

# Kraft Pulping of Softwood Chips with Mild Hot Water Pre-hydrolysis to Understand the Effects of Wood Chip Thickness

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Hemicelluloses consume alkali during kraft pulping and dissolve in the black liquor as a low energy fuel. Acidic pre-hydrolysis of softwood chips removes hemicelluloses but preserves cellulose content prior to pulping. This study compared mild pre-hydrolysis (140 °C) kraft pulping with conventional kraft pulping of commercial softwood chips at two *H*-factors for wood chips with thickness ranging from less than 2 mm to over 6 mm. The chip thickness less than 2 mm increased hemicelluloses oligomer yield and showed little influence on pulp fiber yield. However, the kraft pulp fiber length decreased 5.6%. Kappa number and fiber reject increased dramatically when chip thickness was greater than 6 mm. The detailed compositional analysis of kraft pulp and fiber quality analysis indicate that pre-hydrolysis followed by kraft pulping enhanced delignification with limited reduction of fiber length and width, and increased kinks. Strategic considerations for the integration of pre-hydrolysis into kraft pulping for future biorefineries were outlined.

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## INTRODUCTION

Kraft pulping separates cellulosic fibers from wood by dissolving hemicelluloses and lignin from fiber walls and middle lamella (Mimms *et al.* 1989). Under typical kraft pulping conditions, approximately 75% of hemicelluloses dissolves in black liquor as complex sugar acids, such as aldonic acids under oxidative conditions (Mimms *et al.* 1989; Ek *et al.* 2009); 80 to 90% of lignin is fractionated into smaller molecules of mono- or oligo-lignols and dissolves in black liquor due to cleavage of phenolic  $\beta$ -O-4 and  $\alpha$ -O-4 structures by hydroxide and hydrosulfide ions (Mimms *et al.* 1989; Arato *et al.* 2005; Ek *et al.* 2009).

Carbohydrates consume a large portion of alkali during kraft pulping. Approximately 30 to 40% of total alkali is consumed during chip impregnation by neutralization reactions with acidic groups from carbohydrates and is then unavailable for delignification reactions (Mimms *et al.* 1989; Gullichsen and Fogelholm 2000). The

dissolved hydroxy acids, acetic and formic acid, constitute 25 to 31% of concentrated black liquor (Ek *et al.* 2009). Additionally, it has been demonstrated that the heating value of dissolved lignin is double that of dissolved hemicelluloses (van Heiningen 2006; Lu *et al.* 2012; Fišerová *et al.* 2014; Farhat *et al.* 2017). Thus, extraction of hemicelluloses prior to pulping could serve as a source of valuable chemicals without a major impact on energy generation. Further, pre-hydrolysis can also help reduce pulping energy requirements as discussed below. Lastly, pre-hydrolysis kraft pulping is also an effective way to produce dissolving pulp with increased pulp yield, minimum hemicelluloses retention, and less chemical consumption compared to conventional kraft pulping (Sixta 2006; Li *et al.* 2010; Bi *et al.* 2021).

Hot water hydrolysis or autohydrolysis is an environmentally friendly approach for hemicelluloses extraction, during which a portion of hemicelluloses and lignin will dissolve, cellulose crystallinity may be reduced, and wood chip porosity will increase (Mosier *et al.* 2005; Lu *et al.* 2012; Chen *et al.* 2017; Ibrahim and Kruse 2020). These structural changes facilitate subsequent pulping by increasing chemical mass transfer and reducing energy requirements (Liu *et al.* 2015). Some recent studies focused on the fiber and wood morphology after pre-hydrolysis kraft pulping and demonstrated an increase in cellulose degradation, exposure of less-ordered cellulose (Bi *et al.* 2021), and an increase in internal hydrophilicity of wood chips (Guo *et al.* 2021).

Autohydrolysis has been applied as a pretreatment prior to kraft pulping to extract hemicelluloses and produce pulp fibers. It has been shown that pre-hydrolyzed chips are more susceptible to pulping and bleaching when the pre-treatment is mild (Yoon and van Heiningen 2008; Smith 2011; Fišerová *et al.* 2014). Under mild hydrolysis conditions, some carbohydrates together with a portion of the acid-soluble lignin, as defined by absorption at 240 nm, is removed from the wood matrix; consequently the time to reach a target Kappa number in the final pulp, is reduced (Smith 2011; Chen *et al.* 2017; Guo *et al.* 2021). Severe hydrolysis conditions, such as high temperature or low pH, will cause lignin to crosslink with lignin or other degradation products (Li *et al.* 2007; Hu and Ragauskas 2014). The subsequent cooling process leads to lignin agglomeration as spherical droplets that block pores and make lignin degradation more difficult, resulting in longer pulping time (Smith 2011; Zhuang *et al.* 2017; Guo *et al.* 2021). Similar trends were reported by other scholars studying pre-hydrolysis pulping (Yoon and van Heiningen 2008; Lu *et al.* 2012; Borrega *et al.* 2013). The viscosity of pulp also exhibits a two-stage pattern. Mild pre-hydrolysis removes hemicelluloses and low molecular weight cellulose, resulting in higher pulp viscosity (Lu *et al.* 2012). Harsh conditions, however, cause degradation of cellulose and a significant loss of pulp viscosity (Vila *et al.* 2011; Borrega *et al.* 2013).

Chip size influences pre-hydrolysis, delignification, post-pulping fiber separation, and subsequent fiber properties (Borlew and Miller 1970; Grace and Malcolm 1989; Niskanen 1998; Gullichsen and Fogelholm 2000; Song *et al.* 2008; Rissanen *et al.* 2014a,b; Kyyrö *et al.* 2020). Mass transfer within wood chips during pulping is mainly by diffusion. The rate of diffusion is anisotropic and depends on liquor pH (Grace and Malcolm 1989). Thickness is the mass transfer limiting dimension during pre-hydrolysis, chip impregnation, and delignification (Borlew and Miller 1970; Grace and Malcolm 1989; Niskanen 1998; Gullichsen and Fogelholm 2000). The influence of chip thickness on pulping has been explored for thickness varying from 0.5 to 15 mm (Cable *et al.* 1927; Borlew and Miller 1970). Hartler and Onisko's (1962) investigation of kraft pulping of pine chips with thickness of 2 to 7 mm found that the screened yield was highest for the thinnest chips and that unbleached pulp viscosity was not influenced by chip thickness.

Colombo *et al.* (1964) kraft pulped spruce chips while varying thickness from 0.5 to 15 mm. When chip thickness was lower than 4 mm, the cooking rate increased rapidly with decreasing thickness resulting in lower pulp yield. Hartler and Ostberg (1959) evaluated yield and rejects after kraft pulping of pine chips with thickness ranging from 3 to 7 mm. They concluded that 3 mm was the optimum thickness, as it resulted in highest screened yield (47.6%) with the shortest cook time, 90 min. When the chip thickness increased to 5 mm, at least 135 min cooking was required to achieve a screened yield 44.8%. Overall, the literature suggests that the optimum chip thickness falls within the range 2 to 5 mm. Therefore, to comprehensively understand the trade-off between yield and delignification, in this study, chip thickness was varied from less than 2 mm to greater than 6 mm to assess the effect of chip thickness on pre-hydrolysis and kraft pulping.

From the literature, it is clear that mild pre-hydrolysis conditions are preferable in comparison to the severe pre-hydrolysis to retain a portion of hemicelluloses for higher yield, minimize cellulose degradation and lignin condensation for non-dissolving pulp production. Details of hydrolysate and final fiber composition are also missing from literature reports and this information is needed for process design, product control, and economic assessment of biorefining opportunities. In this study, mild hydrolysis of softwood chips with thickness varying from less than 2 mm to greater than 6 mm was conducted prior to kraft pulping. The fiber composition and pulp properties after pre-hydrolysis kraft pulping were evaluated. The major challenges to implementation of pre-hydrolysis will be identified, and a more promising direction for integration of pre-hydrolysis with kraft pulping will be suggested.

## EXPERIMENTAL

### Materials

Softwood chips, a mixture of white spruce (*Picea glauca*), lodgepole pine (*Pinus contorta*), and subalpine fir (*Abies lasiocarpa*), were manually screened to remove knots and other contaminants. All chips were then screened using a 7-mm round hole tray. Chips were next separated by thickness on bar screens: fines (under 2 mm), 2 mm (2 to 4 mm), 4 mm (4 to 6 mm), and 6 mm (over 6 mm). The softwood chips and white liquor were supplied by the Canfor Pulp Innovation Centre (Burnaby, Canada). Sulfuric acid (98 wt%) was purchased from Sigma Aldrich (Oakville, Canada) and diluted to desired concentration. The carbohydrates kit (CAR10-1KT) used to calibrate the high-performance liquid chromatography (HPLC) was purchased from Sigma Aldrich (Oakville, Canada) and contained mannose, glucose, galactose, xylose, and arabinose. The purity of the standards was greater than 98%.

