Analysis of entrapped and free liquor to gain new insights into kraft pulping

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Abstract Most of our knowledge on kraft pulping comes from studies on dissolved lignin in the freely drainable black liquor and isolated residual lignin in pulp. However, entrapped liquor in the delignified chips has been shown to differ significantly from the free liquor. The present study has compared three liquor fractions: free, lumen and fiber wall liquor. The free liquor was obtained by draining the delignified chips, the lumen liquor was separated by centrifugation and the fiber wall liquor by subsequent leaching. The liquor in the fiber wall had the lowest concentration of lignin and hydrosulfide ions and the highest concentration of monovalent cations. The dissolved lignin in the fiber wall liquor had the highest molar mass and the highest content of xylan. The highest concentration of dissolved lignin was in the liquor filling the lumen cavities. The lignin in the free liquor had the lowest molar mass and the lowest content of lignin structures containing β -O-4 linkages and aliphatic hydroxyl groups. The lowest mass transfer rate of dissolved lignin was from the lumen liquor to the free liquor probably restricted by the tortuosity of the chip.

Keywords Delignification · Lignin · Mass transfer · Non-process elements · Softwood

Abbreviations

Al-OH	Aliphatic hydroxyl groups
C5-sub	C5-substituted
COOH	Carboxylic acid
d.s.	Dry solids
G	Guaiacyl
H	Hydroxyphenyl
ICP-OES	Inductively Coupled Plasma-Optical Emission spectrometry
o.d.	Oven dry
MMD	Molar mass distribution
Mn	Number average molecular mass
Mp	Peak molecular mass
Mw	Weight average molecular mass
PD	Polydispersity
SEC	Size exclusion chromatography

Introduction

The kraft process is a beauty, it can digest all kinds of raw material and produce pulp fibers suitable for soft tissue paper, tough sack paper and strong board. Furthermore, the recovery process is able not only to get back the cooking chemicals in high yield but also to recover the heating value of the dissolved

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components. It enables modern pulp and paper mills to be self-sufficient and even net-producers of heat and electricity. The drawback of the process is the low yield. It would be of great interest to perform the kraft cooking more selectively, enhancing delignification while preserving more carbohydrates. Although kraft delignification has been extensively studied, the previous knowledge on kraft delignification reactions is mainly based on studies of dissolved lignin in black liquor and residual lignin in pulp fibers (e.g. Gellerstedt and Lindfors 1984; Sjöholm et al. 1993; Santos et al. 1997; Svärd et al. 2016).

However, some studies have compared the lignin in freely drainable black liquor with the entrapped liquor pressed from within delignified chips and seen that there is quite a large difference. In the entrapped liquor, the lignin concentration is significantly higher as well as the molar mass of the dissolved lignin (Egas et al. 2002; Simão et al. 2011; Pakkanen et al. 2013). It has been shown by Simao et al. (2011) that changes in process conditions may affect the entrapped liquor to a greater extent than free liquor. They reported that an increase in effective alkali charge had no effect on the concentration of lignin in the free liquor, whereas in the entrapped liquor it resulted in a higher lignin concentration.

Since the entrapped liquor is in close proximity of the reaction sites within the chip, it can be presumed that a study on the entrapped liquor may give a more accurate picture of the delignification kinetics. It has been suggested by Mattson et al. (2017) that the delignification reactions are completed very early in the cook and the rate determining step in delignification is the mass transfer of dissolved lignin. Studies on dissolved lignin in free liquor would thus not give the correct picture on reaction kinetics. The purpose of the present study is to characterize the entrapped and free liquor with the aim to get a better understanding of the delignification kinetics.

Methods and materials

Materials

Industrially produced softwood chips of Norway spruce (*Picea abies*) were screened, keeping the fraction with a thickness of 4–8 mm. They were dried

to a moisture content of approx. 8% after which chips with bark and knots were removed by hand.

Chemicals

NaOH pastilles of puriss grade (VWR International AB, Radnor, PA, USA) and Na₂S technical grade flakes (VWR International AB) were dissolved in deionized water to obtain stock solutions of NaOH and Na₂S for cooking.

Methods

Batches of 100 g o.d. (oven dry) chips were delignified in steel autoclaves of 2.5 dm³ volume. Air was removed from autoclaves by vacuum suction, followed by addition of 1500 mL deionized water to each autoclave. A pressure of 5 bar was applied by nitrogen gas. After 30 min, the gas was released, water was drained from the chips and the water impregnated chips were weighed. Cooking liquor, 4.5 L/kg o.d. wood, with an effective alkali charge of 22% and sulfidity of 35% was added. The autoclaves were placed in a glycol bath at 25 °C and the temperature was increased by 3 °C/min to 110 °C. As the autoclaves are mounted with a slight inclination, the rotation in the glycol bath causes a movement back and forth of the liquor within the autoclaves, thus ensuring homogeneous mixing of chips and cooking liquor. To ensure good impregnation of the chips with cooking liquor prior to delignification, the autoclaves were kept at 110 °C for 30 min. Next, the temperature was increased by 3 °C/min to 160 °C. The kraft pulping was terminated after a certain cooking time, given as H-factor. After cooling, the delignified chips were poured into a sieve and drained for 30 min, thus obtaining the free black liquor. The volume of free liquor was recorded. The liquor from within the lumen was obtained by subsequent centrifugation for 10 min at 3500 rpm. The centrifugation time was chosen based on pre-trials with centrifugation for 5 to 30 min, where the lignin concentration was analyzed in the liquor obtained after centrifugation. From 10 min and onwards, the lignin concentration remained constant and thus 10 min was chosen as an appropriate centrifugation time, see [Appendix](#). Pre-trials were also performed to determine a suitable g-force in centrifugation. 1000, 3500 and 5000 rpm were tested. The suitable rpm was based on the volume of liquor/g.

