Reductive Modification of Alkaline Pulping of Southern Pine, Integrated with Hydrothermal Pre-extraction of Hemicelluloses

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This study was to investigate the effect of modification of the kraft cooking process integrated with hemicellulose pre-extraction on the properties of pulp produced from softwood chips. Loblolly pine wood chips were extracted with pressurized hot water at an elevated temperature and then subjected to conventional and modified kraft pulping. A reductive pretreatment using sodium borohydride (SBH) in a mild alkaline sodium sulfide solution was adopted for a modification of kraft pulping preceded by water extraction. The presence of SBH in pretreatment caused a pronounced increase in pulp yield of the water pre-extracted kraft pulps. This reductive modification strategy for water-extracted kraft pulping was evaluated in two different ways including double extraction (SBH-alkaline extraction preceded by water extraction) followed by AQ-kraft pulping (DE-AQKP) and water extraction followed by pretreated AQ-kraft pulping (WE-SB-AQKP). The DE-AQKP using 1% SBH showed the same pulp yield as normal kraft cooking at 12% water-extraction weight loss along with approximately 3% of additional sugar extracts from the second extraction stream. In the case of WE-SB-AQKP with 1% SBH, the same yield as the kraft control was achieved around 14% water-extraction weight loss. The SBH demand for zero-yield-loss in pretreatment was in proportion to water-extraction weight loss in kraft pulping preceded by water extraction. Pulps from the modified processes showed faster PFI mill refining responses than the corresponding kraft pulps. No significant changes in paper strength properties were observed in handsheets prepared from the modified kraft pulping preceded by water extraction except for some reductions in tear strength.

Introduction

Pre-extraction of hemicelluloses from woody biomass prior to pulping has recently gained increased attention in the pulp and paper industry. A renewable resource such as hemicelluloses can be identified as a feedstock for the production of higher value-added products such as transportation biofuels, biopolymers, sugar-based chemicals, consumer products, and electrical energy to reduce our reliance on fossil fuels, in addition to pulp.[1,2] However, since the value of pulp is still the most important concern in the paper industry, it is required that the pulp yield based on the original dry wood weight and pulp properties be maintained after the pre-extraction process. In the hemicellulose extraction study using pure water, a maximum of about 12% of the wood mass was extracted as sugars at an H-factor of 1500 h when Loblolly pine chips were treated with pressurized hot water.[3,4] In the kraft pulping study using water pre-extracted wood chips, the total pulp yield based on the original wood at a given kappa number was 3% and 6% lower than the control when 5% and 8% of wood weight were extracted with hot water prior to pulping, respectively.[5] It has also been reported that reduced refining response and reduced tensile strength were observed in the kraft pulp extracted before pulping but it had comparable pulp viscosity, zero-span wet tensile strength, and tear resistance.[5] A manipulation of the yield of final pulp and extract has been suggested to be possible by changing the conditions of prehydrolysis using online monitoring and manipulating pH of the extracts.[6] It can also be speculated that yield and strength losses in kraft pulping of water-extracted wood chips can be minimized or completely recovered if an effective method for carbohydrate stabilization is used before practicing the alkaline pulping. In the kraft pulping process, the alkaline peeling reaction and the hydrorolysis of the glycosidic bonds are considered to be responsible for most of the yield loss during pulping.[7] The stepwise degradation (peeling) initiated at the reducing end groups and the alkaline hydorolysis of the glucosidic bonds occur and influence the dissolution and the degradation through peeling when the temperature and the alkali concentration are sufficiently high. Peeling can be prevented or at least retarded by selective modification of the reducing end groups.[8] It would be of greatest practical significance if this strategy is applied to the stabilization of residual carbohydrates in the water-extracted wood chips prior to pulping or during pulping used in the different technical processes in alkaline medium.[9] The objective of the current study was to investigate the effect of modification of the kraft cooking process integrated with hemicellulose pre-extraction on the properties of pulp produced from softwood chips. Loblolly pine wood chips were treated with pressurized hot water at an elevated temperature of 170 °C until the H-factor reached several targeted values. The pre-extracted wood chips were then subjected to the conventional and modified kraft pulping at different effective alkali charges to various kappa numbers. Reduction of carbohydrate end groups with reducing agents was adopted for a modification of kraft pulping. Sodium sulfide and sodium borohydride were used as reducing agents. AQ was also added in all cooking stages to maximize the yield recovery.[10] The hemicellulose contents of extracts, pulp yield, and kappa number of the different conditions of modified kraft cooks with water extraction were determined. Pulp and paper properties of the pulp produced with modified process were compared to reference kraft pulp.

Experimental Section

Fresh southern pine chips were obtained from Rock-Tenn Company in Demopolis, Alabama. Chips with major defects including barks, knots, and decayed parts were removed prior

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10.1021/ie100005v
Published on Web 06/07/2010