### Pre-hydrolysis

Hot water pre-hydrolysis experiments were conducted in 400-mL batch reactors at the Canfor Pulp Innovation Centre in Burnaby, British Columbia, Canada. The final slurry was 419 g and the solids consistency was 10% for all chip thickness. Pre-hydrolysis was conducted at *H*-factors of 77 (Eq. 1) in triplicates. The batch reactors were submerged in a 20-L digester with a hot water circulation system. The isothermal reaction time was 1 h at 140 °C. The slurry was filtered using 20- $\mu$ m porous filter paper. The hydrolysate was stored at 4 °C for further analysis and the pretreated chips were washed multiple times with

deionized water, air dried, and the moisture content was determined in preparation for kraft pulping. Equation 1 defines the  $H$ -factor,

$$H = \frac{\int_{t_{100}}^{t_{\text{rxn}}} T dt}{T-100} + t_{\text{iso}} \quad (1)$$

where  $t_{100}$  is the time to heat up to 100 °C in minutes,  $t_{\text{rxn}}$  is the time to heat up to isothermal temperature in minutes,  $t_{\text{iso}}$  is the isothermal reaction time in minutes,  $T$  is the isothermal reaction temperature in °C, and  $H$  is the calculated  $H$ -factor in minutes.

### Compositional Analysis

The carbohydrate and lignin composition of the raw chips, hydrolyzed chips, and liquid hydrolysate were determined according to the National Renewable Energy Laboratory (NREL) Laboratory Analytical Procedures (LAP) (Sluiter *et al.* 2005, 2006, 2008; Hames *et al.* 2008). Oligomer yield was calculated by the difference between monomer concentration before and after treatment of the liquid hydrolysate. Acid soluble lignin was measured by ultraviolet-visible (UV-Vis) spectroscopy (UV-1800; Shimadzu, Kyoto, Japan), and acid insoluble residue (acid insoluble lignin + ash) was determined by gravimetric analysis (Depyrogenation oven; VWR, Edmonton, Canada) before and after combustion.

Monomer concentration was analyzed by Dionex AS50 HPLC (Thermo Scientific, Burnaby, Canada) coupled with an ion exchange PA1 column (Dionex), an ED50 electrochemical detector (pulsed amperometric detector) with a gold electrode, and an AS50 autosampler (Dionex, Burnaby, Canada). De-ionized water was used as eluent with a flow rate of 1 mL/min. An auxiliary pump added 0.2 M NaOH at 0.5 mL/min. The samples were filtered through a 0.22- $\mu\text{m}$  nylon syringe filter before injection. The injection volume was 10  $\mu\text{L}$ .

### Kraft Pulping

Kraft pulping was conducted using the same reactor system used for pre-hydrolysis. The final slurry was 285 g, and the solids consistency was 13.3%. The liquor to solid ratio was 6.5 with 18 wt% effective alkali of oven-dried (o.d.) chips and 27% sulfidity in white liquor. Chips were soaked overnight in white liquor before pulping to ensure complete chemical impregnation. An  $H$ -factor of 1600 (Eq. 1) was used for kraft pulping of pre-hydrolyzed chips. Temperature was ramped up at 1 to 2 °C/min until a maximum temperature of 170 °C was reached. Raw chips of the same thickness and consistency were pulped for comparison to pre-hydrolyzed chips. Two  $H$ -factors (Eq. 1) were tested for kraft pulping: 1600 and 1900. The cooked chips were washed with de-ionized water to remove residual alkali and transferred to a disintegrator (Lorentzen & Wettre, serviced by ABB, Kista, Stockholm, Sweden) for 10 min (6000 revolution) to separate the fibers. The fiber suspension was filtered with nylon filter mesh fabric. The fiber pad was washed with de-ionized water and oven-dried to determine the fiber pad weight.

Oven-dried pulp fibers were blended in the disintegrator for 5 min. The fiber suspension was transferred to the pulp screening machine (Voith Sulzer, Appleton, Wisconsin, United States of America) with continuous water input. After all fibers passed through the screen to the bottom tray, residual shives on the top screen (0.15 mm) were collected, dried, and weighed to determine the oven-dried weight of the rejects. All screened fibers were collected for further analysis. Fiber yield (Eq. 2) is defined as the pure

fiber fraction to the total o.d. unprocessed, raw chips input before pre-hydrolysis/kraft pulping:

$$\text{Fiber yield} = \frac{\text{Post fiber pad o.d.} - \text{Reject o.d.}}{\text{Initial o.d. chips}} \times 100\% \quad (2)$$

### Kappa Number

Kappa number was determined according to TAPPI standard method TAPPI T236 om-99 (2003). Klason lignin content ( $X_k$ , Eq. 3) has a linear relationship with Kappa number for pulps with less than 70% yield (Smook and Kocurek 1982; Mimms *et al.* 1989):

$$X_k(\%) = 0.147 \times \text{Kappa number} \quad (3)$$

### Fiber Compositional Analysis

Fiber composition was determined using a modified alkaline hydrolysis procedure (Zhao *et al.* 2017). One gram of oven-dried pulp was mixed with 10 mL 17.5% NaOH and kept in a 20 °C water bath for 45 min. Then, 50 mL of de-ionized water was added, and the slurry was filtered in a 30-mL medium-porosity fritted glass crucible until at least 20 to 30 mL of liquor was recovered. This liquor was retained for further analysis. The solid fiber was sequentially washed in the crucible with 9.5% sodium hydroxide (NaOH), a large amount of de-ionized water, and finally, 2 M acetic acid. The crucible and solid fiber pad were oven-dried at 105 °C to determine fiber moisture content. The oven-dried sample was weighed ( $X_d$ ) to determine the percentage of alkaline insoluble carbohydrates content in pulp ( $X_\alpha$ ). The percentage of alkaline insoluble carbohydrates content in initial o.d. pulp samples ( $X_i$ ) was calculated according to Eq. 4. Equation 4 is as follows:

$$X_\alpha = \frac{X_d - X_k}{X_i} \times 100\% \quad (4)$$

The carbohydrate content of 15 mL of the alkaline filtrate was determined. The pH of the liquor was slowly acidified, and the amount of added acid was recorded. A 10 mL sample of the pH adjusted liquor was hydrolyzed to determine the monomer sugar content according to NREL LAP (Sluiter *et al.* 2006). Acid soluble lignin content was determined by UV-vis spectroscopy (Sluiter *et al.* 2008).

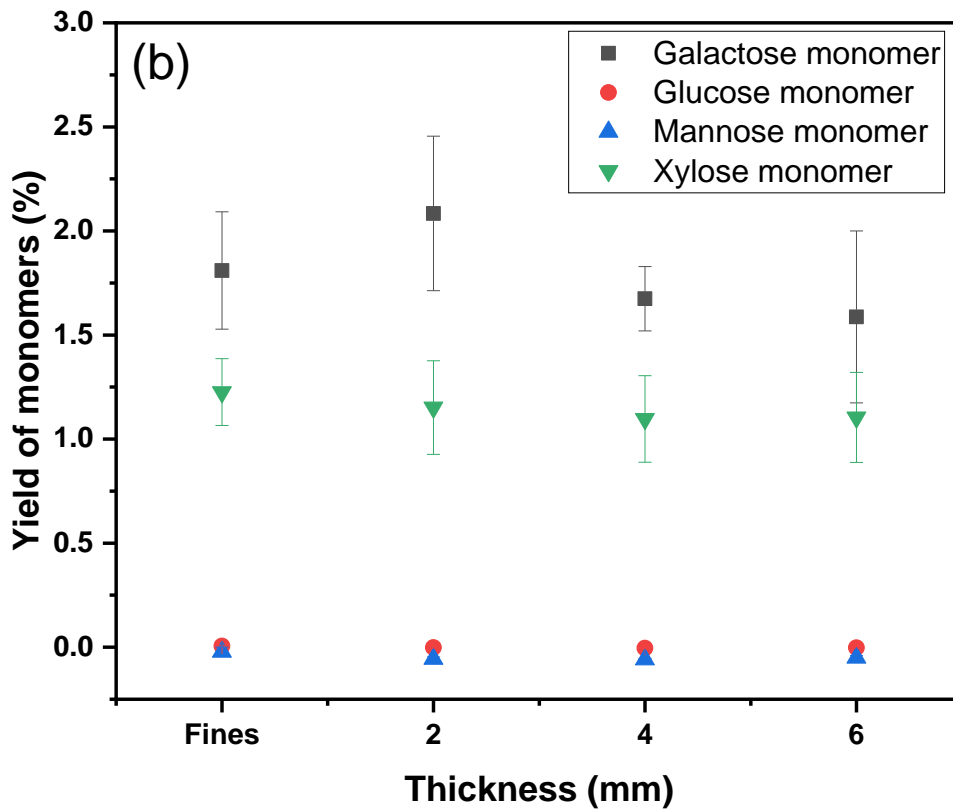
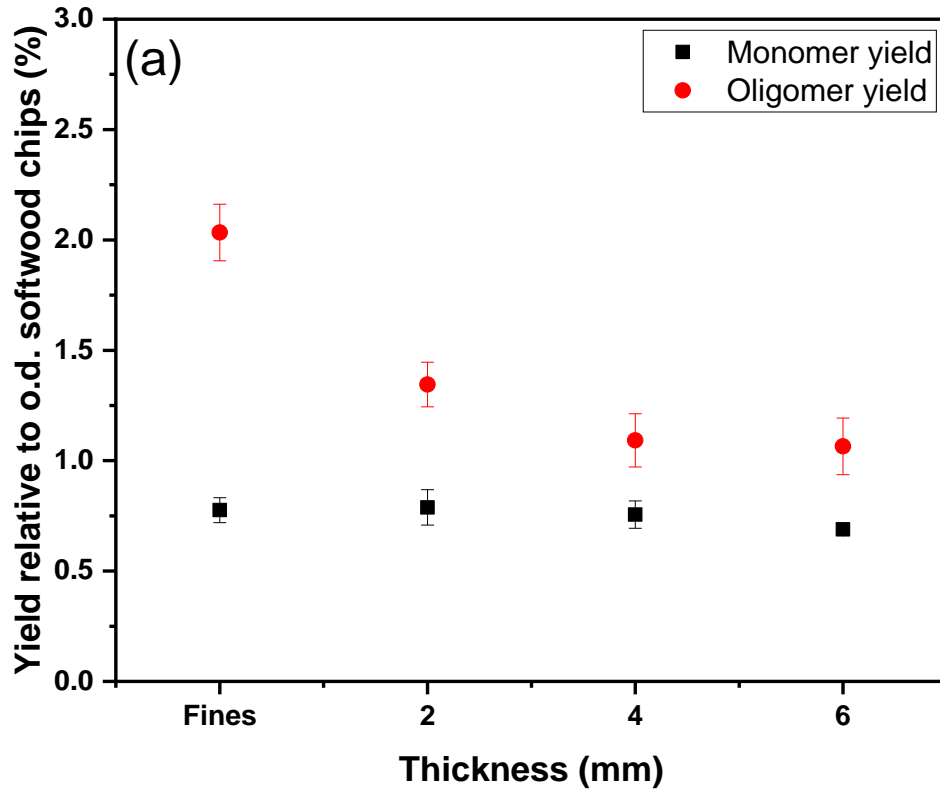
### Pulp Properties

