

Polysulfide-borohydride modification of southern pine alkaline pulping integrated with hydrothermal pre-extraction of hemicelluloses

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ABSTRACT: We studied three process modifications to investigate their effects on the property and yield recovery capabilities of kraft pulping integrated with hemicellulose pre-extraction of southern pine. Loblolly pine chips were pre-extracted with hot water until the sugar extraction yield reached the targeted value of 10% and then subjected to conventional and modified kraft pulping. Modification included polysulfide pretreatment; polysulfide-sodium borohydride dual pretreatment, and polysulfide followed by polysulfide-sodium borohydride dual pretreatment two-stage pretreatments prior to kraft pulping. In the first modification, about 5% of the lost pulp yield (total 7%) caused by hemicellulose pre-extraction could be recovered with 15%-20% polysulfide pretreatment. Complete recovery (7%) was achieved with simultaneous pretreatment using 15% polysulfide and 0.5% sodium borohydride with 0.1% anthraquinone in polysulfide-sodium borohydride dual pretreatment. Two-stage pretreatment using recycled 15% polysulfide followed by simultaneous treatment of 6% polysulfide and 0.4%–0.5% sodium borohydride with 0.1% anthraquinone also achieved 100% yield recovery. Continuous recycling of 15% polysulfide employed in the two-stage process modification maintained its yield protection efficiency in a repeated recycling cycle. No significant changes in paper strength were found in handsheets prepared from the three process modifications, except for a minor reduction in tear strength.

Application: Information about the effectiveness of polysulfide-borohydride dual pretreatment on the recovery of pulp yield and kraft pulping properties will be useful for integrated forest products biorefineries that practice hemicellulose extraction prior to pulping.

The kraft pulping process, which is predominantly used worldwide to release the highest-quality fiber for pulp production from essentially all hardwood and softwood species with minimal environmental impact, has only about 50% pulp yield. This low yield is mainly caused by the alkaline dissolution of most wood hemicelluloses in the spent pulping liquor along with almost all the lignin. The black liquor is combusted for steam and electricity generation, while the dissolved inorganic cooking chemicals, sodium hydroxide and sodium sulfide, are recovered and recycled for pulping. Considering that the heating value of the carbohydrates is only half that of lignin, the combustion of dissolved hemicelluloses does not constitute optimal economical use of this valuable resource [1]. As a result, the pulp and paper industry has given more attention to pre-extraction of hemicelluloses from woody biomass prior to pulping. The pure extract of hemicelluloses can be used 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 [2, 3]. In previous work,

hot water was demonstrated to be an effective solvent in the extraction of hemicelluloses from wood chips [4,5], although hot water pre-extraction caused significant and permanent loss in pulp yield and paper strength in subsequent kraft pulping [6]. Because the value of pulp is still the most important concern in the pulp and paper industry, the economic limitation related to yield loss emphasizes the need to search for alternatives or modifications to the kraft process.

The aim of our initial investigation was to develop a modified process that would extract substantial amounts of hemicelluloses from wood while maintaining the pulp yield and paper strength at the same levels of conventional kraft pulp [7]. That work focused on a reductive pretreatment using sodium borohydride (SBH), sodium sulfide (SS), and anthraquinone (AQ) to stabilize residual carbohydrate in the water-extracted wood chips against alkaline degradation during kraft pulping. The combination of 1% SBH, 6% SS, and 0.1% AQ in pretreatment of water-extracted wood chips caused complete recovery of pulp yield in the subsequent kraft pulping. No significant changes in paper strength properties were observed in handsheets prepared from the reductively modified

kraft pulping preceded by water extraction, except slight reductions in tear strength [8,9]. The use of SBH to stabilize the end groups (via the reduction of the aldehyde to an alcohol group) to prevent alkaline peeling reactions during pulping had already been proposed by Meller, Ritman, Aurell, and Hartler [10–12]. Our previous research [9] revealed a new important fact: the SBH should be used with a low-alkalinity SS solution for pretreatment of wood chips to maximize its effectiveness at stabilizing residual carbohydrates against alkaline degradation in the subsequent kraft pulping. The reductive modification of kraft pulping using SBH with SS in the pretreatment stage clearly showed a promising effect on preserving pulp yield and handsheet strength properties, even though 14% of wood mass was dissolved in the form of sugar extracts. However, SBH is still so costly that it may be desirable to find a way to minimize or replace its use to economically justify its use on a technical scale in the pulp and paper industry.

The objective of our latest research was to develop a more cost-effective modification of kraft pulping integrated with hot-water pre-extraction of hemicelluloses. We designed three process modifications to investigate their effects on the recovery of pulp yield and properties that would otherwise be lost due to hydrothermal pre-extraction of wood chips. The modifications were (1) oxidative pretreatment using polysulfide (PS) solution; (2) oxidative-reductive dual pretreatment using PS and SBH simultaneously, and (3) oxidative pretreatment followed by oxidative-reductive two-stage pretreatment using PS and dual treatment (PS+SBH) with PS recycling. We treated loblolly pine chips with pressurized hot water at 170°C until the sugar yield reached the targeted value of 10% and then determined the pulp yield and kappa number of the different conditions of modified kraft cooks with water extraction. Pulp and paper properties of pulp produced with the modified process were then compared to reference kraft pulp.