Table 1. Results of HPLC Sugar Analysis of Water Extract after Acid Hydrolysis with 4% H_2SO_4

water extraction at 170 °C			HPLC sugars in water extracts (g/L)					polysaccharides and total sugar (% on ODW)		
time (min)	*H*	wt. loss (%)	Glu	Xyl	Gal	Ara	Man	cellulose	hemi celluloses	total sugar
0	115	4.24	0.33	0.74	0.91	0.53	1.81	0.00	2.24	2.24
11	277	5.83	0.56	1.20	1.18	0.69	2.39	0.00	3.12	3.12
25	483	8.57	1.07	2.23	1.79	1.05	4.47	0.00	5.50	5.50
45	839	11.64	1.60	3.13	2.53	1.48	6.69	0.00	8.00	8.00
80	1356	14.94	2.40	4.05	3.11	1.83	9.71	0.03	10.91	10.94

to screening on a CHIP CLASS laboratory screen equipped with a stack from top to bottom of 45-mm round screens, 8-mm bar screens, 6-mm bar screens, and 4-mm round screens. The wood fraction passing 45-mm round screens and 8-mm bar screens and retained on 6-mm bar screens was collected, well mixed, and air-dried before use. The extractions, pretreatments, and cooks were conducted using three 500-mL cylindrical bomb digesters that were placed inside a computer profiled M/K laboratory digester filled with water as a heat transfer fluid. Seventy grams of oven-dried softwood chips were used in each bomb digestion at a liquor-to-wood ratio of 5.8. The digester temperature was ramped from room temperature to preset maximum temperatures of 170 °C at a rate of 3.2 °C per minute. At the end of the digester operation, each bomb was then quenched in a cold water bath. In the water-extraction stage, extraction times at the preset extraction temperature (170 °C) varied from 0 to 90 min to attain various wood weight loss levels ranging from 0 to 16% based on oven-dry wood. After completion of water extraction, extract was drained from the wood chips (about 70% of the total liquor) and collected to be used for chemical analysis. The sugar contents of the extract and pulps were determined using HPLC analysis before and after hydrolysis of the samples with 4% sulfuric acid for 1 h at 121 °C in an autoclave according to methods published by the National Renewable Energy Laboratory.[11] In subsequent treatment stages, the water-extracted wood chips were treated with sodium-based borohydride-sulfide solution at a preset temperature of 140 °C for 90 min. In the kraft pulping experiments, cooking times at 170 °C were varied to obtain different kappa numbers. Unless otherwise specified, 0.1% AQ was added in all kraft cooks except for control. Pulps obtained from each cook were disintegrated in a laboratory blender and thoroughly washed on a 200-mesh screen with warm tap water. The pulps were then air-dried for measurement of pulp yield and kappa number. For the evaluation of papermaking properties, bleachable grade pulps were obtained after modified kraft cooking of hot-water pre-extracted wood chips up to 1100 H-factor hours. These pulps were subjected to PFI mill refining to be prepared 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.[11] TAPPI standard T205 was used to prepare handsheets from the refined pulps. The basis weight, tensile strength, tearing resistance, and folding endurance were measured according to procedures described in TAPPI standards T494 and T414.

Results and Discussion

Water Pre-extraction of Softwoods. Hot water has proved to be an effective solvent for the extraction of hemicelluloses from wood.[2] When about 8% of hemicelluloses were extracted with water, only a minor amount of lignin (0.5% on ODW) and celluloses (0.3% on ODW) could be removed.[3] In the initial stage of this study, loblolly pine chips were subjected to the hot-water pre-extraction at 170 °C from 0 to 80 minutes. As wood chips are extracted, their weights can be expected to decrease due to components dissolved and diffused from the wood into the extraction media. The wood weight loss data were calculated from the difference between the weight of fresh wood chips and that of thoroughly washed wood residue. The sugar contents in terms of arabinose (Ara), galalactose (Gal), glucose (Glu), mannose (Man), and xylose (Xyl) were obtained by HPLC analysis after acid hydrolysis of the extracts with 4% H_2SO_4 at 120 °C for 1 h in an autoclave. The carbohydrate composition was calculated from the sugar analysis following the procedure described by van Heiningen et al.[12] Table 1 shows the water-extraction condition, weight loss of wood chips, and the concentrations of glucose, xylose, galactose, arabinose, and mannose after acid hydrolysis, expressed in g/L.

The total amount of cellulose, *C*, and hemicelluloses, *H*, which led to these concentrations were then calculated using the following equations:

$$C = \mathrm{Glu}\cdot\left(\frac{162}{180}\right) - \frac{\mathrm{Man}}{b}\cdot\left(\frac{162}{180}\right) \quad (1)$$

with $b = 4.15$ (average value for number of mannose units per glucose unit in hemicellulose of pine/spruce wood, based on Janson[14]):

$$H = (\mathrm{Ara} + \mathrm{Xyl})\cdot\left(\frac{132}{150}\right) + (\mathrm{Gal} + \mathrm{Glu} + \mathrm{Man})\cdot\left(\frac{162}{180}\right) - C \quad (2)$$

The weight loss increases with extraction time from almost 4% at the mildest extraction condition (0 min, 115 H-factor hours) to about 15% at the most severe condition (80 min, 1356 H-factor hours). The extracted amount of hemicelluloses increased up to about 11% with increasing H-factor from 0 to 1356 h. In the case of the extracted amount of cellulose, however, only a small trace (0.03%) was detected over a higher H-factor of 1300 h. This indicates that there is almost no change to the cellulose content of wood chips because the sugar contribution is dominated by hemicelluloses within this weight loss range. Total sugar represents the sum of cellulose and hemicelluloses dissolved at a given weight loss. Total sugar contents were plotted against wood chip weight loss as shown in Figure 1. As expected, a linear relationship was observed between total sugar in extracts and weight loss of wood chips measured after water extraction ($R^2 = 0.997$) indicating that the weight loss could be an important control parameter which makes the sugar contents of the extracts predictable in a reasonable way (i.e., 14% weight loss of wood chips predicts 10.04% of total sugar in the water extracts).

