

IMPROVEMENTS IN PULP PROPERTIES BY ALKALI PRE-EXTRACTION AND SUBSEQUENT KRAFT PULPING WITH CONTROLLING H-FACTOR AND ALKALI CHARGE

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The objective of this study was to determine the processing conditions for obtaining improved pulp properties from the kraft pulping process with an alkali pre-extraction stage. Before the kraft pulping, a pre-extraction of hemicelluloses from mixed hardwood chips was performed with two different alkali concentrations (3% and 12% as Na₂O) at 150 °C for 90 minutes. The kraft pulping of the pre-extracted chips was then conducted in two ways: with either the H-factor alone controlled or with both the H-factor and the alkali charge controlled. When the chips were pre-extracted with the 3% alkali charge and with the kraft pulping controlled to an H-factor of 500, the yield and properties of the pulp were higher than those of the reference kraft pulp. The 12% alkali pre-extraction and kraft pulping resulted in a low yield of screened pulp. However, when the alkali charge and the H-factor were adjusted together, the pulp yield remained constant and the pulp properties improved in comparison to the reference pulp for both the 3 and 12% cases.

Keywords: Hemicelluloses; H-factor; Kraft pulping; Pre-extraction; Pulp properties

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INTRODUCTION

Kraft pulping, which is the most popular chemical pulping process, has many advantages. This process makes it possible to remove lignin efficiently and to produce fibers with high strength. The strength properties are superior to those of other chemical pulps such as acidic sulfite pulp. The kraft pulping process is also economically beneficial, because the chemicals used in the cooking can be recovered and recycled effectively. For more efficient utilization of energy and raw materials in the kraft pulping process, the pulp yield must be increased. Moreover, the possibility of converting the processing infrastructure from a pulp mill to a biorefinery in order to produce valuable materials from degraded wood components has been raised (Sixta and Schild 2009).

Carbohydrates such as hemicelluloses react with hydroxyl ions produced during kraft pulping (Mimms *et al.* 1993). As a result, approximately 50% of the hemicelluloses in wood chips are dissolved during the kraft pulping process and removed as black liquor along with lignin when producing pulp with a yield of 50% (Smook 2002). The hemicelluloses are burned in a recovery boiler to produce a portion of the energy for the operations of the pulp mill. However, the higher heating value (HHV) of the hemicelluloses (13.6 MJ/kg) is much lower than that of lignin (27 MJ/kg) (van Heiningen 2006; Walton *et al.* 2010). Therefore, it may be desirable for hemicelluloses to be used as value-added products rather than be burned as black liquor.

Hemicelluloses are the third most abundant renewable biopolymer, following cellulose and lignin (Cunningham *et al.* 1986). Hemicelluloses can be used in their native or modified forms in various applications (Ebringerová and Heinze 2000; Ebringerová *et al.* 2005). Since hemicelluloses are extracted from non-woody or woody materials, they are utilized as gels, films, coatings, adhesives, and stabilizing and viscosity-enhancing additives in the food and pharmaceutical industries (Ebringerová 2006). They also can be used as papermaking additives. It has been reported that the adsorption of hemicelluloses such as xylans onto cellulose fiber surfaces improves the strength of the bonding between fibers (Linder *et al.* 2003). Hemicelluloses obtained from a waste degumming liquor of ramie fiber are used as additives to reduce the energy consumption during the beating operation and to improve paper strength (Bhaduri *et al.* 1995). Lima *et al.* (2003) showed that xyloglucans could be used as wet-end additives to improve the mechanical properties of the paper sheet. Köhnke *et al.* (2010) showed that the adsorption of birch glucuronoxylan reduced the degree of drying-induced fiber wall cross-linking, resulting in the higher tensile strength of the paper sheet.

Several studies on the extraction of hemicelluloses from black liquor have been reported. Lisboa *et al.* (2005) isolated polysaccharides from black liquor by acid precipitation. Wallberg *et al.* (2006) also extracted hemicelluloses from the kraft black liquor using ceramic membranes. However, such hemicelluloses are difficult to use because both the molecular weight and the yield of the hemicelluloses are very low.

In the bioenergy industry, the extraction of hemicelluloses has been considered a pretreatment necessary for improving the accessibility of the cellulose to the enzymes. One of the most popular pretreatments is the dilute-acid pretreatment, which is usually carried out using acid at high temperature. Varga *et al.* (2004) and Yang *et al.* (2009) extracted hemicelluloses with yield of maximum 82% and 80% from switchgrass and cornstover using sulfuric acid. Lu and Mosier (2007) and Kootstra *et al.* (2009) used maleic acid to extract hemicelluloses from lignocellulosics. However, the purpose of this kind of pretreatment was just to remove hemicelluloses from the biomass as mono- or oligosaccharides using a strong acid for better enzymatic hydrolysis and fermentation. Dilute-acid pretreatment may be more suitable in the bioenergy industry than in the pulp and papermaking industries.

The pre-extraction of hemicelluloses from lignocellulosic biomass prior to the kraft pulping process has drawn the attention of the pulp industry. Various solvents have been used for the pre-extraction. Furthermore, the effects of the pre-extraction process on the subsequent kraft pulping has been evaluated via measurements of the pulp properties. Al-Dajani *et al.* (2009) showed that kraft pulping after hot-water pre-extraction resulted in improved delignification due to a reduced kappa number, although the total pulp yield decreased. Yoon and van Heiningen (2008b) also observed a decrease in the pulp yield and in the tensile strength compared to the control pulp, even though the H-factor was controlled. Generally, treatment of the chips with hot water or steam is conducted in the first stage for dissolving pulp grade production in order to remove most of the hemicelluloses (Lora and Wayman 1978). This is usually called 'autohydrolysis', and there have been several studies about its effects on the chemical composition of wood chips (Caparrós *et al.* 2007; Leschinsky *et al.* 2009). Pre-extraction using hot water causes acidic conditions due to the release of acetic acid formed during autohydrolysis of the acetyl groups in the hemicelluloses (Song *et al.* 2008; Tunc and van Heiningen 2008; Yoon and van Heiningen 2008b), and this acidity may accelerate the degradation of the