At 5000 rpm, the repeatability was poor, specially at higher degrees of delignification when the high g-force severely deformed and compressed the delignified chips, probably causing lumen cavities to collapse. At 1000 rpm, the liquor remaining in the fiber wall was 2.5 mL/g, which is too high considering levels of WRV (Water Retention Value) commonly obtained for kraft pulps. Centrifugation at 3500 rpm gave more realistic values for the fiber wall liquor volume, 1.6–1.9 mL/g fiber. Thus, 3500 rpm was considered as a reasonable choice for centrifugation. The volume of liquor removed by centrifugation and the weight of the delignified and centrifuged chips were recorded. The centrifuged chips were leached with 0.5 M NaOH for 24 h to obtain the concentration in the fiber wall liquor. Subsequently the leached delignified chips were washed for 10 h with deionized water, dried and the weight was recorded.

Analysis

Residual alkali and hydrogen sulfide ion concentration were determined according to SCAN-N 33:94 and SCAN-N 31:94 respectively and kappa number according to ISO 302:2004. The carbohydrate composition according to SCAN-CM 71 by acid hydrolysis followed by ion chromatography; the measurement uncertainty was ± 2 mg/g for monosaccharides at the level of 1–10 mg/g and $\pm 20\%$ for monosaccharides at a level > 10 mg/g. The monosaccharides were converted to cellulose and hemicellulose according to Janson (1974). The xylan content is calculated as the sum of xylose and arabinose and a uronic acid content of 4.1%. The galactoglucomannan was calculated using a mannose to glucose ratio of 4.2. Concentration of dissolved lignin in black liquor was determined by UV absorption after dilution with 0.5 M NaOH to obtain absorbance in the range 0.2–0.7 at 280 nm, using an absorptivity constant of 24 L/g cm.

The lignin mass balance was calculated. Amount of residual lignin in pulp was determined as the sum of acid insoluble and acid soluble lignin after acid hydrolysis according to SCAN-CM 71. The amount of lignin in the different liquor fractions was calculated according to Eqs. 1–3:

$$\text{Free Liquor} \rightarrow c_{\text{free_lignin}} \cdot \frac{V_{\text{free}}}{m_{\text{wood}}} \left[\frac{\text{glignin}}{\text{gwood}} \right] \quad (1)$$

$$\text{Lumen liquor} \rightarrow c_{\text{lumen_lignin}} \cdot \frac{V_{\text{lumen}}}{m_{\text{fiber}}} \cdot Y \left[\frac{\text{glignin}}{\text{gwood}} \right] \quad (2)$$

$$\text{Fiber wall liquor} \rightarrow c_{\text{FW_lignin}} \cdot \frac{V_{\text{FW}}}{m_{\text{fiber}}} \cdot Y \left[\frac{\text{glignin}}{\text{gwood}} \right] \quad (3)$$

where $c_{\text{free_lignin}}$, $c_{\text{lumen_lignin}}$, and $c_{\text{FW_lignin}}$ are the concentration of lignin, g/L, obtained from UV absorption. V_{free} and V_{lumen} are the volume, L, of free liquor and liquor removed by centrifugation. The volume of liquor in the fiber wall, V_{FW} , was calculated as $m_{\text{centr.chips}} - m_{\text{fiber}} - m_{\text{H}_2\text{O}}$, g, where $m_{\text{centr.chips}}$ is the weight of the centrifuged chips, $m_{\text{H}_2\text{O}}$ the amount of water in centrifuged chips and m_{fiber} the weight of the washed and dried chips. Y is the yield, g pulp/g wood.

The hydroxy acids formed in the peeling reaction were quantified by analytical pyrolysis coupled with mass spectrometry (Py-GC/MS), see Brännvall and Reimann (2018) for details. The liquor samples were kept frozen prior to analysis.

The carbohydrate composition of delignified chips was determined according to SCAN-CM 71 by acid hydrolysis followed by ion chromatography.

To determine the metal content in the liquors, the samples were oxidized with hydrogen peroxide and subsequently wet digested with nitric acid in a microwave oven before analysis by ICP-OES (Inductively Coupled Plasma-Optical Emission spectrometry). Amount of carbonate was analysed in a Total Organic Carbon-V CPH from Shimadzu Corporation, where the inorganic carbon in the sample is reduced to carbon by acidification and detected spectroscopically. The carbon value is multiplied by five for conversion to carbonate.

Molecular mass distribution, MMD, and NMR were made on lignin precipitated from the liquor fractions. The fiber wall liquor fraction was evaporated prior to precipitation, obtaining a dry solids content between 20 and 30%. Sulphuric acid, 5 M, was added during mixing by magnetic stirrer to a given volume of liquor until pH approx. 5.5 was reached. The temperature was 60–70 °C. The precipitate was recovered by centrifugation.

