

Near-neutral pre-extraction of hemicelluloses and subsequent kraft pulping of southern mixed hardwoods

SUNG-HOON YOON, MEHMET SEFIK TUNC, AND ADRIAAN VAN HEININGEN

ABSTRACT: Southern mixed hardwood chips were extracted with alkaline solutions at different chemical charges, times (45-110 min), and temperatures (125°C-160°C). At high alkali charges (10% and 20% sodium hydroxide [NaOH] as sodium oxide [Na₂O]), the extract was strongly alkaline (pH about 13) and 17%-40% of the wood was dissolved. Subsequent kraft cooking of the extracted chips yielded 5%-7% less pulp than that of control kraft pulps. However, at reduced alkali charge, just sufficient to approximately neutralize the acids released during pre-extraction, the pulp yield (on original wood) after subsequent kraft pulping was not affected. In this case, about 5%-10% of the wood substance is removed during pre-extraction with 3% NaOH or 3% green liquor (+0.05% anthraquinone) at 140°C and 160°C for 60, 90, and 110 min. The green liquor extract obtained after 110 min at 160°C contained 2.1% (oven-dry weight basis) of sugars, 2.1% acetic acid, and 1.6% lignin accounting for 64% of the wood weight loss. Kraft pulping of the pre-extracted wood chips performed at 12% effective alkali charge showed significantly improved delignification rates and approximately the same or slightly higher yield than the kraft control at 15% effective alkali. The near-neutral green liquor+anthraquinone pre-extraction kraft pulps showed lower refining response but higher tear resistance and similar tensile strength compared to control kraft pulps.

Application: The results of this study might help industry planners in their efforts to integrate the biorefinery concept of hemicellulose pre-extraction with existing pulp production.

Fundamental global developments are making energy supply one of the central issues in the coming decades. At the same time, increased concern about greenhouse gas emissions and decreasing competitiveness of traditional pulp and paper producers in temperate climates has increased the challenges and urgency for pulp mills to increase revenues. This may be achieved by transforming chemical pulp mills into integrated forest biorefineries (IFBRs) that produce new biomaterials and export renewable energy, while continuing to meet growing demand for pulp and paper products [1]. In an IFBR, hemicelluloses are partially pre-extracted from residual wood chips before pulping. The rationale for the pre-extraction is that the fuel value of hemicelluloses is only half that of lignin (13.6MJ/kg vs. 27MJ/kg), so that simultaneous combustion of the dissolved carbohydrates (half of the hemicelluloses: 24%-33% in wood) in the recovery boiler is not the optimal economic use [2,3]. The transition to an IFBR will be enabled by economic returns from improved ongoing pulp and paper production, while producing additional biomaterials and renewable energy [1].

In our previous studies [4-6], softwood chip pre-extraction using pure water produced acidic conditions caused by release of acetic acid from hemicelluloses. Although the extracted hemicelluloses could be used as feedstock for transportation fuels (e.g., ethanol and butanol) and commodity chemicals (e.g., acetic acid), the acidity during high temperature pre-

extraction with water leads to a significant loss in pulp yield and paper strength in the subsequent pulping step. In another paper, the economic and technical feasibility of the biorefinery concept of the near-neutral hemicellulose pre-extraction process integrated within an existing hardwood kraft mill was analyzed [7]. Pulp production and quality were maintained, and the energy balance was compared with that of a kraft mill where no hemicelluloses were pre-extracted. Pre-extraction of poplar wood chips at strong alkaline conditions (1-2 molar sodium hydroxide [NaOH] at a liquor-to-wood ratio of 4 kg/L) and relatively low temperatures (50°C-90°C) was reported by Al-Dajani and Tschirner [8,9]. At these conditions, about 40-50 kg of hemicellulose oligomeric sugars could be extracted without detrimental effect on overall pulp yield when the extracted wood was subjected to modified kraft pulping. Amidon et al. [10] reported that hot-water pre-extraction (HWP-E) of sugar maple decreased alkaline reaction times by 2.0%-87.5% and severity of HWP-E, and comparable yields and kappa numbers were attainable.

The biorefinery concept has been well recognized in the pulp and paper industry; however, relatively little work has been reported on extracting and using hemicelluloses before the pulping process. Hemicellulose removal from wood chips as a pretreatment is being practiced commercially in the production of dissolving pulps using hot water autohydrolysis [11]. In our study, we focused on extraction of southern

mixed hardwood chips with alkaline solutions at different chemical charges (0%-20% as sodium oxide [Na₂O] on wood), times (45-110 min), and temperatures (125°C-160°C). Sodium hydroxide and sodium carbonate were tested as a major source of alkali for extraction. We then pulped the extracted chips to bleachable grade pulp at different reduced effective alkali charges compared to the control kraft cook and measured pulp yield, kappa number, viscosity, and extraction weight loss. The composition of the near-neutral extract obtained at an alkali charge that approximately neutralizes the acids released during pre-extraction was determined, and we quantified the refining and strength properties of the near-neutral green liquor and anthraquinone (AQ) pre-extraction kraft pulps.

