by the literature to correlate with a solvent's ability to dissolve cellulose. A high β-value, indicating a pronounced capability of the solvent to accept hydrogen bonds, is vital to interact sufficiently with the OH-groups of cellulose or hemicellulose in order to dissolve the biopolymers. It has also been reported that the cellulose solubility in ionic liquids correlates with the so-called net-basicity (β-α). However, this could not be confirmed in our studies. This might be because the solvent systems used herein are biphasic in nature. Further, we do not aim for complete dissolution, but for selective hemicellulose removal.(Kamlet et al. 1983; Lungwitz et al. 2010; Hauru et al. 2012)

3.6 Biopolymer dissolution with ionic liquids

Swatloski et al. were the first to report the dissolution of cellulose in ionic liquids in 2002. Since then, all three lignocellulosic polymers: lignin, hemicellulose and cellulose have been shown to dissolve in specific ionic liquids. Degrading pretreatment of wood and other lignocellulosic materials with ionic liquids has been applied widely to enhance enzymatic degradability of cellulose, which is advantageous for bioethanol production. Several authors have shown attempts to fractionate the wood constituents by means of complete or partial dissolution in ionic liquids. However, a considerably large portion of undissolved residues, limited selectivity, and contamination of the spent ionic liquid with wood extractives and other impurities, represent obstacles that still need to be overcome. (Swatloski et al. 2002; Li et al. 2010; Lan et al. 2011; Pinkert et al. 2011; Anugwom et al. 2012; Hossain and Aldous 2012; Hauru et al. 2013; Gupta and Jiang 2015) Cellulose, as the Earth's most abundant biopolymer and raw material for many products, has been the most intensively investigated lignocellulosic polymer in connection with ionic liquids. From these ionic liquids, the [emim] based ones have been the most studied group. These studies aim largely to use cellulose as a glucose source for ethanol production, but cellulose processing in ionic liquids is also under profound investigation. Particularly textile fiber spinning with ionic liquids has been examined as an alternative for the viscose fiber process. The key advantages in ionic liquid textile fiber spinning is that in this single step process, the cellulose is directly dissolved and no derivatization with toxic carbon disulfide or other chemicals is needed. (Kilpeläinen et al. 2007; Kosan et al. 2008; Pinkert et al. 2009; Mäki-Arvela et al. 2010; Hong et al. 2013; Hummel et al. 2015; Michud et al. 2015)

3.6.1 Cellulose dissolution mechanism in ionic liquids

Aiming for an understanding of biopolymer dissolution in ionic liquids, many studies have been conducted in particular using cellulose as the model solute. Cellulose crystal is very recalcitrant towards solvation, not only due its inter and intramolecular hydrogen bond network, but also due to the lattice packing of the polymers. The hydrophobic interactions between the sheets bind the layers strongly together. Microfibrils form macrofibrils by direct interactions (polar to polar and non-polar to non-polar) of surfaces of cellulose crystals, bringing more complexity to cellulose solvation.(Oehme et al. 2015; Oehme et al. 2015) Despite intensive research, there is no conclusive explanation on the dissolution mechanism of cellulose in ionic liquids. Ionic liquids are non-derivatizing cellulose solvents. This means that the cellulose can be dissolved directly in the solvent, without chemical reactions of the OH-groups and polymer degradation. Low melting point, low viscosity, and a strong anion basicity (the ability to receive hydrogen bonds) are generally connected with the ionic liquid's strength to dissolve cellulose. (Remsing et al. 2008; Vitz et al. 2009) Also short alkyl chains in both, cation and anion, and electron-withdrawing groups in the cation, but not in the anion, have been associated with good cellulose dissolving capability. (Zhao et al. 2012; Zhao et al. 2013) By contrast, hydrogen bond donating functional groups, like –OH or –OCH3, in the cation backbone, hinder the cellulose solvation. This is because these groups decrease the cation proton acidity and compete with the cellulose for the anion hydrogen bonds. (Zhang et al. 2010; Lu et al. 2014) Yet, the role of the cation is not as well understood as the anion's ability to accept hydrogen bonds. There are both studies which claim that the cation is rather irrelevant, and studies, where the cation has identified to have a major role in the cellulose dissolution. (Lu et al. 2014) The situation is further complicated by the large number of possible ion combinations, which makes it almost impossible to postulate a universal unambiguous solvation mechanism.

Bypassing the experimental limitations for a thorough understanding of the cellulose dissolution on a molecular level, computational simulation studies have been performed to gain insight into the dissolution mechanism. It is essential to keep in mind that the computation capacities to date are still limited and that respective simulations implement only small cellulose fragments and short time periods, meaning that even though these studies provide useful information, they do not fully describe the reality yet. In practical applications, the cellulose polymer is present in bundles of long-chain cellulose and the dissolution time is considerably longer. (Gupta and Jiang 2015) In computational studies, the anions have been reported to form a steady hydrogen bond network with the cellulose OH-groups and surround the cellulose polymer more tightly than the cations. (Youngs et al. 2007; Huo et al. 2013; Rabideau et al. 2013) Studies investigating dissolution of crystalline cellulose, illustrate anions forming negatively charged complexes with the surface cellulose polymer, weakening the intramolecular hydrogen bonding, making the cellulose strand more flexible and easier to peel off. Breaking the intermolecular hydrogen bonds eventually detaches the cellulose polymer from the bundle. (Cho et al. 2011; Rabideau et al. 2013) Cations interact with the anions and move between the detaching strand and the remaining cellulose bundle, acting as a lever and pushing the dissolved strand off the bulk cellulose. This behavior also might explain why the aromatic cations seem to be more efficient than non-aromatic ones. The aromatic ring is a sterically more demanding structure to peel the cellulose strand off. The importance of the levering effect provided by the cation depends on the present anion. For example, Cl^- is not able to separate the strands by itself, but needs the bulk of the cations to peel off the dissolved cellulose chains. Cellulose solvation could not be demonstrated with ionic liquids, which could not form steady hydrogen bonds with the cellulose OH-groups. (Rabideau et al. 2013)

In another simulation study by Rabideau et al., chloride, acetate and dimethylphosphate anions were investigated in combination with 1-alkyl-3-methylimidazolium cation. The authors found that the acetate anion has the largest amount of stable binding states for hydrogen bonds, followed by chloride and then by dimethylphosphate. This means that acetate is the most potential and agile anion for cellulose solvation, as it can form the biggest variety of bonds, increasing the lifetime of the interaction between the anion and cellulose. (Rabideau and Ismail 2015)

3.6.2 Co-solvent in cellulose dissolution

Many ionic liquids have a high viscosity, which is often a draw back for their use in processes. High viscosity of the solvent hampers the dissolution of these long polymers that are organized in highly crystalline structures. This problem can be partly overcome, by adding an aprotic co-solvent to the actual cellulose dissolving ionic liquid. Typical examples of co-solvents are dimethyl sulfoxide, (DMSO), dimethylformamide, (DMF). DMSO is one of the most investigated co-solvents used with ionic liquids. DMSO is a polar, aprotic solvent and decreases the ionic liquid viscosity, facilitating mass transfer during cellulose dissolution, without disturbing the anion – cation or ionic liquid – cellulose interactions (the ability to accept and donate hydrogen bonds). The solvent system's ability to accept hydrogen bonds (Kamlet-Taft β-value), needs to remain high enough to dissolve cellulose. The ratio of the solvent and co-solvent depends of their solvent properties and interactions. The molar fraction of the co-solvent can be surprisingly high, without hampering the ionic liquid's ability to dissolve cellulose, if the co-solvent does not disturb the hydrogen bond forming.(Rinaldi 2011; Froschauer et al. 2013; Huo et al. 2013; Zhao et al. 2013; Andanson et al. 2014; Rabideau and Ismail 2015)

3.6.3 Water in cellulose dissolution

Water is generally perceived to act as an anti-solvent with ionic liquids. Water has low hydrogen basicity and high hydrogen acidity. Thus, water forms strong hydrogen bonds with the anions of the ionic liquid, blocking the sites from forming hydrogen bonds with the cellulose. These hydrogen bonds hinder the anion-cellulose interactions, leading to reduced cellulose dissolution. Water influences the solvent properties of the system gradually by its molar fraction as described for co-solvent in the previous chapter.(Liu et al. 2011; Zhao et al. 2013; Rabideau and Ismail 2015)
In the previously mentioned study of Rabideau et al. where OAc, DMP and Cl anions combined with the [emim] cation, were compared as cellulose solvents, they also simulated the formation of hydrogen bonds between ionic liquid and cellulose, when water was added into the mixture. The result was that in general, water addition decreases the formation of hydrogen bonds between the anion and cellulose, but that the acetate anion is slightly less influenced by the water than DMP and Cl. This might be attributed to acetate's higher potential to accept hydrogen bonds in different states. (Rabideau and Ismail 2015) In a simulation study of Liu et al. it was demonstrated that water disrupts the interaction of the anion and the cellulose OH-groups, but also changes the way that cations are organized. Water dislodges the cation from the nearness of the anion, eliminating the levering power, which pushes off the peeling cellulose chains from the fibril. (Liu et al. 2011)

3.7 IONCELL-P(ulp) process

As described earlier, the currently used hemicellulose solvation methods have their problems in their effectiveness, yield and economics. Hemicellulose extraction by nitren-water solution provided the idea, that nitren, which needs nickel to operate, could be replaced with ionic liquids.

The original hypothesis of the IONCELL-P process was that if a high β-value is needed for cellulose solvation, the short, hydrophilic, amorphous hemicelluloses should be soluble in solvents with lower β-values. If this was true, the dissolution power of the ionic liquid could be impaired gradually by adding water, and conditions for selective hemicellulose solvation found. This discovery of the ionic liquid based hemicellulose dissolution from paper grade pulp, was patented first by US provisional patent (US61/646383) and subsequently by a full patent application (WO 2013/171364 A1). The finding was published in 2012 by Froschauer et al. Meanwhile, similar studies were performed in the US, by Celanese International Corporation, who filed their own patent shortly after Aalto University. The patent of Aalto University was bought by Metsä Fibre, who extended the original patent with two additional ones (WO 2014170546 A1 and CA 2907608 A1).

In this so-called IONCELL-P(ulp) process a paper grade pulp is treated at a mild temperature of 60 °C for 3h, in a mixture of ionic liquid and water, during which the hemicelluloses are dissolved selectively. The dissolved hemicelluloses are then removed via filtration, resulting in purified cellulose and a polymeric hemicellulose solution. The hemicelluloses are reprecipitated from the solvent by adding more water to the system. Unlike in the prehydrolysis Kraft and cold caustic extraction procedures, there are no yield losses or polymer degradation on either of the collected fractions. In addition, the treatment is so mild, that the cellulose fully remains in cellulose I crystalline form, which keeps the pulp in a more reactive state after drying. The polymeric hemicelluloses can be easily collected and used as a platform for new hemicellulose based products increasing the overall material efficiency. (Froschauer et al. 2013; Sixta et al. 2013; Li et al. 2014; Reilama and Turunen 2014)

In the initial study of Froschauer et al. the dissolution of artificially blended cotton linter cellulose and cold caustic extracted birch xylan was tested in [emim][OAc] with increasing water content. It was found that xylan could be dissolved completely in mixtures with higher water contents, lower temperatures and in shorter time than cellulose. These differences in dissolution behaviour provided a set of parameters to optimize the treatment conditions in terms of selective pulp hemicelluloses extraction. The solubility of pure xylan as a function of the solvent water content, in different temperatures is illustrated in **Figure 8**. In practise, when applied to pulp, the extraction efficiency is not as high as with pure cellulose and hemicellulose. When embedded into paper grade pulp, the polymers have interactions that need to be overcome in order to extract the hemicellulose, which narrows the conditions window. Regardless of the narrowing of the differences, bleached birch Kraft pulp was successfully purified with [emim][OAc] containing 15 wt% of water. The IONCELL-P process decreased the xylan content from 25.4 wt% to 2.8 wt%. The experiments were repeated with NMMO, which is the only commercially used direct cellulose solvent, with which a partial hemicellulose removal was obtained (residual xylan content of 11.4 wt%). (Froschauer et al. 2013)

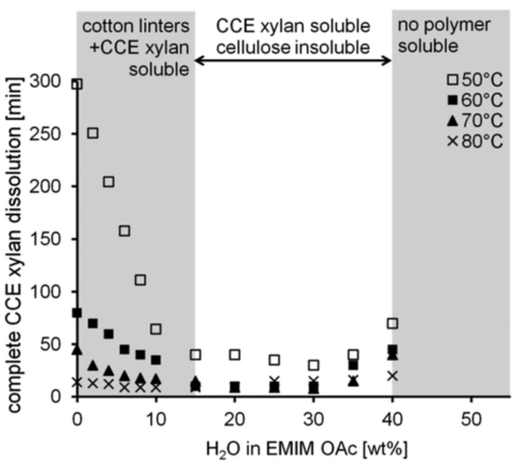

Figure 8. Solubility of CCE xylan and cotton linters in different temperatures and water concentrations in [emim][OAc]. Reprinted with permission. (Froschauer et al. 2013)

The findings of Forschauer et al. was the starting point of this thesis work. The paper is included in the study, but the research methods and equipment were further developed and refined so much that the experimental details of Paper I are not covered completely in the experimental part. As an example, the NMMO experiments in Paper I resulted 11.4 wt% of residual xylan, while in following studies the xylan content was reduced to 5 wt%, equalling to a 56% improvement. In addition, the interpretations of the Kamlet-Taft parameters evolved when more solvents were tested and the material balance became more accurate after substantially improving the washing protocol of the fractions.

In this thesis, the features affecting the extraction process efficiency and selectivity are examined thoroughly. The processes influencing the properties of the substrate and the solvent system are investigated. Reaction conditions (t, T and χH_2O) are optimized and the quality of the resulted polymers (cellulose and hemicellulose) fractions are studied. From the results, a general empirical relationship between the physicochemical properties of the solvent system and the xylan removal efficiency from paper grade pulps was established.