Effect of Water Pre-extraction on Kraft Pulp Yield. When the kraft pulping is preceded by water pre-extraction, the residual hemicelluloses are extensively degraded and dissolved in the alkaline liquor, primarily due to the presence of a large amount of reducing end groups formed during the autohydrolytic

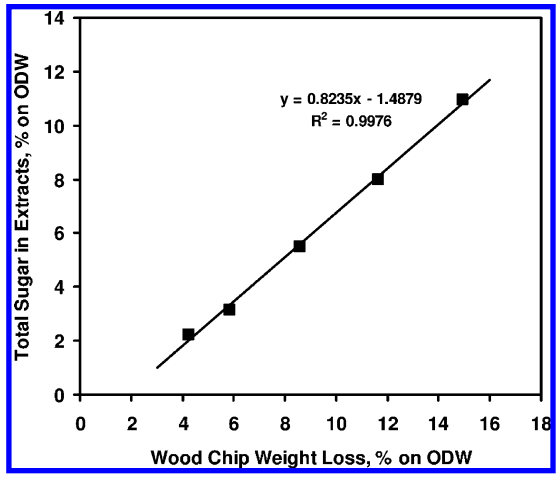

Figure 1. Plots of total sugar in extracts versus extraction weight loss.

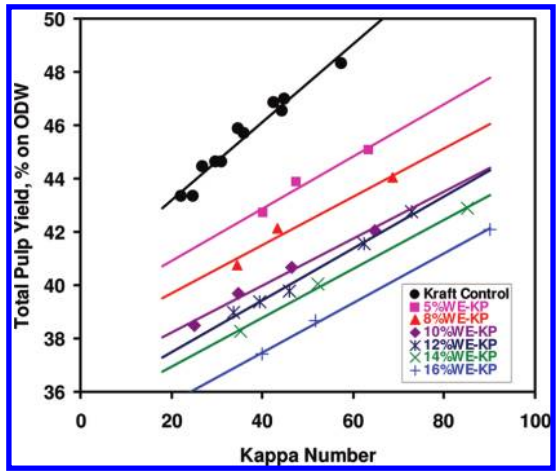

Figure 2. Total pulp yield versus kappa number for kraft pulping of water pre-extracted wood chips (WX) compared to kraft control.

cleavage of the glycosidic bonds mostly catalyzed by released acetic acids from wood. To quantify the effect of pure water pre-extraction on kraft pulp yield, wood chips were pre-extracted with water at a preset temperature (170 °C) varied from 8 to 96 min to achieve the extraction weight loss of 5, 8, 10, 12, 14, and 16%. The pre-extracted wood chips were then subjected to kraft pulping at 17% effective alkali charge and 30% sulfidity (without AQ addition) including reference cooks at 18, 19, and 20% EA and 30% sulfidity. Figure 2 shows the plot of total pulp yield versus kappa number of pulps at different levels of water pre-extraction of Loblolly pine chips. The results shows that all the total pulp yield versus kappa number relationships run parallel to each other with $R^2 = 0.96-1.00$ and, to some extent, to that of the kraft control cooks over a wide range of kappa numbers. Total pulp yield based on wood at a given kappa number significantly decreases as the water-extraction level increases. Total pulp yields at kappa numbers 30 and 40 were calculated using regression equations and plotted against water-extraction weight loss as shown in Figure 3.

The pulp yield decreases significantly as the water-extraction weight loss increases. A linear relationship was also observed between total pulp yields and water-extraction weight loss with the linear coefficients of determination (R^2) of 0.99 for both kappa numbers of 30 and 40. The slopes of the regression equations indicate that the total yield of kraft pulp preceded by water extraction decreases with increasing water-extraction weight loss by a factor of about 0.5 (i.e., there should be 7% loss in the kraft pulp yield compared to control when about

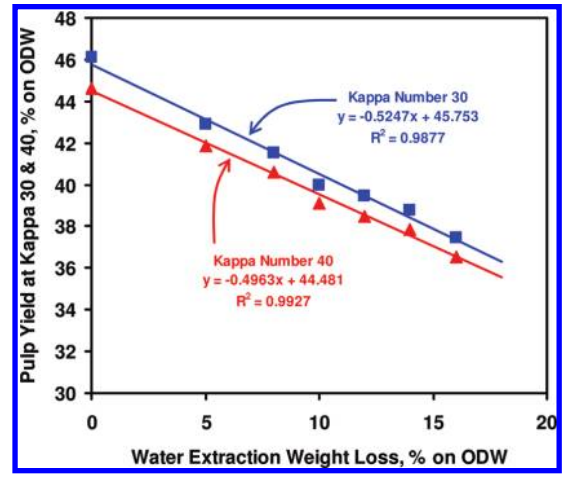

Figure 3. Total pulp yield versus weight loss for kraft pulping of water pre-extracted wood chips compared to kraft control at kappa number 30 and 40.

14% wood mass was dissolved in the water extraction stage). Clearly, with pure water extraction it is not possible to extract a significant amount of hemicelluloses from wood chips without also causing a sizable loss in yield of the final pulp. Since the value of pulp is still the most important concern in the pulp and paper industry, this economic limitation related to yield loss caused by sugar pre-extraction emphasizes the need to search for alternative or modification to the existing kraft process for its transition to an integrated forest biorefinery.