EXPERIMENTAL

Fresh mixed southern hardwood chips (35% sweet gum and black gum, 35% southern red oak, 15% red maple, 12% poplar and sycamore, and 3% southern magnolia) were obtained from International Paper. Extraction and cooking experiments were conducted using a profiled pilot digester equipped with an external heat exchanger and a forced liquor circulation system. The wood chips were subjected to pre-extraction at a liquor-to-wood ratio of 4.5 L/kg under the following conditions:

- 0%, 3%, 10%, and 20% NaOH (% as Na₂O) at various temperatures (125°C-160°C) and times (45, 60, and 90 min)
- 3% (as Na₂O) sodium carbonate (Na₂CO₃) at 140°C for 90 min
- 3% green liquor (as Na₂O) and 0.05% AQ for 90 min at 140°C, 60 min at 160°C, and 110 min at 160°C

The green liquor sulfidity was 30% on the basis of total titratable alkali. Wood weight loss was determined from the oven-dry (o.d.) weight difference between the weight of fresh wood chips and that of thoroughly washed wood residue. The chemical composition of wood (e.g., cellulose, hemicelluloses, lignin, ash, and extractives) was determined by the procedure described in TAPPI Standards T 249 ("Carbohydrate composition"), T 249, T 222 ("Acid-insoluble lignin content"), T 244 ("Acid insoluble ash content"), and T 204 ("Solvent extractives determination"), respectively. The monosugar contents were obtained by high-performance anion-exchange chromatography (HPAEC) analysis after double acid hydrolysis of the extracted wood [12,13]. The uronic anhydride content was determined using the chromophoric group analysis method developed by Scott [14]. The compositions of the green liquor extracts were determined by HPAEC (monosugars), high-performance liquid chromatography (acetic acid) and ultraviolet (lignin), as described in detail by Tunc and van Heiningen [15]. After completion of pre-extraction, the liquor was drained from the chips (about 66% of the total liquor), and 30% sulfidity white liquor plus fresh water was added to obtain a liquor-to-wood ratio of 4.5 L/kg at the required effective alkali charge. The effective al-

kali charges were 12%, 13%, or 15% for pre-extraction kraft pulping and 15% (all as Na₂O) for the kraft control. The cooking time for the kraft control and kraft cooks on pre-extracted chips varied from 100 min to 240 min at the maximum cooking temperature of 160°C. Pulps obtained were disintegrated in a laboratory pulper, passed through a pilot vibrating reject screen, and thoroughly washed and collected on a 200-mesh screen with flowing tap water. The wet pulps were then placed in a refrigerator without air-drying for measurement of pulp yield, kappa number, reject contents, residual effective alkali concentration, and intrinsic viscosity (ASTM Standard D 1795-62) using standard testing methods. The residual effective alkali concentration of black liquor was determined using a modified SCAN-N 33:94 method [16]. In all experiments, data were collected from several replicate runs and used to determine the reproducibility of the procedures and the reliability of the analytical data. Completely randomized design and the covariance design were used in the analysis of kraft pulping results. Duncan's multiple range test and t-test were used to determine if any difference among treatment means existed. The best-fit linear regression procedures also were used to determine the relationship between pulping variables and papermaking properties.

RESULTS AND DISCUSSION

Pre-extraction with NaOH

Southern hardwood chips were pre-extracted using 0%, 3%, 10%, and 20% NaOH (on o.d. weight as Na₂O). The extraction conditions, wood weight loss and residual pH of the extracts are summarized in **Table I**. The wood weight loss during extraction increases from almost 3% at the mildest condition (pure water, 130°C, 90 min) to about 40% at the most severe condition (20% NaOH, 150°C, 90 min). The solids content of the water extracts were an order of magnitude smaller (0.16%-1.6%) than those obtained with NaOH (5%-15%). The solids content for the most severe NaOH extraction is similar to that of regular black liquor. The final pH of alkaline extraction varied from acidic (with water), to near-neutral (at 3% NaOH) to alkaline (at 10% and 20% NaOH). The pH drop during mild alkaline or water extraction is caused mostly by acetic acid formed by hydrolysis of acetyl groups in the hemicelluloses.

The wood weight loss data (Table I) are plotted against H-factor during extraction in **Fig. 1**. The weight loss increases with increasing H-factor for water and alkaline extraction. The increase in the wood dissolution with respect to increasing NaOH charge compared at 261 h H-factor was statistically significant at the 99% probability level ($p=0.004$).

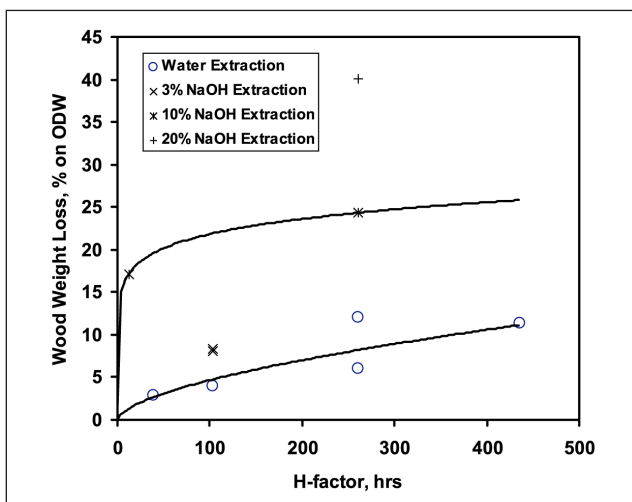
Table II shows the composition of the original wood and that of the extracted and well-washed wood after extraction at three different NaOH charges (0%, 10%, and 20%) for 90 min at 150°C (H-factor: 261 h). All percentages are based on original oven-dry wood. The carbohydrate composition (cellulose and hemicelluloses) was calculated from the monosugar analysis following the procedure described by van Heiningen et al. [17].

