Department of Chemistry
Faculty of Science
University of Helsinki
Helsinki

MODIFICATION AND CHARACTERIZATION OF WOOD COMPONENTS

Tia-Annette Kakko

ACADEMIC DISSERTATION

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public examination in lecture room A 110 Chemicum, on 1st of February 2019, at 12 noon.

Helsinki 2019

Supervisor

Professor Ilkka Kilpeläinen
Department of Chemistry
University of Helsinki
Helsinki, Finland

Reviewers

Professor Tapani Vuorinen
Department of Bioproducts and Biosystems
Aalto University
Espoo, Finland

Associate Professor Henrikki Liimatainen
Fiber and Particle Engineering
University of Oulu
Oulu, Finland

Opponent
Professor Stefan Willför
Department of Chemical Engineering
Åbo Akademi University
Turku, Finland

ISBN 978-951-51-4836-0 (pbk.)
ISBN 978-951-51-4837-7 (PDF)

Unigrafia
Helsinki 2019

ABSTRACT

The separated wood components cellulose, hemicelluloses, and lignin allow for the production of various materials via chemical modifications. In addition to modifications, understanding the structural features of these products is important for enabling tailored processes for commodities.

In this thesis, the introduction covers background information concerning cellulose chemistry. The dissolution of cellulose in various solvent systems is compared, and the usability of these solvents in acetylation of polysaccharides is assessed. Typically, the solvents used in Viscose or Lyocell processes are not suitable for chemical modifications, mainly due to their reactivity with either cellulose hydroxyls or used reagents. Furthermore, in current industrial cellulose acetate (CA) processes, the degree of polymerization (DP) of the product decreases.

The results and discussion present the possibility of using ionic liquids as a reaction media for homogeneous acetylation of hemicelluloses and cellulose. The aim is to produce new methods in ionic liquids, in which tunable substitution is possible for acetylated hemicelluloses and CAs without substantial losses in DP. Furthermore, the procedure is upscaled and acetate fibers are produced with good spinnability and fiber characteristics in collaboration with Aalto University.

Another issue under study is lignin chemistry, especially the structural characterization of hydrothermally (HT) treated Kraft lignin. The results demonstrate that diphenyl methanes are formed during HT treatment of Kraft lignin.

ACKNOWLEDGEMENTS

This work was conducted in the Department of Chemistry at the University of Helsinki during the years 2013–2018. I am grateful for the financial support and travel funds I have received from the University of Helsinki, The Alfred Kordelin Foundation, the Finnish Concordia Fund, and the Doctoral School of Chemistry and Molecular Sciences (CHEMS).

I am grateful for my supervisor, Professor Ilkka Kilpeläinen, for giving me the opportunity to conduct this survey with his team. He has always been supportive and positive with his feedback. He has always believed in me and for a while was the only person who thought I could do this. Thank you.

As most of us know, I have worked at the University of Helsinki for quite a long time now. So, there are numerous people I want to thank. I would like to acknowledge all who have contributed to this work.

I am very grateful to have coworkers with such broad knowledge. I would like to thank Dr. Alistair King for his help of all kinds, Dr. Sami Heikkinen for his NMR expertise, and Dr. Petri Heinonen for discussions and suggestions in analytics.

From the former and current personnel of the Organic Chemistry laboratory, I would like to thank friends and colleagues Dr. Pirkko Karhunen, Dr. Maarit Lahtinen, Maiju Soikkeli, Hanna Niemikoski, and Katja Sievänen. Thank you for your endless support, comments, and discussions.

In addition, I would like to thank the “coffee groups” for their academic and non-academic discussions. These include Dr. Leena Kaisalo, Tom Lagerwall, D. Sc. Tech. Lauri Hauru, Dr. Karoliina Joutsiniemi, Olli Kostiainen, and Martin Söderström.

Furthermore, I would like to thank technical personnel Gudrun Silvennoinen, Seija Lemettinen, Hassan Haddad, Sami Virtanen and Kauko Kauhanen for all their help.

Balancing work, a family with kids, and renovations at home has not always been easy to handle. Without the support of my family, especially my husband, Tommy Kakko, I would not have been able to conduct this long and demanding project. Thank you, my dear. Last, I want to thank Julia and Leon for understanding my need for peace and quiet while writing this thesis.

Tia Kakko

September 2018
Vantaa

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications:

I Tia **Kakko**, Alistair W. T. King, and Ilkka Kilpeläinen. *Homogenous esterification of cellulose pulp in [DBNH][OAc],* Cellulose 2017, *24* (12), 5341-5354 doi:10.1007/s10570-017-1521-5

II Shirin Asaadi, Tia **Kakko**, Alistair W.T. King, Ilkka Kilpeläinen, Michael Hummel, and Herbert Sixta. *High-Performance Acetylated Ioncell-F Fibers with Low Degree of Substitution,* ACS Sustainable Chemistry & Engineering 2018, 6 (7), 9418-9426 doi:10.1021/acssuschemeng.8b01768

III Tia **Kakko**[†], Juulia Talvitie[†], Pirkko Karhunen, and Ilkka Kilpeläinen. *Structural Changes to Lignin During Hydrothermal Carbonization (HTC),* Submitted

IV Agnes M. Stepan, Alistair W. T. King, Tia **Kakko**, Guillermo Toriz, Ilkka Kilpeläinen, and Paul Gatenholm. *Fast and highly efficient acetylation of xylans in ionic liquid system*, Cellulose 2013, 20 (6), 2813-2824 doi:10.1007/s10570-013-0028-y

The publications are referred to in the text by their Roman numerals.

Some unpublished results are also included.

Other related publications:

V Uula Hyväkkö, Tia **Kakko**, Jussi Kontro, Joona Mikkilä, Paula Nousiainen, Petri Kilpeläinen, Eric Enqvist, Panu Tikka, and Jussi Sipilä. *Comparison of recently developed pulping methods by using microwave reactor,* Manuscript

VI Tiina Laaksonen, Jussi K. J. Helminen, Laura Lemetti, Jesper Långbacka, Daniel Rico del Cerro, Michael Hummel, Ilari Filpponen, Antti H. Rantamäki, Tia **Kakko**, Marianna Kemell, Susanne K. Wiedmer, Sami Heikkinen, Ilkka Kilpeläinen, and Alistair W. T. King. *WtF-Nano: One-pot dewatering and water-free topochemical modification of nanocellulose in ionic liquids or gamma-valerolactone,* ChemSusChem 2017, 10 (24), 4849-4890 doi:10.1002/cssc.201701344

VII Somdatta Deb, Sara R. Labafzadeh, Unna Liimatainen, Arno Parviainen, Lauri K. J. Hauru, Shoaib Azhar, Martin Lawoko, Tuomas Kulomaa, Tia **Kakko**, Juha Fiskari, Marc Borrega, Herbert Sixta, Ilkka Kilpeläinen, and Alistair W. T. King. *Application of mild autohydrolysis to facilitate the dissolution of wood chips in direct-dissolution solvents*, Green Chemistry 2016, 18 (11), 3286-3294 doi:10.1039/C6GC00183A

Author contribution in publications I–IV

I TK performed all the experiments and method development including analytics and the synthesis of ionic liquids. TK wrote the article and participated in the editing process.

II TK conducted the syntheses at Aalto University, planned, and performed the experimental scale-up. TK studied the reaction products by ATR-IR and ^{31}P NMR. TK participated in drafting the article and in the editing process.

III Both TK and JT performed the Py-GC/MS experiments. JT produced the experimental and analytical data (shared first authorship). TK wrote the manuscript, and the final version was modified and approved by all authors.

IV TK and AS performed the experiments. TK participated in the article editing process.

ABBREVIATIONS

2D	two-dimensional
Ac_2O	acetic anhydride
[admim]Br	1-allyl-2,3-dimethylimidazolium bromide
AGU	anhydroglucose unit
AGX	arabinoglucuronoxylan
[amim][Cl]	1-allyl-3-methylimidazolium chloride
AX	arabinoxylan
ATR-IR	attenuated total reflectance infrared spectroscopy
[bdmim]Cl	1-*N*-butyl-2,3-dimethylimidazolium chloride
[bmim][Cl]	1-butyl-3-methylimidazolium chloride
CA	cellulose acetate
$Cl_2CHCOOH$	dichloroacetic acid
CP-MAS	cross polarization magic angle spinning
CS_2	carbon disulfide
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
[DBNH][OAc]	1,5-diazabicyclo[4.3.0]non-5-enium acetate
[DBNH][OPr]	1,5-diazabicyclo[4.3.0]non-5-enium propionate
DMA	*N,N*-dimethylacetamide
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulfoxide
DP	degree of polymerization
DP_w	weight average molecular weight
DR	draw ratio
DS	degree of substitution
EC	effective concentration
e.g.	exempli gratia
[emim][Me_2PO_4]	1-ethyl-3-methylimidazolium dimethylphosphate
[emim][OAc]	1-ethyl-3-methylimidazolium acetate
etc.	et cetera
[$etNH_3$][NO_3]	ethylammonium nitrate

FTIR	fourier transform infrared spectroscopy
GC/MS	gas chromatography mass spectrometry
GPC	gel permeation chromatography
HCOOH	formic acid
H_2SO_4	sulphuric acid
HTC	hydro thermal carbonization
HTL	hydro thermal liquefaction
i.e.	id est
IL	ionic liquid
Ip*e*Ac	isopropenyl acetate
HSQC	heteronuclear single quantum coherence
LC	liquid chromatography
LiCl	lithium chloride
MALLS	multi angle laser light scattering
MM	molar mass
MWL	milled wood lignin
m/z	mass-to-charge ratio
*N*MMO	*N*-methylmorpholine-*N*-oxide
NMR	nuclear magnetic resonance
NaOH	sodium hydroxide
N_2O_4	dinitrogen tetraoxide
Na_2S	sodium sulfide
OH	hydroxyl group
PF	phenol-formaldehyde
p-TsOH	*p*-toluenesulfonic acid monohydrate
PSIL	phase separable ionic liquid
Py-GC/MS	pyrolysis gas chromatography mass spectrometry
$[R_2PO_4]$	dialkylphosphate
$[R_2SO_4]^-$	dialkylsulphate
RID	refractive index detector
RTIL	room temperature ionic liquid
$[SCN]^-$	thiocyanate
SIL	switchable ionic liquid

TBAF	tetrabutylammonium fluoride
TG	thermogravimetric
[TMGH][CO2Et]	1,1,3,3-tetramethylguanidinium propionate
t_R	retention time
VinAc	vinyl acetate
VinPr	vinyl propionate

1 Introduction

The chemistry of wood and its components have been under intense investigation during the last two centuries. Scientists and engineers have been studying cellulose, hemicellulose, and lignin to improve usage of the materials and increase profits.

This thesis is mainly a combination of cellulose and lignin chemistry, but hemicelluloses are also examined. The main focus of the study is in the modification of cellulose with tunable degree of substitution and increase the commercial usability of wood-based cellulose products such as films and fibers. The need to replace cotton-based products with biomass-derived ones (*e.g.,* pulp cellulose) is essential since the demand of cropland needed for cotton production is growing. Simultaneously, the world population is increasing, and the cultivated land is needed for food production.[1]

In the pulping industry, the methods of producing pulp and lignin are well-established. Both pulp and cotton contain cellulose. The use of pulp for traditional applications like printing paper is declining and concurrently the usage for packaging is increasing. In addition, other uses have been developed (*e.g.,* fibers for clothing). Viscose and Lyocell fibre production processes are being used at present. Finding new applicable solvents and methods for environmental and economical use of wood-based materials is also necessary. Ioncell is one such method.[2-3] In addition to cellulose yarns, the need for functionalized textiles with different kinds of properties such as water-repellency or fire-retardancy is increasing.

Lignin chemistry is an endless field of investigation due to its aromatic non-uniform structure and various applications. The pulping industry produces large amounts of lignin, of which the majority is burned for energy. As an energy-rich and carboneous material, the use of lignin as a raw material in various applications is attractive. At present, separated lignin is used in composites, thermoplastics, car tires, and more, and novel uses are constantly being developed.[4] Thus, an understanding of the alterations in lignin substructure under various treatments is essential.

1.1 Wood and its components

In botany, trees belong to seed plants and are perennials. Trees consists of a broad variation of species, and occasionally, larger herbaceous plants are also considered trees. In general, trees consist of roots, stems, and branches and grow upward so that the leaves or needles are above the ground. Trees are also divided into soft- and hardwoods. The majority of hardwoods grow in tropical forests, and softwoods mainly grow in borealic forest areas (taiga), also called coniferous woods.[5-6]

Wood is used in many ways, and this thesis discusses the materials obtained from the forest industry, mainly via Kraft processing. In general, wood pulping produces different raw materials for paper and board industries, *e.g.*, paper-grade and dissolving pulp to produce chemicals and fibers. The dissolving pulp has a lower hemicellulose content as a result of pretreatment processes in which hemicelluloses are separated and used as raw materials for various applications. The production of paper-grade pulp accounts for 98% of pulp production from wood. However, dissolving pulp is important for cellulose-derived commodities. In addition to cellulose and lignin, extractives and electricity are produced during wood pulping.[7]

1.1.1 Wood biopolymers

The wood cell walls are dynamic and constantly changing during growth. This fast wood evolution ends when the cell dies. Along with water, the main components of plant cell walls are cellulose, hemicelluloses, pectins, proteins, and lignin. The amount of components in the cell wall depends on the type of cell wall. A primary cell wall (P) is a thin-growing cell with low cellulose content (**Figure 1**). A secondary cell wall comprises three layers (S1–S3), of which the middle is thickest and is the one with importance in fibre production. When secondary cell walls have attained their final shape, the main component is cellulose. On the surface of the S3 layer, a thin layer called the warty layer (W) exists. It mainly contains lignin and can be found in coniferous trees. The middle lamella (ML) binds the cells together and consists mainly of lignin and pectins. The composition of these cell macromolecules varies between plant species and cell wall types.[5-6, 8]

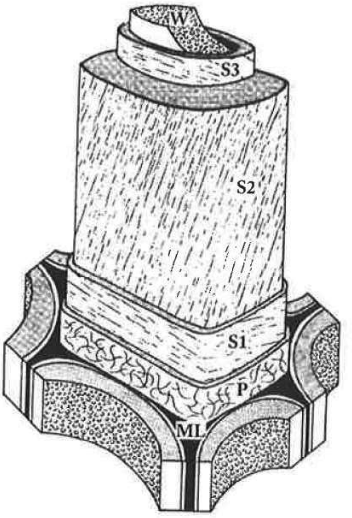


Figure 1 A simplified structure of a wood cell. [9]

1.1.2 Cellulose

Cellulose is the most abundant component in the plant cell wall. In wood cells, mainly in secondary cell walls, cellulose comprises 40% of the dry weight.[5] The cellulose primary structure, *e.g.,* covalent pattern, is rather simple, being a linear homopolysaccharide. It is composed of β-D-glucopyranose units, which are bonded together with (1→4)-glycosidic linkages. The β-D-glucopyranose units are in $^4C_1$ chair conformation, and the free hydroxyl (OH) groups are in the positions of C-2, C-3, and C-6 with equatorial orientation.[10]

The conformation and orientation of the glucose units in cellulose chains cause the cellulose to form both intra- and intermolecular hydrogen bonds *e.g.,* hydrogen bonds within a chain (intramolecular) and between chains (intermolecular).[5, 11-13] In addition, the linearity of cellulose chains requires a 180° rotation of every second β-1,4-glucopyranosyl unit (**Figure 2**), thus the repeating unit in a cellulose chain has two anhydroglucose units (AGU) and is a disaccharide cellobiose.[8, 14-15]

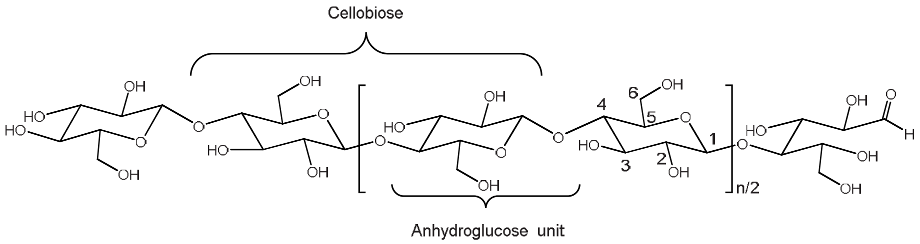


Figure 2 Molecular structure of cellulose. Modified from [10]

The ends of cellulose molecules differ. One end has a terminal aldehyde (reducing end) at the C-1 position in hemiacetal form, and the other end has a free hydroxyl group at the C-4 position.[10] The secondary structure of cellulose varies in native and regenerated cellulose. The secondary structure is formed with hydrogen bonds and interactions between cellulose chains with the aid of van der Waals forces and hydrophobic interactions.[16]

In plant cell walls, cellulose chains form microfibrils, which consist of approximately 36 β-D-glucan chains, forming macrofibrils or bundles and further cellulose fibers and chains (**Figure 3**).[8] The microfibrils are *para*-crystalline, meaning that both crystalline and amorphous sites exist in fringed fibrillar forms. The crystalline (*e.g.,* highly ordered) sites are in majority of cellulose fibers, and amorphous sites are less dominant. The crystalline structure affects the properties of cellulosic materials and provides, for example, mechanical strength in wood.[15]

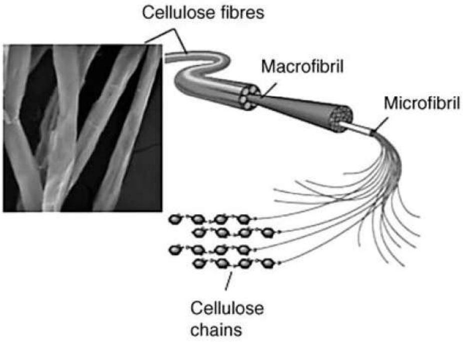


Figure 3 The fiber morphology of plant cellulose.[15] With permission of Wiley

Cellulose has four allomorphs (I–IV), of which the main ones are cellulose I and II. Cellulose III and IV are less important, manmade structural forms. In cellulose I, which is the native form of cellulose, the microfibrils are oriented in the same direction and the chains are parallel to each other. Cellulose II is formed when native cellulose is dissolved and regenerated (or mercerized by strong alkali immersion).[14] Simultaneously, the original lattice of cellulose I is destroyed and cellulose II is formed with antiparallel chains. Another difference between allomorphs I and II is that in cellulose II, hydrogen bonds are formed in different positions in the chains, changing the lattice. Cellulose I has intermolecular hydrogen bonds between C-3 hydroxyl oxygen (C-3-O-H) and C-6 hydroxyl hydrogen (C-6-O-H). Cellulose II has intermolecular hydrogen bonds that are formed between C-6 hydroxyls hydrogen (C-6-OH) and C-2 hydroxyls oxygen (C-2-O-H) (**Figure 4**). Cellulose II is thermodynamically more stable than cellulose I. In addition, both cellulose I and II have intramolecular hydrogen bonds between adjacent glucose units. The intramolecular hydrogen bonds contribute to the linear structure of cellulose and give stiffness to the chains.[5-6, 16]

