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A comparative study of the cell wall level delignification behaviour of four Nordic hardwoods during kraft pulping

Wood Chemistry

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Abstract: Wood is a heterogeneous material with significant variation among species. This inherent complexity poses a challenge to the continuous expansion of our understanding of the kraft process; yet previous pulping research has mainly been limited to a few species. This study investigates variations among some less studied species and their cell wall level delignification behaviour during kraft pulping. Ground wood of birch, beech, aspen, and alder were pulped at near-constant composition and temperature conditions. Minor, yet significant, differences in the rates of their delignification were observed: aspen had a pronounced fast rate during the initial stage, whereas alder delignified more slowly relative to its high initial lignin content. The dissolution of xylan was substantially faster for birch. In contrast, no substantial differences were detected between the species in the molecular weight and structure of the dissolved wood components, suggesting that the different delignification behaviours stem from variations in the residual phase. The molecular weight distribution of dissolved lignin was uniform during the initial stage of pulping, which is indicative of rapid and extensive fragmentation. Subsequently, the weight increased continuously for the remainder of the process, suggesting that the mass transfer within the cell wall influenced the overall delignification kinetics.

Keywords: hardwood; kraft delignification; mass transport; precipitated lignin

1 Introduction

The kraft pulping process, in the form of a combined pulp mill and biorefinery, will play an important role in the global shift towards a biobased circular economy because it is essential in the quest to replace materials procured from non-renewable sources. The amount of biomass available on Earth is nevertheless finite and improving the resource efficiencies in all areas is therefore paramount (EC 2004). A modern kraft pulp mill has a material yield of roughly 40–60 %, depending on the products, whilst running at an energy surplus. There is therefore a potential for extracting even more material, thereby increasing the total material yield, without disrupting the energy balance. However, liberating the fibres in wood to produce pulp requires treatment under harsh process conditions, which degrades large parts of the initial wood material. Pulping is thus a trade-off between maintaining an acceptable yield and producing a final product with the desired purity and properties, and especially so if various wood components are being extracted simultaneously in side streams where the optimal process conditions probably differ significantly from those of the main product. However, achieving this goal requires an even more comprehensive understanding of the pulping process than is currently held. This stems mainly from the inherent complexity of processing such a heterogeneous material as wood, as it is a network of various connected wood cells of different dimensions, orientations, and purposes. Each cell, in turn, consists of a cell wall, which itself is a disparate multilayered structure of (hemi)celluloses and lignin in various concentrations and levels of order (Fengel and Wegener 1983).

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A key step in the pulping of wood is delignification, which entails the transport of small ions and large polymers, multiple reactions and macrostructural changes all happening simultaneously (Sixta et al. 2006). In conjunction with the complexity of wood, a complete understanding of the interplay between the different mechanisms remains incomplete: for example, even recent modelling attempts rely mainly on reaction kinetics (Rahman et al. 2020) as delignification kinetics have traditionally been assumed to be pseudo homogeneous and determined by the reaction rate of aryl ether bond cleavage in lignin (Gierer 1980). This is despite the fact that properties such as chip thickness, which affects mass transport but not reaction kinetics, are known to have a large impact on the overall delignification process (Dang and Nguyen 2008; Svedman et al. 1998; Tripathi et al. 2018). The liquor within the wood chips creates significantly different environments compared to the bulk, further emphasizing the need to account for mass transfer when studying delignification (Brännvall and Rönnols 2021; Kron et al. 2023; Pakkanen and Alén 2012; Simão et al. 2011).

Thus, it is crucial to decouple the various mechanisms in order to gain a better understanding of the delignification process. Ground wood has been used in kinetic studies to eliminate the effects of transport through the wood chip (Dang 2017; Fearon et al. 2020; Jara et al. 2019). It has also been suggested that transport phenomena have a significant impact even at the level of the cell wall (Dang et al. 2016; Mattsson et al. 2017; Mortha et al. 1992) but these types of studies are, however, limited in number and have typically focused on a single (often softwood) wood species. However, due to the fact that various hardwood species have different compositions and chemical structures, they may exhibit differences in pulping behaviour, potentially even so within the same genus, as found in studies on eucalyptus (Pinto et al. 2005a; Santos et al. 2011). Consequently, there is a need to expand current knowledge of cell wall transport mechanisms in general, and the effects due to compositional and structural differences among wood species in particular.

As a first step towards improved understanding of hardwood delignification, this study investigates the general delignification behaviour of wood meal samples of four common Nordic hardwood species, namely birch, beech, aspen and alder, during kraft cooking. Delignification studies incorporating several hardwoods simultaneously (outside of the eucalyptus genus) are sparse, and a comparative study on these four species has never, to the authors' knowledge, been conducted before. A flow-through cooking process is employed to study simultaneously the interplay between reaction kinetics and mass transfer on the cell wall level from the perspective of the dissolved wood components. The four hardwood species are compared with respect to the rate of dissolution of lignin and carbohydrates at different temperatures. Additionally, the molecular weight distribution of the dissolved wood components of all four species is studied, along with its variation over time.

