Kraft pulping of model wood chips: Local impact of process conditions on hardwood delignification and xylan retention

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Abstract: Local evolution of delignification and xylan removal inside wood chips was investigated throughout the initial stages of kraft cooking. Model chips of birch sapwood were pulped at 145, 155 and 165 °C, utilizing white liquors with hydroxide content ranging from 0.25 to 0.55 mol/kg. The composition of different sections in each cooked sample was then determined. Xylan was isolated from selected samples and analyzed using size exclusion chromatography and HSQC NMR. Most changes in concentration and structure of residual xylan occurred early in the process (<45 min). Furthermore, xylan samples isolated from the tissue of different cooked chips had similar average molecular weights, indicating that temperature and alkali content had little impact over the extent of reactions affecting residual xylan. In contrast, xylan dissolution was significantly dependent on pulping conditions, increasing with hydroxide concentration. The lignin profile inside the cooked chips also varied with alkali content and temperature, and it was shown to be more uniform when applying low cooking temperatures (145 °C). Finally, increased delignification and xylan removal were detected close to the transverse surfaces of chips (likely due to the fast mass transport in vessels/lumen), implying that anatomical features of wood can have a significant impact on pulping.

Keywords: kraft cooking; delignification; xylan; hardwood; mass transport

1 Introduction

Kraft pulping is a well-established process and the preferred method for chemical pulp production. Yet, further process development and optimization is required in order to maintain its competitiveness in the face of rising wood costs, changes in feedstocks and new pulp quality specifications (Hujala et al. 2013; Mboowa 2024). In this sense, a thorough understanding of how delignification and carbohydrate losses progress during the process is essential, as it allows, for example, fine-tuning of the pulping conditions to reduce rejects and improve pulp yields.

Not surprisingly, several studies regarding the effect of process conditions (such as temperature, effective alkali, sulfidity and ionic strength) over the composition and/or quality of the pulp can be found in literature, e.g., Favaro et al. (2021); Jansson and Brännvall (2014); Lan et al. (2024) and Segura et al. (2012). Others focused on the kinetics of delignification and dissolution of wood components, e.g., Bogren et al. (2007), Dang et al. (2013) and Lindgren and Lindström (1997). In addition, some investigated mass transport during pulping, with emphasis on the distribution of cooking chemicals after impregnation, e.g., Määttänen and Tikka (2012) and Zanuttini et al. (2000).

Nevertheless, despite the large body of work on the subject, there is no consensus on the rate limiting steps of kraft pulping. This is reflected in the various approaches utilized to model the operation. The majority of the models available in literature present some variation of the kinetics proposed in the 3-stage model (Gustafson et al. 1983) or in the parallel reaction model, i.e., the Purdue model (Smith 1974). The effect of mass transport is sometimes included, with varying degrees of complexity. Dang and Nguyen (2008), for instance, developed a delignification rate constant that is a

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function of chip thickness. Gilbert et al. (2021) proposed a model considering a solid phase (uniformly subjected to pulping reactions) and two liquid phases: entrapped liquor (subjected to pulping reactions and mass transport) and free liquor (only subjected to mass transport).Bijok et al. (2022) went even further and suggested including these three phases and different values of mass flux in each surface of the wood chip (depending on the diffusion coefficients in each coordinate).

In this scenario, the present study is focused on mapping delignification and xylan removal inside model wood chips from *Betula pubescens* sapwood during kraft pulping, assessing local changes in composition and how they are affected by the cooking temperature and hydroxide content. The goal is to provide a detailed description of the system under the initial stages of pulping and to identify the main phenomena taking place. This analysis can serve as a guide when adjusting kraft cooking conditions. Moreover, the results can be valuable for the development of new kraft pulping models, especially regarding which assumptions or mechanisms are relevant.

2 Materials and methods

2.1 Wood sample

A wood log from a 27-year-old birch tree (*B. pubescens*) grown in southern Sweden was kindly provided by Södra Skogsägarna. The log (height: 1 m, diameter: approximately 16.5 cm) was cut into model sapwood chips according to the procedure described in item 2.3. Only sapwood was utilized in order to ensure a more homogeneous raw material and to avoid the presence of deposits of extractives in the wood structure. Then, the hand-cut chips were air dried and stored at room temperature. The air-dried samples had an average dry content of 94.6 ± 0.2 % (w/w).

2.2 Chemical reagents

All chemicals were of analytical grade. The Pullulan standards (PL2090-0100, 0.180–708 kDa) used in the analysis of molecular weight distribution of xylan were purchased from Varian Inc.

2.3 Model sapwood chips

The procedure applied to prepare the model chips is illustrated in Figure 1. First, the birch log was divided into thin wood disks (30 ± 1 mm) by successively performing transverse cuts with a vertical bandsaw. Next, each disk was further divided into different pieces, to separate sapwood-rich parts (borders) from heartwood (inner region, with sides of about 85 mm). For the purpose of this study, the sapwood-rich material will be simply referred to as "sapwood".

Still using the vertical bandsaw, the sapwood fractions were sliced into slabs (8 ± 1 mm thick). Then, in order to remove the remaining bark and produce chips with uniform dimensions, the slabs were sawed into smaller pieces (45 ± 1 mm long) using a handsaw. Finally, any non-uniformities (e.g., rough edges and coarse surfaces) were fixed with a hand plane, and chips containing knots were discarded. The final model chips had the following dimensions: length = 30 ± 1 mm, width = 45 ± 1 mm and thickness = 8 ± 1 mm. These dimensions were selected to be within the usual limits adopted during chip screening, but also allowing for subsequent sectioning after the pulping experiments.

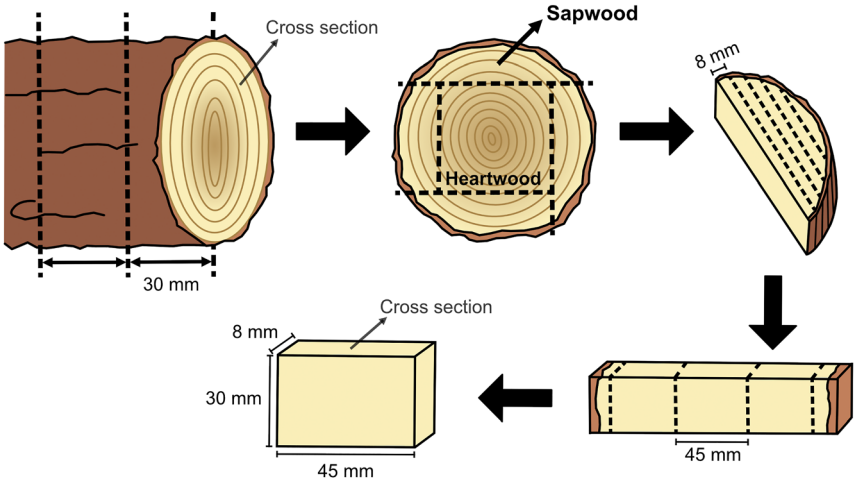

Figure 1: Scheme describing the preparation of sapwood model chips.

