

Kraft pulping and papermaking properties of hot-water pre-extracted loblolly pine in an integrated forest products biorefinery

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ABSTRACT: Our objective in this research was to investigate the effect of hot-water pre-extraction of softwood on the behavior and papermaking properties of kraft pulp. Loblolly pine wood chips were treated with pressurized hot water at an elevated temperature of 170°C until the H-factor reached 200 and 500 hours. Kraft pulping of the extracted wood chips, performed at 15% effective alkali charge and 30% sulfidity, showed significantly improved delignification rates with 40% to 60% higher rate constants than corresponding kraft control cooks. The total pulp yield based on the original wood at a given kappa number was 3% and 6% lower than the control at the pre-extraction H-factors of 200 and 500 hours, respectively. The water pre-extracted kraft pulps showed a reduced refining response to PFI mill refining. The handsheets prepared from bleachable-grade pulps, after kraft pulping of hot-water pre-extracted wood chips for 400 H-factor hours, showed reduced tensile strength because of the lower percentage of hemicelluloses, compared to the control; but comparable pulp viscosity, zero-span wet tensile strength and tear resistance.

Application: This study can aid kraft pulp mill operators who are considering hot-water extraction of hemicellulose sugars for the development of new revenue streams.

BACKGROUND

Managed forests in the United States have enormous untapped potential as sources of bioenergy and biomaterials. Realizing this potential requires an approach that integrates new separation and conversion technologies with existing forest products procurement, production and delivery infrastructures. The objective of integrated forest products biorefineries (IFBR) is to adapt existing chemical pulp mills to produce new biomaterials and export renewable energy while continuing to meet growing demand for pulp and paper products [1].

In an IFBR a significant amount of hemicelluloses are extracted from the residual wood chips prior to kraft pulping [2]. The relatively pure extract of hemicellulose oligomers or polymers may then be used as feedstock for sugar-based transportation fluids, polyester polymers and chemicals. The rationale for the pre-extraction is that the fuel value of the hemicelluloses is only half of that of lignin (13.6 MJ/kg versus 27 MJ/kg) [3]. In addition, the hemicelluloses degrade during kraft pulping to a complex mixture of sugar acids, which are difficult to separate and purify into sizable streams of value-added products [4].

However, since the value of kraft pulp is still the most important concern, it is important that the pulp yield based on the original dry wood weight be maintained after the pre-extraction process. In a companion publication [5], it has been reported that a maximum of about 12% of the wood mass was extracted as wood sugars at an H-factor of about 1,500 hours and a maximum of about 8% of hemicelluloses were extract-

ed as polymeric sugars with a minor removal of lignin (0.5% on ODW) and cellulose (0.3% on ODW) at an extraction H-factor of about 500 hours. During kraft pulping of softwoods, about 15%-20% of the wood weight as hemicellulose (25%-30% in wood) ends up in spent pulping liquor [4]. Therefore the combined amount of softwood hemicelluloses removed in the pre-extraction and pulping processes should be no more than 15% - 20% (based on wood). Our investigation explores whether this objective can be achieved with pure water pre-extraction and subsequent kraft cooking of loblolly pine chips. We investigated the effect of time and temperature on hemicellulose extraction and on the yield and properties of the resulting pulp. We then compared the results to regular kraft pulps of the same kappa number.

EXPERIMENTAL

International Paper Co. supplied fresh loblolly pine chips. Chips with defects, including barks, knots and decayed parts, were removed before screening in a Weyerhaeuser classifier equipped with 10mm wide slots and 7/8 in., 5/8 in. and 5mm round screens. In the first stage of experiments, we subjected the wood chips to hot-water pre-extraction for 6 min and 25 min at a preset extraction temperature (170°C) to attain 200 and 500 H-factor hours, respectively. After completion of pre-extraction, we replaced about 60% of the total volume of the extract with kraft cooking liquor for subsequent pulping. The effective alkali charges were 15% for pre-extraction kraft pulping and 15% and 17% (all as Na₂O) for the kraft controls. In all cases, we employed a constant sulfidity of 30% and liquor-to-

wood ratio of 4:5. The profiled digester used in both pre-extraction and kraft pulping works was a 6-L stainless steel high-pressure vessel equipped with an external heat exchanger and a forced liquor circulation system.