4. Experimental

4.1 Materials

Three bleached Kraft pulps were used as substrates in this thesis work: Metsä Fibre pine pulp from Rauma mill, Stora Enso's birch pulp from Imatra mill, and eucalyptus pulp from a Brazilian pulp mill. The sugar compositions and intrinsic viscosities of the pulps are listed in **Table 3**. Cold caustic extracted (CCE) xylan from eucalyptus pulp, applied in the viscosity studies of the solvent-hemicellulose mixtures, was obtained by a method described earlier by Froschauer et al. (Froschauer et al. 2013)

Table 3. Characteristics of the used pulps.

Pulp (Kraft)	**Cellulose** (wt %)	**Xylan** (wt %)	**Mannan** (wt %)	**Intrinsic viscosity** (ml/g)
Pine	84.8	8.1	7.1	893
Birch	74.6	25.4		808
Eucalyptus	83.4	16.6		813

The ionic liquids used in this work were commercial, synthetized by Helsinki University (Ilkka Kilpeläinen group), or synthetized in-house, by 1:1 acid-base reaction. The solvents, their abbreviations and the origins are listed in **Table 4** and their structures are presented in **Figure 9**. DBN was purchased from Fluorochem, UK; acetic acid, propionic acid and trimethylphosphate were from Sigma, Germany. Endoxylanase, Pulpzyme® HC, applied in this thesis study, was purchased from Novozymes. Thermostable mannanase ManAd3 from Caldibacillus cellulovorans (Sunna et al. 2000) was produced in *Pichia pastoris* by Hubei Wuhan and Hairong Xiong at Huazhong University of Science and Technology, China. Endoglucanase Ecopulp R. (EC3.2.1.4) was obtained from AB Enzymes Oy (Finland). Reichardt's dye (RD) and 4-nitroaniline (NA) were purchased from Sigma Aldrich, Germany, *N,N*-diethyl-4-nitronaniline (DENA) from Flurochem, UK, and 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio) phenolate (WB) was a kind gift from Professor Omar El Seoud from the University of Saõ Paulo. The chemicals needed for acetylation experiments were: sulfuric acid (95–97 % for analysis, Merck Millipore), acetic acid (100 %, glacial, VWR), and acetic anhydride (>98 %, for synthesis, Merck Millipore).

Table 4. List of ionic liquids and their origins.

Abbreviation	Solvent	Origin	Purity
1. [emim][OAc]	1-ethyl-3-methylimidazolium acetate	BASF, Germany	95%
2. [emim][DMP]	1-ethyl-3-methylimidazolium dimethylphosphate	IoLiTec, Germany	98%
3. [emim] Cl	1-ethyl-3-methylimidazolium chloride	IoLiTec, Germany	98%
4. [mDBN][DMP]	1-methyl-1,5-diazabicyclo[4.3.0]non-5-enium dimethylphosphate	Helsinki University	-
5. [DBNH][OAc]	1,5-diazabicyclo[4.3.0]non-5-enium acetate	Helsinki/Aalto University	-
6. [DBNH][EtCOO]	1,5-diazabicyclo[4.3.0]non-5-enium propionate	Helsinki/Aalto University	-
7. NMMO	*N*-methyl-morpholine *N*-oxide	Sigma, Germany	97 %

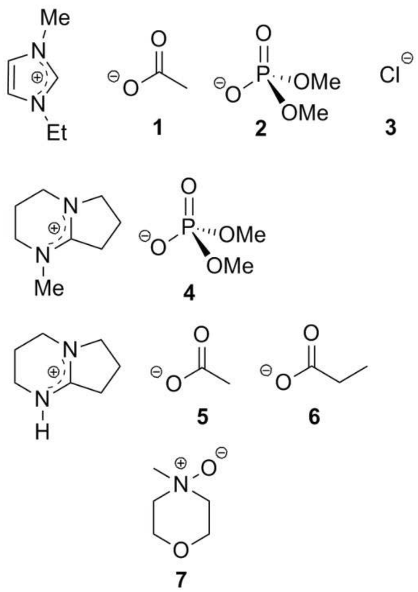

Figure 9. Structures of the used solvents.

4.2 Ioncell-P(ulp) experimental set up

The IONCELL-P process is a simple method, where the pulp hemicelluloses are directly dissolved into a mixture of ionic liquid and water at a moderate temperature of 60 °C. The dissolution is followed by filtration, which removes the liquefied hemicelluloses, and is continued by washing of the fractions. A theoretical flow scheme is presented in **Figure 10**. The residual ionic liquid is removed from the extracted fractions with hot water and the hemicelluloses are collected from the liquid phase via centrifugation after reprecipitation with water. With hemicellulose fraction from eucalyptus, 1/3 of the centrifuge bottle was filled with isopropanol and 2/3 with the pine extract, in order to enhance the pelleting of the sugars. Better pelleting is achieved as isopropanol decreases the density and dielectric constant of the liquid. Isopropanol was not needed with the birch xylan in order to collect the hemicelluloses quantitatively.

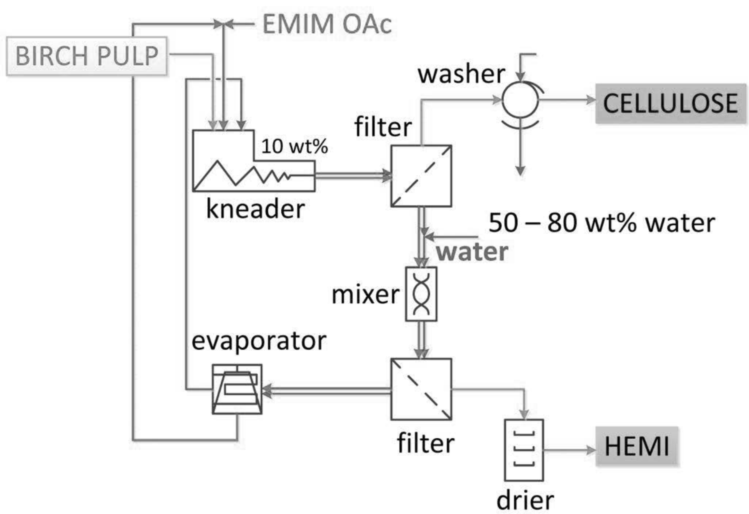

Figure 10. A theoretical flow scheme of the IONCELL-P process. The recycling of the solvent is not in use in the laboratory experiments. Reprinted with permission. (Froschauer et al. 2013)

The instructions to perform IONCELL-P extraction are presented below.

<u>IONCELL-P extraction procedure:</u>

1. Blend pulp with an ionic liquid-water mixture.
2. Heat for 3h in 60 °C. Mixing is needed with larger scale experiments.
3. Filtrate the hemicelluloses containing liquid fraction from the pulp.
4. Wash the pulp with ionic liquid-water mixture and filtrate again.
5. Wash the pulp with hot water two times
6. Dry the pulp.
7. Combine the ionic liquid-water mixtures, containing hemicelluloses with cellulose washing water.
8. Centrifuge 15 min 4500 rpm.
9. Decant the supernatant and wash the hemicelluloses containing pellet two times with hot water. Enhance pelleting with isopropanol if needed.
10. Freeze dry the hemicelluloses.

4.3 Equipment (Scaling up)

The IONCELL-P process has been used in different scales, from 1 g of pulp to 6, 50, and 400 g of pulp in different projects. The 400 g test was performed at the

Technical Research Centre of Finland LTD (VTT) and the performed test resulted in a collaboration paper, (Laine et al. 2016), which is not a part of this thesis, but is partly presented here, as it provides essential information about the up-scaling of the process.

4.3.1 Devices used for the heating step

The IONCELL-P process proved to be highly flexible for different equipment needed for different scales. As the heating step demands nothing more than a hermetic environment at a moderate temperature of 60 °C, almost any kind of reactor is suitable for the heating period. In the 1 g scale, even continuous mixing was not necessary if the pulp was blended into the solvent thoroughly before heating. Continuous mixing becomes more important with larger amounts of pulp, as it is impossible to insure that the pulp is properly immerged into the solvent if mixed only shortly by hand. The heating period in the 1 g scale was performed in falcon tubes in a water bath, while a glass reactor, used for a larger scale (6 g in this thesis work) is presented in **Figure 11** (left). The steady mixing and adjustable volume of the glass reactor provided optimal conditions for the hemicellulose solvation step. The reactor volume could be adjusted by a tightly fitted lid that could be pushed deeper into the reaction vessel, when small volume experiments were performed. Adjustable reactor volume limits the water evaporation and condensation on the lid. A prototype model for the glass reactor is presented in **Figure 11** (right). This so-called bottle reactor was submerged into a water bath and mixing was conducted through a sealed hole in the lid by a manually operated mixing rod. The 50 g studies are not part of this thesis, but in these experiments the heating was performed in an oil heated kneader, which was used for the experiments in Paper I. The problem with this reactor was the large head space and that the reactor was not hermetic. Water of the solvent system was condensed on the reactor lid and some of the water was evaporated away from unsealed, glass covered peek holes on the lid. For these reasons, in this reactor it was impossible to maintain precisely the water content of the solvent system and the optimum water content of [emim][OAc] and NMMO changed after the new equipment was set up.

Figure 11. (Left) The glass reactor. A= electric motor, B= mixing rod, C= the inner vessel, D= the gas phase limiting, adjustable lid, E= hot water inlet of the heating jacket. (Right) F = mixing rod, G = seal.

4.3.2 Filtration equipment

The filtration of the dissolved hemicelluloses after the heating stage was performed in the 1 g test scale with 25 ml or in 50 ml syringes, containing Supelco polyethylene frits. Sufficient pressure was maintained with a manually operated screw press (custom made), which is presented in **Figure 12** (right). On a scale from 5 g to 50 g of pulp, a manually operated (custom made) hydraulic press was used (**Figure 12** left). The applied filter material was a metal mesh (GKD, Germany), with a pore size of 30 µm. The filtration pressure was varied from 30 to 40 bars with the hydraulic press. With both devices, the filtration continued as long as a liquid phase could be extracted. The pressure was released when there was more than 10 seconds between each drop of extract. There were differences in the residual solvent content of the filter cakes as some of the ionic liquids had the tendency to swell the pulp, retaining more liquid within the cellulose fraction. This means that there is no standard procedure of how dry the filter cake should be pressed. Washing carry over was minimized by washing the pulp from the remaining dissolved xylan with an ionic liquid-water mixture and filtrating once again before water washing. The 400 g test, performed by VTT, was filtered in a filter bag with a pore size of 100 µm. The filter bag was applied with an automatic hydraulic press. The pore size of the filter bag was slightly too wide for a selective filtration, leading to increased amount of cellulose in the liquid fraction.

Figure 12. (Left) Hydraulic press for filtrating from 5 g to 50 g scale experiments. A= piston lifting springs, B= hydraulic piston, C= heating jacket, D= Cylinder holders for lifting piston. (Right) Filtration system for experiments performed in 1 g scale. E= screw press, F= frit containing syringe, G= the filtrate collecting flask.

4.4 Testing different reaction conditions (Paper I, II, III and IV)

Different solvents, their optimal water contents, reaction times and temperatures have been tested through this thesis study. The primary objective in testing different ionic liquid-water mixtures, was to measure their effectiveness in the IONCELL-P process and find a correlation to their Kamlet-Taft β-values. As the research evolved, additional solvent properties were investigated. Viscosity of the liquid phase as a function of increasing xylan content, pH, influence of high pulp consistencies, and the effect of the solvent molar mass to the liquid to pulp ratio were studied. In addition, CCE trials were performed in-house and compared to the IONCELL-P process in the Paper II.

All the extraction conditions for all the pulps and solvents are listed below. **Table 5** contains the experiments performed on the birch pulp, **Table 6** on pine and **Table 7** on eucalyptus pulp including the CCE tests.

Table 5. Birch pulp extraction conditions (Paper III and IV)

Birch pulp	Co-Solv	CoSolv/	mol	mol	Pulp	Pulp	Mix/	T	t
Solvent	wt%	mol/mol	χH2O	χIL	wt%	Odg		°C	h
NMMO	22.5	1.89	0.65	0.35	5	5	G/ F	90	3
NMMO	23.5	2.00	0.67	0.33	5	5	G/ F	90	3
NMMO	24.5	2.11	0.68	0.32	5	5	G/ F	90	3
NMMO	25.5	2.23	0.69	0.31	5	5	G/ F	90	3
NMMO	28.0	2.53	0.72	0.28	5	5	G/ F	90	3
[emim][DMP]	7.1	1.00	0.50	0.50	4	1	T/S	60	3
[emim][DMP]	10.0	1.46	0.59	0.41	4	1	T/S	60	3
[emim][DMP]	13.2	1.99	0.67	0.33	4	1	T/S	60	3
[emim][DMP]	6.5	0.91	0.48	0.52	4	1	T/S	60	3
[emim][DMP]	7.1	1.00	0.50	0.50	4	1	T/S	60	3
[emim][DMP]	18.5	2.97	0.75	0.25	4	1	T/S	60	3
[mDBN][DMP]	25.3	4.99	0.83	0.17	10	1	T/S	60	3
[mDBN][DMP]	28.9	5.99	0.86	0.14	10	1	T/S	60	3
[mDBN][DMP]	15.5	2.70	0.73	0.27	5	1	T/S	60	3
[mDBN][DMP]	16.9	2.99	0.75	0.25	5	1	T/S	60	3
[mDBN][DMP]	15.0	2.60	0.72	0.28	5	1	T/S	60	3
[mDBN][DMP]	15.3	2.66	0.73	0.27	5	1	T/S	60	3
[DBNH][OAc]	16.3	2.00	0.67	0.33	10	1	T/S	60	3
[DBNH][OAc]	22.6	3.00	0.75	0.25	10	1	T/S	60	3
[DBNH][OAc]	28.0	4.00	0.80	0.20	10	1	T/S	60	3
[DBNH][OAc]	16.3	2.00	0.67	0.33	4	1	T/S	60	3
[DBNH][OAc]	15.0	1.81	0.64	0.36	5	1	T/S	60	3
[DBNH][OAc]	16.3	2.00	0.67	0.33	5	1	T/S	60	3
[DBNH][EtCOO]	15.3	2.00	0.67	0.33	10	1	T/S	60	3
[DBNH][EtCOO]	21.3	3.00	0.75	0.25	10	1	T/S	60	3
[DBNH][EtCOO]	26.5	4.00	0.80	0.20	10	1	T/S	60	3
[DBNH][EtCOO]	31.1	4.99	0.83	0.17	10	1	T/S	60	3
[DBNH][EtCOO]	14.2	1.83	0.65	0.35	5	1	T/S	60	3
[DBNH][EtCOO]	15.5	2.03	0.67	0.33	5	1	T/S	60	3
[emim][OAc]	15.0	1.67	0.63	0.37	5	5	B/ F	60	3
[emim][OAc]	16.1	1.81	0.64	0.36	5	5	B/ F	60	3
[emim][OAc]	17.0	1.93	0.66	0.34	5	5	B/ F	60	3
[emim][OAc]	20.0	2.36	0.70	0.30	5	5	B/F	60	3
[emim][OAc]	25.0	3.15	0.76	0.24	5	5	B/ F	60	3
[emim][OAc]	14.0	1.54	0.61	0.39	5	1	T/S	60	3
[emim][OAc]	15.0	1.67	0.63	0.37	5	1	T/S	60	3
[emim][OAc]	16.0	1.80	0.64	0.36	5	1	T/S	60	3
[emim][OAc]	30.0	4.05	0.80	0.20	3	1	T/S	60	3
[emim][OAc]	25.0	3.15	0.76	0.24	3	1	T/S	60	3
[emim][OAc]	20.0	2.36	0.70	0.30	3	1	T/S	60	3
[emim][OAc]	15.0	1.67	0.63	0.37	3	1	T/S	60	3

