

Effect of Hot Water Extraction on Hardwood Kraft Pulp fibers (*Acer saccharum*, Sugar Maple)

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ABSTRACT: This study focuses on the properties of fibers obtained from the kraft pulping of pre-extracted sugar maple wood chips. Hot-water pre-extraction was carried out for different times characterized by P-factors in the range of 12 and 600 h. It was found that pre-extraction of the chips significantly accelerates delignification during Kraft pulping such that the H-factors necessary to obtain equivalent delignification (i.e., the same κ numbers) were substantially smaller than control cooks (i.e., with unextracted chips). Unbleached pulps of κ numbers of 35, 25, and 15 were prepared, and their papermaking properties were tested. The hemicellulose content of the pulps decreased with pretreatment, whereas the cellulose contents increased. Pretreatment also resulted in an increase in the pulp viscosity. The fiber lengths showed no change, but the fines content was reduced. The kink index of pre-extracted pulps showed large increases. The porosity of the cell wall also increased with extraction severity as did the mean pore size. The water retention values (WRV) also increased with extraction probably because of the increased fiber porosity. The ζ potential of the fines remained unaffected, whereas the total charge (cationic) demand of the pulps decreased with pre-extraction. There is also a significant loss of tensile and burst strengths of handsheets made with extracted pulps possibly as a consequence of the increased kink and curl index and decreased interfiber bonding ability.

INTRODUCTION

An increasing concern about the environment, especially greenhouse effect and the shortening availability of (cheap and accessible) fossil fuels, have intensified efforts to developing alternative and renewable energy sources. Lignocellulosic materials such as wood constitute an important natural resource for the production of biofuels and biodegradable plastics and can be a component for sustainable industrial development (Ragauskas et al.¹). Biofuels can help alleviate climate change by reducing greenhouse gas emissions, while bioresources can substitute for fossil-based carbon resources as a raw material for plastics. Forest biorefineries process forest biomass feedstock, such as wood, into a spectrum of fuel and material products, similar to the operation of conventional petroleum refineries (Amidon et al.² and Liu et al.³). Mills producing papermaking pulps can be converted into integrated biorefineries producing biofuels, acetic acid, and bioplastics, while still producing pulp and paper (Goyal et al.⁴). Current chemical pulping processes in effect remove a sizable fraction of the wood hemicellulose in the black liquor and ultimately burn it. The present hot-water extraction aims to separate the hemicelluloses prior to pulping and use them to manufacture biofuels and platform chemicals of higher value, thus augmenting the products from conventional pulp mills.

Several researchers have studied hemicellulose extractions, using hot-water (autohydrolysis), alkaline, and acidic liquors for different wood species. Extract properties including particle size, distribution, and flocculation potential were investigated and reported by Duarte et al.⁵ and Duarte.⁶ Separation of such extracts and their subsequent use for biofuel production has been reviewed by Huang et al.^{7,8} Goyal et al.⁴ used hot water to extract hemicelluloses from Sugar Maple and Eucalyptus wood

chips and subsequently prepared kraft pulps from them. They found that the extracted chips are easier to pulp and bleach, but the pulp had poorer refinability and tensile strength. Yoon et al.⁹ found that pre-extraction of loblolly pine chips also results in kraft pulps of poor refinability and lower tensile strength but the pulping and bleaching processes are significantly accelerated. Pre-extraction has no impact on pulp viscosity, zero span tensile strength (ZSTS) or tear, on the basis of which they suggest that the individual fiber strength remains unaffected, but that the interfiber bonding decreases. Similarly, Liu et al.¹⁰ found that for hot-water extracted sugar maple chips, kraft pulping is accelerated but the resulting pulps showed significantly lower tensile and burst strengths.

Santos et al.¹¹ studied the influence of hemicellulose content on the properties of bleached kraft pulp of *Eucalyptus globulus*. They noticed that pulps with low hemicellulose had slightly smaller fiber length, higher amounts of fines, and substantially higher kink when compared to the control. These pulps also exhibit higher wet fiber flexibility (WFF) and viscosity, but lower relative bonded area (RBA). The water retention value (WRV) seems to decrease with the removal of hemicellulose, reducing the swelling and interfiber bonding ability. The removal of hemicelluloses (from approximately 19% to 8.5%) negatively affected tensile and tear indexes and zero span tensile strength. They also found lower intrinsic fiber strength which was attributed to the higher number of defects in the fibers. Dodge et al.¹²

Received: April 3, 2011

Accepted: July 12, 2011

Revised: July 11, 2011

Published: July 12, 2011

obtained kraft pulps from Scandinavian birch, which was pre-extracted using hot water and dilute acid treatments. They found that pre-extraction increased the brightness of the pulps slightly and also the tear strength increased. Other properties were in line with earlier results cited above.

There have been investigations of the surface properties of pulp fibers and their relationship to fiber compositions in the earlier literature^{13–15} although they did not consider specific pretreatment or pre-extraction of hemicelluloses. The ζ potential and surface charge of fibers depends on their chemical composition. Sousa et al.¹⁶ found that a change in hemicellulose content from 20 to 15% decreased the cationic demand but did not affect the ζ potential, whereas the removal of lignin contributes to a decrease of the ζ potential. Goulet¹⁷ showed that it is the weak acid content of pulp that most affects the electrophoretic mobility and thus the ζ potential. Interestingly, the electrophoretic mobility changes with the weak acid content of the pulps, but only when the total acid content is low. At higher acid values, corresponding to those in unbleached kraft pulps, the mobility is relatively independent.

Hemicellulose extraction can be integrated with the pulp and paper industry, but the lack of clear understanding of the pulp properties is one of the barriers to its commercial implementation. Since the hemicellulose content directly affects the surface properties of pulp fibers, the present work investigated how pretreatment processes can impact pulp fiber quality. For this purpose, we prepared kraft pulps from control and pretreated wood chips and studied the fiber quality, surface charge, and potential, in the wet state to understand the impact of removing hemicellulose on papermaking operations, particularly in the wet end of the papermachine. We also measured the change in porosity and pore size distributions of the fibers because of hemicellulose removal. These properties affect water absorption and retention in the wet state and thus alter the structure of the paper sheets. Furthermore, they also affect the adsorption of polymeric and ionic species in functional and process aids, such as retention polymers and different sizing agents. Therefore, improving our knowledge of these properties enables successful application of hemicellulose extracted fibers to different paper grades.