EXPERIMENTAL

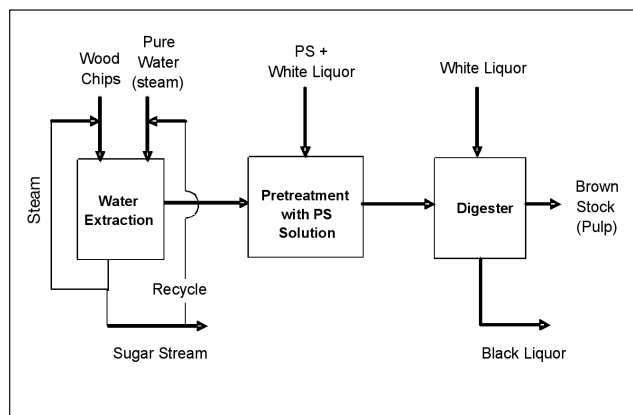
Methods

Fresh southern pine chips were obtained from Rock-Tenn Company in Demopolis, AL, USA. Chips with major defects including barks, knots, and decayed parts were removed before screening on a Chip Class laboratory screen (Testing Machines Inc.; Newcastle, DE, USA). The screen was 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 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 (M/K Systems; Peabody, MA, USA) filled with water as a heat transfer fluid. Seventy grams of o.d. 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 a preset maximum temperature of 170°C at a rate of 3.2°C per min. At the end of

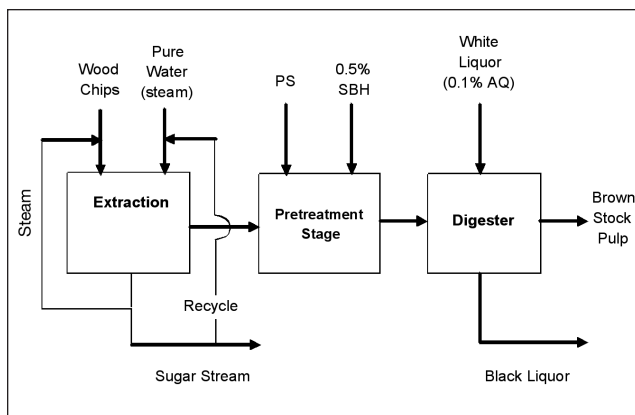
the digester operation, each bomb was then quenched in a cold water bath. In the water extraction stage, extraction time at the preset extraction temperature (170°C) was 66 min (H-factor: 1021 h) to attain 14% wood weight loss level (10% sugar extraction) based on o.d. wood. In subsequent treatment stages (either one or two stages), the water-extracted wood chips were treated with sodium-based PS solution without SBH at a preset temperature of 120°C for 120 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 h. These pulps were subjected to PFI mill refining to prepare them for evaluation of the refining response and handsheet properties over a broad range of degrees of refining. Handsheets from the refined pulps were prepared and tested according to TAPPI standards (“Forming handsheets for physical tests of pulp” [T205 sp-95]; “Laboratory beating of pulp” [T248 sp-00]; “Tensile breaking strength and elongation of paper and paperboard” [T404 cm-92]; “Internal tearing resistance of paper” [T414 om-88]).

Process design for modification

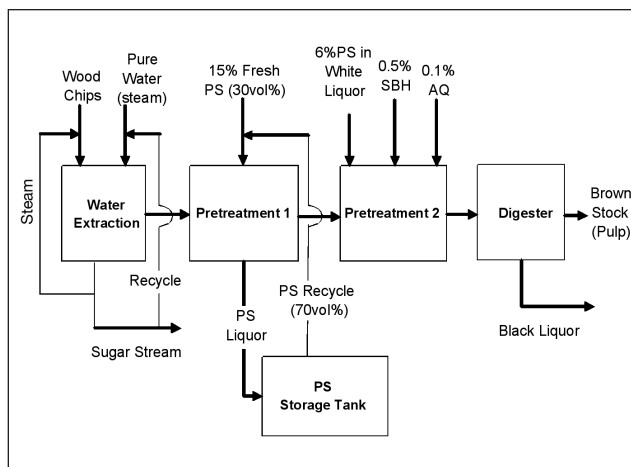
Figure 1 shows the conceptual block diagram of an oxidative modification process composed of a hemicellulose extraction stage and a PS pretreatment stage, followed by alkaline pulping of wood chips. In this process, pure water was added to the fresh wood chips in the extraction stage. The wood and water mass was then treated at 170°C. The organics released from the chips during this pre-extraction operation were mostly wood hemicelluloses, acetic acid, and a small amount of lignin. The extract was flashed to produce preheating



1. Block diagram for oxidative modification process: Single-stage polysulfide (PS) pretreatment process for alkaline pulping of hemicellulose pre-extracted wood chips with PS recycle.