cellulose at high temperatures, resulting in a significant loss in the pulp yield (Yoon *et al.* 2010). The pulp yield is related to productivity and economy, and a decrease in the pulp yield is disadvantageous to any kraft pulp mill. Al-Dajani and Tschirner (2010) observed a pulp yield similar to that of the control during alkaline pre-extraction and subsequent ASAM (alkaline sulfite anthraquinone methanol) pulping. However, the tensile strength, burst strength, viscosity, and brightness of the pulp had decreased. Kämpfi *et al.* (2010) increased the pulp yield to a level similar to that of the reference kraft pulp using polysulfide and anthraquinone; however, the strength and optical properties decreased. Although Yoon *et al.* (2011) also achieved a similar pulp yield after hot water pre-extraction compared to the control cook, one or two more pretreatment stages using polysulfide and sodium borohydride in addition to the pre-extraction stage are required. More treatment stages, more chemicals, and a longer cooking time, however, must be avoided if possible in the interest of productivity and economic efficiency.

Another important issue is the utilization of pre-extractives obtained by pre-extraction. For this, the hemicelluloses dissolved into the pre-extractives should be separated out, as their heating value is very low and they have great potential to be used in many other fields. Some researchers have tried to extract or separate hemicelluloses from non-woody or woody materials using various solvents such as 1, 4-dioxane, DMSO, ethanol, KOH, *etc.* (Kitayama *et al.* 2000; Sun *et al.* 2005; Jin *et al.* 2009). Converting a kraft pulp mill into an Integrated Forest Biorefinery (IFBR), will permit the production of higher value-added products (van Heiningen 2006). For example, the hemicelluloses separated from biomass could be further processed for fermentation and conversion into bioethanol (Yang *et al.* 2009).

As reported in many studies, the application of pre-extraction in the kraft pulping process is likely to cause a decrease in the pulp properties. Nevertheless, it is desirable and important to maintain these pulp properties despite the inclusion of the pre-extraction treatment while also reducing the energy requirement. Therefore, the objective of this study was to investigate the effects of alkali pre-extraction on the kraft pulping process and to determine the processing conditions for obtaining pulp properties superior to those of the reference kraft pulping. The pre-extraction, kraft pulping, and analysis of the pre-extractives and pulp properties were carried out according to the experimental scheme shown in Fig. 1. Two different conditions for kraft pulping were used: one, controlling for only the H-factor, and the other, adjusting both the H-factor and the alkali charge.

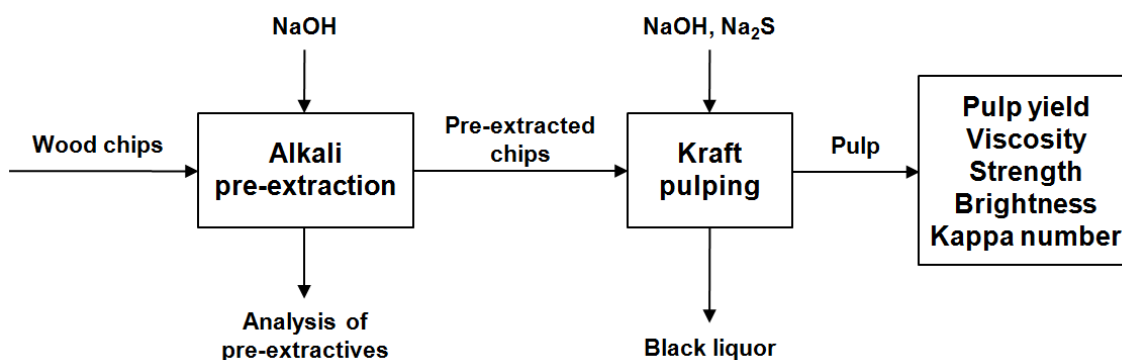


Fig. 1. Schematic for pre-extraction, kraft pulping, and evaluation of the pulp properties

EXPERIMENTAL

Materials

The wood chips used in this study were mixed hardwoods chips, of which the main species was oak. They were obtained from Moorim P&P Co. in Korea. The chips were conditioned at 23 ± 2 °C and RH $50 \pm 2\%$ and then used for pre-extraction. The chips consisted of $45.9 \pm 0.2\%$ cellulose, $21.4 \pm 0.1\%$ hemicelluloses, $26.6 \pm 0.7\%$ lignin, $2.5 \pm 0.4\%$ alcohol-benzene extractives, and $0.5 \pm 0.03\%$ ash. Both the sodium hydroxide and sodium sulfide were purchased from Samchun Pure Chemical Co. in Korea.

Alkali Pre-Extraction

The pre-extraction for the chips with only sodium hydroxide was conducted using a laboratory batch digester (10 L). The pre-extraction was carried out at 150 °C for 90 minutes in accordance with a previous study (Cho *et al.* 2011), with conditions that preceded a high pre-extraction yield. The levels of addition of alkali sodium hydroxide, were 3% (as Na₂O) and 12% (as Na₂O) based on the oven-dried weight of the chips. The liquor-to-wood ratio was 4:1. After pre-extraction, the pre-extractives were removed, and the pre-extracted chips to be used for kraft pulping were not washed.

Kraft Pulping

Kraft pulping was carried out with the alkali pre-extracted chips using the same digester as described above. White liquor was prepared according to the following conditions: alkali charge of 17% (expressed as Na₂O), sulfidity of 25% (expressed as Na₂O), and liquor-to-wood ratio of 4:1. The cooking temperature during the kraft pulping was 170 °C, and the cooking time was controlled such that the H-factor was 200, 500, or 1000. The activation energy of 134 kJ/mol was used to calculate the H-factor during the pre-extraction and kraft pulping processes. The cooking conditions, such as temperature, active alkali, sulfidity, and the liquor-to-wood ratio, of the reference kraft pulping were the same as those of the kraft pulping of alkali pre-extracted chips. The cooking time was 2 hours, and the H-factor was about 1940.

