Thesis for The Degree of Licentiate of Engineering

Hardwood delignification

Understanding chemistry and mass transport fundamentals

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Gothenburg, Sweden, 2024

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Cover:
Illustration of the multiscale transportation of alkali and lignin during kraft delignification.

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Abstract

For the necessary transition into a sustainable and circular society, lignocellulosic resources are set to play a crucial role in replacing fossil-based materials. In the valorisation of lignocellulosic materials, kraft pulping is one of the key processes. However, challenges regarding increasing the resource efficiency and expanding the scope of products mean that an improved understanding of the mechanisms behind the process is needed. The work presented in this thesis summarises two studies aimed at investigating the interplay between transport and reaction mechanisms in the kraft delignification of hardwood.

In the first study, the impact of mass transport during the pulping of wood chips has been investigated by comparing the liquor fraction within the chip, with that of the bulk. The study observed considerable differences in the concentration and structure of dissolved wood components between the liquor inside the wood chip and the surrounding bulk liquor, implying that the transport between these two fractions is slower than the reactions involved. In addition, even under mild impregnation conditions, the transport of alkali has been found to have a minor, yet persistent, effect on the subsequent delignification.

The second study compared the delignification behaviour of milled wood from four hardwood species: birch, beech, aspen, and alder. Small, yet significant, differences in the delignification rate were found among the species, although these differences could not be attributed to variations in the molecular weight or structure of the dissolved wood components. However, the molecular weight of the dissolved lignin continuously increased throughout pulping, indicating that transport mechanisms within the cell wall influences the overall rate of delignification. Lastly, parts of the xylan have been found to extract rapidly in polymeric form at the start of pulping, while other parts remained as residuals in the pulp.

Keywords

Black liquor, Hardwood, Kraft delignification, Mass transport, Precipitated lignin

List of publications

This thesis is based on the following appended papers:

Paper I **Kraft cooking of birch wood chips: differences between the dissolved organic material in pore and bulk liquor**
Linus Kron, Carolina Marion de Godoy, Merima Hasani, Hans Theliander
Holzforschung, 77, 2023, 598-609.

Paper II **A comparative study of delignification behaviour during kraft pulping of four Nordic hardwoods**
Linus Kron, Merima Hasani, Hans Theliander
Manuscript, submitted

Contribution report

Paper I Shared first author together with Carolina Marion de Godoy. Both first authors were responsible for planning and conducting all experimental work, except running the NMR measurements. Results were analysed together with co-authors. Both first authors were responsible for drafting the manuscript, revised together with co-authors.

Paper II First author. Responsible for planning and conducting all experimental work, except running the NMR measurements. Results were analysed together with co-authors. Responsible for drafting the manuscript, revised together with co-authors.

List of abbreviations

ASL	Acid-soluble lignin
BL	Bulk cooking liquor *or* Black liquor
CL	Centrifuged cooking liquor
DP	Degree of polymerisation
GPC	Gel Permeation Chromatography
HPAEC-PAD	High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection
HSQC-NMR	Hetero-nuclear Single Quantum Coherence Nuclear Magnetic Resonance spectroscopy
IL	Impregnation liquor
IS	Ionic strength
LCC	Lignin Carbohydrate Complexes
MeGlcA	4-O-methylglucuronic acid
MWD	Molecular weight distribution
PEG	Polyethylene glycol
RI	Refractive index
S/G	Syringyl to Guaiacyl ratio
UV	Ultraviolet light
WL	White liquor

Contents

Chapter 1

Introduction

In order to mitigate the irreversible changes threatened by global warming, the world needs to transition towards sustainable and circular economies [1]. This entails greatly reducing reliance on fossil-based raw materials and instead converting to bio-based alternatives. Lignocellulosic materials from trees and plants are the main candidates for bio-based raw materials, and consequently the pulp and paper industries will play a key role in this transition. In combination with biorefineries, these technologies can produce materials ranging from textiles and packaging, to speciality chemicals and pharmaceuticals [2]. Nevertheless, the global supply of lignocellulosic biomass is, albeit massive, limited and efficient use of all resources is of paramount importance for a sustainable process industry.

The dominating technology for providing the primary separation of wood components is, at present, the kraft pulping process. A key step in this process is the delignification, in which lignin and hemicelluloses are partly removed to produce liberated cellulose-rich fibres for various purposes. In modern kraft pulp mills the total yield is typically around 50%, chiefly because most of the lignin and hemicelluloses are solubilised during pulping. The dissolved hemicelluloses and lignin (which make up roughly half of the woods weight) remain, today, largely unutilised for material applications, and are instead mainly used as fuel. This stems, in part, from the inability to recover the cellulose fibres without heavily degrading the lignin and parts of the hemicelluloses. An improved understanding of the underlying mechanisms of pulping is necessary in achieving an increased resource efficiency, as well as for the development of new types of materials that can replace fossil-based alternatives.

Nevertheless, delignification is a complex process comprising of several simultaneous reactions of lignin and carbohydrates, as well as the transport of reactants and dissolved wood components through the porous structure of wood. Moreover, wood is made up of a highly heterogeneous network of fibres and pores of different orientations and sizes, whose structure also varies throughout the delignification process. As a consequence, models of delignification often

reduce the complexity of the process by focusing on only a few of the main mechanisms. In most cases it has been assumed that the delignification can be described as a pseudo-homogeneous operation, and that the overall kinetics follow the rate of the cleavage of bonds in the lignin structure [3].

However, many other factors besides reaction kinetics have an impact on the overall delignification. One factor that has been investigated earlier is the impregnation, which demonstrates the impact of mass transfer of the cooking chemicals, prior to the cooking step, in order to achieve a uniformly cooked chip [4]. Research on the mass transfer of dissolved wood components within wood chips, on the other hand, have obtained less attention, especially compared to the vast amount of studies on reaction kinetics (which often investigate the overall delignification kinetics rather than the true reaction kinetics) [5–9]. Yet, it has been demonstrated that large variations in the concentration of dissolved wood components exist between the liquor inside of the wood chips and the bulk liquor [10–12], which suggests that a considerable transport resistance exists for these components. Studying the kinetics of delignification thus requires consideration of transport mechanisms in addition to the reactions. One way of decreasing the effect of transport resistance is to study pulping with ground wood instead of chips. Then, the fibre walls are exposed directly to the pulping liquor, thus removing the necessity to transport components in and out of the porous network inside of the wood chips [13]. Nevertheless, even transport within the cell wall of the wood fibres has been suggested to affect the overall delignification kinetics [14]. However, a full understanding of the relative importance of transport and reaction mechanisms is far from complete and, consequently, there is a need for further research into this field.

Furthermore, large differences, both structural and chemical, exist between different tree species, and yet past studies have largely been limited to only a selected few species; mostly softwoods and eucalyptus. Thus, additional knowledge on variations among species and their effect on kraft delignification is required in order to utilise the full potential of the available lignocellulosic biomass.

1.1 Objectives

The main goal of this work has been to improve the general understanding of the main mechanisms of kraft delignification of hardwoods, by relating the relative effects of reaction kinetics and mass transfer. More specifically, in the conducted studies this can be summarised as three objectives:

1. To study the difference between the liquor inside of wood chips and the bulk liquor during kraft pulping.

2. To study delignification at the cell wall level through the pulping of wood meal.

3. To compare the relative delignification behaviour among hardwoods.

This thesis provides a summary of two studies targeting these goals. In the first study, birch wood chips were subjected to kraft pulping, separated from the spent liquor, and then centrifuged to separate a second fraction of cooking liquor corresponding to the environment inside of the chips. The two liquor fractions were compared at different pulping times as well as for different impregnation conditions. The second study conducted a comparative study on ground wood from four hardwoods: birch, beech, aspen, and alder. A flow-through reactor was employed to continuously analyse the rate of extraction and structure of dissolved wood components.

Chapter 2

Wood

2.1 Wood morphology

Wood is a highly hierarchical structure, consisting of a network of various types of cells, each with different characteristics and purposes, and is typically classified into two categories: softwood, coming from gymnosperms (i.e conifers), and hardwood, coming from angiosperms (i.e deciduous trees). Softwood consists up to 95% of a longitudinally oriented cell type called tracheids, which provide both structural support as well as transportation of water and nutrients. Hardwood, on the other hand, has separate cells for providing support (called libriform fibres and fibre tracheids), and much larger cells for transportation of fluids in longitudinal direction (called vessels). Both wood types also have radially distributed cells, consisting of parenchyma cells providing storage of nutrients, while softwoods also have tracheid rays which provide radial transport of fluids [15]. Additionally, hardwood fibres are in general shorter and thinner, compared to softwood tracheids, as well as having thicker cell walls [16].

The cell walls of tracheid and hardwood fibres consist of several layers, each containing cellulose fibrils of different orientations depending on the layer. A schematic illustration of this structure is displayed in Figure 2.1. The outermost layer of the fibre, called the primary cell wall, is relatively thin, with disordered orientation of the fibrils. Next comes the secondary cell wall, which in itself is typically split into three layers (S1, S2 and S3), each containing highly oriented cellulose fibrils. The S1 and S3 fibrils are slightly inclined in counter-running helices, whereas the S2 layer fibrils are almost vertically angled, although the angle differs in regard to the position in the stem, between juvenile and mature wood, as well as in wood grown under stress (so called reaction or compression wood). Additionally, the S2 layer is the thickest, constituting roughly 70-80% of the total wall thickness [16]. The region between the cell walls is called the middle lamella, which consists mainly of lignin. However, due to the relative thickness of the S2 layer, approximately 70% of the total lignin content is found there rather than in the middle lamella [17].