The MMD was determined by size exclusion chromatography (SEC). The SEC system consisted of a pre-column followed by two analytical columns,

PSS MCX 105 and 103 Å, connected in series. The mobile phase was NaOH pH 12 and flow rate was 0.5 mL/min. The samples were dissolved in the mobile phase to suitable concentrations and filtered using cellulose acetate syringe filters, 0.20 µm prior to injection. The injection volume was 250 µL. Detection was performed using a refractive index detector (Shodex RI-101) and a UV detector (Knauer K-2501). The SEC system was calibrated using sulfonated polystyrene standards with molecular masses ranging from 246 to 200 000. MMD, peak molecular mass (Mp), weight average molecular mass (Mw), number average molecular mass (Mn) and polydispersity (PD) index (Mw/Mn) were calculated using Cirrus GPC software version 3.1 by Polymer laboratories (Agilent). The integration limits used were the times for elution of Mp 100 and 100,000.

^1H , ^{13}C NMR spectroscopy was carried out at 9.4 T. Lignin samples were dissolved in dimethylsulfoxide- d_6 at a concentration of 100 mg/mL and transferred to NMR tubes. 2D ^1H , ^{13}C -HSQC experiments were measured, in addition to 1D. ^{31}P NMR was performed according to Biorefinery test Method L7:2017.

Fig. 1 Illustration of porous system in fiber wall and location of liquor fractions in a section of wood. The dotted red arrows show diffusion paths for dissolved lignin from fiber wall, through the chip and to the free liquor

Results and discussion

Porosity of wood

Figure 1 illustrates the diffusion path of dissolved lignin. Cooking chemicals react with lignin in wood, degrading and solubilizing it. The dissolved lignin diffuses through the pore system of the fiber wall to the lumen cavities. From the lumen, diffusion continues through pit openings connecting adjacent fibers and enters the next lumen cavity. As lignin, as well as hemicelluloses, are solubilized and transported away, pores and channels are created within the fiber wall and in the middle lamellae, creating more pathways for diffusion. Finally, the dissolved lignin will reach the free liquor surrounding the chips.

Pores thus play an important role in the mass transport of lignin. Theoretically, the void fraction in wood, ϵ_i , is given by Eq. 4 (Saeed et al. 2012).

$$\epsilon_i = 1 - \frac{\rho_c}{\rho_w} \quad (4)$$

where ρ_c is the wood chip density, o.d. weight of wood/green volume of wood, and ρ_w is the solid density, 1500 kg/m³. As an example, at a wood chip density of 400 kg/m³ the void fraction is 73%, which gives a volume of 1.83 mL/g wood available for liquor.

To measure the pore volume available within the chips, trials were performed where chips were treated with water and cooking liquor at room temperature. In Table 1, the measured volumes of liquor in lumen and

Table 1 Liquor volume in lumen and fiber wall of chips treated with deionised water or cooking liquor at room temperature for 3 h

		H ₂ O	Cooking liquor
Volume of liquor mL/g wood	Lumen	0.9 ± 0.4	0.9 ± 0.2
	Fiber wall	1.1 ± 0.4	1.3 ± 0.4
	Total volume	2.0	2.2
Residual [OH [−]]	Free	–	0.8 ± 0.1
	Lumen	–	0.8 ± 0.1
	Fiber wall	–	0.5
Yield, %		100	98

The concentration of the cooking liquor was [OH[−]] = 1.3 M and [HS[−]] = 0.4 M. The values are at 95% confidence level

in fiber wall are given. The total volume, i.e. the sum of liquor in lumen and fiber wall, was approx. 2 mL/g, whether water or the alkaline cooking liquor was used to impregnate the chips, which fits well with the calculated value of 1.8 mL/g. The water uptake by the fiber wall was 1 mL/g. This is larger than the fiber saturation point, 0.4 mL/g, previously reported for wood (Stone and Scallan 1967) but similar to what was obtained for spruce TMP fibers (Eriksson et al. 1991). The lumen volume was approx. 1 mL/g. Previously, the lumen volume in pine wood has been determined to 1.4 mL/g (Yamauchi 2007).

The yield after the chips had been treated with alkali for 3 h at room temperature was 98%. This is higher compared to Paananen et al. (2010), who obtained a yield of 92–93%. However, they used wood meal in their experiment, which can explain why more material was dissolved. As seen in Table 1, a considerable amount of alkali was consumed during treatment in room temperature, the alkali concentration was reduced from 1.3 M to 0.8 M in free and lumen liquors and to 0.5 M in the fiber wall liquor. The consumption is mainly due to cleavage of acetyl groups.

Figure 2 shows the free, lumen and fiber wall liquor volumes at different degrees of delignification. In Fig. 2a, the volumes are given as mL g⁻¹ wood, i.e. the liquor volume for a constant number of fibers. Initially, the volume of the lumen cavities increased and the void volume of the fiber wall decreased with delignification. This was unexpected as the lumen volume should stay fairly constant and the fiber wall volume should increase with delignification (Andreasson et al. 2003). However, this can be an effect of

lumen and fiber wall volumes being determined by centrifugation at constant conditions. The entrapped liquor is held within delignified wood due to capillary suction, the smaller the radius of the pore, the larger the capillary force. Since the lumen cavities are the largest pores, they are emptied first when wood and pulp are subjected to centrifugation. Liquid can also be expelled from pores within the fiber wall if their size will result in a capillary suction lower than the centrifugal force. Upon increased delignification, centrifugation might expel more liquor from the fiber wall. The sum of the entrapped liquor volume remained fairly constant, 2.2 mL g⁻¹ wood, at all cooking times. In Fig. 2b, the liquor volumes are given as mL g⁻¹ d.s. (dry solids, i.e. pulp) and in this case the fiber wall volume increased from 1.4 to 1.6 mL g⁻¹ d.s. as delignification proceeded. This is quite similar to WRV, water retention value, for pulps, e.g. (Andreasson et al. 2003) obtained 1.7 g g⁻¹ at 60% yield, which corresponds to H-factor 300 in the present study, where 1.5 mL g⁻¹ was obtained.