Table 1: Process conditions and composition of the white liquor used in the kraft pulping experiments.

Parameter[a]	Level (−1)	Level (0)[b]	Level (+1)
Temperature (°C)	145	155	165
$[HO^-]$ (mol/kg liquor), (EA, %)	0.25 (22)	0.40 (35)	0.55 (48)
Liquor:wood (w:w)[f]	22:1	22:1	22:1
$[SH]^-$ (mol/kg liquor)[f], (S, %)	0.25 (100)	0.25 (77)	0.25 (63)
Na_2CO_3 (mol/kg liquor)[f]	0.10	0.10	0.10

[a]Parameters marked with "f" were kept fixed in all experiments. EA, effective alkali (expressed as NaOH); S, sulfidity. [b]The center point conditions (155 °C and 0.40 mol HO^-/kg liquor) were used in triplicate to measure the repeatability of the pulping experiments and to provide error estimates.

2.4 Kraft pulping experiments

Batch kraft pulping experiments were conducted with different temperatures and hydroxide ion concentrations, as described in Table 1.

The experiments were carried out in autoclave vessels (1.5 L) containing four model chips each (approximately 24 g of dry wood). After adding white liquor (liquor:wood = 22:1, w:w), the autoclaves were sealed and the impregnation step took place: the vessels were deaerated and left under vacuum (10 min), followed by pressurization with nitrogen (5 bar) for 20 min.

At the end of impregnation, the pressure inside the vessels was released and they were placed in a pre-heated PEG-bath under constant agitation. The autoclaves were kept in the bath for different times (15, 30, 45, 60, 90 or 120 min), depending on the process conditions under evaluation. It is worth mentioning that the vessels took approximately 25 min to reach the targeted temperature – therefore, samples collected at 15 min never reached the temperatures presented in Table 1. The temperature profiles inside the autoclaves are reported in the Supplementary Material.

In order to terminate the cooking process, the vessels were moved to a water bath. After cooling for about 10 min, the autoclaves were opened, and the black liquor was separated from the treated chips by vacuum filtration in a polypropylene mesh. The cooked chips were then washed and leached in distilled water (4 L, changed every other day). Leaching was terminated when the leaching water was colorless and the pH neutral.

2.5 Sectioning of cooked chips

After being cooked and leached, the model chips were divided into sections, as shown in Figure 2. The adopted procedure was inspired by the methodology described by Wojtasz-Mucha et al. (2017). First, while the chips were still wet, a hand saw was used to split them into nine pieces (approximately 1 cm × 1.5 cm × 8 mm). The pieces were classified as center, side or corner. Then, with the aid of a microtome, each piece was divided into three layers (refer to Figure 2c). The outer and intermediate layers had approximately 3 mm of thickness (1.5 mm on top and 1.5 mm at the bottom), while the inner layer had about 2 mm.

Therefore, each pulping experiment generated nine different samples (sections): three layers (inner, intermediate and outer) for each of the three different wood pieces (corner, side and center). The material was dried at 105 °C overnight and stored at room temperature.

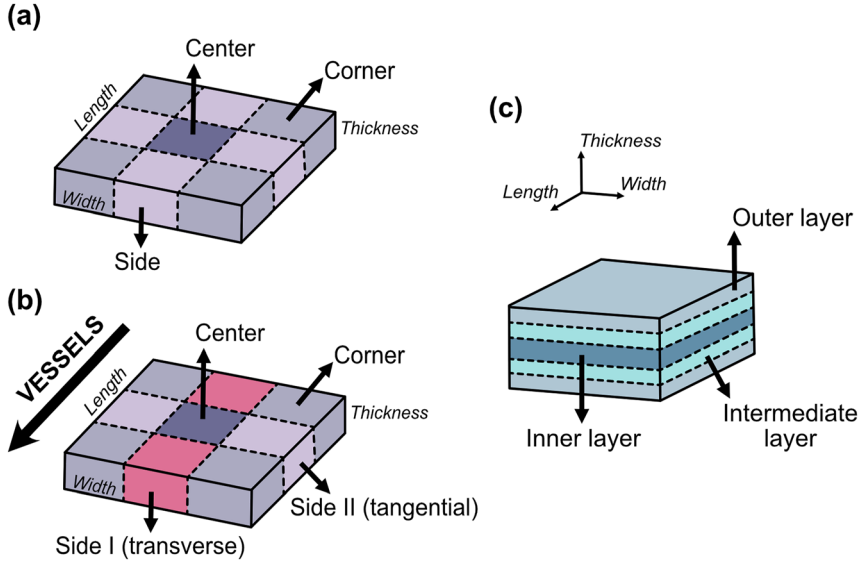

Figure 2: Sectioning of the cooked wood chips. (a) Division into three regions (corner, side and center). (b) Special case considering two different lateral regions: one in which the cross section of vessels (and fibers) was exposed (side I) and one with no exposed cross sections (side II). (c) Division of each piece into three different layers.

During the experiment conducted at Level (0) conditions (refer to Table 1), a different sectioning strategy was used (Figure 2b), considering four different regions: center, corner, side I and side II. This distinct procedure was adopted to compare how lateral pieces with exposed transverse surfaces (side I) and with exposed tangential surfaces (side II) behave during pulping. Thus, in this case, 12 samples were generated instead of nine.

2.6 Determination of Klason lignin

Klason lignin was quantified in untreated wood and in different sections of the cooked chips using an adapted version of the methodology reported by Sluiter et al. (2012). Given the small quantities of material attained after sectioning, no extraction was conducted prior to the Klason lignin analysis.

The samples were grinded in a Wiley mill (particle size <1 mm) and dried at 105 °C overnight. Next, duplicates of 75.0 ± 1.0 mg were transferred to 50 mL beakers and 1.125 ± 0.005 mL of sulfuric acid (72 %, w) was added. The samples were stirred with glass rods and subjected to vacuum for 15 min. Then, the beakers were placed in a water bath (30 °C/1 h) and the mixture was stirred every 20 min. Afterwards, the samples were diluted (31.50 ± 0.01 g of distilled water), covered with aluminum foil and placed in an autoclave at 125 °C for 1 h.

The hydrolyzed samples were vacuum filtered in glass microfiber filters (Whatman GF/A, diameter: 24 mm). The filtrate was collected and transferred to a 100 mL volumetric flask and the volume was completed with distilled water. This solution was further diluted with distilled water (1:3.75, v:v) and used in the analyses of acid-soluble lignin (ASL) and carbohydrates content (refer to items 2.7 and 2.8, respectively). The solid residue attained after filtration was dried overnight (105 °C) and weighted.

2.7 Acid-soluble lignin (ASL) measurement

The ASL content was determined by the absorbance of the filtrate solutions obtained during the Klason lignin analysis. The procedure was carried out at 205 nm using a UV spectrophotometer (Specord 205, Analytik Jena) and 1 cm quartz cuvettes. If the absorbance values were outside the 0.2–0.7 range, filtrate solutions with different dilutions were prepared. The absorptivity constant used to calculate the ASL concentrations was 110 $dm^3\,g^{-1}\,cm^{-1}$, as described by Dence (1992).