2. Block diagram for oxidative-reductive dual modification process: Single-stage PS-sodium borohydride (SBH) pretreatment process for alkaline pulping of hemicellulose pre-extracted wood chips without PS-SBH recycle.



3. Block diagram for oxidative treatment followed by oxidative-reductive two-stage modification process.

steam, and a portion of the aqueous extract was recycled back to the extraction vessel to raise the sugar content of the extract. In the PS pretreatment stage, the pre-extracted wood chips were treated with white liquor containing a sufficient amount of alkali metal PS at 120°C for 2 h. PS is an important oxidative agent that stabilizes wood polysaccharides against alkaline degradation by oxidizing aldehyde end groups to carboxyl groups via glucosone intermediates [13,14].

Figure 2 shows the block diagram of a single-stage dual treatment using PS and SBH together with 0.1% AQ for the alkaline cooking of 10% sugar pre-extracted wood chips. This scheme was designed to improve the yield recovery capabilities of the PS process mentioned previously. The process comprised a hemicellulose extraction stage and PS-SBH dual pretreatment stage (for 2 h at 120°C) followed by alkaline pulping of wood chips. The PS in this process was prepared in a portion of the alkaline white liquor and no PS recycle was involved.

Figure 3 shows the block diagram for two-stage treatment for alkaline pulping of hemicellulose pre-extracted wood chips. This two-stage process was designed to reduce the PS charge required in the oxidative-reductive modification process. In the first treatment stage, the hemicellulose pre-extracted wood chips were treated with 15% PS liquor at about 120°C for 2 h. The PS liquor was then withdrawn for recycling. This first treatment with PS presumably converted substantial parts of carbonyl groups of residual wood carbohydrates into carboxyl groups. In the second pretreatment stage wood chips were treated with kraft white liquor containing PS and SBH with 0.1% AQ at 120°C for 2 h; subsequent and continuous alkaline cooking delignified the wood chips into separable papermaking fibers. In the second treatment, significant end groups of residual polysaccharides in wood were converted to alditols and carboxyl groups.

RESULTS AND DISCUSSION

Hydrothermal pre-extraction effects

Hemicellulose sugars extracted from wood can be converted

into multiple products, including fuels and high value added chemicals and materials [15]. When about 8% of hemicelluloses were extracted with water, only a minor amount of lignin (0.5% on o.d. weight) and celluloses (0.3% on o.d. weight) can be removed [4]. 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 min. As wood chips are extracted, their weights can be expected to decrease as components dissolve and diffuse 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), galactose (Gal), glucose (Glu), mannose (Man), and xylose (Xyl) were obtained by high-performance liquid chromatography (HPLC) analysis after acid hydrolysis of the extracts with 4% sulfuric acid (H₂SO₄) 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. [16]. **Table I** shows the water extraction condition, weight loss of wood chips, and the concentrations of Glu, Xyl, Gal, Ara, and after acid hydrolysis, expressed in g/L.

The total amount of cellulose (C) and hemicelluloses (H) that led to these concentrations were then calculated using Eqs. (1) and (2):

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

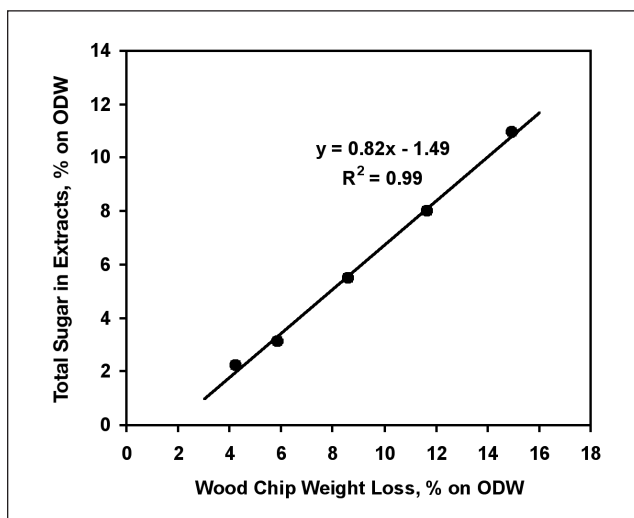
With $b = 4.15$ (average value for number of Man units per Glu unit in hemicellulose of pine/spruce wood, based on Janson [17]):

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

The weight loss increases with extraction time from almost 4% at the mildest extraction condition (0 min, 115 H-factor h) to about 15% at the most severe condition (80 min, 1356