Delignification and diffusion

Mass transfer of dissolved lignin from the entrapped liquor within the chip to the free liquor was monitored by measuring the lignin concentration at different degrees of delignification of spruce chips. Free liquor is the liquor drained from the delignified chips. Subsequently the chips were centrifuged, and it was assumed centrifugation removed the liquor from the lumen cavities. After centrifugation, the chips were leached with alkali, to obtain the lignin concentration in fiber wall liquor.

Fig. 2 Free, lumen and fiber wall liquor volumes given as **a** mL g⁻¹ wood and **b** as mL g⁻¹ d.s. (dry solids, i.e. delignified wood)

In Fig. 3, the lignin concentration in the different liquor fractions is shown. In the free and lumen liquor, the lignin concentration increased relatively rapidly up to an H-factor of 450, which corresponds to a kappa number of approx. 100 or 80% degree of delignification. Prolonged cooking resulted in a minor increase in lignin concentration in the free liquor, while the lignin concentration in the lumen liquor remained constant. The concentration of dissolved lignin in the fiber wall remained practically at the same level through the cooking. This was somewhat surprising, as it has been previously shown that the most important factor restricting diffusion from fiber wall is the size of pores (Favis et al. 1981, 1983; Favis and Goring 1984). It was thus expected that dissolved lignin would accumulate in the fiber wall liquor until defragmentation reactions had modified the size so it would be small enough to escape through the channels and pores within the fiber wall. It is also puzzling that the concentration was much lower in the fiber wall liquor compared to the lumen liquor and yet diffusion of dissolved lignin continued from fiber wall to lumen. However, the observation can be explained by considering the porous structure as well as electrostatic interactions between fiber wall and lignin macromolecules and intramolecular electrostatic interactions between functional groups in the macromolecule. The fiber wall has channels along the fiber axis, formed by the lamellar structure of fibril layers, connected radially by openings (Goring 1984; Favis and Goring 1984). The porous structure is thus a system of cavities with smaller orifices leading into larger pores. Dissolved lignin fragments make their way out from a pore through the orifice and into the

next pore. Once the dissolved lignin fragments have entered the lumen cavity, the repulsive interactions between negatively charged lignin molecules and negative charges on the fiber wall components prevent lignin to enter back into the fiber wall. Additionally, the concentration of cations is higher in the fiber wall due to the Donnan effect, which might influence the hydrodynamic volume of the dissolved lignin fragments. At higher ionic strength, the hydrodynamic volume of the lignin is lower as the phenolic groups in the lignin structure are shielded by cations (Chen and Li 2000). In the lumen, where the ionic strength is lower, the hydrodynamic volume increases, thus restricting re-entrance into the fiber wall.

The lumen cavities seem to play a highly important role for transport of dissolved lignin, and it has previously been shown that if the lumen is filled with polymer, the delignification rate is reduced (Treimanis 1996).

In Table 2, the calculated amounts of lignin, g/kg wood, are given.

Rates of mass transfer are calculated by making mass balances between pulp and liquor fractions, schematically shown in Fig. 4. Delignification rate was calculated as the amount of lignin solubilized from wood matrix to fiber wall liquor per unit h-factor. The difference in the amount of lignin in pulp obtained at H-factors HF1 and HF2 was used and the rate of solubilization thus calculated according to Eq. 5

$$\frac{P_{H1} - P_{H2}}{HF2 - HF1} \quad (5)$$

Fig. 3 The lignin concentration in free, lumen and fiber wall liquor at different cooking times, given as H-factor

Table 2 Amount of lignin remaining in partly delignified pulp fibers and the different liquor fractions

H-factor	Lignin, g/kg wood				
	Pulp	Fiber wall	Lumen	Free	Sum
0	308	0	0	0	308
100	188	24	46	49	307
150	152	32	52	66	302
300	110	36	70	94	310
450	84	34	97	118	333
650	46	35	99	134	313
1100	24	28	97	141	289

Fig. 4 Schematic presentation of mass flows

where P_{HF1} is the amount of lignin in pulp at H-factor HF1 and P_{HF2} is the amount of lignin in pulp at H-factor HF2.

The rate of diffusion from lumen to free liquor can be obtained by analyzing the amount of lignin in the free liquor at H-factor HF1 and HF2 and calculated as the rate of increase in amount of lignin in the free liquor according to Eq. 6

$$\frac{Free_{HF2} - Free_{HF1}}{HF2 - HF1} \quad (6)$$

where $Free_{HF1}$ is the amount of lignin in the free liquor at H-factor HF1 and $Free_{HF2}$ is the amount of lignin in the free liquor at H-factor HF2.

