Pre-extraction of hemicelluloses and subsequent kraft pulping Part I: alkaline extraction

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ABSTRACT: A mild alkaline treatment was applied to aspen chips prior to kraft pulping in order to extract hemicelluloses for use as biofuels. The extraction was performed at 50-90° C, and did not require costly pressurized reaction vessels. It resulted in a recovery of 40-50 kg of hemicellulose per ton of chips, and yielded the same amount of pulp after subsequent pulping of the extracted chips residue, as compared to a control cook. The pre-extraction process requires careful optimization of the pulping process, and allows shorter cooking time and lower chemical charges.

Kraft pulps obtained from pre-extracted chips have a slightly higher cellulose/hemicellulose ratio, and demonstrate a small decrease in tensile index (~10%), but improved brightness and shive content. While the hemicellulose yield for this process is low, this problem is outweighed by the fact that pulp properties and pulping yield can be maintained at a high level. The recovered hemicellulose can be concentrated/isolated more easily than furfural-containing smaller fragments obtained by autohydrolysis or dilute-acid treatment.

Application: High-quality hemicellulose can be pre-extracted using NaOH before kraft pulping. With careful optimization of the subsequent pulping steps, the same yield and high pulp quality can be maintained. Successful implementation of hemicellulose pre-extraction has the potential to provide additional income for a pulp mill.

BACKGROUND

During kraft pulping, hemicelluloses are degraded into low molecular weight isosaccharinic acids and end up in the black liquor, with degraded lignin. To prevent an environmental impact and recover energy, black liquors are concentrated and burned. As the heating value of hemicelluloses is considerably lower than that of lignin, extracting the hemicelluloses before the pulping stage for generation of high value products has the potential to improve overall economics. Hemicelluloses can be used directly in polymeric form for novel industrial applications such as biopolymers [1], hydrogels [2], or thermoplastic xylan derivatives [3]; or, once hydrolyzed, they can serve as a source of sugars for fermentation to fuels, such as ethanol, or chemicals, such as 1,2,4-butanetriol, a less hazardous alternative to nitroglycerine [4].

Little work has been done on extracting and utilizing hemicelluloses prior to the pulping process. Removal of hemicelluloses from wood as a pretreatment step is presently being practiced commercially in the production of dissolving pulps. The hemicelluloses are removed to allow the production of pure cellulose. Dissolving pulps are processed into products such as cellulose nitrate, cellulose xanthate (rayon fibers) and cellulose acetate.

The most common commercial procedures for extracting hemicellulose are pre-steaming to release natural wood acids (autohydrolysis) followed by water extraction or acid hydrolysis with small amounts of mineral acids (sulfuric acid or hydrochloric acid). Pretreatments of lignocellulosic materials by water or steam are referred to in literature as autohydrolysis [5], hydrothermolysis or hydrothermal pretreatment [6], aqueous liquefaction or extraction [7]. Microwave heat-fractionation of wood has been recently used to extract hemicelluloses [8, 9]. This method requires a treatment temperature of 180-200° C for 2-5 minutes. Other methods for hemicellulose extraction include mild alkaline solutions with and without addition of cations such as Na, K, Li, and borate at low temperatures [10-12]. In this paper, we focused on extraction of hemicelluloses with NaOH, a chemical already used and recovered in conventional kraft mills.

Pre-extraction of hemicellulose can provide a totally new feedstock for biofuel/bioethanol production, thus increasing the total revenue stream for the pulp and paper industry [13, 14]. It is therefore desirable to develop a pretreatment process that can solubilize hemicellulose sugars with minimal formation of fermentation inhibitors, while preserving the fiber integrity. Our study relates to a method for extracting some of the xylan-rich-material in aspen wood, through a mild and selective treatment that leaves high-quality cellulosic material for papermaking.

EXPERIMENTAL

Wood chips

We carried out all the experiments in our study in duplicate, using commercial aspen chips (*Populus tremuloides*). The

chemical composition of aspen chips is shown in **Table I.** After air-drying, the chips were screened and the fraction passing 1.0″ but not 0.5″ holes was sorted manually before storage to remove knots and bark.