ID	NaOH charge (% as Na ₂ O)	Tmax (°C)	Time at Tmax (min)	H-factor (hours)	Weight Loss (% on o.d. wood)	Residual pH	Residual Effective Alkali (% as Na ₂ O)
X-01	0	150	90	261	12.03	4.06	0.00
X-02	0	130	90	39	2.88	4.40	0.00
X-03	0	140	90	103	3.98	4.12	0.00
X-04	0	160	60	436	11.34	3.56	0.00
X-05	0	150	90	261	5.95	3.67	0.00
X-06	3	140	90	103	8.01	7.04	0.00
X-07	3	150	90	261	8.39	6.23	0.00
X-08	10	125	45	12	17.1	13.25	3.63
X-09	10	150	90	261	24.34	12.88	0.84
X-10	20	150	90	261	40.14	13.70	15.25

I. Water and alkaline extraction results of southern mixed hardwoods.

ID	NaOH Charge (%)	Tmax (°C)	Time at Tmax (min)	Monosugars (% on o.d. wood)					Cellu-lose (%)	Hemi-cellulose (%)	Gluco-mannan (%)	Xylan (%)	Lignin (%)	OTHERS		Total (%)
				Ar	Ga	Gl	Ma	Xy						Ash (%)	EtOH-Benzene Extracts (%)	
CTRL	Original wood			0.50	1.04	44.19	2.36	16.74	42.80	26.83	4.76	22.04	29.43	0.52	0.42	100
X-01	0	150	90	0.13	0.59	41.76	1.73	12.77	40.74	18.97	3.35	15.63	26.96	0.28	1.02	87.97
X-08	10	125	45	0.34	0.46	38.68	0.56	11.85	38.35	16.11	1.35	14.76	27.15	1.19	0.11	82.91
X-09	10	150	90	0.29	0.28	37.63	0.38	10.81	37.40	13.93	0.88	13.04	22.95	1.24	0.14	75.66
X-10	20	150	90	0.18	0.18	37.14	0.53	7.72	36.83	9.70	1.03	8.68	12.79	0.48	0.06	59.86
Ar = arabinan, Ga = galactan, Gl = glucan, Ma = mannan, Xy = xylan																

II. Composition of original and extracted wood after NaOH extraction (percentages based on o.d. weight of the original wood).

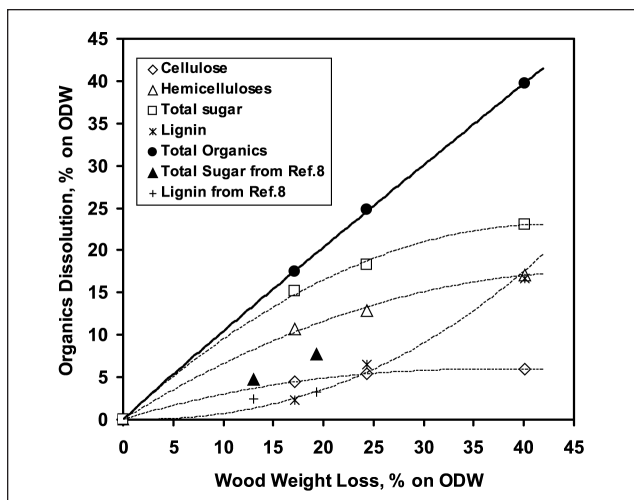


1. Wood weight loss vs. extraction H-factor.

The original southern mixed hardwood is identified as the control. The original wood contained 22.0% xylan (including the 4-O-methylglucuronic acid groups), 4.8% glucomannan, 42.8% cellulose, and 29.4% lignin. With increasing severity of extraction (i.e., for sample X-01 to X-10), more of the wood components were progressively removed with increasing al-

kali charge ($R^2 = 0.99$, $p < 0.05$). Table II shows that the lignin removal is modest (about 2%) when extraction is performed with pure water or 10% NaOH at 125°C for 45 min (X-08). However, a significant amount of lignin is removed (6.5%-16.6%) when using 10%-20% NaOH at 150°C for 90 min ($R^2 = 0.94$, $p = 0.15$). Furthermore, the amount of cellulose and glucomannan extracted with NaOH is roughly the same (4.5%-6.0% and 3.4%-3.9%), irrespective of extraction time, temperature, and NaOH charge. However, the removal of xylan with respect to extraction severity was statistically significant at the 90% probability level ($R^2 = 0.98$).

Figure 2 shows the total amount of organics, carbohydrates, and lignin removed from wood chips during NaOH extraction plotted against wood weight loss. The total sugar amount (Fig. 2) represents the sum of cellulose and hemicelluloses removed at a given weight loss, and the total organics are the sum of total sugar and lignin removed. The slope of the line through the total organics removed is close to 1, which indicates that the measurements of the wood components are internally consistent. Although the carbohydrate removal levels off as the wood weight loss increases, lignin removal shows an exponential increase with increasing wood weight loss. Al-Dajani et al. [8] extracted hemicelluloses from



2. A material balance plot for wood organics dissolution vs. wood weight loss during NaOH extraction of southern mixed hardwoods.

aspen chips using two different mild alkaline solutions containing 2.08 M (25.78% on o.d. weight as Na₂O) and 1.67 M (20.70% on o.d. weight as Na₂O) of NaOH for 4 h at 50°C and 90°C, respectively. Based on the data provided, we calculated that 4.7% and 7.7% of total sugars and 2.4% and 3.3% of Klason lignin were removed at 13% and 19.3% weight loss extractions, respectively. Figure 2 also shows these data for comparison. Results of lignin removal appear to be in good agreement with those of Al-Dajani and Tschirner [8], but a significantly lower sugar removal was observed compared with our results. This is likely because of the much higher temperature used in the present experiments.