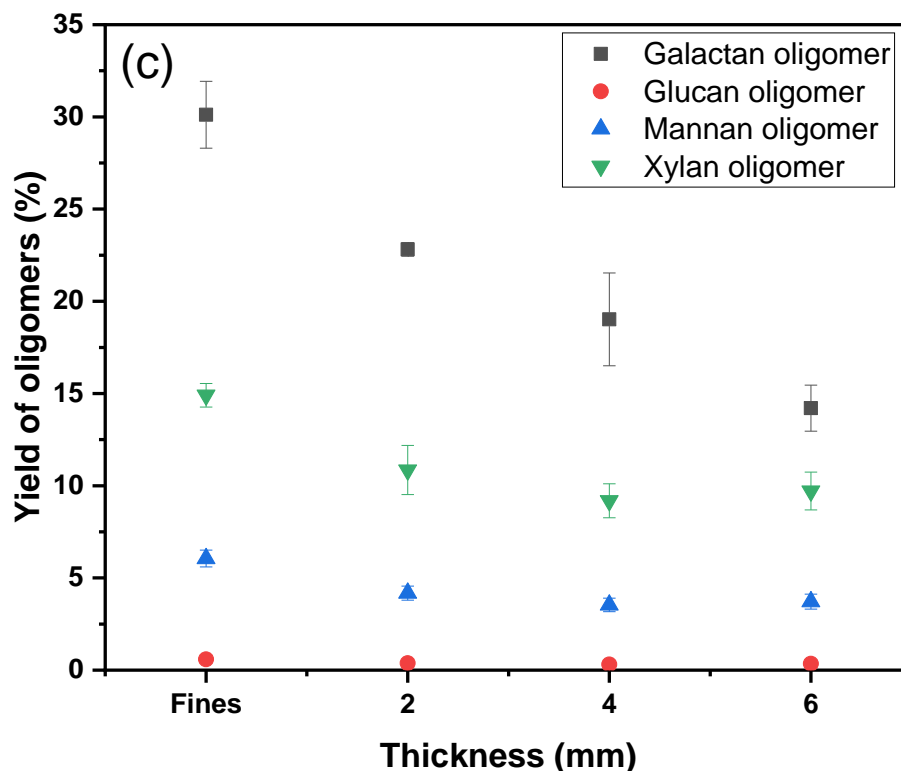
All the fiber properties were analyzed by PulpEye, an online pulp fiber analyzer from Eurocon (Domsjö, Sweden).

## RESULTS AND DISCUSSION

### Hemicelluloses Content in the Hydrolysate and Pre-hydrolyzed Chips

Hemicelluloses oligomer and monomer yields in the hydrolysate are shown in Fig. 1a. The maximum yield of oligomer came from the fines, and oligomer yield decreased with the increasing thickness. This was consistent with previous studies that showed that small thickness favors high oligomer yield (Song *et al.* 2008; Rissanen *et al.* 2014a,b). Monomer yield, by contrast, was constant with varying thickness, suggesting that monomer production is unaffected by mass transfer limits within wood chips.





**Fig. 1.** (a) Hydrolysate hemicelluloses yield relative to o.d. chips as a function of wood chip thickness. Hydrolysate hemicelluloses (b) galactose, glucose, mannose, and xylose monomer yield, and (c) galactan, glucan, mannan, and xylan oligomer yield relative to initial galactan, glucan, mannan, and xylan within o.d. chips as a function of thickness

Wood chip thickness effects on the yield of xylose, galactose, glucose, and mannose in the hydrolysate were negligible (Fig. 1b). This result further established that monomer generation was independent of thickness. Galactose and xylose are the major monomers. Softwood hemicelluloses contain arabino-4-O-methylglucurono-xylans (AGX) (up to 10% of o.d. softwood) and O-acetyl-galactoglucmannans (GGM) (14 to 20% of o.d. softwood) (Sjostrom 1993; Hon and Shiraishi 2000; Fengel and Wegener 2011; Kim *et al.* 2014).

The AGX, the pentose-based polymer, was easily hydrolyzed to monomers with the high xylose yield (Fig. 1b). The GGM, which is hexose-based, was mainly hydrolyzed to oligomers. Glucose and mannose were the most stable hemicelluloses components as demonstrated by their low monomer yields in Fig. 1b. Galactose is found as branches on the glucomannan backbone of GGM (Fengel and Wegener 2011) and is thus more reactive.

Oligomer yield by sugar species was influenced by wood chip thickness (Fig. 1). Small chip thickness favored oligomer production, regardless of sugar type, reflecting total oligomer yields (Fig. 1a). The majority of oligomers consist of mannan and galactan (Fig. 1c). This reflects their high initial concentration in wood and the recalcitrance of the glucomannan backbone. As the Man:Glu:Gal ratio of softwood in water-soluble GGM is 3:1:1 (Fengel and Wegener 2011), calculation of the mannan to glucan ratio can provide an indirect measure of degree of GGM hydrolysis. For all wood chip thickness, the Man:Glu:Gal ratio was 1.9 to 2.1:1:1.5 to 2.3, which suggested incomplete release of mannan and glucan.

The fraction of solubilized solids after pre-hydrolysis is listed in Table 1. The fraction of material solubilized decreased with increasing chip thickness. The fines lost

twice the amount of material lost from the other thickness. The differences in degree of solubilization among 2, 4, and 6 mm were small. From Fig. 1a, the hemicelluloses yield from fines was less than 1.5 times of yield from 4 mm and 6 mm, indicating that other components, such as extractives, were also readily removed during the pre-hydrolysis of fines.