2.8 Carbohydrates quantification (anhydro sugars)

The carbohydrates were quantified using the filtrate solutions attained during the Klason lignin analysis. The solutions were analyzed via anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD Dionex ICS-5000, Thermo Fisher Scientific), in a system equipped with Dionex CarboPac PA1 columns (2 × 50 mm guard column and 2 × 250 mm analytical column) and a gold reference electrode. Elution conditions were as described by Kron et al. (2023). The measured concentrations of monosaccharides were corrected by the yield after acid hydrolysis (Wojtasz-Mucha et al. 2017) and the final results were expressed as anhydro sugars (Janson 1974).

2.9 Calculation of yield and local composition

Equation (1) was used to provide estimates for the pulping yield in each section of the model chips, and Equation (2) provided the contents of the main wood components present in the cooked material (i.e., Klason lignin, ASL and anhydro sugars) in grams per gram of dry wood (g/g odw).

$$\mathrm{Yield_i} = \frac{G_{\mathrm{wood}}}{G_{\mathrm{i}}} \tag{1}$$

$$X_{\mathrm{i}} = x_{\mathrm{i}}\,(\mathrm{Yield_i}) = x_{\mathrm{i}}\left(\frac{G_{\mathrm{wood}}}{G_{\mathrm{i}}}\right) \tag{2}$$

In which, $\mathrm{Yield_i}$ is the yield of pulping in a given section i, G_{wood} is the content of glucan in the untreated wood (g of glucan/g of wood) and G_{i} is the content of glucan measured in the section (g of glucan/g of cooked material in section i). In Equation (2), X_{i} stands for the content of X in section i given in g/g odw (X = Klason lignin, ASL or anhydro sugars), and x_{i} is the content of X in section i given in g/g of cooked material.

2.10 Preparation of holocellulose (peracetic acid delignification)

Holocellulose samples were prepared according to the experiments described by Chang and Holtzapple (2000) and Kumar et al. (2013). In short, delignification was carried out in beakers containing 5 % (w/w) of dry solids (sapwood meal or milled kraft cooked sections, particle size <1 mm) and 5.5 g of peracetic acid/g of solids. The reaction occurred at 25 °C for 48 h. The beakers were covered with parafilm and kept under constant stirring (300 rpm).

At the end of the process, the slurry was vacuum filtered in a glass microfiber filter (Whatman GF/A 55 mm, Cytiva) and washed with distilled water (4× the volume of the slurry). Next, the solid residue was washed with a 50:50 (v:v) mixture of ethanol and acetone (2× the volume of the slurry). Then, the material was dried in an oven (40 °C) for four days and stored at room temperature inside a desiccator. Finally, 100 mg samples were separated for the molecular weight analysis (refer to Supplementary Material) and the remaining material was subjected to extraction with DMSO (dimethyl sulfoxide), as described in item 2.11. Yield: 74–95 %.

It is worth mentioning that, when performing the peracetic acid delignification of kraft cooked chips, different pieces of a same layer were combined (i.e., center, corner and side). Therefore, each cooked sample resulted in three different holocellulose fractions (associated to the outer, intermediate and inner layers).

2.11 Extraction and isolation of xylan

The extraction of xylan from holocellulose was based on the procedure described by Evtuguin et al. (2003). In this process, holocellulose was treated with DMSO (1:60, w) under nitrogen atmosphere for 20 h. The system was kept at 50 °C and under constant stirring (300 rpm).

At the end of the process, the DMSO extract was separated from the solid residue by vacuum filtration in a glass microfiber filter (Whatman GF/A 55 mm, Cytiva). During filtration, the residue was washed with approximately 25 mL of fresh DMSO. Afterwards, in order to precipitate xylan, ethanol was added to the filtrate (2:1, v) together with enough acetic acid to cause the system to become a suspension. Then, the suspension was left at 4 °C overnight, followed by centrifugation at 4500 rpm/30 min/4 °C, as described by Corradini et al. (2018). Finally, the isolated xylan was freeze-dried and stored in a desiccator. Estimated xylan recovery (based on results attained using holocellulose from untreated sapwood): 33 %.

2.12 Molecular weight distribution measurements

The MWD of the xylan fractions (item 2.11) was analyzed using a PL-GPC 50 Plus Integrated GPC system (Polymer Laboratories, Varian Inc.) with two 300 × 7.5 mm PolarGel-M columns and one 50 × 7.5 mm PolarGel-M guard column. A solution of LiBr (10 mM) in DMSO was used as mobile phase with a flow rate of 0.5 mL/min at 50 °C. Detection was made using both a UV detector (280 nm) and a refractive index detector. Pullulan standards (0.180–708 kDa) were used for calibration and data processing was carried out with the Cirrus GPC Software 3.2. Sample preparation involved dissolving the xylan fractions in mobile phase overnight (10 mg/mL), followed by diluting the material (final concentration: 1.67 mg/mL) and filtering with 0.2 µm PTFE filters.

2.13 NMR

The isolated xylan was also analyzed using the 2D NMR HSQC methodology. The samples were dissolved in DMSO-d_6 (140 mg/mL) and placed in 3 mm tubes. The spectra were recorded with a Bruker Avance III HD (Rheinstetten, Germany) using a 5 mm TXO cold probe working at 800 and 200 MHz for ^{1}H and ^{13}C, respectively. More details about the experimental settings are described by Kron et al. (2023). TopSpin 4.2.0 (Bruker) was used for data analysis.

3 Results and discussion

3.1 Composition of untreated wood

The composition of the sapwood used to prepare the model wood chips is given in Table 2. The measured holocellulose content (63.6 %) and the concentrations of the individual carbohydrates are within the range of values reported for *B. pubescens* wood (Luostarinen and Hakkarainen 2019; Mulat et al. 2018; Pettersen 1984). In regard to the lignin, the acid soluble fraction (5.3 %) is in line with the findings of Luostarinen and Hakkarainen (2019), whereas the Klason lignin content was closer to the result reported by Pettersen (1984). However, the comparison between literature and the data observed in Table 2 is affected by the fact that only sapwood (and not the whole wood) has been analyzed in this study.

Table 2: Composition of birch sapwood; detected amount: 88.2 ± 0.5 %.

Component	Content ± SD (%, w/w)[a]
Klason lignin	19.3 ± 0.4
Acid-soluble lignin	5.3 ± 0.1
Glucan	37.0 ± 0.2
Xylan	23.2 ± 0.2
Arabinan	0.3 ± 0.0
Galactan	0.8 ± 0.0
Mannan	2.3 ± 0.1

[a]Based on measurements of six replicates.

3.2 Effect of kraft cooking conditions: xylan removal

To get an overall picture of how temperature and hydroxide content have impacted xylan removal, the distribution of xylan inside chips subjected to the same time of cooking has been compared. Figure 3 shows these profiles after 45 min of reaction (time point in which defibration started to occur in the outer layer of the sample treated at 165 °C with 0.55 mol HO^-/kg liq.).