Using a lignin mass balance one can calculate that the rate of diffusion of dissolved lignin from the fiber wall liquor into the lumen liquor as being equal to the dissolution rate of lignin from the fibre into the fiber wall liquor minus the rate of lignin accumulation in the fibre wall liquor. The dissolution rate of lignin from the fibre into the fibre wall liquor is $(FW_{HF2} - FW_{HF1}) / (HF2 - HF1)$, while the rate of lignin accumulation in the fibre wall liquor is $(P_{HF2} - P_{HF1}) / (HF2 - HF1)$. Thus, the rate of diffusion of dissolved lignin from the fiber wall liquor into the lumen liquor is described by Eq. 7.

$$\frac{FW_{HF1} + P_{HF1} - P_{HF2} - FW_{HF2}}{HF2 - HF1} \quad (7)$$

In Fig. 5, the rate of solubilization and diffusion rates are presented. The rate of solubilization of lignin from the wood matrix, i.e. the delignification rate, is denoted Pulp to fiber wall liquor and calculated from

Fig. 5 Rate of delignification and diffusion. Lines are as guide for the eye

the amount of lignin in pulp according to Eq. 5. The rates are calculated from H-factor 100, i.e. only bulk delignification is taken into account and the impregnation and fast solubilization during the initial phase delignification is omitted.

The slowest mass transport was of dissolved lignin from lumen to free liquor. The rate of solubilization was similar to the rate of diffusion from the fiber wall to lumen.

In the subsequent brown stock washing stage, it can be assumed that the washing liquor easily displaces the lumen liquor (Andersson et al. 2003). It is thus fortunate that the highest lignin concentration was found in the lumen liquor, as this lignin will easily be removed by washing. Some of the dissolved lignin in

the fiber wall may be displaced or diffuse out of the fiber wall as well but some will remain entrapped within the fiber wall. It has been shown that a certain amount of dissolved lignin remains in pulp after brown stock washing and is only possible to remove by prolonged leaching (Trinh and Crostogino 1987; Ala-Kaila et al. 2003).

Hydroxy acids

In the peeling reaction, different hydroxy acids are formed. Three different types of hydroxy acids were analyzed by pyrolysis and the results are presented in Table 3. The concentration of these degradation acids was lower in the fiber wall liquor compared to lumen and free liquor. This is contrary to results by Pakkanen et al. (2013), who had much higher concentration of hydroxy acids in the entrapped liquor, compared to free liquor. They however obtained the entrapped liquor mainly originates from the lumen. Furthermore, they studied the very initial stage of pulping, i.e. the heating period up to 140 °C, and the concentration of hydroxy acids in free liquor approached the concentration in the entrapped liquor at higher temperature. In the present study, the bulk delignification phase is studied and the lower hydroxy acid concentration in the fiber wall liquor may imply that either hydroxy acids have diffused from the fiber wall liquor or that carbohydrates dissolved as oligomers have been further degraded once they have diffused to the lumen liquor.

Fig. 6 Concentration of carbonate in different liquor fractions

Carbonate

In Fig. 6, the concentration of carbonate in the different liquor fractions is shown. The fiber wall liquor had a much higher concentration of carbonate compared to lumen and free liquor. The ratio of the carbonate concentration between the fiber wall liquor and the other liquor fractions was much higher than the ratio of the lignin concentration. This suggests that diffusion of dissolved carbonate from the fiber wall was slower than diffusion of lignin. The concentration increased up to H-factor 650 after which it decreased abruptly. The reason could be formation of calcium carbonate precipitate. No carbonate was added to the cooking liquor for the cooking trials presented so far. However, carbonate is formed in kraft cooking (Hartler and Libert 1973; Chai et al. 2003; Li et al. 2014) and it has been proposed that the carbonate derives from decarboxylation of glucuronic acid

Table 3 Concentration of degradation acids formed in the peeling reaction in free, lumen, and fiber wall liquor

H-factor	Liquor fraction	2,5-dihydroxy-pentanoic acid $\pm 0.5 \text{ g L}^{-1}$	α -iso-saccharinic $\pm 0.2 \text{ g L}^{-1}$	β -iso-saccharinic $\pm 0.5 \text{ g L}^{-1}$	Sum hydroxy acids g L^{-1}
300	Free	1.2	1.2	3.5	5.8
	Lumen	1.4	1.4	3.8	6.6
	FW	0.8	0.7	1.1	2.6
450	Free	1.6	1.4	4.2	7.2
	Lumen	1.7	2.0	6.0	9.7
	FW	0.6	0.6	1.5	2.7
650	Free	1.7	1.4	4.3	7.4
	Lumen	1.8	1.3	4.2	7.3
	FW	0.9	0.6	1.5	3.0

groups (Hartler and Libert 1973) and degradation of lignin (Li et al. 2017).

Characteristics of dissolved lignin

The weight average molar mass, M_w , and number average molar mass, M_n , of lignin in the different liquor fractions is given in Fig. 7, calculated both from UV and RI signals. The UV signal derives from lignin whereas presence of carbohydrates affects the RI signal. The molar mass of dissolved lignin increased significantly at the early stages of delignification, reaching a maximum between H-factor 400–600. The lignin in the free liquor had significantly lower molar mass compared to lumen and fiber wall liquor. This is in accordance with a study on leaching by Vilpponen et al (1993) showing that larger lignin molecules are left within the fiber wall compared to those found in the black liquor. This may indicate the effect of mass transfer resistance of dissolved lignin from the fiber wall. Dang et al. (2016) have shown that mass

transport rate is slower for lignin with high molar mass. However, fiber wall liquor contains the most recently solubilized lignin fragments while the free liquor holds lignin dissolved longer ago. The lower molar mass in free liquor may also be an effect of longer exposure time to hydroxide and hydrosulfide ions.