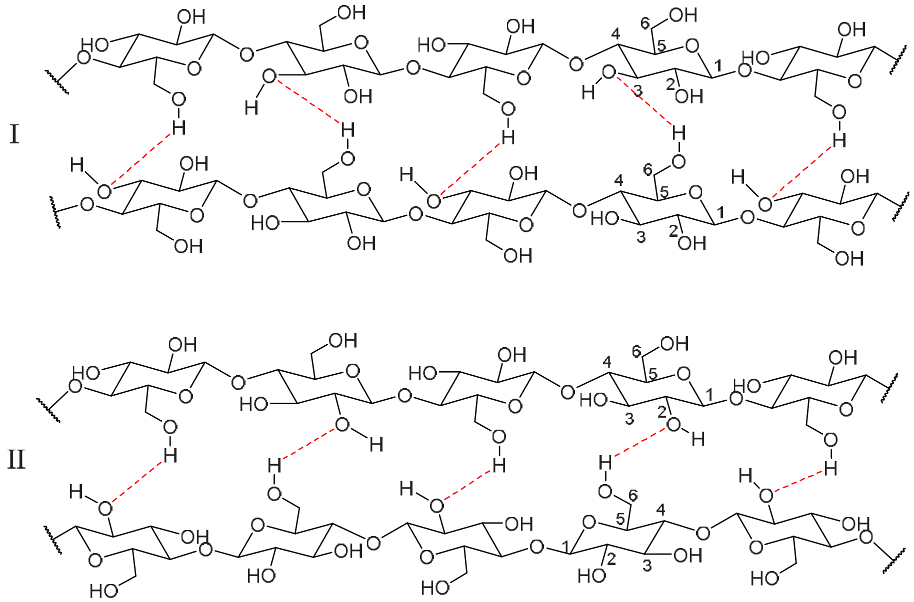


Figure 4 Cellulose I (I)[12] and II (II)[13] and their intermolecular hydrogen bonds between cellulose chains. Modified from Gardner and Blackwell and Kolpak and Blackwell

The length of the cellulose chains (cellulose polymer) can be defined as the degree of polymerization (DP), which describes the amount of anhydroglucose units (AGUs) in the fiber (*e.g.*, chain length in anhydroglucose units). The chain length varies between the different sources of cellulose. For native wood, the DP_w is approximately 10,000,[5, 10] but in chemically produced pulp cellulose, for example, the DP_w varies greatly, usually between 1000-8000 due to the different origins of the cellulose and various processing methods.[17] In this study (**I** and **II**), the used cellulose is from eucalyptus prehydrolysis Kraft pulp, which has a DP of approximately 1700–2300.

1.1.3 Hemicelluloses

Hemicelluloses are one of the three major components of wood cells, comprising approximately 20–30% of the wood's dry weight. They exist in the cell wall between the cellulose microfibrils. Hemicelluloses are heteropolysaccharides *i.e.* the polymer consists of different monosaccharide units.[5] The backbones of hemicelluloses are comprised of *β*-(1→4)-linked glucose, mannose, or xylose moieties (**Figure 5**). In addition, a variety of substituents are attached to the backbone. The composition and structure of the hemicelluloses vary between different species and between soft- and hardwoods. In hardwoods, the hemicelluloses consist mainly of glucuronoxylan (O-acetyl-4-O-methylglucuronoxylan) and glucomannan (**Figure 5**). The glucuronoxylans have 4-O-methylglucuronic acids in approximately every tenth xylan unit, and many C-2 or C-3 hydroxyls in the xylopyranosyls have acetyl substituents. The glucomannan structure, on the other hand, is linear and relatively free from substituents.[6]

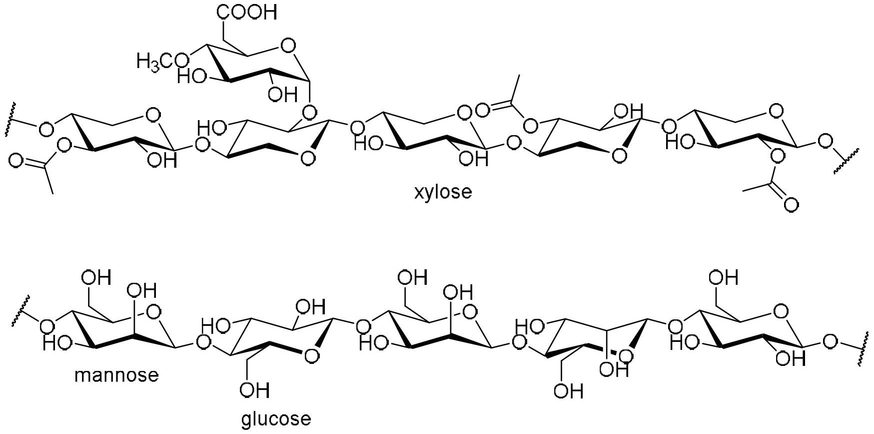


Figure 5 Hardwood glucuronoxylan (upper) and hardwood glucomannan (lower) structures[5]

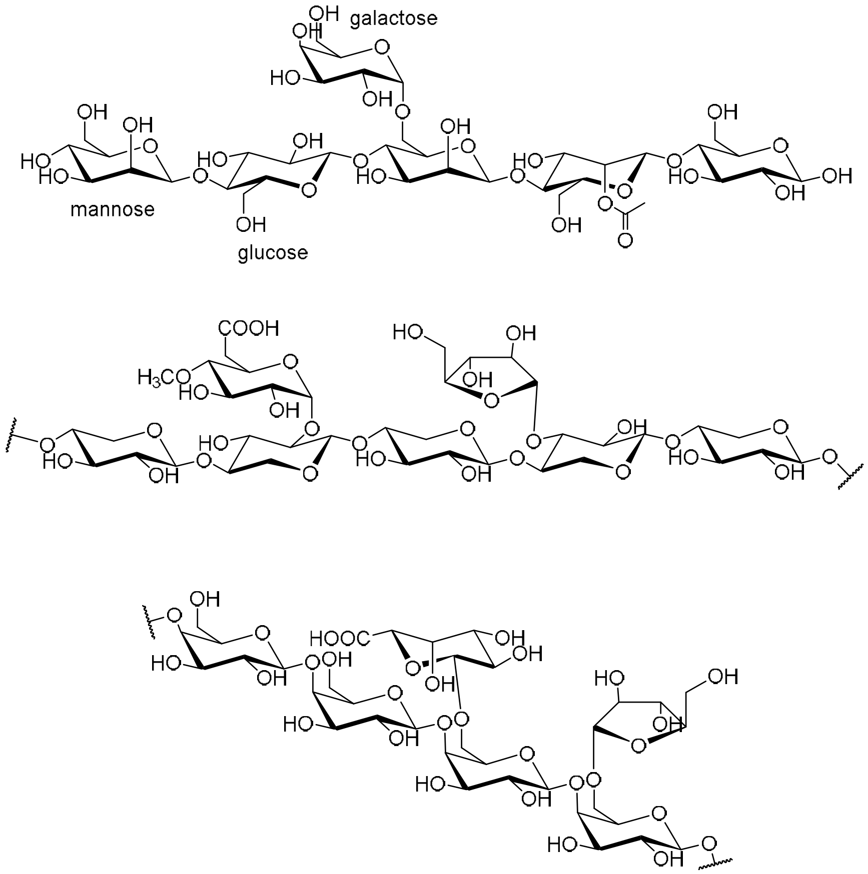


Figure 6 Softwood galactoglucomannan (upmost), arabinoglucuronoxylan (middle), and arabinogalactan (bottom) structures[5]

In softwoods, most hemicelluloses are galactoglucomannas, arabinoglucuronoxylans (arabino-4-O-methylglucuronoxylan), and arabinogalactans (**Figure 6**). Figures 2 and 3 are schematic, and the distribution of the backbone units and substituents differ according to plant species.

As can be seen in **Figures 5** and **6**, the structures of hemicelluloses are often branched. In addition, the variety of substituents in the branches (methoxyl, acetyl, and acid groups in example figures) prevents ordered crystal structure of hemicelluloses. The branching and amorphicity of hemicelluloses make them usually more easily dissolvable than cellulose, thus enhancing the reactivity.[6] On the other hand, linkages with cell moieties, *e.g.,* proteins, reduce solubility. Hemicelluloses can be extracted with water or alkali from plant tissues;[5] pressurized extraction methods are also used.[18] In the case of alkali extractions the acetyl substituents are removed. This occurs in the extraction process of hemicelluloses from wood. The degree of polymerization (DP) of hemicelluloses is usually less than 200, which is considerably lower than for cellulose (DP 1000-8000) (see 1.1.2).

1.1.4 Lignin

Lignin is the second most abundant macromolecule in wood. The amount of lignin depends on the wood species, but approximately 20% of hardwood and 30% of softwood dry matter is lignin. The main structural phenyl propane precursors, or monolignols, of lignin are *p*-coumaryl alcohol, coniferyl alcohol, and sinalpyl alcohol (**Figure** 7). In the lignin macromolecule, these units are called *p*-hydroxyphenyl-, guaiacyl-, and syringyl units (H-, G-, and S- units), correspondingly. The abundance of the units differs according to the species and the growing conditions of the plant. In softwood, the majority consists of guaiacyl units (monolignol coniferyl alcohol). Hardwood lignin has two major components, guaiacyl and syringyl units *(*monolignols coniferyl alcohol and sinapyl alcohol). Grass lignin has all three units but mainly guaiacyl. The notable difference between grass and wood lignin is in the amount of *p*-hydroxyphenyl units; in wood, the amount is only a few percent, but in grasses, it is up to 33%. [5, 19]

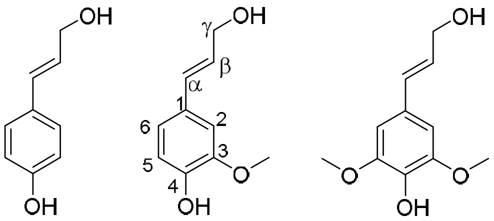


Figure 7 The precursors of lignin: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol.

The biosynthesis of lignin monolignols and the production of lignin in different plant parts has been reviewed by Boerjan *et al.* [20] In this thesis, the main structural units are handled according to the necessity for background information connected to publication **III**.

1.1.5 Native lignin

Native lignin and its structure have been explored widely. Lignin has a complex structure including both aromatic and aliphatic moieties. The phenyl propane precursors are connected with randomly distributed carbon-carbon and ether bonds, forming a kind of three-dimensional web or network.[19] An example of the main structural features of lignin is shown in **Figure 8**.[21] The method for discovering different lignin components is to analyze native lignin with NMR. Usually milled wood lignin (MWL) or enzymatically produced lignin is used. In addition, model compounds are synthesized and also analysed, and the obtained data is compared.

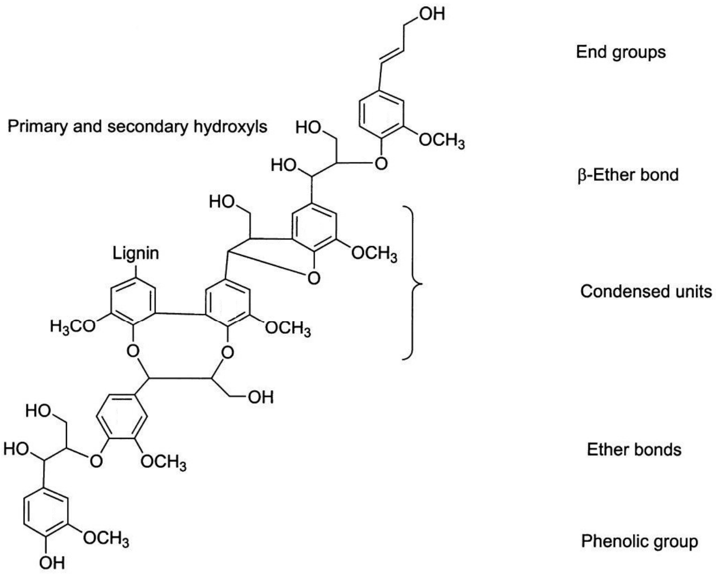


Figure 8 An example of lignin bonding patterns.[21] With permission of Wiley

As a macromolecule, lignin's structure has been debated, and several models have been suggested.[21-26] Major structural units found in the lignin polymer are products of radical coupling reactions of the phenolic radical of lignin precursors (**Figure 9**).

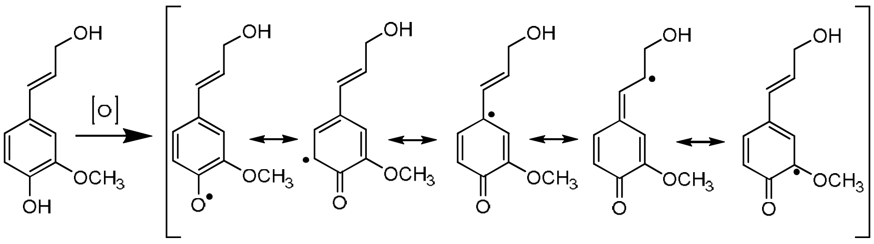
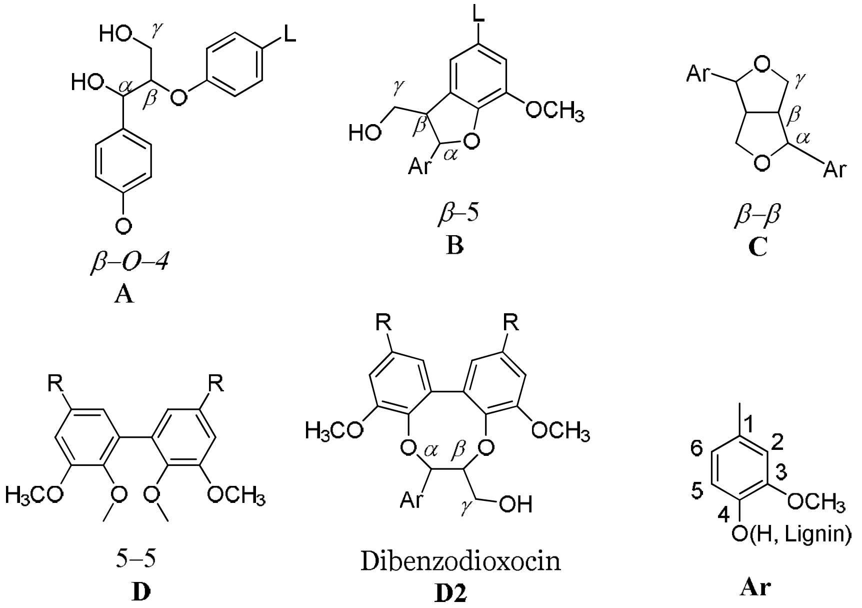


Figure 9 Formation of different radicals in the first step of lignin polymerization. In the figure, an example of resonance structures for coniferyl alcohol is shown

The abundance of different dimer structures has been evaluated, and the most abundant structure in soft- and hardwood has a *β*-aryl ether bond (*β*-O-4, **A** in **Figure 10**). Other common structures in wood lignin are phenylcoumaran (*β*-5, **B**), resinol (*β*-*β* **C***)*, diarylethers (4-O-5), and 1,2-diaryl propane (*β*-1) structures. Biphenyl (5-5, **D**) structures can be found in softwood lignins but not in harwoods.[6, 27-29] Also, the majority of 5-5 structures reform to an eight-membered ring via crosscoupling to a dibenzodioxocin structure (**D2**), [30-31] found in both hard- and softwood species.



β-O-4
A

β-5
B

β-*β*
C

5–5
D

Dibenzodioxocin
D2

Ar

Figure 10 Some common linkages in native lignins[6, 32-35]

1.2 Fractionation of wood biomass

Kraft lignin is obtained from the Kraft pulping process, which is the dominant pulping process in the world. During the pulping process, lignin is removed from the wood and separated. Currently, the majority of the lignin is burned for energy. However, new ideas for the usage of lignin are being sought, and thus the interest to use (Kraft) lignin is increasing.

1.2.1 Kraft process

The Kraft process is highly optimized, and its economic feasibility lies in the circulation of reagents and the obtained products. The main product is chemical pulp that is used in raw materials for paper products and other important products such as methanol. When using pine wood, tall oil and turpentine are also obtained as side products.

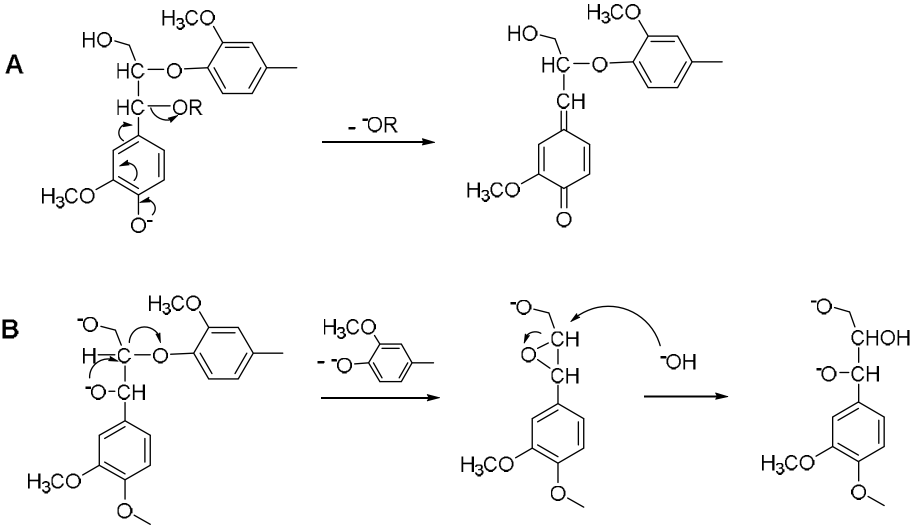
The process is a continuous system. At first, the wood (chips) are impregnated with cooking liquor, which consists of water, sodium hydroxide, and sodium sulfide (NaOH and Na_2S). The purpose of Na_2S is to promote and fasten the delignification reactions. It also protects carbohydrates from hydrolysis and dissolution, thus increasing the yield. The mixture is heated at high temperatures (135–175°C) for approximately 2 h, and the wood fibers are liberated from the lignin and from each other. The lignin macrostructure is degraded, and smaller fragments and degradation products of hemicelluloses, in addition to waxes and resins dissolve in the cooking liquor. Due to the alkalinity of the cooking liquor, lignin fragments are in a phenolate form and thus soluble. The heating is terminated before all the lignin has been removed, since a cook is a balance of retaining the cellulose chain length and removal of lignin.[36] After cooking, the liquid mixture, which is called black liquor, is separated from the pulp. The pulp mass is washed and bleached to remove the rest of the lignin. Most of the water is evaporated from the black liquor, the cooking chemicals are recovered for reuse in the recovery boiler, and the lignin is used for energy. Alternatively, lignin can be separated from the black liquor and used in applications including production of hydrocarbons, phenols, oxidized chemicals, macromolecules, and/or syngas.[37] The separation of lignin from the black liquor is usually obtained by the precipitation with carbon dioxide, followed by the removal of water and re-dissolution. Then the lignin slurry is acidified and washed to liberate pure Kraft lignin. The amount of lignin that can be separated from the black liquor without affecting the chemical recovery is approximately 10–15%.[38] At present, most lignin is used for energy, and only a small percentage is used in the production of isolated lignin.

