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RESEARCH

Uniformity of delignification during kraft pulping of hardwood chips: impact of wood structure and the importance of impregnation

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Abstract

This study examines the homogeneity of lignin and xylan removal in model sapwood chips of alder (*Alnus glutinosa*), birch (*Betula pubescens*), beech (*Fagus sylvatica*), and aspen (*Populus tremula*) during batch kraft pulping. The first experiments focused on investigating the effect of hardwood morphology on the evolution of pulping. By comparing the gradients of lignin and xylan inside the chips at different stages of delignification, it was established that the process is more uniform in hardwoods of lower density (high porosity), like aspen. Hence, characteristics such as large and frequent vessels, thin fiber walls, and large lumens may help to achieve pulps with more homogeneous composition and to avoid shives. The influence of other morphological features was not clear. The results also suggested that the impact of morphology was mostly connected to the impregnation step, as the porosity of the sapwood dictated the initial concentration of hydroxide ions within the chips. Thus, a second set of experiments was conducted to evaluate the possibility to overcome this impact by utilizing liquors with high alkali content during pulping. Among the evaluated conditions, the use of liquor containing 2 mol HO^-/kg during impregnation followed by cooking with 0.55 mol HO^-/kg was shown to be a reasonable approach to increase the uniformity of delignification.

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Introduction

The pulp industry has faced major shifts for the past decades, from alterations in consumption patterns to the rise of pulp and paper production capacity outside of the Europe-North America axis (Hujala et al. 2013; UNECE/FAO 2024b). Yet, the sector is still undergoing profound changes. For example, the development of innovative paper materials for hygiene and packaging purposes is a current trend, as well as the valorization of pulping side-streams (e.g., lignin). At the same time, fiber security remains a concern, especially considering the increasingly high costs of wood and the challenges posed by climate change (UNECE/FAO 2024a, b).

In this scenario, diversifying the feedstocks used in pulp mills can be of interest (Mboowa 2024; UNECE/FAO 2024b). For instance, a larger number of hardwood species could be employed for pulp production. However, to ensure pulp quality and resource efficiency, it is essential to understand how different raw materials behave during pulping, particularly in the context of the kraft process (which is the dominant method used for pulp production globally). This is especially relevant for hardwoods, given their great complexity and variability, both in terms of chemical composition and morphology.

Still, the number of studies focusing on kraft pulping of hardwoods is small when compared to softwoods, and most of them focus on fast growing species – like eucalyptus. Among these studies, some evaluate the impact of process conditions on pulp production. For example, Santiago et al. (2008) investigated the effect of alkali splitting on kraft pulping of eucalyptus finding that, contrary to what is observed in other wood species, the profiling led to no significant impact on the overall pulping performance. The impact of effective alkali and temperature has also been explored. Favaro et al. (2021), for instance, reported that low cooking temperatures increase the screened pulp yield, favor the retention of xylan, and increase the hexenuronic acid content in brown pulp of eucalyptus.

Even fewer studies provide comparisons between the pulpability of different hardwood species. In these cases, it is common to focus on differences in pulping yields and/or pulp properties, as is the case of the works developed by Patt et al. (2006) and Neiva et al. (2015). Patt et al. (2006) compared *Eucalyptus globulus* and three European hardwoods (beech, birch, and poplar), finding that poplar resulted in the highest yields. Pulp properties, with the exception of runnability, varied depending on morphology and composition. A similar but more extensive analysis was conducted by Neiva et al. (2015). In their work, 12 species of eucalyptus were compared, considering pulpability, fiber characteristics and handsheet properties. Unsurprisingly, *Eucalyptus globulus* showed the best overall performance, but other species showed potential for specific applications, such as printing and tissue paper.

In-depth investigation of the delignification behavior of different hardwoods is rare. Pinto et al. (2005b); Santos et al. (2011), for example, emphasized differences in reaction kinetics and lignin structure. Pinto et al. (2005b) compared the behavior of three eucalyptus species, as well as birch and acacia, suggesting that the ease of delignification (which was higher in eucalyptus) was linked to the syringyl/guaiacyl (S/G) ratio and to the proportion between noncondensed/condensed units in lignin. Santos et al. (2011) found a similar trend regarding the rate of delignification and the S/G ratio when comparing 10 hardwoods, although birch was an outlier. The impact of mass transport during delignification has been studied for selected hardwoods (Egas et al. 2002; Simão et al. 2008; Kron et al. 2023), but direct comparisons of this impact among different species remain scarce.

One aspect that could be further investigated is the impact of wood morphology on delignification. While some impregnation studies provide insight regarding liquor penetration and the initial distribution of cooking chemicals inside hardwood chips (Stone and Green 1959; Wardrop and Davies 1961; Zanuttini et al. 2005), the implications of wood anisotropy to the progression of delignification are yet to be fully explored. Hence, this work aimed to investigate how wood morphology influences the progression of lignin and hemicellulose removal during kraft pulping. This analysis was performed by comparing local changes in composition inside hand-cut chips of different species after batch kraft cooking experiments. The study considered four hardwoods commonly found in the Nordic countries, namely: alder, aspen, beech, and birch. The local composition was assessed utilizing a sectioning procedure described in our previous work (Marion de Godoy et al. 2024), followed by quantification of Klason lignin and structural carbohydrates. Additional pulping experiments were also included to evaluate the use of impregnation liquors with high alkali concentration as possible alternatives to improve the uniformity of lignin removal.

Materials and methods

Sample preparation

Logs of alder (*Alnus glutinosa*), aspen (*Populus tremula*), beech (*Fagus sylvatica*), and birch (*Betula pubescens*), all grown in southern Sweden, were kindly provided by Södra Skogsägarna. The age of the specimens was approximately 27 ± 1 years old for birch, 28 ± 1 years old for aspen, 43 ± 2 years old for alder and 44 ± 5 years old for beech. All logs were cut from the stems at breast height.