Kraft pulping was also performed by adjusting the alkali charge at the kraft pulping stage. Since the total alkali charge during the pre-extraction and kraft pulping was the same as that during reference pulping, the alkali charge in the kraft pulping was determined as the difference between the total charge and the NaOH charge in the pre-extraction stage. The sulfidity was calculated based on the sum of the active alkali charge during the pre-extraction and kraft pulping processes. The H-factor of the pre-extraction at 150 °C for 90 min was about 260, and this was subtracted when the kraft pulping was performed. The cooking temperature, time, and liquor-to-wood ratio were the same. All the conditions for the pre-extraction and kraft pulping are shown in Table 1. After cooking, the black liquor was removed, and the pulp obtained from the kraft pulping was washed thoroughly with tap water.

Analyses

For analysis of the pre-extracted chips, the chips were washed with tap water after pre-extraction and then dried in an oven at 105 °C for 24 hours. The pre-extraction yield was determined. The pre-extraction yield was defined as the weight loss of the chips, that is, the ratio of the reduced oven-dried weight of the chips to the initial oven-dried weight

of the chips. The pre-extractives were collected and freeze-dried so that the amount of pre-extracted hemicelluloses and lignin could be determined. Analyses of Klason lignin, acid soluble lignin, and sugar content were performed according to the National Renewable Energy Laboratory (NREL) Analytical Procedure: determination of structural carbohydrates and lignin in biomass (Sluiter *et al.* 2008). The freeze-dried pre-extractives were treated with 72% sulfuric acid at 30 °C for 1 hour, followed by hydrolysis with 4% sulfuric acid at a temperature of 121 °C for 1 hour using an autoclave. Acid-soluble lignin was determined by a UV-Vis spectrophotometer (UV-1601PC, Shimadzu, Japan) at 205 nm. A sugar analysis was conducted by high-performance liquid chromatography (HP-1100, Hewlett Packard, USA) equipped with an Aminex-87H column and refractive index detector. The ratio of hemicellulose or lignin content in the pre-extractives to the total amount in the initial chips was defined as the relative hemicellulose or lignin yield. These analyses were carried out in triplicate.

Table 1. Pre-extraction and Kraft Pulping Conditions *

	Reference	Kraft pulping after pre-extraction			
		I	II	III	IV
Pre-extraction					
Active alkali charge (NaOH), % on O.D. wood chips (as Na ₂ O)		3	12	3	12
Extraction temperature, °C		150	150	150	150
Extraction time, min		90	90	90	90
H-factor		260	260	260	260
Liquor-to-wood ratio		4:1	4:1	4:1	4:1
Kraft pulping					
H-factor	1940	200, 500, 1000	200, 500, 1000	1680	1680
Active alkali charge, % on O.D. wood chips (as Na ₂ O)	17	17	17	14	5
Sulfidity, % (as Na ₂ O)	25	25	25	25	25
Cooking temperature, °C	170	170	170	170	170
Liquor-to-wood ratio	4:1	4:1	4:1	4:1	4:1

* Kraft pulping that was controlled by only the H-factor (I, II) and adjusted for both the alkali charge and H-factor (III, IV) was conducted and compared.

All measurements of the pulp and paper properties in this study were carried out according to TAPPI test methods and ISO standards. After the washed pulp was screened with a Somerville type screen (TAPPI T 275), the screened pulp yield was determined. The screened pulp yield is defined as the ratio of the final oven-dried mass of pulp after screening to the initial oven-dried mass of chips before pre-extraction. The viscosity (TAPPI T 230) and kappa number (TAPPI T 236) of the pulp were also determined. After each kraft pulp was formed into handsheets according to TAPPI T 205 without beating treatment, the following paper properties were analyzed: tensile index, TAPPI T 494; tear index, TAPPI T 414; and brightness, ISO 2470.

RESULTS AND DISCUSSION

Alkali Pre-Extraction

Figure 2 shows the pre-extraction yield, expressed as the weight loss of the chips after alkali pre-extraction at the different alkali charges and reaction times (Cho *et al.* 2011). The pre-extraction yield increased as the alkali charge increased from 3% to 12%. The maximum yield, about 30%, was obtained under the following pre-extraction conditions: alkali charge of 12% at 150 °C for 90 minutes. The impact of reaction time on the pre-extraction yield at the same alkali charge was small. The alkali charges of 3% and 12% were chosen as the pre-extraction conditions because they led to relatively low and high pre-extraction yields, respectively. The effects of each pre-extraction condition on the properties of kraft pulp were then evaluated.

In the pre-extraction stage, the weight of the chips decreased due to dissolved components such as hemicelluloses and lignin. The relative yields of the hemicelluloses and lignin are shown in Table 2. Both yields increased with the increase in the alkali charge. The significant increase in the pre-extraction yield at the alkali charge of 12% might have been caused by the higher extraction of lignin. A small increase in the relative hemicellulose yield was observed together with an increase in the alkali charge. Due to the high amount of lignin in the pre-extractives, this alkali pre-extraction process can be considered as a pre-delignification process. It would seem that the amount of pre-extracted hemicelluloses and lignin influenced the properties of the pulp through subsequent kraft pulpings.

In terms of utilization of the pre-extractives, pre-extraction with an alkali charge of 3% could be appropriate, as it was relatively easy to separate the hemicelluloses from the pre-extractives that contained a small amount of lignin. Furthermore, the molecular weight of the pre-extracted hemicelluloses after pre-extraction with an alkali charge of 3% must be high because the molecular weight decreases with an increase in pre-extraction yield according to Cho *et al.* (2011). The pHs of the pre-extractives with alkali charges of 3% and 12% were about 5 and 13, respectively. In other studies, when the pre-extraction was carried out using hot water, the final pH of the pre-extractives became acidic (Song *et al.* 2008; Yoon *et al.* 2008a; Cho *et al.* 2011); thus, such processing may have brought about a reduction in the pulp yield due to the degradation of the cellulose. In contrast to the hot water pre-extraction (pH 3 to 4), the pH was higher or still alkaline after the alkali pre-extraction. Therefore, autohydrolysis was inhibited by neutralization in the alkali pre-extraction, which prevented the pulp yield of the alkali pre-extracted chips from being reduced.