Extraction with NaOH

Air-dried chips corresponding to 30.0 g oven-dry matter were extracted with NaOH in a stainless steel autoclave that rotated for 4 h in an oil bath at 32°, 50°, 70°, and 90° C and a liquor-to-wood ratio of 4:1. The concentrations of NaOH we investigated were 1.04, 1.67, and 2.08 M. After the extraction, the liquor was thoroughly drained and the chips residue was washed repeatedly with deionised water until the solution remained colorless. At this point, we determined the oven-dry weight of the residue. For pulping experiments, we subjected the residue directly to kraft pulping without washing. We calculated the charges of chemicals after taking the alkali content in wood residue into consideration. **Figure 1** illustrates the extraction process.

Pulping

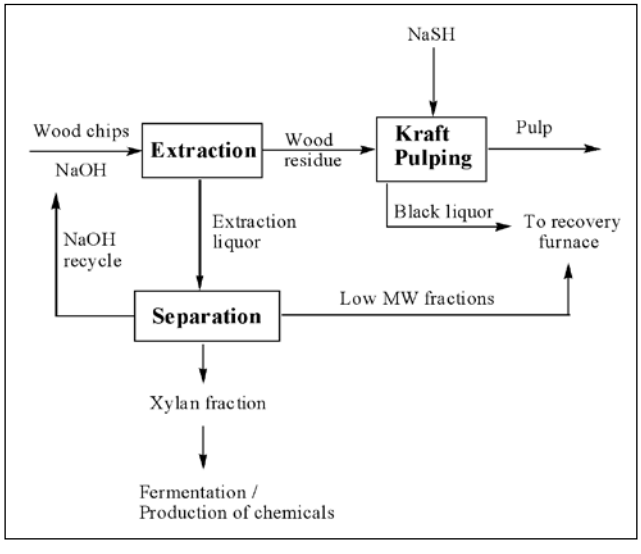
We applied a liquor-to-wood ratio of 4:1. After the addition of white liquor, the mixture was rotated in a stainless steel autoclave at room temperature for 1 h to ensure complete wetting of the chips. Subsequently, the temperature was raised at a rate of 3.5° C/min to the final cooking temperature, 170° C. Cooking parameters were varied so that a desired kappa number was attained (see Results and Discussion).

Analyses

We measured the following values: Klason lignin content, TAPPI T 222 om-23; viscosity of pulp, TAPPI T 230 om-94; tensile index, TAPPI T 494 om-96; residual alkali, SCAN-N 33:94; hydrogen sulfide ion concentration, SCAN-N 31:94.

We determined the carbohydrate content of chips/pulps by using the filtrate obtained after Klason lignin removal. A Waters HPLC system was employed with a Waters 1525 Binary Pump, a Waters 717 plus Autosampler, a Waters 2414 Refractive Index Detector and Breeze software for operation control and data processing. We used BIO-RAD De-Ashing Refill Cartridges, 30 x 4.6 mm (guard column) in line with VARIAN MetaCarb 87P, 300 x 7.8 mm (analytical column). The eluant was deionized and degassed water flowing at 0.3 mL/min. The operating pressure was 541 psi and the column temperature was 80° C.

We used the same Waters system for size exclusion chromatography determinations (SEC). We performed the separations using two Waters ultrahydrogel columns connected in series (300 x 7.8 mm; pore size 250 and 120 Å) and packed with hydroxylated polymethacrylate-based gel. We used water flowing at 0.5 mL/min as eluant. The columns temperature was kept at 30°C. We used polyethylene glycol standard (PEG, Mp (g/mol)=21030 from Polymer Laboratories) and xylose (Acros) to estimate the molecular weight of the isolated xylan fractions.