In some variations of the Kraft process, a pre-hydrolysis step is utilized before pulping. In the system, a woody mass is heated with water steam (with or without mineral acids), removing acetic acid from the wood. This promotes acid hydrolysis (*e.g.,* cleavage of water-soluble carbohydrates). The aim is to remove hemicelluloses and improve economy while also affecting the pulp quality.[39]

1.2.2 Lignin reactions during Kraft process

During the Kraft process, the lignin structure is changed. Two types of reactions occur during Kraft pulping: degradation and condensation.[40] The degradation reactions are favorable, since these reactions liberate the lignin fragments, promoting dissolution of the fragments into the black liquor. On the other hand, condensation reactions can form strong linkages, which tolerate alkaline conditions and are thus undesirable.

Originally, the main degradation reactions have been suggested to be the cleavage of α–aryl and β–aryl ether bonds. These cleavage types are prominent if phenolic -OH is in para position. Thus, the formation of a quinone methide structure is possible (**Scheme 1 A**). However, this reaction path seems unlike since such α–O–4 bonds have not been confirmed with NMR studies (**Table 1**).[32, 35, 38] In the case of nonphenolic units, the cleavage involves the attack of an anionic hydroxyl from α- or γ- carbon. Thus, new phenolic end groups are formed (**Scheme 1 B**). Another similar cleavage of γ-hydroxyls from β–aryl ethers is the formation of vinyl ethers (or styryl ethers) (**M** in **Figure 11**); both reactions occur during Kraft pulping. The sulfide used in the Kraft process promotes the cleavage of β-ether units in lignin, and the amount of β-O-4 bonds is reduced during cooking from approximately 40% to 8%.[33, 40-41] It has been suggested that when the α–aryl ether cleavage occurs from phenylcoumaran (**B** in **Figure 10**) units, the formed product has a stilbene structure (**E** in **Figure 11**) and the side product is formaldehyde. [32, 42] In addition, demethylation from aryl ether bonds form corresponding catechol structures.[38, 43]



Scheme 1 Cleavage of α–aryl ether in phenolic units (A) and cleavage of β–aryl ether from α-carbon in nonphenolic units (B)[7, 44]

The condensation reactions occur at position 5- (and 6-) of the aromatic ring. Dominantly, these take place in the structures, which have a good leaving group (*e.g.,* OAr) in the *β*-carbon, and the formation of a quinone methide intermediate is possible. The condensation reaction is a competitive reaction with either internal or external nucleophiles, *e.g.,* an anionic lignin fragment or hydrosulfide anion, respectively. In another condensation reaction, formaldehyde reacts with two phenolates, resulting in diarylmethane.[33, 44]

1.2.3 Structural differences between native and Kraft lignin

The main structural elements (**A–C**) of lignin are the same within native and Kraft lignin, but the relative amount of side chain structures varies, and the amount of coniferyl alcohol end groups increase in Kraft lignin due to the breakage of *β*-O-4 bonds. The relative amounts of condensed structures with C-C bonds, such as *β*-*β* and *β*-5 structures, also increase due to their resistance to alkaline pulping cleavage reactions.[33] This can be expected, as the main reactions occurring during the Kraft process are the ones with ether cleavage. According to the chemistry of Kraft pulping, it is also proposed that new structures are formed.[40] Stilbene (**L** in **Figure 11**) structures are formed via cleavage of *β*-5 structures occurring via *γ*-hydroxyl elimination.[45] On the other hand, clear evidence of some of these new structures such as diphenylmethane (**N** in **Figure 11**)[40] in Kraft lignin have not been published.

A structural analysis of lignins is made with nuclear magnetic resonance (NMR) techniques. Typical two-dimensional (2D) or 3D NMR analysis techniques are not quantitative methods, but relative assessments of the amounts of different structures can be made. 1D NMR techniques often fail in quantitating high-molecular-weight lignin samples due to poor resolution, overlapping signals, or low sensitivity.[46] In addition, from quantitative ^{13}C, only relative information from peak clusters of different substituent groups such as aliphatic, methoxyl, aromatic, and acetate groups is obtained.[47] In **Table 1**, the amounts of different structures and possible structures in lignin have been listed according to 2D HSQC and 3D HSQC-TOCSY spectral analyses performed by Liitiä *et al.*[32] and 2D HSQC data from Hu *et al.*[9] The corresponding structures (**A–D2** and **E–R**) are illustrated in **Figures 10** and **11**.

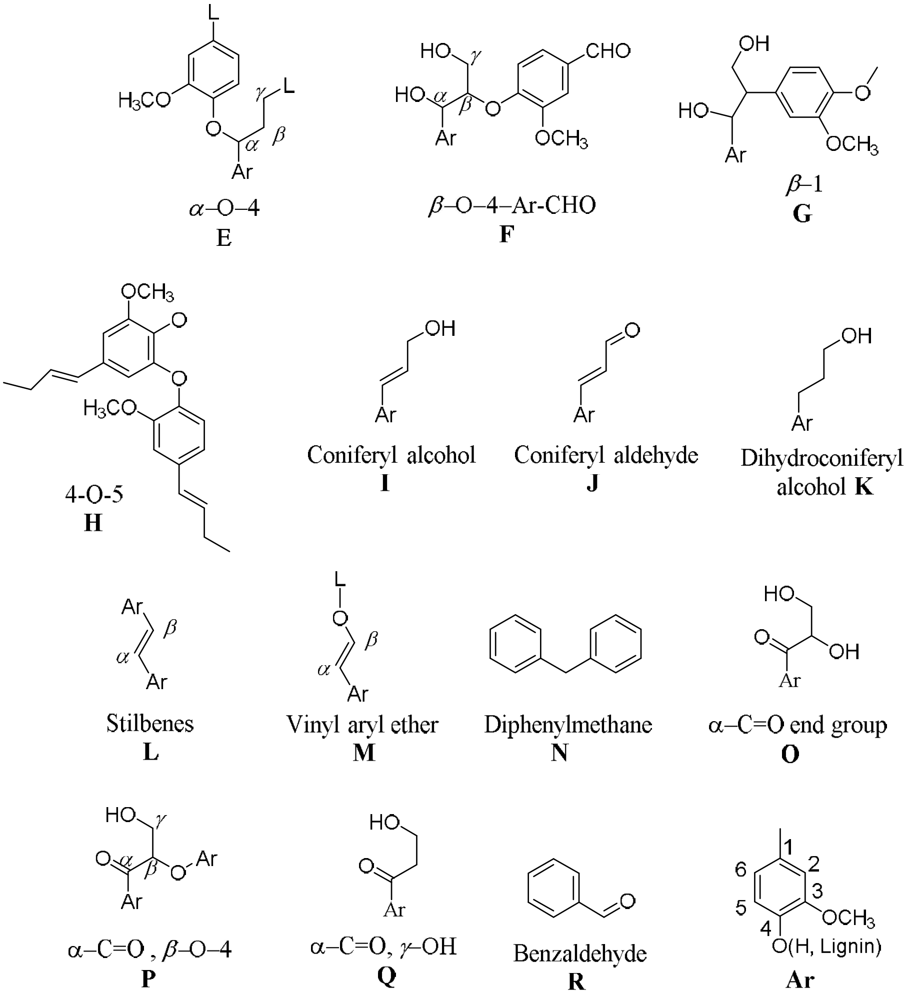


Figure 11 Other possible side chain structures in lignin[32]

Table 1. Lignin side chain structures in pine and spruce MWL and Kraft lignin. Combined data from [32, 38] n.r. = not reported

	Substructure	MWL[a]	MWL[b]	Kraft[a]	Kraft[b]
A	β-O-4	41	++	2,2	++
B	β-5	9	++	1,6	++
C	β-β	6	++	4	++
D2	Dibenzodioxicin	0,8	+	8	(+)
E	α-O-4	n.r.	(+)[c]	n.r.	n.r.
F	β-O-4-Ar-CHO	n.r.	+	n.r.	-
I	Coniferyl alcohol	4	+	0,7	++
J	Coniferyl aldehyde	n.r.	+	n.r.	-
K	Dihydroconiferyl alcohol	n.r.	+	n.r.	++
L	Stilbene	0	-	7,3	+
M	β-vinyl ether	0	-	2,2	-/(+)*
N	Diphenyl-methane	n.r	n.r	n.r	n.r
O	α-carbonyl end group	n.r	+	n.r	-
P	α-carbonyl with β-O-4	n.r	+	n.r	-
Q	α-carbonyl with γ-OH	n.r	+	n.r	-
R	Benzaldehyde	n.r	+	n.r	-

*[a] is the substructure amount per 100 Ar unit from Hu et al. [b] is the strength of the correlation (++ strong, + moderate, (+) weak, and – no correlation) from Liitiä et al., *uncertain result from 2D spectra [c] is data from Ede and Kilpeläinen[35]*

1.2.4 Hydrothermal treatment for lignin

Hydrothermal (HT) processes for biomass treatment have been studied intensively in recent years.[48-59] The effect of reaction conditions,[55] different temperatures,[60] water-biomass ratios, and possible catalysts such as H_2SO_4, $FeCl_2$, NaOH,[54] have been investigated. Hydrothermal carbonization (HTC) or wet torrefaction is a method to alter biomass to a solid, coal-like mass.[61] In the process, the biomass is mixed with water and possibly additives in high temperatures (from 180–260°C) and self-generated 20–30 bars pressure. Reaction times vary from 0.5 hours to four days, and the obtained product is hydrochar.[56, 62] With higher (>280°C) temperatures, the method turns to HT liquefaction (HTL), since the product turns to liquid, or bio-oil.[49, 52]

During the hydrothermal process, the combination of heat and pressure causes the loss of CO, CO_2, and H_2O, hence decreasing the hydrogen and oxygen content, especially in the case of whole biomasses. Thus the relative carbon number of the mass increases. Reactions include dehydration, condensation polymerization, aromatization, hydrolysis, and decarboxylation. Due to the decrease in hydrogen and oxygen in the product, the system is called carbonization and the product is hydrochar.[50, 63-65] For Kraft lignin, some of the cleavage and condensation reactions have already taken place during the pulping process, and the increase in carbon number is not as evident.[49] However, the observation that the highest yields of hydrochar can be produced from lignin promotes the idea of exploring separated lignin fractions instead of raw biomass.[62]

Biochar is an alternative for hydrochar and is produced mainly with pyrolysis techniques *i.e.,* without water, oxygen, or other additives. The hydrochar, which is produced in HT conditions, has lower ash content and the surface has more oxygen-containing groups (in phenolic structures) than biochar, thus the usability of HTC lignin is broader than for biochar. It is also possible to use hydrochar as a replacement for more expensive materials such as carbon black.[66]

The chemical characterization of hydrochar is rather challenging due to its condensed chemical structure and low solubility. On the other hand, to expand the usability of HTC lignin, a structural analysis of the products is needed. Characterization methods have included Py-GC/MS, solid-state NMR, and FTIR techniques. With pyrolysis, the idea is to vaporize the degradation products of the material. Pyrolysis is usually done in high temperatures for a short time, volatile components are separated with GC, and mass spectra of different components are obtained.[49, 67-69] From solid-state NMR and FTIR studies, it is possible to determine functional groups in the product such as double bonds, aromaticity, and ether functionalities as methoxy groups, but no complete structural analysis can be obtained with these techniques.[49]

1.3 Ionic liquids

Ionic liquids (ILs) are molten salts that have a melting point under 100°C. Their structure includes an organic component and often a delocalized charge. In addition, the irregular structure of the cation lowers the melting point of the salt. [70] ILs have usually low vapor pressure, are non-flammable, and some have high thermal stability (>200°C). The properties of ILs are tunable. In principle, the possibilities to pair anions and cations to adjust solvent properties are countless. For example, melting point, density, and miscibility with water or organic solvents can be tuned.

Research on new ionic liquids has been growing rapidly during recent years. A selection of example cations are alkylimidazolium, alkylpyrinidium, tetraalkylammonium, tetra-alkylphosponium, and more recently, suberbase cations such as 1,5-diazabicyclo[4.3.0]non-5-enium ([DBNH]$^+$), 7-methyl-1,5,7-triazabicyclo-[4.4.0]-dec-5-enium ([MTBDH]$^+$), and 1,8-di-azabicyclo[5.4.0]undec-7-enium ([DBUH]$^+$) (**Figure 12**).[71] Superbase-based ionic liquids' basicity lies with the strong proton affinity, which is in relation to the multiple nitrogen atoms. The structure enables the distribution of the resonance forms after protonation, thus creating a stronger base.[72]

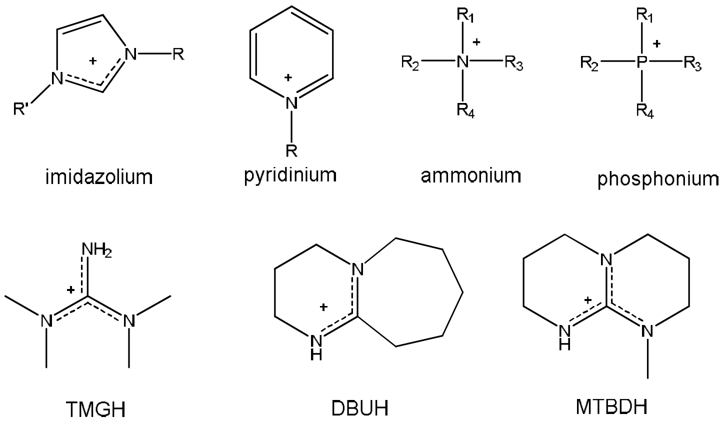


Figure 12 Examples of cations used in ionic liquids. TMGH = 1,1,3,3-tetramethylguanidinium, DBUH = 1,8-di-azabicyclo[5.4.0]undec-7-enium, and MTBDH = 7-methyl-1,5,7-triazabicyclo-[4.4.0]-dec-5-enium [71, 73]

The anions of the ionic liquids also have a wide range, including halogenides (Cl^-, Br^- and F^-), hexafluorophosphate $[PF_6]^-$, thiocyanate $[SCN]^-$, tetrafluoroborate $[BF_4]^-$, formate $[HCOO]^-$, acetate $[CH_3OO]^-$, propionate $[CH_3CH_2COO]^-$, dialkylsulphate $[R_2SO_4]^-$, and dialkylphosphate $[R_2PO_4]^-$.[70, 74-76]

An IL can thus be understood as a “sum of its components”, even though some properties may change drastically as an ion pair. It needs to be recognized, that the usability of some ILs at large scale is often hindered or prohibited due to toxicity or accumulation in the environment.

1.3.1 Ionic liquid subgroups

As mentioned, the structure of ionic liquid has an effect on the physio-chemical features of the IL, and in addition to “normal” ionic liquids, four subspecies are clarified here. First, there are room-temperature ionic liquids (RTILs). These have melting points below room temperature, some even as low as −96°C.[77-79] Ethylammonium nitrate $[etNH_3][NO_3]$ was discovered by Walden in 1914; an industrially produced RTIL, 1-ethyl-3-methylimidazolium acetate [emim][OAc], also exists, but so far it is only used in laboratory applications.[80] Secondly, the term "distillable ionic liquid" has been adopted;[81] the main importance of these ILs is the possibility to convert ionic liquids back to their starting compounds. For cellulose dissolution, King *et al.* studied 1,1,3,3-tetramethylguanidine (TMG) conjugates with several carboxylic acids and found out that tetramethylguanidium propionate $[TMGH][CO_2Et]$ was able to dissolve cellulose and could also be distilled with high recovery.[82] This work has been continued in further studies, and other superbase-based distillable ILs such as 1,5-diazabicyclo[4.3.0]non-5-enium acetate [DBNH][OAc] and propionate [DBNH][OPr] have emerged.[71, 83]

Switchable ionic liquids (SILs) comprise a third subgroup of ionic liquids. These were first introduced in 2005 by Jessop *et al.*[84] The name “switchable” comes from the switchable properties of the solvents; the polarity and viscosity of the SILs are different from either molecular solvent used for the SIL.[85] The preparation is done by bubbling "acidic gas" like carbon dioxide to the mixture of two non-ionic compounds such as alcohol and a superbase to induce ionic liquid. On the other hand, bubbling the IL with inert gas (like nitrogen) breaks down the ionic form of the SIL consequently, starting solvents can be separated (**Figure 13**).[84] SILs have been studied for absorbence use in CO_2 capture,[86] biomass fractionation,[87] and cellulose derivatization with DMSO as a co-solvent.[88]

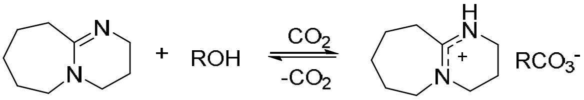


Figure 13 Protonation of DBU with alcohol and carbon dioxide[84]

The fourth subgroup of ionic liquids is phase separable ILs (PSILs). These can be composed of two ionic liquids[89] or, more often, of IL and aprotic organic solvents such as DMSO and DMF;[90-92] even combinations of IL and water exist in this subgroup.[93-94] Some of these PSILs have been used for biomass separation processing[91] and in cellulose dissolution.[90, 92]

1.3.2 Toxicity of ILs

One important factor to consider with all chemicals is their impact on the environment and toxicity, especially in cases of potential usability on a large industrial scale. For ILs, evaluating toxicity is a major issue. A recent review discussed four aspects that need to be taken into consideration when judging the toxicity of IL: i) the nature of anions or cations, ii) the length of an alkyl chain in the cation, iii) the degree of functionalization in the side chain of the cation, and iv) the mutual influence of both cations and anions.[95]

Ruokonen *et al.* and Witos *et al.* studied the toxicity of biomass-dissolving ILs for zebrafish and the biomimetic system of phospholipid layers and found that long (C8 and C14) hydrocarbon "tails" in cations have a greater impact on EC_{50} (effective concentration) than shorter ones.[96-97] The EC_{50} values specify a 50% reduction of processes such as reproductive activity, for example, of the exposed organisms relative to the test control. A "cation effect" *i.e.* increased lipophilicity has also been revealed with modeling studies for ILs in general, not just for biomass-dissolving ILs.[98]

Anions have also been demonstrated to be toxic to the environment, demonstrating an "anion effect" that is sometimes dependent on the cation.[99] Halides, especially the fluoro-anion[100] and boron[101] or phosphorous anions, are toxic. Furthermore, sulphates, sulphonates, and phosphates can have toxic effects. The bis(trifluoromethyl-sulfonyl)imide anion $[(CF_3SO_2)_2N]^-$ has especially shown intrinsic toxicity to different species.[102] For carboxylate anions, less information is available, but some conclusions can be made. Larger anions, more than six carbons long, are more toxic,[103] and with shorter chains such as formate and acetate,[104] the toxicity depends greatly on the cation of the IL.