**Table 1.** Fraction of Solids Solubilized During Pre-hydrolysis and Composition of Pre-hydrolyzed Chips (% o.d. Chips, Average  $\pm$  Standard Deviation)

	Raw Chips	Fines	2 mm	4 mm	6 mm
<b>Fraction Solubilized</b>	N.A.	5.84	2.66	2.59	2.34
<b>Arabinan</b>	0.44 $\pm$ 0.04	0.00	0.00 $\pm$ 0	0.00 $\pm$ 0	0.00 $\pm$ 0
<b>Galactan</b>	1.65 $\pm$ 0.05	1.86	1.90 $\pm$ 0.02	1.88 $\pm$ 0.01	1.64 $\pm$ 0.03
<b>Glucan</b>	49.40 $\pm$ 0.78	48.13	50.86 $\pm$ 0.11	49.49 $\pm$ 0.2	49.18 $\pm$ 0.38
<b>Xylan</b>	2.11 $\pm$ 0.55	1.48	1.61 $\pm$ 0.20	1.85 $\pm$ 0.45	1.50 $\pm$ 0.12
<b>Mannan</b>	9.19 $\pm$ 0.47	6.29	7.74 $\pm$ 0.15	7.56 $\pm$ 0.03	8.22 $\pm$ 0.27
<b>Acid Soluble Lignin</b>	5.26 $\pm$ 0.43	5.10	5.19 $\pm$ 0.10	5.11 $\pm$ 0.15	5.38 $\pm$ 0.11
<b>Acid insoluble residue</b>	26.16 $\pm$ 0.14	27.83	28.69 $\pm$ 0.13	27.46 $\pm$ 1.71	26.40 $\pm$ 0.51
<b>Extractive</b>	3.04 $\pm$ 0.03				
<b>Total</b>	97.24 $\pm$ 2.49	96.45	98.45 $\pm$ 0.31	94.76 $\pm$ 1.78	94.48 $\pm$ 1.45

Note: No standard deviation for fines due to inaccurate operation for one replicate

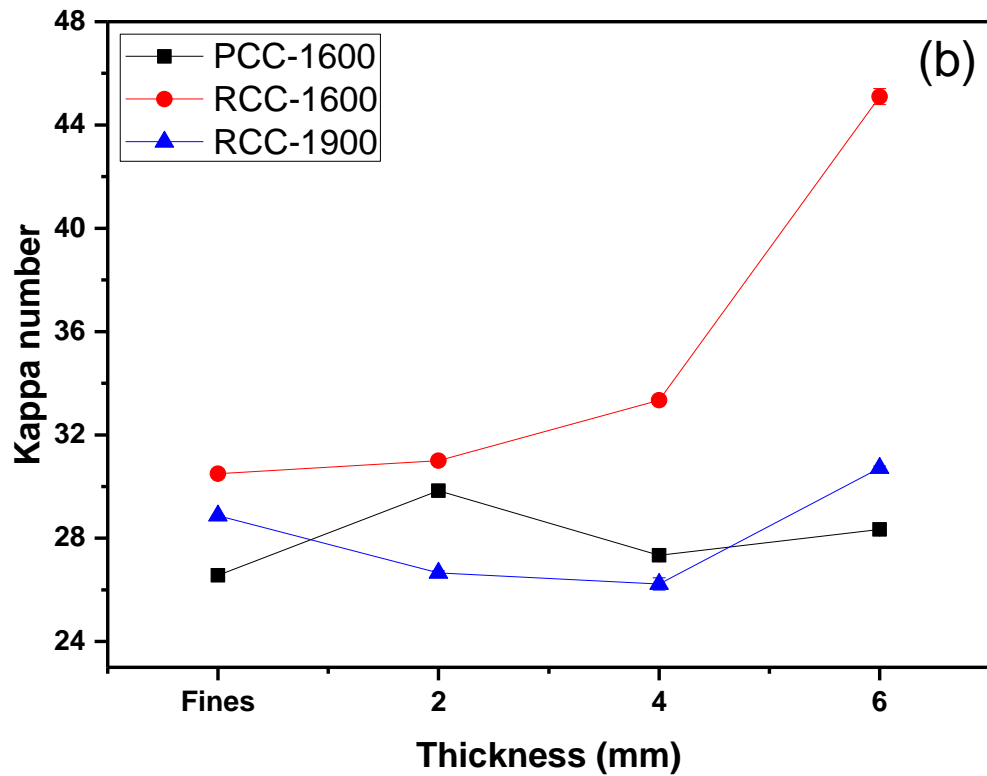
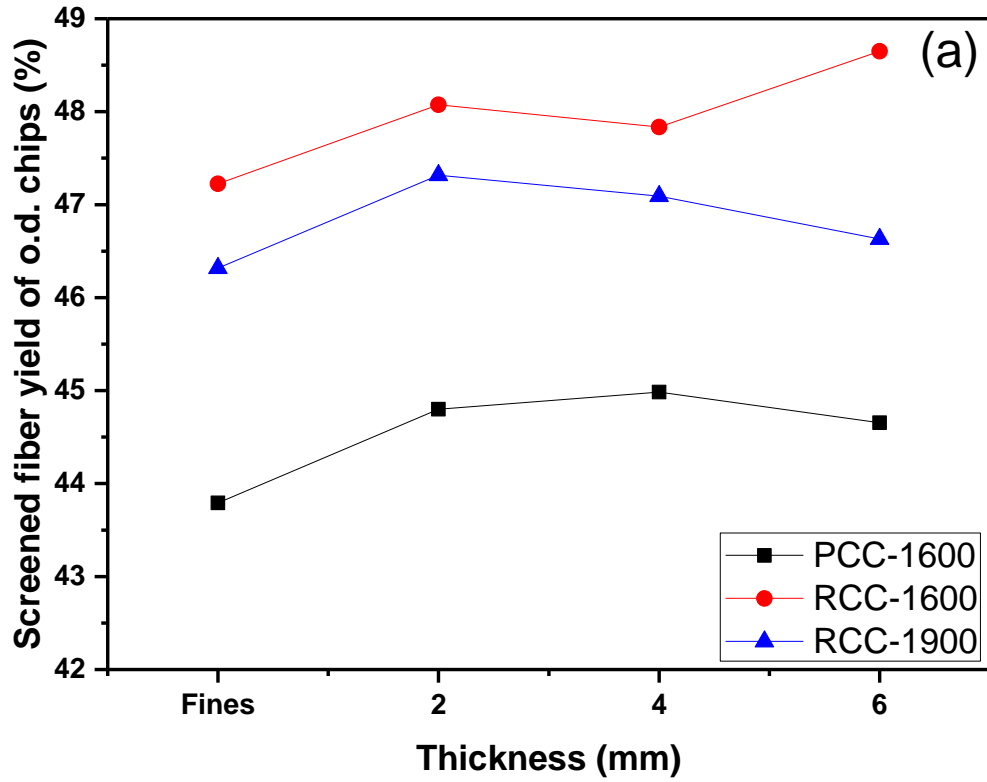
The composition of raw and pre-hydrolyzed chips is summarized in Table 1. The most striking difference was the disappearance of arabinan from the pre-hydrolyzed chips, reinforcing the observation that AGX is the most reactive hemicelluloses component. Mannan and xylan content decreased for all wood chip thickness. Glucan, which includes cellulose and hemicelluloses-derived glucan, was constant with respect to thickness and the amount was comparable to the raw chips, which implied that the selected hydrolysis condition did not substantially degrade glucan. The total carbohydrates content was consistent with oligomer and monomer yields reported in Fig. 1. The acid-soluble lignin and insoluble residue content were independent of chip thickness (Table 1), which could arise from limited lignin removal.

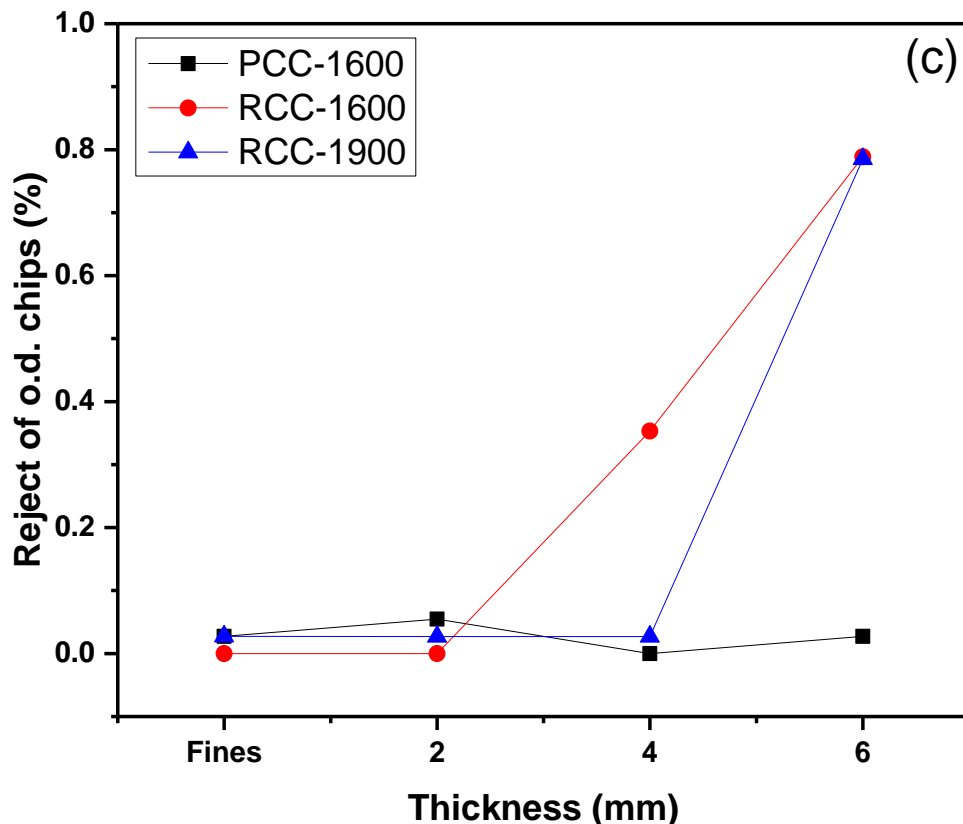
### Kraft Pulping Fiber Yield and Kappa Number

In the subsequent discussion, the abbreviation PCC-1600 represents pre-hydrolyzed chips cooked to an H-factor of 1600; RCC-1900 is raw chips cooked to an H-factor of 1900; RCC-1600 is raw chips cooked to an H-factor of 1600.