2 Materials and methods

2.1 Raw materials

Pulp mills in southern Sweden supplied the wood used in this study, all of which are hardwoods: alder (*Alnus glutinosa*), aspen (*Populus tremula*), beech (*Fagus sylvatica*) and birch (*Betula pubescens*). In the case of the latter, no distinction is usually made between *B. pubescens* and *Betula pendula*: the one used in this study has been tentatively identified as *B. pubescens* according to the precipitation method described by Lundgren et al. (1995), although decomposition of the platyphylloside used to distinguish the two species may have occurred due to the long storage time of the bark sample prior to analysis. A single log of stem wood (approximately 15–20 cm in diameter) of each species was chipped, and bark and knots removed, before being left to dry in ambient conditions to a dry content of 89–92 %. The chips were then ground and sieved into particles passing a 1-mm mesh. Photographs of the ground wood meal are found in Supplementary Figure S1. The dry content of each wood meal was measured prior to each cook.

2.2 Flow-through reactor delignification

Kraft delignification of the wood meal was performed in a tube reactor with a continuous flow of cooking liquor, see Figure 1. In the set-up, approximately 4.5 g of wood meal was distributed evenly inside the column reactor with inner dimensions of 300 × 7.8 mm (length × diameter). The cooking liquor had a concentration of OH^- and HS^- of 0.35 and 0.15 mol/kg liquor, respectively. Impregnation of the wood meal was performed at room temperature using a continuous flow of the same liquor as during the proceeding cook, for a total volume of approximately 30 ml. At the start of each cook, the reactor was lowered into a hot polyethylene glycol bath at either 140 °C or 150 °C, with negligible heat-up time due to the pre-heated liquor and thin reactor. Initially, an increased flow rate of 10 ml/min ensured a minimal impact of alkali-consuming reactions occurring in the early stage of delignification (Bogren et al. 2009). The flow rate was lowered stepwise, with 2.5 ml/min being used from 22 min onward, and the total cooking time was varied up to 180 min.

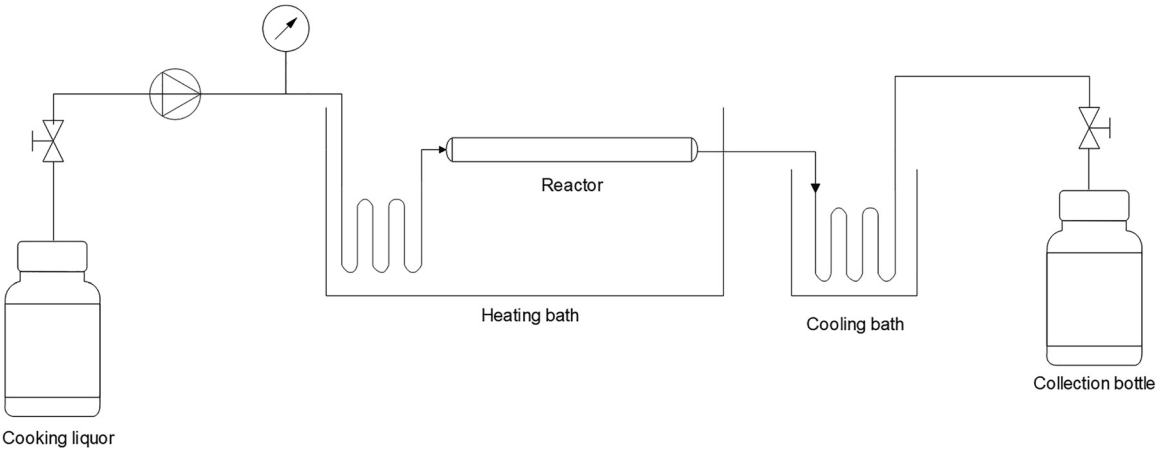

Figure 1: Schematic diagram of the reactor set-up.

Delignification was discontinued by placing the reactor into a water bath at room temperature for 10 min. After termination of the cook, the pulp was suspended in approximately 300 ml deionized water and defibrillated with an immersion blender. The suspension was then filtered through a fine nylon mesh and washed with 700 ml water; the resulting filter cake was dried at 105 °C overnight. A more detailed description of the set-up can be found elsewhere (Bogren et al. 2009).

The immediate cooling of the reactor outflow minimised further reactions of dissolved material, thus allowing continuous sampling of the black liquor (BL) representative of the conditions within the reactor at that time: the intervals of BL sampling are given in Table 1.

2.3 Lignin precipitation

The lignin dissolved in the black liquor was precipitated using sulphuric acid to pH 2.5 and freezing overnight, as described by Dang et al. (2016). After thawing, the solids were separated using glass fibre filters, washed with water acidified to pH 2.5 and then dried over P_2O_5 at 40 °C for 3 days. This method can cause some carbohydrates to co-precipitate along the lignin, as was found in the following characterisation using gel permeation chromatography (GPC) and nuclear magnetic resonance microscopy (NMR).

Table 1: Sampling intervals of BL.

Name	Time (min)	Approx. volume (ml)
Impregnation	−5 to 0	30
BL 5	0 to 5	50
BL 10	5 to 10	50
BL 20	10 to 20	90
BL 40	20 to 40	70
BL 60	40 to 60	50
BL 90	60 to 90	80
Bl 120	90 to 120	80
BL 150	120 to 150	80
BL 180	150 to 180	80

2.4 Analytical procedures

The contents and compositions of lignin and carbohydrates in the pulps and black liquors were analysed, as well as the molecular weight distributions and structural motifs in the precipitated lignin. Detailed descriptions of the analytical procedures are reported in a previous work (Kron et al. 2023), a summary of which is given here.