As a summary of toxicity of ionic liquids, there are several independent factors, which might cause toxic effects. Therefore, the toxicity of chemicals (and ILs) needs to be evaluated separately. The role of entire system must also be taken into account when judging the environmental impact of ILs.

1.3.3 Ionic liquids as cellulose solvents

In 1934, Graenacher patented a method of cellulose solubilization in which molten salt *N*-ethylpyridinium chloride with nitrogen-containing bases was used to dissolve cellulose.[105] The turning point in the use of ionic liquids occurred in 2002 when Swatloski *et al.* published a study on cellulose dissolution in imidazolium based ILs.[75]

For the purpose of cellulose dissolution and modification, many different cellulose ILs have been studied and developed, but just a few have the potential to be utilized in controllable and homogenous esterification reactions for cellulose. Some properties such as viscosity and reusability affect greatly the usability of IL. For example, when considering imidazolium-based ILs, when the cation has a long hydrocarbon end (more than six carbons), it increases viscosity; but on the other hand, branching and double bonds reduce viscosity. With anions, the most viscous ILs are formed with chlorides, but formates and acetates form less viscous ILs.[73, 79] One method to reduce viscosity is to add a (typically polar aprotic) co-solvent such as DMSO,[91] *N,N*-dimethylacetamide (DMA), or 1,3-dimethyl-2-imidazolidinone (DMI).[106] Without the use of co-solvents, examples of effective cellulose-dissolving ILs include 1-butyl-3-methylimidazolium chloride [bmim]Cl,[107] 1-ethyl-3-methyl imidazolium acetate [emim][OAc],[108-109] and 1-ethyl-3-methylimidazolium dimethyl-phosphate [emim][Me_2PO_4].[79] However, Heinze *et al.* reported the reactivity of [emim][OAc] with cellulose, as it can form cellulose acetate and thus consume the IL.[110] A similar downside is the imidazolium ILs reaction with the C-1 carbon of the cellulose reducing end, which further emphasizes the importance of evaluating the inertness of ILs.[111] Other documented ILs in cellulose dissolution and modification are *N*-ethylpyridinium chloride and 1-allyl-3-methyl-imidazolium chloride [amim]Cl, among others.[73, 112-113] More recently, superbase-based ionic liquids have been noted to dissolve cellulose,[82] although it has high viscosity, the ability to spin that IL-cellulose dope ([TMGH][CO_2Et]+cellulose) for textile fiber production was not successful. As a consequence, an evaluation of possible cellulose-dissolving ILs and explanations for the dissolution of cellulose was published by Parviainen *et* *al.*[71] In the current thesis (**I, II, IV**), the IL [DBNH][OAc] has been shown to have good properties for cellulose dissolution as a homogeneous reaction media.

The dissolution mechanisms of ILs for cellulose have been studied extensively, and different suggestions for dissolution mechanisms have been reported. The main theory deals with the solvents' ability to break down the hydrogen bonding network of cellulose and replace it with the solvent ions. Theoretical studies for cellulose dissolution in [emim][OAc] have suggested that acetate anions form strong hydrogen bonds, and on the other hand, cations act with a polysaccharide or cellulose backbone via hydrophobic interactions.[114-115] As mentioned earlier, both anions and cations affect the dissolution capability. Calculations and experimental studies of the solubility of cellulose in imidazolium-based ILs with fluoro-, acetate-, and alkyl phosphate anions have also been conducted, and it was noted that acetate and phosphonate anions have stronger interactions with cellulose than halides.[116] Anions of the ionic liquid act as hydrogen bond acceptors, thus hydrogen bond basicity affects the dissolution mechanisms.[79] In addition, hydrogen bond acceptability and proton affinities with the basicity of the cation have been evaluated with Kamlet-Taft parameters.[78-79, 117-119] However, these parameters are measured separately without accounting for the impact of IL and cellulose interactions. Therefore, the obtained data need to be combined with experimental results.

Parviainen *et al.* proposed a simplified model for evaluating cellulose dissolution in ionic liquids (**Figure 14**). In this system, the enthalpy of acid-base conjugates of the ionic liquid has a great effect on dissolving properties. Cation acidity was found to be an important role in cellulose dissolving capacity, along with viscosity of the ionic liquid.[71] More recently, Kuzmina *et al.* conducted a detailed study of superbase-derived ILs compared to [emim][OAc] and [emim] diethylphosphate.[119] It was noted that when the acetate anion was replaced with a longer anion chain, the maximum cellulose solubility decreased, resulting in an unsuitable mixture for processing (*e.g.,* spinning of fibers). In the same study, the mixture of two ILs, 1,5-diazabicyclo[4.3.0]non-5-enium hexanoate [DBNH][Hex] and [DBNH]

[OAc], showed promising dissolving and processing properties of cellulose fibers.[119]

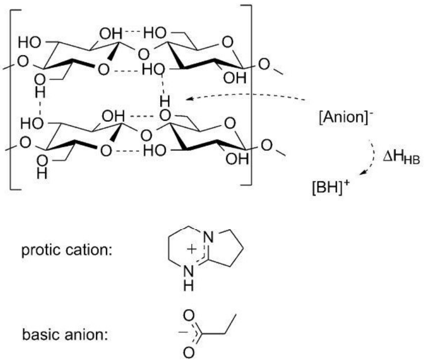


Figure 14 Protic ionic liquids with competitive hydrogen bond donation from cellulose and the protic cation with the basic anion.[71] With permission of Wiley

The dissolution of cellulose in ionic liquids is dependent on various circumstances. The purpose of the end product determines the selection of appropriate IL. The main issues are the dissolution process itself, the required time and temperature, and the solubility (*e.g.*, the amount of dissolved cellulose). Other important aspects are the recyclability, robustness, and chemical stability of the ionic liquid. In addition, toxicity and environmental impact need to be evaluated, especially if the process is used on an industrial scale. The quality of the obtained product might depend on the IL as well. Finally, the suitability of the IL system for cellulose modifications must be assessed.

1.4 Dissolution of cellulose

Cellulose structure and its tendency to form hydrogen bonds makes the dissolution of cellulose difficult. Despite having a great deal of hydroxyl groups, cellulose is not soluble in water or organic solvents. This is due to the chain length and crystalline structure with hydrogen bonds. The hydroxyl groups in cellulose are able to react only from the surface of the cellulose fibers and from the amorphous areas of the cellulose chains. Consequently, the requirement for cellulose dissolution is to replace the hydrogen bonding network with more favorable ones. There are non-derivatizing and derivatizing solvents/solvent mixtures for cellulose dissolution, which can be aqueous or non-aqueous. More recently, ionic liquids have been added to the list of non-derivatizing solvents.[15, 75, 120] Ideally a cellulose solvent does not cause hydrolysis and is chemically inert.[120] In this thesis, the dissolution of cellulose has been achieved with an ionic liquid and with a fairly small reduction in molecular weight and DP of the material.

In addition to cellulose fiber production, the objective is to prepare cellulose solutions in which chemical modifications of the cellulose are possible and plausible. Ideally, a cellulose solvent would accomplish the dissolution of cellulose, easy regeneration of cellulose, and furthermore should be an inert solvent to enable conducting chemical reactions with cellulose. These properties would allow for the production of cellulose derivatives in one process. There are numerous applications for cellulose commodities, not only in replacing fossil fuel usage, but also in producing biodegradable materials.[14]

1.4.1.1 *Derivatizing cellulose solvents*

A derivatizing cellulose solvent is one in which the cellulose dissolution is obtained via chemical modification. Cellulose hydroxyl groups react in the system and form a derivative, which is dissolved in the solvent due to disruption of the hydrogen bonds in the cellulose.[121] The Viscose process is the most important process for the production of manmade cellulose materials more than 3,000,000 tons per year.[10] Viscose process was discovered by Cross, Bevan, and Beadle in 1891 and has been used in industrial production since 1910.[122] In the Viscose process, after mercerization and aging (in which the DP of the cellulose chains is lowered from ~800 to ~300), the cellulose is converted to xanthogenate with the aid of carbon disulfide (CS_2) and sodium hydroxide in a water mixture (**Figure 15**). The product dissolves and is further ripened for re-distribution of the chains and loss of CS_2 groups with the aid of sulfuric acid; thus, Viscose fibers are formed after filtering and spinning.[123] Similar derivative forming systems include dinitrogen tetraoxide (N_2O_4) in dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO), formic acid with sulphuric acid $HCOOH/H_2SO_4$, trifluoroacetic acid (CF_3COOH), and dichloroacetic acid ($Cl_2CHCOOH$). These form corresponding derivatives, including cellulose nitrite, -formate, -trifluoroacetate, and -dichloroacetate.[124-125]

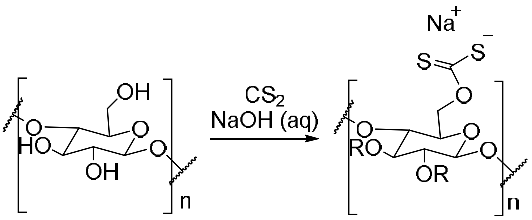


Figure 15 Cellulose xanthogenate used in Viscose process, R is H or xanthogenate

1.4.1.2 Non-derivatizing solvents

Methods for dissolving cellulose in non-derivatizing solvents include aqueous inorganic complexes, organic solvents with salts, aqueous alkali solutions, organic amine-containing solvents, and ionic liquids. In contrast with derivatizing systems, these dissolve cellulose directly and form a homogeneous solution; they are also called direct solvents. The disadvantage of many of these solvent systems lies in the difficulties in upgrading production to an industrial scale *e.g.*, narrow dissolution window or challenging recyclability of the solvents. Consecutively, they are mainly used for analytical or laboratory purposes.[120, 126] However, there are exceptions such as the *N*-methylmorpholine-*N*-oxide (*N*MMO) process, which is used to produce textile fibers industrially. Other drawbacks to non-derivatizing solvent systems are the possibility of side reactions, as some systems include toxic chemicals and must be used in strictly controlled conditions.

In 1865, Schützenberger synthesized cellulose acetate in cuprammonium hydroxide solution, which is one example of an aqueous inorganic complex. The complexing systems dissolve cellulose with the aid of deprotonation of cellulose hydroxyl groups and coordinative binding of copper complex to C-2 and C-3 hydroxyl groups, simultaneously reducing the amount of hydrogen bonds within and between cellulose chains (**Figure 16**).[127]

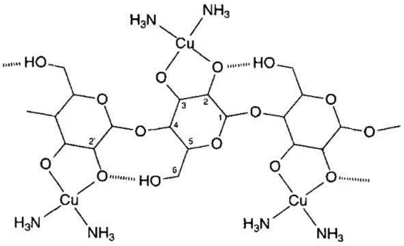


Figure 16 Copper complex formation in cuprammonium hydroxide solutions[127]

The dissolution of cellulose can be conducted in organic solvents with salts such as lithium chloride in *N,N*-dimethylacetamide (LiCl/DMA)[128] and tetrabutylammonium fluoride in dimethylsulfoxide (TBAF/DMSO).[129] Of these, DMA with LiCl are more commonly used despite the need for an activation step of either heating or solvent exchange.[130] The general use of DMA/LiCl over DMSO/TBAF is due to the simplicity of performing chemical reactions in a laboratory. In addition, with DMSO/TBAF, the DMSO can mediate oxidation reactions for alcohols.

In the dissolution of cellulose with DMA/LiCl, cellulose hydroxyl hydrogen is believed to have an intermediate with Cl^- ions along with macrocation ($^+$Li-DMA). This is bound to the cellulose hydroxyl groups' oxygen atom with an ionic bond (**Figure 17**). There, the solvent causes charge repulsion and coordination between the cellulose chains' intra- and intermolecular hydrogen bonds and solvent ions. The macromolecular structure of cellulose is broken down and cellulose is dissolved. Several mechanisms for dissolution in LiCl/DMA have been suggested.[128, 131-133]

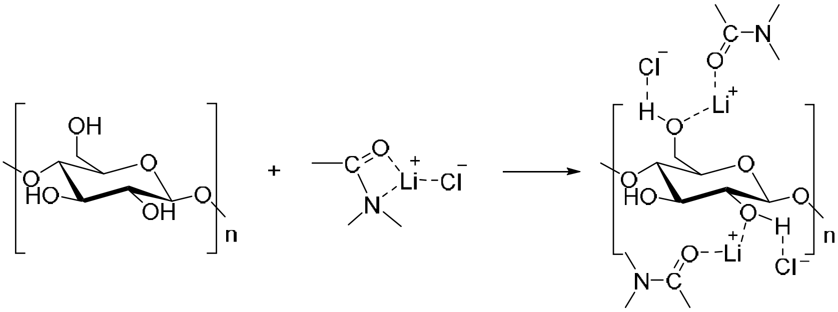


Figure 17 Cellulose dissolution in DMA/LiCl system[120, 128]

Merceration is a method in which cellulose is soaked in strong alkali to produce cellulose II. Other alkaline systems with aqueous alkali hydroxides, such as sodium hydroxide and lithium hydroxide water solutions, are able to dissolve cellulose with low DP values (under 200).[124] Cotton linters with DP of 850 have also been dissolved in lower temperatures (-15 and -20°C) in 6% NaOH water solutions,[134] but for wood pulps, such systems are not effective.[135] In addition, in solvent systems with thiourea- or urea-NaOH, the urea stabilizes the swollen cellulose molecules and helps the alkali to reach crystalline regions with the aid of a freeze–thaw cycle.[136-137]

In the Lyocell process, cellulose is dissolved in *N*-methylmorpholine-*N*-oxide (*N*MMO), which has been proven to be a successful alternative to the Viscose process for producing synthetic cellulose fibers. With *N*MMO (**Figure 18**), the dissolution of cellulose is obtained without derivatization and significant change in DP.[138] In the Lyocell process, the dissolution of cellulose relies on the dipolar character of amine oxide, and the *N*MMO is said to rupture the ionic forces of cellulose.[10, 139] The amount of water in the *N*MMO is crucial as only the monohydrate is able to dissolve cellulose. Larger water amounts lead to regeneration, and precipitation of cellulose occurs.[125] One major problem with the Lyocell process is the instability of *N*MMO, as it is a labile compound and an oxidant that can result in thermal runaway reactions.[140] Despite limitations of the *N*MMO and Lyocell processes, such as thermal instability and small dissolution windows, the industrial production of Lyocell fibers is at approximately 100,000 tons per year.[14, 125, 139]

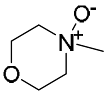


Figure 18 Structure of *N*-methylmorpholine-*N*-oxide (*N*MMO)

1.5 Acetylation of wood polymers

1.5.1 Acetylation of polysaccharides

Acetylation changes the chemical moiety of polysaccharides from free hydroxyls to more hydrophobic acetyl groups. Hemicelluloses have different amounts of hydroxyl groups depending on the backbone sugar units due to the variation in their structures. On the other hand, polysaccharide structures have two main reaction sites for reactions to occur. These reactions are either primary or secondary hydroxyl group reactions. In general, the primary groups are more prone to react. In addition, the cellulose and hemicellulose chains have glycosidic bonds between monomer units. These are prone to hydrolytic cleavage reactions, especially under acidic conditions, resulting in chain degradation and lowering the degree of polymerization.[10] Usually, lowering of DP is avoided and can be solved with the selection of a solvent system, reagents, and reaction conditions.

Polysaccharide modifications and especially acetylation have been studied widely in common cellulose solvents and ionic liquids. Acetylation can be performed with acetic anhydride (**I**) and acetyl chloride (**IV**), but isopropenyl acetate and vinyl acetate have also been used (**I, II**). The most common route for cellulose acetate (CA) production has been patented by Eastman Company.[141] This system produces CA in a heterogenous system using acetic anhydride, acetic acid as reagents, and sulfuric acid as a catalyst. The process itself produces cellulose triacetate, which is then hydrolyzed with aqueous alkali to the desired degree of acetylation. The disadvantage is that the DP of the cellulose chain is reduced due to acid hydrolysis.

From the organic solvents, an important route for preparing cellulose acetate in laboratory is the DMA/LiCl system in which the reaction is usually performed with acetic anhydride. Mixed cellulose esters can also be obtained, such as acetate-butyrate with corresponding butyric anhydride.[142] The solvent DMA, unreacted acetic anhydride, and side product acetic acid are usually removed by distillation or washing. McCormic and Callais conducted similar reactions of cellulose esterification with anhydrides (or acyl chlorides) with an amine catalyst.[143] In DMA/LiCl, the cellulose has been activated by either heat or a solvent exchange to enhance the reactivity of the cellulose hydroxyl groups. The role of activation is to further break down the hydrogen bonds between the cellulose chains and improve the reactivity of the hydroxyl groups.