EXPERIMENTAL SECTION

Sugar Maple (*Acer saccharum*) chips were obtained from a hardwood forest (Heiberg Forest Properties, SUNY ESF in Tully, NY, USA). The logs were manually debarked and chipped using a Carthage chipper. All chips were air-dried and screened through a series of screens with circular opening of 9/8, 7/8, 5/8, and 3/8 in. in diameter. The chips retained in the 7/8 and 5/8 in were considered accepts and used in the laboratory experiments (Smook¹⁸). The extractions and cooks were carried out in a 4.5 L M&K Digester, using 500 g of OD chips. DI water was added in order to reach 4:1 liquid to wood ratio. Extractions were carried out at 160 °C, the heating time was of 30 min and the time at temperature varied from 30, 60, 90 to 120 minutes. The Kraft cooks were performed similar to the extractions. The white liquor was prepared in order to have 16% active alkali (AA) and 25% sulfidity, while maintaining 4:1 L:W ratio. The heating up time was 60 min, and the H-factor varied to achieve three different κ numbers –15, 25, and 35. Cooks were performed with all of the extracted chips (after 30, 60, 90, and 120 min extraction), as well as with unextracted chips (control) for comparison. When

performing a Kraft cook on extracted chips, the cook was done right after the extraction, and therefore, the chips were never dried. However, two washes with DI water at 80 °C for 15 min were performed between the extraction and the cook. In these cases, experiments were done until two pulps with similar κ (± 2) were obtained.

The ζ potential was determined using a Brookhaven (BIC) Zeta Potential Analyzer (ZetaPlus). Since ζ potential is determined by measuring the electrophoretic mobility of particles, these need to be small enough not to be affected by gravity. Therefore, to avoid sedimentation (in the time frame of the measurements), this analysis was performed with the fine fraction of the pulps that were able to pass through a paper machine wire. Each value reported is the average of 10 measurements.

Lignin was quantified in all the initial chips, extracted chips and pulps. For the chips, both Klason (or acid insoluble) lignin and acid soluble lignin tests were performed, according to the respective TAPPI Standard T222 and TAPPI Useful Method 250. In case of the acid insoluble lignin, the standard was slightly modified since the all the reagent amounts were cut in half. For the acid soluble lignin, a PerkinElmer Lambda 650 UV/vis spectrophotometer was used. For the pulps, the residual lignin was measured via an indirect method, by measuring the κ number of the pulps, according to TAPPI Standard T 236, with the exception that the amounts of chemicals used was cut in half. Klason lignin was performed in duplicates. Acid Soluble lignin was performed in triplicate.

¹H NMR analysis was used to determine the cellulose and hemicellulose content (from the quantification of monomeric sugars, glucan, xylan, mannan, arabinan, rhamnose, and galactan) of wood chips, extracted wood chips and pulp samples. The NMR methods used in this research are described in detail earlier (see, e.g., Bolton,¹⁹ Mittal,²⁰ Barber,²¹ Bose et al.,²² Alves et al.²³). The wood and pulp samples (milled using a Willey Mill with a 60 mesh screen) were first digested to yield sugars and then analyzed using ¹H NMR. In a first digestion stage, a 50 mg OD sample (milled wood/pulp) is dispersed in 16 mL of 72% sulfuric acid at room temperature for 2 h, stirring it every 15 min to ensure proper dissolution. In a second stage, 21 mL of DI water are added to the mixture, bringing the acid content down to 40%. This mixture is then placed in a water bath at 80 °C for one hour, being shaken every 15 min. The tubes are then cooled down and kept in the refrigerator overnight, for the residual solid matter to precipitate. When necessary the tubes are centrifuged at 2500 rpm for 7 min to further settle the solid matter and allow the collection of 1 mL of the clean supernatant, which is transferred to a NMR tube and mixed with 0.1 mL of a standard solution. The standard solution is a mixture of known amounts of trimethylamine hydrochloride (TMA) and glucosamine. This analysis was done in duplicate.

The cationic demand of pulps was measured using a Mutek particle charge detector (PCD-02) with an automatic titrator (PCD-T2). A known amount (approximately 0.8 g) of pulp was dispersed in 100 mL of water, and an aliquot of 10 mL was used per test. The pulp was allowed to reach a steady streaming potential for 3 min and then it was titrated against a commercial solution of poly-DADMAC with a concentration of 0.001 N. The reported value is an average of three measurements.

The pore size distributions were measured at the Labgran—Granulometry Laboratory and the University of Coimbra, Portugal. The pore size distribution measurements were performed in duplicate using an AutoPore IV Mercury Porosimeter from

micromeritics, in Norcross, GA, U.S.A. The fiber analysis and the Water Retention Value (WRV) measurements were done at the Specialty Minerals Research Center facilities in Allentown, PA. The first was done using an OpTest HiRes Fiber Quality Analyzer (FQA) from OpTest Equipment Inc., Hawkesbury, ON, Canada. The analysis provided a fiber length distribution (different length averages, fines content, among others), as well as fiber curl and kink information. The operating procedure consists of a series of dilutions to obtain a representative sample at very low consistency (0.04%). The dilution was done once, and triplicate aliquots were taken for measurement. The methodology used for the WRV was similar to TAPPI Useful Method T256. 1.94 OD g of pulp were weighed and transferred into the crucibles (forming a 1400 g/m² pad), with the assistance of a vacuum to ensure a neat pulp pad at the bottom of the crucible. The crucibles were then placed in the centrifuge for 30 min and 2500 rpm's (900 G's). After the centrifugation, the crucibles and pulp were weighed and placed in an oven at 105 °C for drying. Once dried, they were weighed again to determine the weight of the dry pulp. Because of time constraints, not all of these tests were performed in duplicates. Roughly 60% of the tests were carried out in duplicate to ensure that the variability between them was small enough.

The viscosity of the pulps were determined in duplicates, using TAPPI Standard T230, with the exception that no nitrogen purge was used. Since this method is only valid for lignin amounts below 4%, the pulps with κ 35 were not tested.

Handsheets were prepared and tested according to the standard TAPPI Methods. Only nonextracted pulps (control pulps) and 120 min extracted pulps (for all kappa levels) were used for paper testing.

RESULTS

Kinetic Analysis of Pre-extraction. Hot water pretreatment removes hemicelluloses and a small fraction of lignin depending on the extent of treatment. The hydrolysis reaction can be characterized by a reaction coordinate, which is a composite of the treatment time and temperature. The severity factor is one such reaction coordinate used for many different types of lignocellulosics including straw, corn stover, wood, and other types of biomass.^{24–27} The pulping H-factor has also been used.^{28,29} The H-factor was originally developed as an effective way of measuring the extent of the chemical pulping reactions combining temperature and time into a single variable. Since prehydrolysis or pre-extraction reactions involve the solubilization of hemicellulose oligomers rather than delignification as in the kraft pulping process, the activation energies are slightly different leading to different constants in the reaction coordinate definition. The resulting factor has been referred to as the P-factor (standing for prehydrolysis, Sixta³⁰). The P-factor has been used as a reaction coordinate by Testova et al.,³¹ Sixta,³⁰ and also by Tunc et al.³² Thus three alternates can be used for the severity of pre-extraction and its impact on the properties of the extracts and the pulps.

$$R_0 = \int_0^{t_x} \exp\left(\frac{T(t) - T_{REF}}{14.75}\right) dt \quad (1)$$

$$H = \int_0^{t_x} \frac{k_{KP}[T(t)]}{k_{KP,REF}} dt = \int_0^{t_x} \exp\left(A - \frac{B}{T(t)}\right) dt \quad (2)$$