Following a slightly modified version of the standard procedures by NREL (Sluiter et al. 2012), lignin was quantified into acid-insoluble (Klason lignin) and acid-soluble (ASL) parts. However, emphasis was placed on Klason lignin during subsequent analysis since measurements of ASL are subject to variations due to extractives, side products and different absorptivity constants (Dence 1992; Shin et al. 2004). After the separation of Klason lignin, the filtrate was used for carbohydrate quantification using anion exchange chromatography with a pulsed amperometric detector (HPAEC-PAD). The carbohydrate monomers detected were corrected for yield of the hydrolysis as reported by Wojtasz-Mucha et al. (2017), and given as their anhydrous form (Janson 1974). Extractives were not removed prior to characterisation, which may inflate the lignin value reported and underestimate the carbohydrate content (Shin et al. 2004).

The molecular weight distribution (MWD) of the precipitated lignin was determined by gel permeation

chromatography. The system used dimethyl sulphoxide (DMSO), with 10 mM LiBr as the eluent, and was calibrated with pullulan standards in the range 0.180–708 kDa. Two detectors were run in series: an ultraviolet (UV) detector operating at 280 nm and a refractive index (RI) detector.

Finally, 2D NMR spectroscopy, using a heteronuclear single quantum coherence sequence (HSQC), was employed to characterise the precipitated lignin further. The acquisition was made using the same pulse programme as described earlier, but with a probe operating at 700 and 176 MHz for ^{1}H and ^{13}C. The spectral width (in ppm) was kept the same, resulting in an acquisition time of 109 ms and 7 ms, respectively. The precipitated lignin was dissolved at a concentration of 140 mg/ml using DMSO-d_6 as solvent, with the exception of the 120 min fraction of aspen: this was dissolved to 70 mg/ml, as less precipitated lignin was available due to the low concentration in this particular fraction. The solutions were centrifuged at 12.5 krpm for 5 min to remove undissolved particles (<5 w%).

3 Results and discussion

3.1 Characterisation of the raw materials

The four species of wood were characterised according to their chemical compositions, Table 2. In general, the results concur with those reported previously, namely that birch is relatively high in xylan and low in lignin, aspen is high in glucan and mannan but low in xylan and lignin, and beech and alder are both high in lignin (Borovkova et al. 2022; Fengel and Wegener 1983; Gabrielii et al. 2000; Henriksson et al. 2009; Kotilainen et al. 2001; Pinto et al. 2005b; Santos et al. 2011, 2017). However, the range of values reported varies considerably, and differences in characterisation techniques necessitates caution when making comparisons.

Table 2: Composition of the raw materials. Values indicate an average of four replicates and corresponding standard deviation (% 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.

Additionally, neither the content of substituents on the hemicelluloses, such as methyl glucuronic acid and acetyl groups, nor the extractives were quantified in this study.

3.2 Comparison of delignification rates

The changes in the lignin content of the pulp recorded during delignification are shown in Figure 2A and B, where the data is presented on the conventional basis of amount of lignin per initial mass of wood charged to the reactor. The same data is plotted in Supplementary Figure S2 but normalised with the initial content of lignin in each wood species.

It should be noted that aspen, regardless of temperature, experiences an initial removal of lignin greater than the three other species. After 180 min at 140 °C, aspen still has the lowest (both absolute and relative) amount of residual lignin, whereas after the same time at 150 °C, all of the other species have surpassed aspen. Moreover, it appears that alder, regardless of temperature, experiences the lowest rate of delignification. Many factors affect the removal of lignin, however, especially during the early part of the process when it is likely that a fraction of lignin is readily available due to a partially exposed middle lamella stemming from the use of wood meal rather than whole chips. Thus, at this point, the apparent difference in delignification rates between wood species cannot be attributed to any individual mechanism.

As expected, the same trends are seen when investigating the cumulative amount of lignin found in the BL, see Figure 2C and D. Again, these data is skewed by the initial content of lignin, and differences between species are more easily discerned in the relative data, see Supplementary Figures S2C and D. Regardless of this, aspen shows an initial high rate of delignification but seems to benefit less from the increased temperature compared to the other three species.

The total amount (pulp and liquor) of detected Klason lignin surpasses 100 % for all species after 60 min and onwards during 150 °C cooking, to a total detected amount of 108–123 % after 180 min. This most likely stems from an overestimation of the lignin content in the BL fraction. The cumulative content at this time represents the sum of 10 measurements, hence it is susceptible to stacking experimental errors. For example, furfurals from pentose degradation may to some degree show as lignin (Wan et al. 2019). Nevertheless, these measurements are still of value when comparing the relative differences between the wood species, which are also confirmed by the more conventional measurements of residual lignin content in the pulp.