At this early stage of the process, one of the main factors contributing to xylan removal is the dissolution of the polysaccharide chains (Pinto et al. 2005). When focusing on the effect of hydroxide content, higher concentrations of alkali led to increased removal of xylan, which agrees with reported data (Lehuedé et al. 2023). The influence of temperature, however, is not as straightforward. Increasing temperature has been shown to improve xylan dissolution (Jun et al. 2012), which agrees with the experimental data attained when comparing the samples treated with 0.55 mol HO^-/kg liquor. Nevertheless, when lower concentrations of hydroxide were applied, higher temperatures did not increase xylan removal. Rather the opposite occurred; the sample treated at 165 °C showed slightly higher retention of xylan in the inner layers.

These contrasting results suggest that there is a significant reduction in the hydroxide ion content available within the wood chips, when compared to the bulk liquor – which is initially caused by fast alkali-consuming reactions, such as neutralization of acid groups. Then, as pulping progresses, the HO^- concentration inside the chips will be determined by the balance between the rates of hydroxide consumption and transport from the bulk towards the center of the chips. Hence, if low hydroxide concentrations are utilized in the white liquor, the use of high cooking temperatures can result in increased HO^- consumption (due to faster reaction rates), which may not be met by the rate of transport of ions. Therefore, depending on the content of alkali that is utilized in the white liquor, the increase in xylan solubility due to applying higher temperatures may be upstaged by the decrease in xylan solubility caused by the lower hydroxide levels inside the chips.

Re-adsorption of xylan in the delignified material is also a factor that must be considered when analyzing xylan retention. However, since the extent of delignification is quite modest in the experiments performed in this study, re-adsorption would be expected only at the outer layers of the most delignified samples. Another important aspect that can influence xylan removal is the structure of xylan itself. Characteristics such as degree of branching, type of side groups and molecular mass – all which may change throughout pulping – have been shown to significantly affect xylan solubility (Palasingh 2022). Thus, in order to better understand how the pulping conditions affect xylan structure and how the residual xylan in the treated chips compare to the native birch xylan, the molecular weight distribution (Figure 4) and structural motifs (Figure 5 and Table 3) of xylan fractions isolated from sapwood and from different layers of the kraft cooked chips were analyzed.

Xylan samples isolated from the outer layers of chips cooked for 45 min exhibited similar MWD, with average molecular weight (Mw) within 24.6–26.3 kDa. This result, combined with the similar NMR spectra of xylan samples isolated from chips cooked under different conditions (refer

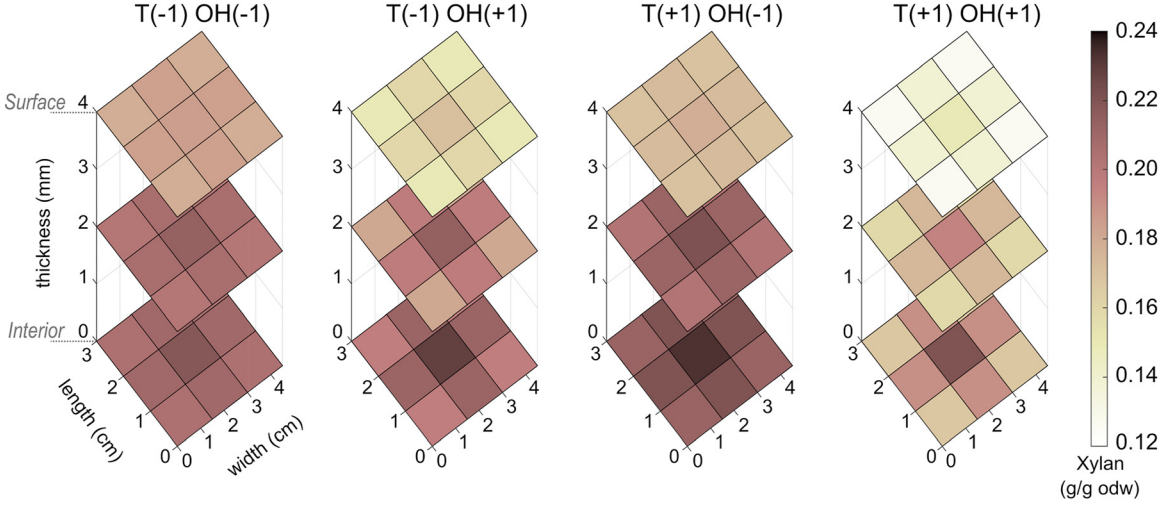

Figure 3: Distribution of xylan (g/g of dry wood) in the nine sections of wood chips after 45 min of batch kraft cooking. Cooking conditions from left to right: 145 °C & 0.25 mol HO^-/kg liq., 145 °C & 0.55 mol HO^-/kg liq., 165 °C & 0.25 mol HO^-/kg liq., 165 °C & 0.55 mol HO^-/kg liq. Estimated error = 4 % (refer to Supplementary Material).

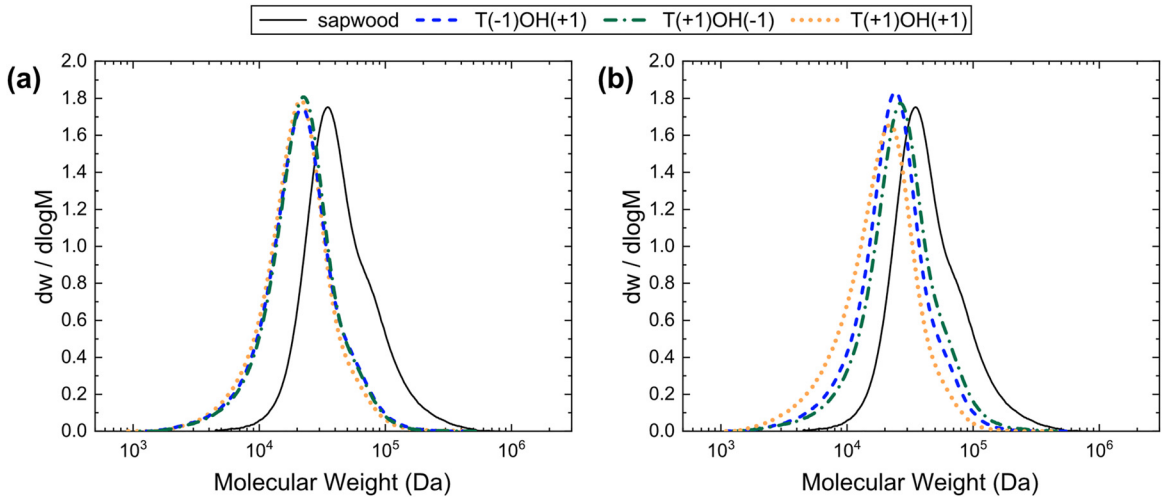

Figure 4: Molecular weight distribution of xylan isolated from birch sapwood and birch chips cooked for 45 min at 145 °C & 0.55 mol HO^-/kg liq., at 165 °C & 0.25 mol HO^-/kg liq. and at 165 °C & 0.55 mol HO^-/kg liq. (a) Results observed in the outer layer of the chips, with all three regions (corner, side and center) combined. (b) Results observed in the inner layer of the chips, with all three regions (corner, side and center) combined.