Birch pulp	Co-Solv	CoSolv/ Solv	mol fractio	mol fractio	Pulp cons	Pulp	Mix/ Sep	T	t
Solvent	wt%	mol/mol	χH2O	χIL	wt%	Odg		°C	h
[emim]Cl	20.0	2.03	0.67	0.33	5	1	T/S	60	3
[emim]Cl	23.5	2.50	0.71	0.29	5	1	T/S	60	3
[emim]Cl	27.0	3.01	0.75	0.25	5	1	T/S	60	3
[emim]Cl	33.0	4.01	0.80	0.20	5	1	T/S	60	3
[emim]Cl	11.3	1.04	0.51	0.49	5	1	T/S	60	3
[emim]Cl	6.3	0.55	0.35	0.65	5	1	T/S	60	3
[emim]Cl	6.0	0.52	0.34	0.66	5	1	T/S	60	3
[emim]Cl	18.0	1.79	0.64	0.36	5	1	T/S	60	3

F = press filter, G = glass reactor, B = bottle reactor, T/S= heating performed in Falcon tube and filtration in syringe.

Table 6. Pine pulp extraction conditions. (Paper III)

Pine pulp	Viscosity	Co-Solv	CoSolv/ Solv	mol fractio	mol fractio	Pulp cons	pulp	Mix / Sep	T	t
Solvent	ml/g	wt%	mol/mol	χH2O	χIL	wt%	Odg		°C	h
[emim][DMP]	450	6.3	0.881	0.468	0.532	5	1	T/S	60	3
[emim][DMP]	450	6.8	0.956	0.489	0.511	5	1	T/S	60	3
[emim][DMP]	450	7.3	1.032	0.508	0.492	5	1	T/S	60	3
[emim][DMP]	450	7.8	1.108	0.526	0.474	5	1	T/S	60	3
[emim][DMP]	450	7	0.986	0.497	0.503	10	5	G/F	60	4
[emim][DMP]	660	6.3	0.881	0.468	0.532	5	1	T/S	60	3
[emim][DMP]	660	6.8	0.956	0.489	0.511	5	1	T/S	60	3
[emim][DMP]	660	7.3	1.032	0.508	0.492	5	1	T/S	60	3
[emim][DMP]	660	7.8	1.108	0.526	0.474	5	1	T/S	60	3
[emim][DMP]	660	6.8	0.956	0.489	0.511	5	6	G/F	60	3
[emim][DMP]	893	6.8	0.956	0.489	0.511	5	1	T/S	60	3
[emim][DMP]	893	6.8	0.956	0.489	0.511	5	1	T/S	60	4
[emim][DMP]	893	6.5	0.911	0.477	0.523	5	1	T/S	60	3
[emim][DMP]	893	6.8	0.956	0.489	0.511	5	1	T/S	60	3
[emim][OAc]	893	15	1.667	0.625	0.375	5	1	T/S	60	3
[emim][OAc]	893	16	1.799	0.643	0.357	5	1	T/S	60	3
[emim][OAc]	893	17	1.935	0.659	0.341	5	1	T/S	60	3
[emim][OAc]	893	13	1.411	0.585	0.415	5	1	T/S	60	3
[emim][OAc]	893	14	1.538	0.606	0.394	5	1	T/S	60	3
[emim][OAc]	893	15	1.667	0.625	0.375	5	5	G/F	60	3
[emim][OAc]	893	15	1.667	0.625	0.375	5	5	G/F	60	3
[emim][OAc]	893	15	1.667	0.625	0.375	5	1	T/S	60	3
[emim][OAc]	893	15	1.667	0.625	0.375	5	1	T/S	60	3

F = press filter, G = glass reactor, B = bottle reactor, T/S= heating performed in Falcon tube and filtration in syringe.

Table 7. Eucalyptus extraction conditions. (Paper II and II)

Eucalyptus	Co-Solv	CoSolv/ Solv	mol fractio	mol fractio	Pulp cons	pulp	Mix / Sep	T	t
Solvent	wt%	mol/mol	χH2O	χIL	wt%	Odg		°C	h
[emim][DMP]	6.5	0.9	0.477	0.523	5	1	T/S	60	3
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	60	3
[emim][DMP]	9	1.3	0.564	0.436	5	1	T/S	60	3
[emim][DMP]	6.5	0.9	0.477	0.523	5	1	T/S	60	3
[emim][DMP]	6.5	0.9	0.477	0.523	5	1	T/S	60	3
[emim][DMP]	6.5	0.9	0.477	0.523	5	1	T/S	80	3
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	80	3
[emim][DMP]	9	1.3	0.564	0.436	5	1	T/S	80	3
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	80	3
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	80	3
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	60	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	60	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	60	4
[emim][DMP]	6.5	0.9	0.477	0.523	5	1	T/S	60	4
[emim][DMP]	6.5	0.9	0.477	0.523	5	1	T/S	60	4
[emim][DMP]	6.5	0.9	0.477	0.523	5	1	T/S	60	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	60	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	60	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	60	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	80	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	80	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	80	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	80	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	80	4
[emim][DMP]	7.1	1.0	0.500	0.500	5	1	T/S	80	4
[emim][DMP]	6.5	0.9	0.477	0.523	5	1	T/S	80	4
[emim][DMP]	6.5	0.9	0.477	0.523	5	1	T/S	80	4
***[emim][DMP]**	6.5	0.9	0.477	0.523	5	5	G/F	60	4
NAOH	12				5	5		RT	1
NAOH	10				5	5		RT	1
NAOH	12				5	5		30	1
NAOH	10				5	5		30	1

* Repeated five times. F = press filter, G = glass reactor, B = bottle reactor, T/S= heating performed in Falcon tube and filtration in syringe.

4.4.1 Kamlet-Taft parameters (Paper IV)

The determination of the Kamlet-Taft parameters, α and β, was conducted according to Hauru et al.(Hauru et al. 2012) The α-values of [emim][DMP],

[emim]Cl, and [DBNH][OAc] were measured by applying 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio) phenolate (WB) (a gift from Professor Omar El Seoud from University of Saõ Paulo) colorimetric probe instead of Reichardt's dye (RD) (Sigma Aldrich, Germany) which could not tolerate these solvents. The correlation between RD and WB was calculated, such as in the study of Tada et al.(Tada et al. 2000) N,N-diethyl-4-nitroaniline (DENA) (Fluorochem, UK) and 4-nitroaniline (NA) (Sigma Aldrich, Germany) were used to determine the β-value of the mixtures. 7.5 mg of RD, and 0.3 mg of Na and DENA were dissolved in acetone, and pipetted into Eppendorf tubes. The acetone was removed via evaporation. Subsequently, 500 µl of solvent mixture was added and mixed with the dye and kept at 100 °C for five minutes, in which this time the dye dissolved. The absorption spectrums of the probes were measured at 60 °C (90 °C for NMMO) by means of a Varian UV-VIS spectrophotometer using a quarts-cuvette (0.1 cm x 1 cm). The parameters, α and β, were calculated according to Doherty et al. from the wavelength that gave the numerical maximum absorption.(Doherty et al. 2010)

4.4.2 Shear viscosity (Paper IV)

The shear viscosity of the solvent mixtures were studied in the optimal water content for xylan removal, as a function of increasing xylan concentration, The xylan model compound was isolated from eucalyptus Kraft pulp by a cold caustic extraction. The preparation of the cold caustic extracted xylan was described by Froschauer et al.(Froschauer et al. 2013) The xylan was solvated for 3h at 60 °C in ionic liquid mixtures and at 90 °C in NMMO mixtures. The shear viscosity measurements were then performed with an Anton Paar MCR 300-device with a plate and plate geometry (25mm diameter, 1mm gap). Measurements were taken from a steady shear test over a velocity shear rate range of 0.1/s–100/s, and the zero-shear viscosity was calculated as an average of the Newtonian plateau.

4.5 Direct comparison of various solvent systems to study a common dissolution behaviour (Paper IV)

In order to identify a general dissolution behavior valid for all the tested solvents, a second test series was performed on birch pulp. The same solvents, NMMO, [emim][OAc], [emim][DMP], [emim]Cl, [DBNH][OAc], [DBNH][EtCOO] and [mDBN][DMP] were applied. The pulp consistency was adjusted to 1 g of pulp per 0.152 mol of the solvent system including the water. The 1 g/0.152 mol consistency was chosen based on a study by Stepan et al. where it was shown that the efficiency of [DBNH][OAc], which is the most challenging of the tested ILs in the IONCELL-P process, could not be further improved by decreasing the pulp consistency (Stepan et al. 2016). This test series did not aim for optimization of the extraction conditions but to compare the tested ionic liquids while taking their different molecular weights into account.

According to our hypothesis, the results were to be comparable to Kamlet-Taft β-value of the solvent systems. Also the pH of the solvent mixtures were investigated in order to identify the extraction influencing features.

In this test series, the process was performed in the 1 g scale in Falcon tubes and syringes, as described earlier. The dissolution temperature for all solvents was kept at 60 °C, which, however, limited the use of NMMO at the optimum water content, due to the high melting point of NMMO. Detailed information of the tested solvent mixtures is listed in **Table 8**.

Table 8. Solvent properties of the second test series on birch pulp.

Birch pulp	**CoSolv/Solv**	**mol fraction**	**mol fraction**	**Pulp cons**
Solvent	mol/mol	χ_{H2O}	χ_{IL}	wt%
NMMO	2.8	0.736	0.264	3.941
NMMO	2.2	0.684	0.316	4.223
NMMO	2.0	0.666	0.334	4.307
NMMO	2.2	0.684	0.316	4.223
NMMO	2.0	0.666	0.334	4.307
[mDBN]DMP	5.0	0.833	0.167	1.858
[mDBN]DMP	3.7	0.786	0.214	1.989
[mDBN]DMP	3.0	0.751	0.249	2.064
[DBNH][OAc]	3.0	0.750	0.250	2.756
[DBNH][OAc]	2.6	0.720	0.280	2.849
[DBNH][OAc]	2.3	0.693	0.307	2.920
[DBNH][OAc]	2.00	0.667	0.333	2.981
[DBNH][OAc]	2.3	0.693	0.307	2.920
[DBNH][EtCOO]	4.0	0.799	0.201	2.433
[DBNH][EtCOO]	2.8	0.734	0.266	2.648
[DBNH][EtCOO]	2.3	0.694	0.306	2.747
[DBNH][EtCOO]	1.8	0.647	0.353	2.840
[emim][OAc]	4.0	0.802	0.198	2.713
[emim][OAc]	3.1	0.759	0.241	2.907
[emim][OAc]	2.4	0.703	0.297	3.100
[emim][OAc]	1.7	0.625	0.375	3.294
[emim][OAc]	2.4	0.703	0.297	3.100
[emim]Cl	1.8	0.641	0.359	3.689
[emim]Cl	0.9	0.475	0.525	4.049
[emim]Cl	0.7	0.414	0.586	4.139
[emim]Cl	0.5	0.354	0.646	4.215
[emim]Cl	1.2	0.549	0.451	3.914
[emim]Cl	0.9	0.475	0.525	4.049
[emim][DMP]	3.1	0.755	0.245	2.263
[emim][DMP]	2.0	0.666	0.334	2.425
[emim][DMP]	1.5	0.593	0.407	2.514
[emim][DMP]	1.0	0.500	0.500	2.595
[emim][DMP]	2.0	0.666	0.334	2.425
[emim][DMP]	1.8	0.641	0.359	2.458
[emim][DMP]	1.5	0.593	0.407	2.514

4.6 The effect of the substrate properties

In order to study the factors that make a pulp a suitable substrate for the IONCELL-P process, different pulp species were tested and cellulose and hemicellulose degrading pre-treatments were examined.

4.6.1 Testing different wood species (Paper III)

Three different kinds of wood species were tested in the IONCELL-P process, birch, eucalyptus and pine. The bleached Kraft pulps differed in composition and content of hemicelluloses, and molar mass distributions of the polymers. The primary purpose of implementing pine pulp was to elucidate how softwood mannan would behave in the process, as paper pulp mannan is known to be more demanding to remove than xylan. Reasons for this are that mannan is more evenly distributed in the fiber structure, while the xylan is predominantly located on the fiber surface. After Kraft pulping, the remaining mannan is alkali stable and is left in a straight unbranched form, and typically has a higher DP than xylan. This type of mannan condensates densely on the cellulose fibers and is thus hard to remove.(Yllner 1957; Simonson 1971; Sjöholm et al. 1997; Jacobs and Dahlman 2001; Puls et al. 2006) Eucalyptus, as an important feedstock for different grade pulps, was studied as the second hardwood species after birch. Yields, carbohydrate compositions and molar mass distributions of the fractions were followed throughout the experiments.