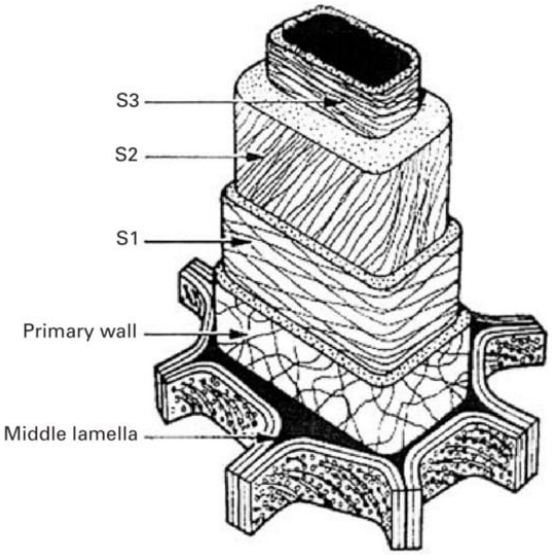

Figure 2.1: Schematic drawing of wood fibre cell wall. CC BY [18].

2.2 Wood chemistry

The main components of wood can be divided into three groups of polymers/macromolecules: cellulose, lignin, and hemicelluloses. Apart from the polymers/macromolecules, wood also contains various low molecular weight components, such as fatty acids, sterols, and terpenes, which are usually grouped into one category termed *extractives*. The total content of extractives typically ranges from <1 to 5 % [19].

2.2.1 Cellulose

Cellulose is the main component of all trees, and hence, by far the most common biopolymer on earth. It consists of linearly 1→4-glycosidic linked β-D-glucose units (see Figure 2.2), typically with a degree of polymerization (DP) of 7000 to 15000 [16]. The presence of the equatorially oriented hydroxy groups in the glucose pyranose rings contribute to amphiphillic properties of cellulose chains, and enables both intra- and intermolecular interactions and stabilisation. This results in a supramolecular structure consisting of ordered sheets of intramolecularly bonded units, which are then further stacked, creating crystalline structures separated by less ordered regions. Although, there is still a debate regarding whether these are to be treated as separate regions or not [20]. Nevertheless, the consequence of this supramolecular arrangement is elementary fibrils, which are then further arranged into microfibril bundles of roughly 15 to 20 nm in width [21]. These bundles are conjoined together with a network of hemicellulose and lignin to form the macrofibrils, which make up the majority of the cell walls in wood.

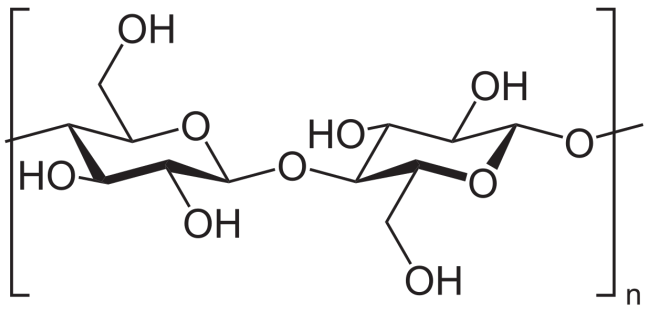

Figure 2.2: A cellobiose unit: the smallest repeating unit of cellulose.

2.2.2 Lignin

Lignin is the second most abundant component in wood. The function of lignin is manifold: It gives support both within the cell wall and between separate cells, provides hydrophobicity for the cell wall to improve water transport, as well as aids in protecting from microbial degradation [22]. Lignin, as opposed to cellulose, is not a true polymer but rather a complex network of phenyl propane base units, randomly connected through various ether and carbon-carbon linkages. The most common monolignols are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, as presented in Figure 2.3, although these are more commonly referred to in their non-propyl forms: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively.

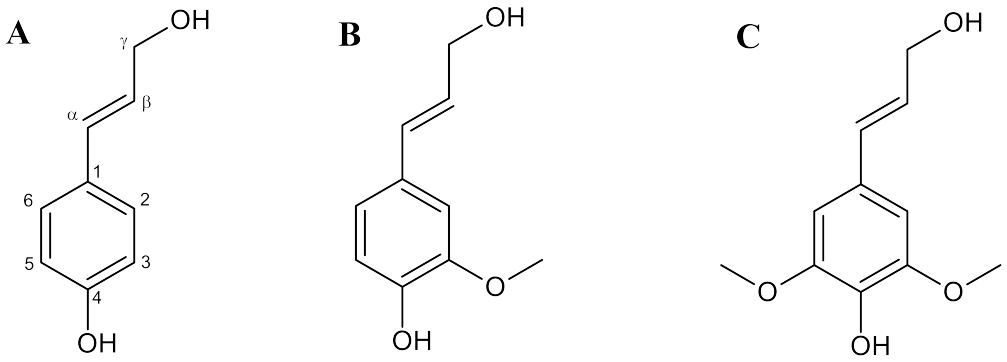

Figure 2.3: Structure of the three monolignols (A) p-coumaryl alcohol, (B) coniferyl acohol, and (C) sinapyl alcohol. Conventional naming of the C atoms is indicated in Sub-figure (A).

Some of the most common inter-lignin linkages are shown in Figure 2.4. Aryl ether linkages (mainly β-O-4, but also some α-O-4) account for roughly 50-60% of all lignin bonds, followed by β-5, 5-5' and β-1', each occurring in the order of 5-10% [16, 22, 23]. Determining the molecular weight of native lignin is troublesome, as any isolation of lignin is accompanied with condensation or degradation reactions that may alter the lignin structure. Reported values of the weight-averaged molecular weight (M_W) of isolated "native-like" lignin typically fall in the range 2-20 kDa [16].

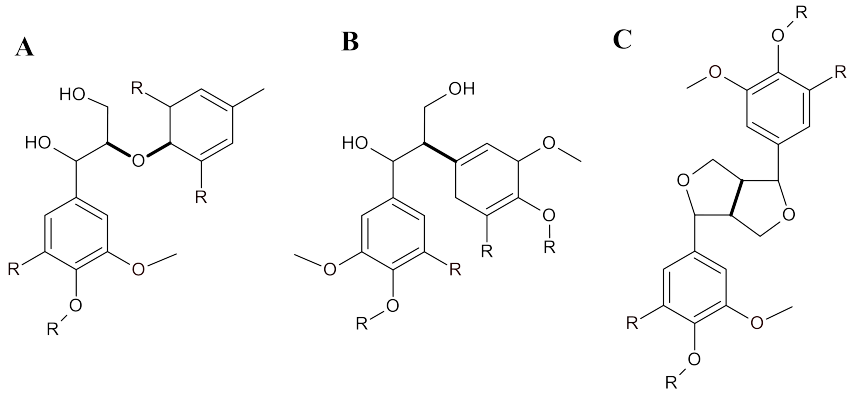

Figure 2.4: Schematic representation of three common inter-lignin linkages, with the relevant bond highlighted with bold lines: (A) β-O-4, (B) β-1, and (C) β-β.

2.2.3 Hemicelluloses

While hemicelluloses are also polysaccharides, unlike cellulose, they consist of different sugar units, may be branched, and are also generally substituted by different groups. The sugar units that comprise most wood hemicelluloses are glucose, mannose, xylose, galactose, and arabinose. Typically, they occur as (galacto)glucomannan and (arabino)glucuronoxylan, both commonly substituted by O-Acetyl groups (although, not when simultaneously substituted with arabinose), and the latter also substituted with 4-O-methylglucuronic acid (MeGlcA) (see Figure 2.5). They are also much shorter polymers compared to cellulose, with DP's around 100 to 200 [16]. The biological functions of hemicelluloses are not fully understood. They likely grant structural support within the cell wall through the linear backbone, but are also possibly enabling the interaction between lignin and cellulose as well as affecting the crystal structure and arrangement of cellulose fibrils [24].

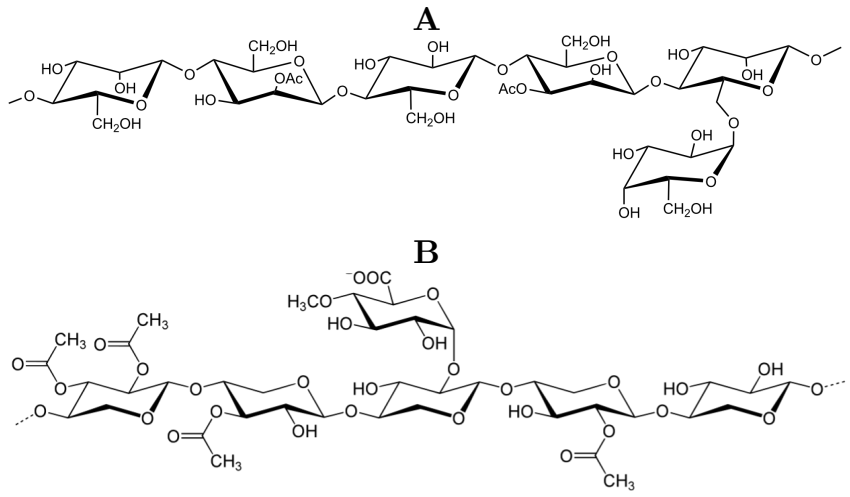

Figure 2.5: Schematic representations of hemicelluloses. (A) A glucomannan polymer with a galactose substituent. (B) A xylan polymer with a 4-O substituted MeGlcA. Both polymers contain acetyl groups.

2.3 Tree species

Softwoods

The morphological difference between the two groups of wood was briefly discussed in Section 2.1, however there are major differences in the chemical composition as well. The main hemicellulose in softwoods is glucomannan, substituted to various degrees with galactose and acetyl groups, followed by arabinoglucuronoxylan. Consequently, the amount of mannose units found in softwood is roughly twice that of xylose [16]. Softwood lignin consists up to 95% of guaiacyl and small amounts of p-hydroxyphenyl, but virtually no syringyl units, hence, it is sometimes described as G-lignin.