The M_n from the RI signal was significantly lower at H-factors 150–300, probably due to dissolution of many low molar mass compounds originating from carbohydrates, such as acetic and hydroxy acids.

The main delignification reaction in kraft pulping, cleavage of β -aryl ether bonds, creates both new free phenolic units and introduces new aliphatic hydroxyl groups. According to Table 4, the dissolved lignin found closest to the reaction site, i.e. in the fiber wall liquor, had significantly higher content of aliphatic hydroxyl groups (Al-OH), but less free phenolic groups (G + H) and condensed structures (Σ C5-sub Ph-OH) compared to dissolved lignin in lumen and free liquor. Condensation reactions may have taken

Fig. 7 Weight-weighted molecular mass of lignin in the liquor fractions at different H-factor

Table 4 Lignin structures characterized by ^{31}P NMR. G = guaiacyl, H = hydroxyphenyl, C5-sub. = C5-substituted, COOH = carboxylic acid. Values as mmol/g organic content in sample, i.e. lignin and any co-precipitated hemicellulose

H-factor	100			150			300			
Liquor fraction	Free	Lumen	FW	Free	Lumen	FW	Free	Lumen	FW	
Σ C5-sub Ph-OH	0.5	0.51	0.45	0.53	0.52	0.50	0.61	0.51	0.48	± 0.02
G + H	1.49	1.43	1.33	1.47	1.42	1.39	1.56	1.24	1.19	± 0.03
Al-OH	1.66	2.65	2.78	1.65	2.31	2.85	2.27	2.20	2.29	± 0.06
COOH	0.46	0.45	0.37	0.38	0.41	0.61	0.39	0.45	0.56	± 0.03
Ph-OH/Al-OH	0.90	0.54	0.48	0.89	0.61	0.49	0.69	0.56	0.52	

Table 5 Lignin structures characterised by 2D NMR

H-factor	100			150			300			
Liquor fraction	Free	Lumen	FW	Free	Lumen	FW	Free	Lumen	FW	
G2	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	
G5	98.5	99.1	99.0	99.7	99.2	103.1	101.1	95.5	92.8	
β -O-4	17.3	20.4	23.6	16.0	21.0	17.2	12.3	13.7	13.5	
Pinoresinol	5.2	5.9	7.2	5.3	6.6	5.6	4.9	5.9	4.8	
Epi-pinoresinol	2.0	2.3	2.7	2.1	2.5	2.3	2.1	2.3	1.7	
β -5	3.7	4.5	5.8	4.1	5.4	4.0	3.6	4.1	3.7	
Coniferyl alcohol	4.4	4.1	5.7	3.8	4.4	2.6	3.4	3.7	2.8	
Dehydroconiferyl alcohol	3.1	3.0	3.0	3.0	2.9	3.2	3.2	2.9	2.9	
Seco-isolarisiresinol	2.7	2.2	3.4	2.7	3.4	2.2	2.9	2.4	3.0	
Enol ether	3.5	3.9	3.8	3.6	3.4	4.8	6.2	4.4	5.3	
1.5-Stilbene	9.3	7.2	4.5	10.0	7.7	4.2	7.5	7.7	2.9	
1.1-Stilbene	8.2	5.5	1.8	7.8	4.0	2.0	6.8	5.3	1.6	
Xylan	0.4	0.5	0.8	0.5	0.6	1.9	1.4	1.4	3.3	

place along the diffusion path from the reaction site to the free liquor, indicated by higher amount of condensed structures and lower amount of aliphatic hydroxyl groups in the lumen and free liquors. In the free liquor, condensation reactions may have continued to occur.

^1H , ^{13}C -2D HSQC NMR measurements on the precipitated lignins showed high similarities when comparing the lignins isolated from the lumen and free liquor fractions, Table 5. The free liquor however, had lower content of β -O-4 structures, which is in agreement with the higher content of free phenolic groups seen by ^{31}P NMR, Table 4. Stilbene structures were more abundant in the free liquor, especially compared to the fiber wall liquor. These structures are formed

during alkaline pulping (Gierer and Pettersson 1977; Gellerstedt and Lindfors 1984; Gierer 1985). The lower content of β -O-4 and higher content of stilbene structures in free liquor shows that the lignin in the free liquor has been subjected to longer exposure time to cooking chemicals compared to the lignin more recently solubilized into the fiber wall liquor.

The xylan content in the precipitated lignins increases with H-factor in all liquor fractions. This is in accordance with previous studies showing that xylan dissolves from the wood matrix at the early stages of cooking (Yllner and Enström 1957; Jansson and Brännvall 2011). The lignin from the fiber wall liquor had much higher xylan content compared to lignin from free and lumen liquor. This may imply that

xylan remaining in the fiber wall liquor has more linkages to lignin while the xylan leaving the fiber wall might be less interconnected to lignin and thus can more freely diffuse out to the lumen and free liquors.