4.6.2 Enzymatic pre-treatment of the pulp (Paper II and III)

Both, pulp hemicellulose and cellulose have been subjected to enzymatic degradation prior to the IONCELL-P process during the studies. The hemicellulase treatment was tested on hard (eucalyptus) and soft wood (pine) pulps to evaluate a possible enhancement of hemicellulose removal. The hypothesis was that short hemicelluloses would dissolve easier than intact ones. The endomannanase and endoxylanase dosages were 200 U g^{-1} and 500 U g^{-1} of pulp, respectively. The xylanase treatment conditions for eucalyptus pulp were as follows: 3 % pulp consistency, 120 min, 60 °C, pH 7 in a phosphate buffer (11 mM NaH_2PO_4, 9 mM Na_2HPO_4). The conditions for combined xylanase and mannanase treatment for pine pulp were a compromise between the optimal conditions of the enzymes: 3 % pulp consistency, 180 min, 70 °C, pH 5.5 in a phosphate buffer (19.6 mM NaH_2PO_4, 0.269 mM Na_2HPO_4). The treatment temperature was set between 60 and 85 °C, which were the optimal temperatures for the xylanase and mannanase respectively, and the pH was set according to the mannanase enzyme. As the conditions were not completely optimal for the enzymes, the reaction time was prolonged by one hour compared to the regular xylanase treatment to compensate for a possible loss in effectiveness. Sugar composition and molar mass distributions of the pulps were determined after the hemicellulase treatments in order to see, how effectively the hemicelluloses were degraded.

The purpose of the cellulose degrading endoglucanase pre-treatment was to adjust the intrinsic viscosity of the pulp to a level that is suitable for possible subsequent process steps, *e.g.* acetylation or textile fiber spinning. Especially for ionic liquid based textile fiber spinning this would be beneficial, as this could bypass the need of residual IL removal from the extracted pulp. Furthermore, this study aimed at identifying the effect of the endoglucanase treatment on the hemicellulose extraction efficiency. The hypothesis was that enzymatically opened pulp structure would yield the hemicelluloses more easily than pristine pulp. Respective experiments were performed using pine pulp (Paper III), in which the pulp viscosity was adjusted enzymatically from 893 to 660 and 450 ml g^{-1}. The endoglucanase dosages were optimized to 0.04 and 0.22 mg protein per gram of dry pulp, respectively. The enzymatic treatment was performed at VTT in 6% pulp consistency, 50 °C, 120 min and the initial pH was adjusted to 5 with sulfuric acid.

4.6.3 IONCELL-P extraction of unbleached pulp

In order to see, how unbleached pulp would behave in the IONCELL-P process, unbleached eucalyptus pulp was prepared in-house, as a substrate. Eucalyptus chips were delignified by Kraft pulping using the conditions listed in **Table 9**.

The pulp yield was 54 % of raw wood, with a kappa number of 21 and intrinsic viscosity of 950 ml/g. 50 g of this unbleached pulp was subjected to IONCELL-P extraction, using [DBNH][OAc] with 15 wt% of water. The heating period was performed in the oil heated kneader and filtration in the manually operated hydraulic press as described earlier. (Unpublished data)

Table 9. Cooking conditions of the eucalyptus chips.

Effective alkali charge	19 % on ODW
Sulfidity	32 % on ODW
Liquid to wood ratio	4:1
T	155 ˚C
H-factor	250

4.7 The properties of the extracted fractions

In order to assess the suitability of the IONCELL-P for various applications, the extracted fractions were characterized thoroughly. The gravimetrical yield, sugar composition, intrinsic viscosity, crystallinity, molar mass distribution, pore volume and reactivity of the cellulose fraction were investigated. Yield, sugar composition, and molar mass distribution of the extracted hemicellulose-rich fraction were studied likewise. The main purpose was to close the material balance and prove that there are no material losses in the process. Moreover, the quality of the fractions were examined in order to prove that there is no polymer degradation and that the dissolving pulp produced is highly reactive and thus suitable for acetylation and other cellulose OH-groups derivatizing processes.

4.7.1 Gravimetrical yield and pulp intrinsic viscosity

The gravimetrical yield of the extracted pulp was determined by the NERL/ TP-510-42618 standard. The dry matter content of the xylan fraction was determined by infrared scale.

Changes in the intrinsic viscosity of the pulp before and after the IONCELL-P process were investigated in Paper I, II and III. The intrinsic viscosity was measured according to the SCAN-CM 15:99-standard.

4.7.2 Sugar composition analysis

The carbohydrate compositions of both dissolved and solid fractions were analyzed according to standard NREL/TP-510-42618. In this method the dry sample material is acid-hydrolyzed to monosugars and analyzed by high performance anion exchange chromatography (HPAEC) connected to a pulsed amperometric detector (Dionex ICS-3000). The monosugar content is then converted to polymers (anhydrous sugars) and normalized to correspond to 100 % of analyzed material according to the Janson formula.(Janson 1970)

4.7.3 Molar mass distribution

The MMD of the respective fractions was determined by using gel permeation chromatography (GPC) as presented by Borrega et al. (Borrega et al. 2013) In this method the samples are subjected to a solvent-exchange sequence. First the samples are activated in water and then the water is replaced by acetone. After acetone removal the samples are activated in *N,N*-dimethylacetamide (DMAc). Finally, the samples are dissolved in a lithium chloride-DMAc solution and analyzed with a Dionex Ultimate 3000 system. Pullulan standards (343 Da – 708 kDa, Polymer Standard ServiceGmbH, Mainz, Germany, and 1 600 kDa, Fluka GmbH, Germany) were used to calibrate the system. The molar masses (MM) of the pullulan standards were converted to correspond to the molar masses of cellulose polymers ($MM_{cellulose} = q * MM_{pullulan}^{p}$), as proposed by Berggren et al. The coefficients q = 12.19 and p = 0.78 were found by the least-squares method, using the data published in their report. (Berggren et al. 2003; Borrega et al. 2013)

4.7.4 Cellulose crystallinity analysis

The share of cellulose II crystalline form in IONCELL-P extracted pulps was determined with wide angle x-ray scattering (WAXS) analysis. WAXS intensities were measured by using Cu Kα (k 1.54 Å) perpendicular transmission geometry. The equipment applied was a Seifer ID 3003 X-ray generator, 36 kV, 25 mA, a Montel multilayer monochromator, and a MAR345 image plate detector. Scherrer equation was used to calculate the crystal size from WAXS intensities. The crystallinity was calculated by fitting Gaussian functions on a 2θ range from 12° to 49°. The analyses were performed at Helsinki University by Paavo Penttilä and the method is described in detail by Penttilä et al. (Penttilä et al. 2013)

4.7.5 Pore volume of the purified pulp (Paper II)

In order to evaluate the accessibility and thus reactivity of the IONCELL-P extracted pulp, the pore volume was measured and compared to the original Kraft pulp and to commercial dissolving pulp. The fiber swelling was determined by the solute exclusion method, which determines the fiber saturation point (FSP). The FSP means the point in drying when only the water bound to the fiber walls is present. This water is inaccessible to a dextran probe with a Stokes diameter of 54 nm (T2000 by Pharmacia), because it is too large to penetrate the pores in the fiber wall. Thus, only the accessible water will dilute the dextran probe. The change in the probe concentration is detected optically.

The measurement was done by adding 0.8 g of dry pulp to 35 ml of 2 % dextran probe solution. The mixture was rotated for one hour, after which the solids were centrifuged and the dextran supernatant removed. The dextran concentration was determined by measuring optical rotation to 3 decimal points precision at 357 nm wavelength in a Rudolph Research polarimeter. The pore volume determined by the FSP was calculated by **Equation (1)**.

(1)
$$FSP = \frac{w_{dex} - w_{water}}{w_{pulp}} - \frac{w_{dex}}{w_{pulp}} * \frac{c_i}{c_f}$$

In Equation (1) w_{dex}, w_{water} and w_{pulp} stand for the masses of dextran solution, sample water and dry pulp, respectively, and c_i and c_f stand for initial and final dextran concentration of the solution. Microfibril swelling was determined similarly, but the used probe was 3.6 nm dextran (T6, Pharmacia). This considerably smaller probe could penetrate the pores of the cell wall, but not the fibrils, leaving the water in the fibrils inaccessible. The total accessible surface area (ASA), was calculated from the fiber and microfibril saturation points with **Equation (2)**.

(2)
$$ASA = \frac{FSP - V_{3.6}}{0.0116}$$

In **Equation (2)** the $V_{3.6}$ is the pore volume determined with a 3.6 nm diameter dextran and 0.0116 is a geometric constant based on the assumption of cylindrical pores with a diameter of 3.6 nm. The analyses were performed by the research group of Professor Thaddeus Maloney at Aalto University.

4.7.6 Acetylation

Acetylation is an efficient method to test the pulp reactivity as any chemical or physical defect, like hemicelluloses or compressed fibers, prevents the cellulose OH-groups from interacting with the chemicals and restrain the acetylation reaction. Unevenly acetylated pulp will result in hazy cellulose triacetate solutions and residual hemicelluloses lead to an increase in so-called yellowness. The IONCELL-P process extracted pulp was compared to commercial acetate grade pulp and cold caustic extracted pulp (all pulps derived from bleached eucalyptus Kraft pulp).

The cellulose triacetate production method was adopted from Solvay Rhodia, and was set up at the premises of Aalto University by Lidia Testova. In this method the pulp is chemically dried via solvent exchange in glacial acetic acid, followed by activation in a mixture of glacial acetic acid and sulfuric acid. The acetylation is initiated by adding acetic anhydride at 35 °C, while thoroughly mixing the suspension. The reaction progress is typically monitored via a simplified falling-ball viscosity, where the outflow time of the suspension from a standardized tube was measured. The method is described in more detail by Testova et al. (Testova et al.). The completed acetylation was stopped by adding a mixture of sodium acetate, acetic acid and water, preventing degradation of the cellulose. Air bubbles were removed from the cellulose acetate solution by vacuum and the yellowness and turbidity were measured immediately. The yellowness was measured by Shimadzu UV-2550 spectrometer according to **Equation (3)**. The haze was determined by the Turbiscan MA 2000.

$$Cy = \frac{10^{-abs\ 640\ nm} - 10^{-abs\ 440\ nm}}{10^{-abs\ 640\ nm}} \tag{3}$$

4.7.7 Measuring residual ionic liquid content from the extracted fractions

The purity of the extracted fractions increased considerably when the washing steps were performed at an elevated temperature. The improvement was reflected in the gravimetrical yields and over all mass balance. However, in order to determine the amount of possible ionic liquid residues, preliminary C-, H- and N- elemental analysis were conducted. The amount of ionic liquid was calculated from the nitrogen content and correlated to the sample weight. Two cellulose fractions and two hemicellulose fractions were analysed by Perkin Elmer CHNS/O 2400 series II system. The elemental analysis were performed at a core service at Aalto University. The IONCELL-P extractions were performed at standard conditions (60 °C, 3h) using the ionic liquids [emim][OAc] and [DBNH][OAc] with a water content of 15 % and 16.3 %, respectively. (Unpublished data.)

5. Results and discussion

5.1 The advances of the IONCELL-P process

The most significant advantages of the IONCELL-P process are reflected in the selectivity and effectiveness when compared to current methods in use (PHK and CCE). The selectivity refers to the ability to solely dissolve hemicelluloses in certain conditions, while cellulose remains undissolved. The effectiveness portrays how thoroughly the hemicelluloses can be removed under the selective conditions. The selectivity of the IONCELL-P influences the effectiveness profoundly, as the extraction efficiency diminishes, when the cellulose starts to dissolve. In general, the selected process conditions aim for a compromise between selectivity and effectiveness. Second key asset of the IONCELL-P process is the substantial decrease in yield losses and polymer degradation. CCE is very selective, but only towards xylan, and the yield losses increase with high effectiveness. The preservation of the yield of the IONCELL-P has been proven by the gravimetrical yields of the purified cellulose and dissolved hemicellulose fractions and supported by GPC analyses, (example given in **Figure 13**).

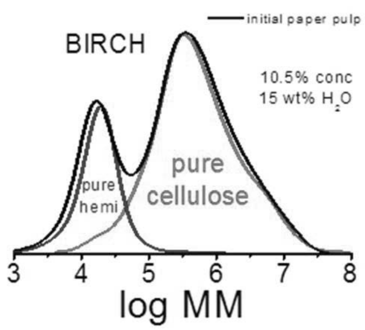

Figure 13. The GPC analysis of the initial birch pulp and the separated cellulose and hemicellulose fractions. Treatment conditions: 15 wt % water, 60°C, 3 h, pulp consistency, 10.5 wt %. (Adapted from Paper I)

Thirdly, the diluted ionic liquid leave the cellulose undisturbed in its cellulose I crystalline form, which limits pulp hornification during drying. The topic is discussed in more detail in Chapter 5.8. Due to these initial findings of Froschauer et al., the IONCELL-P process was studied thoroughly and the results cover the screening of the optimal process conditions, testing the applicability of different ionic liquids and pulp species in the process and investigation of the properties of the extracted fractions, resulting in the recognition of a common dissolution behaviour between the tested solvents.

5.2 Optimizing the general reaction conditions

In general, the reaction conditions for optimal hemicellulose removal were as follows: 60 °C, 3h, and 1:20 pulp to solvent ratio. The best kind of reactor for the heating was a vessel with a limited headspace, in order to prevent water evaporation and condensation on the reactor lid. Mixing during heating was necessary for larger scale experiments than 1 g of pulp. The 60 °C temperature was found to be the most efficient, as it allows for the solvent water to remain neatly in the mixture, while enough energy is introduced to the system, to enhance the hemicellulose solvation. Increasing the temperature did not improve hemicellulose removal, but lead easily to cellulose solvation. The reasons for this, was either evaporation of the water (increasing the effective ionic liquid content) leading to too harsh reaction conditions, and swelling of the crystalline structure of the cellulose. The 3h retention time was chosen through various tests during this thesis study. The heating time has been varied from 0.5 h to 6h (Paper I). While 3h was efficient to dissolve the hemicelluloses, increasing the time did not bring direct advantages. This implies that the solvation is not so much limited by reaction rate or mass transfer, but by the individual substrate and solvent properties. The optimum pulp consistency is dependent on the used solvent system and is discussed later in more detail. The 1:20 pulp to solvent mixture ratio seemed to provide enough bulk liquid in the laboratory scaled experimental set-up for all the tested solvents to allow for an efficient hemicellulose removal.