Reductive Pretreatment of Kraft Pulping Preceded by Water Extraction. Carbohydrates with aldehydic end groups are sensitive to alkali, and they are degraded through successive cleavages of acidic products originating from the aldehydic end group in the alkaline pulping process. The degradation of a 1,4-glycosidic polysaccharide proceeds by a peeling mechanism in which the aldehydic end group is liberated from the chain by elimination of the rest of the chain as a glycoxy anion. This peeling reaction is a major factor that causes pulp yield to decrease throughout the pulping process. Peeling can be prevented by stabilization of the carbohydrate aldehydic end groups. It is logical therefore to try to improve the pulp yield of the kraft cook preceded by water pre-extraction by reacting the carbonyl groups with a reducing agent prior to or in the early stages of the cook.[15] Sodium borohydride (SBH) is effective as a reducing agent unless the hemicelluloses were degraded too extensively during the water pre-extraction. It is theoretically capable of liberating eight hydrogen equivalents per mole in alkaline solution according to the schematic eq 3:

$$NaBH_4 + 2NaOH + H_2O \rightarrow Na_3BO_3 + 4H_2 \qquad (3)$$

The stabilization of polysaccharides of wood chips by pretreatment of sodium borohydride is attributed to the reaction by which the terminal aldehyde end groups are reduced to primary alcohols according to the following equation:[16]

$$4RCHO + 4H_4 \rightarrow 4RCH_2OH \qquad (4)$$

In this laboratory study of reductive modification for kraft pulping of water-extracted wood chips, a two-stage cooking process was carried out with a pretreatment (reductive stabilization) and a kraft cooking stage with 0.1% AQ. To maximize the reducing effectiveness, sodium borohydride was dissolved in a mild alkaline solution of sodium sulfide and its mixture was used as pretreatment liquor for carbohydrate end-group

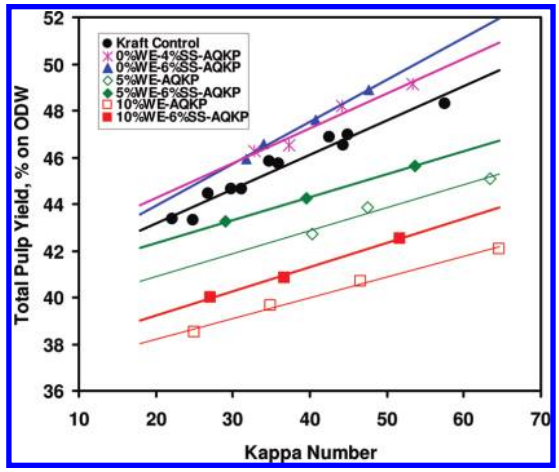

Figure 4. Total pulp yield vs kappa number for kraft pulping of water pre-extracted wood chips (5% and 10% weight loss) compared to that of regular kraft cook.

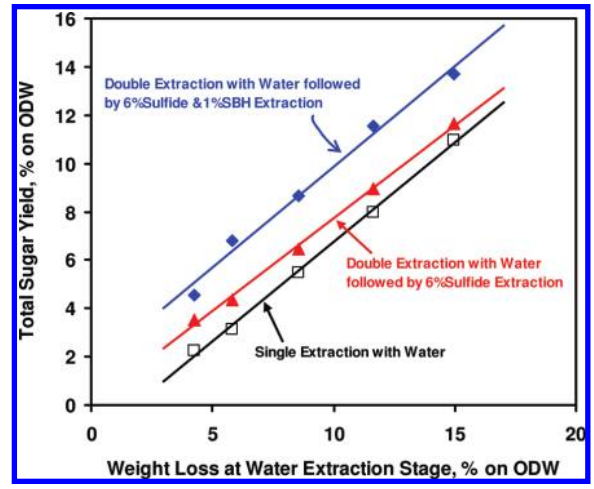

Figure 5. Total sugar yield vs weight loss in water-extraction stage in a single (water only) and double extraction (water followed by sulfide extraction) process.

stabilization of water-extracted wood chips prior to pulping. Sodium sulfide undergoes hydrolysis in aqueous solutions, which is governed by pH-dependent equilibria, to generate hydroxide ion, hydrogen sulfide, and hydrosulfide ions. Since the pK_a value of hydrogen sulfide is about 7 at room temperature, the amount of the un-ionized species (hydrogen sulfide) should be significant at the near-neutral or mild alkaline pH level of the pretreatment process.[17,18] Therefore, it is reasonable to assume that additional end-group stabilization can also be taking place by the thiolation with hydrogen sulfide, derived from sodium sulfide, by which some of the aldehyde end groups are reduced to thioalditols as:[18]

$$\mathrm{RCHO} \xleftarrow{\mathrm{H^+,\ HS^-}} \mathrm{RCH(OH)SH} \xleftarrow{-\mathrm{H_2O},\ \mathrm{H_2S}}$$

$$\mathrm{RCH(SH)_2} \xrightarrow{-\mathrm{H_2S}} \mathrm{RCHS} \xrightarrow{\mathrm{H_2S},\ -\mathrm{S}} \mathrm{RCH_2SH} \qquad (5)$$

To investigate the presumed beneficial effects of sulfide on kraft pulp yield, a pulping experiment was conducted using 0, 5, and 10% water-extracted wood chips. Sodium sulfide charge in the pretreatment was 6% in water-extracted wood chip cooking (Controls 2 and 3) and 4 and 6% in regular kraft cook (Kraft Control). 0.1% AQ was added in all cases except for Kraft Control. The pulp yield data are plotted against kappa number in Figure 4.

As expected, a linear relationship was observed between total pulp yield and kappa number for the sodium sulfide pretreated kraft pulping with R^2 ranging from 0.96 to 0.99. Approximately 1−1.5% yield gain was observed in 6% sulfide pretreated kraft cooks (+0.1% AQ) in both cases of water pre-extracted kraft cooks and regular ones. No significant difference existed between 4% and 6% treatments of sodium sulfide in kraft control. Considering about 0.5% yield gain with the addition of 0.1% AQ, the sulfide treatment for both regular kraft pulping and water pre-extracted kraft pulping led to increase in pulp yield about 0.5−1.0% based on the original wood chip charge.