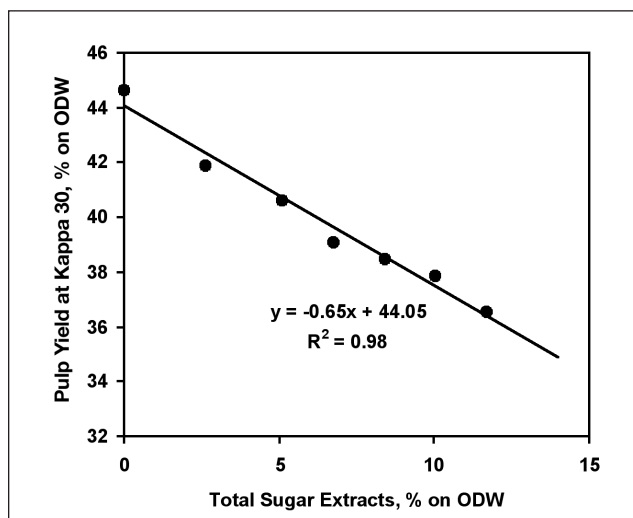
Water Extraction at 170°C			HPLC Sugars in Water Extracts (g/L)					Polysaccharides and Total Sugar (% on o.d. weight)		
Time (min)	H-factor	Wt. loss (%)	Glu	Xyl	Gal	Ara	Man	Cellulose	Hemi-celluloses	Total Sugar
0	115	4.24	0.33	0.74	0.91	0.53	1.81	0.00	2.24	2.24
11	277	5.83	0.56	1.20	1.18	0.69	2.39	0.00	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	1,356	14.94	2.40	4.05	3.11	1.83	9.71	0.03	10.91	10.94

1. Results of high-performance liquid chromatography sugar analysis of water extract after acid hydrolysis with 4% sulfuric acid.



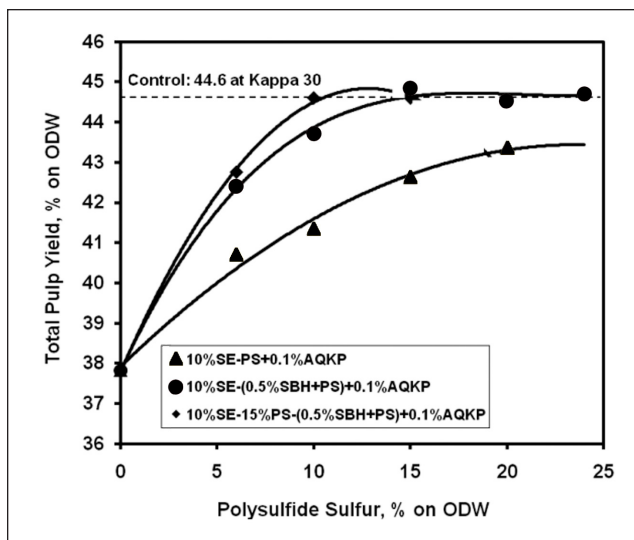
4. Plots of total sugar in extracts versus extraction weight loss.

H-factor h). The extracted amount of hemicelluloses increased up to about 11% with increasing H-factor from 0 to 1356 h. For the extracted amount of cellulose, however, only a small trace (0.03%) was detected over a higher H-factor of 1300 h. That finding indicated that there was almost no change to the cellulose content of wood chips because the sugar contribution was dominated by hemicelluloses within this weight loss range. Contents of total sugar, which represents the sum of cellulose and hemicelluloses dissolved at a given weight loss, were plotted against wood chip weight loss (**Fig. 4**). As expected, a linear relationship was observed between total sugar in extracts and weight loss of wood chips measured after water extraction (linear coefficient of determination $[R^2] = 0.99$), indicating that the weight loss could be an important control parameter that makes the sugar contents of the extracts reasonably predictable (i.e., 14% weight loss of wood chips predicts 10.04% of total sugar in the water extracts). When the kraft pulping was preceded by water pre-extraction, the residual hemicelluloses were extensively degraded and dissolved in the alkaline liquor, primarily due to the presence of a large amount of reducing end groups



5. Total pulp yield versus total sugar extracts for kraft pulping of water pre-extracted wood chips compared with kraft control at kappa no. 30.

formed during the autohydrolytic cleavage of the glycosidic bonds mostly catalyzed by acetic acids released 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 extraction weight losses of 5%, 8%, 10%, 12%, 14%, and 16%. The pre-extracted wood chips were then subjected to kraft pulping at 17% effective alkali (EA) charge and 30% sulfidity (without AQ addition), including reference cooks at 18%, 19%, and 20% EA and 30% sulfidity. Total pulp yield based on wood at a given kappa number significantly decreased as the water extraction level increased. Total pulp yields at kappa no. 30 were determined and plotted against total sugar extracts (**Fig. 5**). The pulp yield decreased significantly as the total sugar extracts increased. A linear relationship existed between total pulp yields and total sugar extracts with $R^2 = 0.98$. The regression equations indicated that the total yield of kraft pulp decreased as a function of total sugar extraction in the pre-extraction stage by a factor of about 0.7 (i.e., about 7% loss in the kraft pulp yield can be calculated compared to control



6. Plot of total pulp yield at kappa no. 30 versus PS sulfur charge (0%, 6%, 10%, 15%, 20%, and 24%) in three types of process modifications using PS, PS + SBH, and PS - (PS + SBH) pretreatments, respectively, for pulp yield recovery in kraft pulping preceded by hydrothermal pre-extraction up to 14% weight loss (10% sugar extraction).