Figure 2a presents the screened fiber yield (Eq. 2) as a function of wood chip thickness for PCC-1600, RCC-1600, and RCC-1900 while Fig. 2b presents Kappa number. The screened fiber yield of RCC-1600 was greatest for all chip sizes (Fig. 2a). The RCC-1900 screened fiber yields were 0.7 to 2.0% lower and screened fiber yields from PCC-1600 were lower still. As the discussion below will demonstrate, these differences were due to variation in hemicelluloses and lignin removal.







**Fig. 2.** (a) Screened fiber yield from o.d. raw chips, (b) Kappa number of kraft pulp, and (c) percent rejects in pulp after screening based on o.d. chips as a function of chip thickness

There are two key features to note in Fig. 2b. The first is that there was a slight increase in Kappa number of RCC-1600-4 mm followed by a larger increase in Kappa number of RCC-1600-6 mm, indicating increasing lignin content. It was noteworthy that the Kappa number of the RCC-1900 and PCC-1600 series were comparable and showed little variation with chip thickness.

The percentage of screened rejects (Fig. 2c) exhibited similar behavior to Kappa number. Rejects occur when pulped wood chips are not fully separated into fibers by the disintegrator. There was an increase in the percentage of rejects for RCC-1600-4 mm and a second increase in the percentage of rejects for RCC-1600-6 mm. The percent of rejects from RCC-1900 was negligible for all sizes except RCC-1900-6 mm. The percentage of rejects from RCC-1900-6 mm chips was equal to the percentage of rejects from RCC-1600-6 mm. Finally, there was a negligible percentage of rejects from PCC-1600-treated chips at all sizes.

The differences in RCC-1600 and RCC-1900 were discussed first so that the effects of pre-hydrolysis relative to increasing pulping severity could be delineated. Increasing the *H*-factor from 1600 to 1900 caused an increase in lignin removal and thus a decrease in screened fiber yield. Increasing the *H*-factor also reduced the effect of chip size on the percentage of rejects. The low percentage of rejects at an *H*-factor of 1900 for chips smaller than 6 mm was due to better delignification and indicated complete pulping of the wood chips. The percentage of rejects was equal for chips with a thickness greater than 6 mm at an *H*-factor of 1600 and *H*-factor of 1900. This equivalence suggested mass transfer limitations during pulping, which resulted in uneven cooking. Pulping under the conditions

of RCC-1600 was found to be undesirable despite the high yield because it resulted in a high Kappa number and was accompanied by a high percentage of rejects.

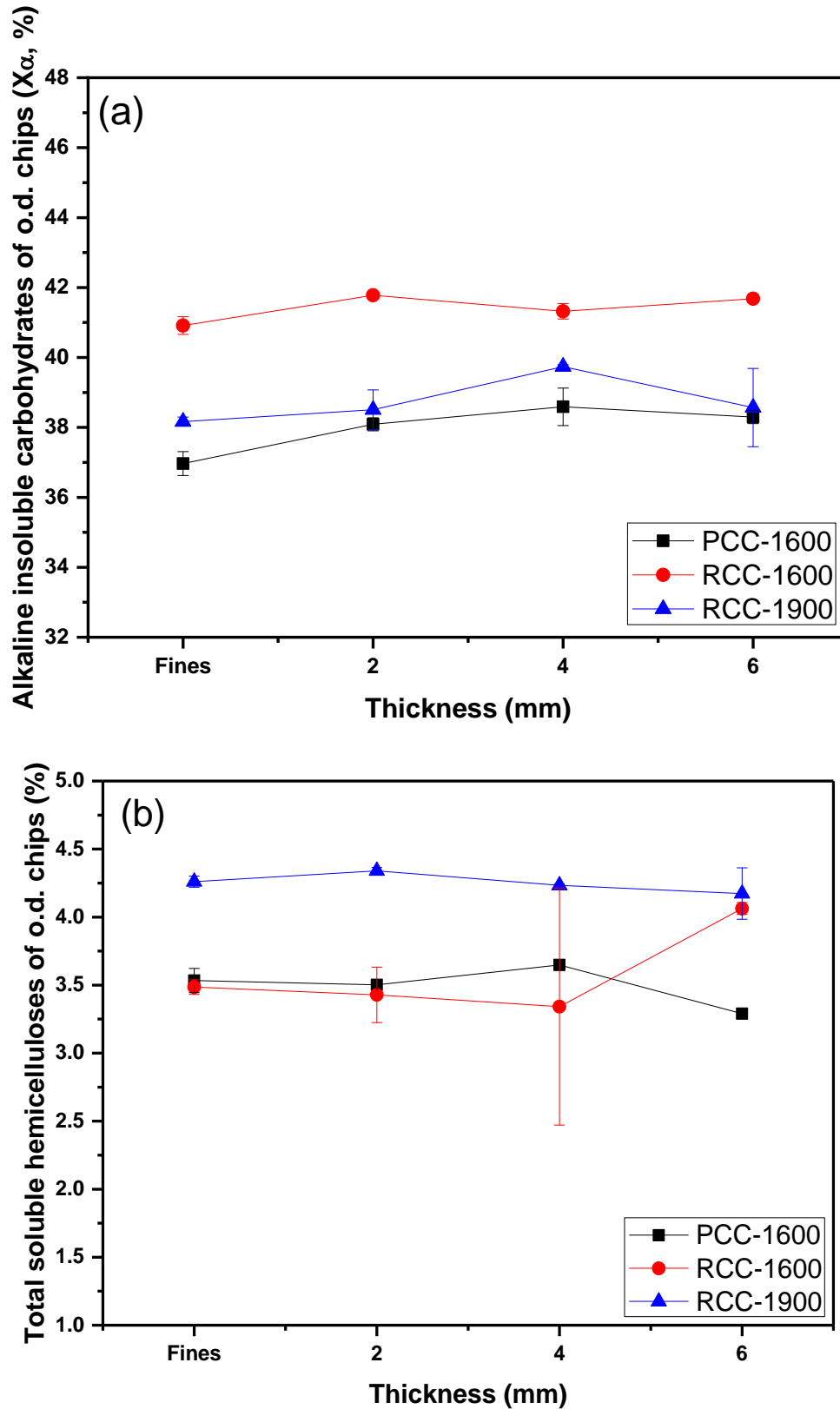
The Kappa numbers and lignin content of PCC-1600 and RCC-1900 were comparable, although the pre-hydrolyzed chips were subjected to a milder pulping process. Despite similar lignin content, the screened fiber yield of PCC-1600 was 2.0 to 2.5% lower than that of RCC-1900. The sum of PCC-1600 fiber yield and pre-hydrolysis hemicelluloses yield was equivalent to the RCC-1900 fiber yield. Thus, the difference in RCC-1900 and PCC-1600 fiber yields was due to hemicelluloses removal during pre-hydrolysis.

Hemicelluloses removal during pre-hydrolysis has two effects. During pulping, hemicelluloses are converted to organic acids, which then neutralize alkali, thus reducing its availability for delignification reactions (Mimms *et al.* 1989; Niskanen 1998). This neutralization effect is reduced by removing hemicelluloses during pre-hydrolysis. Hemicelluloses removal also increases wood chip porosity (Mosier *et al.* 2005; Lu *et al.* 2012; Chen *et al.* 2017; Guo *et al.* 2021), which improves chemical penetration during the subsequent pulping step. These effects explain why pulping pre-hydrolyzed chips to an *H*-factor of 1600 resulted in the same Kappa number as pulping raw chips to an *H*-factor of 1900. As discussed in the introduction, there is a two-stage response to pre-hydrolysis: enhanced lignin removal resulting in a decrease in *H*-factor to reach a target Kappa number and condensation of lignin resulting in the need to increase the *H*-factor to reach a target Kappa number. The equal Kappa numbers for PCC-1600 and RCC-1900 indicated that the selected pre-hydrolysis condition was sufficiently mild that lignin condensation was minimal. Similar observations have been reported by others (Yoon and van Heiningen 2008; Smith 2011; Borrega *et al.* 2013). Pre-hydrolysis makes it possible to decrease the *H*-factor required to meet a target Kappa number while hemicelluloses removal is simultaneously increased. Energy and chemical savings may be attainable through reductions in *H*-factor or in application of pulping chemicals.

Unlike the raw chips, the percentage of rejects produced from pre-hydrolyzed pulp was negligible at all thicknesses. This was noteworthy as the residual lignin content of RCC-1900-6 mm was only slightly higher than that of PCC-1600-6 mm but the percentage of rejects from RCC-1900-6 mm was more than 27 times higher. The low percentage of rejects could relate to the greater porosity created during pre-hydrolysis and the subsequent facilitation of mass transfer during kraft pulping (Lu *et al.* 2012; Rissanen *et al.* 2014a,b; Chen *et al.* 2017).