To prepare the samples utilized in this work, the logs were sawn to separate the sapwood from the heartwood and bark. The sapwood portions were then cut to form small blocks, hereafter referred to as "model chips" or simply "chips". These model chips had specific dimensions to allow comparing the local composition in different samples. The dimensions were: length = 3.0 ± 0.1 cm, width = 4.5 ± 0.1 cm, and thickness = 8 ± 1 mm (refer to Supplementary Information). More details about the sawing process can be found in previous work (Marion de Godoy et al. 2024).

The model chips were air dried and stored at room temperature. Their water content was measured before each cooking experiment via oven-drying (105 °C / overnight).

Density measurement and porosity estimation

The density of the air-dried model chips of each wood species (ρ_i) was determined by measuring their volume and their oven-dried mass. The volume of the chips was calculated based on measurements of length, width, and thickness (accuracy: ±1 mm^3). Afterwards, the same chips were dried at 105 °C overnight, and their dry mass was then measured.

With the density results, it was possible to estimate the porosity of the samples using Eq. 1:

$$\epsilon_i = 1 - \frac{\rho_i}{\rho_w} \tag{1}$$

where ϵ_i is the porosity of species i, ρ_i is the wood chip density of species i, and ρ_w is the density of the wood substance. This value was assumed to be 1500 kg/m^3, as described elsewhere (Malkov et al. 2001).

Kraft cooking

Batch kraft cooking experiments were conducted using autoclave vessels. Initially, the vessels were filled with model chips (about 24 g) and white liquor, i.e., a solution containing HO^-, HS^-, and additional carbonate, as specified in Table 1. Next, the chips were impregnated by subjecting the loaded vessels to vacuum (10 min) followed by pressurization with nitrogen (5 bar / 20 min).

After impregnation, the vessels were placed in a pre-heated polyethylene glycol bath, in which they took approx. 25 min to reach the target cooking temperature. The detailed temperature profile is described by Bogren et al. (2007). The vessels were kept in the bath under constant agitation until reaching the final cooking time. The experimental conditions utilized in the tests are summarized in Table 1.

Delignification was stopped by placing the vessels in a cooling bath. Then, the cooked chips were separated from the black liquor via vacuum filtration. Finally, the chips were washed and leached in distilled water to remove all the residual liquor (leaching water was changed every other day for about 2 weeks).

Lignin and carbohydrate analysis

To determine the local chemical composition inside the samples, the cooked wood chips were divided into different sections, as shown in Fig. 1. First the chips were cut with a hand saw to separate the corners, sides (both transverse and tangential), and center. Then each of these pieces was sliced into three layers (outer, intermediate, and

Table 1 Cooking conditions and white liquor composition

Parameter[a]	Value
Target cooking temperature, °C	155, 165
Time, min	0, 30, 45, 60
$[HO^-]$, mol/kg liquor, (mmol/cm^3)	0.55 (~0.57) 2.00 (~2.20)
$[HS^-]$, mol/kg liquor, (mmol/cm^3)[f]	0.25 (~0.27)
Na_2CO_3, mol/kg liquor, (mmol/cm^3)[f]	0.10 (~0.11)
Liquor: wood (w: w)[f]	22:1

[a] Parameters marked with “f” were the same in all tests. The temperature of 155 °C was only applied in the set of experiments used to evaluate the impact of high alkali during pulping

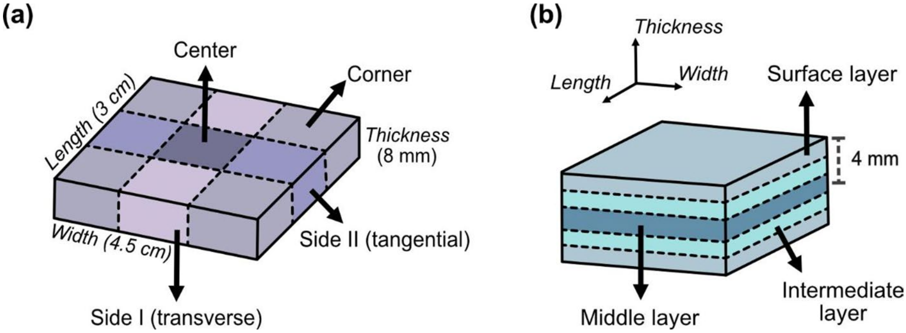

Fig. 1 Sectioning of the cooked chips. **a** Division of the model chip into four different pieces: center, corners, side I (transverse), and side II (tangential). **b** Division of each piece into three layers: surface layer, intermediate layer, and middle layer. Adapted from Marion de Godoy et al. (2024).

inner) with the aid of a microtome. In total, each chip resulted in 12 different sections, except for the samples cooked at 155 °C. In this case, sides I and II were treated as the same, resulting in 9 different sections per chip.

Afterwards, the sections were subjected to acidic hydrolysis, following a slightly modified version of the NREL's procedure for determination of structural carbohydrates and lignin (Sluiter et al. 2012). The final hydrolysate was filtered in glass microfiber filters (Whatman GF/A), and the solid residue (Klason lignin) was dried and weighed. The filtrate was used to determine the contents of acid-soluble lignin and carbohydrates. Acid-soluble lignin was measured via spectrophotometry (Specord 205, Analytik Jena) using $\lambda = 205$ nm and the absorptivity constant $= 110$ L g^{-1} cm^{-1}. The carbohydrates were analyzed via anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD Dionex ICS-5000, Thermo Fisher Scientific). The system was equipped with two 250 mm Dionex CarboPac PA1 columns and a gold reference electrode. The amount of sugars was corrected by the yields of hydrolysis, as determined by Wojtasz-Mucha et al. (2017), and the results were expressed as anhydro sugars, using the approach described by Janson (1974).

A more detailed description of both the sectioning procedure and the methods used for compositional analysis is given in previous work (Marion de Godoy et al. 2024). All measurements were conducted in replicates (2–6) using samples from two different model chips for each species under each experimental condition.