For each pre-extraction and kraft cook, we charged 400 g (oven-dry basis) of wood chips into the digester in addition to the prepared liquor containing the desired amounts of chemical and water. Cooking times at 170°C were varied to obtain different kappa numbers. Pulps obtained from each cook were disintegrated in a blender and thoroughly washed on a 200-mesh screen with warm tap water. We then air-dried the pulps for measurement of pulp yield, kappa number and intrinsic viscosity, using standard testing methods. We determined the residual effective alkali concentration of the final black liquor using a modified SCAN-N 33.94 Method. In this method 10 mL samples are diluted ten times and then titrated with 0.5N HCl up to the end point of pH 11.3 [6,7].

In the second stage of experiments, bleachable-grade pulps obtained after kraft cooking were hot-water pre-extracted up to 400 H-factor hours. We subjected these pulps to PFI mill refining to prepare them for evaluation of the refining response and handsheet properties over a broad range of degrees of refining. The Canadian Standard Freeness (CSF) was determined using TAPPI standard T227 [8]. TAPPI standard T205 was used to prepare handsheets from the refined pulps. The basis weight, tensile strength, wet zero-span tensile strength and tearing resistance were measured according to procedures described in TAPPI standards T494 and T414 [8].

RESULTS AND DISCUSSION

Kraft pulping of pre-extracted and control loblolly pine chips

To obtain a relatively high yield of polymeric hemicellulose in the extract, but at the same time minimize the degradation of cellulose, we pre-extracted the loblolly pine chips using pure water before pulping at H-factors of about 200 and 500 hours. We then subjected the pre-extracted wood chips to pulping at 15% effective alkali charge and 30% sulfidity. The cooking results were compared with two reference controls (at 15% and 17% effective alkali charge and 30% sulfidity). We estimated the wood weight loss of the loblolly pine chips at about 5.0% and 7.9% after pre-extraction with water at 200 and 500 H-factor hours, respectively, based on the results in our previous publication [5].

Rate of kraft delignification

We calculated the percentage of residual lignin (as % on wood), L_r , as:

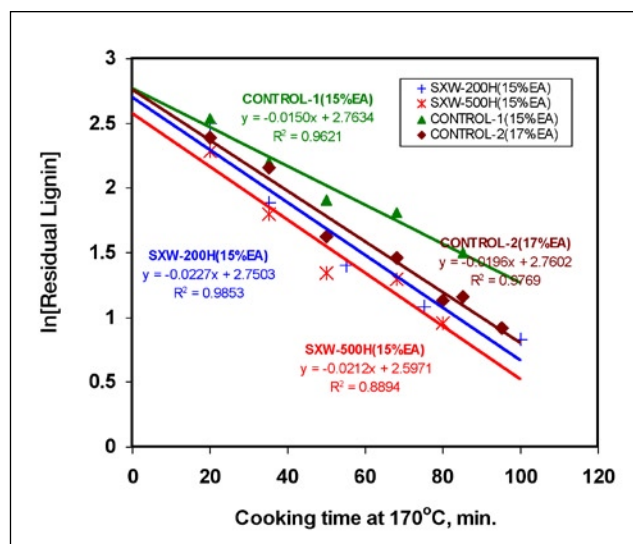
$$L_r = 1.5 \times 10^{-3} [Kappa] \cdot [Yield(\%)] \quad (1)$$

The overall rate of delignification in the bulk or late bulk kraft pulping phase, during which the variation in hydroxyl and hydrosulfide ion concentrations are considered to be moder-