Hardwoods

There are, in general, larger differences among hardwoods, compared to softwoods (with the exception of larch wood deviating from typical softwoods). Hardwood hemicelluloses are mainly in the form of glucuronoxylans, containing little to no arabinose units, and with a frequency of MeGlcA roughly half that of softwood xylans. Glucomannans are present to a lesser extent, but without any galactose substituents. On the other hand, hardwood hemicelluloses are heavily acetylated on the C2 and C3 position of the polymer backbone [16]. Hardwood lignins consist of both syringyl and guaiacyl units, with a ratio of syringyl to guaiacyl, S/G, between 1:2 and 4:1. The fraction of β-O-4 linkages are slightly higher in hardwoods, whereas β-5 and 5-5' exist to a greater extent in softwoods [22].

Table 2.1: Reported distributions of chemical components in different tree species

Species	Glc	Man	Xyl	Ara	Gal	Klason	ASL[a]	Extractives	References
Black alder	48.1[b]	-[b]	31.9[b]	-[b]	-[b]	19.9[c]	-[c]	-	[25]
Alnus glutinosa	50.9[b]	-	-	-	-	21.8[c]	-[c]	4.9	[26]
	43.4[b]	-[b]	23[b]	-[b]	-[b]	23.9[c]	-[c]	3.8	[16]
Silver birch	46.5	2.0	26.7	0.6	1.2	19.6	-	-	[27]
Betula pendula[d]	44.5	2.1	23.6	0.7	0.8	21.5	-	2.24	[28]
	37.4	1.5	20.3	0.3	0.5	19.6	3.1	-	[29]
	41.0[b]	2.3[b]	27.5	-	-	22.0[c]	-[c]	3.2	[23]
	34.2[b]	4.8[b]	32.5[b]	-	1.7	26.3[c]	-[c]	-	[16]
Betula pubescens[e]	42.2[b]	-	-	-	-	19.2	0.76	2.1	[30]
European beech	39.4[b]	1.3[b]	27.8[b]	-	-	24.8[c]	-[c]	1.2	[23]
Fagus sylvatica	42.9[b]	5.2[b]	23.0[b]	1.9[b]	-[b]	23.4	1.1	0.0	[31]
	43.3[b]	1.4[b]	27.8[b]	-	2.6	24.4[c]	-[c]	-	[16]
	49.1[b]	-[b]	22.0[b]	-[b]	-[b]	23.8[c]	-[c]	0.8	[16]
	44.5[b]	-[b]	20.6[b]	-[b]	-[b]	22.2[c]	-[c]	-	[16]
European aspen	41.1	3.9	16.7	0	0	19.3	2.9	-	[32]
Populus tremula	51.1	2.6	22.9	0.5	0.6	21.7[c]	-[c]	-	[33]
	51.2	2.3	22.7	0.6	0.7	19.3	-	-	[27]
Norway spruce	41.7[b]	16.3[b]	8.6[b]	3.4[b]	-[b]	27.4[c]	-[c]	1.7	[23]
Picea abies	44.9[b]	14.7[b]	8.2[b]	1.1[b]	-[b]	28.2	0.8	-	[31]

[a] Acid-soluble lignin. [b] Data reported as cellulose/glucomannan/xylan. [c] Data reported as total lignin (both ASL and Klason). [d] *B. pendula* is also known as *B. verrucosa*. [e] English name: Downy birch

Chapter 3

Pulping

For many applications, such as paper and board products, wood needs to undergo severe treatments to become a pulp before transforming it into the final products. The general procedure in common for all modern methods of pulping is to debark and cut the logs into smaller chips, which may then undergo various pre-treatments before being subjected to the main step, in which the wood fibres are liberated and separated from each other through mechanical or chemical means. The liberated fibres are then washed, and may subsequently undergo several bleaching treatments in order to adjust pulp properties to application requirements, such as increased brightness and/or even further reduced lignin content [34]. The dominant method of pulping is the kraft method, which was developed beginning in the late 19th century, and accounts for over 80% of all pulp produced [35].

3.1 Kraft delignification

The defining step in kraft pulping is the delignification, in which the fibres in wood chips are liberated through the dissolution and removal of up to 85% of the initial lignin. However, *delignification* is not a single reaction taking place, but rather a complex process consisting of several steps with different kinetics and dependencies acting in parallel. This can be summarised as:

1. Transfer of chemicals from bulk liquor to chip surface.
2. Transfer of chemicals from chip surface to cell wall surface via the porous network of connected lumens.
3. Transfer of chemicals from cell wall surface to reactive sites within the cell wall.
4. Cleavage of bonds within the lignocellulosic network.
5. Dissolution of cleaved wood components.

6. Transfer of dissolved wood components from reactive sites to cell wall surface.

7. Transfer of dissolved wood components from cell wall surface to chip surface via the porous network of connected lumens.

8. Transfer of dissolved wood components from chip surface out into bulk liquor.

However, while the list above summarises the steps that need to occur for complete delignification, several additional factors affect the overall process as well. For example, competing reactions, such as the hydrolysis, peeling, and deacetylation reactions of the carbohydrates, affect the availability of reactants for the lignin cleavage reactions [36]. Moreover, dissolved products from both lignin and carbohydrate reactions will alter the chemical environment, such as the ionic strength or presence of certain compounds, affecting both reactions and transport mechanisms [13]. In addition, wood is a highly heterogeneous structure and, consequently, separating the effects of the different steps in the process and the effect of variations in the raw material poses a great challenge.

3.1.1 Lignin reactions

Solubilisation of lignin requires fragmentation reactions to decrease the molecular weight and introduce hydrophilic groups. This mainly occurs through the cleavage of ether bonds, while carbon-carbon linkages remain relatively stable. Due to its prevalence, the cleavage of β-O-4 bonds is considered the main fragmentation reaction, and its pathway depends on whether the linkage is part of a phenolic or non-phenolic structure. In phenolic structures, a quinone methide intermediate is formed at alkali conditions, after which a nucleophilic attack by hydrogen sulphide ions is required for a subsequent cleavage of the interunit linkage. A simplified reaction pathway is displayed in Figure 3.1. The cleavage of β-O-4 in non-phenolic structures is, on the other hand, independent of hydrogen sulphide ions, and requires only the presence of hydroxide ions. In both cases, a new phenolic structure is formed when the previous bond is cleaved, which may continue to react if it, in turn, is part of similar ether linkages [23].

However, there is also another main group of reactions occurring simultaneously that counteracts the solubilisation of lignin, namely carbon-carbon forming condensation reactions. These are considered to generally occur at the 5-position in guaiacyl units, although there is no conclusive evidence for any given pathway. It may be the case that these types of condensed structures are not formed in the residual lignin, but instead already existing ones accumulate as other types of structures are degraded. It has also been shown that some condensed structures more common in hardwoods, such as α-5 linkages, are more prevalent in the dissolved lignin compared to the residual. [38]

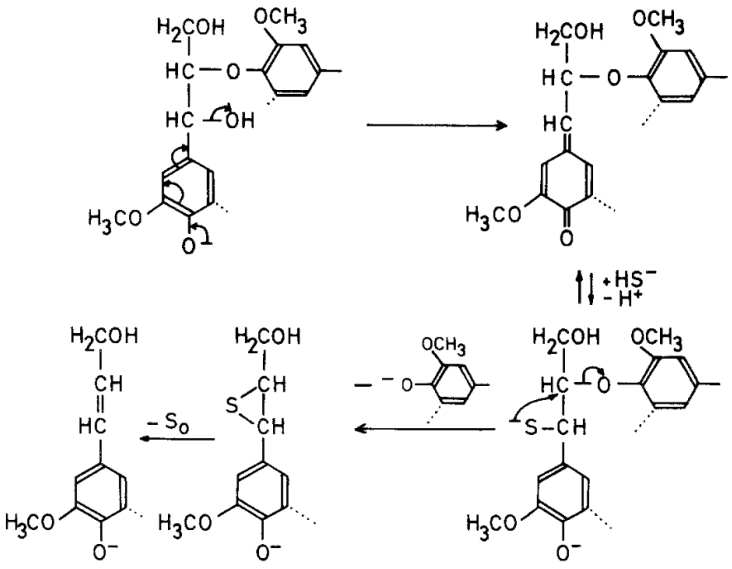

Figure 3.1: Schematic reaction pathway of β-O-4 cleavage in phenolic structures. Reprint in edited form with permission [37].

3.1.2 Carbohydrate reactions

The degradation of carbohydrates during kraft pulping stems mainly from two types of reactions, peeling and alkaline hydrolysis, but is also affected by reactions of the substituents. In alkaline conditions at intermediate temperatures (>70°C), the reducing end of polysaccharide chains can be removed through β-elimination. This peeling reaction then forms a new reducing end, which will continue to split off, until at some point a so-called stopping reaction forms a stable end-group [38]. Due to high DP and decreased availability in the crystalline regions, cellulose is, in general, not influenced by peeling to any large extent, whereas glucomannans are very susceptible leading to substantial degradation during pulping. Xylans are less prone to peeling due to the frequent substitution of MeGlcA and arabinose units (for softwoods) at the 2 and 3 position, respectively, which then favours the stopping reactions [39], and is possibly also shielded by close association to cellulose [40].