Determination of liquor uptake and hydroxide concentration

The content of hydroxide ions inside the wood chips throughout the pulping process was determined in selected samples with low porosity (birch) and high porosity (aspen). The chips were collected after impregnation and after cooking for 30 min (cooking temperature = 165 °C). In addition, a third condition was considered: samples were collected after cooking at 105 °C for 30 min, i.e., a point at which the rates of carbohydrate reactions are significant, but delignification is still negligible.

In all cases, the liquor uptake was determined by measuring the initial mass of the chips and the mass after impregnation or cooking. The degree of penetration was estimated according to Eq. 2:

$$p\,(\%) = \frac{(m_f - m_0) + (m_0 w_{H2O})}{\left[\epsilon_{\,i}\rho_{\,H2O}\frac{m_0}{\rho_{\,i}}\,(1 - w_{H2O})\right]} \times 100 \tag{2}$$

where p is the degree of liquor penetration, m_f is the final mass of the chip after impregnation or cooking, m_0 is the initial mass of the chip, w_{H2O} is the initial mass fraction of water in the chip, $\epsilon_{\,i}$ is the estimated porosity of the wood species i, $\rho_{\,i}$ is the chip density of species i, and $\rho_{\,H2O}$ is the density of water at 20 °C.

To determine the hydroxide concentration, the treated chips were placed in liquid nitrogen for 5 min (to stop reactions and minimize mass transport). Next, with the aid of a hand saw, they were divided into four different pieces: corners, side (transverse), side (tangential), and center, as seen in the first step of Fig. 1. These pieces were leached in distilled water overnight under constant agitation. Finally, the hydroxide concentration in each piece was measured by titrating the leaching water with $HCl_{(aq)}$ 0.02 M or 0.2 M. The titrations were performed in replicates (2–4) using samples from two different model chips for each species and each studied condition.

Results and discussion

Wood composition and structure

Table 2 shows the composition, water content, density, and porosity of the sapwood chips from the different hardwoods investigated in this study. In terms of wood composition, the results were within the ranges reported for each hardwood in previous works (Pettersen 1984; Gabrielii et al. 2000; Patt et al. 2006; Santos et al. 2011; Kron et al. 2024). More importantly, although the absolute values of individual com-

Table 2 Composition, water content, density, and estimated porosity of the different hardwood chips

	Alder (*A. glutinosa*)	Aspen (*P. tremula*)	Beech (*F. sylvatica*)	Birch (*B. pubescens*)
Water content (%)	5.9–9.7	5.9–8.8	9.7–10.9	5.3–10.1
Density (kg/m^3)	500 ± 15	428 ± 27	603 ± 18	575 ± 01
Porosity[a]	0.667	0.715	0.598	0.617
Composition (%, w/w dry)				
Klason lignin	24.9 ± 0.4	19.6 ± 0.6	21.3 ± 0.1	19.3 ± 0.4
Acid-soluble lignin	3.5 ± 0.0	5.1 ± 0.1	5.2 ± 0.1	5.3 ± 0.1
Glucan	40.0 ± 0.6	43.0 ± 0.8	36.4 ± 0.4	37.0 ± 0.2
Xylan	17.6 ± 0.2	16.5 ± 0.3	20.6 ± 0.4	23.2 ± 0.2
Arabinan	0.4 ± 0.0	0.3 ± 0.0	0.4 ± 0.0	0.3 ± 0.0
Galactan	1.0 ± 0.0	0.5 ± 0.0	0.6 ± 0.0	0.8 ± 0.0
Mannan	1.6 ± 0.1	3.0 ± 0.2	2.0 ± 0.1	2.3 ± 0.1

[a] Porosity estimated considering the density of the wood substance = 1500 kg/m^3

ponents varied, the overall trends across different species were consistent with the literature. For instance, the Klason lignin content in alder was significantly higher than in the other hardwoods. In addition, the proportion between glucan and xylan changed accordingly among the species. The highest glucan concentration was measured in aspen while the highest xylan content was detected in birch.

Regarding the density results, the samples showed good agreement with the literature data reported for these hardwoods (Patt et al. 2006; Kiaei and Moya 2015; Ruffinatto and Crivellaro 2019), with aspen exhibiting the lowest value (428 kg/m^3) and beech the highest (603 kg/m^3). This variation between the hardwoods implies substantial differences in porosity and reflects their distinct structures. For example, high densities can be associated with thicker fiber walls, smaller lumens, smaller vessels, and/or lower number of vessels. In the case of the four species under analysis, micrographs showed (refer to the Supplementary Information) that some of the main differences are the presence of larger vessels in aspen, less frequent vessels in birch, and both thicker fiber walls and smaller lumens in beech. Other structural differences that were observed involve the distribution and size of the rays in the samples. Alder is the only one to display aggregate rays, and some rays in beech are wider than in the other species (even wider than their vessels).

Alkali distribution

To better understand the impact of wood structure during pulping, the content of hydroxide ions inside selected wood chips was determined at different conditions. These measurements were conducted with aspen and birch samples (materials with low and high density, respectively) and the results are shown in Fig. 2.

In all the evaluated conditions, the ratios between the mass of the absorbed liquor and the mass of wood indicated a high degree of penetration in the samples. In fact, when compared to the degree of penetration achieved with pure water (Malkov et al. 2001), all samples showed more than 100% penetration, which is reasonable due to the swelling of the chips in the alkaline medium. Also, in the case of the thermally treated samples, a high penetration is expected due to the increase in porosity caused by the removal of hemicelluloses and lignin.

When comparing the penetration of liquor between the species, both aspen and birch achieved elevated degrees of liquor uptake. Still, the high porosity of aspen (71.5% against 61.7% in birch), allowed more liquor inside the chips, as seen by the liquor to wood ratios in Fig. 2.

However, the distribution of alkali in the samples suggested low concentrations of hydroxide ions in the inner layers. In the first samples, analyzed right after impregnation, the average concentration of alkali was substantially lower than in the bulk liquor (about 0.17 mmol/cm^3 in aspen and 0.10 mmol/cm^3 in birch against approximately 0.57 mmol/cm^3 in the bulk). It is likely that during penetration the hydroxide ions were quickly consumed (in neutralization reactions, for example), and diffusion was not fast enough to equilibrate the concentration of ions between the middle and the surface of the chips. This behavior is similar to what has been previously modeled for softwood chips (Gustafson et al. 1989).