Non-process elements

Table 6 shows the concentration of non-process elements (NPE) and sodium and sulfur in the different liquor fractions. The highest concentration of sodium and potassium was in the fiber wall liquor. This can be explained by the Donnan equilibrium as the chemical constituents in the partly delignified wood contain negatively charged groups, mainly carboxyl and free phenolic groups, which attract the monovalent cations. Consequently, anions are repelled from the fiber wall liquor resulting in lower hydroxide and hydrosulfide ion concentration. As seen, the sulfur concentration, which can represent the hydrosulfide ion concentration, was lowest in the fiber wall liquor.

The highest concentration of divalent cations on the other hand was in the lumen liquor. The divalent cations seemed to be related to the lignin as the concentration of the sum of calcium, magnesium and manganese correlated linearly with the lignin concentration, Fig. 8.

Fig. 8 Sum of divalent cations in the different liquor fractions versus the respective lignin concentration

Effect of ionic strength on delignification

Higher ionic strength decreases the delignification rate (e.g. LéMon and Teder 1973; Bogren et al. 2007). The reason is a decreased solubility of lignin at higher salt concentration (Dang et al. 2013). The ionic strength in the present study was lower compared to industrial conditions, as a synthetic white liquor was prepared without addition of any sodium carbonate. To study the effect of increased ionic strength, pulping was performed with addition of sodium carbonate. Increased ionic strength had no effect on total yield while the alkali consumption was slightly higher at higher concentration of sodium carbonate, Table 7. The concentration of dissolved lignin was slightly

Table 6 Concentration of NPE, sulfur and sodium in free lumen and fiber wall liquors

H-factor	mg L ⁻¹	Ca	Mg	Mn	P	K	Na	S	Na/S
100	Free	20	0.8	1.7	3.4	60	36 328	13 473	2.7
	Lumen	78	2.5	3.6	4.6	68	39 261	13 783	2.9
	FW	49	1.6	2.6	4.2	103	97 026	12 437	7.8
300	Free	52	1.6	2.6	3.2	75	33 154	12 414	2.7
	Lumen	102	3.3	5.1	4.1	80	36 419	13 762	2.8
	FW	79	1.7	3.6	3.6	120	101 464	11 431	8.9
450	Free	63	1.9	3.1	3.5	67	31 776	12 218	2.6
	Lumen	120	4.0	5.3	4.5	75	36 199	13 926	2.6
	FW	65	2.2	2.5	3.6	90	67 640	8 219	8.2
650	Free	68	2.2	3.4	3.0	71	33 764	12 768	2.6
	Lumen	122	4.4	5.6	3.8	75	37 886	14 111	2.7
	FW	61	3.3	4.9	4.0	108	74 531	9 796	7.6
1100	Free	77	2.2	3.3	3.1	52	34 639	12 248	2.8
	Lumen	118	3.6	5.2	3.2	59	38 857	13 472	2.8
	FW	64	4.2	6.3	5.6	63	91 119	9 707	9.4

Table 7 Effect of ionic strength on total yield, residual alkali and concentration of dissolved lignin in liquor fractions

H-factor	Conc. of added [Na ₂ CO ₃]	Yield. %	Residual alkali. mol/l	UV lignin concentration g L ⁻¹		
				Free ± 1.5	Lumen ± 2.0	Fiber wall 2.0
150	0	68.5	0.54	27.9	46.2	33.5
	0.1	68.4	0.53	25.0	44.8	26.2
	0.25	68.1	0.46	26.2	39.5	27.2
300	0	61.8	0.40	39.0	57.5	38.8
	0.1	61.8	0.45	36.4	55.1	32.6
	0.25	61.8	0.37	34.4	56.3	32.9
450	0	57.1	0.41	49.8	68.2	38.1
	0.25	57.3	0.39	48.0	61.5	34.4

Table 8 Effect of ionic strength on chemical composition of partly delignified chips

H-factor	Conc. of added [Na ₂ CO ₃]	% on wood			
		Lignin	Xylan	GGM	Cellulose
150	0	15.2	4.8	5.4	43.0
	0.1	17.6	4.3	4.9	41.6
	0.25	18.2	4.6	5.0	40.3
300	0	11.0	4.3	5.1	41.4
	0.1	12.5	4.0	4.5	40.8
	0.25	12.7	4.3	4.8	40.3
450	0	8.4	4.1	4.7	39.9
	0.25	15.2	4.8	5.4	43.0

lower at higher ionic strength, the decrease being significant in the fiber wall liquor.

From Table 8 it is apparent that the delignification rate was slower at higher ionic strength. The amount of residual lignin was higher after pulping at higher sodium carbonate concentration to a given H-factor. The decreased delignification rate was reflected by a lower concentration of dissolved lignin in the fiber wall liquor. A decrease in lignin concentration at higher ionic strength was also seen in the free liquor, but not as pronounced as for the fiber wall liquor. Thus it appears that a higher ionic strength does not restrict diffusion of dissolved lignin from fiber wall to free liquor.

Significantly more cellulose was dissolved at higher ionic strength, in accordance with Johansson and Germgård (2008). They also showed that sodium ion concentration has no effect on the alkaline hydrolysis rate, so the lower cellulose yield at higher

Fig. 9 Effect of higher ionic strength on the weight average molar mass of lignin in the liquor fractions by addition of sodium carbonate to the cooking liquor

ionic strength should therefore be attributed to a more extensive primary peeling, not secondary peeling. The Donnan effect is diminished with increasing sodium ion concentration. The negative charges are shielded

Fig. 10 Lignin concentration in the liquor after centrifugation at 3500 rpm. The value at 0 min is the concentration in the free liquor

by cations which enables a higher hydroxide ion concentration in the fiber wall liquor. As an example, Dang et al. (2013) calculated that with a hydroxide ion concentration in the bulk of 0.26 M, the concentration was 0.11 M in the fiber wall without addition of sodium carbonate and 0.21 M with addition.