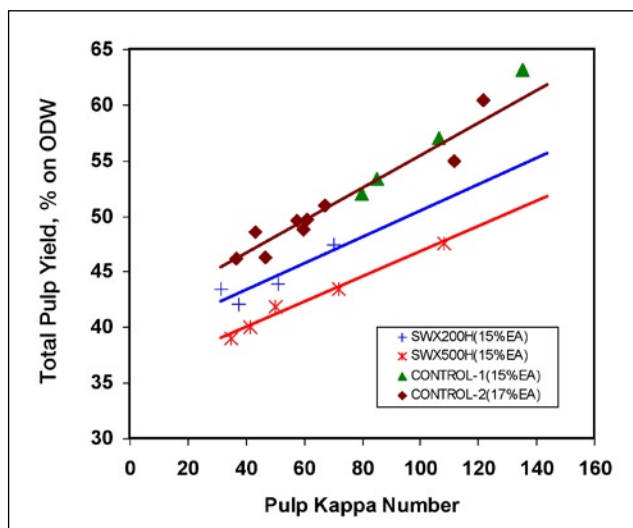
ate, would follow homogeneous pseudo-first order reaction kinetics [9] as:

$$-\frac{dL_r}{dt} = kL_r \quad (2)$$

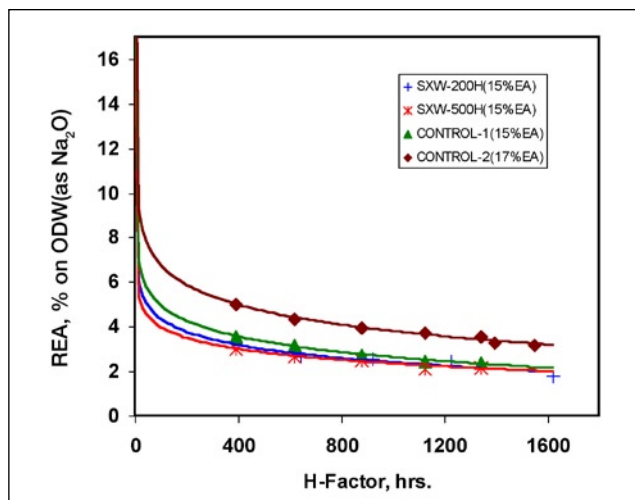
where t is time at the maximum temperature and k is the delignification rate constant. The delignification rate constant, k , can be calculated from the slope of the regression lines through data plots of $\ln(L_r)$ against t . **Fig. 1** shows the semi-log plots of the delignification as a function of pulping time at 70°C for both the pre-extracted and control cooks. All the pre-extraction-kraft cooks showed significantly higher delignification rates than the kraft control cooks. The im-



1. Semi-logarithmic plots for residual lignin (based on wood) as a function of pulping time at 170°C. (SXW-200H or -500H in legend indicates the kraft cook conducted with softwood extracted with water for 200 or 500 hrs of H-Factor, respectively).



2. Total pulp yield (on wood basis) versus pulp kappa number for 170°C kraft pulping of loblolly pine chips.



3. Plot of residual effective alkali concentration versus H-factor.

provement in delignification rate may possibly be due to an increased accessibility of the cell wall and cleavage of lignin-carbohydrate covalent bonds during pre-extraction [10]. The semi-log plot of the delignification rate is shown in **Fig. 2**.