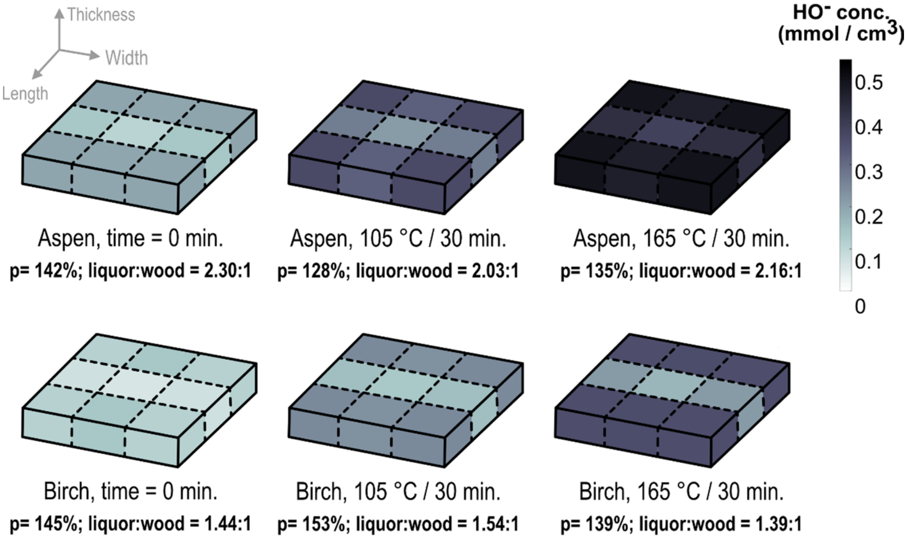

Fig. 2 Degree of liquor penetration (*p*), liquor uptake and distribution of hydroxide ions in wood chips of aspen and birch in three different conditions: after impregnation (20 °C, time = 0 min.), after impregnation and mild treatment (105 °C/30 min), and after impregnation and kraft cooking (165 °C / 30 min). The concentration of hydroxide was measured in different parts of the chips (corners, transverse sides, tangential sides, and center). The results are in mmol of hydroxide ions per volume of impregnated wood (calculated based on measurements of length, width, and thickness) with max. RSD = 18%

In the impregnated samples that were subjected to 105 °C for 30 min, it was possible to observe the evolution of the alkali distribution still under conditions in which delignification was negligible. In this case, the concentration of hydroxide ions nearly doubled in all regions of the wood chips of both birch and aspen, as diffusion and further swelling allowed more alkali to be transported in. Furthermore, under this mild treatment it seems that the rates of hydroxide transport were sufficiently high to balance the consumption of HO^- in carbohydrate reactions, as the concentrations of alkali within the chips increased evenly.

Nevertheless, when the samples were treated at 165 °C, the increase in alkali content was less uniform, and it differed between the hardwoods. In aspen, the concentration of hydroxide ions increased more in the center of the chip than in the corners, whereas in birch the increase was more pronounced in the corners. Such contrast between the species is probably a result of the differences in initial alkali concentration inside the chips and the high rates of hydroxide consumption at high temperatures. In birch, it is possible that the inner layers of the chip experienced a depletion of HO^-, resulting in less swelling and lower diffusivities. On the other hand, the higher initial alkali content in aspen probably minimized these issues.

Thus, to achieve similar qualities of impregnation in hardwoods with high and low porosities, the latter might require higher hydroxide concentrations in the impregnation liquor and/or longer impregnation times. Still, other factors may also need to be considered. For instance, in heartwood the presence of tyloses results in low permeability and it is known to compromise the penetration of liquor even in highly porous species (Stone and Green 1959). At the same time, it is also important to stress that impregnation issues are lessened when working with industrial chips, mostly due to their lower thickness and the existence of cracks in their structure.

Delignification

The main differences regarding the delignification behavior of the four hardwoods under study are illustrated by the results shown in Fig. 3. The lignin contents in the corners of the surface layers indicate that the delignification extents were similar in all hardwoods, except for aspen, which displayed higher lignin removal. Since the conditions in the surface corners are likely to be close to the ones in the bulk liquor (as the transport of cooking chemicals is less limited by the wood structure than in the other sections), the differences in lignin content suggest higher rates of lignin depolymerization reactions and/or faster mass transport of dissolved lignin at the fiber wall level in aspen than in the other species. This observation is in line with previous studies conducted with wood mill (Kron et al. 2024). Yet, further investigation is needed to establish the cause.

In the inner layers, the extents of delignification become considerably different between the hardwoods. The uniformity of lignin removal seems to decrease as the density of the chips increases, with beech displaying the highest gradient of lignin content and aspen the lowest. Moreover, in the inner layers there is a noticeable difference in the lignin removal in each section of the chip (i.e., when comparing corners, center, and even the different sides of the chip). This behavior arises due to the heterogenous distribution of alkali inside the chips (refer to Sect. 3.2), as both lignin solubility and the rate of lignin depolymerization have been shown to be strongly dependent on the concentration of hydroxide ions (Bogren et al. 2007; Puss et al. 2023).

Similar trends could also be observed in other time points during cooking, as detailed in Fig. 4.