5.3 Relationship between the molar mass of the dissolved polymer and the water content of the solvent system

Birch pulp was treated with [emim][OAc]-water mixtures, containing decreasing amounts of water. GPC analysis showed that when the system contained a lot of excess water, only the shortest hemicellulose polymers were dissolved. Decreasing the water content of the solvent system lead gradually to solvation of longer polymer chains, until only the purified cellulose fraction was remaining. Ionic liquid which is diluted enough not to dissolve long chain polymers is still able to dissolve short polymers as they have higher entropic contribution than long ones. As the entropy gain is molar mass dependent the gradual increase in the dissolved polymer length could be visualised via GPC. The results are shown in **Figure 14** and are supported by the study of Stepan et al. (Stepan et al. 2016) The crystalline structure of cellulose seems to give some resistance towards the dissolution, as the low molar mass cellulose polymers remain intact, while same size hemicelluloses are dissolved. The recalcitrance of the cellulose crystal is strong due to both the hydrophobic stacking between cellulose polymer layers and the interlayer hydrogen bonding.(Oehme et al. 2015)

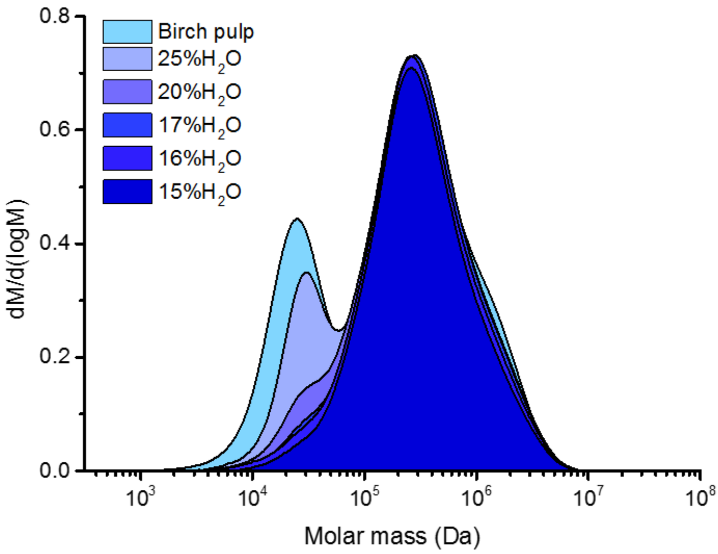

Figure 14. GPC results of birch pulp before and after extraction with [emim][OAc] with varying water content. Treatment conditions: 3h 60 °C, pulp consistency 5 wt % (Reprinted with permission from Paper IV)

5.4 Testing different ionic liquids.

In this thesis study, seven solvents were tested and all of them could selectively dissolve hemicelluloses, when mixed with water, but there were significant differences in their extraction efficiency and selectivity. The range of water content allowing for hemicellulose dissolution varied strongly between the solvents as well as the optimum water content for best xylan removal. In order to achieve the best hemicellulose removal efficiency, the water content needed to be as low as possible for maximum hemicellulose solubilization, but high enough not to dissolve cellulose. Even partly dissolved cellulose forms a highly viscose dope, which hampers the filtration step considerably, leading to ineffective hemicellulose removal. Through the optimization tests with different solvents, the xylan removal gradually increased with decreasing water molarity until the cellulose started to dissolve, leading to complications described above. **Figure 15** shows the water content range for selective hemicellulose dissolution for each of the tested solvents.

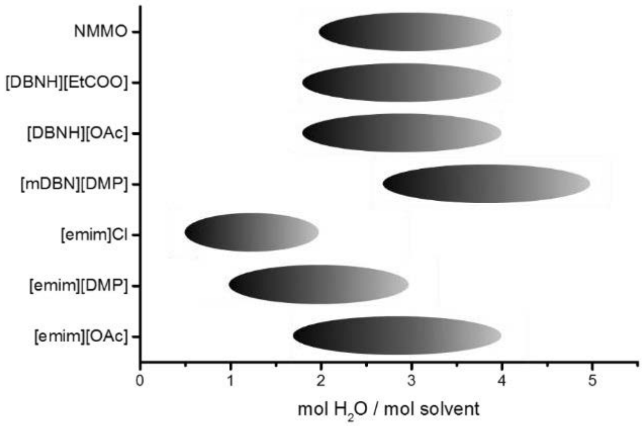

Figure 15. The hemicellulose dissolving water concentration areas for the tested solvents. (Reprinted with permission from Paper IV)

The residual xylan and dissolved cellulose amounts were followed through the optimization of different ionic liquids and the results are presented in **Figure 16**. The loss of the dissolution selectivity towards hemicelluloses already at too high water contents, limited the number of ionic liquids that could be tuned to produce high purity pulps.

Solvent properties, the amount of residual xylan and dissolved cellulose in optimum conditions for each tested solvent, are presented in **Table 10**. From the three different kinds of cations ([emim], [mDBN] and [DBNH]) that were tested, [emim] seems to be more favorable for selective hemicellulose dissolution. A possible explanation could be that the structure [emim]-cation is relatively small, when compared to the double ring structure of [mDBN] and [DBNH]. The large cation structure might be too invasive, leading to cellulose solvation and providing only a little room to tune the solvent properties by the addition of water. Amongst the tested anions [DMP] seems to be the best for the IONCELL-P process with both type of cations. This is in line with Rabideau's findings that the [DMP] is the weakest one to form hydrogen bonds, when compared to Cl and [OAc] anions. (Rabideau and Ismail 2015) This would suggest that the weaker the anion is, the easier it is to optimize the reaction conditions with water to influence only the hemicelluloses. This behavior is confirmed with the DBN based ionic liquids, where the [mDBN][DMP] resulted 3.56 wt % residual xylan, while the [DBNH][OAc] could only reach 6.56 % xylan content before cellulose started to dissolve.

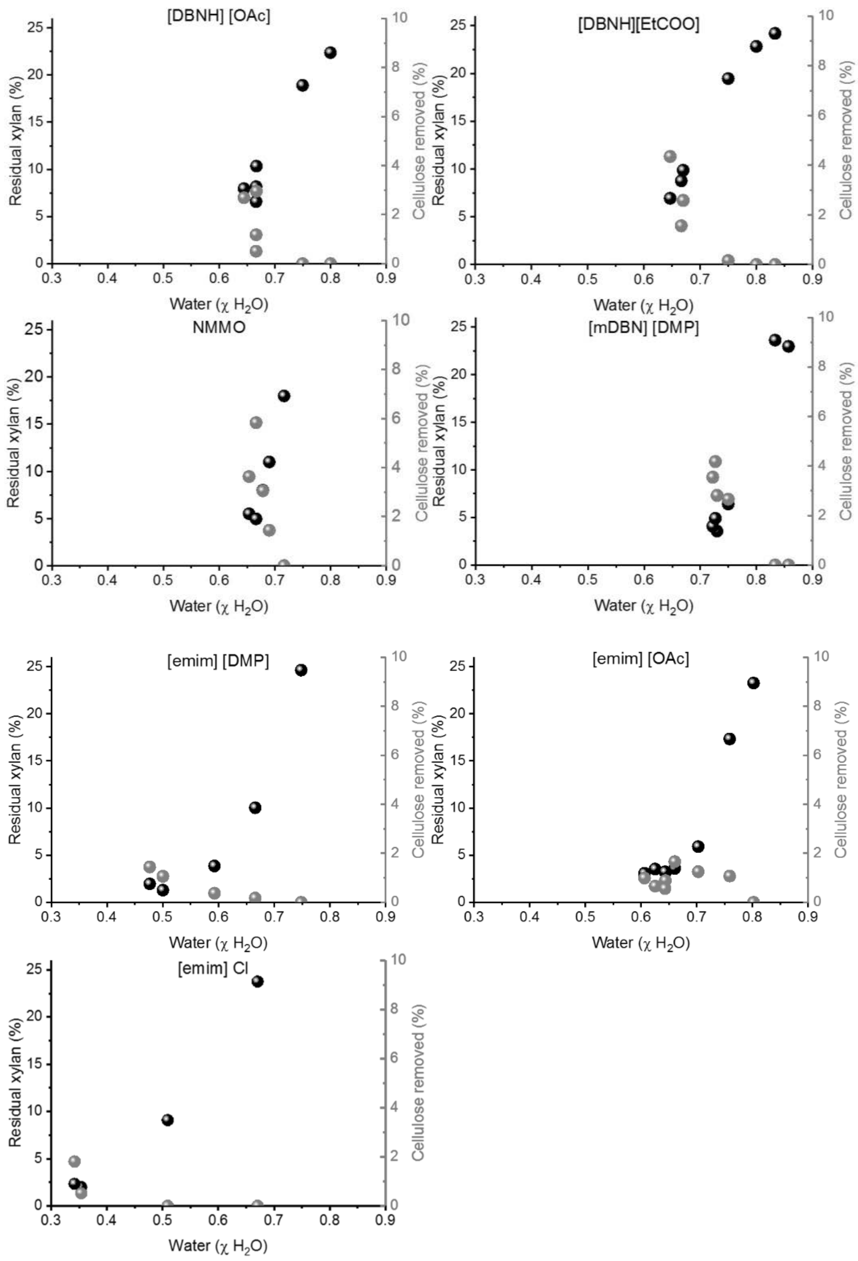

Figure 16. Residual xylan and the amount of dissolved cellulose through the optimization tests of each ionic liquid.

Table 10 shows that the optimum water content varied strongly between the solvents, and that the Kamlet-Taft parameters did not correlate unambiguously with the dissolution efficiency, even though the β-value has been connected in the literature to the ability to dissolve cellulose. Interestingly, when the β-value is divided with the water molar fraction ($\beta/\chi(H_2O)$-value) a common behavior is revealed. This trend is illustrated in **Figure 17** (B) and compared to the plain β-value in **Figure 17** (A).

Table 10. Optimized properties and extraction results of the tested solvents for bleached birch Kraft pulp, with original xylan content of 25.4 wt%. (Data from Paper IV)

Solvent	χH_2O	α	β	$\beta/\chi\ H_2O$	T °C	Residual xylan %	Dissolved cellulose %
[emim][OAc]	0.63	0.52	0.87	1.38	60	2.37	2.40
[emim][DMP]	0.50	0.53	0.97	1.94	60	1.28	1.44
[emim]Cl	0.35	0.47	0.65	1.86	60	1.99	1.35
[mDBN][DMP]	0.73	0.27	0.98	1.35	60	3.56	2.81
[DBNH][OAc]	0.65	0.48	0.85	1.26	60	6.56	1.18
[DBNH][EtCOO]	0.65	0.55	0.88	1.31	60	6.94	4.35
NMMO	0.67	0.32	0.76	1.13	90	4.95	5.83

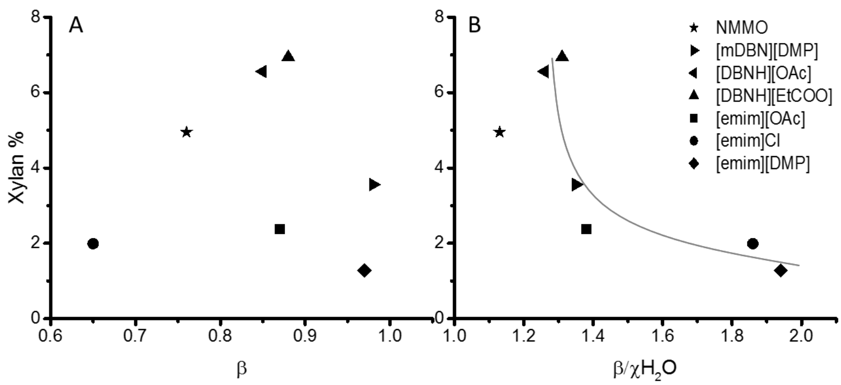

Figure 17. The residual xylan content in the optimal conditions correlated to Kamlet-Taft β-value (A) and $\beta/\chi H_2O$ (B).

This common behavior might result from the water shielding the anions and competing with the hemicellulose OH-groups for the hydrogen bonds. NMMO is not following this $\beta/\chi(H_2O)$-trend, which is most likely caused by the inevitably higher treatment temperature of 90 °C. At this temperature two factors might influence the hemicellulose removal: higher energy input and that the water is inclined to evaporate and not to stay neatly in the solvent mixture. This might lead to a gradual decrease in water content during the dissolution, which would affect the $\beta/\chi(H_2O)$-value.

In the formed trend, the fact that the experiments were done in 1:20 pulp to solvent mixture weight ratio is unaccounted for. The dissolution, however, is based on the relationship of the number of anions to accessible hemicellulose OH-groups. A new test series was then performed in which the pulp consistency was fixed as gram of pulp per 0.152 mol of solvent and the extraction temperature set to 60 °C. These results are discussed in the next chapter (5.4.1).

5.4.1 Common dissolution behavior between the tested ionic liquids (Paper IV)

As stated above, in this second test series the hemicellulose extraction was investigated with systems in which the pulp consistency was defined as g of pulp per 0.152 mol of solvent mixture and not as weight ratio. This approach compensated for the issue that the studied IL mixtures differed in molecular weight and water content, leading to different amounts of ions available, when the pulp consistency is considered as weight ratio. The xylan removal efficiency was once more compared to the Kamlet-Taft β-value, describing the solvent's ability to accept hydrogen bonds. As expected, the residual xylan content showed no correlation with the β-value (see **Figure 18 A**). However, when the β-values were divided with the solvent water molar fraction, the data was reorganized on a master curve and the different solvents depicted a common behavior (**Figure 18 B**).