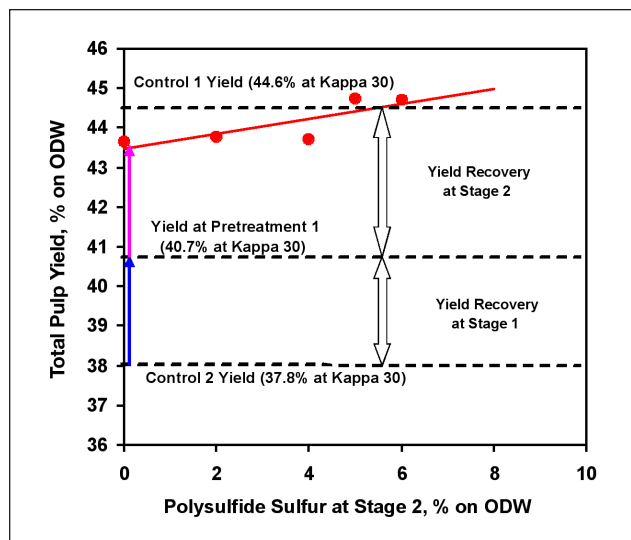
when about 10% wood sugar was dissolved in the pre-extraction with water). Clearly, with pure water extraction it was not possible to extract a significant amount of hemicelluloses from wood chips without also causing a sizable loss in yield of the final pulp.

Modification effects on yield recovery

Figure 6 shows the results of the three modifications in pulp yield recovery for kraft pulping preceded by 14% weight loss hydrothermal pre-extraction (10% sugar extraction).

In the first type of modification, pretreatment with PS increased the total pulp yield of 10% sugar pre-extracted wood chips with increasing PS charge. However, the increase in pulp yield appeared to level off at around 15% PS charge and reach about 2% lower yield level than the target yield of conventional kraft pulp, even at 20% PS charge. This indicated that additional treatment would be required to achieve a complete recovery of pulp yield from kraft pulping of water pre-extracted wood chips with 10% sugar extraction.

The result of the second type of modification showed that when PS was used in combination with SBH in the treatment of 10% sugar pre-extracted wood chips with hot water, more than one-half of the SBH could be saved for a complete recovery of pulp yield to the level of convention kraft pulp. The yield recovery increased with increasing PS charge from 6% to 20% at constant charge of 0.5% SBH. Approximately 15% or higher PS sulfur together with 0.5% SBH was required for this process to reach the target pulp yield (Fig. 6). Of note, an oxidizing agent such as PS can be used simultaneously with a reducing agent such as SBH in the yield-protective treatment of wood chips pre-extracted with water. These two different types of

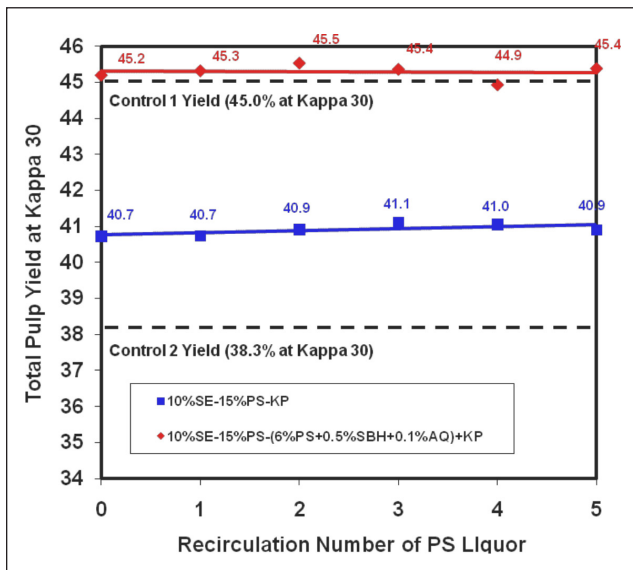


7. Yield recovery contribution of each pretreatment stage in the oxidative treatment followed by oxidative-reductive modification.

chemical species possess completely opposite chemical reactivity but have not shown any apparent interference or a negative interaction in their carbohydrate-protective potential against alkaline degradation in the kraft pulping process.