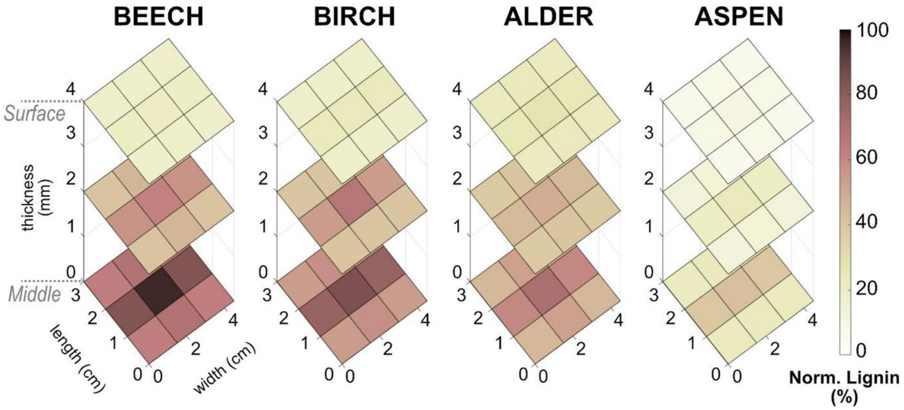

Fig. 3 Distribution of Klason lignin (%) within wood chips after 45 min of batch kraft cooking. Cooking conditions: 165 °C, 0.55 mol HO^-/kg liquor. The results were normalized based on the original Klason lignin content present on each wood species. Max. RSD = 13%

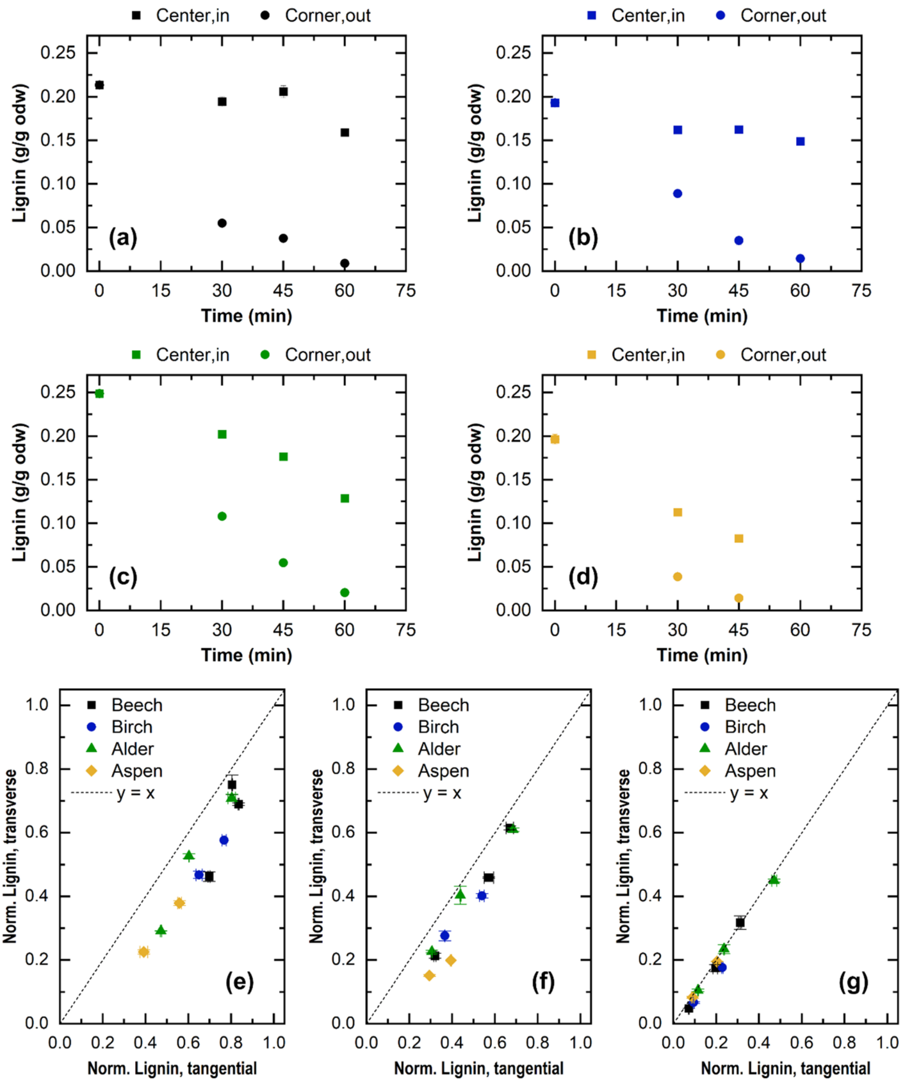

Fig. 4 Delignification profiles in different sections of the wood chips. Upper rows: comparison between the Klason lignin (g/g odw) in the center of the middle layer (squares) and in the corners of the surface layer (circles) for **a** beech, **b** birch, **c** alder, and **d** aspen. Bottom row: comparison between the normalized Klason lignin content in the tangential side (x axis) and in the transverse side (y axis) throughout pulping in the **e** middle layer, **f** intermediate layer, and **g** surface layer. Cooking conditions: 165 °C, 0.55 mol HO^{-}/kg liquor. Error bars, although small, are included for all data points and represent the standard deviation

The gradients of lignin shown in Fig. 4a–d confirm that delignification was more uniform in the species with lower densities (aspen and alder). In addition, the plots displaying the differences in lignin content in the tangential and transverse sides of the chips (Fig. 4e–g) indicate that, while no significant differences were seen in the surface layer, in the inner layers delignification was always faster in the longitudinal direction. This result also arises from the uneven distribution of hydroxide ions within the samples, as different concentrations of alkali lead to heterogeneous effects on the lignin of each part of the chip and cause substantial differences in the rates of diffusion in the tangential direction. The tangential effective capillary cross-section area, for example, has been shown to experience a sharp decrease when the pH drops from 13 to 12 in aspen (Stone 1957) and from 13.5 to 12.5 in eucalyptus (Inalbon and Zanuttini 2008).

Regarding the effect of specific morphological features on pulping, it was evident that the high porosity of aspen (a result of the high number of large vessels) contributed to a more homogeneous delignification. Still, the impact of other features, especially the ones related to ray cells, was not clear. For instance, one could expect that different distributions and sizes of ray cells would result in different rates of mass transport (of both cooking chemicals and dissolved wood components) in the radial and tangential directions of the hardwoods under study. However, the implications of this hypothesis were not confirmed by the lignin profiles, as the gaps between the extents of delignification in the tangential and longitudinal directions (i.e., distances to the y = x line in Fig. 4e–g) were similar among all wood species. Hence, further investigation is necessary to clarify the effect of rays and other cells.