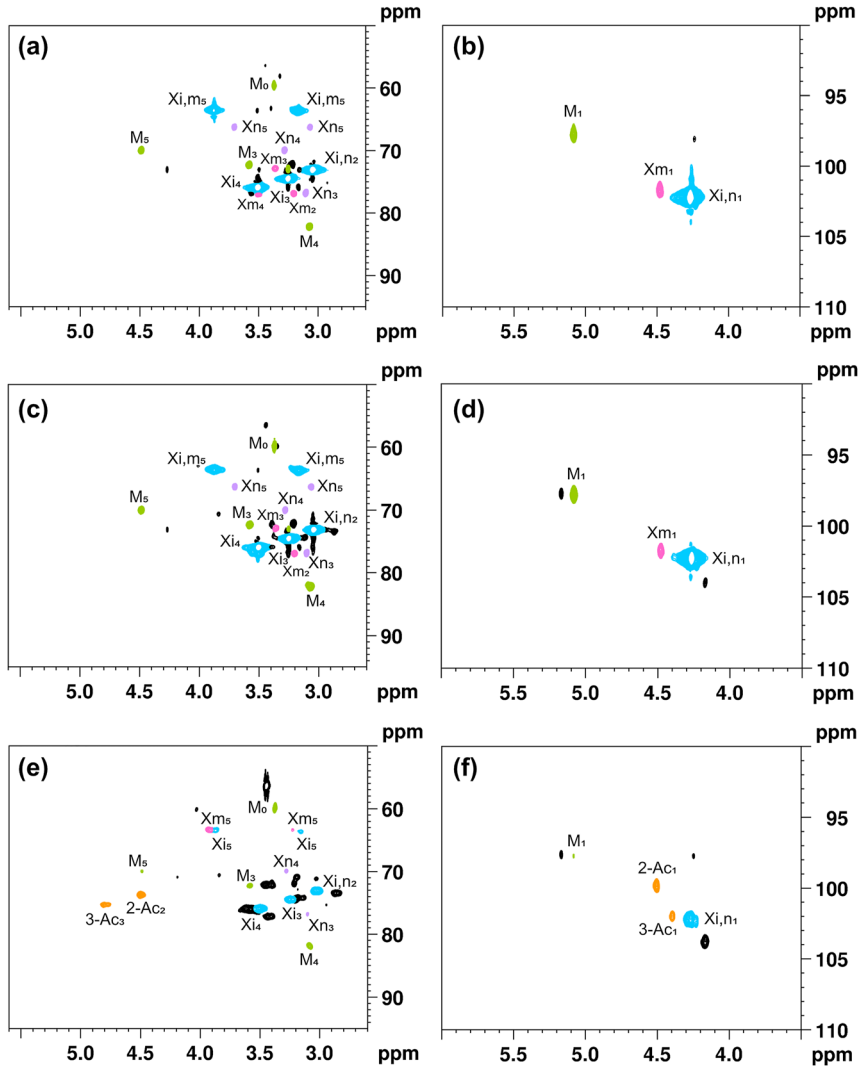

Figure 5: HSQC spectra of isolated xylan dissolved in DMSO-d_6. (a) Aliphatic and (b) anomeric regions of the sample isolated from the outer layer (corner, side and center combined) of the material treated at 165 °C & 0.55 mol HO^-/kg liq. (c) Aliphatic and (d) anomeric regions of the sample isolated from the inner layer (corner, side and center combined) of the material treated at 165 °C & 0.25 mol HO^-/kg liq. (e) Aliphatic and (f) anomeric regions of the sample isolated from sapwood. Annotated peaks are detailed in Table 3.

Table 3: Assigned peaks in the HSQC data of isolated xylan samples (solvent: DMSO-d_6)[a].

Symbol	Unit	$^{13}C/^{1}H$ chemical shifts (ppm)
M_O	C–H in MGA[b] (–OCH_3)	59.7–60.1/3.37
M_5	C_5–H_5 in MGA[b]	70.1/4.49
M_2	C_2–H_2 in MGA[b]	73.2/3.25
M_3	C_3–H_3 in MGA[b]	72.3/3.58
M_4	C_4–H_4 in MGA[b]	81.8–82.2/3.07–3.09
M_1	C_1–H_1 in MGA[b]	97.8/5.08
Xi_5	C_5–H_5 in xylan (internal)	63.6/3.17 & 3.88
Xi_2	C_2–H_2 in xylan (internal)	73.2/3.04
Xi_3	C_3–H_3 in xylan (internal)	74.6/3.25
Xi_4	C_4–H_4 in xylan (internal)	75.9/3.51
Xi_1	C_1–H_1 in xylan (internal)	102.2/4.27
Xn_5	C_5–H_5 in xylan (non-reducing end)	66.3/3.07 & 3.70
Xn_4	C_4–H_4 in xylan (non-reducing end)	70.1/3.28
Xn_2	C_2–H_2 in xylan (non-reducing end)	73.2/3.04
Xn_3	C_3–H_3 in xylan (non-reducing end)	76.9/3.10
Xn_1	C_1–H_1 in xylan (non-reducing end)	102.2/4.27
Xm_5	C_5–H_5 in xylan (MGA[b])	63.4/3.23 & 3.93
Xm_2	C_2–H_2 in xylan (MGA[b])	76.9/3.20
Xm_3	C_3–H_3 in xylan (MGA[b])	73.0/3.36
Xm_4	C_4–H_4 in xylan (MGA[b])	77.1/3.50
Xm_1	C_1–H_1 in xylan (MGA[b])	101.7/4.48
2-Ac_2	C_2–H_2 in acetylated xylan (2-*O*-acetyl-β-D-xylopyranose)	73.8/4.50
2-Ac_1	C_1–H_1 in acetylated xylan (2-*O*-acetyl-β-D-xylopyranose)	99.8/4.50
3-Ac_3	C_3–H_3 in acetylated xylan (3-*O*-acetyl-β-D-xylopyranose)	75.3/4.80
3-Ac_1	C_1–H_1 in acetylated xylan (3-*O*-acetyl-β-D-xylopyranose)	102.0/4.40

[a]The assignment of the peaks in Figure 5 was based on the works of Kim and Ralph (2010, 2014). [b]4-*O*-methyl-α-D-glucuronic acid (MGA).

to Figure 5a–d), indicates that differences in cooking temperature and concentration of hydroxide seem to have little impact over the final structure of the residual material (in the range of conditions studied in this work). Such behavior is expected, since the rates of the main reactions affecting xylan at this stage of cooking are quite fast (Sjöström 1993). In the inner layers, the differences in MWD became more significant, with Mw ranging from 22.8 kDa in the sample treated at high temperature with high hydroxide content, T(+1)OH(+1), to 28.4 kDa in the sample cooked at low temperature, T(–1)OH(+1), and 32.8 kDa in the sample treated with low hydroxide concentration, T(+1)OH(–1). These results agree with the idea of a decrease in hydroxide content inside the chips due to chemical reactions (when compared to the conditions in the bulk liquor), as the sample treated with low alkali and high temperature displayed Mw closer to the one observed in native xylan.