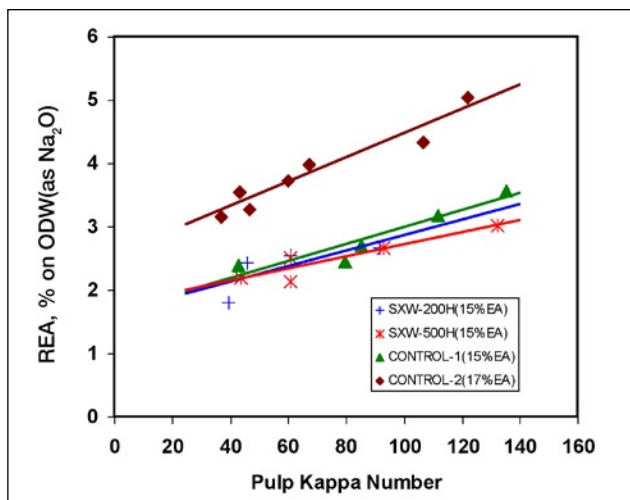
The delignification rate constants determined from each regression result, with R^2 's ranging from 0.89 to 0.99, were 0.0227, 0.0212, 0.0150, and 0.0196 min^{-1} for SXW-200H(15%EA), SXW-500H(15%EA), Control-1(15%EA), and Control-2(17%EA), respectively. The delignification rate constants for 15% effective alkali kraft cooking of water pre-extracted chips were 40% to 60% higher than the kraft control cooks at 15% effective alkali charge. Compared to the 17% effective alkali control cooks, the 15% effective alkali cooks of water pre-extracted chips still showed a 10% to 20% higher k value. This improvement in delignification rate for water pre-extracted chips leads to a pulp production rate increase.

Total pulp yield

In order to evaluate the delignification selectivity of the water pre-extracted wood chip cooking, total pulp yields were plotted against pulp kappa numbers as shown in Fig. 2.

As expected, we observed a linear relationship between total pulp yields and pulp kappa number for the water pre-extracted kraft and kraft control cooks. Total pulp yield based on wood at the same kappa number decreases as the H-factor for water pre-extraction increases from 100 to 500 hrs. A total pulp yield decrease at Kappa 30 of approximately 3%, compared to the control cooks, was observed for the 200 hour H-factor pre-extracted chips. For the 500 hour H-factor pre-extracted chips the yield loss approximately doubles to 6%. These values compare to extraction yields (based on wood) of 5% and 8%, respectively.

These results show that additional wood sugars are removed during kraft pulping of pure water pre-extracted chips, compared to those which end up in the black liquor during conventional kraft cooking to the same kappa number. More research is needed to understand better the mechanism



4. Residual effective alkali versus pulp kappa number for 170°C kraft pulping of loblolly pine chips.

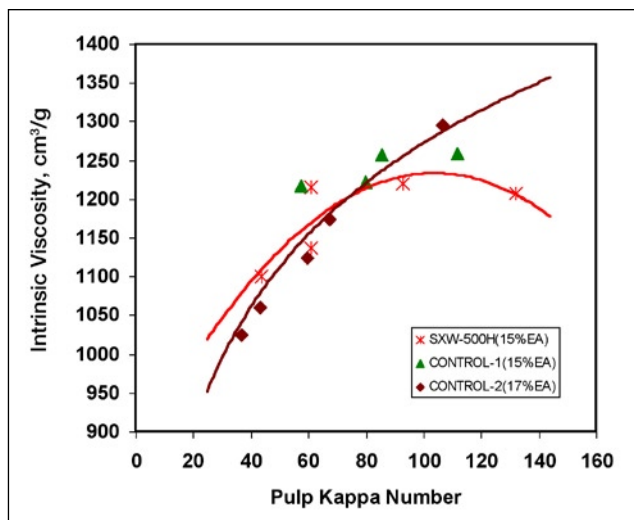
for this additional wood sugar loss, so that operating procedures can be defined to minimize this loss.

Effective alkali consumption

The residual effective alkali concentration (REA) was plotted as a function of H-factor, as shown in **Fig. 3**. This figure shows that approximately 70% to 80% of the charged effective alkali is consumed at an H-factor of 400 hours for the two control kraft cooks (15% EA and 17% EA charges) and that of the kraft cooks after water-extraction (15% EA charge). This result is in good agreement with literature on alkali consumption before the onset of the main delignification reactions [11]. The alkali is consumed by end-wise degradation of polysaccharides, neutralization of acetyl groups cleaved from hemicelluloses and neutralization of the acid groups formed during kraft pulping [11]. In the bulk stage of delignification, however, relatively little alkali is consumed. No significant difference in REA was observed between the 15% EA kraft cook with water-extracted wood chips and the 15% EA conventional process. This indicates that water-extraction before kraft cooking of softwood chips has no significant effect on alkali consumption compared to the conventional kraft cooking.