Xylan removal

When compared to delignification, xylan removal was more uniform inside all samples, with the highest gradient, i.e., difference between the xylan content in the center of the middle layer and in the corners of the surface, being 0.10 g/g odw (against 0.17 g/g odw measured for lignin). The results in Fig. 5 summarize the main trends regarding xylan removal in the different hardwoods.

Just as observed with lignin, the uniformity of xylan removal increased with the decrease in chip density. However, unlike delignification, the extents of xylan removal in the corners of the surface layers (sections that are more exposed to the

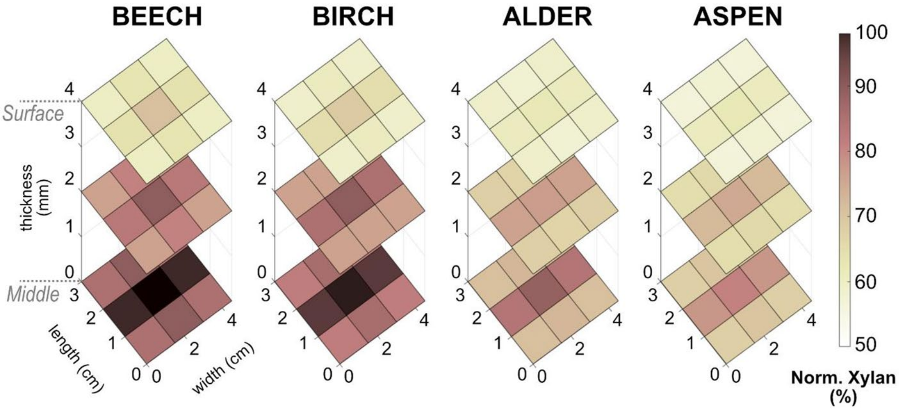

Fig. 5 Distribution of xylan (%) within wood chips after 45 min of batch kraft cooking. Cooking conditions: 165 °C, 0.55 mol HO^-/kg liquor. The results were normalized based on the original xylan content present on each wood species. Max. RSD = 4%

cooking liquor) were similar in all species. The gradients of xylan at different stages of pulping are shown in Fig. 6.

During hardwood kraft pulping, most of xylan removal readily occurs due to dissolution in the alkaline medium (Pinto et al. 2005a). Thus, the minor decrease in xylan content measured in the middle of the samples might indicate that the pH was quite lower than at the surface—especially for beech and birch—confirming the results

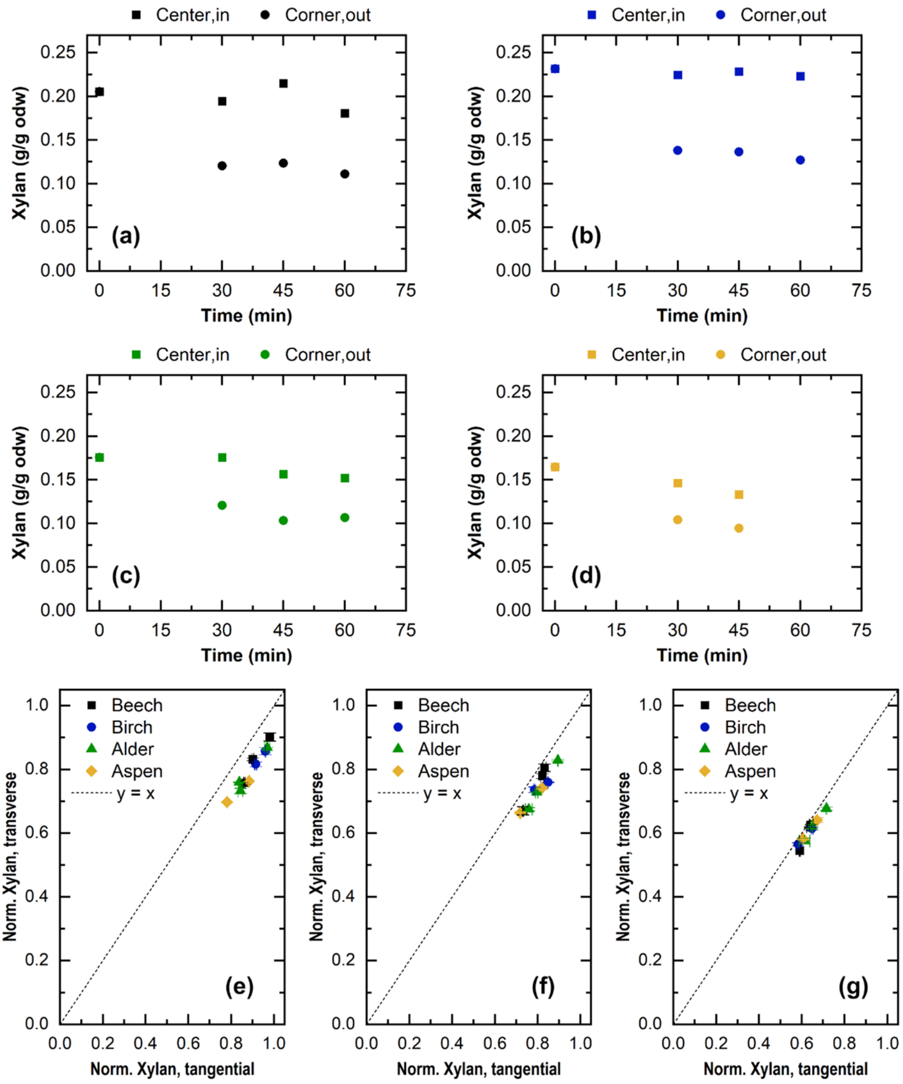

Fig. 6 Xylan removal in different sections of the wood chips. Upper rows: comparison between the xylan (g/g odw) in the center of the middle layer (squares) and in the corners of the surface layer (circles) for **a** beech, **b** birch, **c** alder, and **d** aspen. Bottom row: comparison between the normalized xylan content in the tangential side (x axis) and in the transverse side (y axis) throughout pulping in the **e** middle layer, **f** intermediate layer, and **g** surface layer. Cooking conditions: 165 °C, 0.55 mol HO$^-$/kg liquor. Error bars, although small, are included for all data points and represent the standard deviation