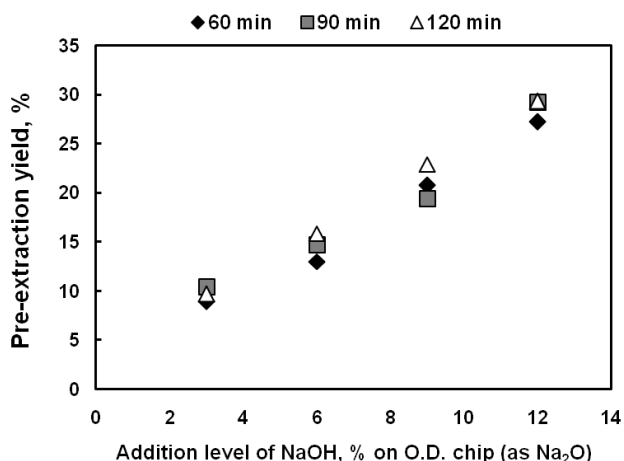


Fig. 2. Pre-extraction yield after alkali pre-extraction with different alkali charges and reaction time at 150 °C (Cho *et al.* 2011)

Table 2. Relative Hemicellulose and Lignin Yield of the Pre-extractives Obtained by Pre-extraction with Alkali Charges of 3% and 12% at 150 °C for 90 minutes

	Alkali charge at pre-extraction stage, % on O.D wood chips (as Na ₂ O)	
	3	12
Relative hemicellulose yield, %	8.8	12.4
Relative lignin yield, %	7.5	31.4

Effects of H-factor Control

In order to evaluate the applicability of the pre-extraction on the kraft pulping process, the pre-extraction of hemicelluloses using sodium hydroxide and the subsequent kraft pulping at different H-factors were carried out. The properties of the obtained kraft pulp, *i.e.*, the pulp yield, viscosity, brightness, mechanical properties, and kappa number, were measured in order to evaluate the effects of the pre-extraction on the kraft pulping.

Figure 3 (a) shows the screened yield of the kraft pulp produced from the chips that were pre-extracted with the alkali charges of 3% and 12% based on the initial oven-dried weight of the chips before pre-extraction. A lower H-factor (200 to 1000) than that of the reference pulping, 1940, was chosen for the kraft pulping stage. As expected, a lower pulp yield than that of the reference pulping was found, along with an increase in the H-factor during the kraft pulping process because the pre-extraction treatment already removed a part of lignin and hemicelluloses from the chips, as shown in Table 2. When the chips were pre-extracted with an alkali charge of 3% and cooked at an H-factor of 500, however, the pulp yield did not differ from that of the reference kraft pulping. In contrast, the pulp yield decreased slightly when cooked at an H-factor of 1000. This result indicated that an H-factor of 500 was appropriate for the given conditions. On the other hand, at the H-factor of 1000, more carbohydrates such as cellulose and hemicelluloses decomposed into cooking liquor and were then removed as black liquor along with lignin. This was because the alkali used in the pre-extraction and kraft pulping was consumed during the degradation of the polysaccharides as well as during the

removal of the lignin. In a similar study, a pulp yield similar to that of the reference kraft pulp was also obtained via pre-extraction with a higher alkali charge, lower temperature, and shorter time (Al-Dajani and Tschirner 2008). However, a decrease in pulp properties such as viscosity and tensile strength was observed. The pulp yield was also slightly low at an H-factor of 200, which might have resulted from incompletely cooked wood such as knots. Although the initial pulp yield was higher than that of the reference pulp yield, the final screened pulp yield decreased due to a large number of knots. In the case of the 12% alkali charge, the screened pulp yield decreased continuously as the H-factor increased from 200 to 1000, resulting in a lower yield than that of the reference kraft pulping. The pre-extraction with an excessive sodium hydroxide charge such as 12% was apparently a severe condition, resulting in many carbohydrates being degraded during the subsequent pulping.

Figure 3 (b) shows the viscosities of the kraft pulp after the alkali pre-extraction and after the reference kraft pulping. The pulp viscosity decreased as the H-factor increased. A more significant loss of viscosity was found in conjunction with the 12% alkali pre-extraction pulp than it was with the 3% alkali pre-extraction pulp. However, the viscosity of the pulp from the 3% alkali pre-extraction and subsequent kraft pulping at H-factors of 200 and 500 was higher than that of the reference kraft pulp. The viscosity at an H-factor of 1000 was similar to the viscosity of the control. This meant that the degradation of cellulose was minimal, because the pre-extraction with the 3% alkali charge and the lower H-factor was a mild treatment. This process showed better results than that of kraft pulping combined with hot water pre-extraction (Yoon and van Heiningen 2008b) but required control of the operating parameters in order to increase the yield of the pulp.

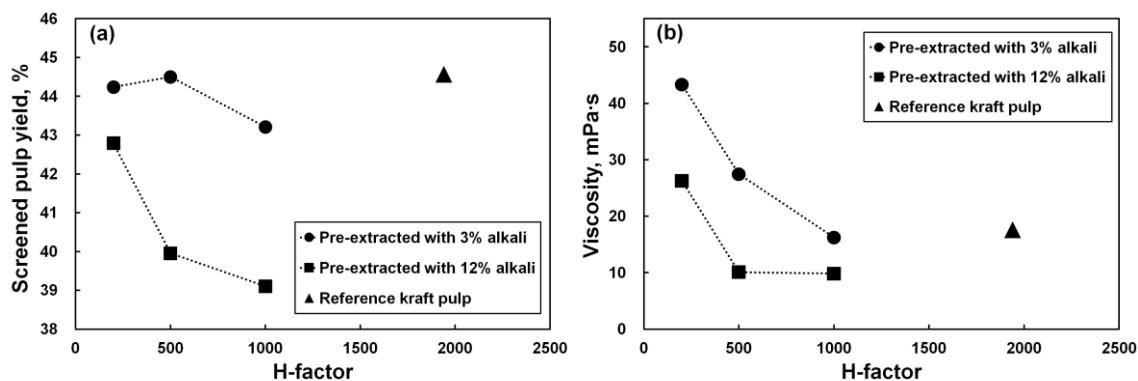


Fig. 3. Screened pulp yield (a) and viscosity of the pulp (b) with different H-factors after alkali pre-extraction of mixed hardwood chips at 150 °C for 90 minutes