The REA was plotted as a function of pulp kappa number as shown in **Fig. 4**.

The results show that the REA of 15% EA kraft cooks for water-extracted wood chips is approximately 1% lower than the 17% EA control cook at bleachable grade kappa numbers (30-40 kappa). However, the data also show that the alkali consumption of the water-extracted 15% EA kraft cook is essentially the same as that of the 15% EA control cook. This result implies that the alkali consumption savings during kraft pulping due to pre-extraction of sugars are offset by additional alkali consumption due to additional carbohydrate removal during kraft cooking. Thus it appears that pre-extraction leads to additional peeling of wood sugars that



5. Intrinsic viscosity versus pulp kappa number for 170°C kraft pulping of loblolly pine chips.

are retained in the control pulp. The mechanism underlying this additional consumption of alkali should be studied in order to define operating conditions that would lead to savings in effective alkali consumption during kraft cooking after pre-extraction.

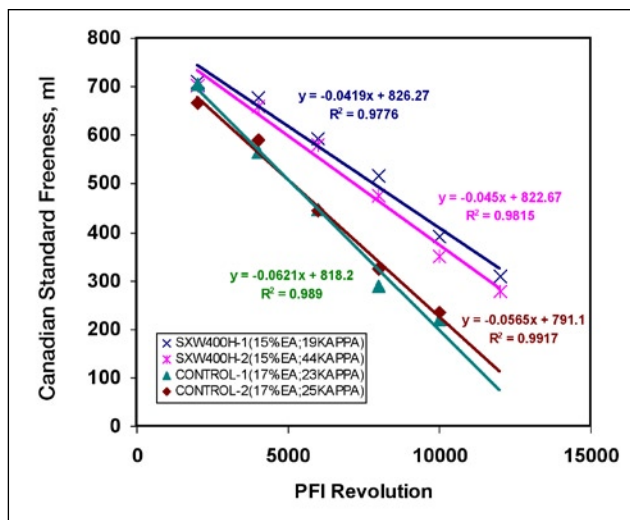
Pulp viscosity

The high kappa number pulp samples above 35, both from conventional kraft cooks and kraft cooks from water pre-extracted wood chips (500 H-factor), were subjected to mild chlorite delignification for the measurement of intrinsic viscosity. **Figure 5** shows the intrinsic viscosity of the pulps versus kappa number. It shows that the cellulose - lignin selectivity during kraft pulping is not affected by mild pre-extraction with pure water at a 500 H-factor. This means that these pre-extraction conditions are mild enough so that acid hydrolysis of cellulose during extraction is minimal. It also suggests that the fiber strength properties of the pre-extracted pulps will be similar to that of the control pulps. Further physical testing of the pulps beaten to different freeness values is needed for conformation and for paper strength evaluation.

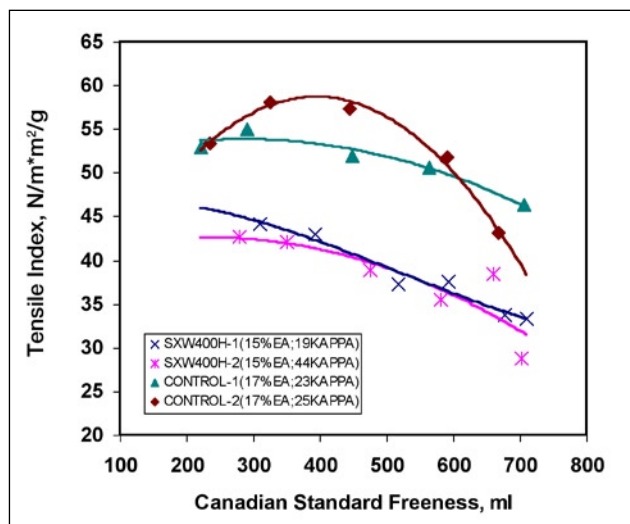
Refining response

The PFI mill refining responses of pulps obtained from kraft cooks with hot-water pre-extracted wood chips and conventional kraft process are shown in **Fig. 6**.