Table 1. Experimental Conditions and Constants in eqs 1–3^{27,28}

temperature	$T(t) = T_0 + ((T_f - T_0)t)/(t_R)$	$0 < t < t_R$
	$T(t) = T_f$	$t_R < t$
initial temperature	T_0	298.16 K (25 °C)
final temperature	T_f	433.16 K (160 °C)
ramp time	t_R	30 min
	T_{REF}	373.16 K
	A	43.186
	B	16 115
	A'	40.48
	B'	15 106

Table 2. Mass Removal Data with Extent of Pre-extraction, Severity, H, and P Factors

extraction time, min	R_0	$\log R_0$	P-factor, h	H-factor, h	mass removed, %
30	1944.2	3.2887	147.87	214.47	7.9
60	3697.3	3.5679	283.93	412.60	14.4
90	5450.0	3.7364	419.95	610.99	18.5
120	7202.8	3.8575	555.98	809.22	21.1

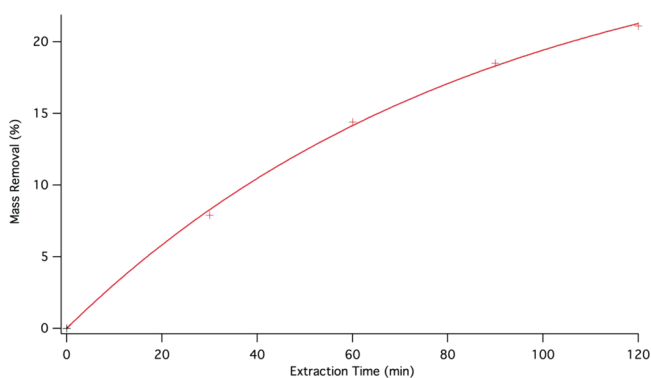


Figure 1. Mass removal of sugar maple chips as a function of time. Correlation coefficients shown for correlation of eq 4 ($\alpha = 28.99 \pm 1.37$, $\beta = 0.011438 \pm 0.000949$, $R^2 = 0.99954$).

$$P = \int_0^{t_x} \frac{k_{PX}[T(t)]}{k_{PX,REF}} dt = \int_0^{t_x} \exp\left(A' - \frac{B'}{T(t)}\right) dt \quad (3)$$

The absolute temperature is used in the above equations. The kraft pulping reaction rate constant is denoted by k_{KP} and the preextraction rate constant by k_{PX} . The scaling rate constants are those taken at a reference temperature, T_{REF} .³⁰ Table 2 shows the values of these three parameters calculated for our experiments (and their constants), as well as the fraction of the initial o.d. chip mass removed by the extraction. All the parameters serve adequately as reaction coordinates but for further analysis, we chose the P-factor since it incorporates the kinetics of the prehydrolysis reactions. Figure 1 shows the mass removal, $m(t)$ as a function of extraction time along with a simple exponential fit of the experimental data. The extraction times reported in all the figures are the time at maximum temperature. All extractions had

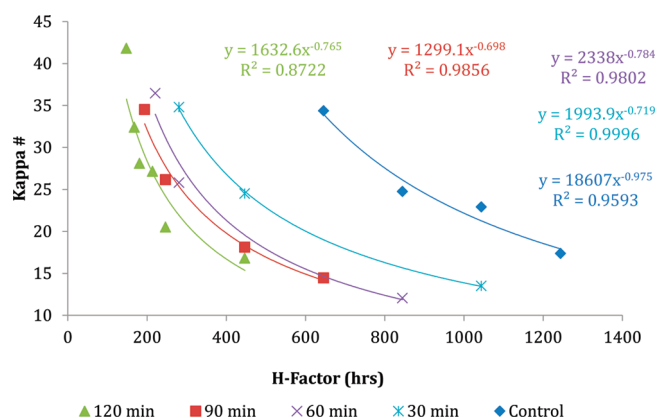


Figure 2. κ number of pulp vs H factor of pulping.

the same heating time of 30 min (see Experimental Section).

$$m(t) = \alpha[1 - \exp(-\beta t)] \quad (4)$$

The coefficient α can be interpreted as the maximum dissoluble fraction of wood (comprised in its majority by hemicellulose and only a small fraction of lignin) and coefficient β would be a pseudofirst order reaction rate constant (at 160 °C). This model was used to fit the data, with very high R^2 values. The coefficients are also given in Figure 1.

Figure 2 shows the κ number of the kraft pulps as a function of the pulping H-factor, at different pre-extraction levels. The conventional hyperbolic correlation of the kappa number with H-factor is obtained for the control (i.e., nonextracted) pulps. As pretreatment severity is increased, delignification is enhanced resulting in significantly lower κ numbers for the same H-factors.

Prehydrolysis treatment is known to accelerate the delignification of wood chips (see e.g., Sixta³⁰). That is, the time or temperature (H-factor) necessary to attain a certain kappa number is substantially reduced. The enhancement in delignification rate by pre-extraction can be correlated to a combination of the pre-extraction severity and the pulping H factors. Since the P factor expression is algebraically closest to the H factor, pre-extraction kinetics described through the P factor would be more suitable for the correlation.

Let us assume that kappa number is linearly proportional to the lignin content, denoted by L.

$$\kappa = AL \quad (5)$$

The delignification reactions in kraft pulping are represented by pseudo-first-order kinetics with a rate constant k_{l0} , (for an unextracted pulp). Then,

$$\kappa = AL_0 \exp(-k_{l0}t) \quad (6)$$

is a suitable model for the variation of the kappa number with time. For the sake of simplification, we ignore the H-factor during the ramp-up time. The H-factor is then the product $t \cdot k_{l0}/k_{\text{REF}}$. Denoting b as a scaling constant, eq 6 is given by

$$\kappa = AL_0 \exp(-bH) \quad (7)$$

When pulping pre-extracted chips, the pre-extraction kinetics changes the lignin content while enhancing the rate of delignification during subsequent pulping. This enhancement has been attributed to the increased porosity and probable decreased tortuosity in the chip.³³ Bolton et al.¹⁹ however concluded that although the chip porosity increased, this alone could not account for the increased delignification rates of extracted wood

Table 3. Coefficients in eq 14 via Multiple Linear Regression^a

parameter	estimate	standard error of estimated coefficient
A	3.7963	0.1059
b	7.3064×10^{-4}	1.445×10^{-4}
c	-5.2345×10^{-5}	2.741×10^{-5}
d	2.682×10^{-6}	4.096×10^{-7}
R^2	0.9436	

^a Standard errors of regression estimates are also provided.