NaOH pre-extraction effects on kraft pulping

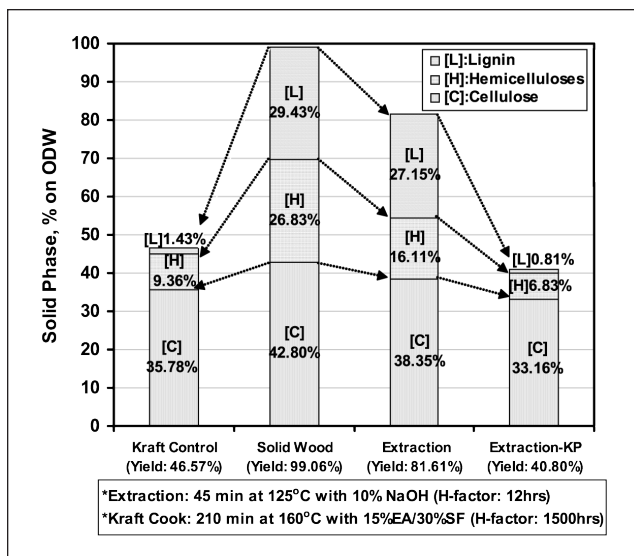
Table III lists the results of 0%, 3%, 3.5%, and 10% NaOH pre-extraction and subsequent kraft pulping. Table III also lists a control cook at 160°C, 15% effective alkali charge, a liquor-to-wood ratio of 4.5 L/kg, and an H-factor of about 1600 h, which produced a pulp of 46.6% total yield at 16 kappa number and TAPPI viscosity of about 41 cP pulp. The data show that, for pure water extraction, the total pulp yield decreases significantly below that of the control at extraction temperatures of 140°C or higher. At 150°C, the total pulp yield is more than 5% lower than the control, and at 160°C, the yield loss is almost 7%.

The only exception is experiment X02-KP04, a water extraction at 130°C for 90 min, which leads to the same total pulp yield. This pretreatment process is similar to very long pre-steaming, and leads only to a very small amount extracted (Table I) with wood weight loss of only 2.88%. Thus, with pure water extraction, it likely is not possible to extract a significant amount of organics from hardwood without also causing a sizable loss in yield of the final kraft pulp. When 10% NaOH is added to keep the extraction medium alkaline during 60 min extraction (leading to 17.4% wood substance removal, as in experiment X08-KP10), the total pulp yield after cooking is 40.8% (i.e., similar to that obtained with pure water extraction at 45 min and 150°C). The reduction in total pulp yield after high temperature pure water extraction is mostly the result of a loss of xylan, as shown through carbohydrate analysis (Table II). Although pure water extraction at 150°C leads to a loss of hemicellulose and cellulose in the kraft pulp relative to that of the control of 4.6% and 0.5%, respectively, addition of 10% NaOH reduces the hemicellulose loss to about 2.0% and the

I	PROCESS 1 [ExtractionD (L/W = 4.5)]					PROCESS 2 [Kraft Pulping (L/W = 4.5)]						Carbohydrates	
	NaOH Charge (%)	Tmax (°C)	Time at Tmax (min)	H-factor	Wood yield (%)	EA charge (%)	Tmax (°C)	H-factor	Total yield (%)	Screen Reject (%)	Kappa No.	Cellulose (%)	Hemi-celluloses (%)
Raw wood	NA					NA						42.80	26.83
Control	NA					15.0	160	1617	46.57	0.07	16.5	35.78	9.36
X01-KP1	0	150	90	261	87.89	15.0	160	1777	40.53	0.01	12.6	-	-
X12-KP2						12.0	160	1499	41.50	1.45	20.3	35.30	4.69
X13-KP3						13.5	160	1500	41.19	0.59	16.2	35.14	4.81
X02-KP04	0	130	90	39	97.12	13.5	160	1500	46.59	0.12	-	-	-
X03-KP05	0	140	90	103	96.02	13.5	160	1500	44.79	0.17	-	-	-
X04-KP06	0	160	60	436	88.66	13.5	160	1496	38.71	0.16	13.1	34.89	2.86
X06-KP07	3	140	90	103	91.99	13.5	160	1500	45.27	0.02	-	-	-
X07-KP08	3	150	90	261	91.61	12.0	160	1500	45.64	0.08	-	-	-
X11-KP09	3.5	150	90	261	-	12.0	160	1500	45.84	0.05	-	-	-
X08-KP10	10.0	125	45	12	82.90	15.0	160	1588	40.80	0.02	10.5	33.16	6.83