Ionic liquids have been used in cellulose esterifications and acetylations for almost two decades now. In this application, the ionic liquid acts (usually) as a base catalyst in the reactions, enabling the reactions to proceed without additional catalysts. The first study was published by Wu *et al.* (2004), in which the homogeneous acetylation of cellulose was accomplished with acetic anhydride in [amim]Cl.[144] Other imidazolium-based ILs such as [emim]Cl,[110] [bmim]Cl,[145] 1-allyl-2,3-dimethylimidazolium bromide [admim]Br, and 1-*N*-butyl-2,3-dimethyl-imidazolium chloride [bdmim]Cl[107] have also been applied in the synthesis of CAs. Granström *et al.*[146] proposed the use of an additional base with anhydrides for enhancing reactivity and trapping the formed acid, hence reducing the chain degradation of the cellulose.[146] More recently, co-solvents such as DMSO, DMA, DMI, acetone, and acetonitrile have also been applied with [DBNH][OAc],[147] [bmim][OAc],[148] [bmim]Cl,[149] and [amim]Cl[150] in cellulose acetylation. In addition, SILs with a co-solvent have been applied, and a rapid reaction was observed in a “relatively homogeneous” system.[88]

Another reagent, isopropenyl acetate, is usually used in esterification reactions of tertiary alcohols, hydroxy esters, and nitriles, which have the tendency to dehydrate with acetic anhydride.[151] It has also been used in cellulose acetylations in [emim]Ac[152] and other imidazolium-based ILs with and without co-solvents.[153] In addition, DMSO as a co-solvent and [amim]Cl with a DBU base catalyst have been reported.[154] In the current thesis (**I, II**), isopropenyl acetate was used in cellulose acetylations in [DBNH][OAc] without additional solvents or bases.

1.5.2 Pros and cons of solvents in cellulose modifications

One could presume that the Viscose and Lyocell processes, which are the main processes for producing cellulose fibers, would be feasible routes for cellulose functionalization, especially acetylation. In the Viscose process, the hydroxyls are already substituted by xanthogenate esters. In addition, the amounts of water and base (sodium hydroxide) would prevent acetylation reaction due to hydrolysis of the acetic anhydride to acetic acid. The Lyocell process, on the other hand, has *N*MMO monohydrate as a solvent and includes water. In addition, the chemical stability of *N*MMO is limited (runaway accidents with explosions have occurred).[140] While some experiments of acetylation with vinyl acetate have been conducted in *N*MMO, the degree of substitution of the product has been low.[155] This could be expected due to the probable hydrolysis of vinyl acetate to acetic acid and acetaldehyde in dissolution conditions (water solutions). The *N*MMO monohydrate is also used as a catalyst and oxidant in organic reactions, thus the use of *N*MMO in chemical modifications, especially at industrial scale, is questionable.

In DMA/LiCl, various reactions have been conducted, although its recyclability is challenging and DMA is a toxic, carcinogenic, and mutagenic solvent. With DMSO/TBAF, even small amounts of water increase viscosity and swell the cellulose, complicating the dissolution process.[131] Side reactions are also plausible, especially oxidation reactions with DMSO since it is an oxidant. In addition, the purification and recyclability of such solvent systems is quite tedious.

When comparing ILs, the commonly used [emim][OAc] is a good comparison for [DBNH][OAc]. The lower melting point and viscosity of [emim][OAc] are good characteristics, but it has poorer thermal stability with chain degradation of cellulose (especially when stored at elevated temperatures).[156] Moreover, with [emim][OAc], a side reaction with acetate anions and cellulose hydroxyl groups limits its use.[157] A less important side reaction occurs between the C-1 carbon of the reducing end of the cellulose chain and the imidazolium part of the IL.[111] On the other hand, the tolerance for impurities such as water is moderate with [DBNH][OAc], although some hydrolysis of the IL occurs.[158] The need for catalysts and co-solvents depends on the used reagents and solvent systems. The use of a catalyst can be important to promote reactivity. On the other hand, addition of a base as an acid scavenger is often used for preventing hydrolysis of cellulose. However, one should determine whether is it possible to select the base in such a way that no side products nor impurities accumulate to the solvent. With [DBNH][OAc], the solution is quite easy: add DBN. The need for a co-solvent, on the other hand, is usually related to reducing viscosity, which concomitantly increases the reactivity. However, the recovery (and recyclability) of the reagents and solvent usability can be hindered, especially on a large scale. In addition, difficulties purifying ionic liquids may occur with the use of co-solvents.

1.5.3 Acetylation of lignin

Acetylation of lignin is a method to modify lignin to become more soluble in organic solvents. One important reason is the use of lignin in manufacturing processes. For example, partially acetylated Kraft lignin has been used in lignin-based synthetic polymers[159-160] and carbon fibers.[161] In addition, acetylated alkaline lignin from wheat has been used to prepare colloidal spheres.[162] Acetylation of lignin is also used in solvent state NMR studies, since acetylated lignin is usually soluble in common deuterated NMR solvents such as chloroform or dimethylsulfoxide. Milled wood lignin, or Björkman lignin,[163] does not necessarily need to be acetylated to be analyzed in DMSO-d_6 or in dioxan-water solutions, although the resolution of the plain ^{13}C NMR spectra is limited.[164] Nowadays, more efficient two-dimensional NMR techniques are used for structural identification.[46] Via acetylation, the product is soluble and the possibility of obtaining clear signals in NMR spectra increases. On the other hand, residual (or thermally processed, see 1.2.4) Kraft lignin is more condensed and thus requires chemical modification to obtain soluble products.[32, 165]

2 Aims of the study

The aims of this work is to discover new possible routes to modify wood-based cellulose. The original idea started during the laboratory work for **Article IV** with Agnes Stepan in which hemicelluloses were acylated in ionic liquids to form transparent films. As a continuum, the idea was to test the novel ionic liquid, which has been developed and tested in our research group[71, 158] to cellulose modifications. The aims were to develop a homogeneous reaction route in an ionic liquid, [DBNH][OAc], to produce cellulose acetates and develop a method, in which different degree of substitutions were obtained. Furthermore, the objective was to produce spinnable cellulose acetate with diverse degree of substitutions.The formation of cellulose acetates (**Article I**) in the IL was successful. Therefore, the collaboration with Aalto University and Shirin Asaadi began, and the most promising reaction route for cellulose acetate was adopted and modified for fiber spinning, hence **Article II** was published.

During the cellulose work, lignin was also studied and the reaction routes of **Article I** were tested for lignin. Some unpublished data is included to this thesis, and while working with lignin, some special notifications of the structure of hydrothermally treated lignin were made, leading to the **Article III** as a natural continuation.

3 Results and discussion

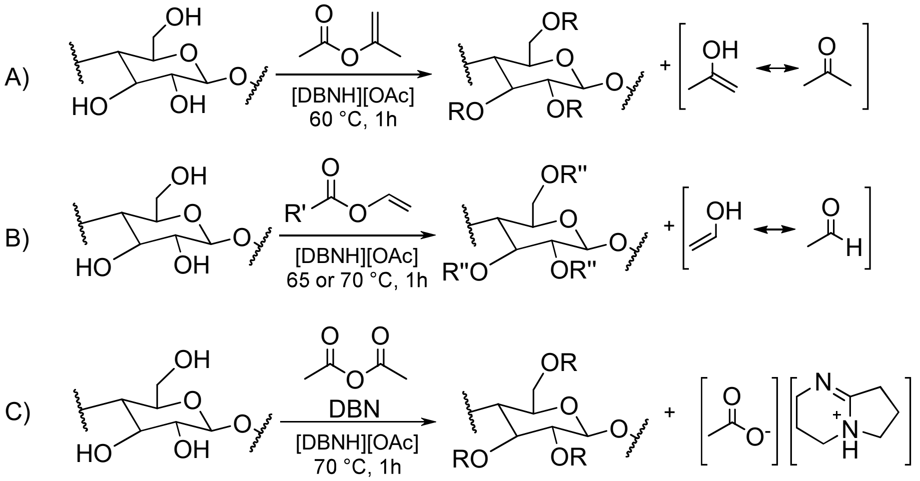
3.1 Experimental notes

Experimental procedures and analytical methods can be found in the original publications **I–IV**. Other unpublished lignin studies included in this thesis were prepared for Protobind 1000 wheat straw lignin, Lignoboost lignin, and milled wood lignin from birch, spruce, pine, and eucalyptus, which were prepared by ball milling.[166]

3.2 Esterification of cellulose in [DBNH][OAc]

The most important cellulose derivative with a wide range of industrial products is cellulose acetate.[112] In current industrial processes, the preparation of cellulose acetates is based on heterogenous processes, which were first invented by Schüzenberger (1865) and patented in 1927 by Herbert Mallabar[167] and later by Eastman company in 1956.[141] The acetylation reaction itself produces cellulose triacetate, with acetic acid and acetic anhydride as reagents and sulfuric acid as a catalyst. To achieve a lower substitution level to the cellulose, the product needs to be hydrolyzed, hence the process involves several steps.[10] More recently, homogeneous systems have been developed, providing a method to obtaining uniform distribution of substituents. The most common media for homogeneous reactions include ionic liquids,[88, 107, 144, 147, 152] non-aqueous organic solvents with salts (LiCl/DMA) and (DMSO/TBAF)[168] or *N*MMO.[169]

In study **I**, tunable esterification of cellulose was obtained in [DBNH][OAc] with both acetic anhydride (Ac_2O) and isopropenyl acetate (Ip*e*Ac). A lower, but tunable, degree of substitution (DS) was obtained using vinyl acetate (VinAc) or vinyl propionate (VinPr). The reagents were chosen in such a way that the byproduct would be easily removable, or at least would not contaminate the used ionic liquid. Further, with acetic acid, excess base (DBN) of the IL was used to bind the formed side product acetic acid (C) in **Scheme 2**.



Scheme 2 Acylation of cellulose in [DBNH][OAc]. The forming side products are acetone for IpeAc (A) and acetaldehyde for VinAc and VinPr (B). With Ac_2O, excess DBN is used (C), and thus the released acetic acid is bound to the base and [DBNH][OAc] is formed. R= CH_3CO (Ac), R'= methyl or ethyl and R''= Ac or CH_3CH_2CO (Pr) (Article I)

When comparing the reaction with isopropenyl acetate (route A in **Scheme 2**) with the literature, acetylation in [DBNH][OAc] does not require a remarkable excess of reagents or activation for the reaction to occur.[152-153] Also, the [DBNH][OAc] has other advantages. First, the superbase salts are recyclable.[82] Secondly, the dissolution and reaction times are shorter with [DBNH][OAc] than with *e.g.* imidazolium based ILs. Furthermore, catalysts and co-solvents are not needed, as is the case with imidazolium-based ILs. [145, 147-149, 170-171] Typically, with imidazolium ILs the co-solvents are needed when the formed cellulose ester is not soluble to the IL media.

Acetylation was also performed with acetic anhydride in [DBNH][OAc], as this is still the main industrial method to produce cellulose acetates.[172] With acetic anhydride, an additional base is usually required to prevent possible cellulose chain hydrolysis, especially if water is present, leading to lower DP of the polymer. Previously, Abe[173] used both acid chlorides and Ac_2O in imidazolium-based ionic liquids, Wu[144] and Cao[174] used Ac_2O in [Amim]Cl without the addition of a base. However, no GPC data were reported, and some hydrolysis of the cellulose is likely to occur. Also, the recycling of these ILs is difficult, and the formed side product, acetic acid, might be difficult to separate from the used ILs. In this study, these problems were overcome with the equimolar addition of DBN (vs. Ac_2O), which in practice forms new IL in the system, simultaneously reducing viscosity.

Vinyl esters with long carbon chains (C_8 to C_{16}) have previously been used in cellulose esterification in [emim][OAc] with successful esterification but had undesirable side reactions with the IL.[175] Other studies have been conducted but only in organic solvents with the use of activation or catalysts.[168, 176-179] Chen *et al.* obtained high DS values (2.5) when using NaOH activation in their reactions, but the DP of the product decreased significantly.[179] In our case with vinyl acetate, the maximum obtainable DS was 1.5, but the decrease of DP was not substantial (**Figure 20**).

The reaction of Ip*e*Ac and Ac_2O in [DBNH][OAc] was almost instantaneous. For example, with higher loadings of Ip*e*Ac, the reaction side product, acetone, could be seen from the formation of vapors in the flask. Short 0.5–2 h reaction times were enough for a complete reaction with both Ip*e*Ac and Ac_2O. In the case of vinylic reagents, the reaction was also fast but did not form high DS products, although the reaction time and (or) amount of reagent was increased to 24 h and 9 eq/AGU.

Dried reaction products were analyzed with ATR-IR, ^{31}P NMR, and GPC. The DS of the reaction products were analyzed with ^{31}P NMR with a slightly modified method from King *et al.*[180] The determined DS values were between 0.23 and 3, which corresponded with the amount of used reagent. Furthermore, the recovery of the products was very high—more than 80% according to the calculated DS in all cases (**Table 2**).

Table 2. *Values of DS for different reagents where variable amounts of reagent were used. The results have been calculated from 1 h reaction samples made from eucalyptus pulp cellulose, which were analyzed using* ^{31}P *NMR*

Reagent	0.25 eq/AGU		1 eq/AGU		3 eq/AGU	
	DS	Yield %	DS	Yield %	DS	Yield %
Ac_2O	0.23	95	0.85	88	2.80	88
VinAc	0.24	98	0.84	88	1.58	90
VinPr	0.23	94	0.85	86	1.34	85
IpeAc	0.23	92	0.89	82	2.97	95

The functional group analysis for the reaction products was done with ATR-IR. The reactions and reactivity were followed with the reduction of hydroxyl signal intensity with the simultaneous increase of the carbonyl signal intensity. It was noticed quite quickly during the syntheses and screening of the products that there seemed to be a clear correlation between the amount of reagents used and carbonyl signal intensity in the IR spectra. This led to the idea of comparing the results of the two analysis methods, ^{31}P NMR and ATR-IR. When the results of two separate methods are plotted against each other and a good (over 80 %) linear correlation is obtained, the two methods can be used separately with the use of the linear equation. On the other hand, to evaluate and quantify IR data, there must be some signals that stay stagnant during the process. The cellulose chain has C-O-C signals, which belong to the glucopyranose ring and are in the cellulose backbone. These are unaltered in the acetylation reactions. Thus, a correlation between the ^{31}P NMR results and ATR-IR signal intensity was found (**Figure 19**). This is a good observation, since in principle IR can be used as a screening method for cellulose acetate samples. In the cases in which the method can be taken into operation, there would not be a need for routine ^{31}P NMR analysis. Only an occasional update to the linear correlation of data points might be necessary.

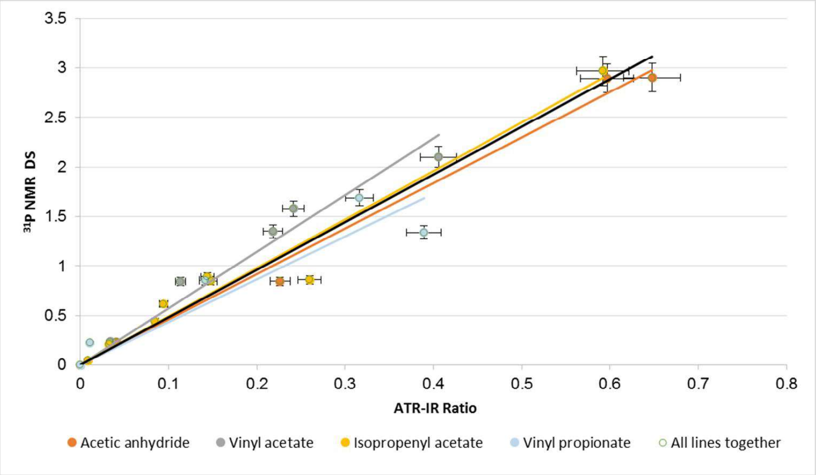


Figure 19 The correlations of the ^{31}P NMR and ATR-IR results for determination of degree of substitution. Reactions from: Ac_2O (orange), Ip*e*Ac (yellow), VinAc (gray), and VinPr (blue). The correlation of all data points is represented as a black line (Article I)

The degree of polymerization of the products was analyzed by GPC with an RI detector, which means that the obtained values are relative and not exact. In addition, pullulan standards were utilized. Pullulan is a polymer with *α*-(1-4) glycosidic linkages between glucopyranose units and thus has a different hydrodynamic volume than cellulose. Berggren *et al.* proposed a method in which correction factors are used to calculate pullulan standards to represent cellulose.[181] This method is reasonable, but the fact that analytical systems differ from each other greatly prohibited the use of the correction method in **Article I**. The hydrodynamic volume of cellulose derivatives might also change due to differences in molecular structure. A multi-angle laser light scattering (MALLS) technique would give more precise results, especially when the samples are functionalized cellulose products and not pure cellulose with free OH groups.[17]

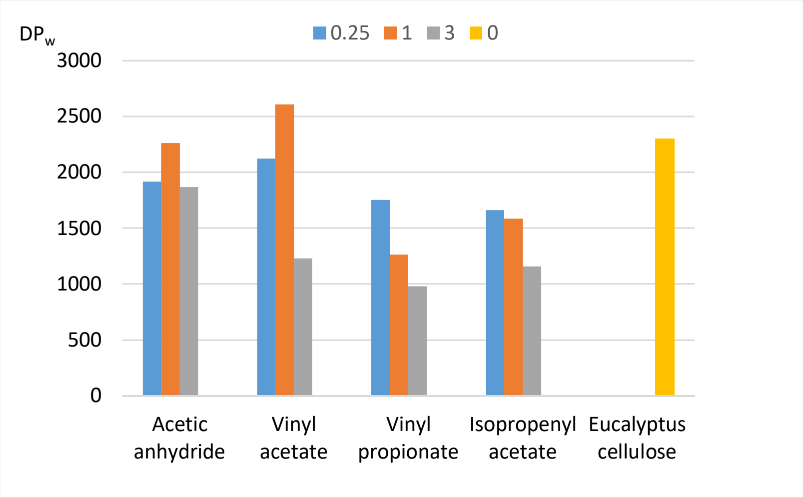


Figure 20 Weight average degree of polymerization DPw of the cellulose acetates obtained with different reagents and used equivalents of the corresponding reagent. DP$_w$ is calculated with DS obtained with ^{31}P NMR from the corresponding M$_W$

The weight average degree of polymerization (DP$_w$) results from the reaction samples are represented in **Figure 20**. It can be seen that the molecular weight drops in almost all cases, although the drop is smallest with acetic anhydride. Unfortunately, an appropriate explanation for the apparent chain degradation has not been found. Evidence of a uniform structure is proven by the GPC graphs, which show a nice Gaussian curve and only a small shoulder in the smaller mass range area. This can also be seen in the blank sample (**Figure 21**).