of alkali distribution presented in Sect. 3.2. In addition, the sharp contrast between the initial fast decrease in xylan content in the surface of the samples and the minor losses of xylan observed afterwards suggests the existence of xylan fractions that are resistant to the alkaline conditions applied during kraft pulping in all evaluated species. Also, in Fig. 6e–g it is possible to compare the concentrations of xylan in the tangential and transverse sides. In this case, the differences were not as pronounced as for lignin—probably because the removal of xylan is not only affected by the rates of hydroxide diffusion, but also by the interactions of the dissolved polysaccharide with cellulose and lignin (Dammström et al. 2009; Gomes et al. 2020).

Kraft pulping with high alkali concentration

The use of high effective alkali during impregnation has been shown to result in more homogeneous delignification of softwood chips (Brännvall and Bäckström 2016). So, a short test was conducted to evaluate if it would be possible to use this approach to eliminate or minimize the influence of wood structure in the evolution of kraft pulping of hardwood chips. Aspen and birch chips were treated considering three conditions: the base case, in which the chips were impregnated and cooked using a liquor with 0.55 mol HO^-/kg; the high alkali impregnation, in which the chips were impregnated with a liquor containing 2.00 mol HO^-/kg and cooked using a liquor with 0.55 mol HO^-/kg; and the high alkali cook, conducted using a liquor with 2.00 mol HO^-/kg for both impregnation and cooking.

When using liquors containing high alkali concentration, the average content of hydroxide ions inside the chips after impregnation had a ninefold increase. The details about the extents of impregnation and the new distributions of hydroxide ions inside the samples are described in the Supplementary Information. Regarding the effect of the different pulping conditions on delignification and xylan removal, Figs. 7 and 8 present the profiles of normalized Klason lignin and xylan inside the wood chips for each situation under study.

When focusing on delignification (Fig. 7), the use of high alkali resulted in significant improvement in the uniformity of lignin removal. In aspen, the increase in HO^- resulted in seemingly homogeneous delignification of the chips, with the lignin gradient dropping from 0.072 g/g odw in the base case to 0.010 and 0.019 g/g odw when applying high hydroxide concentrations. In birch, the increase in uniformity was more modest, with the gradients moving from 0.097 g/g odw to 0.051 and 0.041 g/g odw. Still, the results confirm that the impact of wood structure can be overcome by adjusting the impregnation conditions.

The analysis of the xylan distribution (Fig. 8) revealed that, while the homogeneity of delignification was increased by both impregnating and cooking with high alkali, the same was not true for xylan removal. In this case, only impregnating with high alkali resulted in better uniformity: in birch the xylan gradient went from 0.097 g/g odw in the base case to 0.074 g/g odw when impregnating with high alkali, and in aspen the gradient decreased from 0.047 to 0.036 g/g odw. When the whole kraft cook was conducted with high concentration of hydroxide ions, the samples showed a more extensive removal of xylan than in the base case, but, at the same time, slightly larger gradients of xylan (0.099 g/g odw in birch and 0.054 g/g odw in aspen).

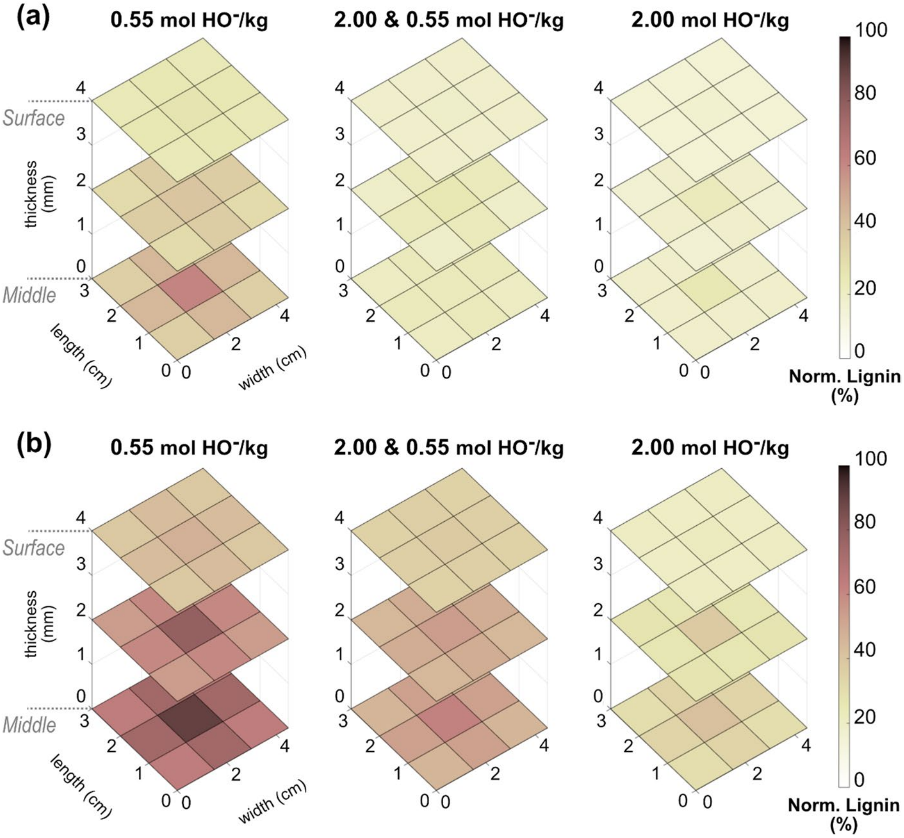

Fig. 7 Distribution of Klason lignin (%) within wood chips after 45 min of batch kraft cooking at 155 °C for **a** aspen and **b** birch. Evaluated conditions: (1) impregnation and cooking liquors containing 0.55 mol HO^{-}/kg liquor; (2) impregnation using 2.00 mol HO^{-}/kg liquor and cooking with 0.55 mol HO^{-}/kg liquor; (3) impregnation and cooking liquors containing 2.00 mol HO^{-}/kg liquor. The results were normalized based on the original lignin content present on each wood species. No distinction was made between transverse and tangential sides. Maximum RSD = 13%