L/W = liquor-to-wood ratio

III. Results of 0%, 3%, 3.5%, and 10% NaOH pre-extraction and subsequent kraft pulping.



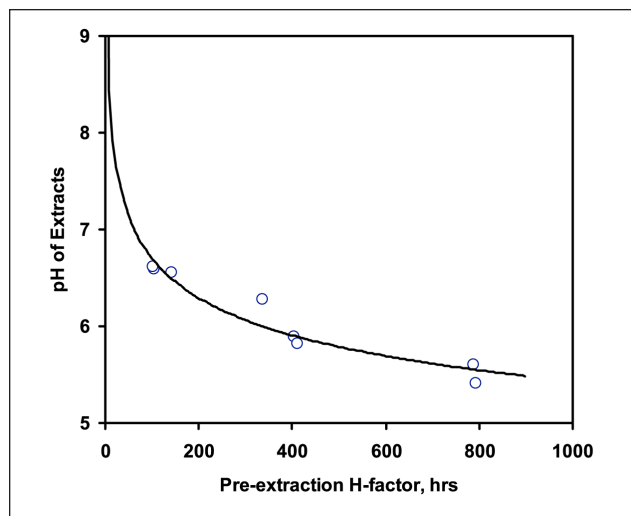
3. Effect of 10% NaOH pre-extraction on the chemical compositions of extracted wood and kraft pulps.

cellulose loss increases to about 2.0%. These results show that a final acidic extract (pH of about 4 resulting from release of acetic acid) or alkaline extract (pH of about 13) during high temperature extraction are detrimental with respect to the total pulp yield. Therefore, three extractions and subsequent kraft cooks were performed with 3% or 3.5% NaOH (on o.d. weight) during extraction to neutralize the acetic acid released in the extraction process (X06-KP07, X07-KP08, and X11-KP09). In all three cases, about 8% of wood substance was removed during extraction and the total pulp yield was only about 1% lower than that of the control at about the same total alkali charge as the control. Thus, it appears that the pH of the extract must be kept near neutral at high temperature treatment to avoid a significant loss in total pulp yield.

Figure 3 shows the chemical composition changes of southern mixed hardwoods with 10% NaOH pre-extraction and subsequent kraft pulps. Figure 3 also shows that approximately 4.5% cellulose, 10.7% hemicelluloses, and 2.3% lignin (leading to about 17.5% wood substance removal) were removed from the original wood during 10% NaOH extraction. As the extracted wood chips were subjected to subsequent kraft cooking, additional amounts of 5.2% cellulose, 9.2% hemicelluloses, and 26.3% lignin were removed from the extracted wood. This mass balance analysis on the pre-extraction and kraft cook indicates that approximately 15% of wood sugars could be pre-extracted for IFBR with only about 5% loss in carbohydrate yield of the pulp, compared to kraft control.

Near-neutral pre-extraction with green liquor and subsequent kraft pulping

Because practical implementation of the near-neutral pre-extraction process would favor the use of mill-available alkali sources such as green liquor or Na_2CO_3 , a new set of pre-extraction experiments were performed with green liquor +AQ.



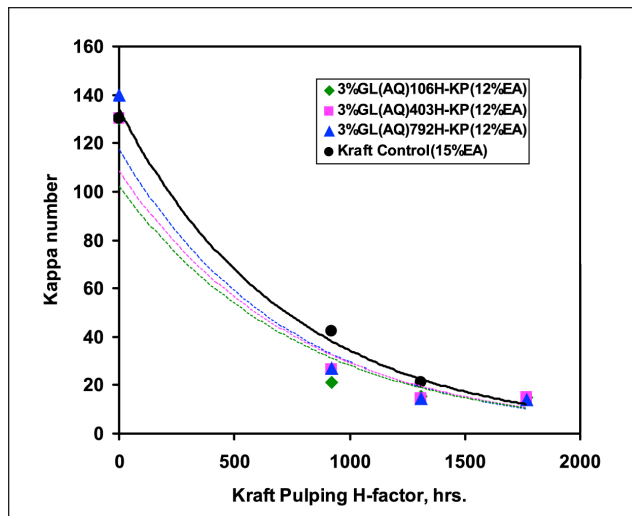
4. pH of 3% green liquor (+anthraquinone [AQ]) extracts vs. pre-extraction H-factor.

AQ possesses a marked capability for stabilizing the polysaccharides toward alkaline degradation according to the redox mechanism. AQ was added in the pre-extraction stage for the maximum beneficial effect on the pulp yield gain in the subsequent kraft pulping [18]. The alkali charge during pre-extraction was 3% on wood as Na_2O , and the AQ charge was 0.05% on o.d. wood. No AQ was added during cooking, including the control kraft cooks. The sulfidity of the green liquor was 30% based on total titratable alkali. Pre-extraction with 3% green liquor (as Na_2O) +0.05% AQ pre-extraction for 90 min at 140°C, 60 min at 160°C, and 110 min at 160°C (liquor-to-wood ratio = 4.5 L/kg) led to the removal of about 4.5%, 8.3%, and 9.6% of wood substance, respectively. The 4.5% weight loss value obtained with 3% green liquor (+AQ) at 140°C is lower than that with 3% NaOH (8.0%) at 140°C. The extraction at 140°C-160°C for 60-110 min may seem to consume additional thermal energy. However, in our preliminary experiments (data unpublished), the near-neutral pre-extraction using 3% Na_2CO_3 for 90 min at 140°C (106 h H-factor) revealed that that the H-factor required to reach the targeted kappa number (16.3-16.4) in subsequent kraft pulping was 1650 h for 15% effective alkali kraft control, 884 h for 13% effective alkali, and 1290 h for 12% effective alkali kraft cooks after near-neutral pre-extraction. This indicates that the near-neutral extraction with 106 h H-factor leads to the savings of 360 h and 766 h H-factors for 12% effective alkali-cook and 13% effective alkali-cook with 3% Na_2CO_3 pre-extracted hardwood chips, respectively. Similar results are expected in the green liquor pre-extraction followed by kraft pulping.