According to our hypothesis, the β-value describes the solvent system's potential to accept hydrogen bonds, but the solvent mixture's water content affects the anion's ability to form H-bonds. Water decreases the overall power to form hydrogen bonds (the β-value) but also competes with the hemicellulose hydroxyl groups and accessible hydroxyl groups of the cellulose for the forming hydrogen bonds. Thus, this decrease in the ability to form hydrogen bonds with the pulp needs to be considered, leading to the $\beta/\chi(H_2O)$-value. [Emim]Cl is a prominent example, as it has the lowest β-value, but at the same time, it is one of the strongest and most selective hemicellulose solvents in the IONCELL-P process. When the β-value is corrected by dividing it with the water molar fraction, it turns out that the [emim]Cl has a similar $\beta/\chi(H_2O)$-value with [emim][DMP] at the optimum water content of the solvent system, and the ability to produce high purity pulp. A mathematical fit (created by Kaarlo Nieminen) describes the xylan removal efficiency as a function of $\beta/\chi(H_2O)$-value (See **Figure 18 B)** and **Equation (**4**)**). This would allow for the estimation of the theoretical optimum water content of a new ionic liquid.

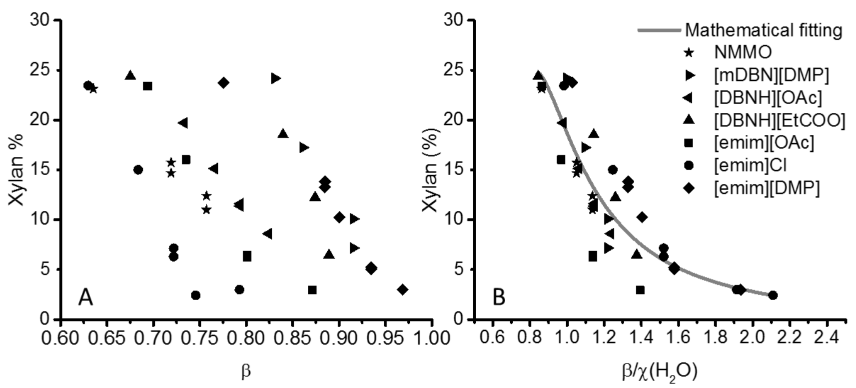

Figure 18. Residual xylan compared to β-value (A) and $\beta/\chi(H_2O)$. (Reprinted with permission from Paper IV)

(4) $$y = \frac{25.4\ \%\ \text{xylan}}{5.857(x-0.84)^{1.537}+1} \qquad R^2: 0.9477$$

However, this model has to be regarded as a rough estimation because the Kamlet-Taft parameters are influenced by impurities and possibly by preferential dissolution of the probe chromophore. This means that the probe might interact more intensively with one of the ions or with the water of the solvent mixture. Nonetheless, the values give a valid empirical approximation of the potential of the solvent mixtures. Furthermore, the availability of accessible OH-groups is not considered in this simple model. Pulps may differ in the number of accessible OH-groups due to differences in the hemicellulose content and crystallinity. Also, extractions at higher pulp consistency would induce more competition for the hydrogen bonds and could tilt the optimum water content to lower values. In these cases, the dissolution factor could be modified by adding the accessible OH-groups of the pulp to the divisor, leading to the term: $\beta/(\chi H2O+\chi OH_{accessible})$.

5.4.2 pH of the solvent systems (Paper IV)

As stated before, the optimal water content of the solvent system varied strongly between the ionic liquids. The $\beta/\chi(H_2O)$-value can describe the potential efficiency of xylan removal, but it does not explain why some ionic liquids can be optimized further, without losing their selectivity towards hemicelluloses. In order to understand the solvent selectivity, pH of the solvent systems were measured as a function of an increasing water content. The results are presented in **Figure 19** and the optimal water contents for the IONCELL-P process are marked with gray symbols.

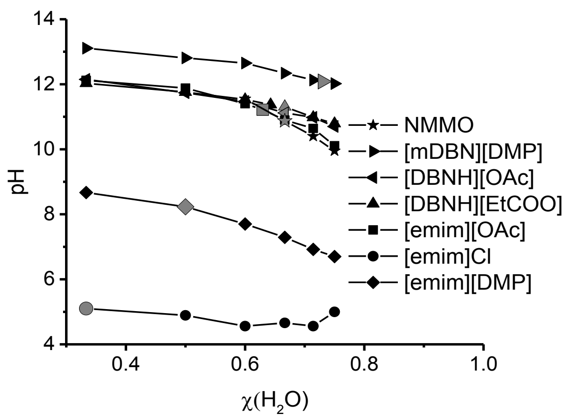

Figure 19. The pH of the ionic liquids with increasing water content. The optimal water contents for the IONCELL-P extraction are emphasized with gray markers. (Reprinted with permission from Paper IV.)

As seen in **Figure 19**, the pH decreases moderately, when the water content is increased. An interesting phenomenon is that the lower the pH, the less water seems to be needed for the optimal xylan removal conditions. This does not mean that the pH affects the hemicellulose solvation, as the pH at the optimum conditions varies from an acidic pH of 5 to nearly a pH of 13. Rather, this means that the high pH ionic liquid-water mixtures seem to be more inclined to swell and dissolve cellulose. This could explain why the high pH ionic liquids demand higher amounts of water in order to reduce the solvation capacity to affect only the hemicelluloses. The tendency of high pH to swell cellulose could also explain why [emim][OAc] dissolves more cellulose than [emim][DMP] or [emim]Cl, even though these three ILs share the same cation.

5.4.3 Viscosity measurements of the solvent systems

The zero shear viscosity of the optimal solvent mixtures are shown in **Figure 26** as a function of an increasing xylan content. Water in the solvent system reduces the viscosity considerably, facilitating the execution of certain process steps. The shear viscosities are plotted against gram of xylan per mol of solvent in **Figure 20 A)** and per gram of solvent in **Figure 20 B)**, which visualizes the effect of the molar mass of the solvent system. In addition, the samples in which the xylan was not fully dissolved even when the heating time was extended from 3h to 6h are plotted with gray symbols. These results support the observation that the viscosity is more dependent on the individual properties of the ionic liquid as the viscosity increases rather systematically throughout the solvent mixtures. It can be concluded that low viscosity is an advantage for agitation, pumping, and filtration, but it does not seem to affect directly the xylan dissolution, when a 3h heating period is applied. The effect of the ionic liquid molar mass in **Figure 20 B)** shows that the low MM ionic liquids carry more xylan in terms of weight ratio. An interesting finding was that the most efficient and selective solvent mixtures in the IONCELL-P process are the ones that could not dissolve the highest xylan concentrations fully, supporting the theory that weaker ionic liquids are easier to tune into selective hemicellulose solvents. [Emim][DMP] and [emim]Cl could fully dissolve only 5 g of xylan per mol of solvent and [emim][OAc] 10 g per mol of solvent, while the rest of the solvents could easily dissolve 20 g of xylan. This difference to the DBN based ILs is neither explained by the viscosity nor by the mass ratio of the xylan and the solvent mixture, as can be seen in **Figure 20**, where it is clearly shown that [DBN] based ionic liquids dissolve xylan easily even at higher mass ratios. The [DBN] based cations seem to promote strong interaction with the substrate and they dissolve cellulose unless excess amount of water is provided, which in turn weakens the ability of the anions to solvate the hemicelluloses. This balance within the alkaline ionic liquids leads either to unselective dissolution and/or to a higher residual hemicellulose content.

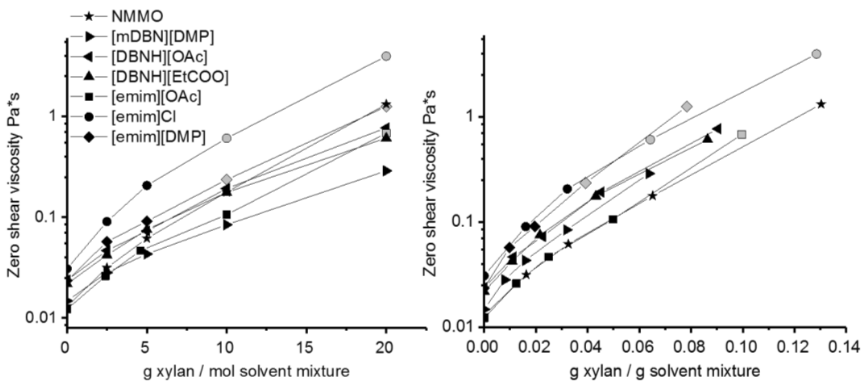

Figure 20. Zero shear viscosity measurements of the solvent systems with increasing xylan content. The solvent mixtures are at their optimal water contents, presented in **Table 10**. (Adapted from paper IV.)

5.4.4 Extraction efficiency at different pulp consistencies. (Paper IV)

The maximum pulp consistency in the IONCELL-P process is solvent dependent as demonstrated for [emim][OAc], [mDBN][DMP] and [DBNH][OAc] in **Figure 21 A)**. From the three tested ionic liquids, [emim][OAc] was superior when working at high pulp consistencies. [Emim][OAc] achieves an efficient xylan removal even at 20 % pulp consistency, whereas the performance of the other tested ionic liquids started to decrease already at 10 % pulp consistency. Several factors affect the ability to cope with high pulp loads. One is the molar mass of the solvent, demonstrated in **Figure 21 B)**, where the pulp consistencies are translated to mols of anions per g of pulp. The [mDBN][DMP] has the highest molar mass and water content in the solvent mixture, and thus the lowest anion-to-pulp molar ratio. When selecting the pulp consistency for a certain IL-water extraction system, the pulp loading needs to be low enough to ensure that there is enough solvent to interact with the hemicellulose OH-groups. Furthermore, the solvent system must facilitate a rapid transfer of the solubilized carbohydrates into its bulk. A good dispersion of the dissolved carbohydrates is a prerequisite for an effective filtration and washing of the extracted pulp, preventing washing-induced carry-over. The viscosity of the neat IL-water mixtures seems to be a minor factor, as [mDBN][DMP] has a very low viscosity, but its efficiency is strongly influenced by the pulp loading. A notable phenomenon is that the solvent needs to interact with more OH-groups at high pulp consistencies, which might decrease the optimal water content of the system.

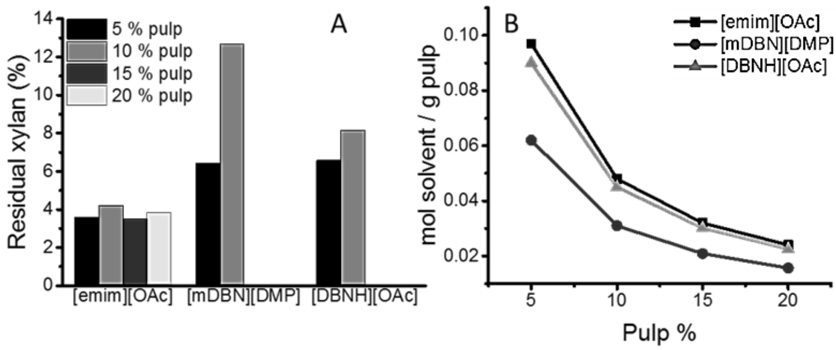

Figure 21. (A) The effect of pulp consistency to extraction efficiency. **(B)** The solvent mol ratio to pulp compared to pulp consistency. (Adapted from Paper IV)

5.5 Influence of the wood pulp properties on the extraction efficiency (Paper III)

Testing hardwood and softwood pulps in the IONCELL-P process revealed that the IONCELL-P process is not dependent on the pulp species, but the efficiency is conditional to the molar mass distribution of the pulp. Pine, birch and eucalyptus Kraft pulps were extracted with [emim][OAc] and [emim][DMP]. The results are presented in **Figure 22**. The optimal water content did not differ between the pulp species, but it was striking to see that [emim][OAc] was more effective and selective for pine pulp, while in the case of hard wood pulps, it was [emim][DMP]. The divergence of pine pulp is routed in the mannan extractability, as mannan was removed more effectively with [emim][OAc]. In summary, the pine pulp mannan content could be decreased from 7.1 wt % down to 2.9 wt %, while the xylan content was lowered from 8.1 wt % to 0.93 wt %. Birch and eucalyptus xylan contents were purified from 25.4 and 16.6 wt% to 1.3 and 2.3 wt % respectively.

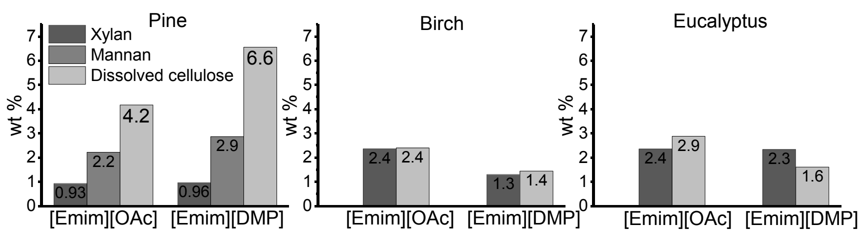

Figure 22. Extraction results of different pulp species. (Reprinted with permission from Paper III.)

Between the pulp species, there were differences in the selectivity of the IONCELL-P extraction. 4.2 wt % of the pine cellulose was dissolved (extracted with [emim][OAc]), while 1.4 and 1.6 wt % of birch and eucalyptus cellulose respectively, were dissolved with [emim][DMP]. 6.6% of pine cellulose was dissolved when extracted with [emim][DMP] and 2.4 % and 2.9 % of birch and eucalyptus cellulose when extracted with [emim][OAc]. These differences could be explained by the MMD of the pulps, which are presented in Figure 30(A) and discussed below.

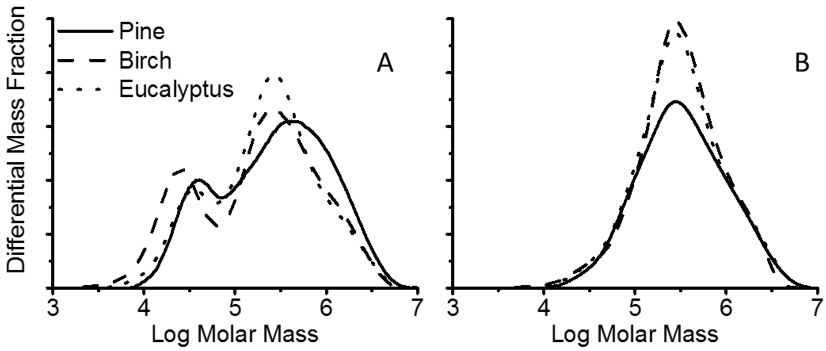

Figure 23. Molar mass distributions of the pulps (A) and purified cellulose fractions (B). (Reprinted with permission from Paper III.)