### **Kraft Pulp Fiber Carbohydrates**

Alkaline-insoluble carbohydrates are the carbohydrates that are resistant to strong alkaline treatment. As can be seen in Fig. 3a, RCC-1600 had the highest alkaline insoluble carbohydrates content of the three materials. Pre-hydrolysis (PCC-1600) and high *H*-factor pulping (RCC-1900) decreased the alkaline-insoluble carbohydrates content of the final pulp relative to RCC-1600. Wood chip thickness did not affect the alkaline insoluble carbohydrates and hemicelluloses content of PCC-1600 and RCC-1900. This indicated that the carbohydrate reaction rates during pre-hydrolysis and pulping were not mass transfer limited. This trend was validated by comparable hemicelluloses molar mass in hydrolysate for varying chip thickness (Fig. S1). Similarly, the Kappa number was comparable for the different thicknesses (Fig. 2b), indicating that the delignification reactions were not influenced by the mass transfer. The trend in hemicelluloses was less clear for RCC-1600 due to the size of the error bars (Fig. 3b).



**Fig. 3.** (a) Alkaline insoluble carbohydrates content (wt%) and (b) total soluble hemicelluloses content (wt%) of screened pulp fiber relative to o.d. chips as a function of wood chip thickness. Total soluble hemicelluloses are the sum of soluble arabinan, xylan, galactan, mannan, and glucan.

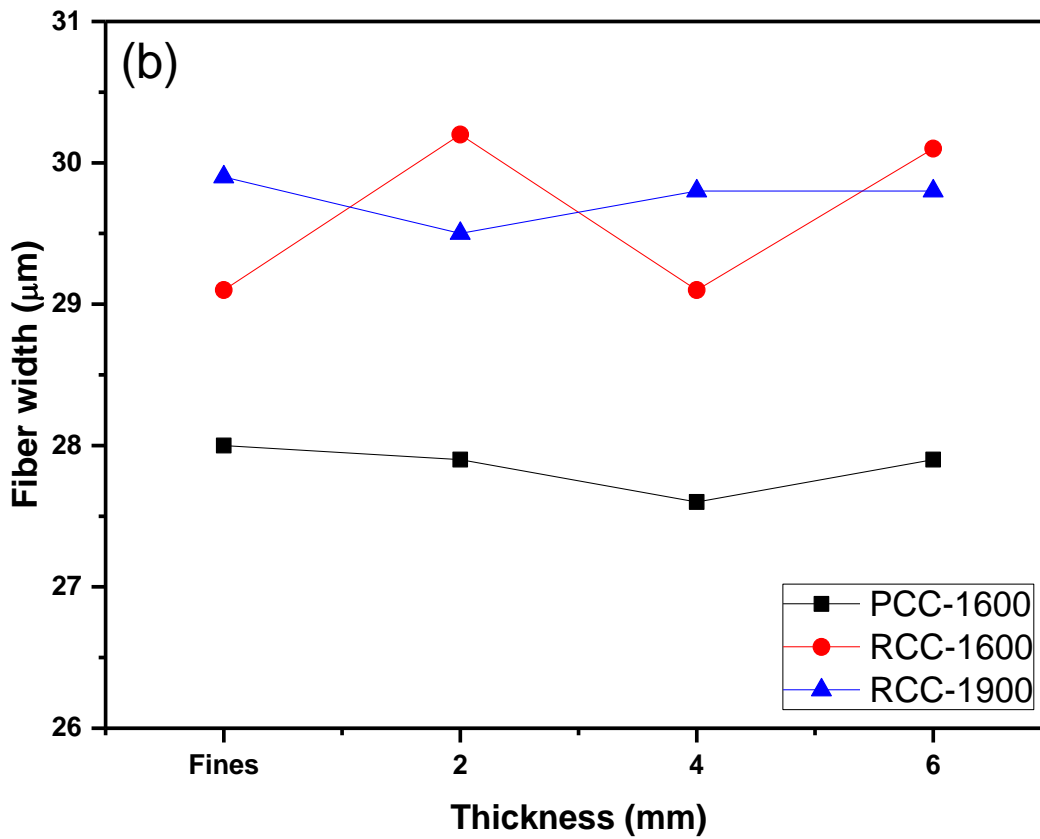
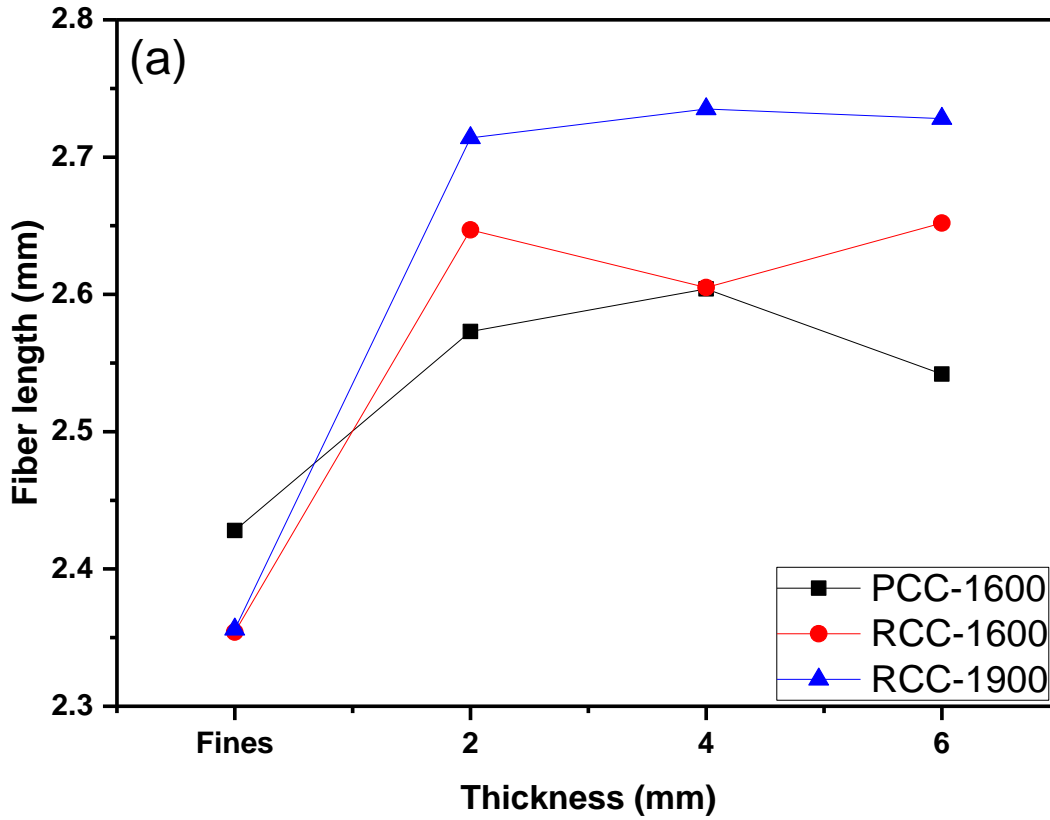
The total soluble hemicelluloses content, the sum of soluble galactan, glucan, mannan, xylan, and arabinan, of RCC-1600 was unexpectedly close to that of PCC-1600 (Fig. 3b), as it was demonstrated in Fig. 1 that hemicelluloses were removed during pre-hydrolysis. It was also unexpected that the soluble hemicelluloses content of RCC-1600 was less than that of RCC-1900 (Fig. 3b), as increasing the *H*-factor increases hemicelluloses removal (Ek *et al.* 2009). These observations were most likely an artefact of the methods used to prepare the samples for analysis. Residual lignin may tether hemicelluloses through lignin-carbohydrate complexes (LCC) in the fiber during the alkaline extraction process (Lawoko *et al.* 2003). The elevated lignin content of RCC-1600 may have hindered complete hemicelluloses release from the fiber during sample preparation. This restriction on hemicelluloses release may be due to shielding of hemicelluloses from sodium hydroxide and by reducing hemicelluloses solubility through shared LCC bonds.