Figure 4 shows the kappa numbers of the pulp after pre-extraction and after the reference kraft pulping. The kappa number of the pre-extracted pulp decreased as the H-factor increased during the cooking. The wood chips had already been pre-treated at high temperatures using an alkali solution so that delignification during the cooking could be easily activated due to the easy accessibility of inside of the chips to the chemicals. Therefore, the kappa number of the pulp was lower than that of the reference kraft pulp, even though less energy, denoted by the low H-factor, was consumed in the kraft pulping after the pre-extraction. The H-factor would be limited to the 300 to 400 range to obtain the same kappa number as the reference pulp, as the kappa number of the pulp was higher

than that of the reference pulp under this limit. Generally, the bleaching process requires additional chemicals for delignification. Thus, savings on chemical costs as well as on energy costs could be achieved by introducing the alkali pre-extraction process to the kraft pulp mill.

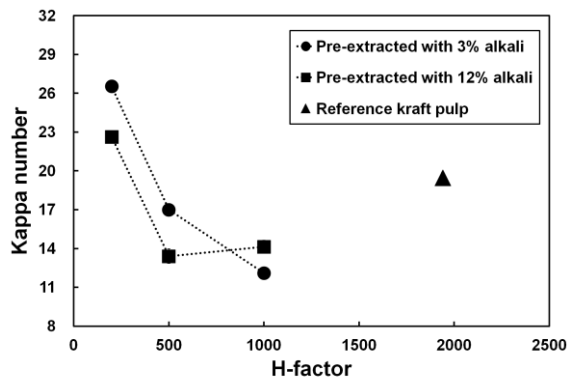


Fig. 4. Kappa numbers of the pulp against different H-factors after alkali pre-extraction of the mixed hardwoods chips at 150 °C for 90 minutes

The tensile strengths of the kraft pulp after alkali pre-extraction and after the reference kraft pulping are plotted in Fig. 5. It was observed that the tensile strength of the 3% alkali pre-extracted pulp was higher than that of the reference kraft pulp over a range of H-factors from 200 to 1000. The tensile strength of the 12% alkali pre-extracted pulp, however, decreased as the H-factor increased during cooking and was lower than that of the reference kraft pulping. These tensile strength results are related with the screened yield and viscosity of the pulp, as shown in Fig. 3. When only the H-factor was controlled and the alkali charge was the same as that of the reference kraft pulping, much of the lignin was already removed with the 12% alkali pre-extraction, and consequently, the degradation of the cellulose chains occurred easily in the subsequent kraft pulping. Therefore, the pulp yield decreased due to the decomposition of cellulose, and the tensile strength decreased as the H-factor increased because of a decrease in the pulp viscosity.

As in Fig. 5, the tensile strength of the pulp pre-extracted with a 3% alkali charge increased as the H-factor increased. This result disagreed with the behavior of the viscosity of the pulp, which decreased with the increase in the H-factor (Fig. 3 (b)). In the case of the pulp pre-extracted with 12% alkali, the viscosity of the pulp might have been the main factor that influenced the tensile strength of the pulp sheet. On the other hand, when the chips were treated with mild conditions (3% alkali) in the pre-extraction stage and cooked at a low H-factor such as 200, only a small amount of lignin was removed. Therefore, the bonding ability of the pulp fibers decreased due to low flexibility, resulting in a tensile strength of the pulp sheet that was lower than that of the pulps with H-factors at 500 and 1000. This explanation could be supported by the kappa number result in Fig. 4. The kappa number of the pulp that was pre-extracted with 3% alkali at an H-factor of 200 was the highest among the H-factor-controlled kraft pulps, and even higher than the kappa number of the reference kraft pulp. Thus, it could be concluded that the residual amount of lignin in the fiber was the major factor that affected the tensile strength of the pulp when the lignin was insufficiently removed.

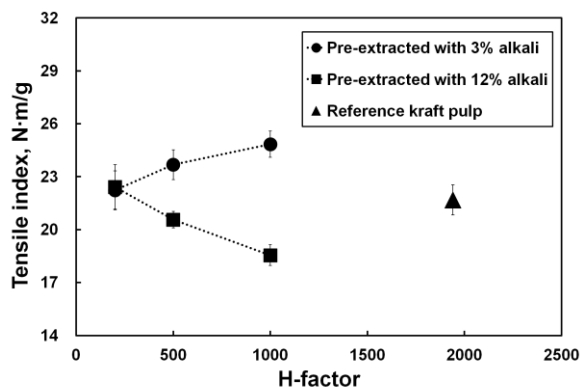


Fig. 5. Tensile strength of the pulp sheet against different H-factors after alkali pre-extraction of mixed hardwood chips at 150 °C for 90 minutes

Figure 6 represents the brightness values of the kraft pulp sheets after pre-extraction with alkali charges of 3% and 12% and after reference kraft pulping. The brightness of the pre-extracted pulp sheet was higher than that of the reference kraft pulping with H-factors ranging from 200 to 1000, and the brightness increased as the H-factor increased during cooking. In other studies, when chemicals such as polysulfide and anthraquinone were used in the kraft pulping, no decrease in the pulp yield was observed. The brightness was equal to or only a little higher than that of the reference pulp (Al-Dajani and Tschirner 2010; Kämpfi *et al.* 2010). However, in this study it was possible to maintain the pulp yield and increase the brightness using only pre-extraction and control of the H-factor but not other chemicals. There was little difference in brightness between the pulp produced with an alkali charge of 3% and pulp produced with an alkali charge of 12%.