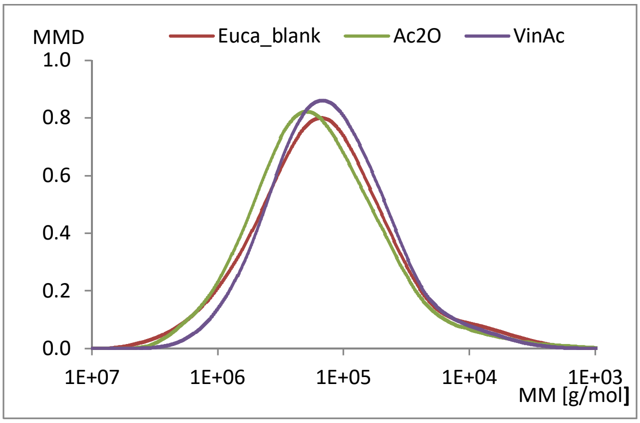


Figure 21 GPC graphs of the reaction products from the reactions made with acetic anhydride (Ac_2O) in green and vinyl acetate (VinAc) in purple; for reference, the blank sample (Euca_blank) of eucalyptus pulp is shown in red

In **Article I,** it was found that both acetic anhydride and isopropenyl acetate produce cellulose acetates in [DBNH][OAc] with variable substitutions according to the amount of acetylation reagent. Because Ip*e*Ac does not need any additional base, as is the case with Ac_2O, the reaction was chosen to be upscaled for production of cellulose acetate fibers.

3.3 Cellulose acetate fibers

The Ip*e*Ac was found most suitable for acetylation of cellulose, thus a collaboration with Aalto University was initiated to produce cellulose acetate fibers. For fiber spinning, the reaction mass balances, reaction times, and reagent additions (obtained DS) with Ip*e*Ac were optimized. Fiber spinning and fiber characteristics were performed and determined by Asaadi *et al.* (Aalto University).

Large scale reactions with 13m-% of cellulose in [DBNH][OAc] were performed with successful reactivity and spinnability of all the dopes. The conversion of the acetylation reaction with Ip*e*Ac was found between 83–100%. This is excellent, since the added amount of reactant (0.05, 0.25, 0.5, and 0.75 eq) in the syntheses was small in volume compared to the reaction dope (mass). Additionally, uniform distribution of substituents in all reaction products was successful. Furthermore, all the dopes were spinnable using dry-jet wet spinning. Spinnability means that aligning cellulose molecules along the chain and stretching the filament are done with a reduction of linear density but without breaking the cellulose structure. The maximum draw ratios (DR) (*e.g.*, the ratio of the take-up velocity to the extrusion velocity) were good, being over eight (DR>8), for all samples.[182] As expected, the hydrophobicity of the fibers increased with DS > 0.5 because the acetyl group is less hydrophilic than hydroxyl groups.

The regenerated fibers were analyzed with ATR-IR (**Figure 22**). The spectra of the fiber filaments show the presence of the acetate groups' carbonyl signal (1725 cm^{-1}). However, with the analysis of very low DS values ATR-IR is inaccurate without a software. When comparing fiber with DS 0.05 to unmodified fiber, there is no visible change in the spectra at the carbonyl region. The first spectrum in which changes in the carbonyl region can be seen is the DS 0.21 sample. The situation could be different with the use of a screening software that compares whole spectra with each other, and not only selected signals with various wavenumbers.

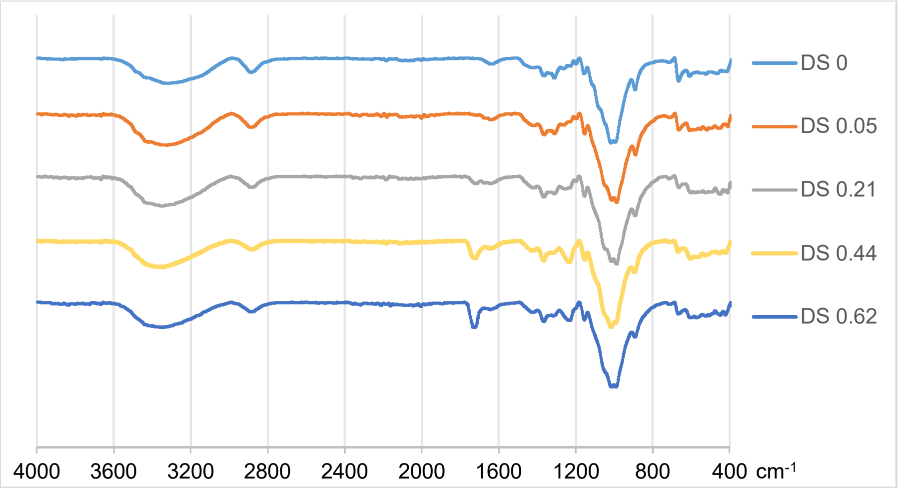


Figure 22 ATR-IR spectra of fibrillated cellulose acetates with various DSs. The reactions were made with isopropenyl acetate in [DBNH][OAc], with variable eq's of reagent.

3.4 Acetylation of xylans

In publication **IV**, rye arabinoxylan (AX) and spruce arabinoglucuronoxylan (AGX) were acetylated in [DBNH][OAc] and [emim][Me_2PO_4]. The study was done in collaboration with Agnes Stepan from the Chalmers University of Technology. Acetylation reactions for galactoglucomannans have been reported with a traditional acetic anhydride route with pyridine catalyst,[183] but for xylan acetylations in ILs had not been published.

The reactions were performed with acetic anhydride in both [DBNH][OAc] and [emim][Me_2PO_4], and with acetyl chloride in [emim][Me_2PO_4]. With the latter IL, the use of a co-solvent improved the results. The idea was to achieve full acetylation to produce transparent films for further processing.

The xylans were solubilized for 2 h to obtain a homogenous solution, but the reaction itself was fast. Full acetylation was achieved in [DBNH][OAc] in only five minutes. The reaction products were analyzed with FTIR (**Figure 23**) and NMR, which confirmed the degree of acetylation. The reactions for AGX made in [emim][Me_2PO_4] produced more condensed products, probably due to crosslinking of AGX carboxyl functionalities. Zoia *et al.* have studied possible crosslinking reactions of wood biopolymers during acetylation.[184] With [emim][Me_2PO_4], the addition of chloroform as a co-solvent promoted the acetylation reaction, presumably via solubilizing the partially acetylated product and thus producing a more homogenous product. This behavior has also been demonstrated by King *et al.,* who used ionic liquids to analyze cellulose phosphite esters.[185] The reaction products made in [emim][Me_2PO_4] with a co-solvent were insoluble in GPC and/or film casting solvents.

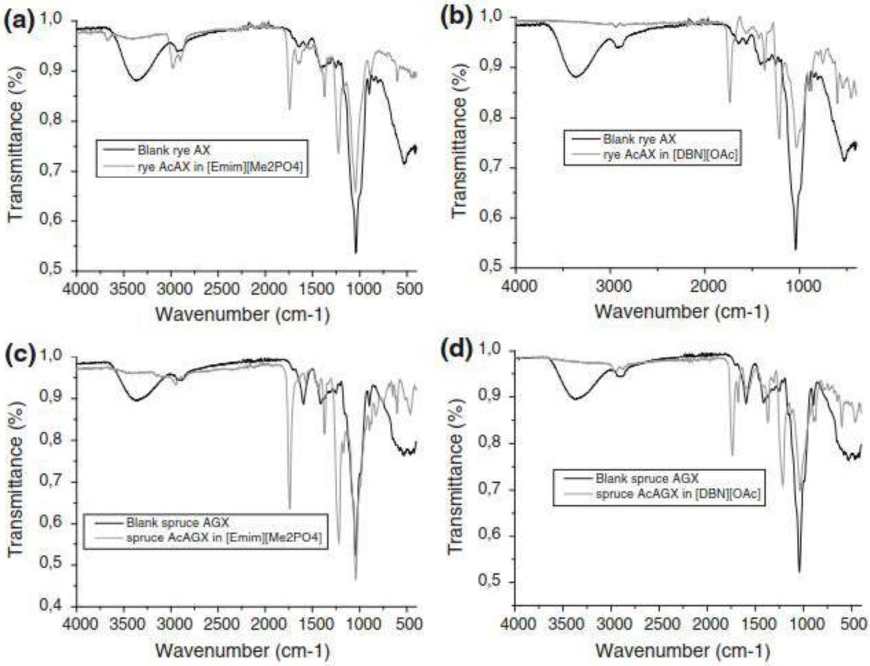


Figure 23 ATR-IR spectra of **a**) blank rye AX and acetylated in [emim][Me_2PO_4], **b**) blank rye AX and acetylated in [DBNH][OAc], **c**) blank spruce AGX and acetylated in [emim][Me_2PO_4], **d**) blank spruce AGX and acetylated in [DBNH][OAc] (Article IV)

The GPC analysis of the produced acetylated xylans showed no reduction in DP between the starting material and acetylated products. In addition, the film formation from chloroform and dimethyl carbonate solutions was successful for the acetylated rye AX samples and spruce AGX made in [DBNH][OAc].

More recently, new studies concerning hemicellulose acetylation in ionic liquids have been reported. These include acetylation of switchgrass hemicelluloses in [amim][Cl], but full acetylation was not achieved.[186] Another group used soy sauce residue as a hemicellulose resource. The acetylations were made in [amim]Cl and [bmim]Cl with acetic anhydride, and the DS results were satisfactory,[187] but no MW (GPC) data were reported.

3.5 Acetylation of lignin

The acetylation method in **Article I** was found to be very suitable for cellulosic samples. The idea for widening the usability of that system for lignin was reasonable, since lignin is acetylated to enhance the solubility of the product(s). Traditionally, acetylation of lignin is performed with acetic anhydride and pyridine for 24 h, but isopropenyl acetate reacts faster at least for cellulose in [DBNH][OAc].

Lignin acetylations were tested for various lignin samples—Kraft lignin, MWL of pine, spruce, and eucalyptus species—with different systems:

A. with the traditional pyridine-acetic anhydride method
B. with a similar system as in **Article I** using acetic anhydride, DBN, and the ionic liquid [DBNH][OAc]
C. with a similar system as in **Article I** using isopropenyl acetate and the ionic liquid [DBNH][OAc]
D. in isopropenyl acetate with and without a catalyst

The results showed (data unpublished) that for lignin, the used ionic liquid [DBNH][OAc] is not an ideal media, since the work-up of reaction products is tedious. However, the reaction itself is completed in 2 h and no hydroxyls can be detected in the IR spectra of several products. For comparison, method A with acetic anhydride and pyridine results in a 24 h reaction at RT, but the evaporation of solvents with the aid of toluene and ethanol is the only purification needed. On the other hand, method D with isopropenyl acetate as a “neat” reaction is quicker, but the use of *p*-toluenesulfonic acid monohydrate (*p*-TsOH) as a catalyst improved the reactivity. This requires washing and drying of the product, hence the work-up is again more tedious than in A.

In **Figure 24,** the ATR-IR spectra of both the unmodified and acetylated MWL from eucalyptus and pine are shown. In the spectra, a clear disappearance of hydroxyl group signals from unmodified samples (gray lines) at ~3440 cm^{-1} can be seen. Furthermore, in both acetylated samples (pine and eucalyptus), new signals are formed to 1732 cm^{-1} and 1370 cm^{-1}, corresponding to carbonyl and methyl group signals. Thus, full acetylation of both pine MWL and eucalyptus MWL can be achieved with pure Ip*e*Ac.

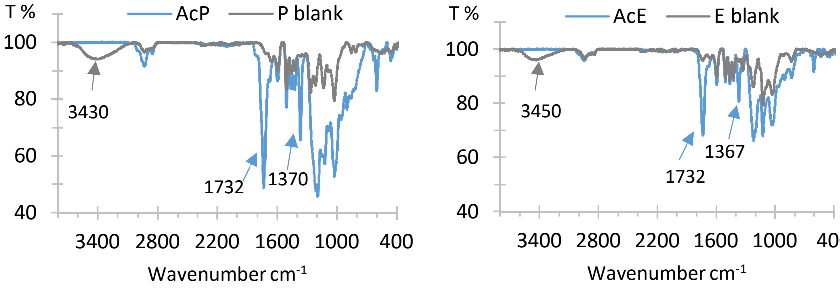


Figure 24 ATR-IR spectra of MWL lignin samples. On the left, acetylated pine (AcP) and unmodified pine (P blank); on the right, acetylated eucalyptus (AcE) and unmodified eucalyptus (E blank)

3.6 Heat treated lignin

Several kinds of starting materials such as agricultural residues, forest product leftovers, grass biomass, or lignin can be used in hydrothermal carbonization (HTC). The majority of the literature concerning hydrothermal carbonization of biomass have studied physical changes of the material such as particle size and porosity, which are of course important for product applicability.[55, 62] However, HTC causes structural changes to biomass and lignin, but the molecular and structural changes that occur during HTC are not understood in detail. This structural information is needed to tailor the properties of the product.

For Kraft lignin, many alterations in the structure have already taken place during cooking. Wikberg *et al.*[49] explored both structural and morphological changes for lignin and reported that in HTC, cleavage of β-O-4 bonds and demethylation occurs with a concomitant (slight) increase of C=C bonds according to solid state NMR and FTIR studies.[49]

The objective in **Article III** was to discover the primary reactions in Kraft lignin during the HTC process. Consequently, the reactions were made for softwood Kraft lignin in a mild alkaline solution (aqueous 1.5% NaOH) for a short reaction time (0.5 and 1 h) in three different temperatures (170, 200, and 235°C). The reactions were made in pressure reactors; the formed gas phase was not examined.

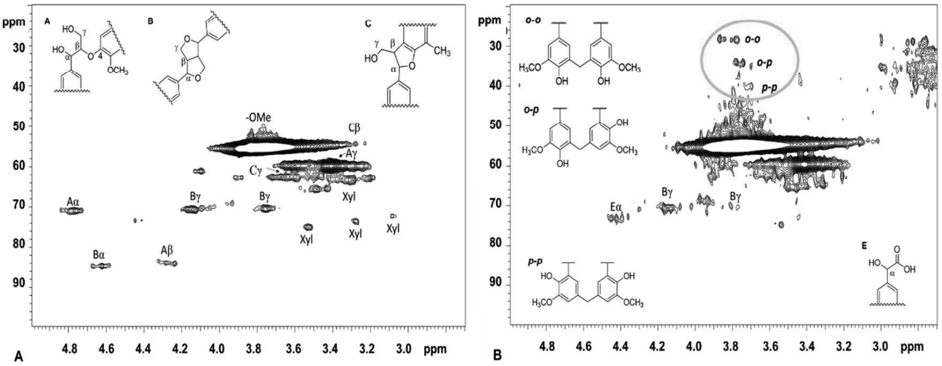
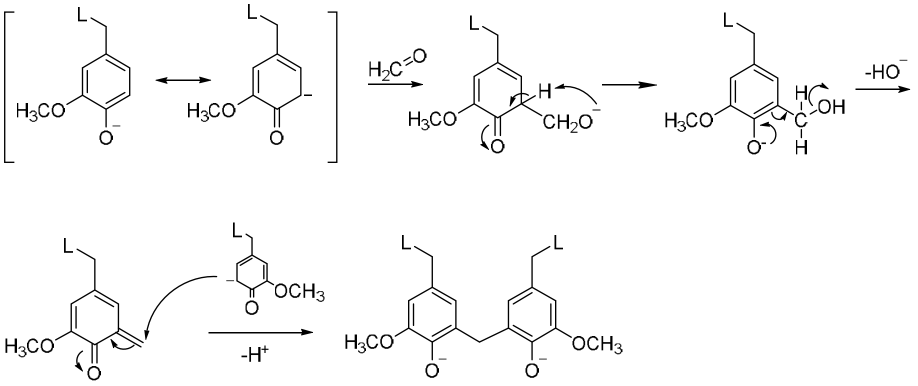


Figure 25 Expansion (side chain region) of the ^{1}H-^{13}C HSQC spectra of (A) Kraft lignin and (B) HTC lignin (170°C for 1 h)

An analysis of the reaction products was done with 2D solution-state NMR, since the products were soluble in DMSO-d_6. For comparison, the starting material was also analyzed. In **Figure 25,** the 2D ^{1}H-^{13}C HSQC NMR spectra of both unmodified Kraft lignin and HTC Kraft lignin are shown. There are clear differences in the spectra. In the Kraft lignin HSQC spectrum, typical lignin side chain structures can be identified (*e.g.*, *β*-O-4, *β*-*β,* and *β*-5, in **Fig. 25 A**, structures **A–C**, correspondingly).[28, 32, 38, 42] However, in the HTC lignin (**B**), all *β*-O-4 bonding patterns have vanished. The resinol (*β*-*β*) and phenylcoumaran (*β*-5) structures' corresponding signal intensities have also been reduced. On the other hand, new signals within the region of 3.7–3.9 ppm in the ^{1}H and 28–40 ppm in the ^{13}C field have appeared. Similar signals were detected in the NMR analysis of pine MWL–phenol-formaldehyde resins[42] but not in Kraft nor in HTC-processed Kraft lignins.

The NMR results for HTC lignin revealed the formation of *o*-*o*-, *o*-*p*-, and *p*-*p*- diarylmethane structures (relative to phenolic OH- groups in lignin subunits), which denotes that the formation of diphenyl methane structures in the HTC process form via a quinone methide route (**Scheme 3**).[42, 44] One would presume that only *o*-*o*-diphenyl methane structures would occur due to steric reasons, as in the softwood Kraft lignin, position 5 in the aromatic ring is already occupied with the lignin side-chain. On the other hand, the fragmentation of lignin is known to produce 2-methoxyphenol *i.e.*, quaiacol, where the ortho- and para- positions are free for condensation reactions and hence the occurrence of *o-p* and *p-p* structure signals is explained.



Scheme 3 An example of the formation of diphenylmethane structures in alkaline reaction conditions L=lignin[42, 44]

Ekman (1965), and later Gierer (1985), suggested that formaldehyde can be liberated under alkaline reaction conditions from lignin's *β*-O-4 and *β*-5 structures, yielding styryl ethers (vinyl ethers) and stilbenes, respectively.[42, 44, 188] In addition, the typical condensation reactions of phenols with formaldehyde forms polymerization products, which consist of diarylmethane structures. Thus, in this study, a model compound (*e.g.*, a guaiacol resin) was prepared with formaldehyde to verify the formation of different diphenylmethane structures. The structural analysis of the formed products show a clear correlation with the diarylmethane signals in both HTC lignin and model resin (**Figure 26**). In addition, the hydroxymethyl corresponding signals are clear in the guaiacol-formaldehyde resin but absent in the HTC lignin. It can be concluded that formaldehyde is formed in situ during the HT process and subsequent condensation reactions are immediate, as no signals for hydroxymethyl intermediate can be found in HTC lignin.