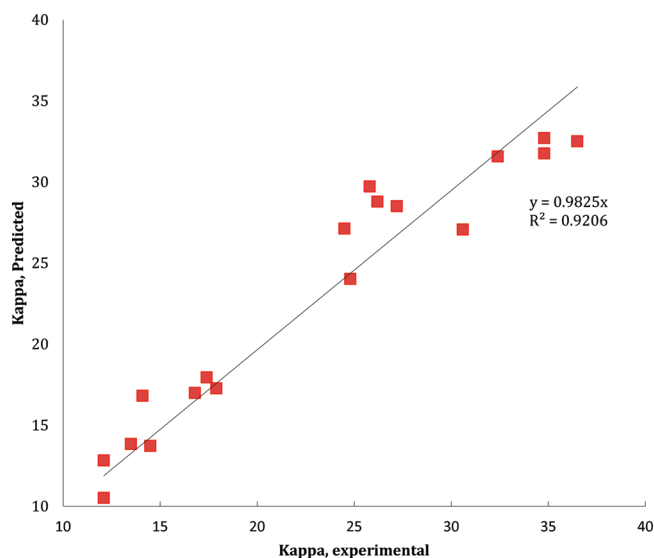


Figure 3. κ number predicted by correlation of eq 14 compared to experimental data of the same. The regression line is fitted to have a zero intercept. Slope of unity indicates perfect fit.

chips. We hypothesize that the delignification of extracted wood chips occurs at an enhanced rate but in a similar manner as the unextracted ones i.e. the kinetic constant (denoted by k_{lX}) is greater than that for the unextracted chips. The resulting κ number equation is given by

$$\kappa = AL_{x0} \exp(-k_{lX}t) \quad (8)$$

We define an enhancement factor, ε , understood as a phenomenological parameter including accelerated chip diffusion and other kinetic effects as

$$\varepsilon = \frac{k_{lX}}{k_{l0}} - 1 \quad (9)$$

Substituting into eq 8, we obtain

$$\kappa = AL_{x0} \exp[-k_{l0}(1 + \varepsilon)t] \quad (10)$$

We hypothesize that this enhancement factor depends on the pre-extraction factor, (the P-Factor) as

$$\varepsilon = c + dP \quad (11)$$

where c and d are suitable parameters. Substituting in eq 10, we obtain for the κ number of the chips

$$\kappa = AL_{x0} \exp[-(k_{l0}t + \varepsilon k_{l0}t)] \quad (12)$$

Table 4. Pulp's Composition for All Extraction Levels and κ Numbers

		components (%)														
		cellulose			xylan			other hemicellulose			lignin			other ^a		
		κ														
extraction time (min)	P-factor (h)	35	25	15	35	25	15	35	25	15	35	25	15	35	25	15
0	0	71.1	70.7	73.9	20.2	21.1	21.9	0.5	0.7	0.6	5.2	3.7	2.6	3.1	3.8	1.0
30	147.87	81.4	82.4	83.2	13.3	13.7	13.8	0.6	0.4	0.2	5.2	3.7	2.0	-	-	0.8
60	283.93	87.0	86.8	89.9	8.0	8.2	7.2	0.4	1.0	0.4	5.5	3.9	1.8	-	0.1	0.7
90	419.95	86.4	88.3	87.0	5.3	5.0	6.1	0.2	0.4	0.7	5.2	3.9	2.2	2.9	2.3	4.0
120	555.98	85.8	86.5	88.8	5.7	6.0	4.5	0.3	0.4	0.3	4.9	4.1	2.5	3.4	3.0	4.0
^a Calculated by difference. - indicates sum over 100%																

^a Calculated by difference. - indicates sum over 100%

and

$$k = AL_{x0} \{ \exp[-bH(1 + (c + dP))] \} \quad (13)$$

The lignin content L_{x0} represents the initial lignin concentration after pre-extraction. We hypothesize that this is given by an exponential dependence on the pre-extraction factor P . The factor f will be positive or negative depending on whether this lignin content is greater or smaller than the initial value.

$$L_{x0} = L_0 \exp(-k_{px}t) = L_0 \exp(-fP) \quad (14)$$

Substituting into eq 13, we obtain the model for the κ number as

$$k = AL_0 \exp\{-[bH + cP + dH.P]\} \quad (15)$$

where we have redefined the constants A , b , c , and d as new parameters to be chosen to fit the experimental data (viz., κ number vs H and P factors).

Table 3 shows the parameters of the correlation and the standard errors of the estimates. The coefficients of the correlation (b , c , and d) are all negative, indicating that the κ number decreases from the initial value with both pre-extraction and pulping. The coefficient b can be used to determine AL_0 and from it, A . The correlation coefficient is 0.951 indicating a reasonably good fit of the data.

Figure 3 shows a plot of the predicted versus experimental κ numbers along with a best fitting line whose slope is 0.984. Since a line with a slope of 1.0 represents a perfect of the model to experimental data, we conclude that the exponential correlation represented by eq 14 is adequate in describing the combined kinetics of pre-extraction followed by pulping.

Fiber Analysis. The composition of the pulp fibers was analyzed for cellulose, xylan, other hemicelluloses and lignin for each treatment level P -factor. Table 4 presents data on the fiber composition with pre-extraction severity indicated by the P -factors. The cellulose fraction in the pulps increases with the P -factor whereas the hemicellulose fraction decreases since pre-extraction yields a wood chip that is already lean in hemicellulose. For the control pulp, xylan accounts for 20–22% of the pulp's composition which decreases to between 4 and 6% after 120 min treatment. Since all the pulps were cooked to the same kappa level (± 1.7) the lignin content can be assumed to be fairly constant. This implies that the fraction of other components must increase. Since hemicellulose has been removed to a greater extent in the pretreated pulps and the lignin remains constant and

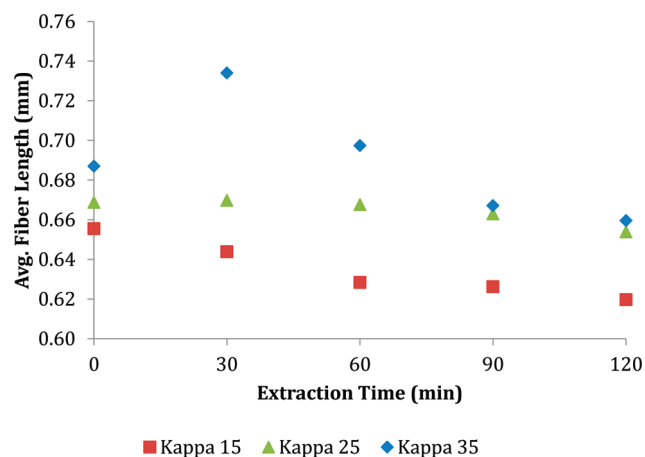


Figure 4. Length-weighted average fiber length versus extraction time, for three different κ numbers.

Table 5. Mass Removal, κ Number, and Cook Yield for All the Pulps Prepared

extraction time (min)	mass removal (%)	κ number	cook yield (%)
0	0	17.4/24.8/34.4	53.1/54.5/56.3
30	7.9	13.5/24.5/34.8	51.4/52.6/55.2
60	14.4	12.1/25.8/36.5	49.4/52.8/53.4
90	18.5	14.5/26.2/34.8	53.0/54.6/54.4
120	21.1	16.8/27.2/32.4	53.0/54.1/53.3

low, the cellulose content increases in the pulp. (We note that this assumes that the relation between the kappa number and lignin content in extracted pulps is similar to that in the unextracted pulps.) The table also shows the entire mass balance and we observe a good closure of the compositional balances. In the worst case, the total mass balance closure is 96% and the best is 99.9%.

Figure 4 shows the average fiber length (length averaged) as a function of extraction time for different κ numbers. It is clear that fiber length is not affected by the extraction, but is affected by the cook. As expected, the longer time of cook yields smaller fibers. This is in accordance with the trend noticed by Santos et al.¹¹ for Eucalyptus pulps.