In Figure 4, it is also possible to notice a steep shift in MWD between the native xylan and the xylan found in the kraft cooked samples. One explanation for such difference could be the presence of LCCs in the native xylan, but the low residual lignin content (less than 2 % of Klason lignin) in the isolated material compromises this hypothesis. Furthermore, no chemical shifts associated with lignin were found in the NMR data presented in Figure 5. The major difference observed in the HSQC spectra was the disappearance of acetyl groups (C_2 and C_3 positions) in xylan isolated from pulped samples, yet the deacetylation of xylan would only partly contribute to the changes in molecular weight. Thus, the initial drop in Mw is likely a combination of deacetylation and peeling reactions taking place at the beginning of the cook (despite xylan's relatively high resistance to alkaline conditions when compared to other hemicelluloses).

One caveat when analyzing the results in Figures 4 and 5 concerns the methodology used for isolating the xylan fractions. Despite resulting in only minor changes in structure (when compared to other methods), the peracetic acid delignification (25 °C/48 h), followed by extraction with DMSO (50 °C/20 h), leads to low xylan yields (Corradini et al. 2018). In the present study, xylan recovery was estimated to be around 33 %. Nevertheless, the reported results seem to capture the overall behavior of xylan in the evaluated samples, as they also agree with the general trends observed when analyzing the MWD of holocellulose samples (refer to the Supplementary Material). Furthermore, the Mw values of xylan isolated from treated chips concur with results reported for birch kraft pulps (Rosa-Sibakov et al. 2016; Westermark and Gustafsson 1994).

In the case of xylan extracted from untreated sapwood, the measured Mw (55.3 kDa) was higher than previous findings. Pinto et al. (2005), for instance, found Mw around 24 kDa for native xylan extracted from holocellulose of *Betula pendula* (extraction conditions: DMSO/50 °C/20 h). However, this discrepancy may be due to the harsher conditions during the peracetic acid delignification (85 °C/30–35 min) utilized in that work, and the subsequent ball milling of the holocellulose.

To further analyze the behavior of xylan during pulping, the contents of xylan in samples treated at 145 °C and at 165 °C were compared over time (until the chips started to defibrate). Figure 6 presents the residual xylan in different regions of the model chips: at the center of the inner layer (least accessible region of the wood chips) and at the corner of the outer layer (region highly exposed to the cooking liquor).

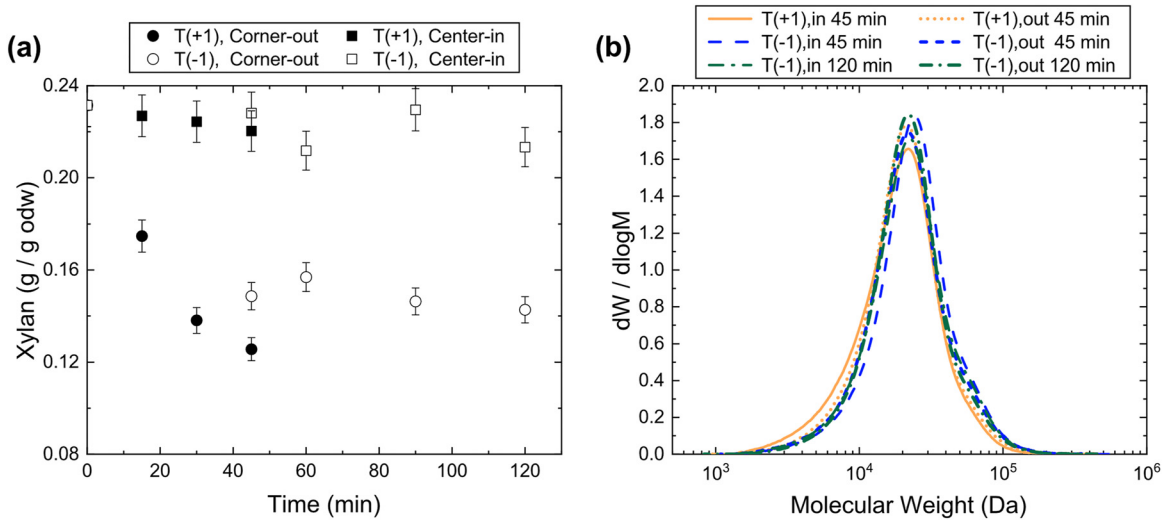

Figure 6: Comparison between xylan retention behavior after kraft cooking at 145 °C and at 165 °C (hydroxide content in both cases: 0.55 mol/kg liq.). (a) Xylan content over time at the corner of the outer layer (corner-out) and at the center of the inner layer (center-in). Estimated error = 4 % (refer to Supplementary Material). (b) Molecular weight distribution of isolated xylan from the inner and outer layers of chips cooked for 45 and 120 min.

The profiles indicate that temperature had a minor impact over the uniformity of xylan removal, since samples treated at 145 °C and 165 °C showed similar differences between the xylan content in the corners and in the center of the chips when defibration started. More interestingly, the xylan content seemed to decrease extremely slowly after the first minutes of pulping. These plateau-like concentration profiles indicate that at low cooking temperatures only a negligible amount of xylan is dissolved and transported out of the chips after the first 45 min of cooking – at least until defibration starts. This behavior hints at the presence of a fraction of xylan that is more resistant to pulping, possibly due to a strong association with cellulose and/or lignin, which reduces xylan's accessibility (Dammström et al. 2009; Gomes et al. 2020). Also, given the differences between the residual xylan in the outer and inner layers of the chips, it is probable that the lower concentrations of cooking chemicals inside the chips (in relation to the concentrations in the bulk liquor) influence the local retention of xylan.

The comparison between the MWD of the material treated at 145 °C – samples T(–1) 45 min and T(–1) 120 min (Figure 6b) – shows that the molecular weight of residual xylan suffers only minor changes after the initial minutes of pulping. Furthermore, samples treated with different temperatures had similar Mw values when defibration began. Thus, in the interval after the first minutes of pulping and before the beginning of defibration, peeling and alkaline hydrolysis do not seem to affect xylan significantly. This result contrasts with previous findings (Pinto et al. 2005), in which the molecular weight of residual xylan in birch kraft pulps was shown to decrease continuously. While this difference can be due to the cooking conditions (for instance, the use of 160 °C instead of 145 °C) and the characteristics of the chips (industrially cut chips instead of hand-cut), it could also mean that further changes in the structure of xylan would occur after defibration, emphasizing that accessibility may be a key factor impacting xylan retention.