Complete recovery of pulp yield at a lowest overall PS charge was observed in the two-stage pretreatment process using recycled PS followed by 0.5% SBH and PS pretreatment. In the first stage, wood chips were contacted with 15% PS solution in all instances. For recycling of PS, about 70% of the PS solution was removed after treatment. About 4.2% of PS sulfur (based on o.d. weight) was supposed to remain in the wood chips and be carried over to the next treatment stage where the wood chips contacted white liquor containing additional PS and SBH with 0.1% AQ. In the experiment to evaluate the effectiveness of the second-stage treatment, the addition level of PS was varied from 0% to 6% and the level of SBH was 0.4%-0.5% based on the o.d. wood charged. The results indicated that the PS level should be at least 6% in the second stage for a complete recovery of the pulp yield (i.e., 4.2% PS in the first stage plus 6% PS in the second stage makes about 10% PS in subsequent alkaline cooking). No significant difference was observed in the effect of SBH level between 0.4% and 0.5% at 6% PS charge.

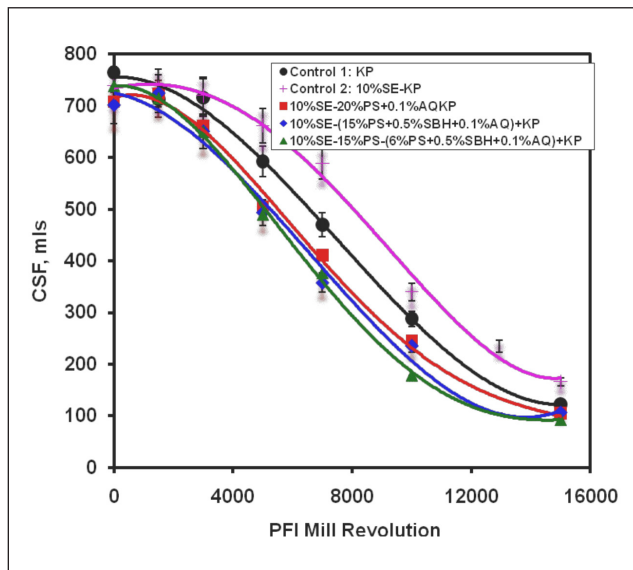
Figure 7 shows the contribution of each stage of pretreatment for the 10% sugar pre-extracted wood chips to the recovery of pulp yield in the two-stage pretreatment process (15% PS followed by [6% PS + 0.5% SBH + 0.1% AQ]). Because approximately 7% yield difference existed between Control 1 (conventional kraft pulp) and Control 2 (kraft pulp from 14% pre-extracted wood chips), this 7% was the target value for the complete yield recovery to reach the pulp yield of Control 1. The results indicated that with an excess PS pretreatment (15% on o.d. weight) in the first pretreatment stage, about 3% of the pulp yield recovery was obtained. In the sec-



8. Recycling effect of 15% PS on total pulp yield of kraft pulping with oxidative modification and with oxidative treatment followed by oxidative-reductive modification compared at kappa no. 30.

ond pretreatment stage, another 3% of pulp yield was recovered with 0.5% SBH and 0.1% AQ without PS. The remaining 1% pulp yield recovery appeared to be attributed to the effect of 6% fresh PS and some PS sulfur carried over with wood chips from the first pretreatment (approximately 4.2%). Therefore, approximately 5% was reduced in PS charge for complete yield recovery in the two-stage pretreatment compared with the oxidative-reductive modification process where 15% PS and 0.5% SBH were required for complete yield recovery.

For a practical application of oxidative treatment followed by oxidative-reductive treatment in the two-stage modification, the first stage for 15% PS treatment was designed to recycle (Fig. 8). To investigate the effect of recirculation of the oxidative treatment stage on final kraft pulping, we conducted an additional set of simulated recycling experiments. Water pre-extracted wood chips (10% sugar yield) were contacted with fresh PS liquor for the oxidative treatment at 120°C for 2 h. After completion of PS treatment, the PS liquor (approximately 70 vol%) was drained from the wood chips and reused with supplementary fresh PS liquor (about 30 vol%) for treatment of the next wood chips pre-extracted with fresh water. PS liquor recycling was conducted a total of five times to examine the effects on both 10% SE-15% PS-KP and 10% SE-15% PS - (6% PS + 0.5% SBH + 0.1% AQ) + KP. Approximately 2% yield was recovered with 15% PS treatment and complete recovery was achieved with 15% PS treatment followed by 6% PS + 0.5% SBH + 0.1% AQ treatment, regardless of the degree of PS recycling. No significant changes in total pulp yields for both 10% SE-15% PS-KP and 10% SE-15% PS - (6% PS + 0.5% SBH + 0.1% AQ) + KP evaluated at kappa no. 30 was observed with increasing PS recycling num-



9. Plot of pulp freeness (CSF) versus PFI mill revolution for modified kraft cooks with oxidative, oxidative and reductive, and oxidative followed by oxidative and reductive modified kraft cooks with 10% sugar-yield water extracted wood chips and control.

bers up to five times. This was an interesting finding that may justify commercial application of PS recycling treatment on a technical scale.