Table 5 shows the mass removal and cook yield for every κ number pulp. As it can be seen the cook yield is not significantly

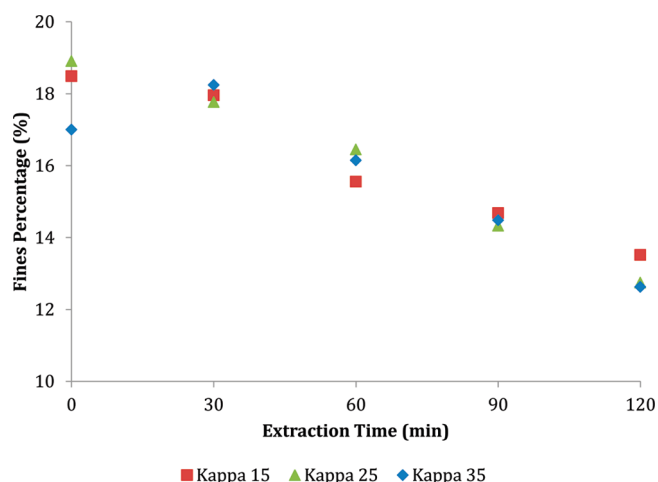


Figure 5. Fines percentage versus extraction time for three different κ numbers.

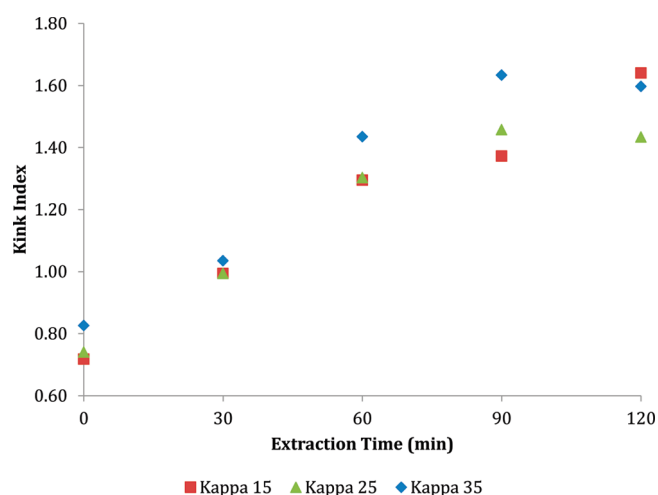


Figure 6. Effect of extraction time on the kink index of the fibers for all κ levels.

affect, if the differences in κ are taken into account. Also, there are evidence that, at least for chips extracted 60 min and more, the chemical conditions of the cooks (active alkali) should be milder (see viscosity results discussion).

The amount of fines, defined as fibrous material with sizes comprised between 0.07 and 0.2 mm, behaves similarly for all kappa levels, decreasing with extraction as shown in Figure 5. When extracted, other hardwood species however showed decreasing fiber length and increasing fines content.^{6,11} Our experiments with sugar maple do not show this behavior, perhaps because the pulping process was not strong enough to degrade the fibers themselves. On the other hand, the kink index of the fibers in Figure 6 shows a significant increase with pre-extraction time. Kinks can be visualized as regions in the fiber, where the crystalline structure is interrupted by damage and the fiber can thus fold and bend over other fibers.

This can be one of the reasons for the observation that these fibers do not refine properly.¹¹ Scanning electron micrographs in Figure 7 show that extracted pulps exhibit a slightly rougher surface than the control pulps for all kappa levels. This roughness is likely to be degradation on the surface as the hemicelluloses removed were

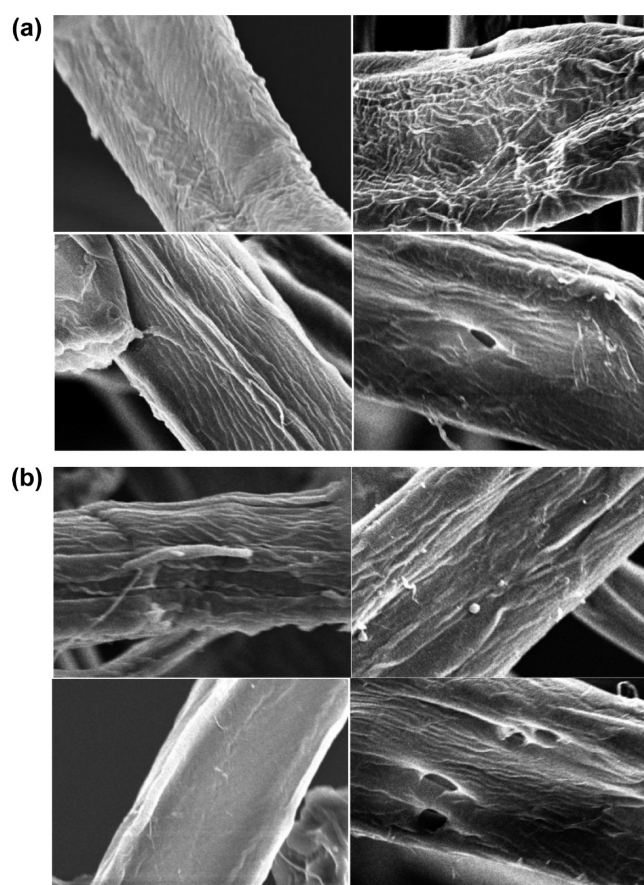


Figure 7. (a) SEM of Sugar Maple fibers with κ 15. Magnification: 7500 \times . Top: Extracted for 120 min. Bottom: Unextracted. (b) SEM of Sugar Maple fibers with κ 35. Top: Extracted for 120 min. Bottom: Unextracted.

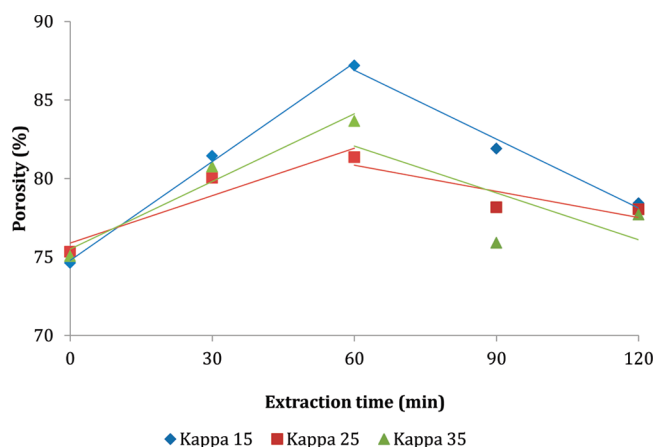


Figure 8. Effect of extraction time in eucalyptus pulp's porosity for all κ numbers.

likely to be on the surface of the fibers. This “damaged” surface may not be able to fibrillate properly when subjected to mechanical action and therefore they may not exhibit typical freeness development behavior when refined.^{16,4} The extracted fibers appear more kinked and curled whereas the control fibers appear straighter.