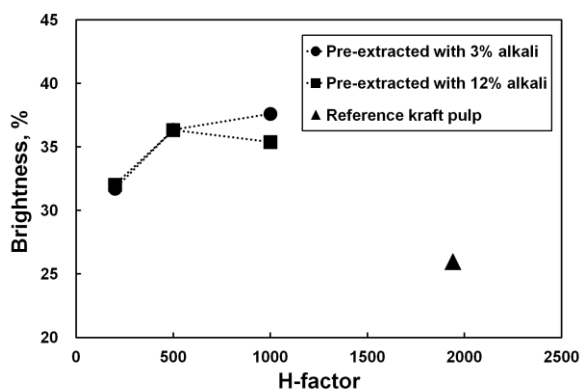


Fig. 6. Brightness of the pulp sheet against different H-factors after alkali pre-extraction of mixed hardwood chips at 150 °C for 90 minutes.

Effects of Alkali Charge and H-factor Control

When only the H-factor was controlled and the overall alkali charge was not adjusted in the pre-extraction or kraft pulping process, an excessive amount of alkali was used. Consequently, pulp properties such as yield, viscosity, and tensile strength decreased in the case of the 12% alkali pre-extraction. Therefore, the charge of sodium hydroxide and the H-factor in the cooking pulping process following the pre-extraction

process were adjusted to be equal to those of the reference kraft pulping in this experiment.

The screened yield of the pulp that was pre-extracted and cooked is shown in Fig. 7 (a). The screened yield was slightly greater for the 3% alkali pre-extracted pulp than for the reference kraft pulp and the H-factor-only controlled pulp. However, a significant increase in the screened pulp yield was observed with the 12% alkali pre-extracted pulp.

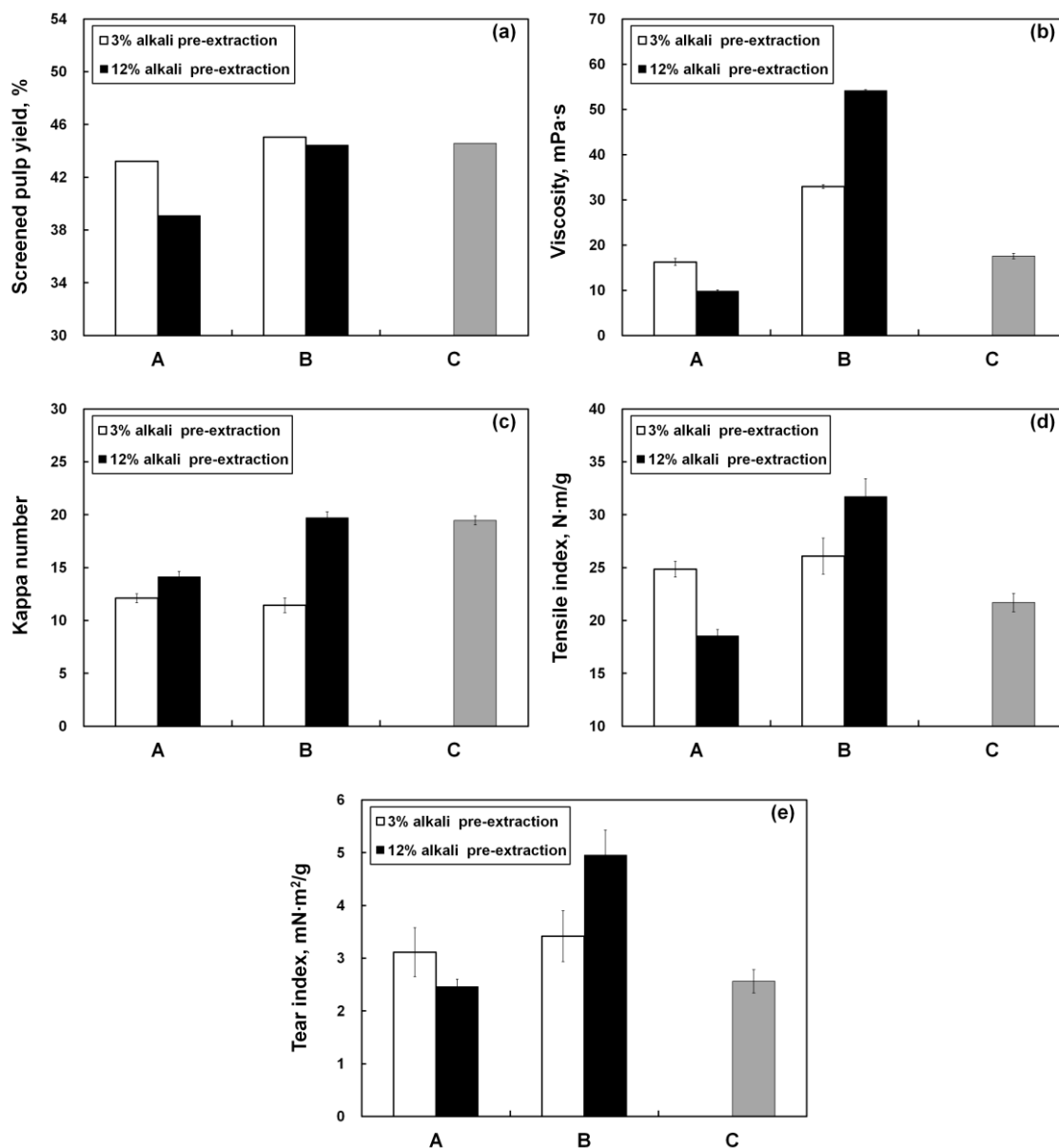


Fig. 7. Screened pulp yield (a), viscosity (b), kappa number (c), tensile strength (d), and tear strength (e) of the pulp after alkali pre-extraction at 150 °C for 90 minutes and subsequent kraft pulping (A, only H-factor was controlled to 1000; B, total alkali charge and H-factor at pre-extraction and pulping were adjusted; C, reference kraft pulping).