Sulfide-Borohydride Dual Pretreatment of Kraft Pulping Preceded by Water Extraction. In the investigation of sulfide-borohydride pretreatment effects in the kraft pulping of water pre-extracted wood chips, experiments were conducted in two different ways including AQ-kraft pulping preceded by water-sulfide double extraction (DE-AQKP) and sulfide-borohydryde pretreated AQ-kraft pulping preceded by water extraction (WE-SB-AQKP). In the DE-AQKP process, about 70% volume of the sulfide-borohydride waste liquor was removed in a second feed stream of sugar extracts after completion of treatment, or recirculated for its economical reuse in the succeeding pretreatment for fresh wood chips preceded by water-extraction. In WE-SB-AQKP, however, the residual sulfide-borohydride liquor left in the pretreatment stage in the WX-MKP was transferred to the cooking stage along with pretreated wood chips. The total sugar yields of the single extraction (water only) and double extraction (water extraction followed by alkaline extraction using sodium sulfide (S) with or without sodium borohydride (B)) are compared over a broad range of water-extraction weight loss as shown in Figure 5.

The double extraction using sodium sulfide solution without borohydride after water extraction showed about 1% higher sugar yield than that of the single extraction with pure water. Some portion of this gain of yield should be caused by washing effects from the residual sugars remaining on the surface of the water-extracted wood chips. The presence of 1% SBH with sodium sulfide in the second extraction caused another increase in the sugar extraction yield (~2%), implying that the treatment with borohydride after water extraction apparently led to an increase in sugar yield as well as the protection of carbohydrates against alkaline hydrolysis in the subsequent alkaline cooking stage. This must be an interesting phenomenon that requires further study. Total pulp yields for 22% and 24%DE-AQKP and 14%WE-SB-AQKP were plotted against kappa number and compared with controls 1(regular KP) and 2(14%WE-KP) in Figure 6. The 24% extraction in the DE-AQKP is the sum of 14% weight loss in water extraction and 10% weight loss in subsequent alkaline extraction using sodium borohydride.

Some of the data for DE-AQKP in Figure 6 are somewhat scattered but suggest that the total pulp yield for kraft pulping with double extraction increases as the extraction level was reduced from 24 to 22%. Similar levels of pulp yield were observed in 22%DE-AQKP (12% sugar yield) using 1% sodium borohydride in the second extraction compared to control 1(regular KP). Total yields for 14%WE-SB-AQKP were slightly lower than control at high kappa number over about 40, but the similar level of yields was observed around the bleachable kappa number below about 35 as that of the reference cook. The residual sodium borohydride carried over to the subsequent kraft pulping in WE-SB-AQKP appeared to give 2% higher yield than DE-AQKP. The pulp yields at kappa 30 for WE-KP, DE-AQKP, and WE-SB-AQKP were interpolated using

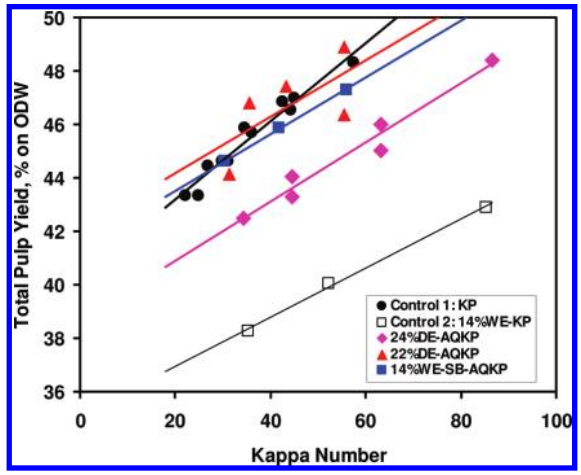

Figure 6. Total pulp yield vs kappa number for 24%DE-AQKP and 14%WE-SB-AQKP.

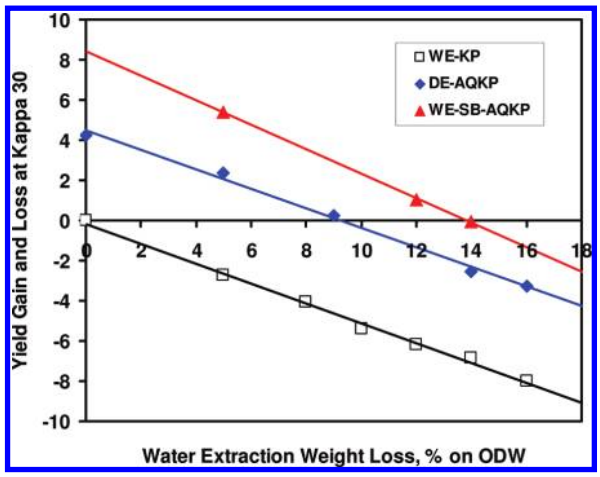

Figure 7. Yield gain and loss diagram for water extraction followed by kraft pulping (WE-KP), double extraction and AQ-kraft pulping (DE-AQKP), and water extraction followed by sulfide-borohydride treated AQ-kraft pulping (WE-SB-AQKP).

simple linear regression of total yields against kappa number and plotted against water-extraction weight loss as shown in the yield gain and loss diagram (Figure 7).