The alkaline hydrolysis reaction becomes relatively fast at higher temperatures (>140°C) as a random cleavage of the glucosidic linkage in polysaccharides. In cellulose, this predominantly targets the less ordered regions and is responsible for the main decrease in DP of cellulose during alkaline pulping [38]. The hydrolysis also introduces new reducing end groups, which will further be subjected to peeling reactions. Apart from peeling and alkaline hydrolysis, some other significant reactions include the degradation of MeGlcA into hexenuronic acids, which affects pulp properties and causes yellowing, as well as extensive deacetylation in hemicelluloses, which consumes substantial amounts of alkali during the early stage of delignification [39].

3.2 Delignification kinetics

No clear consensus has been reached regarding the relative importance of each of the steps presented in section 3.1. While they all occur simultaneously, all of them are necessary for complete delignification. Thus, should any of them be considerably slower than the rest, the overall rate of delignification would then mainly rely on the rate of this step. Hence, in the effort of reducing the complexity of describing the whole process, descriptions and models of delignification are often based on one or a few of these steps. Historically, delignification has been assumed to be a pseudo homogeneous operation, where the cleavage reaction of β-O-4 is the limiting step [37], resulting in many models based mainly around reaction kinetics [3, 41]. In contrast, several studies point out the significant impact of the other mechanisms as well, e.g [42–44], and a growing number of modelling studies incorporate transport and dissolution mechanisms to various degrees along reaction kinetics [11, 45, 46]. Evidently, delignification is truly a complex process, which warrants proper consideration of all underlying mechanisms.

3.2.1 Reaction kinetics

Early studies on lignin model compounds found the rate of cleavage of phenolic aryl ether bonds to be independent of the concentration of OH^- and HS^- (as long as sufficient minimum level is achieved), and relatively fast compared to cleavage of non-phenolic bonds, which in turn is linearly dependent on OH^- [47, 48]. Nevertheless, while these studies reflect the "true" cleavage of aryl-ether bonds, they are based on a limited number of experiments and, in addition, the applicability of model studies-kinetics to predict actual delignification kinetics, during pulping, has been questioned [49].

More commonly, many studies have investigated the kinetics of wood pulping, i.e. delignification, but from the perspective of reaction kinetics. Early on, it was found that the early stage of delignification, assumed to correlate to the cleavage of phenolic aryl ethers, is relatively fast and independent of the studied range of alkali concentrations [50]. It is instead suggested that these reactions are fast enough that the diffusion of alkali is the limiting factor during early delignification. However, diffusion of alkali should also be concentration dependent, although in this study the effect of the heat-up time was not accounted for, which may have influenced the results of the early stage of delignification.

Next, the rate of delignification when the main part of lignin is removed, which is attributed to the cleavage of non-phenolic β-O-4, has been found to be dependent on OH^-, but also to have a slight dependence on HS^- [51, 52], as opposed to the results from the model studies. In addition, an increased concentration of HS^- during the pre-treatment prior to cooking lowered the dependence on HS^- during bulk delignification [52], implying that the concentration of HS^- does have an effect on the reactions occurring early on during delignification. Later studies have found similar results regarding the effect

of alkali and sulphide concentrations [13, 43, 53, 54]. Again, these studies investigate the rate of the overall delignification, rather than the reaction specifically, and will thus be affected by several factors beyond the cleavage of aryl ether bonds.

Another property of lignin that often is attributed with having an affect on the rate of delignification in hardwoods is the ratio between syringyl and guaiacyl units: the *S/G ratio* [55–57]. However, the exact mechanism behind it is not fully understood. Studies on model components found the β-O-4 bonds of syringyl units to be more reactive than that of guaiacyl units, though it remains uncertain whether this occurs when syringyl is the "main" unit [58, 59], or the ether linked "leaving" unit [59, 60]. Again, the ability of model studies to predict actual pulping reactions is debatable. For example, the referred studies are based on lignin dimers, whereas in the actual lignin network, consisting of various bonds and interactions with carbohydrates, the effect of different monolignol units may be diminished.

Alternatively, it has been proposed that the increased frequency of condensed C-C bonds at the 5-position available in guaiacyl limits the rate of delignification [61]. The relative decrease of condensed structures in syringyl-rich lignin would explain the increased yield reported for samples with higher S/G ratios [61–63]. However, this relation is not certain, as other studies found no such correlation [64–66]. Many of the studies investigating the effect of S/G ratio are based on species of eucalyptus which have high S/G ratios and are quick to delignify, such as *E. globulus*. It may thus be the case that the potential correlation between S/G ratio and ease of pulping is overly reliant on data from only a few species, whereas other species, such as birch, does not follow these correlations [29, 67]. Instead, other factors may be the cause of the relative ease of pulping *E. globulus*, such as its interactions with non-process elements like calcium [44].

3.2.2 Transport kinetics

Some aspects of transport mechanisms in pulping has been studied, such as the effect of impregnation [4, 68, 69] and chip thickness [42, 70–72]. Notably, these studies target mechanisms that occur prior to the reaction, that is, the transfer of reactive ions through the chip to the lignin in the cell wall. In contrast, studies on the dissolution and transport of fragmented wood components have obtained far less attention. Nevertheless, there are several reports regarding a significant difference between the liquor inside of the wood chips compared to the bulk [10–12, 45]. The extent to which the fractions differ varies between the reported studies: Simão *et al.* and Pakkanen and Alén report lignin concentrations roughly 4 times higher in the "bound" fraction within the chips [11, 12], whereas Gilbert *et al.* found only a minor increase [45]. The results are likely influenced by the different methods of isolation of the two liquors and, consequently, the difference in volumes of the two fractions. Regardless, the occurrence of distinct fractions indicates that the transport between them indeed has an impact on the overall rate of delignification. This transport obviously depends on the same factors affecting the aforementioned impregnation, such as chip thickness

and presence of vessels, but entails much larger molecules than the ions needed for the reactions. Additionally, the morphology of the chip changes as the delignification progresses, which inherently affects the transportation as well [73].

Moreover, it has been suggested that that the kinetics of transport mechanisms is relevant also at the cell wall level (i.e item 6 in the list of Section 3.1) [10, 14]. Transfer of dissolved wood components within the cell wall is inherently complex, given the heterogeneous composition of both cell wall and dissolved components, which furthermore are not constant but change as the pulping proceeds, along with a changing alkaline environment. Studies on transfer in the cell wall are thus sparse, and most only indirectly investigate this phenomenon. The transport has been suggested to be dependent on the thickness of the cell wall [43], as well as the steric and electrostatic interactions between dissolved lignin fragments and the fibre wall [74, 75]. However, no studies have investigated this in the context of kraft delignification.

Chapter 4

Material & Methods

This chapter presents a brief summary of the materials, equipment, and conditions employed in the pulping experiments, as well as descriptions of the techniques used for characterisation of pulp, process liquors, and raw material.

4.1 Materials

The raw material used in both papers were supplied by a Swedish pulp mill from trees harvested in southern Sweden. Paper I was conducted on industrially cut wood chips of mixed birch (*Betula pendula* and *Betula pubescens*). In Paper II, a single log each of birch (*Betula pubescens*[1]), beech (*Fagus sylvatica*), aspen (*Populus treumla*), and alder (*Alnus glutinosa*) were chosen and cut in a lab-scale chipper. In both studies, the wood chips were sorted to be free of bark and knots and dried in room conditions to a dry content of roughly 90%. The thickness of the chips in Paper I were selected to be within 2-6 mm. In Paper II the chips were instead ground in a knife mill and sieved to particles passing a 1 mm mesh.

4.2 Kraft pulping

4.2.1 Autoclave pulping

The pulping experiments of Paper I were performed in steel autoclaves of 1.5 L, loaded with 25 g of chips and 250 g of one of four impregnation liquors, as described in Table 4.1. The vessels were de-aerated and pressurised with nitrogen at 5 bar for 15 minutes, after which the impregnation liquor was discarded and fresh cooking liquor (500 g of liquor *WL*) was added. They were

[1]No distinction is usually made between *Betula pendula* and *Betula pubescens* [76–80]. The log used in Paper II was tentatively identified according to the method described by Lundgren *et al.* [81], although the results may have been influenced by the long storage time of the sample prior to analysis.

then lowered into a preheated PEG bath at 160°C for defined periods between 10-120 min. The cook was terminated by submerging the autoclaves in cold water. The spent cooking liquor (black liquor) was filtered off and collected (termed bulk liquor, BL). The still-moist pulp was then centrifuged to collect a second fraction of liquor (centrifuged liquor, CL). The pulp was then washed, leached in water until neutral, and dried. More details can be found in the appended Paper I.

Table 4.1: Impregnation liquor composition used in Paper I.

Liquor	Conc. OH^- & HS^- [mol/kg liquor]	NaCl addition [mol/kg liquor]
WL	0.60 & 0.15	-
WLNa	0.60 & 0.15	1.25
W	-	-
WNa	-	2.00

4.2.2 Flow-through reactor

Flow-through experiments were performed in a batch reactor with a continuous flow of cooking liquor (schematically drawn in Figure 4.1). Approximately 4 g of wood meal were uniformly packed in the reactor and impregnated at room temperature with about 30 ml of the cooking liquor. The reactor was then lowered into a hot PEG bath at 140°C or 150°C for 5-180 min, and terminated by submersion into cold water. The pulp was suspended in water, defibrillated with a handheld blender, washed until neutral, and dried.