Figure 4 shows the residual pH of the 3% green liquor (+AQ) extraction liquor plotted as a function of extraction H-factor. It shows a rapid drop from alkaline to a near-neutral level of pH around 6.5 in the very early stage of extraction up to an H-factor of about 100 h. At an H-factor of about 400 h, the residual pH of the 3% green liquor (+AQ) extraction reach-

es 5.9 and then steadily drops below pH 5.5 at H-factors larger than about 800 h. A statistically significant linear relationship exists between pH of extracts and pre-extraction H-factor greater than 150 h ($R^2 = 0.92$; $p=0.000$). The pH drop is mostly caused by continued dissolution of acetic acid formed by hydrolysis of acetyl groups in hemicelluloses.

Table IV shows the composition of near-neutral extracts using 3% green liquor (+AQ) at three different H-factor conditions (106 h, 403 h, and 792 h). In all three cases, acetate is the largest organic component in the extract, followed by lignin. Xylan increases strongly with increasing H-factor ($R^2 = 0.99$; $p=0.03$) and reaches 1.45 (on o.d. wood) at $H = 792$ h. The identified organics in the extract represent 58%-64% of the wood weight loss. This means that 34%-42% of the dissolved wood was not identified. This might be related to degradation of hemicellulose sugars during high temperature treatment at the initial slightly alkaline conditions. Additionally, the amount of dissolved xylan may be underestimated because xylan is quantified as xylose by HPAEC analysis after acid hydrolysis, and this treatment cleaves only a smaller fraction of the bond between the glucuronic acid group that dissolves together with xylan. Acetic acid and furfural from the sugar solution can be separated from the sugar solution using liquid-liquid extraction followed by distillation. Because the sugar concentration of extracts is low (4-9 g/L), a portion of the extract may be recycled back to the extraction vessel for the purpose of raising the sugar contents of the extract. The sugars extracts also may be evaporated for further concentration, and then subjected to acid hydrolysis using sulfuric acid for conversion of the oligomeric carbohydrates into monosugars, filtration to remove precipitated lignin, liquid-liquid extraction followed by distillation to remove other chemicals, liming to raise the pH to that required for fermentation, fermentation of five- and six-carbon sugars and glucuronic acid to ethanol, and, finally, distil-



5. Kappa number vs. kraft pulping H-factor.

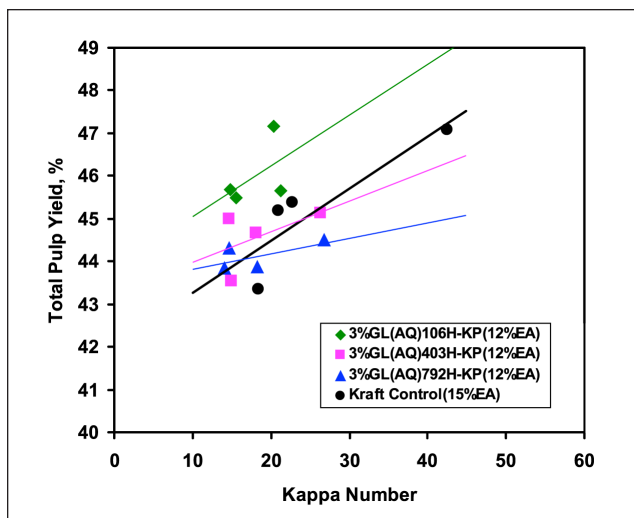
lation and upgrading the product to pure ethanol ($\geq 99\%$).

To evaluate the delignification rate of kraft cooking of 3% green liquor (+AQ) pre-extracted southern mixed hardwood chips, kappa numbers were plotted as a function of kraft pulping H-factor (**Fig. 5**). All kraft cooks with pre-extraction showed higher delignification rates than the kraft control cooks. The significant improvement in delignification rate might result from increased accessibility of the cell wall and increased available alkali for delignification, because major acidic components, including acetic acid, uronic acids, and phenolic acid groups, were partially removed during extraction. There appears to be no significant difference in delignification behavior among kraft cooks of the three different H-factor pre-extracted wood chips.

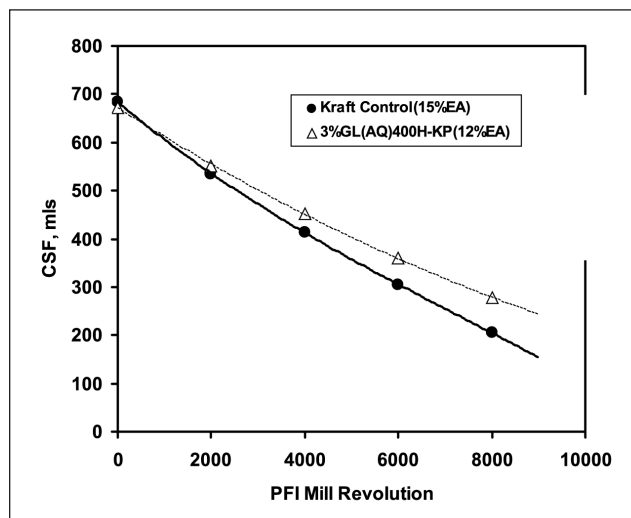
To evaluate the delignification selectivity of kraft cooking of hardwoods after 3% green liquor (+AQ) pre-extraction, we plotted the total pulp yield against kappa number (**Fig. 6**).