The results show that the total pulp yield versus kappa number relationships for the DE-AQKP and WE-SB-AQKP runs parallel to that of the WE-KP over the range of water-extraction weight loss levels from 0 to 16%. The total pulp yield for each process decreases as water-extraction weight loss increases from 0 to 16% at a rate of about 0.5% yield loss per unit weight loss in water extraction. Approximately 4% and 7−8% higher pulp yields were obtained in DE-AQKP and WE-SB-AQKP than WX-KP at a given weight loss level. This result implies that zero-yield-loss could be achieved with 12%DE-AQKP, in which 9% is WE, and with 14%WE-SB-AQKP. In both cases, 1% SBH is used for carbohydrate stabilization against alkali. Among the three processes proposed, the recycled pretreatment process described for DE-AQKP worked out as representing the most economical application of SBH to water-extracted kraft pulping.

The effect of SBH pretreatment levels from 0 to 2% on the pulp yield gain is illustrated in Figure 8. The pulp yield gain appears to increase in proportion to the SBH charge up to about 1% by a factor of 4 to 4.5 and level off beyond 1% addition level.

To investigate the relationship between the water-extraction weight loss and SBH demand for complete yield recovery with

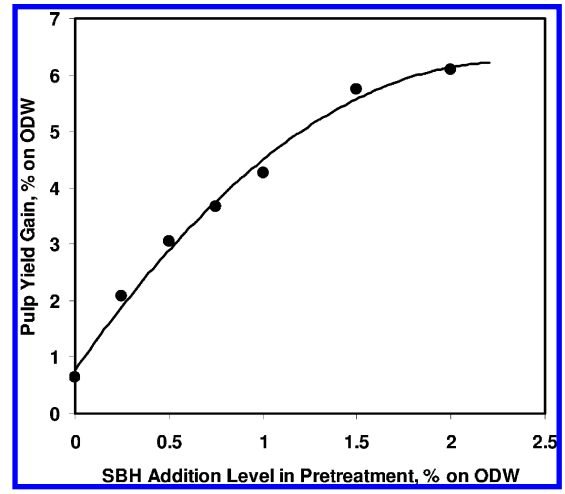

Figure 8. Plot of pulp yield gain versus SBH addition level in pretreatment of Loblolly pine wood chips.

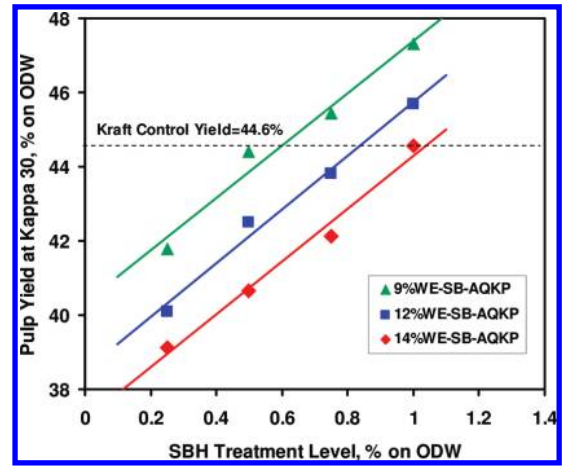

Figure 9. Plots of pulp yield at kappa 30 versus SBH addition level.

the modified kraft pulping preceded by water extraction (WE-SB-AQKP), additional pulping runs were conducted with an experimental design of three different weight loss levels (9, 12, and 14%) in water extraction and four different treatments of SBH (0.25, 0.5, 0.75, and 1%) in pretreatment. Pulp yield data were regressed on kappa numbers for every test block using simple linear regression by which pulp yields at kappa number 30 were then calculated. The plots of pulp yield at kappa 30 versus SBS level are shown in Figure 9.

The results show that a linear relationship ($R^2 = 0.97-0.98$) existed between pulp yield and SBH treatment level. The SBH level required for zero-yield-loss in the kraft pulping of water-extracted wood chips decreased with decreasing water-extraction weight loss. The SBH demands for complete yield recovery for 9, 12, and 14% weight loss were quantified from each regression equation to be 0.60, 0.84, and 1.04%, respectively. The plot for SBH demand against water-extraction weight loss also shows a linear relationship with R^2 of 0.99 as shown in Figure 10. Since the SBH demand is significantly in proportion to water-extraction weight loss, the SBH demand for zero-yield-loss in a modified kraft pulping preceded by water extraction is reasonably predictable, with a somewhat broader range of weight loss from 6 to 18%, using the statistical relationship given (i.e., if the water extraction is operated with 16% weight loss, the SBH demand for zero-yield-loss would be about 1.26% on ODW). SBH pretreatment in combination with mild alkaline sodium sulfide solution clearly showed a remarkable influence

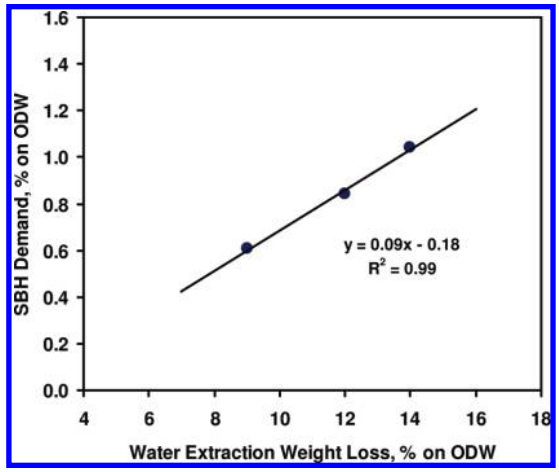

Figure 10. Plot of SBH demand for zero-yield-loss for kraft pulping of water-extracted wood chips versus water-extraction weight loss.