Papermaking properties

Handsheets were prepared from kraft pulps from three types of modified kraft pulping of water-extracted wood chips, kraft process with 10% sugar yield water extraction (Control 2); and conventional kraft control without water extraction or modification (Control 1). The plots for PFI refining response, the tensile (breaking length), and tear index of handsheets prepared at different freeness levels are shown in Figs. 9, 10, and 11, respectively.

Significantly faster 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 (Fig. 9). The results indicated that the pulps from the modified process with water pre-extraction appeared to need much less energy in refining to a given freeness, most likely due to the higher percentage retention of carbohydrates in the pulp fibers. As a broad generalization, pulps that are low in hemicelluloses are very resistant to refining and have poor strength characteristics as shown in Control 2 (10% SE-KP), whereas pulps that contain a high percentage of hemicelluloses beat very quickly and produce stronger sheets [18]. With few exceptions, tensile strength of modified processes did not significantly differ from that of Control 1 pulps, as shown in Fig. 10. These results indicated that the oxidative-reductive modified designs of kraft pulping of water pre-extracted wood chips had a positive effect on recovery of interfiber bonding capabilities and fiber flexibil-

CONCLUSIONS

Loblolly pine chips were pre-extracted with hot water up to the target value of 10% sugar extraction yield and subjected to conventional and modified kraft pulping. Three process modifications were designed to improve the yield recovery capability of kraft pulping preceded by water extraction: (1) oxidative treatment, (2) oxidative-reductive dual treatment, and (3) oxidative treatment followed by oxidative-reductive two-stage treatment. The following results were obtained from this research:

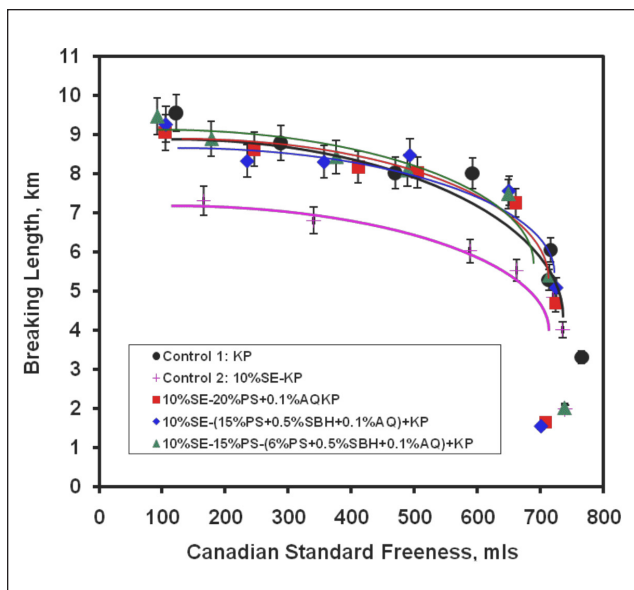
1. About 5% of the lost pulp yield (total 7%) caused by hemicellulose pre-extraction can be recovered with 15%–20% PS treatment prior to pulping.
2. Complete recovery (7%) can be achieved with simultaneous pretreatment of 15% PS and 0.5% SBH with 0.1% AQ.
3. Two-stage modification using recycled 15% PS followed by 6% PS and 0.4%–0.5% SBH with 0.1% AQ also achieved 100% yield recovery.
4. Continuous recycling of 15% PS maintained its yield protection efficiency in the subsequent process.
5. There was no significant change in paper strength, except for a minor reduction in tear. **TJ**

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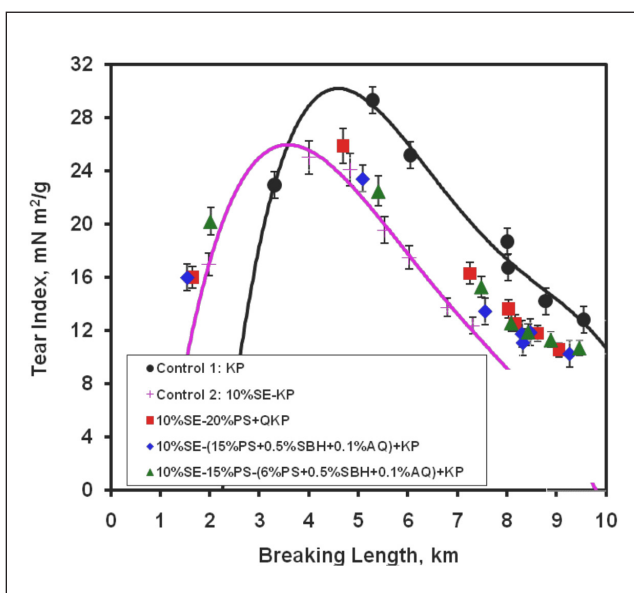
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LITERATURE CITED