Fig. 11 Concentration of lignin in fiber wall liquor after leaching with alkali for 30 min and 24 h. The delignified chips were centrifuged prior to leaching (uncut) or centrifuged and cut by scalpel to strips of 2–3 mm prior to leaching (cut)

Fig. 12 a Fraction of lignin remaining in pulp and dissolved in free, lumen and fiber wall liquor at different H-factor and **b** amount of lignin in pulp and dissolved in free, lumen and fiber

The effect of high sodium ion concentration on hemicellulose is not as straight-forward to assess. Possibly there is a slightly lower amount of hemicellulose left in the partly delignified chips. However, if calculated as yield on wood, the decrease in hemicellulose content is not significant. Earlier studies have shown a decrease in xylan dissolution at higher ionic strength, which has been contributed to a decrease in xylan solubility (Dang et al. 2013).

The molar mass of dissolved lignin at a given H-factor was not affected by higher ionic strength, Fig. 9. This is in contradiction to a study by Dang et al. (2016), which demonstrated a decrease in molar mass of dissolved lignin at higher ionic strength. However, they saw that the effect on molecular weight became more pronounced at longer cooking times and in the present study the analysed samples are from very early in the cook, corresponding roughly to 50–70% degree of delignification, where Dang et al. (2016) only saw a slightly lower molecular weight at higher sodium ion

wall liquor as a function of residual lignin. For chemical composition of fibers, see Fig. 13

Fig. 13 Chemical composition of wood and delignified fibers at different H-factor

concentration. Additionally, they compared $[\text{Na}^+]$ at a broader range, 0.56–3.00 M, while in the present study $[\text{Na}^+]$ was 1.70 M without and 1.95 M with addition of Na_2CO_3 .

Conclusions

The chemical environment in the free and entrapped liquors in lumen and fiber wall differed substantially.

The liquor in the fiber wall had lower concentration of dissolved lignin compared to lumen and free liquor and the concentration remained fairly constant as cooking time increased. The dissolved lignin in the fiber wall liquor had the highest molecular mass and twice as high xylan content compared to lumen and free liquor fractions. The liquor in the fiber wall had the lowest concentration of hydrosulfide ions and highest concentration of sodium and potassium ions.

The highest concentration of dissolved lignin was in the liquor filling the lumen cavities. The lumen liquor also had the highest concentration of calcium and magnesium ions.

The lignin in the free liquor had been subjected to of longer exposure time to hydroxide and hydrosulfide ions shown by the lower molar mass, lower content of lignin structures containing β -O-4 linkages and aliphatic hydroxyl groups and higher content of stilbene structures.

The lowest mass transfer rate of dissolved lignin was from the lumen liquor to the free liquor.

Tortuosity of chip thus affects mass transfer rate more than pore size in fiber wall.

Mass transport of dissolved lignin from fiber wall to lumen was lower than delignification rate at the early stage of delignification, H-factor below 300, corresponding to a degree of delignification less than 50%. When 50% of original amount of lignin had been removed, mass transport rate of dissolved lignin became equal to delignification rate.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

Human and animal rights This article does not contain any studies with human participants or animals performed by any of the authors.

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Appendix

Centrifugation and leaching to obtain lumen and fiber wall liquor

In Fig. 10, lignin concentration in the liquor obtained after centrifugation for different periods of time of chips cooked for 300 and 1100 H-factors is shown. The concentration increased up to 10 min of centrifugation where after it remained constant.

In Fig. 11a, leaching of cut and uncut chips for 30 min and 24 h is shown. The cutting was performed prior to leaching but after centrifugation to expose fiber walls and decrease the path for diffusion, Fig. 11b. Longer leaching time resulted in higher lignin concentration in the leachate. More lignin was removed from the fiber wall after leaching of cut chips for 30 min compared to uncut chips, while quite similar lignin concentration was obtained after 24 h of leaching of cut and uncut chips. The concentration in the leachate after 30 min leaching of cut chips was comparable to leaching for 24 h, suggesting that only diffusion of solubilized lignin was taking place during the leaching procedure and probably no delignification occurred.

Mass balance and lignin content in pulp and liquor fractions

Figure 12a shows the percentage of the original amount of lignin found as residual lignin in pulp or dissolved in free, lumen or fiber wall liquors. The mass balance of lignin was quite accurate. The total amount of lignin added up to 94–108% of the original amount

of lignin. The progress of amount of lignin dissolved from pulp and transported by diffusion from the liquor in the fiber wall to lumen and finally the free liquor is shown in Fig. 12b. The highest amount of lignin was in the free liquor. The amount of dissolved lignin in the fiber wall liquor was lowest and remained fairly constant during cooking.

Chemical composition

The chemical composition of the chips was 44% cellulose, 17% galactoglucomannan, 6% xylan, 31% lignin and 1% extractives. In Fig. 13, the amount of carbohydrates and lignin in fibers is shown as % on wood. After H-factor 300, when approx. 65% of the lignin originally in wood has been dissolved, the cellulose and xylan yield remained quite stable while dissolution of glucomannan continued.

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