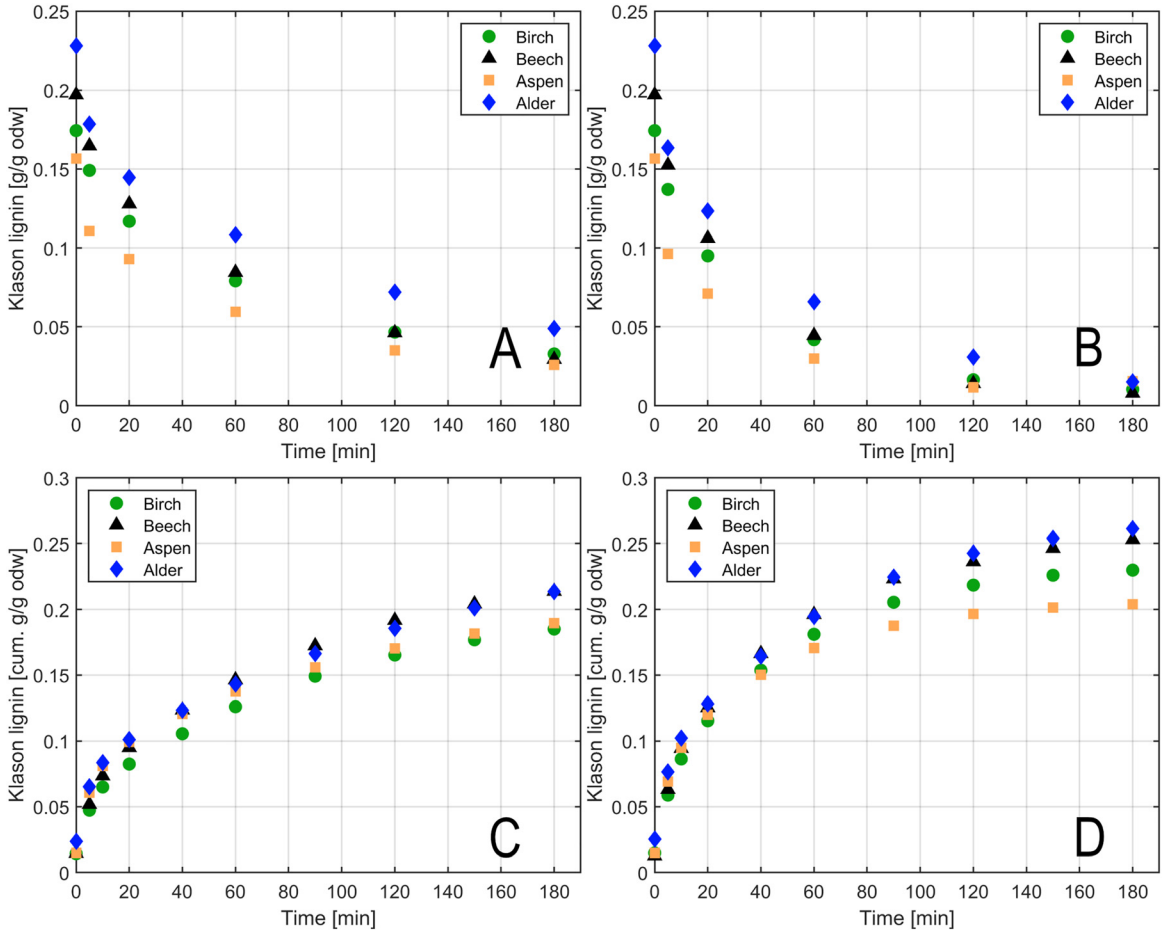

Figure 2: (A, B) Klason lignin remaining in the pulp during pulping at (A) 140 °C and (B) 150 °C. (C, D) Cumulative amount of Klason lignin detected in the BL during pulping at (C) 140 °C and (D) 150 °C. Values are normalised to the amount of wood charged. Values at time zero represent the content of impregnated pulp and impregnation liquor.

3.3 Rate of xylan removal

Compared to delignification, the removal of xylan is rapid. Figure 3C and D shows that not only is approximately 93 % of the dissolved xylan released in the first third of the delignification process, but also that approximately 75 % is released during the first 10 min. Moreover, the amount of xylan dissolved in the birch BL is significantly higher than the other species, even when the initial high content found in birch is corrected for (Supplementary Figure S3). Although it could be expected that the high content of dissolved xylan in birch BL results in correspondingly less residual xylan in the pulp, this was not found to be the case, in either absolute or relative terms, in the pulp data (Figure 3A and B and Supplementary Figures S2A and B). Possible explanations for this discrepancy could be that birch xylan is less prone to alkaline peeling (commonly contributing to losses in detectable monosugars), leading to a higher detection of its xylose units (that would otherwise be converted to xyloisosaccharinic acids), or it is more easily extracted from the cell wall without heavy fragmentation occurring.

The resistance shown by xylans to peeling is generally attributed to the frequent substitution of methyl glucuronic acid groups. On the other hand, previous studies have shown that birch xylan is actually less substituted compared to beech and aspen (Teleman et al. 2000, 2002; Jacobs et al. 2001). Thus, it is unlikely that differences in peeling mechanisms due to degree of substitution can explain the increased content of xylan found in the birch BL in this study. Another possibility could, instead, be differences in the accessibility of the xylans, as suggested in previous reports, which attributed these differences to whether xylan was associated to lignin or cellulose (Dammström et al. 2009; Ruel et al. 2006). It is therefore possible that the increased amount of xylan in birch BL could be due to a larger native fraction of xylan that is more accessible, and thereby more easily removed without being modified or degraded further. For example, the presence of lignin carbohydrate complexes