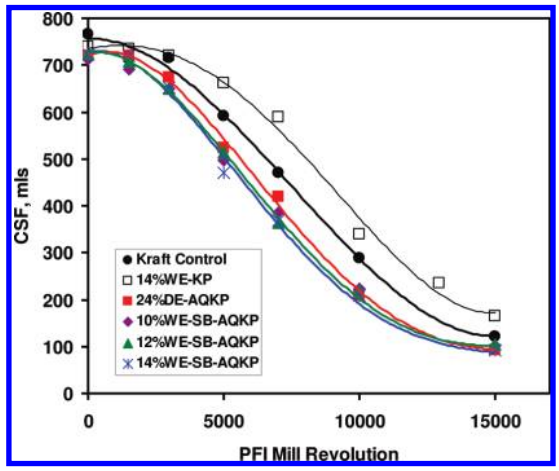

Figure 11. Plot of pulp freeness (CSF) versus PFI mill revolution for modified kraft cooks with 10, 12, and 14% water-extracted wood chips and control.

on the pulp yield recovery in the kraft pulping of water pre-extracted wood chips. The cost of the SBH, however, still runs high compared to other reducing agents in this decade and may prevent its practical application on a technical scale in the pulp and paper industry at present. Further research is required to find the most cost-effective way to use reducing agents for its economical application in the pulp yield recovery of kraft pulping integrated with hemicellulose extraction. Recommendable reducing agents to be tested in the future studies include lithium aluminum hydride, sodium dithionite, amine boranes, potassium borohydride, and sodium metaborate.

Pulp Properties of Modified Kraft Pulping Integrated with Water Extraction. Handsheets were prepared from kraft pulps from modified kraft pulping of water-extracted wood chips, kraft process with water extraction. and conventional kraft control without water extraction or modification. The plots and bar graphs for PFI refining response, the tensile (breaking length), burst index, and MIT fold numbers of handsheets prepared at two different freeness levels (400 and 500 CSF) are shown in Figures 11, 12, 13, and 15 respectively. Tear index was plotted against breaking length as shown in Figure 14.

Significantly higher refining responses were observed in pulps from the modified kraft process with water extraction than those for conventional kraft pulps and kraft pulps with water extraction as shown in Figure 10. The results indicate that the pulps from the modified process with water pre-extraction appeared to need

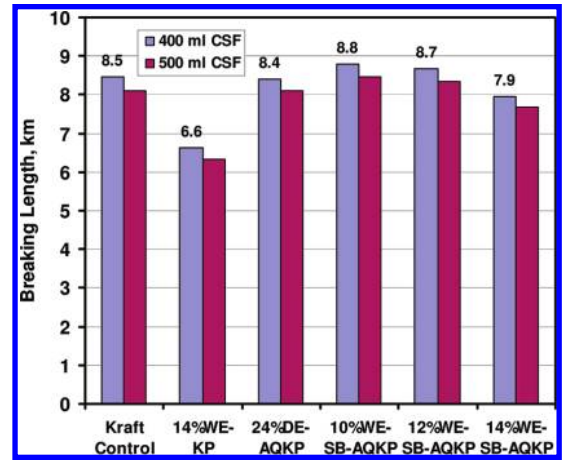

Figure 12. Breaking length of 14%WE-KP, 24%DE-AQKP, and 10, 12, and 14%WE-SB-AQKP and control compared at 400 and 500 mL CSF.

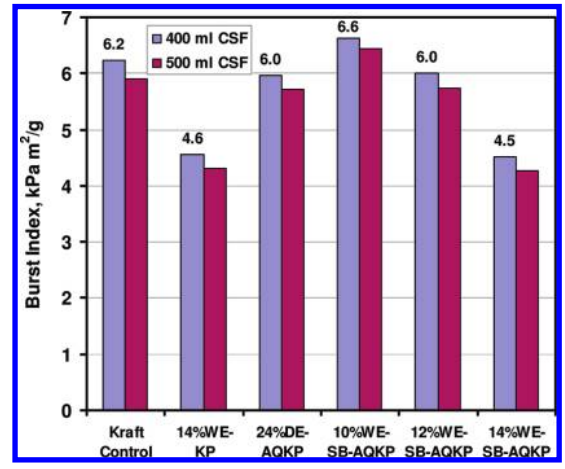

Figure 13. Burst index of 14%WE-KP, 24%DE-AQKP, and 10, 12, and 14%WE-SB-AQKP and control compared at 400 and 500 mL CSF.

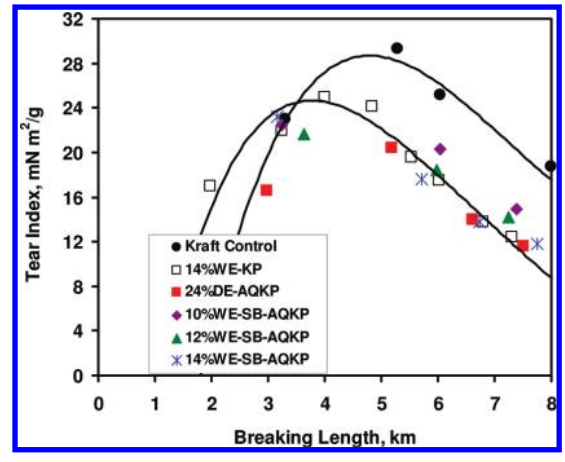

Figure 14. Tear index versus breaking length of 14%WE-KP, 24%DE-AQKP, and 10, 12, and 14%WE-SB-AQKP.

much less refining energy, whereas the pulps from water pre-extraction only showed to require longer beating time to attain the same level of freeness as kraft control. 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.[19] With but a few exceptions, tensile strength, burst strength, and folding endurance values of modified processes did not significantly differ