When the chips were cooked with a controlled H-factor after pre-extraction with a 12% alkali charge, the total alkali charge of the NaOH was about twice that of the reference kraft pulping. This indicated that the pre-extraction and subsequent kraft pulping without controlling the alkali charge removed much of the lignin and degraded the carbohydrates. By controlling the total alkali charge, however, an increase in the pulp yield as well as a reduction in the use of chemicals could be achieved. Furthermore, the pulp viscosity increased greatly, becoming three times higher than that of the reference kraft pulp (Fig. 7 (b)). According to previous studies (Al-Dajani and Tschirner 2008; Al-Dajani and Tschirner 2010; Kämppi *et al.* 2010), the pulp viscosity was constant or slightly increased when the pre-extraction stage was integrated with the alkali solution. This discrepancy might be derived from the pre-extraction conditions.

The adjustment of both total alkali charge and H-factor also caused changes in the kappa number, tensile strength, and tear strength (Figs. 7 (c) – (e)). Although a higher H-factor, of about 1680 (B), in comparison to the case in which only the H-factor was controlled at 1000 (A), was used for the kraft pulping, improvements in the tensile and tear strength were observed when the alkali charge was adjusted in the kraft pulping stage. This indicated that it was possible to prevent cellulose from being degraded by lowering the chemical charge during cooking, resulting in tensile and tear strengths of pulp that were higher than those of the reference kraft pulp. These results correspond to the increase in the pulp viscosity shown in Fig. 7 (b). There was no significant change in the kappa number for the 3% alkali pre-extraction regardless of the chemical charge and H-factor adjustment. After pre-extraction with 12% alkali and kraft pulping with a controlled chemical charge, however, the kappa number increased. The excess amount of alkali, NaOH, used in the pre-extraction stage led to a shortage of NaOH in the kraft pulping stage due to the adjustment for total chemical charge. The reduced amount of NaOH in the kraft pulping was disadvantageous to delignification, but the kappa number still remained at a level similar to that of the reference kraft pulp. These pulp characteristics were slightly different from the pulp of Al-Dajani and Tschirner (2008)'s research, in which the yield increased slightly, the kappa number remained constant, and the viscosity and tensile strength decreased despite the controlling of the alkali charge and H-factor. These results were likely due to the pre-extraction conditions and wood species. Al-Dajani and Tschirner treated commercial aspen chips under mild pre-extraction conditions (50 °C to 90 °C, 4 hours). Despite relatively low temperatures, a longer pre-extraction could cause deterioration in the strength. Therefore, the optimization of the operating conditions during pre-extraction as well as during kraft pulping should be considered. This result means that when pre-extraction is applied to the kraft pulping process, control of the chemical dosage and H-factor is very important for improving the pulp quality. This addition to the process is beneficial in terms of energy efficiency because the integration of the pre-extraction stage with the pulping process requires a lower H-factor.

CONCLUSIONS

1. Improvements in the pulp properties could be achieved by applying alkali pre-extraction technology to the subsequent kraft pulping. The pre-extraction was

conducted using the different alkali charges, and kraft pulping was performed by controlling the H-factor and the alkali charge.

2. When only the H-factor was controlled in the pulping stage, the pre-extraction with 3% alkali charge, which is a mild alkali condition, had a positive effect on the properties of the subsequent kraft pulp. The screened pulp yield and viscosity were equal to and the strength properties and brightness were higher than those of the reference kraft pulp, especially at an H-factor of 500.
3. In the case of the 12% alkali pre-extraction, however, all the measured pulp properties except for kappa number and brightness were inferior to those of the 3% alkali pre-extracted and reference kraft pulp.
4. When both the total alkali charge and the H-factor were adjusted in pre-extraction and kraft pulping, the pulp yield changed little. The viscosity and tensile strength improved significantly. This meant that when pre-extraction was applied to the kraft pulping process, the control of chemical dosage and H-factor was very important for improving the pulp quality.
5. Although there was a drawback in that a relatively small amount of hemicelluloses and a considerable amount of lignin were extracted by alkali pre-extraction, this process is a promising solution to improve the pulp properties and reduce the energy used in a kraft pulp mill. As to the utilization of alkali pre-extractives, it implies that more studies pertaining to high yields of hemicelluloses and the complete separation of hemicelluloses from lignin should be conducted while maintaining the pulp properties.

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REFERENCES CITED

- Al-Dajani, W. W., and Tschirner, U. W. (2008). "Pre-extraction of hemicelluloses and subsequent kraft pulping Part 1: Alkaline extraction," *Tappi J.* 7(6), 3-8.
- Al-Dajani, W. W., Tschirner, U. W., and Jensen, T. (2009). "Pre-extraction of hemicelluloses and subsequent kraft pulping Part 2: Acid- and autohydrolysis," *Tappi J.* 8(9), 30-37.
- Al-Dajani, W. W., and Tschirner, U. W. (2010). "Pre-extraction of hemicelluloses and subsequent ASA and ASAM pulping: Comparison of autohydrolysis and alkaline extraction," *Holzforschung* 64, 411-416.
- Bhaduri, S. K., Ghosh, I. N., and Deb Sarkar, N. L. (1995). "Ramie hemicellulose as beater additive in paper making from jute-stick kraft pulp," *Ind. Crop. Prod.* 4, 79-84.
- Caparrós, S., Ariza, J., Garrote, G., López, F., and Díaz, M. J. (2007). "Optimization of *Paulownia fortunei* L. autohydrolysis-organosolv pulping as a source of xylooligomers and cellulose pulp," *Ind. Eng. Chem. Res.* 46, 623-631.