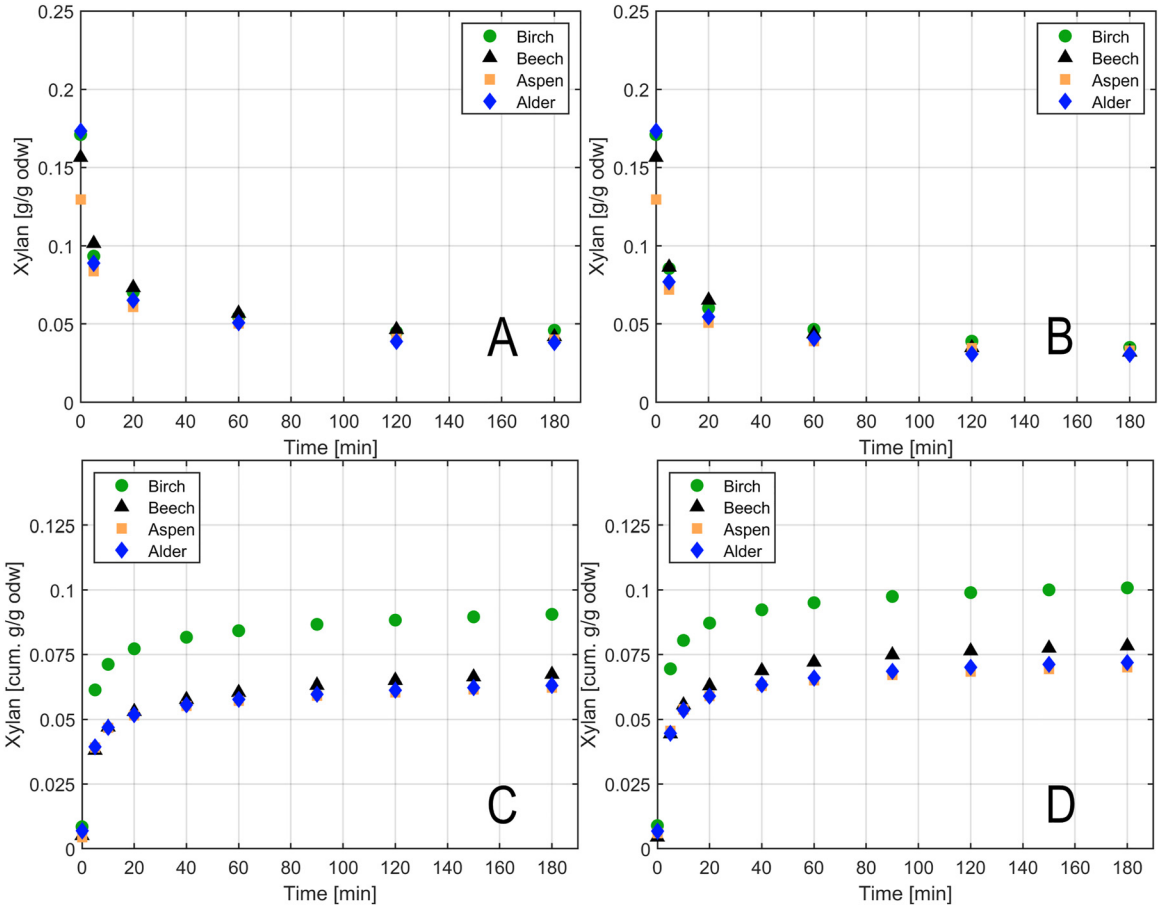

Figure 3: (A, B) Xylan remaining in the pulp during pulping at (A) 140 °C and (B) 150 °C. (C, D) Cumulative amount of xylan detected in BL during pulping at (C) 140 °C and (D) 150 °C. Values are normalised to the amount of wood charged. Values at time zero represent the content of impregnated pulp and impregnation liquor.

(LCCs) could affect the ability of xylan to dissolve. Some of these structures are relatively stable against pulping and would then remain in the pulp (Lawoko et al. 2003), which were not characterized in this work. Possible LCCs occurring in the initial BL fraction were investigated via NMR, though no such linkages were found in concentrations above the detection limit, see Section 3.4.

Moreover, it appears that the amount of dissolved xylan tends to different asymptotic values at 140 °C than at 150 °C, as opposed to the lignin case, where there is clearly still ongoing delignification taking place after 180 min at 140 °C (Figure 2A–C). This may indicate that the total amount of extracted xylan, and the differences between the species in question, do not depend on the rate of xylan fragmentation reactions (such as peeling and alkaline hydrolysis), but rather on the extent of the reactions or subsequent mechanisms: an example of the former could be a more extensive degradation of the cell wall structure at higher temperatures (Joutsimo and Giacomozzi 2015; Stone and Scallan 1965), leading to a higher availability of xylan, whereas differences in solubility with temperature would affect the xylan removal independently of the rate of fragmentation. Another possible explanation could be the re-adsorption of xylan onto the pulp. However, the adsorption has, albeit for birch xylan on cotton, been found to increase with temperature, and it would therefore rather lead to a decrease in the concentration of xylan in the BL at increased temperatures rather than an increase (Danielsson and Lindström 2005). Furthermore, the short residence time of the cooking liquor in the reactor (~5 min) due to the continuous flow is likely to reduce the impact of xylan re-adsorption.

In addition, the effect of temperature on xylan removal is greatest at the beginning of the cook and then decreases, indicating that mechanisms that are highly temperature-dependent take place to a greater extent early on in the process. Once again, the interplay of the mechanisms that occur is complex, making more extensive studies that target

the effect of temperature necessary in order to separate the impact of individual mechanisms.

The total amount of detected xylan is approximately 80 % of the initial xylan content in the untreated wood, independent of tree species. This is mainly due to the fact that the degradation products of peeling, isosaccharinic acids, were not quantified in this work. The detected amount of xylan could also be affected by the relatively low yield of xylose during the acid hydrolysis step prior to the carbohydrate quantification. This was corrected for in the reported data (with an assumed xylan yield of 79 %), but it has been reported that the yield can be as low as 58 % for pure monomers in water solutions (Maitz and Kienberger 2021).