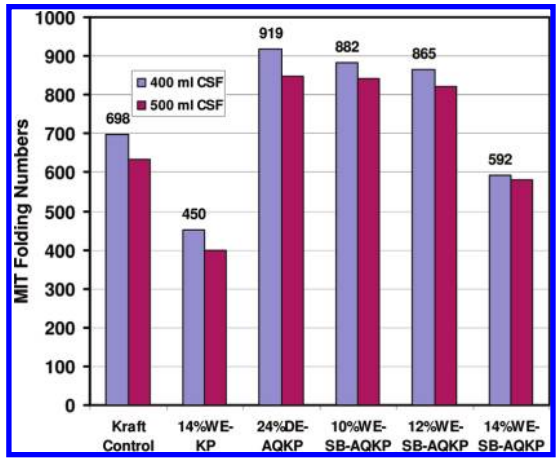

Figure 15. MIT folding endurance of 14%WE-KP, 24%DE-AQKP, and 10, 12 and 14%WE-SB-AQKP and control compared at 400 and 500 mL CSF.

Table 2. Results of HPLC Sugar Analysis of Pulps with Kappa Number near 30 Prepared from Kraft Control, 14%WE-KP, and 14%WE-SB-AQKP

	kraft control	14%WE-KP	14%WE-SB-AQKP
kappa number	30.89	31.93	30.61
pulp yield, %	44.77	38.04	44.63
total sugars, %	38.28	33.41	38.25
glucose, %	37.30	35.03	38.34
xylose, %	3.22	1.41	2.82
galactose, %	0.27	0.19	0.27
arabinose, %	0.16	0.11	0.16
mannose, %	1.66	0.42	1.47
cellulose (*C*),%	33.21	31.44	34.19
hemicelluloses (*H*), %	5.07	1.97	4.07
C/*H*-Ratio	6.55	15.93	8.41

from those of kraft control pulps as shown in Figures 12, 13, and 15, respectively. These results indicate that the modification of kraft pulping of water pre-extracted wood chips has a positive effect on recovery of interfiber bonding capabilities of the sugar pre-extracted kraft pulps. A certain amount of reduction in tear resistance (Figure 14) was observed in pulps from modified kraft pulping after water extraction compared to kraft control. 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.[20] An additional set of experiments was conducted to examine compositional changes of pulps before and after SBH treatment, determining HPLC sugar compositions of pulps with kappa number near 30. Table 2 shows the results of composition analysis for pulps from kraft control, 14%WE-KP, and 14%WS-SB-AQKP. The cellulose and hemicellulose contents were calculated from the contents of glucose, xylose, galactose, arabinose, and mannose in pulps following eqs 1 and 2. The pre-extraction of wood chips with hot water significantly reduced both cellulose and hemicelluloses contents in the order of about 2% and 3%, respectively, in pulps from the subsequent kraft pulping (14%WE-KP) showing remarkably higher *C*/*H*-ratio (15.93) than control. This reduction in cellulose and hemicelluloses contents in pulps accounts for low interfiber bonding ability leading to poor strength characteristics of this type of pulp. In the case of 14%WE-SB-AQKP, however, approximately 1% higher cellulose content, but about 1% lower hemicellulose content was observed in pulps with a similar or slightly higher cellulose/hemicellulose ratio than control. This result indicates that the reductive treatment of water-extracted wood chips tends to more likely increase cellulose retention than that of hemicelluloses at the same cooking condition. The overall retention of carbohydrates, however, caused by the reductive treatment apparently resulted in higher tensile strength, burst strength, and folding endurance except for a certain reduction in tear values. The change in *C*/*H* ratio by reductive treatment would possibly affect the fiber length distribution after refining resulting in some reduction in tear strength. Therefore, future systematic research is required to determine the correlation between *C*/*H*-ratio of pulps and refining fiber length distribution and their impact on tear strength of paper. Tear strength can also be simply improved by performing a mild pre-extraction of wood chips as indicated in Figure 14.

Conclusions

Loblolly pine chips were pre-extracted with hot water and subjected to conventional and modified kraft pulping. Total yield of pulp preceded by water extraction exhibited a linear decrease with increasing water-extraction weight loss. A modification of kraft pulping using sodium borohydride (SBH) in a mild alkaline sodium sulfide solution showed a pronounced effect on the pulp yield recovery. This reductive modification strategy for water-extracted kraft pulping was evaluated in two different approaches including double extraction (SBH-alkaline extraction preceded by water extraction) followed by AQ-kraft pulping (DE-AQKP), and water extraction followed by pretreated AQ-kraft pulping (WE-SB-AQKP). In the case of DE-AQKP using 1% SBH, approximately 3% additional sugar yield was obtained with the second feed stream, and the same pulp yield as normal kraft cooking was achieved at 12% water-extraction weight loss. On the other hand, in WE-SB-AQKP using 1% SBH, the same pulp yield as control was obtained at about 14% weight loss in water extraction. The SBH demand for zero-yield-loss was significantly in proportion to water-extraction weight loss in WE-SB-AQKP. Pulps from DE-AQKP and WE-SB-AQKP beat faster to a given freeness than the corresponding kraft pulps. No significant changes in paper strength properties were observed in handsheets prepared from the DE-AQKP and WE-SB-AQKP except for some reductions in tear strength.

Acknowledgment

This research was supported by Masada Resource Group, LLC, Auburn University Natural Resources Management and Development Institute, and Alabama Center for Paper and Bioresource Engineering. We acknowledge Dr. Y.Y. Lee's group at Auburn University for assistance with the sugar analysis, and Rock-Tenn Company for providing us with Loblolly pine chips.

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Received for review January 1, 2010
Revised manuscript received May 19, 2010
Accepted May 24, 2010

IE100005V