The MMD graphs in **Figure 23 A)** show clearly that the hemicellulose and cellulose fractions are overlapping the least in the birch pulp. This makes it easier to tune the solvent strength with water to affect only the short hemicelluloses. The dissolution of the polymers is based on the anion accepting hydrogen bonds from the polymer OH-groups. It is natural that short polymers are dissolved first, because they have less OH-groups to bind, the entropy gain is thermodynamically more favorable (Stepan et al. 2016), and in addition, their OH-groups are readily accessible, unlike within cellulose crystals. The crystalline structure of cellulose seems to give a bit of resistance against the solvation, as each of the purified cellulose fractions (**Figure 23 B)**) has a tail of short cellulose polymers overlapping with the chain length of the (extracted) hemicellulose fraction. Ergo, in the light of these MMD results, it is understandable why the birch pulp was the most suitable substrate for the IONCELL-P process, with its short and clearly separated xylan. Eucalyptus pulp which had rather long xylan polymers, but a narrow MMD of the cellulose fraction, was the second best substrate for the process. Even though the long hemicelluloses were challenging to dissolve, the extraction maintained the selectivity, due to the narrow MMD of the cellulose fraction, which does not overlap significantly with the xylan fraction. The pine pulp could not be purified as efficiently as the HW pulps because of the larger share of hemicelluloses with higher molar masses, which were overlapping severely with the relatively large fraction of low molar mass cellulose. The finding that overlapping MMDs of the hemicellulose and cellulose fractions hamper the IONCELL-P extraction, was supported by enzymatic studies on the substrate, which are discussed in the next chapter.

An additional difference between the substrates was observed in the further processing of the dissolved fraction. The precipitated birch pulp xylan could be easily isolated via centrifugation, while eucalyptus and pine pulp hemicelluloses needed isopropanol to enhance the pelleting during centrifugation when washed with water. The amount of isopropanol was 1:2 of the volume of the centrifuge bottle with eucalyptus and 2:3 with pine hemicelluloses. It has been reported that short and branched hemicelluloses demand higher alcohol concentrations for precipitation than long and linear polymers. Isopropanol decreases the dielectric constant, and the density of the washing water, enabling more efficient pelleting, as the polar OH-groups are rejected by the washing liquid.(Slusher 2000; Bian et al. 2010)

5.6 Enzymatic pre-treatments of the substrate (Paper II and III)

The hemicelluloses of the eucalyptus pulp were pre-treated with endoxylanase and pine pulp hemicelluloses with a combination of endoxylanase and endomannanase. The hemicellulase pre-treatment degrades the hemicellulosic polymers and amplifies the size difference between the cellulose and hemicellulose MMDs. The residual xylan of the IONCELL-P extracted eucalyptus pulp decreased from 2.4 wt % to 2.1 wt % and pine xylan and mannan contents from 0.93 and 2.2 wt % to 0.76% and 1.89 wt %, respectively. Though the changes seem to be small in absolute values, the relative decrease in the residual hemicellulose contents is remarkable; 13 % for eucalyptus and 15 % for pine pulp.

The importance of the separated molecular sizes of the cellulose and hemicellulose fractions was also demonstrated by cellulase pre-treatment of the pine pulp. The pine pulp viscosity was decreased from 893 ml/g to 660 and 450 ml/g, respectively, by endoglucanase treatment. The extraction selectivity declined nearly linearly with the decreasing viscosity, verifying that the selective solvation of hemicelluloses is strongly dependent on the molecule length. The amount of dissolved cellulose is plotted in **Figure 24** as a function of decreasing viscosity of the pine pulp.

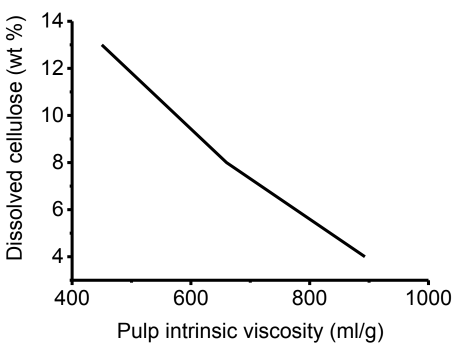

Figure 24. Share of dissolved cellulose as function of the enzymatically adjusted intrinsic pulp viscosity. Tests were performed with bleached pine pulp, treated with endomannanase prior to IONCELL-P extraction with [emim][OAc] containing 15 wt% H_2O.

The solvation of short chain cellulose molecules does not only deteriorate the process efficiency in terms of yield losses of the cellulose fraction, but it also prevents an efficient filtration. In addition, the partly dissolved cellulose molecules remain in the solid fraction, but turn into cellulose II crystalline form during washing. This is a disadvantage for the pulp reactivity, as cellulose II undergoes more severe hornification during drying than cellulose I. Unfortunately, this also limits the possibility to adjust the cellulose molar mass prior to the extraction, to suit the respective following processes. In some applications, for instance, the overall economy might benefit from a process scheme starting with the adjustment of the pulp viscosity. In theory the cellulose fraction could then be followed by extraction of the hemicelluloses and continue directly for example to (textile) fiber spinning, without washing and drying the pulp in between – if the selectivity of the process could be maintained.

5.7 Comparing the yield of the IONCELL-P process to CCE (Paper II)

Cold caustic extraction is becoming an increasingly important method as the demand for higher quality dissolving pulp, needed for speciality products, is rising. The CCE process was compared to IONCELL-P by effectiveness and yield. The residual xylan content of the treatment sequences are summarized in **Table 11** and the process yields in **Table 12**. From these results, it can be seen that the CCE produces 58 % higher residual xylan content than IONCELL-P. In addition, the residual hemicellulose content of the IONCELL-P treated pulp could be further decreased by viscosity adjusting acid treatment resulting in 2.2 wt % xylan, while the CCE pulp xylan content remained at 3.9 wt %.

Table 11. Residual xylan content of IONCELL-P extracted, and CCE eucalyptus pulps.

Stage	EK-I-A xylan (%)	Visco (ml/g)	EK-CCE-A Xylan (%)	Visco (ml/g)
EK-pulp	16.6	813	16.6	813
I	2.4	936		
CCE			3.8	
A	2.2	583	3.9	565

EK = eucalyptus Kraft, I = IONCELL-P extraction, CCE = cold caustic extraction, A = sulfuric acid treatment

The yield is a significant factor, when comparing the CCE process to IONCELL-P. The cellulose yield after CCE is 2.5 wt% lower than after IONCELL-P, even though the pulp purity is distinctly better after the IONCELL-P extraction. In addition, the hemicelluloses can be collected quantitatively through the IONCELL-P process, increasing the total carbohydrate yield of the process. The overall yield of the EK-I-A process was 97.7 %, whereas the yield of the EK-CCE-A process was only 79.5 %. The yield of the CCE process could be enhanced by collecting the dissolved hemicelluloses, which was not done in our laboratory set-up.

The overall yields in **Table 12** are calculated as follows:
Cellulose yield * Acid treatment yield + Collected hemicellulose yield.

Table 12. Overall yields of IONCELL-P extracted and CCE eucalyptus pulps.

Sequence	I_{Solid} (%)	$I_{Dissolved}$ (%)	CCE (%)	A (%)	Total cellulose (%)	Total carbohydrate (%)
EK-I-A	83.8	14.4		99.5	83.4	97.7
EK-CCE-A			81.3	97.8	79.5	79.5
EK = eucalyptus Kraft, I = IONCELL-P extraction, CCE = cold caustic extraction, A = sulfuric acid treatment						

The purity of the IONCELL-P extracted pulp could be enhanced by hemicellulase pre-treatment (described earlier). The final hemicellulose content could be reduced even to 1.7 wt%, but 5 % of the hemicelluloses were lost from the material balance due to the xylanase treatment.

5.8 Reactivity of the purified pulp

Reactivity of the IONCELL-P extracted pulp was examined by investigating the crystallinity and porosity, and by subjecting the pulp to acetylation.

5.8.1 Wide angle x-ray scattering (Paper I and II)

The wide angle x-ray scattering (WAXS) analysis was reported in Paper I for the original and IONCELL-P extracted ([emim][OAc], 15 wt% H_2O, 3h, 60 °C) birch Kraft pulps. The results of the analysis are presented in **Figure 25**, and show that the cellulose maintains fully its cellulose I crystalline form during the IONCELL-P process, as no peak at the diffraction angle of 12° typical for cellulose II is visible. The cellulose crystals seem to be slightly disoriented and the overall crystallinity decreased from 50% to 44% after the IONCELL-P process. This is most likely the result of the accessible OH-groups of the cellulose interacting with the solvent mixture, while the OH-groups inside the crystal will maintain the cellulose chain orientation.

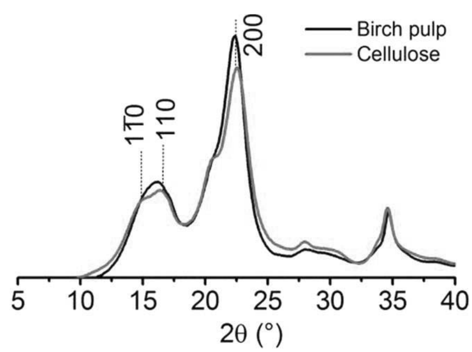

Figure 25. WAXS results of untreated and IONCELL-P extracted birch pulp. (Reprinted with permission from Paper I.)

In Paper II the WAXS analysis was performed for eucalyptus Kraft pulp that had undergone different treatment sequences (**Fig 27**). The treatment sequences and abbreviations for the sequences, presented in **Table 13**, were used in Paper II and will also be used in the following chapters. These treated pulps were compared to a commercial dissolving eucalyptus pulp. IONCELL-P extractions for eucalyptus pulp were performed at 60 °C for 4h, with [emim][DMP] containing 6.5 wt% of water, providing complementary information on another ionic liquid in addition to [emim][OAc]. The four hour retention time was chosen with these experiments according to initial optimization tests that indicated slightly better xylan removal within 4h than within 3h. However, following studies showed that the difference is only minor and may affect the selectivity and thus the 3 h extraction time was defined as the standard treatment time in the following studies.

Table 13. The treatment sequences and their abbreviations applied on Paper II. Abbreviations are referred to in the following figures.

Origin	Abbreviation	Sequence
Lab	EK-I-A	Eucalyptus Kraft pulp-Ionic liquid extraction-Sulfuric acid treatment
Lab	EK-X-I-A	Eucalyptus Kraft pulp-endoxylanase pre-treatment-Ionic liquid extraction- Sulfuric acid treatment
Lab	EK-CCE-A	Eucalyptus Kraft pulp-Cold caustic extraction -Sulfuric acid treatment
Commercial	EPHK-CCE-A	Reference pulp: Eucalyptus prehydrolysis Kraft-Cold caustic extraction-Sulfuric acid treatment.

The conditions for the treatments listed in **Table 13** were as follows: I: [emim][DMP] , 6.5% H_2O, 4h, 60°C. X: 500 EXU/g OD pulp, 2h, 60°C. CCE: 10% NaOH, 1h, RT.

The WAXS intensities of the purified and acid-treated eucalyptus pulps are compared to the EK and EPHK-CCE-A pulps in **Figure 26**. No clear cellulose II indicating peak at the diffraction angle of 12° was detected in any of the pulps. By contrast, the WAXS-pattern of the EK-CCE-A pulp had some changes in the crystal shape around the diffraction angle 15°.

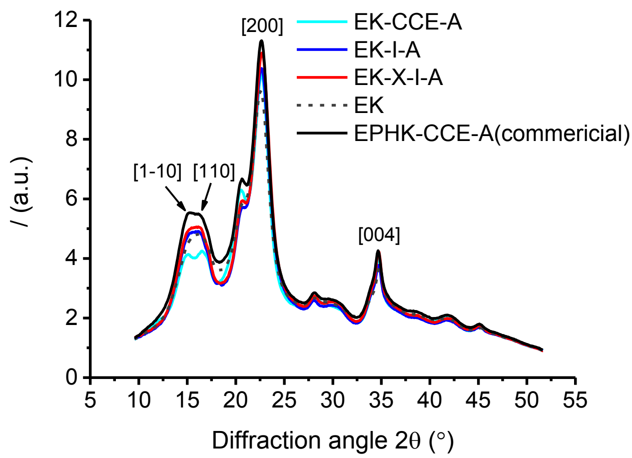

Figure 26. WAXS patterns of the eucalyptus pulps. (Reprinted with permission from Paper II.)

The data of the structural analysis of the WAXS results from the eucalyptus pulps are shown in **Table 14**. The EK-CCE-A pulp is the only one that shows changes in the crystal width in directions measured from 1–10 and 110, resulting in slightly larger crystals than the other pulps. This could indicate aggregation of crystals or organization of some disordered regions. The degree of crystallinity does not vary significantly between the pulps.