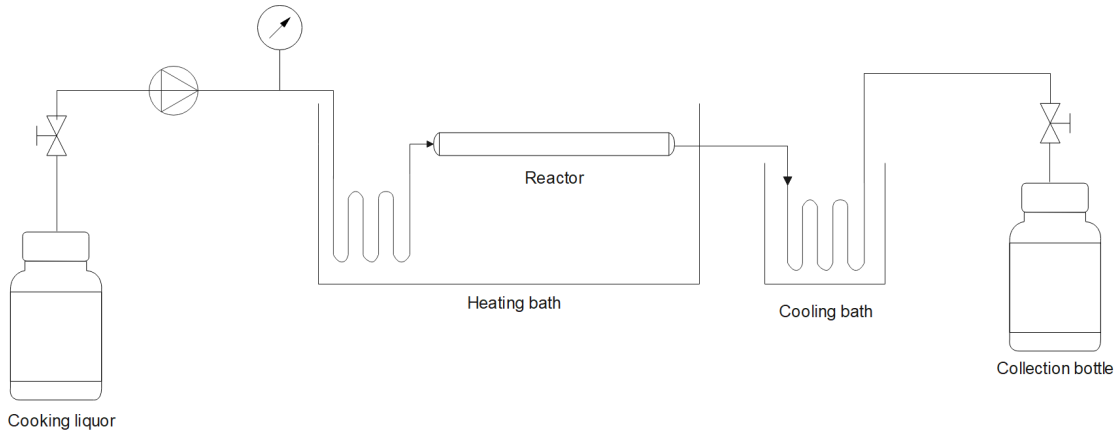

Figure 4.1: Schematic representation of the flow-through reactor setup used in Paper II.

The liquor had a concentration of OH^- and HS^- of 0.35 and 0.15 mol/kg respectively. The flow rate was increased step-wise to 10 ml/min during impregnation, and then lowered step-wise to a final rate of 2.5 ml/min from 22

min onward, in order to ensure near-constant alkali concentration during the entire cook. The black liquor was sampled in intervals, as detailed in Table 4.2.

Table 4.2: Sampling interval of black liquor

Time [min]	Approx. volume [ml]
-5 – 0	30
0 – 5	50
5 – 10	50
10 – 20	90
20 – 40	70
40 – 60	50
60 – 90	80
90 – 120	80
120 – 150	80
150 – 180	80

4.2.3 Lignin precipitation

Lignin dissolved in the liquors of both studies were precipitated prior to structural characterisation. The precipitation procedure followed as described by Dang *et al.* [82]. In short, the liquor sample was acidified with sulphuric acid to pH 2.5, frozen overnight, and then thawed. The produced precipitates were filtered off and washed with water at pH 2.5, followed by drying at 40°C for 3 days.

4.3 Characterisation

4.3.1 Composition analysis

Lignin and carbohydrate composition in pulps and liquor fractions were determined using a modified version of the standard procedures by NREL [83]. After acid hydrolysis treatment, lignin was quantified as an acid-insoluble fraction (Klason lignin), and an acid-soluble fraction (ASL) containing the remaining lignin, as well as various extractives and side products [84]. The soluble hydrolysate was then used for carbohydrate analysis using anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The detected carbohydrate monomers are reported in this work as their anhydrous form [85] and corrected for the yield after hydrolysis, as reported earlier [86].

4.3.2 Molecular weight distribution

The molecular weight distribution (MWD) of the lignin precipitated from all liquor fractions have been measured with gel permeation chromatography (PL-HPC 50 Plus, Varian Inc.). DMSO with 10mM LiBr was used as eluent, and separation was done in two 300 x 7.5 mm PolarGel-M columns, at an eluent rate of 0.5 ml/min. Precipitated lignin samples were dissolved in the eluent overnight and diluted to between 0.25-2.0 mg/ml. Detection was made using both ultraviolet light (UV) and refractive index (RI) detectors acting in series, and the results were calibrated using pullulan standards ranging from 0.18-708 kDa.

4.3.3 Nuclear Magnetic Resonance spectroscopy

Structural analysis of the precipitated lignins was performed through heteronuclear single quantum coherence (HSQC) 2D NMR spectroscopy. The pulse program hsqcedetgpsisp2.3 was used with 24 scans, 1 s relaxation delay, and a FID size of 3072 and 512 points for ^{1}H and ^{13}C respectively. In Paper I, measurements were performed on an 800 and a 200 MHz spectrometer, for ^{1}H and ^{13}C, respectively, whereas in Paper II, a 700 and a 160 MHz spectrometer was used instead. Lignin was dissolved overnight in DMSO-d6 at 140mg/ml and centrifuged at 12.5 krpm for 5 min to remove undissolved particles.

Chapter 5

Results & Discussion

This chapter presents an overview of the key findings and discussions presented in the two appended papers.

5.1 Kraft cooking of wood chips: Pore and bulk liquor comparison

Although the effect of the cooking liquor composition on the rate of delignification has been studied for many years, such studies rarely account for the different environments inside the wood chips, compared to the bulk liquor outside. Hence, the goal of Paper I was to investigate this difference, and in parallel study the effect of the composition of the impregnation liquor.

5.1.1 Influence of impregnation liquor

The effect of impregnation was studied by comparing the initial transport of active ions via advection and diffusion (by impregnating with the cooking liquor), to transport through diffusion only (impregnating with water). Furthermore, the impact of increased ionic strength (IS) was studied through the addition of sodium salt (as NaCl), which are not directly involved in the delignification reactions. The chips impregnated with cooking liquor showed only a slightly higher rate of delignification, compared to impregnation with water (see Figure 5.1). Most noticeably, this was seen as an increased dissolution of both lignin and xylan during the initial stage before final cooking temperature had been reached. This is reasonable, as in the case of impregnation with water, both lignin and xylan extraction occur only when enough OH^- and HS^- ions have diffused into the wood chips to produce an alkaline environment to promote dissolution and degradation reactions, compared to impregnation with white liquor allowing this to happen from the start.

The effect of the sodium addition was minimal and within the experimental error at the concentrations investigated. Donnan Effect theory predicts that an increased IS in the liquor within the wood chip will result in increased OH^- concentration within the fibre cell wall, which then should have benefited delignification. On the other hand, lignin solubility is reported to decrease at higher IS [87]. Therefore, the similarity between impregnation with and without sodium addition could be due to these two effects counteracting each other, or that the effect of the sodium addition in only the impregnation liquor was insufficient to maintain the increased IS throughout the cook.

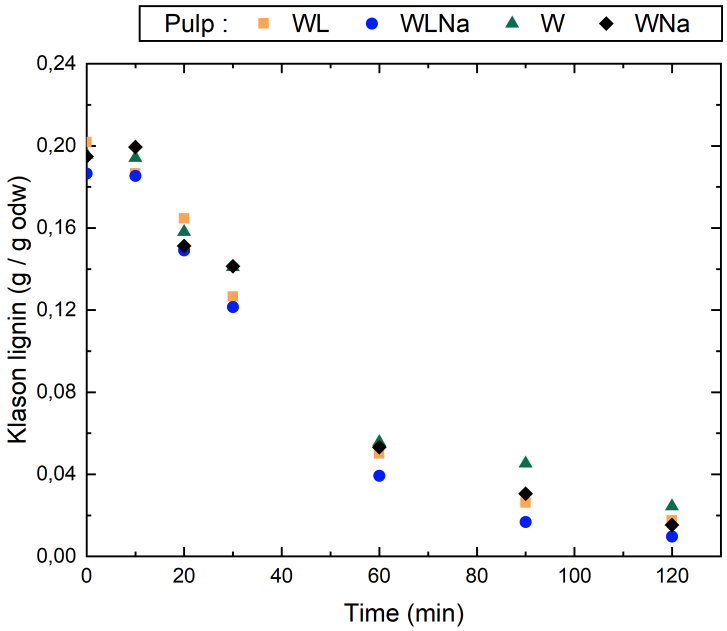

Figure 5.1: Residual Klason lignin content in wood chips after impregnation with different impregnation liquors. Values at 0 represent values in impregnated chips.

5.1.2 Bulk and pore liquor comparison

Comparison of the bulk liquor (BL) and centrifuged pore liquor (CL) revealed a major difference in total concentration of dissolved lignin, as is shown in Figure 5.2. Apart from the increased concentration in the CL, the shape of the profile differed as well: In the bulk, the concentration of lignin steadily increased until after 60 min, after which the rate was significantly decreased and the profile tends towards an asymptote. In contrast, the concentration in the pore liquor increased more sharply, peaked at roughly twice the value in the final BL, but then decreased towards the end of the cook.

This behaviour highlights the interplay between kinetics within the wood chip and transport between the wood chip and the bulk: At the start of the cook, the rate of reaction and transportation in the fibre cell walls within the chip was high, and lignin was quickly fragmented and dissolved in the pore liquor at a higher rate than can be transported out into the bulk, hence the relative

increase in the CL, compared to the BL fraction. Then, as the amount of residual lignin that was readily fragmented and dissolved decreased (c.f. the drop in Figure 5.1 after 60 min), the rate of dissolution of the residual lignin into the CL decreased below that of the transport to the BL, thus decreasing the concentration in the CL until it would reach the same value as the bulk at long residence times. Consequently, these results indicate that the transportation rate of dissolved lignin, from within the chip to the bulk, influence the overall rate of delignification, challenging the notion that the process would be purely reaction limited.

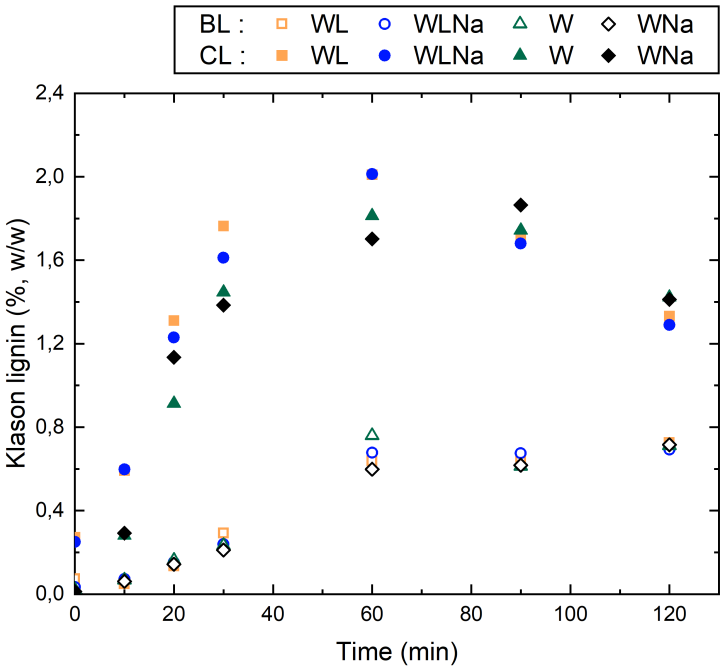

Figure 5.2: Concentration of dissolved Klason lignin in bulk (BL) and centrifuged pore (CL) liquor. Values at 0 min represent values in impregnation liquor.