3.4 Molecular weight distribution of the precipitated material

The change over time of the MWD of the material precipitated from the black liquor from birch is displayed in Figure 4 (for 140 °C cook) and Figure 5 (for 150 °C). Studying the response from the UV detector (Figure 4A and 5A), little difference can be seen in the distributions during the first 20 min. After 40 and 60 min, for 140 °C and 150 °C respectively, the weight distribution is shifted towards larger molecules, which continues to increase with time for the remainder of the cook. This is in line with our earlier research, which found a similar shift in the MWD of birch wood chips as well as spruce wood meal (Dang et al. 2016; Kron et al. 2023). It should be kept in mind, once again, that the present study uses wood meal rather than chips, and the transport of lignin therefore occurs mainly directly from the cell wall into the bulk liquor. Consequently, the increase in the MW of extracted lignin over time corroborates the theory that the transport of the lignin within the cell wall has a substantial effect on the overall delignification rate. Similar effects have been reported previously for a different, but related, process: during the alkaline leaching of oxygen delignification (90–120 °C, 1.65–5.5 g/l NaOH), the relatively slow diffusion of lignin out from the cell wall was found to affect the overall rate of lignin removal (Pahlevanzadeh and Van Heiningen 2023).

Additionally, the GPC data shows very similar distributions during the first 40/20 min for 140 °C and 150 °C respectively, despite that over 50 % of all lignin removal occurs during this time. It has been suggested previously that the cleavage of β-O-4 linkages only occurs early on in the process (Mattsson et al. 2017). Thus, a possible interpretation of the uniform distribution could be an initial high availability of easily cleaved interunit linkages within the lignin structure (such as aryl-ether bonds), leading to extensive fragmentation and the release of relatively uniform fragments. As these easily cleaved structures become depleted, the remaining large lignin fragments undergo only very slow further fragmentation due to inaccessibility, stabilised structures or possibly even condensation reactions. Although occurring simultaneously with the initial fragmentation, diffusion is relatively slow and size-dependent: increasingly large fragments are released continuously into the BL over long periods of time, and still increases between the final two liquor fractions. Consequently, the extraction of the remaining lignin will then probably be strongly influenced by the rate of diffusion of the lignin.

Comparing the difference between the values of RI (Figures 4B and 5B) and UV (Figures 4A and 5A) provides information of the carbohydrates that co-extract along the

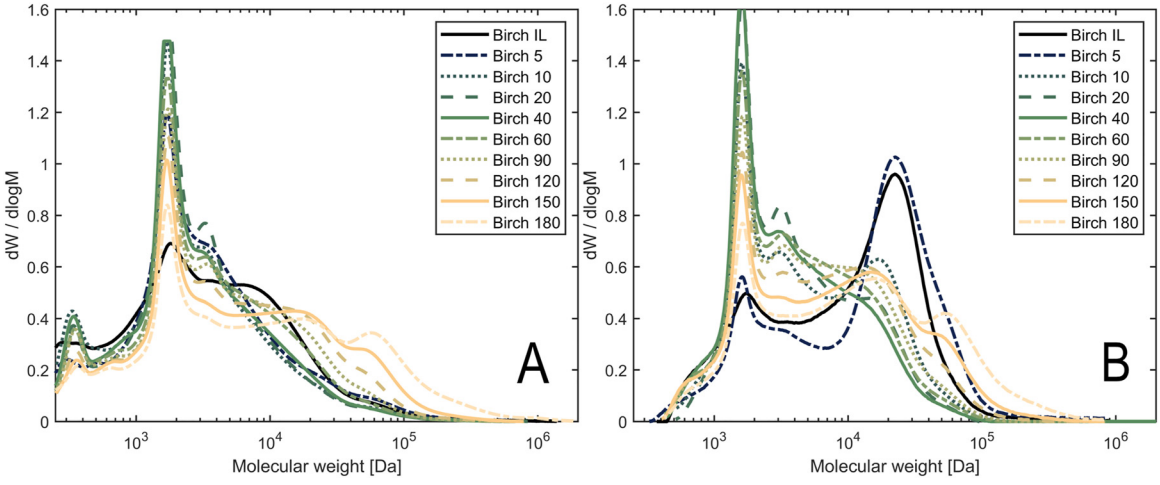

Figure 4: MWD of the material precipitated from all BL fractions during the pulping of birch at 140 °C, as detected by (A) UV and (B) RI.