Figure 8 shows the porosity of the pulps measured as the ratio of the volume of mercury intruded into the pulp pads to the bulk

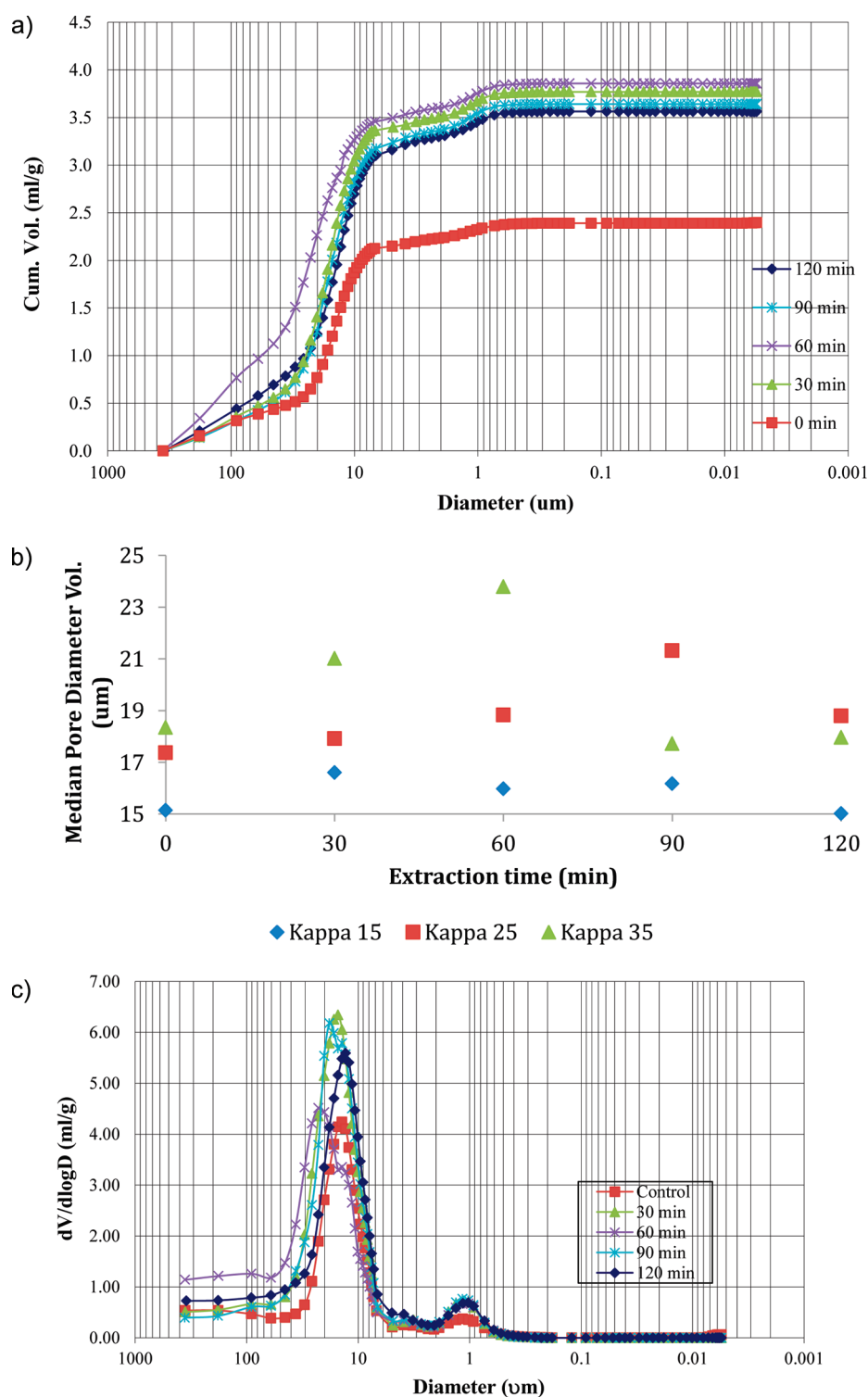


Figure 9. (a) Cumulative pore size distribution measured by mercury intrusion porosimetry (pulp κ number = 15). (b) Median pore diameter for different extraction times. (c) Cumulative pore size distribution measured by mercury intrusion porosimetry. Pulp κ number = 15.

volume. It appears that the porosity increases with pre-extraction time until 60 min after which, it begins to decrease. It is possible that after this time, the fibers lose too much of their cell wall mass and therefore begin to collapse.

Figure 9a shows the cumulative volume distribution for different extraction times. Figure 9b shows the median pore size of the pulp

pads versus extraction times. Both these figures show that as extraction proceeds, the pore size in the handsheets increases at first but reduces at higher levels of extraction. This behavior also indicates more sheet consolidation when the fibers are extracted to higher levels.

Figure 10 shows the pulp viscosity, which initially increases with extraction but starts to decrease after 60 min. All the pulps

showed this behavior in viscosity. Similar observations have been made for eucalyptus pulps.^{6,11} Pulp viscosity depends on the DPs of its components, cellulose and hemicellulose. Since pre-extraction removes increasing amounts of the lower DP hemicellulose, the increase in pulp viscosity can be anticipated.

The following analysis can be used to estimate the viscosity increase because of removal of the hemicelluloses. Assuming that the viscosity can be described by a linear combination of the contributions due to the cellulose and hemicellulose the following equation results.

$$\mu = f_C \mu_C + f_H \mu_H \quad (16)$$

where f_C and f_H are the cellulose and hemicellulose mass fractions and $\mu_{C,H}$ represents the contribution to viscosity from cellulose and hemicellulose. Since the DP of hemicellulose is much smaller than that of the cellulose, we can anticipate that $\mu_H/\mu_C \ll 1$. The relative viscosity increase is given by the following equation where μ^0 denotes the control viscosity.

$$\frac{\mu}{\mu^0} - 1 = \left(\frac{1 - f_H}{1 - f_H^0} - 1 \right) \quad (17)$$

The maximum in the viscosity with pre-extraction severity means that the continued extraction results in fiber damage perhaps because of the increased accessibility of the cooking liquor to the crystalline cellulose. Therefore, to preserve the fiber strength and crystallinity at these extraction levels, the cooking liquor should be weaker. The initial increase of viscosity may be caused by decreased hemicellulose content or by the increase of

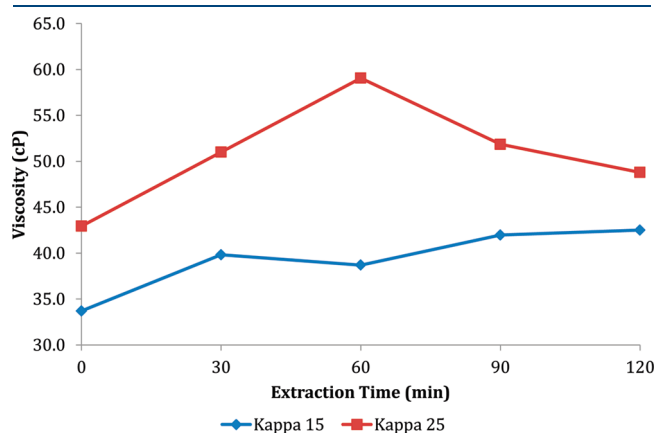


Figure 10. Pulp viscosity as a function of extraction time.