This uneven removal of xylan can be a result of several factors. One of them is the solubility of xylan, which varies in different parts of the chip, depending on the gradient of hydroxide ions within the samples during pulping. This gradient is probably more pronounced when impregnating and cooking with the same concentration of alkali than when using 2.00 mol HO^{-}/kg liquor for impregnation and 0.55 mol HO^{-}/kg liquor for cooking. Other factors to be considered include the interactions of the dissolved polysaccharides with cellulose and/or lignin. For instance, depending on the local pulping conditions, dissolved xylan can adsorb onto the cellulose fibers—a phenomenon that can be hampered by the high concentrations of hydroxide ions in the top layers of the chips impregnated and cooked with 2.00 mol HO^{-}/kg of liquor (Linder et al. 2003; Danielsson and Lindström 2005). Regardless of the cause, it is interesting to note that, when the hydroxide concentration is sufficiently high

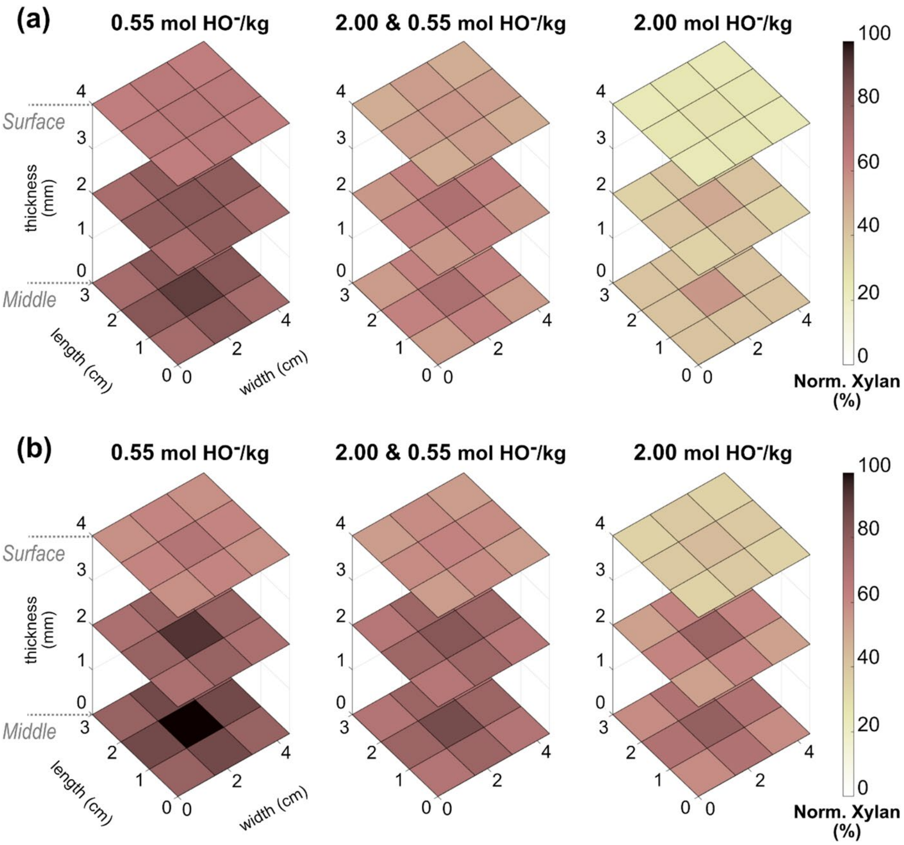

Fig. 8 Distribution of xylan (%) within wood chips after 45 min of batch kraft cooking at 155 °C for **a** aspen and **b** birch. Evaluated conditions: (1) impregnation and cooking liquors containing 0.55 mol HO^-/kg liquor; (2) impregnation using 2.00 mol HO^-/kg liquor and cooking with 0.55 mol HO^-/kg liquor; (3) impregnation and cooking liquors containing 2.00 mol HO^-/kg liquor. The results were normalized based on the original xylan content present on each wood species. No distinction was made between transverse and tangential sides. Maximum RSD = 7%

throughout the chip, xylan removal appears to be more sensitive to the alkali profile inside the samples than delignification.

Finally, when comparing the three pulping strategies shown in Figs. 7 and 8, it is evident that higher extents of lignin and xylan removal were achieved when using high alkali concentration, especially if the chips were subjected to this condition throughout the whole operation. Therefore, if the goal of the process is to attain a more uniform distribution of lignin and xylan inside the chips without compromising the pulping yields substantially, it is preferable to use high concentrations of hydroxide ions in the impregnation step but then performing the cooking step with lower alkali contents.

Conclusion

The homogeneity of delignification and xylan removal varied according to the porosity of the hardwoods: the most uniform process happened in aspen chips (highest porosity), whereas the least uniform occurred in beech (lowest porosity). In terms of wood anatomy, homogeneity of lignin and xylan removal was improved by the presence of big vessels in large numbers throughout the wood tissue, and by the existence of thin fiber walls and large lumens. These features contributed to higher ratios between liquor and wood inside the chips after impregnation and to more uniform distributions of hydroxide ions within the samples. Other morphological features, like ray cells, showed no significant effects on kraft pulping.

When working with highly dense hardwoods, ensuring satisfactory liquor penetration in the chips was shown to be insufficient to achieve uniform delignification. In this case, it is also imperative to guarantee high concentrations of cooking chemicals inside the chips. To accomplish this, the use of impregnation liquors with high alkali content followed by a cooking step applying lower alkalinity levels was proven to be a suitable strategy.

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Data availability The raw data files are available upon reasonable request from the corresponding author.

Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

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