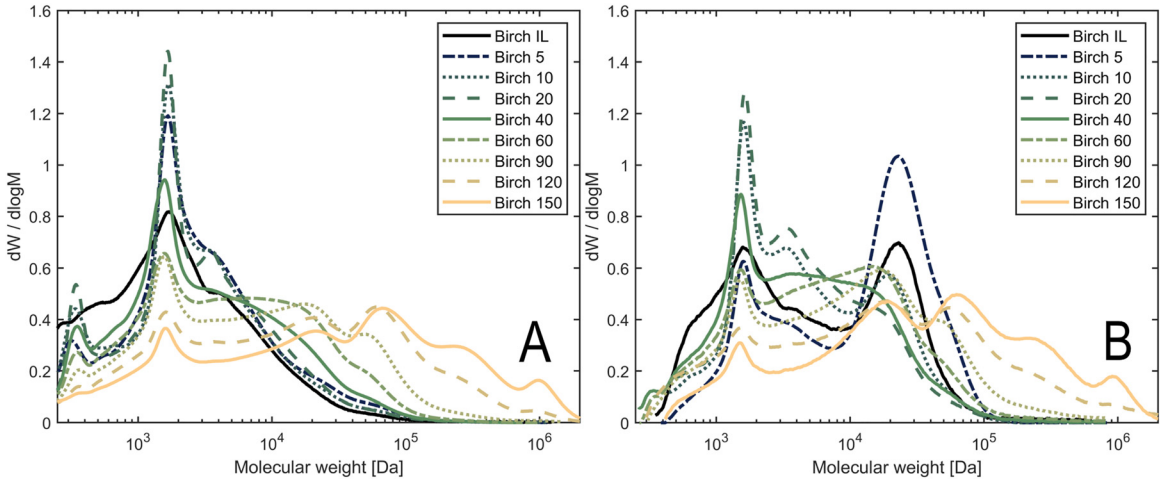

Figure 5: MWD of the material precipitated from all BL fractions during the pulping of birch at 150 °C, as detected by (A) UV and (B) RI. Reliable data could not be collected in the last (180 min) fraction due to the low concentration of lignin, so this point is excluded.

lignin during the precipitation procedure, but which co-elutes independent of the lignin. As expected, the graphs are very similar at long cooking times because that is when the concentration of carbohydrates in the BL is very low. The largest difference is seen during the first 5 min, as this is when the majority of xylan is extracted (which, in turn, accounts for >80 % of the total dissolved carbohydrates). Interestingly enough, the placement of the carbohydrate peak (in the order of 20 kDa) implies that xylan exists in the BL as substantially large polymers, rendering further support towards the suggestion that dissolution mechanisms play an important role in xylan removal in hardwood (Axelsson et al. 1962; Lisboa et al. 2005).

A comparison of the MWD of the material precipitated from the four species is given in Figure 6. The distribution detected via UV (corresponding to lignin) shows very little disparity between the species. These results thus indicate that the difference seen in the delignification rates of the different species (Figure 2) may not depend on the size of the dissolved lignin; other factors that affect the mass transfer beyond lignin size include the interactions with, and the thickness of, the cell wall (Andersson et al. 2003), along with solubility effects pertaining to lignin properties other than size (Saltberg et al. 2009). It is probable, once again, that the initial delignification is influenced by the partially-exposed middle lamella which, in turn, affects the structure of the lignin released, as well as any differences in the exposed surface area of the wood meal from different species stemming from the grinding.

In the case of the RI response (Figure 6B), the peak around 20 kDa mentioned previously appears for all species in the 5 min fraction. It is most pronounced in the

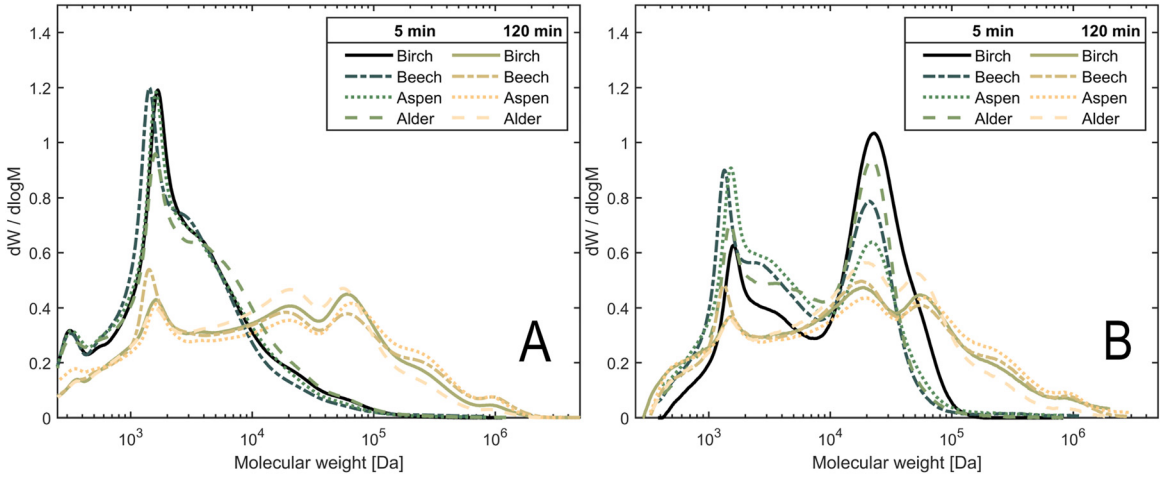

Figure 6: MWD of the material precipitated in the 5 and 120 min fractions of all four species during pulping at 150 °C, as detected by (A) UV and (B) RI.

birch sample, and corresponds to a higher relative concentration of xylan in the precipitated material. This result aligns well with the behaviour seen in Figure 3, since birch had significantly higher amounts of detectable xylan in the BL that are also suspected of having a relatively greater high-molecular (less degraded) content. The rapid extraction of high-molecular birch xylan early on in the process is probably associated primarily with its accessibility (i.e. location in the cell wall) and/or substitution pattern.

Further characterisation of the lignin precipitated from the four species was performed via 2D-NMR. The resulting spectra can be found in Supplementary Figures S4–S7. All samples showed signals corresponding to inter-unit lignin bonds: mainly β-O-4 and β-β′, with trace amounts of β-5 and β-1 structures. The β-1 structures disappeared completely in the 120 min fraction. No signals related to lignin-carbohydrate complexes (benzyl ethers or phenyl glycosides) were found in any sample, although xylan and glucuronic acid signals were present in all samples.