Table 14. Crystallinity results from the WAXS analysis of eucalyptus pulps. (Data from Paper II)

Pulp	Crystal width (nm)			Crystallinity
	(1-10)	(100)	(200)	(%)[a]
EK	-	-	4.9	45±3
EK-CCE-A	4.6	5.7	5.1	44±3
EK-I-A	4	4.6	4.7	46±3
EK-X-I-A	4	4.8	4.8	47±3
EPHK-CCE-A	4.8	4.2	5	44±3

5.8.2 Pore volume (Paper II)

In addition to the determination of the crystalline structure of the pulp, the quantification of the reactivity was pursued via measuring the pulp pore sizes and their changes upon various treatment sequences. The porosimetry measurements (**Table 15**) prove that the accessible surface area of IONCELL-P extracted and acid treated pulp is comparable to commercial dissolving pulp used as the reference. The IONCELL-P did not change the fiber swelling of the Kraft pulp, but the hemicellulose removal in fact opened the fiber structure. The rather low fiber swelling values of the original and extracted pulp are typical for dried pulp and an indication for hornification (typically, never-dried Kraft pulps have a FSP of 1.2–2.0 ml/g). (Newman and Hemmingson ; Maloney and Paulapuro 1999; Röder and Sixta 2004)

Table 15. Porosimetry measurement results of various pulps. (Data from Paper II)

Source	sample	Fibril swelling (ml/g)	Fiber swelling (ml/g)	Accessible surface area (m^2/g)
Lab	EK	0.48	0.51	2.1
Lab	EK-I-A	0.45	0.51	4.7
Commercial	EPHK-CCE-A	0.41	0.47	5.1

5.8.3 Acetylation (Paper II)

As mentioned in the literature review, pulps used for cellulose triacetate production have to reach the highest purity standards, as residual hemicelluloses limit the degree of substitution by blocking the cellulose OH-groups and competing for the acetylation reactions with the cellulose. This manifests as yellowing and haze of the resulting cellulose triacetate solutions. The treated pulps, presented in **Table 13**, were subjected to acetylation in order to receive a relevant quality feedback and to benchmark their quality against commercial acetate-grade pulp. The results presented in **Table 16** show that the resulting yellowness of cellulose acetate from IONCELL-P treated pulp (0.226) is comparable and even lower than the yellowness of the cellulose acetate from the commercial pulp (0.233). Transmittance, measuring the amount of haze, was also on a comparable level with that of a commercial pulp (see **Table 16**). In addition, the IONCELL-P purified pulp, that had undergone xylanase pre-treatment, resulted in remarkably low yellowness (0.174). A notable feature was that the IONCELL-P treated pulps underwent acetylation faster than the commercial pulp. Cold caustic extracted eucalyptus Kraft pulp did not perform well in acetylation due to the high residual xylan content, which resulted in high yellowness and haze of the cellulose triacetate solution.

Table 16. Acetylation results of the eucalyptus pulps. (Data from Paper II)

Sequence	Acetylation time (min)	Xylan (%)	Yellowness -	Transmittance (%)
EK-I-A	22	2.3	0.226	78.6
EK-X-I-A	27	1.6	0.174	81.1
EK-CCE-A	30	3.9	0.302	61.7
EPHK-CCE-A	68	1.8	0.233	83.2

5.9 Unpublished data

The preliminary studies of the extraction of unbleached pulp, and the amount of ionic liquid residues in the extracted fractions, have not been published elsewhere and are presented here as supplementary information. These results are based on single test points and no profound optimization of reaction or washing conditions was performed. Thus, these results should only be regarded as guidelines for future research.

5.9.1 IONCELL-P extraction of an unbleached *Eucalyptus grandis* pulp

Unbleached *Eucalyptus grandis* was extracted with [DBNH][OAc], containing 15 wt% of water, in 3 wt% pulp consistency. The heating was performed with continuous mixing for 3h in 60˚C. The water content was decreased from 16.3 wt % (optimal for bleached pulp) to 15 wt % as the polymers were longer and thus the water content could be decreased slightly, before the cellulose started to dissolve.

The extraction results are presented in **Figure 27**. The xylan content of the unbleached eucalyptus pulp was decreased from 12.93 % to 6.33 %. The final xylan content was identical to the extractions performed on commercial bleached birch Kraft pulp (6.56 %).

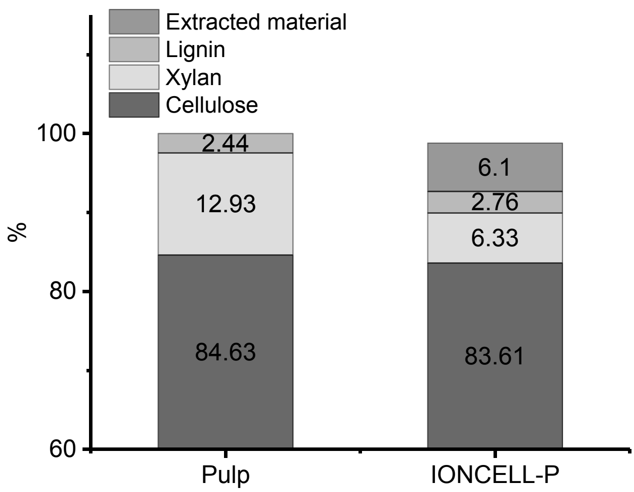

Figure 27. IONCELL-P extraction results of unbleached *Eucalyptus grandis* pulp. Treatment conditions: [DBNH][OAc] containing 15 wt% of water, 3h ,60∘C, 3 wt % pulp consistency.

The GPC results of the extraction experiments on unbleached eucalyptus pulp are presented in **Figure 28**. The molar mass distribution of the unbleached pulp fractions have a considerably larger molar mass than of the bleached Kraft pulp, but the hemicelluloses are well separated from the cellulose fraction in both pulps (no pronounced overlapping with the cellulose fraction). This means that also in this case the IONCELL-P extraction could be optimized to separate the hemicelluloses efficiently, even though the water content had to be decreased from 16.3 % to 15 % in the case of unbleached pulp.

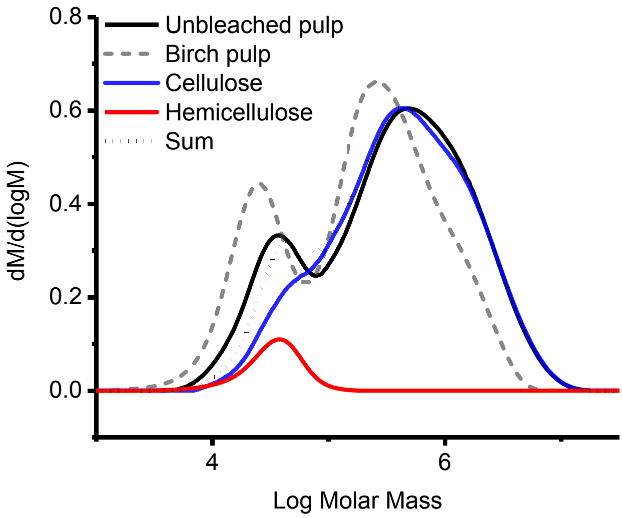

Figure 28. GPC results of the original pulp, IONCELL-P extracted fractions, sum of the fractions and commercial bleached birch Kraft pulp. Treatment conditions: [DBNH][OAc] containing 15 wt% of water, 3h ,60∘C, 3 wt % pulp con-sistency. Birch pulp refers to bleached Kraft pulp.

The IONCELL-P extraction of the unbleached eucalyptus pulp removed some lignin and chromophoric compounds from the pulp. According to the analysis, 10 % of the extracted material was lignin, which would correspond to a lignin removal of 0.61 % of the initial pulp. However, this could not be verified by the component analysis of the extracted cellulose (**Figure 27**). Nonetheless, the colour removal is visualized in **Figure 29**, where it can be seen, that the extracted material has a dark brown colour.

To conclude, the trial was a success, as the removal of hemicellulose was as successful as that of the bleached birch Kraft pulp. This gives support to the hypothesis, that if a more suitable ionic liquid would be applied, high purity dissolving pulp could be produced also from unbleached pulp.

Figure 29. The IONCELL-P extracted unbleached pulp (left) and freeze dried dissolved fraction (right). Treatment conditions: [DBNH][OAc] containing 15 wt% of water, 3h ,60∘C, 3 wt % pulp consistency.

5.9.2 Remaining ionic liquid in the extracted fractions

The results of the elemental analysis of IONCELL-P extracted birch fractions are presented in **Table 17** and compared to untreated commercial eucalyptus dissolving pulp. The dissolved fractions show an increased amount of nitrogen, while the cellulose fractions are virtually clean. However, these were only preliminary tests and should not be over-interpreted as there are many factors influencing the results. Firstly, the nitrogen content of the original Kraft pulp was not measured and from the results of the dissolving pulp, one can assume that untreated Kraft pulp also contains a small amount of nitrogen. Secondly, the washing of the dissolved and coagulated fraction is not optimized. A major improvement is already seen between the [emim][OAc] and [DBNH][OAc] where, in the latter case, the extracted hemicellulose was washed with hot water. Residual ionic liquid is removed more efficiently with hot water, which has been an important finding during this study. A third issue with the dissolved fraction is that pelleting in the centrifuge seems to be improved by ionic liquid contaminations. Salt free hemicellulose tends to float in the water, which leads easily to yield losses during the supernatant decanting. However, these are obviously issues associated with the small-scale laboratory procedure. A different washing and phase separation method could combine high gravimetrical yield with washing efficiency.

Table 17.C, H, N elemental analysis. Values announced as wt %.

Treatment conditions	Fraction	Ionic liquid	C	H	N
15 % water 5 % pulp consistency	Cellulose	[emim][OAc]	42.06	6.37	0.19
15 % water 5 % pulp consistency	Hemicellulose	[emim][OAc]	41.70	6.85	1.14
16.3 % water, 2 % pulp consistency	Cellulose	[DBNH][OAc]	42.56	6.08	0.16
16.3 % water, 2 % pulp consistency	Hemicellulose	[DBNH][OAc]	42.73	6.13	0.53
	Euca. dissolving pulp		42.76	5.69	0.12

6. Conclusions

IONCELL-P is a promising new method for upgrading paper grade pulp into dissolving pulp and thereby producing pure polymeric hemicelluloses. The advantages when comparing to commercial CCE and prehydrolysis Kraft processes are material efficiency, effectiveness and benignity of the process. Paper grade pulp can be purified to acetate grade dissolving pulp without yield losses or polymer degradation. The cellulose structure remains in its cellulose I crystalline form and the hemicellulose removal opens the pulp structure further, making the cellulose eminently more reactive. In CCE or prehydrolysis Kraft processes the hemicelluloses are degraded and removing them from the reaction liquid is complicated and expensive. In the IONCELL-P process the hemicelluloses can be collected quantitatively in their original molecular weight. The IONCELL-P process creates a new platform for hemicellulose based products, as gathering the hemicelluloses is simple and inexpensive, turning the hemicelluloses into a more attractive resource.

The effectiveness of the process is governed foremost by the difference in polymer size of the cellulose and hemicellulose. The MMD of the polymers depends on the raw material source and the pulping treatment. The separation between cellulose and hemicellulose polymer length can be enhanced by hemicellulase treatment. This increases the efficiency of the process as the shortened hemicelluloses can be dissolved more selectively, but also causes hemicellulose yield losses.

Six cellulose dissolving ionic liquids and NMMO were tested in this thesis study. Weaker solvents were more suitable for the IONCELL-P process as they could be optimized more accurately to dissolve even the longest hemicellulose polymers, without influencing the cellulose fraction. In this thesis study, the DBN based ionic liquid-water mixtures have demonstrated a stronger ability to dissolve polymers than [emim] based ones, making the [emim] based ILs more suitable for the IONCELL-P process. Low pH of the solvent system also seemed to be beneficial for maintaining the selectiveness of the process and demanding less water to reduce the anion activity to a selective level.

The Kamlet-Taft parameters of the solvent mixtures did not correlate directly with the hemicellulose removal efficiency. However, a common behaviour of the solvent mixtures was found, when the β-value, describing the anion's ability to accept hydrogen bonds, was divided with the water molar fraction of the solvent system. The resulting $\beta/\chi(H_2O)$-value does give an approximation of the relative strength of the solvent, needed for full hemicellulose solvation, but it does not describe the state, where a certain solvent mixture loses its selectivity. Hemicelluloses dissolve when the $\beta/\chi(H_2O)$-value is approximately between 0.9 and 2.2, approaching maximum hemicellulose removal at 2.2. The $\beta/\chi(H_2O)$-value was determined for bleached birch pulp, that contains 25.4 wt% xylan in low pulp consistency (1 g of pulp per 0.152 mol of the solvent mixture). At a higher pulp consistency or when using a pulp that differs substantially in accessible OH-groups, the OH-groups should be considered when the water molar fraction is determined. A respective $\beta/(\chi H_2O+HO_{groups})$-value could be applied more freely, especially with ionic liquids, which are very sensitive towards water addition.

The IONCELL-P extracted fractions are very pure and intact. The cellulose remains in its cellulose I crystalline form and is highly reactive and suitable for example for acetylation. The dissolved fraction provides a platform for new hemicellulose based products.

7. Future outlook

The IONCELL-P process holds a lot of potential in creating more value for paper grade pulp, by separating the cellulose and hemicellulose fractions, with no yield losses or polymer degradation. However, the overall picture is far from complete to make the process economically feasible.

The major obstacle is the ionic liquid recycling. The recycling level should reach over 99% to render the process commercially viable. The recycling would need to remove the added water and impurities originated from pulp and ionic liquid. A possible recycling pathway could be that the majority of the water would be removed via ultrafiltration and the final water content could be reached by evaporation. In the case of distillable ionic liquids, non-volatile impurities could also be removed by distillation of the ionic liquid itself. However, ionic liquid distillation demands a thin film and short distance evaporation system, and is a very energy consuming process due to the ionic liquid's low vapour pressure. These conditions can lead to degradation reactions and losses, which would impair the overall economy of the extraction process. A possible solution could be in tailored distillable ionic liquids, which dissociate more readily into their conjugate acid and base upon heating.

A second hurdle for up-scaling the IONCELL-P process is that currently no larger markets for hemicelluloses exist. The situation is a bit controversial as many experts say that there is no point in developing hemicellulose based products as there is no steady feedstock of hemicelluloses, and of those that are available, are too expensive. The IONCELL-P process would need to be up-scaled with a parallel production of a hemicellulose product, and meanwhile use the hemicelluloses for example as paper fillers.

The third challenge is, that the process only works best with Kraft pulps that have a clearly separated molar mass distribution of cellulose and hemicellulose, meaning that this upgrading method is more suitable for certain Kraft pulps – at least if acetate grade pulp is targeted. However, viscose grade pulp can be produced easily from any kind of Kraft pulp. It was also proved by Laine et al. that if the dissolved fraction includes cellulose, the dissolving fraction has excellent film forming properties, making even unselective extraction conditions interesting. Compromised selectivity though, can lead to the formation of cellulose II in the purified pulps, which needs to be considered in the demands for the cellulose product.

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