3.3 Effect of cooking conditions: kraft delignification

The distribution of Klason lignin inside chips cooked for 45 min under different conditions is shown in Figure 7. The results regarding acid-soluble lignin are presented in the Supplementary Material, but the trends are the same as seen in Figure 7.

As expected, chips treated at 145 °C showed only minor delignification after 45 min of cooking, which is explained by the low rates of reactions involving lignin at this temperature. Under this condition, the influence of the hydroxide content was quite modest, with the main difference occurring in the surface of the chips, where sample T(–1)OH(+1) showed residual Klason lignin around 0.12 g/g odw, and sample T(–1)OH(–1) had Klason lignin contents of approximately 0.14 g/g odw. Such results reinforce the existence of a significant decrease in the concentration of HO^- inside the chips, mainly due to the initial consumption of these ions in reactions involving carbohydrates.

The samples cooked at high temperature (165 °C) showed a more pronounced delignification, and the difference between utilizing low or high concentrations of

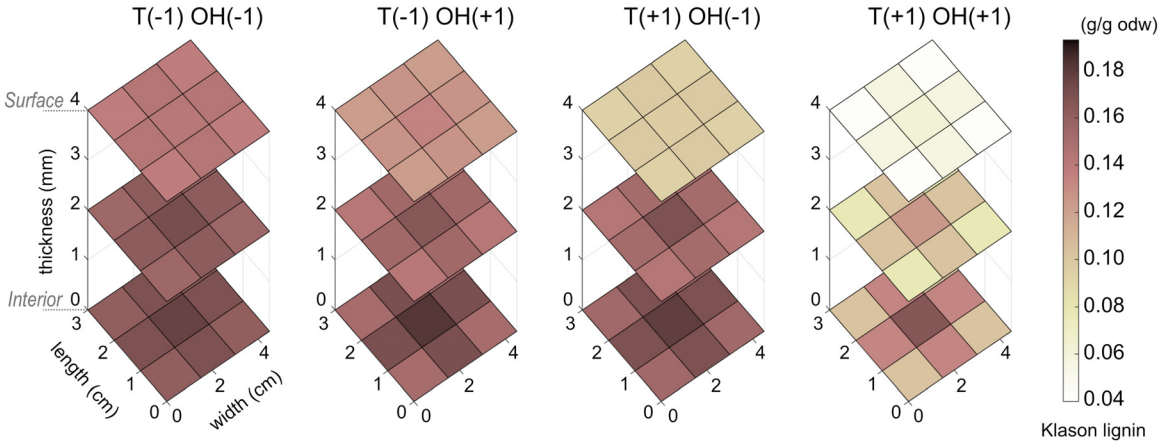

Figure 7: Distribution of Klason lignin (g/g of dry wood) in the nine sections of wood chips after 45 min of batch kraft cooking. Cooking conditions from left to right: 145 °C & 0.25 mol HO^-/kg liq., 145 °C & 0.55 mol HO^-/kg liq., 165 °C & 0.25 mol HO^-/kg liq., 165 °C & 0.55 mol HO^-/kg liq. Estimated error = 5 % (refer to Supplementary Material).

hydroxide ions in the white liquor was striking. When using 0.25 mol HO^-/kg liquor, about 50 % of the original lignin content in the outer layer of the chip was removed, but the delignification in the other two layers was comparable to the ones attained at 145 °C. Such behavior indicates a larger effect of temperature on reaction kinetics than on the mass transport rates of cooking chemicals and lignin inside the chip: if the diffusivity coefficients or the solubility of lignin were impacted to the same extent as the rates of reaction, the delignification of the inner layers would also increase. In addition, comparing the profiles shown in Figure 7 for samples T(−1)OH(−1) and T(+1)OH(−1), it is possible to arrive at the same conclusions drawn when analyzing the xylan results: the increased consumption rate of HO^- (caused by increasing the cooking temperature from 145 °C to 165 °C) led to significantly lower hydroxide contents available in the inner layers of the T(+1)OH(−1) chip, which in this case contributed to the high residual lignin contents measured there.

On the other hand, when both the temperature and the hydroxide concentration levels were high (165 °C and 0.55 mol HO^-/kg white liquor), a substantial increase in lignin removal was observed in all layers. Probably, by using a high content of alkali during the process, it was possible to avoid reaching extremely low hydroxide concentrations inside the chips as pulping progressed, as also suggested by

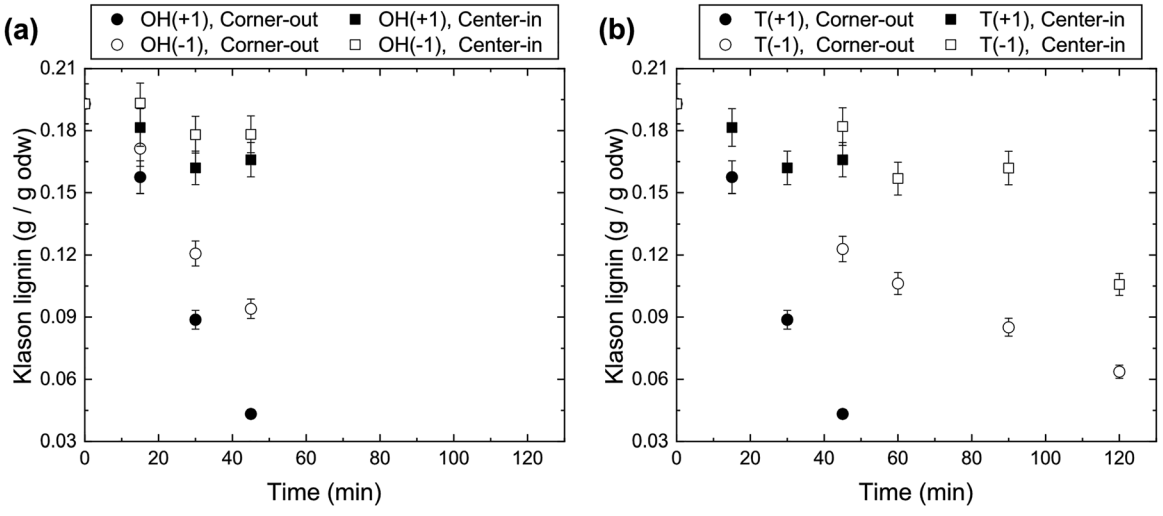

Figure 8: Klason lignin content over time at the corner of the outer layer (corner-out) and at the center of the inner layer (center-in) in chips cooked under different conditions. (a) Comparison between utilizing high and low concentrations of hydroxide (165 °C & 0.25 mol HO^-/kg liq. vs. 165 °C & 0.55 mol HO^-/kg liq.). (b) Comparison between utilizing high and low temperatures (145 °C & 0.55 mol HO^-/kg liq. vs. 165 °C & 0.55 mol HO^-/kg liq.). Estimated error = 5 % (refer to Supplementary Material).

Määttänen and Tikka (2012). This result confirms the significant impact of hydroxide content, not only over the rate of reactions, but also over the mass transport of ions and dissolved products within the chips.