1. Gullichsen, J., *Chemical Pulping in Papermaking Science and Technology*, Book 6B, Tapet Oy, Helsinki, 1999, p. B18.
2. van Heiningen, A.R.P., *Pulp Pap. Can.* 107(6): 39(2006).
3. Al-Dajani, W.W., Tschirner, U.W., and Jensen, T., *TAPPI J.* 7(6): 3(2009).
4. Yoon, S-H., MacEwan, K., and van Heiningen, A.R.P., *TAPPI Eng., Pulping Environ. Conf., Proc.*, TAPPI PRESS, Atlanta, GA, USA, 2006, Conf. CD.
5. Yoon, S-H., MacEwan, K., and van Heiningen, A.R.P., *TAPPI J.* 6(6): 27(2008).
6. Yoon, S-H. and van Heiningen, A.R.P., *TAPPI J.* 6(7): 22(2008).
7. Yoon, S-H., Cullinan, H., and Krishnagopalan, G., Auburn University Technology Disclosure, AU #09-047, April, 2009.
8. Yoon, S-H., Cullinan, H., and Krishnagopalan, G., *TAPPI Eng., Pulping Environ. Conf., Proc.*, TAPPI PRESS, Atlanta, 2009, Conf. CD.
9. Yoon, S-H., Cullinan, H. and Krishnagopalan, G., *Ind. Eng. Chem. Res. in ACS* 49: 5969(2010) Conf. CD.
10. Meller, A., *Tappi* 46(5): 317(1963).
11. Meller, A. and Ritman, E., *Tappi* 47(1): 55(1964).
12. Aurell, R. and Hartler, N., *Tappi* 46(4): 209(1963).



10. Plot of breaking length versus CSF.



11. Plot of tear index versus breaking length.

ity of the sugar pre-extracted kraft pulps without loss of fiber strength. However, pulps from the modified processes showed somewhat reduced tear resistance than that of Control 1 (Fig. 11). This trend can be commonly encountered in most high-yield pulp [19–21]. In a high-yield process, further loading of the carbohydrates on the fibers with an increasing amount of hemicellulose would reduce the proportion of cellulose and the number of fibers in the sheet to critical levels, thereby lowering the tear resistance [22]. However, about 50% of tear strength could be recovered by the oxidative-reductive modification of kraft pulping preceded by hydrothermal pre-extraction of wood chips when compared within regular papermaking freeness levels.

13. Sanyer, N. and Laundrie, J., *Tappi* 47(10): 640(1964).
14. Peckham, J.R. and May, M.N., *Tappi* 43(1): 45(1960).
15. Werpy, T. and Petersen, G., *Top Value-Added Chemicals from Biomass*, Pacific Northwest National Laboratory, Richland, WA, USA, 2004, p. 3.
16. van Heiningen, A.R.P., Sefic Tunc, M., Gao, Y. et al., *PAPTAC Annu. Meet., Proc.*, Montreal, 2003, paper 0610.
17. Janson, J., *Textiltech* 25(9): 375(1974).
18. Casey, J.P., *Pulp and Paper Chemistry and Chemical Technology*, vol. 1., Interscience, New York, 1952, p. 352.
19. Meller, A. and Ritman, E., *Tappi* 47(1): 55(1964).
20. Sanyer, N. and Laundrie, J., *Tappi* 47(10): 640(1964).
21. Hakanen, A. and Teder, A., *Tappi J.* 80(7): 189(1997).
22. Clark, J. d'A., *Pulp Technology and Treatment for Paper*, Miller Freeman, San Francisco, 1985, p. 278.

ABOUT THE AUTHORS

We chose this research topic to evolve existing chemical pulp mills into integrated forest biorefineries that produce new biomaterials and export renewable energy while continuing to meet demand for pulp and paper products. Our study focused on the oxidative-reductive pretreatment effects, mainly using polysulfide and sodium borohydride, on the recovery of pulp yield and paper properties in the kraft pulping of southern pine preceded by hydrothermal hemicellulose pre-extraction. This work differs from our previous research because sodium borohydride was used in combination with alkaline sodium sulfide. We reduced the use of the expensive chemical (sodium borohydride) by one-half by using it together with polysulfide in the pretreatment stage of kraft pulping.

The extraction-pretreatment-cooking experimental sequence was our biggest difficulty, as it required long and cautious work. Our most interesting finding was that a reducing agent (sodium borohydride) can be used with an oxidizing agent (polysulfide) in the alkaline pulping system. It was also surprising to discover that this combination showed a synergetic effect on the recovery of pulp yield and paper properties that were lost in a pre-extraction stage.

The research results might be used by those in the



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pulp and paper industry considering implementation of the biorefinery concept of hemicellulose pre-extraction integrated with existing pulp production without a significant loss in pulp yield and properties. The next step is to study how to increase sugar extraction yield and improve pulp yield and quality more economically.

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