The qualitative nature of the HSQC data makes drawing conclusions based on variations in peak volumes unreliable because differences in T_1 and T_2 relaxation times, along with $^1J_{CH}$ coupling constants, affect the strength of the signal. Given these considerations, no discernible difference between the four wood species was found, which supports the results seen in the MWD data. Indications of a more guaiacyl-rich fraction was seen in the alder samples but, as already noted, further quantitative data is needed before any conclusions can be reached.

3.5 Comparison of the kraft delignification behaviour of the hardwoods studied

The delignification of wood comprises several mechanisms that take place simultaneously, and these must be accounted for when studying the apparent rate of delignification. The reactants required need to be transported through the porous structure of wood and into the cell wall, where they then react with both lignin and carbohydrates to promote their solubility. The dissolved wood components then have to be transported out of the cell wall, through the system of pores in the wood, before being extracted by the liquor. The apparent rate of overall delignification will thus depend on a number of factors: the reactivity and availability of the lignin and cooking chemicals (which affect the reaction kinetics); the size and solubility of the reacted wood components and the thickness and structure of the cell wall (which affect the transport); the carbohydrate reactions (which compete with the availability of the cooking chemicals and alter the porosity and accessibility of the cell wall, and thus affect both the reaction kinetics and mass transport).

This study is based on the pulping of wood powder (less than 1 mm), so any structural differences between the wood species in the form of size and occurrence of vessels, pits, etc., which otherwise influence the overall delignification rate, is not likely to have any significant impact. Nevertheless, despite minimising the contributions made to transport resistance that may be related to the pore structure of the wood, there is a difference in the delignification of the species that remains to be fully understood.

In terms of reaction kinetics, the ratio of syringyl to guaiacyl units (S/G) in the lignin of hardwoods is commonly correlated to delignification rates (Ibarra et al. 2007; Pinto et al. 2005b; Santos et al. 2011). However, this theory fails to predict the delignification rate of birch: despite its reportedly high S/G ratio, it was not the fastest of the species studied, which has also been reported earlier (Nicholson et al. 2016; Santos et al. 2011). Moreover, neither does it explain the significantly faster rate found for the delignification of aspen during the first 20 min despite its reportedly lower S/G ratio (Önnerud and Gellerstedt 2003). It is therefore likely that other factors affect the overall delignification rate. As discussed previously, any differences in the amount of exposed middle lamella and/or surface area of the fibre wall in the wood meal used in this study may affect the availability of lignin in the initial phase of the cook. The wood species could also differ in terms of LCCs and the lignin network itself affecting the availability and reactivity of the lignin (Lawoko et al. 2005). Additionally, it may be possible that, despite the concentration in the bulk liquor remaining virtually constant throughout the cook, there may be local variations in the availability of cooking chemicals in the cell wall due to various carbohydrate reactions; at least so in the early stage, when the majority of carbohydrate degradation and deacetylation takes place. This could, in turn, also affect the kinetics of the delignification reactions.

Regardless of any differences in the reaction kinetics between the species studied, there are other mechanisms that nevertheless affect the overall rate of delignification, as inferred by the continuous increase in the MW seen in the dissolved lignin. However, as the employed NMR methods along with MWD data could not detect any variations between the species, the variations in the delignification rates are likely not associated to the properties of the dissolved lignin. Any conclusions from the NMR data is, however, limited by the qualitative nature of the measurements. There is, also, a possibility that structural differences within the fibre wall and its interactions with lignin are the causes of the different delignification rates obtained in this

work (Andersson et al. 2003). This calls for further investigation into the chemical and morphological changes of the wood tissue that arise during hardwood delignification, as well as into the effects of lignin solubility.

Where xylan is concerned, it is apparent that the majority is removed early on in the process and at seemingly high molecular weights. The rate of xylan removal could not be correlated with that of lignin; it appears, from the NMR measurements, that even though xylan co-extracts along with lignin, no LCCs were detected. It is possible, however, that a tiny amount of LCC is present but is below the detection limit of the NMR measurements, and this is able to affect the extraction of xylan during delignification. Should a suitable separation step be introduced, e.g. after a short impregnation step, the rapid dissolution of xylan could nevertheless be of great use in a future biorefinery concept aiming at extracting and utilising polymeric xylan before it becomes degraded further in the process.

4 Conclusions

A comparative study of the delignification behaviours of four different hardwoods was undertaken. Albeit modestly, the rate of delignification differed to some extent between the species: aspen showed a faster rate of lignin removal during the early stage of cooking, while alder displayed a somewhat lower rate. Analysis of the material dissolved in the black liquor from the four species showed no structural variations in the HSQC NMR measurements, with lignin of essentially identical MWD, and only minor differences in the MWD of xylan in the early samples. Moreover, birch exhibited a significantly higher rate of xylan dissolution in the black liquor compared to the other species, although virtually no difference was observed in the content of residual xylan. Supported by the results obtained from MWD measurements, it was suggested that xylan extraction is probably affected to a great extent by dissolution mechanisms. Finally, it was observed that the MW of dissolved lignin increased continuously throughout the cooking process, thereby indicating substantial resistance to transport even within the cell wall. In conclusion, the result of this work highlights the effect of other mechanisms, besides degradation reactions, on the overall rate of delignification, emphasizing the need to reconsider what constitutes the rate determining steps of kraft delignification.

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