- Cho, H., Shin, H., Sim, K., Youn, H. J., and Lee, H. L. (2011). "Pre-extraction of hemicelluloses from Korean mixed hardwood chips using hot water and alkali solution and its characteristics," *J. KTAPPI* 43(1), 83-91.
- Cunningham, R. L., Carr, M. E., and Bagby, M. O. (1986). "Hemicellulose isolation from annual plants," *Biotechnol. Bioeng. Symp.* 17, 159-168.
- Ebringerová, A., and Heinze, T. (2000). "Xylan and xylan derivatives – Biopolymers with valuable properties, 1. Naturally occurring xylans structures, isolation procedures and properties," *Macromol. Rapid Commun.* 21(9), 542-556.
- Ebringerová, A., Hromádlová, Z., and Heinze, T. (2005). "Hemicellulose," *Adv. Polym. Sci.* 186, 1-67.
- Ebringerová, A. (2006). "Structural diversity and application potential of hemicelluloses," *Macromol. Symp.* 232(1), 1-12.
- Jin, A. X., Ren, J. L., Peng, F., Xu, F., Zhou, G. Y., Sun, R. C., and Kennedy, J. F. (2009). "Comparative characterization of degraded and non-degradative hemicelluloses from barley straw and maize stems: Composition, structure, and thermal properties," *Carbohydr. Polym.* 78, 609-619.
- Kämppi, R., Hörhammer, H., Leponiemi, A., and van Heiningen, A. (2010). "Pre-extraction and PSAQ pulping of Siberian larch," *Nord. Pulp Pap. Res. J.* 25(2), 243-248.
- Kitayama, T., Morimoto, M., Takatani, M., Tamura, Y., Takumi, M., Okamoto, T. (2000). "Isolation of hemicelluloses from sorghum, *Andropogon sorghum* Brot, Kumadake no. 263, and determination of its constituent sugars," *Carbohydr. Res.* 325, 230-232.
- Köhnke, T., Lund, K., Brelid, H., and Westman, G. (2010). "Kraft pulp hornification: A closer look at the preventive effect gained by glucuronoxylan adsorption," *Carbohydr. Polym.* 81, 226-233.
- Kootstra, A. M., Beeftink, H. H., Scott, E. L., and Sanders, J. P. (2009). "Optimization of the dilute maleic acid pretreatment of wheat straw," *Biotechnol. Biofuels* 2.
- Leschinsky, M., Sixta, H., and Patt, R. (2009). "Detailed mass balances of the autohydrolysis of *Eucalyptus globulus* at 170 °C," *BioResources* 4(2), 687-703.
- Lisboa, S. A., Evtuguin, D. V., Neto, C. P., and Goodfellow, B. J. (2005). "Isolation and structural characterization of polysaccharides dissolved in *Eucalyptus globulus* kraft black liquors," *Carbohydr. Polym.* 60(1), 77-85.
- Lima, D. U., Oliveira, R. C., and Buckeridge, M. S. (2003). "Seed storage hemicelluloses as wet-end additives in papermaking," *Carbohydr. Polym.* 52(4), 367-373.
- Linder, Å., Bergman, R., Bodin, A., and Gatenholm, P. (2003). "Mechanism of assembly of xylan onto cellulose surfaces," *Langmuir* 19(12), 5072-5077.
- Lora, J. H., and Wayman, M. (1978). "Delignification of hardwoods by autohydrolysis and extraction," *Tappi J.* 61(6), 47-50.
- Lu, Y., and Mosier, N. S. (2007). "Biomimetic catalysis for hemicelluloses hydrolysis in corn stover," *Biotechnol. Prog.* 23, 116-123.
- Mimms, A., Kocurek, M. J., Pyatte, J. A., and Wright, E. E. (1993). *Kraft Pulping: A Compilation of Notes*, TAPPI PRESS, Atlanta, GA.
- Sixta, H., and Schild, G. (2009). "A new generation kraft process," *Lenzinger Ber.* 87, 26-37.
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2008). "Determination of structural carbohydrates and lignin in biomass," Technical Report: NREL/TP-510-42618.

- Smook, G. A. (2002). *Handbook for Pulp & Paper Technologists*, Third Ed., Angus Wilde Pub., Vancouver.
- Song, T., Pranovich, A., Summerskiy, I., and Holmbom, B. (2008). "Extraction of galactoglucomannan from spruce wood with pressurized hot water," *Holzforschung* 62, 659-666.
- Sun, X., Sun, R., Fowler, P., and Baird, M. S. (2005). "Extraction and characterization of original lignin and hemicelluloses from wheat straw," *J. Agric. Food Chem.* 53, 860-870.
- Tunc, M. S., and van Heiningen, A. (2008). "Hemicellulose extraction of mixed southern hardwood with water at 150°C: Effect of time," *Ind. Eng. Chem. Res.* 47, 7031-7037.
- van Heiningen, A. (2006). "Converting a kraft pulp mill into an integrated forest biorefinery," *Pulp Pap. Can.* 107(6), 38-43.
- Varga, E., Réczey, K., and Zacchi, G. (2004). "Optimization of steam pretreatment of corn stover to enhance enzymatic digestibility," *Appl. Biochem. Biotechnol.* 113-116, 509-523.
- Wallberg, O., Linde, M., and Jönsson, A.-S. (2006). "Extraction of lignin and hemicelluloses from kraft black liquor," *Desalination* 199(1-3), 413-414.
- Walton, S., van Heiningen, A., and van Walsum, P. (2010). "Inhibition effects on fermentation of hardwood extracted hemicelluloses by acetic acid and sodium," *Bioresour. Technol.* 101(6), 1935-1940.
- Yang, Y., Sharma-Shivappa, R. R., Burns, J. C., and Cheng, J. (2009). "Saccharification and fermentation of dilute-acid-pretreated freeze-dried switchgrass," *Energy Fuels* 23, 5626-5635.
- Yoon, S. H., Macewan, K., and van Heiningen, A. (2008a). "Hot-water pre-extraction from loblolly pine (*Pinus taeda*) in an integrated forest products biorefinery," *Tappi J.* 7(6), 27-31.
- Yoon, S. H., and van Heiningen, A. (2008b). "Kraft pulping and papermaking properties of hot-water pre-extracted loblolly pine in an integrated forest products biorefinery," *Tappi J.* 7(7), 22-27.
- Yoon, S. H., and van Heiningen, A. (2010), "Green liquor extraction of hemicelluloses from southern pine integrated forest biorefinery," *Ind. Eng. Chem. J.* 16, 74-80.
- Yoon, S. H., Cullinan, H., and Krishnagopalan, G. A. (2011), "Polysulfide-borohydride modification of southern pine alkaline pulping integrated with hydrothermal pre-extraction of hemicelluloses," *Tappi J.* 10(7), 9-16.

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