the degree of polymerization (DP) of the pulp (i.e., remaining cellulose fraction). Hemicellulose removal cannot increase viscosity by more than 29%, assuming its contribution to viscosity is in proportion to its mass fraction. Since in some cases the increase is higher than 29%, the degree of polymerization of the cellulose component must have been increased, that is, it must have been better preserved than in the control pulp. For the viscosity of pulps from extractions of 30 and 120 min durations, the removal of hemicellulose contributes to increases in viscosity of 10% and 21%, whereas the observed increases at 19% and 26%, respectively. Table 6 gives the measured pulp viscosity at different extraction levels. Estimated increase in viscosity by the composition change, that is, reduced hemicellulose and increased cellulose content is also shown in this table. Most of the viscosity increase can indeed be traced to hemicellulose removal although not all of it. Removal of the hemicellulose fraction is known to increase the crystallinity index of pulp fibers in the case of softwood fibers.³⁴

The Canadian Standard Freeness (CSF) of the pulps increases with extraction, which is in accordance with the decrease of fines content. Figure 11a shows the CSF of the pulps as a function of pre-extraction. The water retention value (WRV) of the pulps is shown in Figure 11b as a function of pre-extraction time for the three pulps. The WRV seems to increase probably because the fiber porosity has increased.

The ζ potential of the pulps decreases with pH and the fibers become more negatively charged. Higher pH results in stronger dissociation of the surface carboxyl groups. Extraction results in a slight increase in the ζ potential perhaps due to the increased porosity resulting in increased accessibility to the surface lignin groups (Figure 12a). Sousa et al.¹¹ did not find a significant change in the surface charge of fibers when the hemicellulose content decreased. Although there is a great difference in hemicellulose content, the total polysaccharide fraction remains in the range of 90–96%. The cationic demand of the pulps initially decreases with extraction as shown in Figure 12b, but it does not seem to change significantly after 30 min. The first decrease is expected since there is a decline in the xylan content, which contributes to the total amount of charged groups in the pulp. Moreover, the decrease of fines with extraction should also contribute to the decrease of the cationic demand of the pulp.

The impact of removing hemicelluloses from the chips prior to pulping results in changes in the fibers. These changes can significantly impact the properties of the paper produced from these pulps. To investigate the impact of such changes, we tested handsheets prepared from a set of control (i.e., from unextracted

Table 6. Pulp Viscosity Increase: Observed and Maximum Expected Resulting from Hemicellulose Removal

extraction time (min)	κ number of pulp	viscosity, mPa s average, (std. dev)	hemicellulose content (%)	observed viscosity increase (%)	maximum increase due to hemicellulose removal (%)	increase difference (%)
0	15	33.7 (0.1)	21.90	0	0	0
0	25	42.9 (0.5)	21.10	0	0	0
30	15	39.8 (0.1)	13.80	18	10	8
30	25	51.0 (0.4)	13.70	19	10	9
60	15	38.7 (n.a)	7.20	15	18	0
60	25	59.1 (1.1)	8.20	38	18	20
90	15	42.0 (0.2)	6.10	21	21	0
90	25	51.9 (1.6)	5.00	25	21	4
120	15	42.5 (1.1)	4.50	14	21	0
120	25	48.8 (0.8)	6.00	26	21	5

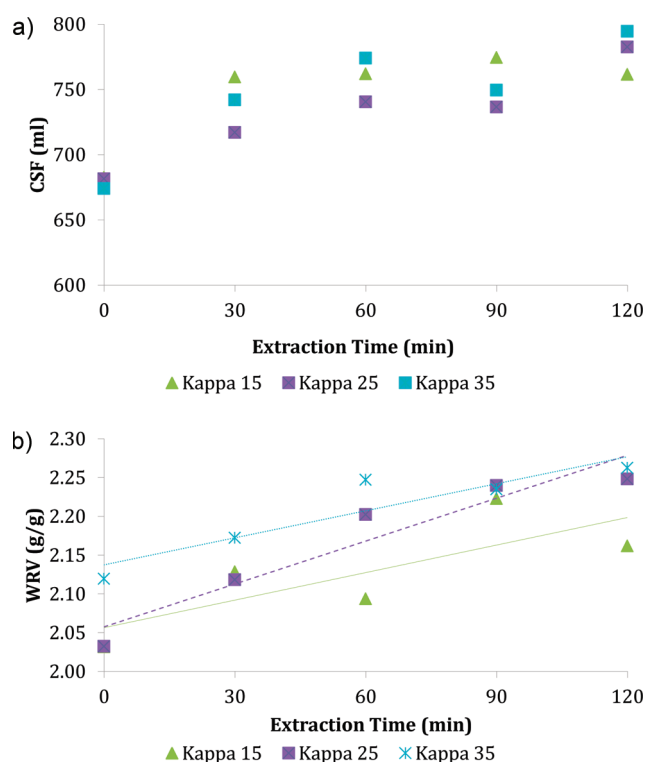


Figure 11. (a) Effect of extraction time in the pulp freeness value. (b) Effect of extraction time in the pulp water retention value.

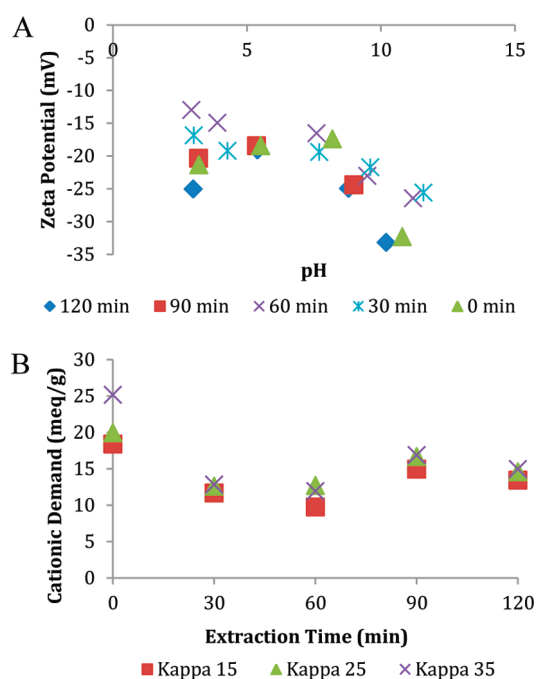


Figure 12. ζ Potential (κ 15) (A) and cationic demand (B) versus pH.

chips) and extracted pulps. The properties of the pulp from chips extracted at the highest severity (120 min) were compared with the properties of the control pulps for all κ levels. Table 7 shows a significant decrease (25–46%) in the tensile index. Pulps containing higher lignin (i.e., higher κ numbers) have lower tensile strength. Lignin containing fibers are less swollen and not as