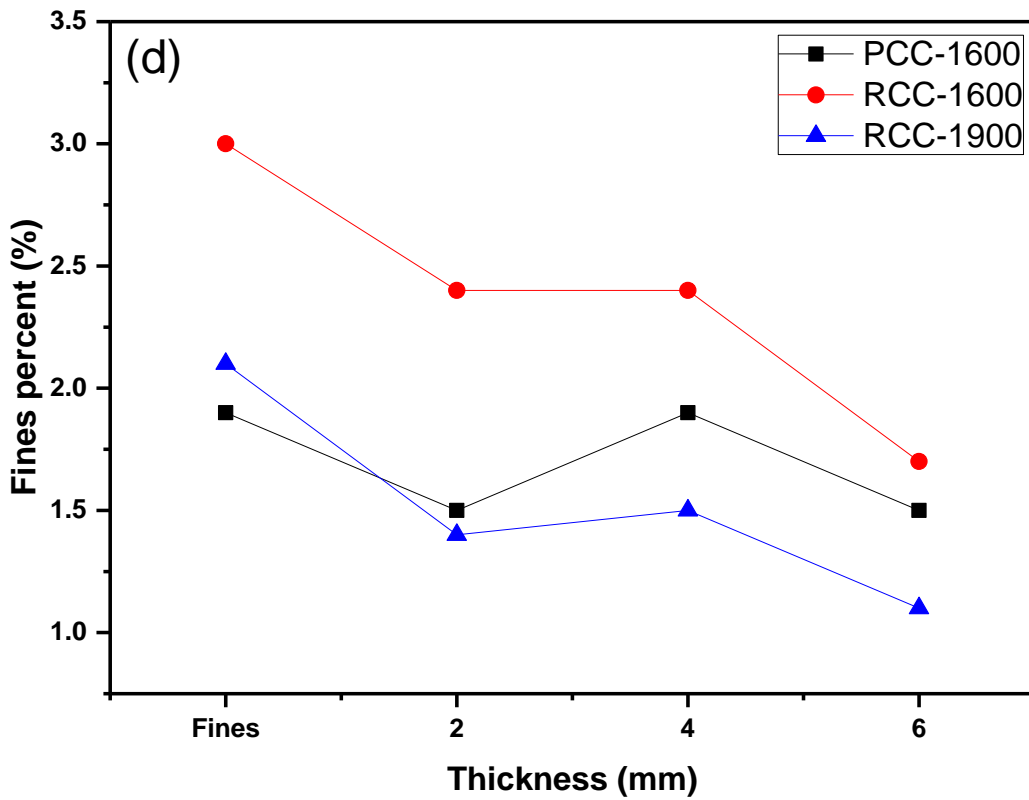
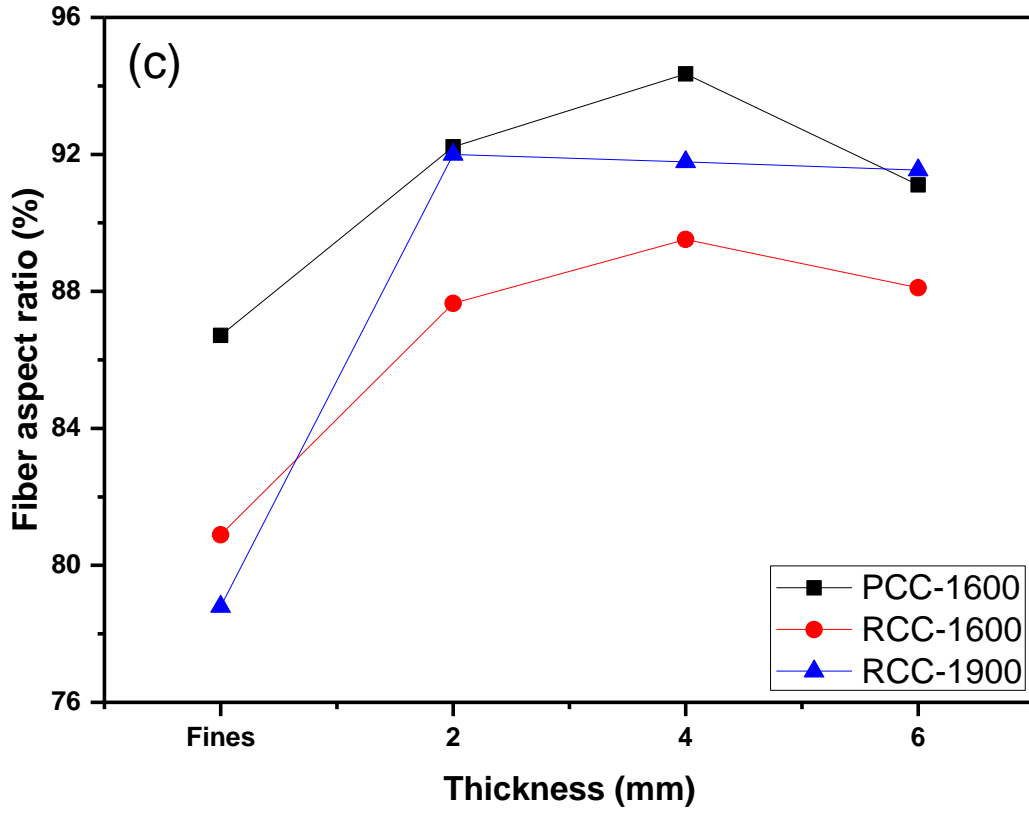
The decrease in soluble hemicelluloses content of PCC-1600 relative to RCC-1900 was attributed to the difference in acidic and alkali hydrolysis. Pre-hydrolysis removes hemicelluloses and lignin from wood chips and increases wood chip porosity (Tarkow and Feist 1969; Mosier *et al.* 2005; Lu *et al.* 2012; Rissanen *et al.* 2014a,b; Li *et al.* 2015; Chen *et al.* 2017) to enhance alkali diffusion and fiber liberation. High *H*-factor pulping produces pulp with high delignification and readily separated fibers. Alkali conditions are more selective for delignification reactions while acidic conditions are more selective for hemicelluloses hydrolysis. When an acidic hemicelluloses removal process was combined with an alkali delignification process, it was possible to produce a pulp with lignin content equal to RCC-1900 (Fig. 2b) but with lower soluble hemicelluloses content.

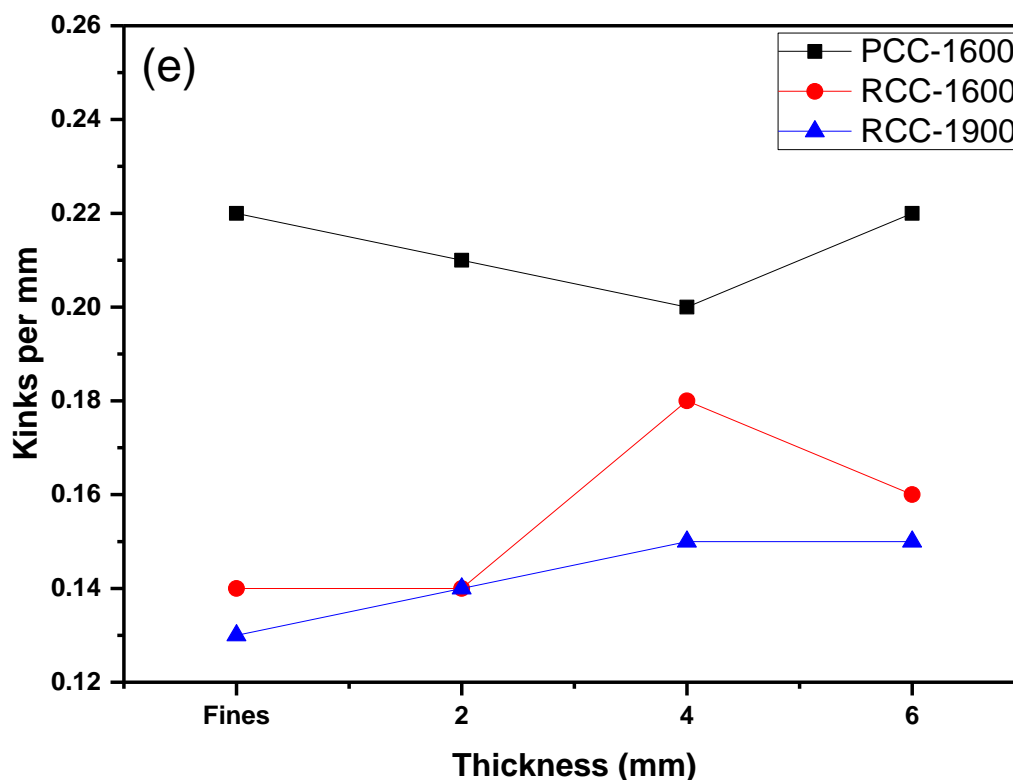
### Kraft Pulp Fiber Properties

Fiber length (length-weighted average) (Fig. 4a) was strongly influenced by chip thickness. Pulping chip fines produced 2.35 to 2.45 mm long fibers. Longer fibers were produced from the thicker chips. Increasing chip thickness increased fiber length for RCC-1600 and RCC-1900; the longest fibers were produced by pulping to an *H*-factor of 1900. Pre-hydrolysis resulted in 0.04 to 4.15% shorter fibers relative to kraft pulping at an *H*-factor of 1600.