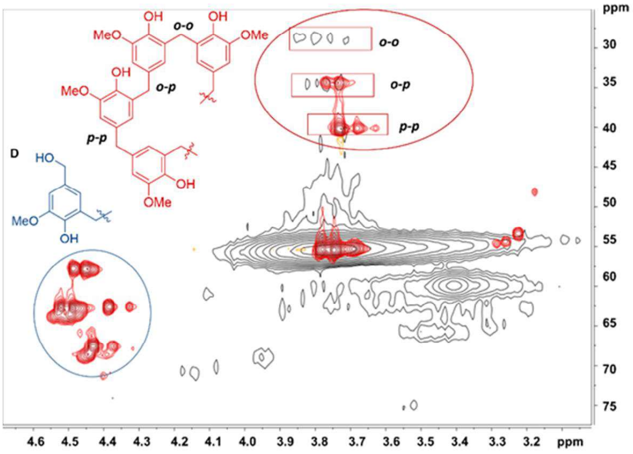


Figure 26 Superimposed ^{1}H-^{13}C HSQC spectra of the guaiacol formaldehyde resin (red) and HTC lignin (200°C,1 h) (black); the signals from the diphenyl methane structures are circled in red, and the hydroxyl methane (D) side group signals are circled in blue

To confirm the role of formaldehyde in the condensation reactions, the thermal liberation of formaldehyde was studied with Py-GC/MS. Previously, thermogravimetric (TG) analysis techniques have been used in analyzing volatiles from lignins. Faix *et al.* studied the evolution of formaldehyde in TG-MS studies to study the carbonization of lignins, but the degradation temperatures were quite high.[189] Zhang *et al.* and Ohra-aho *et al.* studied lignin with Py-GC/MS for analyzing the structural elements in lignin.[69, 190] In the current study, the idea was to ensure the thermal liberation of formaldehyde in mild pyrolysis conditions. Thus, low temperatures (170, 200, and 235°C) for pyrolyzation were used.

The study was done with the aid of a reference compound, thus a chromatogram with the corresponding mass spectra for formaldehyde was obtained. The liberation of formaldehyde was found in all Kraft lignin samples. The retention time (t_R) of formaldehyde was ~2.44 mins in the pyrolysis chromatogram, and m/z 30 as a base peak was found in the corresponding mass spectrum. The ion with m/z 29 was the second highest intensity signal, which could correspond to aldehyde (*m/z* 29) (*e.g.,* formaldehyde with the loss of hydrogen).

Both alkaline and thermal reactions of Kraft lignin produce formaldehyde. In alkaline conditions, condensation reactions occur and diphenylmethane structures are formed. In thermal conditions, the liberation of formaldehyde contributes to the carbonization of lignin.

4 Conclusions

In the current work, a new homogenous acetylation method for cellulose was developed. The reactions allow for adjusting the DS of cellulose acetates from very low to a maximum DS of 3. The reactions were successful for all reagents (Ip*e*Ac, Ac_2O, VinAc, and VinPr), although Ip*e*Ac and Ac_2O were found to be the most suitable. In addition, a method for analyzing the DS of the products using a linear correlation method between ^{31}P NMR and ATR-IR analytics was established.

The best option for acetylation in the used IL, [DBNH][OAc], was isopropenyl acetate. The main advantage of Ip*e*Ac over acetic anhydride (with DBN) was because its side product, acetone, can be evaporated from the system during or after synthesis. The approach of adding only one reagent is also cost-effective. On the other hand, the cellulose acetates obtained with Ac_2O retain their DP better than with Ip*e*Ac. The fibers obtained from large-batch acetylation showed good spinnability and fiber characteristics. The method can be scaled up to produce textiles of non-woven material with tailored properties.

In the future, the IL method could be expanded to other cellulose derivatives, as new IL are invented and produced all the time and the development of new products is never-ending. The possibility of finding and developing more sustainable ILs and applications for products would be rewarding.

The acetylation of hemicelluloses, especially xylans in ionic liquids, was also conducted successfully. The main future challenge lies in combining the modification of xylans into a refinery concept without additional processing steps.

The acetylation of lignin has shown potential, but more work is needed to be able to combine the obtained results. The main issue lies with the heterogeneity of lignin samples and finding a general modification pathway for variable lignin preparates.

The demonstration of diphenylmethane structures with the aid of NMR studies has proven the occurrence of the elimination of formaldehyde during the alkaline process. Understanding the structural changes during various modifications is essential for the controlling of materials to be used in tailored, high-value products.

5 References

1. Hämmerle, F. M., *Lenzinger Berichte* **2011,** *89*, 12-21.

2. Michud, A., Tanttu, M., Asaadi, S., Ma, Y., Netti, E., Kääriäinen, P., Persson, A., Berntsson, A., Hummel, M.; Sixta, H., *Textile Research Journal* **2016,** *86* (5), 543-552.

3. Sixta, H., Michud, A., Hauru, L., Asaadi, S., Ma, Y., King, A. W. T., Kilpeläinen, I.; Hummel, M., *Nordic Pulp & Paper Research Journal* **2015,** *30* (1), 43-57.

4. Ragauskas, A. J., Beckham, G. T., Biddy, M. J., Chandra, R., Chen, F., Davis, M. F., Davison, B. H., Dixon, R. A., Gilna, P., Keller, M., Langan, P., Naskar, A. K., Saddler, J. N., Tschaplinski, T. J., Tuskan, G. A.; Wyman, C. E., *Science* **2014,** *344* (6185).

5. Jääskeläinen, A.-S.; Sundqvist, H., *Puun Rakenne ja Kemia*. Otatieto: 2007; 142 p.

6. Sjöström, E., *Wood Chemistry Fundamentals and Applications*. Academic Press. inc. : Orlando, 1981; 223 p.

7. Gellerstedt, G., Pulping Chemistry and Technology 2009; Vol. Volume 2.

8. Carpita, N. C. R., John; McCann, Maureen C., Biochemistry and Molecular Biology of Plants. Bob, B. B., Ed. Wiley: Chicester, 2012; Vol. Second edition, pp 45-110.

9. Côté, W. A., Jr., *Wood Ultrastructure*. University of Washington Press: Seattle, 1967.

10. Klemm, D., Philipp, B., Heinze, T., Heinze, U.; Wagenknecht, W., *Comprehensive Cellulose Chemistry Functionalization of Cellulose*. Wiley-vch: Weinheim, 1998; Vol. 2, 389 p.

11. Fengel, D.; Wegener, G., Wood : Chemistry, ultrastructure, Reactions. De Gruyter, Inc.: Berlin/Boston, Germany, 2011; pp 20-119.

12. Gardner, K. H.; Blackwell, J., *Biopolymers* **1974,** *13* (10), 1975-2001.

13. Kolpak, F. J.; Blackwell, J., *Macromolecules* **1976,** *9* (2), 273-278.

14. Klemm, D., Heublein, B., Fink, H. P.; Bohn, A., *Angewandte Chemie International Edition* **2005,** *44* (22), 3358-3393.

15. Belgachem, M.; Gandini, A., Production, Chemistry and Properties of Cellulose-Based Materials. In *Biopolymers: New Materials for Sustainable Films and Coatings*, Plackett, D., Ed. John Wiley & Sons, Incorporated: New York, 2011; Vol. 1, pp 151-179.

16. Henriksson, G., Gellerstedt, G.; Ek, M., Wood Chemistry and Wood Biotechnology. In *Pulp and Paper Chemistry and Technology*, De Gruyter: Berlin, 2009; pp 89-94.

17. Potthast, A., Radosta, S., Saake, B., Lebioda, S., Heinze, T., Henniges, U., Isogai, A., Koschella, A., Kosma, P., Rosenau, T., Schiehser, S., Sixta, H., Strlič, M., Strobin, G., Vorwerg, W.; Wetzel, H., *Cellulose* **2015,** *22* (3), 1591-1613.

18. Kilpelainen, P. O., Hautala, S. S., Byman, O. O., Tanner, L. J., Korpinen, R. I., Lillandt, M. K. J., Pranovich, A. V., Kitunen, V. H., Willfor, S. M.; Ilvesniemi, H. S., *Green Chemistry* **2014,** *16* (6), 3186-3194.

19. Henriksson, G., Gellerstedt, G.; Ek, M., Wood Chemistry and Wood Biotechnology. In *Pulp and Paper Chemistry and Technology*, De Gruyter: Berlin, 2009; pp 121-145.

20. Boerjan, W., Ralph, J.; Baucher, M., *Annual Review of Plant Biology* **2003,** *54* (1), 519-546.

21. Brunow, G., Gruber, P. t.; Kamm, B. t.; Kamm, M. t., Eds. Wiley-VCH: Weinheim, 2006; pp 151-163.

22. Adler, E., *Wood Science and Technology* **1977,** *11* (3), 169-218.

23. Nimz, H., *Angewandte Chemie International Edition in English* **1974,** *13* (5), 313-321.

24. Brunow, G., Kilpelainen, I., Lapierre, C., Lundquist, K., Simola, L. K.; Lemmetyinen, J., *Phytochemistry* **1993,** *32* (4), 845-850.

25. Brunow, G., Ammalahti, E., Niemi, T., Sipila, J., Simola, L. K.; Kilpelainen, I., *Phytochemistry* **1998,** *47* (8), 1495-1500.

26. Capanema, E. A., Balakshin, M. Y.; Kadla, J. F., *Journal of Agricultural and Food Chemistry* **2004,** *52* (7), 1850-1860.

27. Ralph, J., Lundquist, K., Brunow, G., Lu, F., Kim, H., Schatz, P. F., Marita, J. M., Hatfield, R. D., Ralph, S. A., Christensen, J. H.; Boerjan, W., *Phytochemistry Reviews* **2004,** *3* (1), 29-60.

28. Ämmälahti, E., Brunow, G., Bardet, M., Robert, D.; Kilpeläinen, I., *Journal of Agricultural and Food Chemistry* **1998,** *46* (12), 5113-5117.

29. Brunow, G.; Lundquist, K., Lignin and Lignans: Advances in Chemistry. Heitner, C., Ed. CRC Press Inc: 2016.

30. Karhunen, P., Rummakko, P., Sipilä, J., Brunow, G.; Kilpeläinen, I., *Tetrahedron Letters* **1995,** *36* (1), 169-170.

31. Karhunen, P., Rummakko, P., Sipila, J., Brunow, G.; Kilpelainen, I., *Tetrahedron Letters* **1995,** *36* (25), 4501-4504.

32. Liitiä, T. M., Maunu, S. L., Hortling, B., Toikka, M.; Kilpeläinen, I., *Journal of Agricultural and Food Chemistry* **2003,** *51* (8), 2136-2143.

33. Chakar, F. S.; Ragauskas, A. J., *Industrial Crops and Products* **2004,** *20* (2), 131-141.

34. Ede, R. M.; Brunow, G., *J. Org. Chem.* **1992,** *57* (5), 1477-80.

35. Ede, R. M.; Kilpeläinen, I., *Research on Chemical Intermediates* **1995,** *21* (3), 313-328.

36. Dimmel, D.; Gellerstedt, G., Chemistry of alkaline pulping. In *Lignin and Lignans: Advances in Chemistry*, Heitner, C., Ed. CRC Press Inc: 2016.

37. Bozel, J. J., Holladay, J. E., Johnson , D.; White, J. F. Pacific Northwest National Laboratory and National Renewable Energy Laboratory: Tennessee, USA, 2007; 87 p.

38. Hu, Z., Du, X., Liu, J., Chang, H.-m.; Jameel, H., *Journal of Wood Chemistry and Technology* **2016,** *36* (6), 432-446.

39. Sixta, H., *Handbook of Pulp*. Wiley-VCH: Weinheim, 2006; 1352 p.

40. Gierer, J., *Wood Science and Technology* **1980,** *14* (4), 241-266.

41. Gellerstedt, G., *Industrial Crops and Products* **2015,** *77*, 845-854.

42. Yelle, D. J.; Ralph, J., *Int. J. Adhes. Adhes.* **2016,** *70*, 26-36.

43. Gellerstedt, G.; Gustafsson, K., *Journal of Wood Chemistry and Technology* **1987,** *7* (1), 65-80.

44. Gierer, J., *Wood Science and Technology* **1985,** *19* (4), 289-312.

45. Crestini, C., Melone, F., Sette, M.; Saladino, R., *Biomacromolecules* **2011,** *12* (11), 3928-3935.

46. Heikkinen, S., Toikka, M. M., Karhunen, P. T.; Kilpelaeinen, I. A., *J. Am. Chem. Soc.* **2003,** *125* (14), 4362-4367.

47. Landucci Lawrence, L., In *Holzforschung - International Journal of the Biology, Chemistry, Physics and Technology of Wood*, 1985; Vol. 39, p 355.

48. Yang, W., Shimanouchi, T.; Kimura, Y., *ACS Sustainable Chemistry & Engineering* **2015,** *3* (4), 591-598.

49. Wikberg, H., Ohra-aho, T., Pileidis, F.; Titirici, M.-M., *ACS Sustainable Chemistry & Engineering* **2015,** *3* (11), 2737-2745.

50. Wikberg, H., Ohra-aho, T., Honkanen, M., Kanerva, H., Harlin, A., Vippola, M.; Laine, C., *Bioresource Technology* **2016,** *212*, 236-244.

51. Wikberg, H., Grönqvist, S., Niemi, P., Mikkelson, A., Siika-aho, M., Kanerva, H., Käsper, A.; Tamminen, T., *Bioresource Technology* **2017,** *235*, 70-78.

52. Wikberg, H., Gronberg, V., Jermakka, J., Kemppainen, K., Kleen, M., Laine, C., Paasikallio, V.; Oasmaa, A., *Tappi J.* **2015,** *14* (3), 195-207.

53. Shen, Y., *Industrial & Engineering Chemistry Research* **2016,** *55* (44), 11638-11644.

54. Mäkelä, M., Benavente, V.; Fullana, A., *Bioresource Technology* **2016,** *200*, 444-450.

55. Lynam, J. G., Reza, M. T., Yan, W., Vásquez, V. R.; Coronella, C. J., *Biomass Conversion and Biorefinery* **2015,** *5* (2), 173-181.

56. Lu, X.; Berge, N. D., *Bioresource Technology* **2014,** *166*, 120-131.

57. Rodríguez Correa, C., Stollovsky, M., Hehr, T., Rauscher, Y., Rolli, B.; Kruse, A., *ACS Sustainable Chemistry & Engineering* **2017,** *5* (9), 8222-8233.

58. Zhai, Y., Peng, C., Xu, B., Wang, T., Li, C., Zeng, G.; Zhu, Y., *Energy* **2017,** *127*, 167-174.

59. Rodriguez Correa, C., Bernardo, M., Ribeiro, R. P. P. L., Esteves, I. A. A. C.; Kruse, A., *Journal of Analytical and Applied Pyrolysis* **2017,** *124*, 461-474.

60. Kim, D., Lee, K.; Park, K. Y., *Journal of Industrial and Engineering Chemistry* **2016,** *42*, 95-100.

61. Kang, S., Li, X., Fan, J.; Chang, J., *Renewable and Sustainable Energy Reviews* **2013,** *27*, 546-558.

62. Kang, S., Li, X., Fan, J.; Chang, J., *Industrial & Engineering Chemistry Research* **2012,** *51* (26), 9023-9031.

63. Curtze, J. H., Baer, F., Steffan, J., Doerr, T.; Vogel, H., *Chem. Eng. Technol.* **2017,** *40* (6), 1190-1195.

64. Funke, A.; Ziegler, F., *Biofuels, Bioproducts and Biorefining* **2010,** *4* (2), 160-177.

65. Fang, J., Zhan, L., Ok, Y. S.; Gao, B., *Journal of Industrial and Engineering Chemistry* **2018,** *57*, 15-21.

66. Dinjus, E., Kruse, A.; Tröger, N., *Chemical Engineering & Technology* **2011,** *34* (12), 2037-2043.

67. Lima, C. F., Barbosa, L. C. A., Silva, M. N. N., Colodette, J. L.; Silvério, F. O., *Journal of Analytical and Applied Pyrolysis* **2015,** *112* (0), 164-172.

68. Liu, C., Deng, Y., Wu, S., Mou, H., Liang, J.; Lei, M., *Journal of Analytical and Applied Pyrolysis* **2016,** *118*, 123-129.

69. Ohra-aho, T., Tenkanen, M.; Tamminen, T., *Journal of Analytical and Applied Pyrolysis* **2005,** *74* (1–2), 123-128.

70. Ge, W.; Wang, X., ILs. In *Ionic Liquids : Synthesis, Characterization and Applications*, Brooks, A., Ed. Nova Science Publishers, Inc: Hauppauge, New York, 2014; pp 154-168.

71. Parviainen, A., King, A. W. T., Mutikainen, I., Hummel, M., Selg, C., Hauru, L. K. J., Sixta, H.; Kilpeläinen, I., *ChemSusChem* **2013,** *6* (11), 2161-2169.

72. Ishikawa, T., *Superbases for Organic Synthesis: Guanidines, Amidines, Phosphazenes and Related Organocatalysts*. John Wiley & Sons: UK, 2009; 326 p.

73. Pinkert, A., Marsh, K. N., Pang, S.; Staiger, M. P., *Chemical Reviews* **2009,** *109* (12), 6712-6728.

74. Holbrey, J. D., Reichert, W. M., Swatloski, R. P., Broker, G. A., Pitner, W. R., Seddon, K. R.; Rogers, R. D., *Green Chemistry* **2002,** *4* (5), 407-413.

75. Swatloski, R. P., Spear, S. K., Holbrey, J. D.; Rogers, R. D., *J. Am. Chem. Soc.* **2002,** *124* (18), 4974-4975.

76. Isik, M., Sardon, H.; Mecerreyes, D., *International Journal of Molecular Sciences* **2014,** *15* (7), 11922-11940.

77. Seddon, K. R., *Journal of Chemical Technology & Biotechnology* **1997,** *68* (4), 351-356.

78. Fukaya, Y., Sugimoto, A.; Ohno, H., *Biomacromolecules* **2006,** *7* (12), 3295-3297.

79. Fukaya, Y., Hayashi, K., Wada, M.; Ohno, H., *Green Chem.* **2008,** *10* (1), 44-46.

80. Wilkes, J. S.; Zaworotko, M. J., *Journal of the Chemical Society, Chemical Communications* **1992,** (13), 965-967.

81. Chowdhury, S. A., Vijayaraghavan, R.; MacFarlane, D. R., *Green Chemistry* **2010,** *12* (6), 1023-1028.

82. King, A. W. T., Asikkala, J., Mutikainen, I., Jaervi, P.; Kilpelaeinen, I., *Angew. Chem., Int. Ed.* **2011,** *50* (28), 6301-6305, S6301/1-S6301/5.