Composition of Extract	% on o.d. weight		
	90 min at 140°C (H-factor 106)	60 min at 160°C (H-factor 403)	110 min at 160°C (H-factor 792)
Wood weight loss	4.45	8.30	9.62
Xylan	0.26	0.70	1.40
Glucan	0.11	0.19	0.35
Mannan	0.05	0.05	0.08
Arabinan	0.03	0.06	0.10
Galactan	0.08	0.12	0.20
4-O-MGA	0.11	0.18	0.37
Acetate	1.45	2.04	2.08
Lignin	0.83	1.51	1.60
Extracts from wood carbohydrates	2.09	3.34	4.58
Dissolved organics	2.92	4.85	6.18

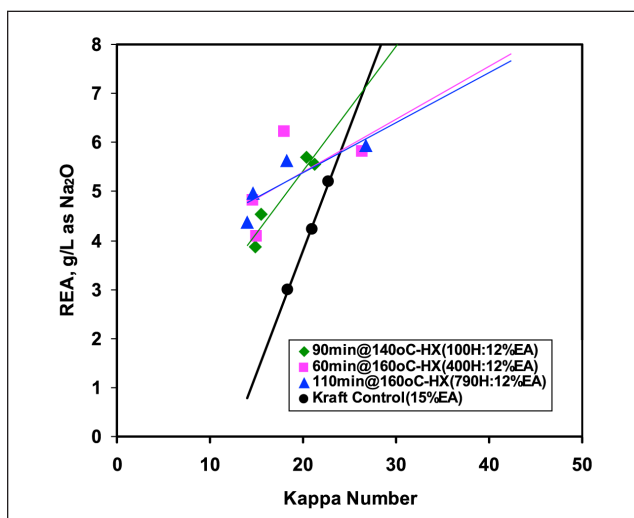
IV. Composition of extraction with 3% green liquor (+AQ) of southern mixed hardwood chips for 90 min at 140°C and 60 and 110 min at 160°C.



6. Total pulp yield vs. kappa number for kraft pulps obtained from kraft cooks with 3% green liquor (+AQ) pre-extracted wood chips and for conventional kraft pulps.



8. Plot of pulp freeness (CSF) vs. PFI mill revolution for 3% green liquor (+AQ) 400 H-factor pre-extracted kraft pulps and control kraft pulps.



7. Plots of residual effective alkali vs. kappa number.

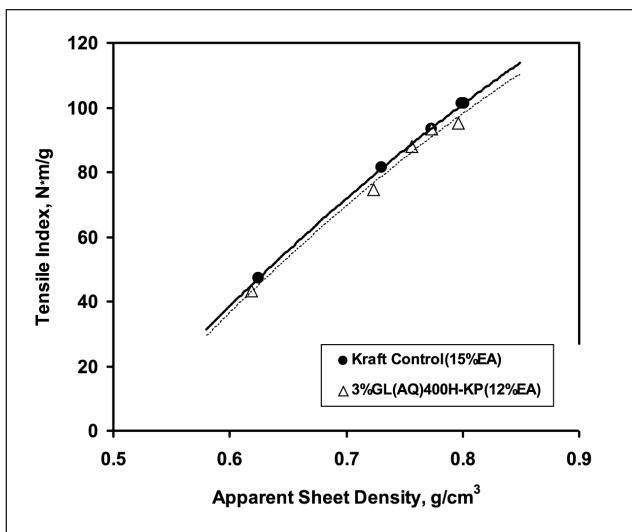
Even though the result shows somewhat scattered data and linear regressions with R^2 of 0.33-0.79, it clearly shows that the total pulp yield for the kraft cooks with near-neutral pre-extraction is as good as or slightly higher than that of the control kraft pulps. The kraft cooks of 3% green liquor (+AQ) pre-extracted hardwood chips with 107 h extraction H-factor shows about 1%-1.5% yield gains compared to control evaluated between the kappa number range of 10-20 at 95% confidence level. No statistically significant difference in total pulp yields was observed between the cooks of 3% green liquor (+AQ) pre-extracted chips at 403 h and 792 h extraction H-factor and kraft control at the kappa number range of bleachable grade ($p > 0.50$). **Figure 7** shows the residual effective alkali concentration plotted as a function of pulp kappa number.

Although 3% lower initial effective alkali was charged to the kraft cooks of the 3% green liquor (+AQ) pre-extracted

wood chips, the final residual effective alkali concentration in the black liquor samples was significantly higher than that of the kraft control when evaluated at the kappa number range of bleachable grade using t-test ($p < 0.007$). The kraft cooks after pre-extraction with 3% green liquor (+AQ) consumed about 2.5%-3% less effective alkali during the subsequent kraft cooks than kraft cooks of the same kappa number in the bleachable grade range. This result implies that the alkali requirements for pre-extraction are balanced by alkali consumption savings during subsequent kraft pulping. In terms of practical applications, there are significant advantages to this process, namely the pulp yield and quality are not degraded, the recovery boiler and the lime kiln are off loaded by about 20%, and two new by-products (ethanol and acetic acid) from the pulping process are generated. The off loading of the recovery cycle allows a potential could increase in production rate if this section of the mill is forms the bottleneck for the production rate. The off loading of the recovery cycle would have a potential to increase the pulp production rate if this section of the mill forms a bottleneck for the production rate.