Average fiber width was independent of wood chip size for all conditions (Fig. 4b). In addition, increasing the *H*-factor from 1600 to 1900 had little effect on fiber width. However, application of pre-hydrolysis resulted in an approximately 3.78 to 7.62% decrease in fiber width relative to kraft pulping (Fig. 4b). This reduction could relate to the removal of more hemicelluloses and lignin during pre-hydrolysis, leading to more delamination or peeling of fibrillar and secondary fines. Scanning electron microscopy (SEM) studies have shown that the ultrastructure of poplar wood during acidic pretreatment undergoes cell wall distortion and shifting of the middle lamella (Blumentritt *et al.* 2016). The subsequent kraft pulping after pre-hydrolysis might further expand the ultrastructure variation. After removal of lignin and hemicelluloses from hardwood chips by alkaline treatment, crack formation (Ji *et al.* 2014), damage to the microstructure (Renders *et al.* 2016), and separated and exposed micro-fibrils (Tarkow and Feist 1969; Li *et al.* 2015) were observed in wood cell walls through SEM images.







**Fig. 4.** Dimensions of kraft pulp fibers: (a) mean fiber length (mm), (b) mean fiber width ( $\mu\text{m}$ ), (c) aspect ratio, and (d) kraft pulp fines content (wt%) as a function of wood chip thickness; (e) fiber kinks number per mm of kraft pulp as a function of wood chip thickness

The fiber aspect ratio is defined as fiber length to fiber width and is presented in Fig. 4c. Pre-hydrolysis generated more slender pulp fiber (Fig. 4c), and the PCC-1600 aspect ratio was higher than RCC-1600. The near parallel trends of PCC-1600 and RCC-1600 indicated that pre-hydrolysis did not change the effect of chip thickness on fiber aspect ratio.

The fines content refers to the fraction of fibers with length equal to or less than 0.2 mm. With increasing wood chip thickness, fines content decreased for RCC-1600 and RCC-1900 (Fig. 4d). Thin wood chips produced more fines compared to thick chips. Better fiber separation due to high delignification at an  $H$ -factor of 1900 resulted in less fiber damage and fines generation; therefore RCC-1900 had the lowest fines content. The residual lignin of RCC-1600 hampered fiber separation, resulting in maximum fines content. The pre-hydrolyzed pulp had a diminished fiber width and cell wall thickness, which could be the result of secondary fines and fibrillar generation. Thus, an intermediate content of fines was demonstrated for PCC-1600, reflecting the balance between enhanced delignification and diminished width and cell wall thickness.

A kink is defined as the abrupt change in the axial direction of fiber curvature that does not naturally exist (Niskanen 1998). As weak points in the fiber, kinks reduce paper tensile strength and elastic modulus but increase stretch by uneven bearing of tensile stress compared to paper formed by straight fibers (Johansson 2011). The pre-hydrolyzed pulp fibers had the greatest number of kinks per unit length (Fig. 4e). The reduction of fiber width makes fiber more flexible and likely provokes subsequent mechanical treatment to



generate more kinks. Under similar mechanical forces, pre-hydrolyzed kraft pulp fibers were easily damaged compared to traditional kraft pulp fiber.

### Practical Implications

The effects of pre-hydrolysis on subsequent kraft pulping and fiber properties are summarized in Table 2. The main advantages are Kappa number reduction of kraft pulp fiber. However, pre-hydrolysis resulted in lower pulp yield, reduced fiber dimensions, and increased kinks, which could lead to fiber strength loss. It was not possible to determine how final paper properties would change as there was insufficient fiber to prepare handsheets for direct testing. Further pre-hydrolysis condition optimization and handsheet property analysis is necessary.

**Table 2.** Summary of Pre-hydrolysis Combination to Kraft Pulping Pros and Cons and Wood Chip Thickness Influence on Pre-hydrolysis and Kraft Pulping

Pre-hydrolysis	
Pros	Cons
Reduce Kappa	Lower fiber yield 1 to 2%
Extracted hemicelluloses for alternative applications	Increased kinks
	Reduced fiber dimension
Wood Chip Thickness Influence	
Pre-hydrolysis	Kraft Pulping
No influence on monomer yield	No impact on fiber yield
Smaller wood chip thickness: Higher oligomer yield	Smaller wood chip thickness: Reduced fiber length, Kappa, and reject; increased fines content
	Little influence on fiber width and kinks

The influences of wood chip thickness on pre-hydrolysis and kraft pulping are summarized in Table 2. Smaller chip thickness favored hemicelluloses oligomer yield and reduced Kappa number, but it also reduced fiber dimension and increased fines content. Thus, chip fines are beneficial for pre-hydrolysis and hemicelluloses production, and the pre-hydrolyzed solids could be used for combustion. Large thickness chips, within the range considered in this work, are favorable for pulp production.

The main challenges associated with integrating pre-hydrolysis with kraft pulping are pulp yield reduction and modification of fiber property. It is critical to balance pre-hydrolysis severity and final fiber quality. Compared to severe pre-hydrolysis with high hemicelluloses yield but low pulp quality, mild pre-hydrolysis at 140 °C (lower than typical autohydrolysis temperature 160 to 200 °C) is more favorable for integration. Under the conditions applied in this work, Kappa number was reduced without serious loss of fiber quality. Further economic analysis is needed to evaluate the differences in profits lost through lower pulp yield and the value of hemicelluloses obtained from the hydrolysates. If pulp products are sensitive to the strength variation, pulp mill waste streams such as chip fines and hog fuel could be an alternative hemicelluloses source (Rangu 2017; Chen *et al.* 2020).

## CONCLUSIONS

1. Mild pre-hydrolysis was integrated with kraft pulping for softwood chips of varying wood chip thickness. Pre-hydrolyzed chips and raw chips were subjected to kraft pulping with an  $H$ -factor of 1600 and 1900.
2. Pre-hydrolysis decreased the  $H$ -factor required to meet a target Kappa number by hemicelluloses removal and enhanced delignification. The detailed compositional analysis of kraft pulp and fiber quality analysis indicated that pre-hydrolysis pulping maintained the fiber properties with limited reduction of fiber length and width and increased kinks.
3. Chip thickness effects on pre-hydrolysis and kraft pulping were analyzed by characterization of hydrolysate, pre-hydrolyzed chips, and kraft pulp fibers. The softwood chip thickness less than 2 mm facilitated hemicelluloses oligomer removal; those with thickness between 2 and 6 mm exhibited sufficient delignification and desirable kraft pulp fiber properties; those with thickness greater than 6 mm were insufficiently delignified.

## Authorship Contribution Statement

Jingqian Chen: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Software; Visualization; Writing - Original draft. Heather L. Trajano and Rodger P. Beatson: Conceptualization; Funding acquisition; Project administration; Resources; Supervision; Validation. Kenny Tam: Data curation; Methodology. Paul Bicho: Resources; Supervision; Validation. All: Writing - Review and editing.

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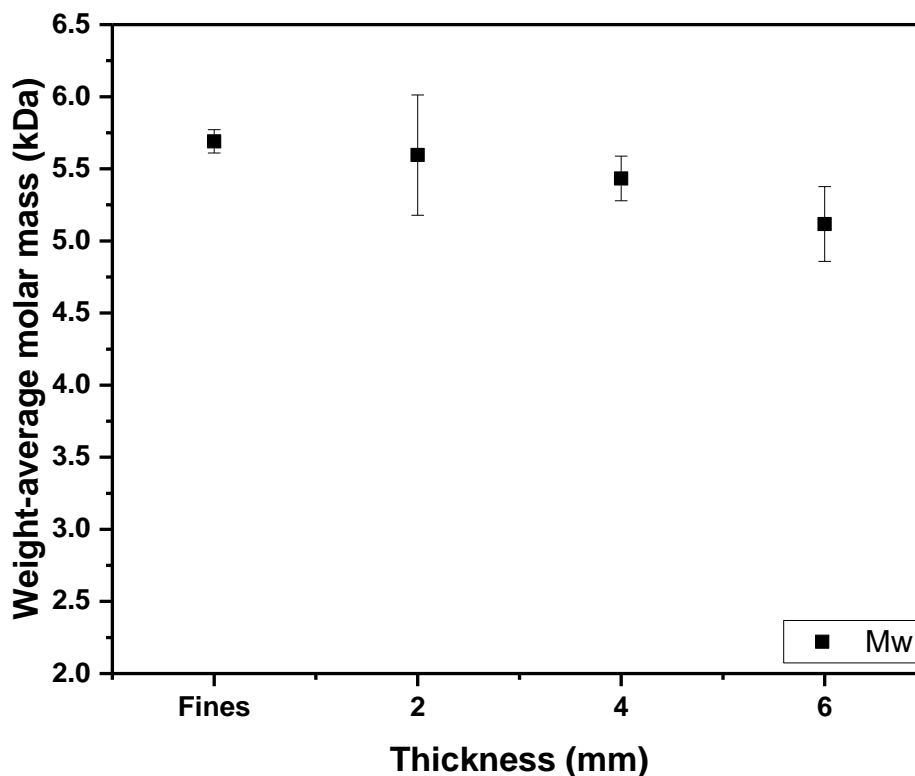
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## APPENDIX

### Supplementary Information



**Fig. S1.** Hydrolysate weight-average molar mass of hemicelluloses as a function of softwood chip thickness after pre-hydrolysis.