In order to further investigate how temperature and hydroxide content can influence the final uniformity of lignin content in kraft pulps, the delignification profiles over time were compared. Figure 8 summarizes this analysis by presenting the residual Klason lignin content in two specific regions of the wood chips: at the center of the inner layer and at the corner of the outer layer.

The profiles in Figure 8a illustrate that utilizing white liquors containing high hydroxide content does not necessarily lead to uniform delignification. The observed behavior indicates that, even though higher HO^- contents in the bulk liquor may lead to higher hydroxide concentrations inside the wood chips (and consequently improved solubilization and transport of lignin), this phenomenon is compromised by the chip surface being exposed to higher alkali levels. In fact, the increased delignification in the inner layers (center-in) of the sample treated with 0.55 mol HO^-/kg liquor is overshadowed by the intense delignification occurring in the outer portions of the chip (corner-out), thus, when the samples start to defibrate, the lignin content in the center remains approximately four times higher than on the surface.

When focusing on the effect of temperature (Figure 8b), the kraft pulping conducted at 145 °C resulted in a more uniform delignification than the one achieved at 165 °C, suggesting that, as temperature decreases, the rates of delignification in different sections of the wood chip become more similar (given the interplay between reaction rates and mass transport). In fact, when defibration started in the samples cooked at low temperature (after 120 min), the lignin content in the center of the chips was less than twice the content of that on the surface. Given these results, the use of low temperatures during kraft cooking has the potential to reduce the incidence of shives and the amount of rejects. Favaro et al. (2021), for instance, reported higher screened pulp yields when kraft cooking eucalyptus at 155 °C than at 160 and 165 °C, moreover, no rejects were produced when pulping was conducted at mild conditions.

3.4 Kraft cooking evolution versus anisotropic nature of wood

As seen in Figures 3 and 7, the evolution of delignification and xylan removal varies with the relative position inside the wood chips, and significant concentration gradients were observed along the thickness of the chip (in the radial direction), between the outer and inner layers. These gradients can be deeply affected by the rates of mass transport inside the pore system of the chips which, in turn, depend on the microstructure of the wood. For hardwoods, this means that the distribution and characteristics of fibers, vessels, longitudinal parenchyma and rays may have an impact on the evolution of pulping. The detailed morphology of the birch sapwood utilized to prepare the model chips can be seen in the Supplementary Material.

In order to briefly assess how substantial the impact of wood structure was during the experiments conducted in this paper, the concentrations of lignin and xylan were compared in two different sections: one in which the transverse surface was exposed to the bulk liquor, and one in which the tangential surface was exposed (sides I and II, respectively – refer to Figure 2). The composition of these

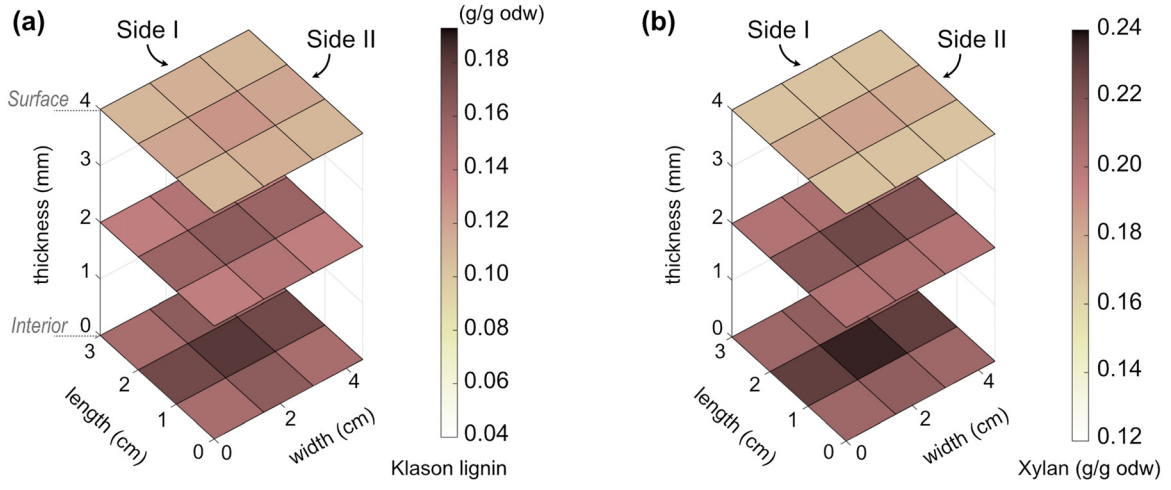

Figure 9: Average chemical composition (g/g of dry wood) of the wood chip sections attained after kraft cooking experiments run in triplicates. Cooking conditions (center point): 45 min of pulping at 155 °C & 0.40 mol HO^-/kg liq. (a) Lignin content, error = 5 %. (b) Xylan content, error = 4 %.

sections was measured in all layers of the chip and the results are presented in Figure 9.

Lateral sections with exposed transverse surfaces showed residual lignin and xylan concentrations similar to the ones measured in the corners of the chip, whereas higher values (5.5 % higher, in average) were found in lateral sections with exposed tangential surfaces. These differences were significant (α = 0.05) in all layers when considering xylan, and in the intermediate and inner layers when considering lignin.

These higher rates of delignification and xylan removal in sections with exposed transverse surfaces (where diffusion and liquor penetration are aided by vessels and lumen of fibers) suggest that the mass transport in the longitudinal direction of wood (along the length of the chips) was more efficient than in the tangential direction (along the width). Such behavior is reasonable, as sections with exposed tangential surfaces are expected to offer higher transport resistance once diffusion is mainly aided by the pits in the walls of fibers and vessels. In addition, this observation agrees with experimental data regarding effective capillarity at high pHs (Stone 1957) and permeability (Siau 1984) in hardwoods.

4 Conclusions

The experiments were able to assess how cooking temperature and hydroxide content can affect delignification and xylan retention inside birch chips during the initial stages of kraft pulping (before defibration starts). The results showed that:

i. The rate of delignification and xylan removal depends on the availability of hydroxide ions inside the chips during pulping, which is impacted by the concentration of alkali in the white liquor and the rate of hydroxide consumption. The latter is substantially affected by temperature.
ii. Wood morphology appears to influence the evolution of pulping inside the chips. Delignification and xylan removal are faster in the longitudinal direction, probably due to lower apparent mass transport resistance, when compared to the ones in the radial and tangential directions.
iii. Xylan retention decreases when utilizing high concentrations of alkali. When high cooking temperatures are used, the solubility of xylan should increase but, if the content of alkali inside the chips becomes significantly low (due to high rates of hydroxide consumption in reactions not being compensated by the slow transport of ions), lower amounts of xylan might be dissolved.
iv. Changes in the native structure of xylan occur early during cooking and are probably due to deacetylation and peeling (to some degree). Within the ranges investigated, temperature and hydroxide content had little impact over the extent of such changes.
v. The uniformity of delignification inside the chips can be improved by using lower cooking temperatures.

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