Similar trends were also found when investigating the concentration of xylan in both liquor fractions, though the peak of the CL profile already appeared after 30 min, which was also simultaneously seen as a corresponding drop in the residual xylan in the pulp. As the reactor did not reach final cooking temperature until 25 min, the quick extraction of xylan confirms that carbohydrate reactions are more prominent than lignin reactions at lower temperatures, resulting in a significant loss already during the heat-up period.

The MWD of the dissolved lignin in both liquor fractions was studied, as shown in Figure 5.3. It was found that the dissolved lignin in the bulk liquor had shifted towards smaller molecules over time. This differs from the previously reported shift over time towards higher molecular weights found when flow-through cooking has been used [82, 88]. The decrease observed in this study was likely caused by a continued degradation in the bulk liquor due to the batch cooking.

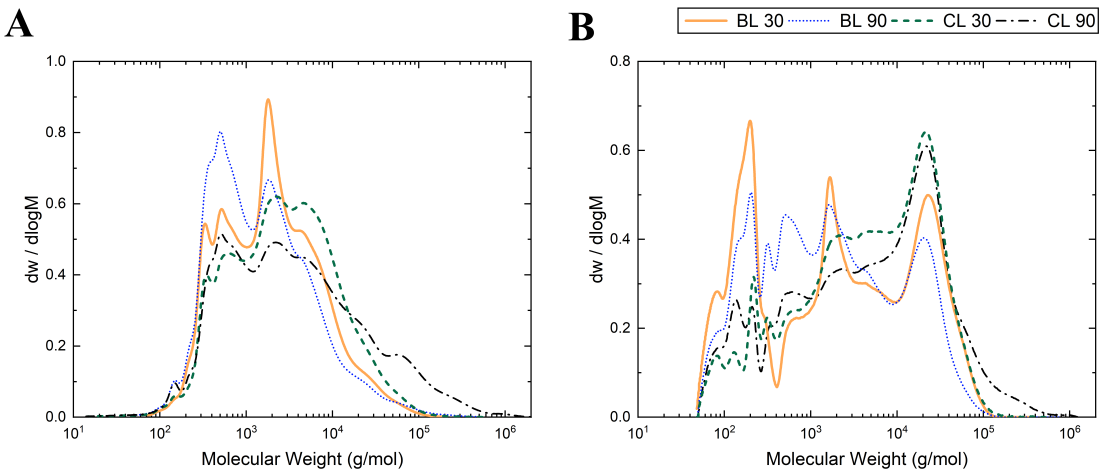

Figure 5.3: Differential molecular weight distribution of precipitated lignin from bulk (BL) and centrifuged (CL) liquors, sampled after 30 and 90 min, based on UV (A) and RI (B) detection.

Furthermore, the molecular weight of the lignin in the CL was found to be higher than that of the bulk, as well as increasing with time. The increasing size of lignin in the CL over time also indicates that the transport within the cell wall, where the larger lignin fragments require longer times to diffuse from the cell wall into the CL, have an impact on the overall kinetics of delignification. This is in agreement with previous findings from pulping of ground softwood [82]. In addition, the peak appearing at approximately 20 kDa in the RI (Figure 5.3 B), compared to the UV data (Figure 5.3 A) corresponds to polymeric xylan in the precipitated material, suggesting that part of the xylan is dissolved rather than degraded.

Lastly, the precipitated lignins were characterised through 2D HSQC NMR. These measurements revealed that signals related to β-O-4 structures were greatly diminished in the BL after 90 min, but were present in both liquor fractions after 30 min, as well as in the Cl fraction after 90 min. It is probable that these bonds will continue to fragment once reaching the bulk given the high availability of cooking chemicals, as previously hypothesised based on the decrease in the molecular weight in the same sample. Likewise, the later bulk sample also showed signs of a more extensive degradation in terms of more oxidised syringyl structures and lesser signals related to MeGlcA. Thus, the NMR data corroborates the theory that the dissolved wood components in the bulk have undergone more severe treatment, compared to the liquid fraction in the pores, again implying that the two fractions have, indeed, some differences, and that the pore fraction represents a more recently dissolved (and, hence, less degraded) lignin. Finally, strong peaks related to xylan were detected in the samples, confirming that the new peak, appearing at 20 kDa in the RI data (Figure 5.3B), resulted from xylan.

5.1.3 Summary of Paper I

The results of the first study concluded that the liquor environment inside the wood chips are distinctly different from that of the bulk. This distinction likely stems from several mechanisms: One is the transport of dissolved wood components from the liquor inside the wood chips to the bulk liquor, which is slower than the rate at which they are dissolved, leading to an accumulation within the lumen fraction. As the dissolution rate from the cell wall drops to levels below that of the mass transport, the concentration in the lumen liquor tends to that of the bulk.

Moreover, dissolved wood components in the bulk liquor appeared to be further degraded compared to those in the liquor within the wood chip. This is likely due to the fact that the components in the chip have been more recently dissolved and have had, on average, less time to be degraded compared to those that have already been transported out into the bulk. Additionally, the availability of alkali is likely greater in the bulk liquor, which would further increase the rate of degradation in the bulk.

5.2 Delignification behaviour of Nordic hardwoods

Past research on kraft delignification of wood has mainly targeted softwoods, such as spruce and pine. While birch has seen considerable research as well, much of the studies on hardwoods have targeted the eucalyptus genus, leaving many species relevant to northern Europe understudied. Paper II conducted a comparative study of the delignification behaviour of four common Nordic hardwoods, which had, to the author's knowledge, never before been compared in a single study. Additionally, this study employed flow-through reactor pulping of wood meal, allowing time-resolved analysis of dissolved wood components decoupled from the effect of transport mechanisms within the wood chip.

5.2.1 Variations among species

The chemical composition of the birch, beech, aspen, and alder wood used in Paper II is presented in Table 5.1. In general, birch contained relatively low amounts of lignin, but had a high content of xylan; aspen was high in glucan and mannan, but low in xylan and lignin; and beech and alder both had relatively high amounts of lignin. These values align with previously reported values for the species [16, 22, 28, 29, 32, 89–91], however comparisons between different studies necessitate caution, as differences in characterisation techniques will influence the results. Additionally, other components of wood that may influence the delignification, such as extractives and hemicellulose side groups, were not quantified in this work.

Table 5.1: Composition of raw material. Reported values are the average of 4 replicates and corresponding standard deviations. [% on odw]

Component	Birch	Beech	Aspen	Alder
Carbohydrates[a]	63.6 ± 0.6	61.1 ± 2.0	65.8 ± 0.4	62.6 ± 0.4
Glucan	39.1 ± 0.4	39.5 ± 1.3	44.8 ± 0.2	41.5 ± 0.2
Xylan	21.9 ± 0.1	19.0 ± 0.6	17.2 ± 0.2	18.1 ± 0.1
Mannan	1.6 ± 0.0	1.4 ± 0.1	2.9 ± 0.0	1.8 ± 0.1
Arabinan	0.3 ± 0.0	0.4 ± 0.0	0.3 ± 0.0	0.3 ± 0.0
Galactan	0.7 ± 0.0	0.8 ± 0.0	0.6 ± 0.0	0.8 ± 0.0
Klason lignin	19.6 ± 0.2	22.4 ± 0.1	19.0 ± 0.2	24.4 ± 0.4
Acid soluble lignin	5.0 ± 0.1	4.4 ± 0.1	4.7 ± 0.1	3.5 ± 0.1
Total	88.2 ± 0.7	87.9 ± 2.0	89.5 ± 0.3	90.5 ± 0.7

[a] Values given in anhydrous form

Changes to the content of lignin in pulp and black liquor were followed throughout pulping, as displayed in Figure 5.4A and B, respectively. The data followed similar (but inverse) trends, though the black liquor data slightly overestimated the amount of dissolved lignin, likely due to experimental errors of the cumulative data. Nevertheless, delignification of aspen was found to be significantly faster during the early stage of pulping at 140°C, whereas alder was slightly slower towards the end, compared to birch and beech. Regarding the liquor data, this is especially clear when comparing the values relative to the initial content of lignin, rather than wood, as illustrated in Figure A.1 in the Appendix.