The refinability of a pulp is the ease with which the pulp fibers can be fibrillated internally and externally and shortened to some extent in water under a mechanical action. Pulp freeness (CSF) indicates the ease with which water drains away from the papermaking fibers while they are being formed into a wet mat on the drainage plate of the Canadian standard freeness tester. As expected, pulp freeness decreased as PFI mill revolution increased for each pulp type.



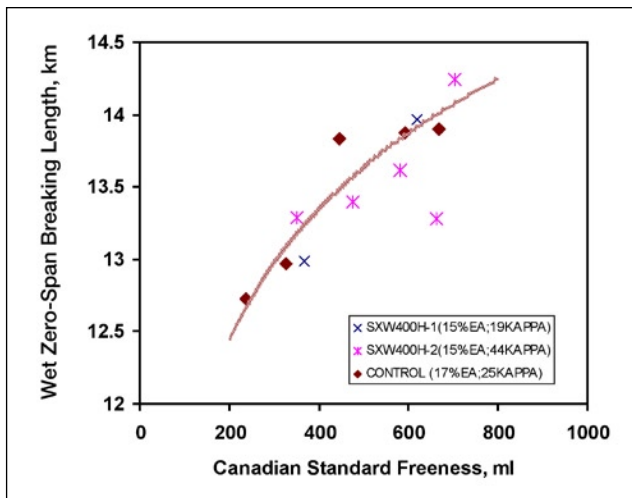
6. Plot of pulp freeness (CSF) versus PFI mill revolution for hot-water extraction Kraft cooks and controls.



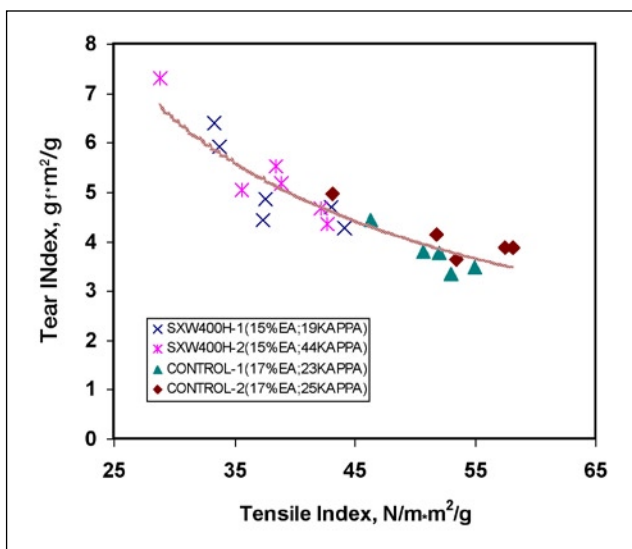
7. Plot of tensile index of handsheets for water pre-extraction kraft pulps versus pulp freeness.

A fairly linear relationship was observed between freeness and degree of refining, as can be seen in Fig. 5. The hot-water pre-extraction pulp appeared to need much more beating to attain the same level of freeness, most likely due to the lower percentage of hemicelluloses. As a broad generalization, pulps that are low in hemicelluloses are very resistant to refining and have poor strength characteristics, whereas pulps that contain a high percentage of hemicelluloses beat very quickly and produce strong sheets [12]. Brauns, et. al., [13] reported that when a wood pulp is purified by alkali extraction to the point where it contains about 99% alpha cellulose, it cannot be refined at all and will not make satisfactory paper, since the fibers do not swell in water and remain shrunken. Leopold [14] reported that the hemicellulose most responsible for the swelling or the increase in the plasticity of cellulose with refining was glucomannan.