83. Ahmad, W., Ostonen, A., Jakobsson, K., Uusi-Kyyny, P., Alopaeus, V., Hyväkkö, U.; King, A. W. T., *Chemical Engineering Research and Design* **2016,** *114*, 287-298.

84. Jessop, P. G., Heldebrant, D. J., Li, X., Eckert, C. A.; Liotta, C. L., *Nature* **2005,** *436*, 1102.

85. Xie, H., Yu, X., Yang, Y.; Zhao, Z. K., *Green Chemistry* **2014,** *16* (5), 2422-2427.

86. Privalova, E., Nurmi, M., Marañón, M. S., Murzina, E. V., Mäki-Arvela, P., Eränen, K., Murzin, D. Y.; Mikkola, J. P., *Separation and Purification Technology* **2012,** *97*, 42-50.

87. Anugwom, I., Eta, V., Virtanen, P., Mäki-Arvela, P., Hedenström, M., Hummel, M., Sixta, H.; Mikkola, J. P., *ChemSusChem* **2014,** *7* (4), 1170-1176.

88. Yang, Y., Xie, H.; Liu, E., *Green Chemistry* **2014,** *16* (6), 3018-3023.

89. Neves, C. M. S. S., Silva, A. M. S., Fernandes, A. M., Coutinho, J. A. P.; Freire, M. G., *The Journal of Physical Chemistry Letters* **2017,** *8* (13), 3015-3019.

90. de Oliveira, H. F. N., Clough, M. T.; Rinaldi, R., *ChemSusChem* **2016,** *9* (23), 3324-3329.

91. Holding, A. J., Heikkilä, M., Kilpeläinen, I.; King, A. W. T., *ChemSusChem* **2014,** *7* (5), 1422-1434.

92. Holding, A. J., Parviainen, A., Kilpelainen, I., Soto, A., King, A. W. T.; Rodriguez, H., *Rsc Advances* **2017,** *7* (28), 17451-17461.

93. Fukumoto, K.; Ohno, H., *Angewandte Chemie International Edition* **2007,** *46* (11), 1852-1855.

94. Fukaya, Y.; Ohno, H., *Physical Chemistry Chemical Physics* **2013,** *15* (11), 4066-4072.

95. Egorova, K. S.; Ananikov, V. P., *ChemSusChem* **2014,** *7* (2), 336-360.

96. Witos, J., Russo, G., Ruokonen, S.-K.; Wiedmer, S. K., *Langmuir* **2017,** *33* (4), 1066-1076.

97. Ruokonen, S.-K., Sanwald, C., Sundvik, M., Polnick, S., Vyavaharkar, K., Duša, F., Holding, A. J., King, A. W. T., Kilpeläinen, I., Lämmerhofer, M., Panula, P.; Wiedmer, S. K., *Environmental Science & Technology* **2016,** *50* (13), 7116-7125.

98. Couling, D. J., Bernot, R. J., Docherty, K. M., Dixon, J. K.; Maginn, E. J., *Green Chemistry* **2006,** *8* (1), 82-90.

99. Stolte, S., Arning, J., Bottin-Weber, U., Matzke, M., Stock, F., Thiele, K., Uerdingen, M., Welz-Biermann, U., Jastorff, B.; Ranke, J., *Green Chemistry* **2006,** *8* (7), 621-629.

100. Wang, H., Malhotra, S. V.; Francis, A. J., *Chemosphere* **2011,** *82* (11), 1597-1603.

101. Garcia, M. T., Gathergood, N.; Scammells, P. J., *Green Chemistry* **2005,** *7* (1), 9-14.

102. Matzke, M., Stolte, S., Thiele, K., Juffernholz, T., Arning, J., Ranke, J., Welz-Biermann, U.; Jastorff, B., *Green Chemistry* **2007,** *9* (11), 1198-1207.

103. Rantamäki, A. H., Ruokonen, S.-K., Sklavounos, E., Kyllönen, L., King, A. W. T.; Wiedmer, S. K., *Scientific Reports* **2017,** *7*, 46673.

104. Costa, S. P. F., Pinto, P. C. A. G., Lapa, R. A. S.; Saraiva, M. L. M. F. S., *Journal of Hazardous Materials* **2015,** *284*, 136-142.

105. Graenacher, C. Cellulose solution. US1.943.176, 1934.

106. Minnick, D. L., Flores, R. A., DeStefano, M. R.; Scurto, A. M., *The Journal of Physical Chemistry B* **2016,** *120* (32), 7906-7919.

107. Barthel, S.; Heinze, T., *Green Chemistry* **2006,** *8* (3), 301-306.

108. Kosan, B., Dorn, S., Meister, F.; Heinze, T., *Macromolecular Materials and Engineering* **2010,** *295* (7), 676-681.

109. Cao, Y., Wu, J., Zhang, J., Li, H., Zhang, Y.; He, J., *Chemical Engineering Journal* **2009,** *147* (1), 13-21.

110. Heinze, T., Dorn, S., Schöbitz, M., Liebert, T., Köhler, S.; Meister, F., *Macromolecular Symposia* **2008,** *262* (1), 8-22.

111. Ebner, G., Schiehser, S., Potthast, A.; Rosenau, T., *Tetrahedron Letters* **2008,** *49* (51), 7322-7324.

112. Heinze T., L. T., Koshella A, Esters of Carboxylic Acids — Conventional Methods. In *Esterification of Polysaccharides*, Springer Berlin Heidelberg: 2006; pp 41-52.

113. Zhang, H., Wu, J., Zhang, J.; He, J., *Macromolecules* **2005,** *38* (20), 8272-8277.

114. Payal, R. S.; Balasubramanian, S., *Phys. Chem. Chem. Phys.* **2014,** *16* (33), 17458-17465.

115. Liu, H., Sale, K. L., Holmes, B. M., Simmons, B. A.; Singh, S., *The Journal of Physical Chemistry B* **2010,** *114* (12), 4293-4301.

116. Guo, J., Zhang, D., Duan, C.; Liu, C., *Carbohydrate Research* **2010,** *345* (15), 2201-2205.

117. King, A. W., Parviainen, A., Karhunen, P., Matikainen, J., Hauru, L. K., Sixta, H.; Kilpeläinen, I., *RSC Advances* **2012,** *2* (21), 8020-8026.

118. Hauru, L. K. J., Hummel, M., King, A. W. T., Kilpeläinen, I.; Sixta, H., *Biomacromolecules* **2012,** *13* (9), 2896-2905.

119. Kuzmina, O., Bhardwaj, J., Vincent, S. R., Wanasekara, N. D., Kalossaka, L. M., Griffith, J., Potthast, A., Rahatekar, S., Eichhorn, S. J.; Welton, T., *Green Chemistry* **2017,** *19* (24), 5949-5957.

120. Medronho, B.; Lindman, B., *Advances in colloid and interface science* **2014,** *222*, 502-508.

121. Sen, S., Martin, J. D.; Argyropoulos, D. S., *ACS Sustainable Chemistry & Engineering* **2013,** *1* (8), 858-870.

122. Cross, C. F., Bevan, E. J.; Beadle, C. PLASTIC COMPOUND OF CELLULOSE. US520770A, 1894.

123. Klemm, D., Philipp, B., Heinze, T., Heinze, U.; Wagenknecht, W., Comprehensive Cellulose Chemistry Functionalization of Cellulose. WILEY-VCH: Weinheim, 1998; Vol. 2, p 389.

124. Heinze, T.; Koschella, A., *Polímeros* **2005,** *15*, 84-90.

125. Olsson, C.; Westman, G., Direct Dissolution of Cellulose: Background, Means and Applications. In *Cellulose* [Online] Van De Ven, T. G. M., Ed. IntechOpen: 2013; pp. 143-178.

126. Pinkert, A., Marsh, K. N.; Pang, S., *Industrial & Engineering Chemistry Research* **2010,** *49* (22), 11121-11130.

127. Burchard, W., Habermann, N., Klüfers, P., Seger, B.; Wilhelm, U., *Angewandte Chemie International Edition in English* **1994,** *33* (8), 884-887.

128. Dawsey, T. R.; McCormick, C. L., *Journal of Macromolecular Science, Part C* **1990,** *30* (3-4), 405-440.

129. Heinze, T., Dicke, R., Koschella, A., Kull, A. H., Klohr, E. A.; Koch, W., *Macromolecular Chemistry and Physics* **2000,** *201* (6), 627-631.

130. Dupont, A.-L., *Polymer* **2003,** *44* (15), 4117-4126.

131. Östlund, Å., Lundberg, D., Nordstierna, L., Holmberg, K.; Nydén, M., *Biomacromolecules* **2009,** *10* (9), 2401-2407.

132. El Seoud, O. A., Nawaz, H.; Areas, E. P., *Molecules* **2013,** *18* (1), 1270-1313.

133. Stryuk, S., Eckelt, J.; Wolf, B. A., *Cellulose* **2005,** *12* (2), 145-149.

134. Wang, Y.; Deng, Y., *Biotechnology and Bioengineering* **2009,** *102* (5), 1398-1405.

135. Isogai, A.; Atalla, R. H., *Cellulose* **1998,** *5* (4), 309-319.

136. Isobe, N., Noguchi, K., Nishiyama, Y., Kimura, S., Wada, M.; Kuga, S., *Cellulose* **2013,** *20* (1), 97-103.

137. Jin, H., Zha, C.; Gu, L., *Carbohydrate Research* **2007,** *342* (6), 851-858.

138. Johnson Dee Lynn, E. K. C. Process for Strengthening Swellable Fibrous Material with an Amine Oxide and The Resulting Material. US3447956A, 1969.

139. Fink, H. P., Weigel, P., Purz, H. J.; Ganster, J., *Progress in Polymer Science* **2001,** *26* (9), 1473-1524.

140. Rosenau, T., Potthast, A., Sixta, H.; Kosma, P., *Progress in Polymer Science* **2001,** *26* (9), 1763-1837.

141. Malm, C. J.; Blanchard, L. W. Method of Preparing Cellulose Acetate. US 2.772.266, 1952.

142. Seoud, O. A. E., Marson, G. A., Ciacco, G. T.; Frollini, E., *Macromolecular Chemistry and Physics* **2000,** *201* (8), 882-889.

143. McCormick, C. L.; Callais, P. A., *Polymer* **1987,** *28* (13), 2317-2323.

144. Wu, J., Zhang, J., Zhang, H., He, J., Ren, Q.; Guo, M., *Biomacromolecules* **2004,** *5* (2), 266-268.

145. Heinze, T., Schwikal, K.; Barthel, S., *Macromolecular Bioscience* **2005,** *5* (6), 520-525.

146. Granström, M., Kavakka, J., King, A., Majoinen, J., Mäkelä, V., Helaja, J., Hietala, S., Virtanen, T., Maunu, S.-L., Argyropoulos, D. S.; Kilpeläinen, I., *Cellulose* **2008,** *15* (3), 481-488.

147. Jogunola, O., Eta, V., Hedenström, M., Sundman, O., Salmi, T.; Mikkola, J.-P., *Carbohydrate Polymers* **2016,** *135*, 341-348.

148. Xu, A., Zhang, Y., Zhao, Y.; Wang, J., *Carbohydrate Polymers* **2013,** *92* (1), 540-544.

149. Rinaldi, R., *Chem. Commun. (Cambridge, U. K.)* **2011,** *47* (1), 511-513.

150. Nawaz, H., Pires, P. R., Bioni, T., Arêas, E. G.; El Seoud, O., *Cellulose* **2014,** *21* (3), 1193-1204.

151. Hagemeyer, H. J.; Hull, D. C., *Industrial & Engineering Chemistry* **1949,** *41* (12), 2920-2924.

152. Kakuchi, R., Yamaguchi, M., Endo, T., Shibata, Y., Ninomiya, K., Ikai, T., Maeda, K.; Takahashi, K., *RSC Advances* **2015,** *5* (88), 72071-72074.

153. Kakuchi, R., Ito, R., Nomura, S., Abroshan, H., Ninomiya, K., Ikai, T., Maeda, K., Kim, H. J.; Takahashi, K., *RSC Advances* **2017,** *7* (16), 9423-9430.

154. Wang, H., Wen, X., Zhang, X.; Liu, C., *Molecules* **2017,** *22* (9), 1419.

155. Klohr, E. A., Koch, W., Klemm, D.; Dicke, R. Regioselectively substituted esters of oligosaccharides and polysaccharides and process for their preparation EP1035135, 21.02.2000, 2000.

156. Michud, A., Hummel, M., Haward, S.; Sixta, H., *Carbohydrate Polymers* **2015,** *117* (0), 355-363.

157. Karatzos, S., Edye, L.; Wellard, R., *Cellulose* **2012,** *19* (1), 307-312.

158. Parviainen, A., Wahlstrom, R., Liimatainen, U., Liitia, T., Rovio, S., Helminen, J. K. J., Hyvakko, U., King, A. W. T., Suurnakki, A.; Kilpelainen, I., *RSC Advances* **2015,** *5* (85), 69728-69737.

159. Jeong, H., Park, J., Kim, S., Lee, J.; Cho, J. W., *Fibers and Polymers* **2012,** *13* (10), 1310-1318.

160. Jeong, H., Park, J., Kim, S., Lee, J., Ahn, N.; Roh, H.-g., *Fibers and Polymers* **2013,** *14* (7), 1082-1093.

161. Zhang, M.; Ogale, A. A., *Carbon* **2014,** *69*, 626-629.

162. Qian, Y., Deng, Y., Qiu, X., Li, H.; Yang, D., *Green Chemistry* **2014,** *16* (4), 2156-2163.

163. Björkman, A., *Nature* **1954,** *174*, 1057.

164. Lundquist, K., *Acta Chem. Scand., Ser. B* **1981,** *B35* (7), 497-501.

165. Balakshin, M. Y., Capanema, E. A., Chen, C.-L.; Gracz, H. S., *J. Agric. Food Chem.* **2003,** *51* (21), 6116-6127.

166. Björkman, A., *Svensk Papperstidning* **1956,** *59*, 477-485.

167. Mallabar, H. J. Manufacture of Cellulose Acetate. US1.652.573, 1927.

168. Heinze, T., Liebert, T. F., Pfeiffer, K. S.; Hussain, M. A., *Cellulose (Dordrecht, Neth.)* **2003,** *10* (3), 283-296.

169. Edgar, K. J., Buchanan, C. M., Debenham, J. S., Rundquist, P. A., Seiler, B. D., Shelton, M. C.; Tindall, D., *Progress in Polymer Science* **2001,** *26* (9), 1605-1688.

170. Schenzel, A., Hufendiek, A., Barner-Kowollik, C.; Meier, M. A. R., *Green Chemistry* **2014,** *16* (6), 3266-3271.

171. Luan, Y., Zhang, J., Zhan, M., Wu, J., Zhang, J.; He, J., *Carbohydrate Polymers* **2013,** *92* (1), 307-311.

172. Fischer, S., Thümmler, K., Volkert, B., Hettrich, K., Schmidt, I.; Fischer, K., *Macromolecular Symposia* **2008,** *262* (1), 89-96.

173. Abe, M., Sugimura, K.; Nishio, Y., *ChemistrySelect* **2016,** *1* (10), 2474-2478.

174. Cao, Y., Zhang, J., He, J., Li, H.; Zhang, Y., *Chinese Journal of Chemical Engineering* **2010,** *18* (3), 515-522.

175. Hinner, L. P., Wissner, J. L., Beurer, A., Nebel, B. A.; Hauer, B., *Green Chem.* **2016,** *18* (22), 6099-6107.

176. Jebrane, M., Pichavant, F.; Sèbe, G., *Carbohydrate Polymers* **2011,** *83* (2), 339-345.

177. Jebrane, M.; Sebe, G., *Holzforschung* **2007,** *61* (2), 143-147.

178. Çetin, N. S., Tingaut, P., Özmen, N., Henry, N., Harper, D., Dadmun, M.; Sèbe, G., *Macromolecular Bioscience* **2009,** *9* (10), 997-1003.

179. Chen, L., Zhang, J., Shi, C., Wang, X., Zhang, B.; Tang, J., *Journal of Chemical Research* **2008,** *2008* (7), 380-382.

180. King, A. W. T., Jalomaki, J., Granstrom, M., Argyropoulos, D. S., Heikkinen, S.; Kilpelainen, I., *Analytical Methods* **2010,** *2* (10), 1499-1505.

181. Berggren, R., Berthold, F., Sjöholm, E.; Lindström, M., *Journal of Applied Polymer Science* **2003,** *88* (5), 1170-1179.

182. Asaadi, S., Hummel, M., Hellsten, S., Härkäsalmi, T., Ma, Y., Michud, A.; Sixta, H., *ChemSusChem* **2016,** *9* (22), 3250-3258.

183. Xu, C., Leppänen, A.-S., Eklund, P., Holmlund, P., Sjöholm, R., Sundberg, K.; Willför, S., *Carbohydrate Research* **2010,** *345* (6), 810-816.

184. Zoia, L., King, A. W. T.; Argyropoulos, D. S., *Journal of Agricultural and Food Chemistry* **2011,** *59* (3), 829-838.

185. King, A. W. T., Kilpelainen, I., Heikkinen, S., Jarvi, P.; Argyropoulos, D. S., *Biomacromolecules* **2009,** *10* (2), 458-463.

186. Ayoub, A., Venditti, R. A., Pawlak, J. J., Sadeghifar, H.; Salam, A., *Ind. Crops Prod.* **2013,** *44*, 306-314.

187. Chen, P., Song, H., Wang, Y., Chen, P., Shen, X.; Yao, S., *J. Mater. Cycles Waste Manage.* **2015,** *17* (3), 574-582.

188. Ekman, K. H., *Tappi* **1965,** *48* (7), 398-402.

189. Faix, O., Jakab, E., Till, F.; Székely, T., *Wood Science and Technology* **1988,** *22* (4), 323-334.

190. Zhang, M., Resende, F. L. P., Moutsoglou, A.; Raynie, D. E., *Journal of Analytical and Applied Pyrolysis* **2012,** *98* (Supplement C), 65-71.