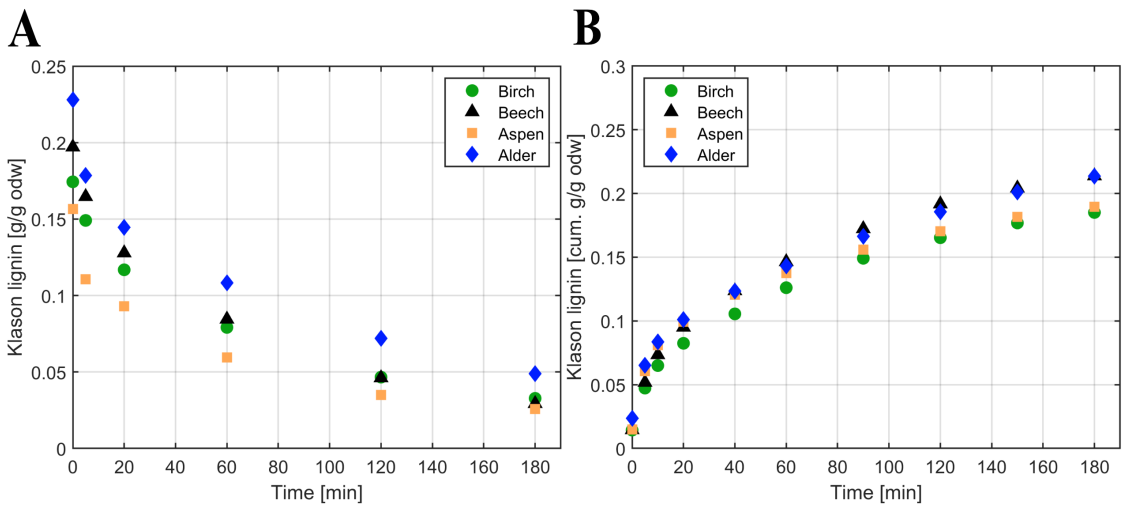

Figure 5.4: Klason lignin remaining in pulp (A) and cumulative Klason lignin content in black liquor (B) during 140°C pulping. The data is normalised to the amount of charged dry wood. Values at time 0 represents content in impregnated pulp or impregnation liquor.

The relative rate of delignification between the four species changed somewhat when pulping at 150°C, possibly suggesting different temperature dependencies exist among the species. However, this difference could not be attributed to any single factor, but could potentially depend on the chemical composition, morphological differences (such as cell wall thickness) and, especially at early pulping times, the extent of exposed middle lamella due to the use of wood meal rather than whole chips.

The extraction of xylan was much faster compared to lignin, with 75% of the total xylan extraction having occurred already after 10 min, as can be found in Figure 5.5. Similar to the results of Paper I, the residual xylan content in the pulp appeared to reach a virtually constant value towards the end of the cook for all studied species, suggesting that the remaining xylan is more resistant to further degradation and/or dissolution. The comparison of the xylan profiles from 140°C and 150°C in Figure 5.5 indicates that the remaining xylan fraction decreases with increased temperature. Different asymptotic values of residual xylan could potentially implicate that the total extent of xylan degradation at the end of the cook is not determined by the rate of the degradation reactions (peeling and hydrolysis), but rather depends on other factors, such as increased availability due to morphological changes during pulping, or re-adsorption effects. Nevertheless, only indications of this could be inferred from this work, and reaching definitive conclusions requires further research into this topic.

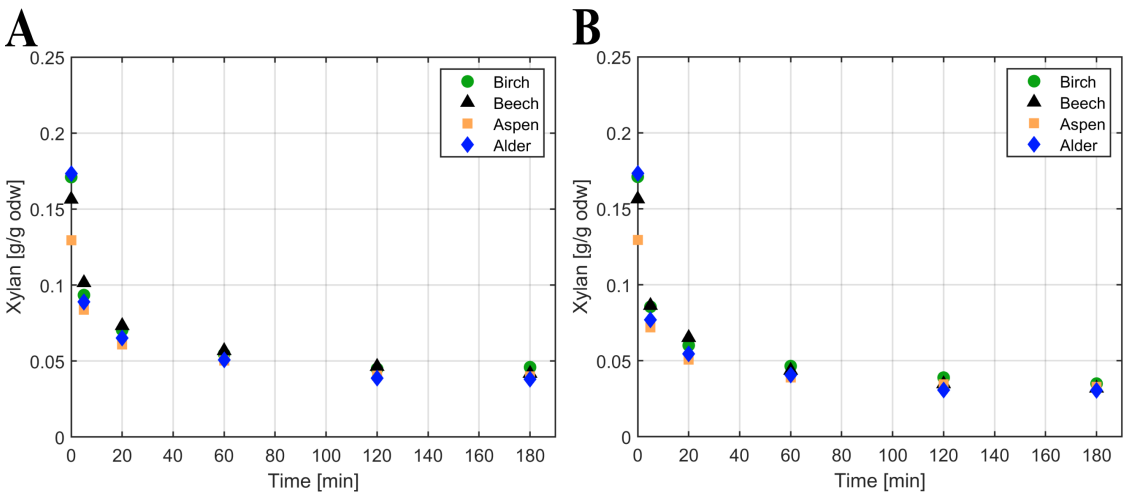

Figure 5.5: Residual content of xylan in pulp during (A) 140°C and (B) 150°C pulping. The data is normalised to the amount of charged dry wood. Values at time 0 represent content in impregnated pulp.

Studying the concentration of xylan in the black liquor (see Figure 5.6), it is evident that the rate of xylan dissolution for birch was distinctly faster than the three other species during the first 5 minutes. Notably, the residual xylan content in the pulps showed only minor differences among the species. That more xylan was detected in birch liquor without corresponding lower levels in the pulp could stem from various rationale. A higher resistance to peeling is one explanation, as peeling otherwise produces degradation products

(not measured in this work), which would then lead to a decrease of xylan in the pulp without a corresponding increase in the liquor. Xylan is generally considered resistant to peeling due to its substituent groups. However, although no characterisation of the substituents was made on the wood used in this work, previous studies found the degree of MeGlcA substitution to be equal or lower in birch, compared to beech and aspen [92–94]. Thus, from the perspective of MeGlcA substitution, it is unlikely that birch has an advantage over the other species. Instead, it is possible that birch xylan is, to a larger degree, linked to lignin rather than cellulose, which would increase the accessibility and, thus, enable xylan removal without further degradation.

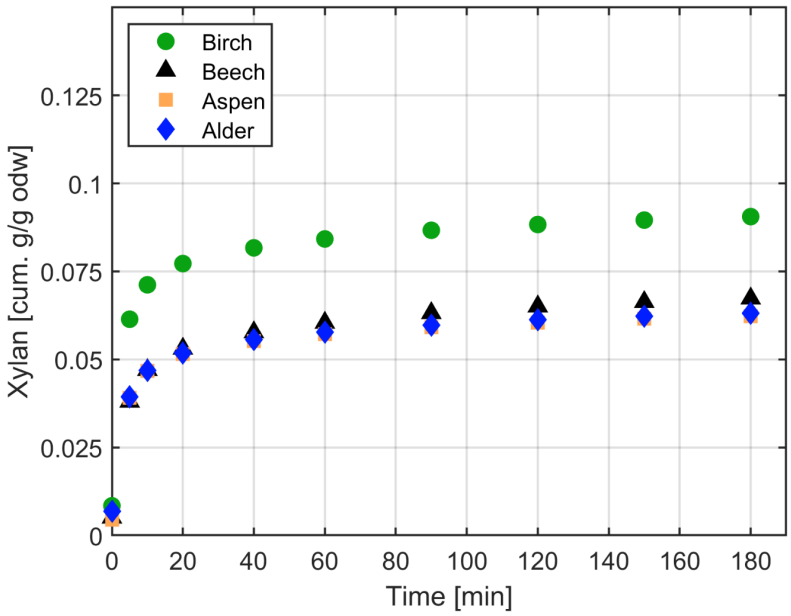

Figure 5.6: Cumulative amount of detected xylan in BL during 140°C pulping. Data is normalised to the amount of charged dry wood. Values at time 0 represent content in the impregnation liquor.

The molecular weight distributions of lignin precipitated from the black liquors sampled after 5 and 120 min for all four species are shown in Figure 5.7. As is evident from subplot A displaying the UV data, the size distribution of the dissolved lignin is very similar between the four species. Consequently, this indicates that the size of the dissolved lignin cannot explain the differences seen in delignification rates. Instead, these differences possibly stem from reaction kinetics (molecular structure or availability of lignin), solubility effects, or transport mechanisms independent of the lignin size (such as size and morphology of cell wall). The RI data seen in Figure 5.7B indicate that birch contains greater amounts of polymeric xylan, as anticipated from the pulping data in Figure 5.6.

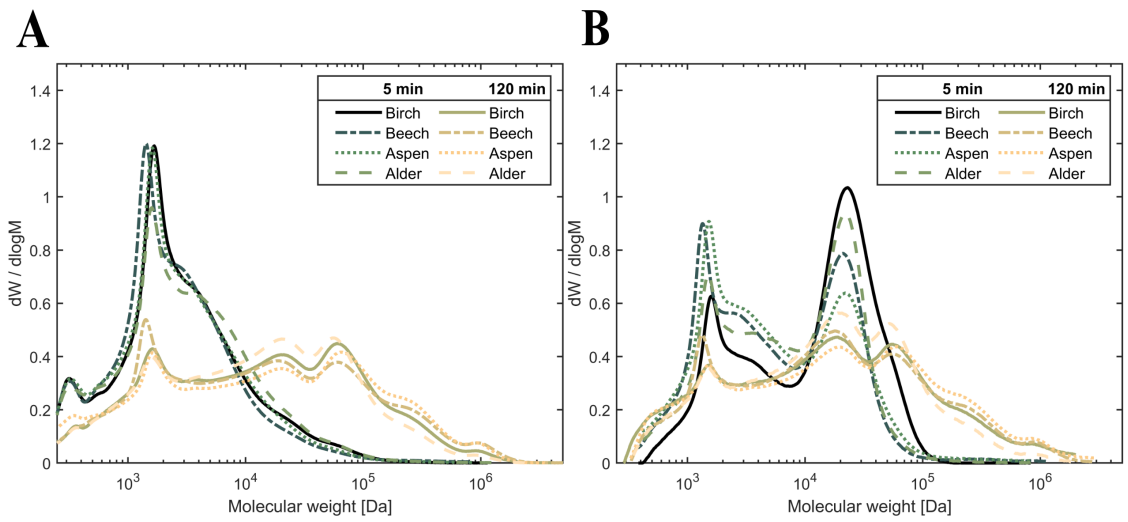

Figure 5.7: MWD of precipitated material in the 5 and 120 min fraction from all four species during 150°C pulping, as detected by (A) UV and (B) RI.