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8. Plot of wet zero-span breaking length as a function of CSF of pulps.



9. Plot of tear index as a function of tensile index of handsheets.

Handsheet properties

We plotted the tensile strength of handsheets versus the CSF of each pulp type as shown in **Fig. 7**. We observed a significant loss in tensile strength of handsheets prepared from the water pre-extraction pulps compared to the controls at a given freeness level. The negative effects of pre-extraction on the tensile strength of kraft pulps could be explained by the low interfiber bonding ability of the hemicellulose-poor pulps after a certain degree of refining. It has been generally accepted that glucomannan in softwood pulp is more effective in fiber bonding than xylan in hardwood pulp because of glucomannan's primary hydroxyl group [15].

Figure 8 shows the zero-span wet tensile strengths of handsheets plotted as a function of CSF. With somewhat scattered data, a higher correlation could be obtained between zero-span wet breaking length and CSF of pulps ($R^2=0.85$). We observed no significant difference in zero-span wet tensile strength between water pre-extraction pulps and the

control pulps. Zero-span wet tensile strength is an index of the average ultimate strength of the randomly oriented fibers and may be regarded as the maximum possible normal tensile strength that can be developed under ideal beating conditions. Therefore, the results shown in **Fig. 7** indicate that pre-extraction of wood chips with water prior to kraft pulping does not significantly reduce the strength of individual fibers obtained from the kraft pulping. This result is clearly in good agreement with the results obtained from the intrinsic viscosity analysis in **Fig. 5**.

Figure 9 shows a plot of tear resistance versus tensile strength of handsheets obtained from water pre-extraction kraft cooks.

We observed no significant difference in tear resistance between the kraft pulps obtained from hot-water pre-extraction followed by kraft pulping and the control handsheets. Tearing resistance is known to depend on total number of fibers participating in the sheet rupture, fiber length, and number and strength of the fiber-to-fiber bonds [16]. Thus, the comparable tear strength observed in handsheets obtained from pre-extraction followed by kraft pulping over a broad tensile strength ranges also suggests that their fiber strength is the same as that of the control fibers.

SUMMARY

We conducted this study to investigate the effect of pre-extraction of loblolly pine with pure water on the pulping behavior and papermaking properties of pulp after subsequent kraft pulping. We determined pulp yields, kappa number, intrinsic pulp viscosity, handsheet properties including tensile strength, zero-span wet tensile strength and tear resistance using standard testing methods. The results were compared to kraft pulps of the same kappa number. The delignification rate constants for kraft cooking of water pre-extracted chips were 40% to 60% higher than corresponding kraft control cooks performed at 15% effective alkaline charge and 30% sulfidity. Unfortunately the total pulp yield based on the original wood at kappa 30 is 3% and 6% lower than the controls at pre-extracting H-factors of 200 and 500 hours, respectively, while the alkali consumption was the same as in the control pulps. The water pre-extraction kraft pulps showed slower refining response and lower tensile strength due to their lower percentage of hemicelluloses in fibers compared to the controls. However, they exhibited comparable pulp viscosity, zero-span wet tensile strength and tear resistance. More research is needed to understand the mechanism underlying the lower pulp yield with water pre-extraction. **TJ**

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INSIGHTS FROM THE AUTHORS

The paper industry today needs to increase revenue streams by producing bioenergy and biomaterials in addition to pulp and paper products. Our research deals with kraft pulping and papermaking properties of pulps from hot-water extracted softwood. Previous studies have been focused only on hemicellulose extractions using hot water. The most difficult aspect of our research was that almost no related data was available. The most surprising finding from our research was that kraft pulping of pre-extracted softwood chips showed 40% to 60% higher delignification rates. Our research results may be used by pulp mills considering implementation of the biorefinery concept of hemicellulose pre-extraction integrated with existing pulp production. The next step is to study how to increase pulp yield and improve pulp quality in an integrated pulp mill biorefinery.



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