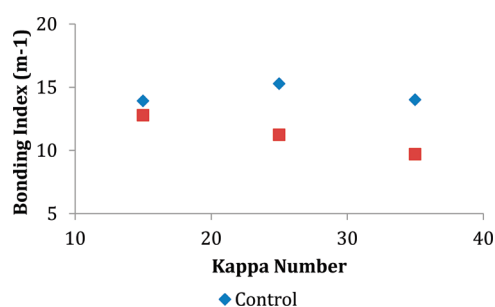


Figure 13. Bonding index as determined by the ratio of tensile strength and zero span strength (according to TAPPI T231).

flexible or collapsible as fibers containing low lignin contents. Flexible fibers drape over each other during paper formation and bond well, leading to higher tensile and other strength properties. The tensile strength of pulps increases as kappa number is lowered. The effect of pre-extraction is to remove some of the hemicellulose resulting in reduced bonding, decreasing the tensile strength. Table 6 provides data on the mechanical properties of handsheets made from extracted pulps and unextracted pulps. It is evident that the extracted pulp has lower strength properties; the tensile and tear indexes are lowered upon extracting the chips. The same is true for the burst strength also. The decrease in strength properties of sheets made from hemicellulose extracted fibers has been widely reported. Hemicellulose flexibilizes fibers and serves as a bonding agent between fibers in paper sheets. It is thus responsible for the bonding area and also its strength in the sheet. Its removal during the pre-extraction process offers less bonding ability in the resultant sheets and therefore reduced strength properties.

The stiffness index on the other hand shows a curious behavior. Paper stiffness is proportional to the elastic modulus of the sheet (E) and its caliper, that is, thickness (t) ($S^b = Et^3/12$). Stiffness increases at the higher κ pulps because although stiffer fibers lower paper strength or elastic modulus, it increases the thickness or sheet bulk which overwhelms the effect on the elastic modulus. Since extracted fibers tend to be bulkier (i.e., of lower density) sheets with the same basis weight will have more fibers. Extracted fibers could also be stiffer because their crystalline fraction has increased. Both these factors can result in an increased sheet thickness (results not shown), which should yield increased stiffness. The results in Table 7, however, do not show stiffness increase upon extraction. When the pulp is delignified further to κ 25, the stiffness suffers a decrease, perhaps because pre-extraction damages the cell wall introducing significant kinks into it. Pre-extracted fibers showed large increases in the kink index observed earlier. Such fibers can twist and break in the paper mat while being pressed and reduce the sheet thickness. Since these fibers do not bond very well, the overall stiffness is lowered because the elastic modulus suffers. The stiffness of the pulp with kappa number 15 seems to increase upon pre-extraction. It is possible that the reduced fines level in the pulp results in increased stiffness although this behavior needs to be investigated in more detail.

The air permeability of paper sheets is represented by the time taken for air to permeate through the sheet (Gurley seconds). The resulting air resistance increases as pulp is delignified, primarily because of sheet densification and better fiber flexibility and bonding. Extraction increases air resistance because the fibers are more kinked and rougher (increased specific surface area). It can also decrease air resistance because the sheets are

Table 7. Mechanical Properties of Paper from Pre-Extracted Wood Chips^a

sample	κ number	tensile index, N·m/g	tear index, mN·m ² /g	stiffness, SU	burst index, kPa·m ² /g	zero span strength, N	Gurley's air resistance, s
0	15	38.7	6.00	2.08	1.77	175	1.48
120	15	28.8	3.73	1.98	1.09	147	1.60
0	25	43.2	6.72	2.31	1.73	185	1.40
120	25	23.1	3.25	1.92	0.76	131	1.32
0	35	35.4	5.85	2.06	1.32	164	1.22
120	35	21.7	3.78	2.18	0.71	154	1.28

^a Sample 0 refers to control wood chips pulped in conventional kraft pulping.

bulkier and may contain fewer fines. These two factors counteract each other and the net result can vary. This can be seen by close examination of the results in Table 7, where extraction seems to increase the air flow resistance at high kappa number but decreases at the intermediate value.

It would be of great interest to measure the individual fiber strength to evaluate the effect that HWE has on the fibers' strength. However, this is very complicated and tedious to do, since it involves a tremendous number of fibers to be tested (to have a representative value), extreme caution when handling the fibers (not to damage them), expensive equipment to test them and highly skilled technicians. Therefore, the zero-span tensile strength (ZSTS) has often been used to quantify the fiber strength.³⁵ From the comparison between the extracted and control paper properties it is clear that there is a significant loss of fiber strength (as measured by ZSTS). This could be due to the enormous increase of kink index and is in accordance with what other researchers have found regarding the effect that the number of kinks on has ZSTS.^{36–38} Furthermore, the ZSTS is highly dependent on the kink index of the pulps (Figure 6). When ZSTS is used in combination with tensile strength, it is also possible to calculate a bonding index. This has the added advantage that both the ZSTS and tensile strength are measured on the same handsheet, and so the state of the fibers tested is the same in the two measurements, which does not happen when testing the fiber strength of individual fibers. Other researchers have measured single fiber strength and compared it with the fiber strength estimated from the ZSTS, obtaining values up to 55% higher than the estimation.³⁸ One final interesting observation pertains therefore to the bonding "ability" of the papers. Figure 13 shows that with extraction, pulp fibers lose their bonding ability, as reflected by the bonding index. This is expected and widely accepted, as hemicelluloses have a great influence in the interfiber bonding. However, the bonding index difference is smaller for lower kappa number. Indeed, at κ 15 the bonding index dropped only 8%, whereas at κ 35 the drop was of 31%.

CONCLUSIONS

It is clear that HWE has a serious affect in several pulp properties and consequently in the paper produced from these pulps. The first and most important parameter that is affected is the pulp composition. As extraction takes place, hemicelluloses are preferentially removed, dropping from 20 to 22% in the control to 4–6% in the highest extraction level. These differences in composition are very significant and can be responsible for the observed differences in the mechanical properties of the paper, WRV, viscosity, and morphological properties. In what concerns xylan content, the difference

between 90 and 120 min extracted pulps is not very significant, and therefore, it may not be advantageous to extract the chips for more than 90 min.

The HWE does not seem to have any significant effect on the ζ potential of the pulps. However, the cationic demand of the pulps initially decreases with extraction (from 0 to 30 min), unexpectedly reaching a plateau, although the fines content keeps on decreasing.

The viscosity of the pulps increases and exhibits a maximum at 60 min extraction. The existence of a maximum in viscosity suggests that the cook might be too harsh for the higher extraction levels. Therefore reducing the chemical used at higher extracting levels may be recommended. It was also evident that the increase of the viscosity is due to two factors: the removal of the lower degree of polymerization fraction (hemicelluloses) and the increase of the degree of polymerization of cellulose, although the first is primarily responsible. The results regarding the WRV are unexpected. The removal of hemicellulose and the decrease in fines content were expected to decrease the WRV. As for the paper properties, there is a general decrease in the paper properties with few exceptions. Therefore, papers produced from these pulps will exhibit weaker properties, unless something is done to compensate the lack of hemicelluloses.

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ACKNOWLEDGMENT

The authors would like to thank Mr. Thomas Haller and Dr. Bruce Evans from Specialty Minerals Inc. for their help and for making their facilities and equipment available when needed.

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