Analysis of 2D HSQC NMR data of the precipitated material revealed the presence of lignin inter-unit linkages (e.g β-O4, β-β' etc.) in all samples. Given that only qualitative measurements were performed, no differences in the structure of the lignin from the four species could be assessed. Despite strong signals related to xylan, no signs of LCC's were found, although they may exist in concentrations affecting the delignification behaviour, yet still fall below the detection limit.

5.2.2 Variations of the MWD over time

Paper II also included more in-depth studies of the MWD of dissolved lignin from birch, presented in Figure 5.8. It was found that the size distribution is relatively uniform during the first 20 min of pulping at 150 °C, despite that over half of the lignin had been removed at this point. Subsequently, the distribution began to shift towards larger sizes and continued to increase for the remainder of the cook. An explanation for this behaviour could be that, early on, there exists an abundance of easily cleaved β-O-4 linkages resulting in a quick fragmentation of lignin into uniform fragments that are easily transported out into the liquor. Meanwhile, transport of larger dissolved fragments is, inherently, much slower and will not be significant until later when the initial fragmenting reactions have decreased, thus explaining the continuously shifted MWD over time. Additionally, due to the impregnation, the concentration of cooking chemicals within the wood meal was initially high, benefiting the reaction rate and contributing to the uniformity. Then, as it was consumed, additional alkali needed to diffuse into the fibre wall, which may have impacted the overall delignification rate as well. Therefore, these results confirm the trends seen in Paper I, and suggest that the transport resistance of dissolved wood species (and potentially alkali) occurs already at the cell wall level.

The RI data of Figure 5.8B shows that the polymeric xylan (as inferred from the peak at approximately 20 kDa) was extracted during the first 5 minutes. This concurs with the majority of the xylan extraction, thus supporting the possibility that dissolution mechanisms are significant for xylan removal in hardwood.

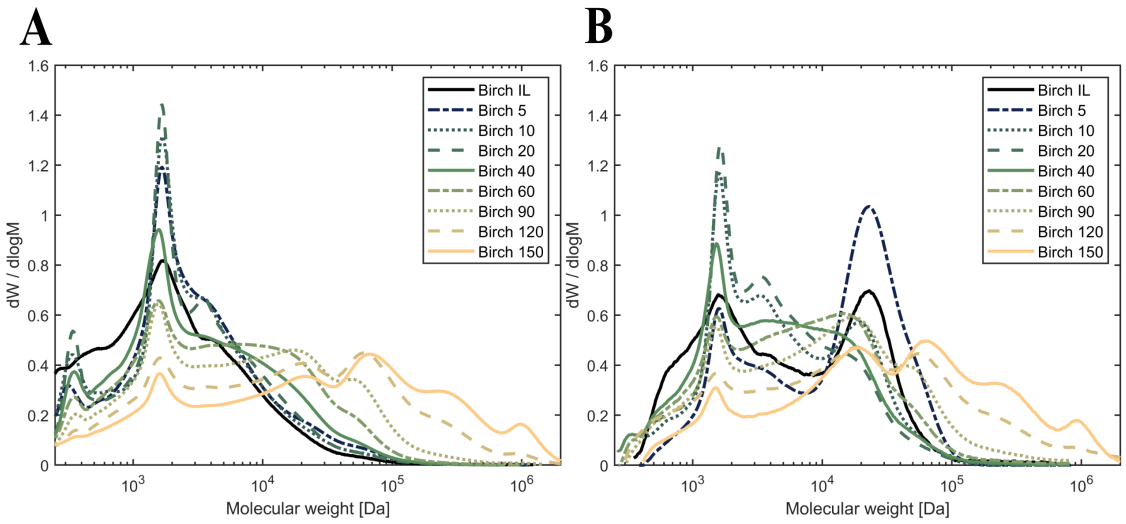

Figure 5.8: MWD of precipitated material from all liquor fractions during pulping of birch at 150°C, as detected by (A) UV and (B) RI. Data from 180 min excluded due to low quantity of lignin in the liquor fraction.

5.2.3 Summary of Paper II

The comparison of kraft pulping behaviour of the hardwoods selected in this work is, to the author's knowledge, the first of its kind. Comparisons between studies investigating the species separately are often problematic given the use of broadly different process conditions and analytical tools. Thus, one of the main benefits of Paper II is as a basis for further investigations into chemical and morphological differences in these hardwoods and their effect on the delignification. In addition, the results revealed differences in delignification rates among the species, though the underlying reasons are still not fully understood. Lastly, MWD measurement indicated once more that, even within the cell wall, transport mechanisms are likely to have an impact on the overall rate of delignification, and yet could not be correlated to the size of the transported lignin.

Chapter 6

Concluding remarks and Future Work

In this work, hardwood kraft delignification was studied in two ways: First, the effect of mass transfer in birch wood chips was studied, based on variations in the liquor composition inside the chips, compared to the bulk. Second, the delignification behaviour of four hardwoods was studied at the cell wall level by pulping of wood meal, specifically focusing on characterisation of the dissolved wood components.

In experiments with birch wood chips, it was found that impregnation with the active cooking ions increased the subsequent delignification rate, whereas the ionic strength in the impregnation liquor did not affect the delignification under the conditions studied. In addition, comparing the content of dissolved wood components in the liquor inside the wood chips revealed substantially higher concentrations of both lignin and carbohydrates, compared to the bulk, implying limited transfer between the two fractions. Measurements of the molecular weight distribution of lignin in the two fractions also indicated an impact of mass transfer, as inferred from the increased weight of the dissolved lignin in the lumen liquor. Moreover, a more degraded lignin and carbohydrates fraction in the bulk, compared to the lumen liquor, was observed through HSQC NMR, confirming that the two fractions are distinct from each other.

Comparing the pulping behaviours of the four hardwoods (birch, beech, aspen, and alder), aspen was found to have a higher rate of delignification during the early stage of pulping, whereas alder appeared to have a somewhat lower rate towards the end. Additionally, only minor variations in the xylan content of the pulp were found between the four species, although in the black liquor, birch xylan was dissolved at significantly higher quantities compared to the other three species. Analysis of the MWD and HSQC data of the dissolved material found no essential differences between the species, with only minor variations in the MWD of xylan at the early stage of pulping. Lastly, additional analysis

of the dissolved material in birch liquor revealed a continuously increasing molecular weight over time, implying a considerable mass transfer resistance at the cell wall level, as well as a rapid extraction of polymeric xylan, confirming the significance of dissolution mechanisms in xylan removal during pulping.

6.1 Future Work

As highlighted by this work, much remains to be investigated regarding the interplay between mass transfer and reaction kinetics during kraft pulping. Further characterisation of the differences among species in terms of e.g. cell wall structure and thickness, as well as their variations during pulping, could grant further insights on delignification mechanisms at the cell wall level. Moreover, quantitative NMR studies on the dissolved material in the liquor would, when combined with a continuous flow-through reactor, allow a more detailed time-resolved perspective of the kinetics of lignin (and carbohydrate) extraction. Finally, studies on the effect of varying the liquor composition during the cook would also be of interest for studying the involvement of different delignification mechanisms.

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Appendix

Figure A.1 presents the same data as Figure 5.4, but normalised to the amount of initial lignin of each species.

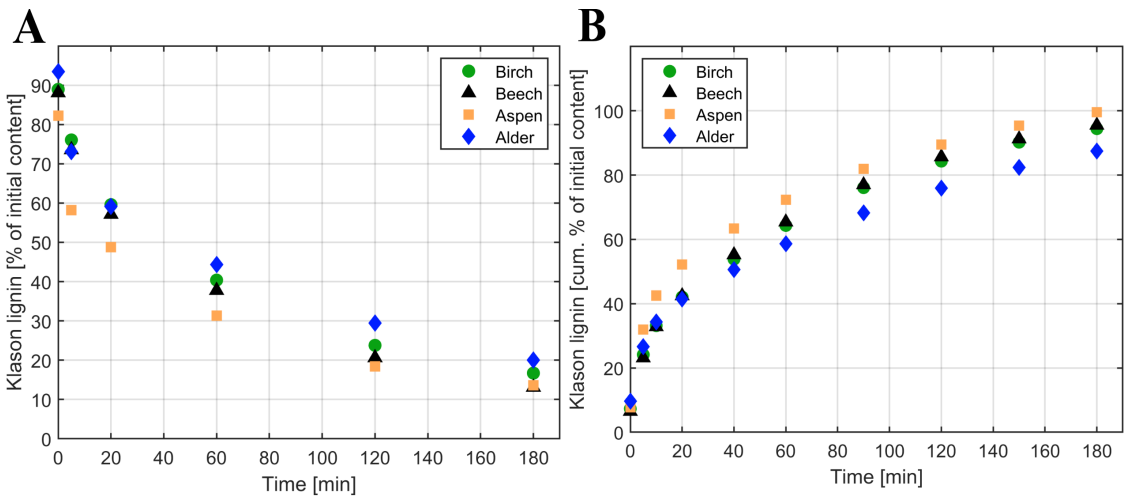

Figure A.1: Klason lignin remaining in pulp (A) and cumulative Klason lignin content in black liquor (B) during 140°C pulping. The data is normalised to the initial amount of Klason lignin in the charged wood. Values at time 0 represent content in impregnated pulp or impregnation liquor.