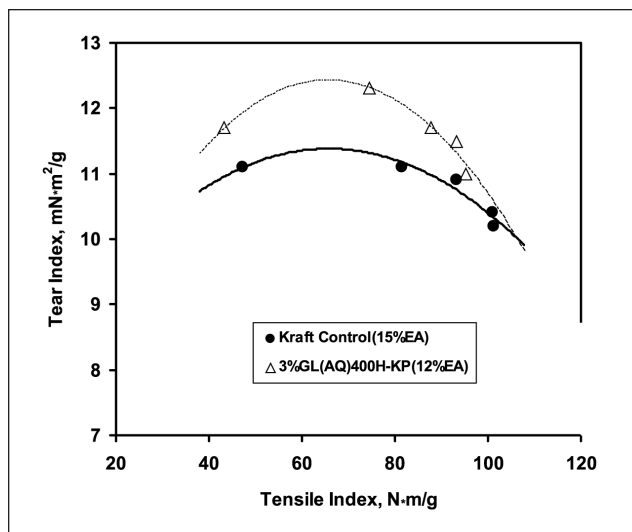
Papermaking properties of kraft pulps with mild alkaline pre-extraction

Three fundamental properties of papermaking (i.e., refining response, tensile strength, and tear resistance) were evaluated for pulps prepared from kraft pulps with 3% green liquor (+AQ) pre-extraction at 400 H-factor and for conventional kraft pulps without pre-extraction. **Figure 8** shows the PFI mill refining responses of the pulps. 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 mechanical action. A linear relationship was observed between freeness and PFI mill revolution for both cases ($R^2 = 0.99$). Statistically significant differences in refinability



9. Plot of tensile index vs. apparent sheet density for 3% green liquor (+AQ) 400 H-factor pre-extraction kraft pulps and control kraft pulps.

were observed between control and pre-extracted kraft pulps at the 95% confidence level. The pre-extracted kraft pulps appeared to need slightly more beating to attain the same level of freeness, most likely because of the lower percentage of hemicelluloses. In general, pulps that are low in hemicelluloses are very resistant to refining and have reduced strength characteristics, whereas pulps that contain a high percentage of hemicelluloses beat quickly and produce stronger sheets [19]. Brauns et al. [20] 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



10. Plot of tear index vs. tensile index for 3% green liquor (+AQ) 400 H-factor pre-extraction kraft pulps and control kraft pulps.

all and will not make satisfactory paper because the fibers do not swell in water and remain collapsed. Leopold [21] reported that the hemicellulose most responsible for the swelling or the increase in the plasticity of cellulose with refining was glucomannan. However, handsheets prepared from 3% green liquor (+AQ) at 400 h H-factor pre-extracted kraft pulps exhibited a tensile strength as good as the kraft control pulps at the 95% confidence level (**Fig. 9**).

Figure 10 shows a plot of tear resistance versus tensile strength of handsheets of the pre-extracted pulps. About 5%-10% higher tear resistance was observed for the near-neutral

ABOUT THE AUTHORS

We chose this topic to help existing chemical pulp mills evolve into integrated forest biorefineries that produce new biomaterials and export renewable energy while continuing to meet demand for pulp and paper products.

The present study focused on near-neutral pre-extraction of hardwoods. It differs from the previous study in which attention was mostly given to hot-water pre-extraction of softwoods.

The most difficult aspect of this research was that quantitative analysis of the extracts was limited to determining the amount of monosaccharides. The most interesting finding was that about 5%-10% of wood substances were removed during the pre-extraction using 3% NaOH or 3% green liquor and 0.05% anthraquinone, without significant loss of pulp yield and papermaking properties.

The research results might be useful to pulp and paper industry planners considering implementation of the biorefinery concept of hemicellulose pre-extraction integrated with existing pulp production.



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The next step is to study how to increase sugar extraction yield and improve pulp yield and quality in an integrated pulp mill biorefinery.

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pre-extracted pulps compared to the control pulps (two sample t-test: $p=0.006$). Tearing resistance depends on total number of fibers participating in the sheet rupture, fiber length, and number and strength of the fiber-to-fiber bonds [22].

CONCLUSIONS

Near-neutral extraction with 3% NaOH or 3% green liquor (+0.05% AQ) at 140°C and 160°C for 60-110 min led to the removal of about 5%-10% of wood substance from southern mixed hardwood chips. When the wood chips extracted at near-neutral conditions with 3% green liquor (+0.05% AQ) were pulped at reduced effective alkali charges (12% effective alkali), the delignification rate increased significantly while the overall pulp yield was similar to that of the kraft control (15% effective alkali). The chips pre-extracted with a charge of 3% green liquor (+0.05% AQ) consumed about 2.5%-3% less effective alkali during the subsequent kraft cooks compared to that of the control kraft cooks. Slightly lower refining response, comparable tensile strength, and significantly increased tear resistance were observed in kraft pulps pre-extracted with 3% green liquor (+0.05% AQ) compared to corresponding conventional kraft pulps. The additional benefits expected from the near-neutral pre-extraction include production of biomaterials or biofuels in addition to traditional paper products, low capital cost requirement because existing pulping equipment and infrastructure are available, in-plant availability of green liquor, and reduction of organic load by up to 5%-10% based on o.d. wood. **TJ**

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