1. Extraction of hemicelluloses from aspen chips prior to kraft pulping.

Component	Weight percent, O.D. basis
Glucan	44.5
Xylan	17.7
Galactan	1.3
Arabinan	0.5
Mannan	1.7
Klason lignin	21.1
Acid-soluble lignin	3.0
Extractives	2.1
Ash	0.5
Acetyl+uronic acids[α]	7.6

[α] *Determined as the difference to get 100% content. This value is in agreement with those reported by Timell [15]; 3.7 and 4.3% for acetyl and uronic acid groups, respectively.*

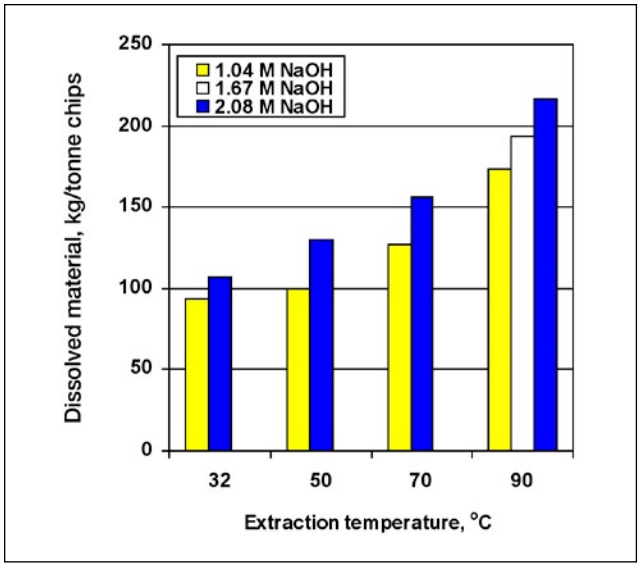
I. Composition of* Populus tremuloides *aspen wood (as the average of 5 replicate measurements).

RESULTS AND DISCUSSION

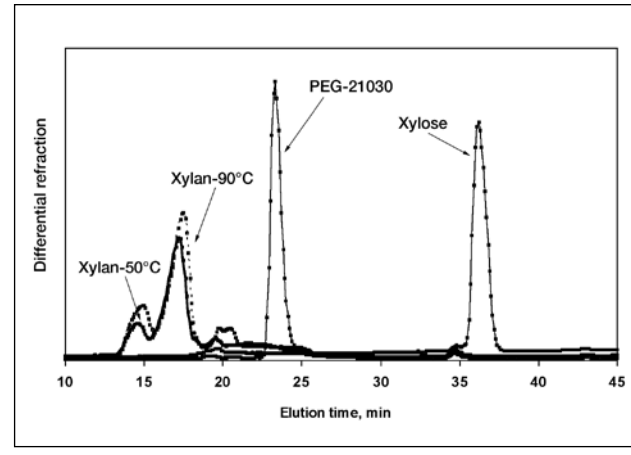
Extraction of hemicellulose

We tested three different concentrations of NaOH in this study: 1.04, 1.67, and 2.08 M, using a liquor-to-wood ratio of 4:1, which corresponds to NaOH charge of 16.7%, 26.7% and 33.3%, respectively (based on dry matter). These concentrations lie within the same order of magnitude as those usually encountered in industrial pulping conditions. As shown in **Fig. 2**, the amount of material dissolved during the extraction increased with increasing temperature as well as increasing NaOH concentration. The study was confined to a maximum temperature of 90° C to avoid the need for pressurized vessels and to minimise carbohydrate modification reactions.

Table II shows mass balances for two different extraction conditions performed at 50° C (2.08 M NaOH) and 90° C (1.67



2. The amount dissolved during alkaline extraction of aspen chips at different temperatures. Extraction time was 4 h and liquor-to-wood ratio 4:1.



3. SEC-Chromatograms for xylose, xylan fractions extracted at 50 and 90°C and polyethylene glycol (PEG).

M NaOH). The dissolved materials (present in both the liquor absorbed by wood residue and the drained liquor) were calculated from the difference between the weight of fresh wood chips and that of thoroughly-washed wood residue, and then distributed according to the volume fraction of each part. More xylan was extracted at 90° C, although higher concentration of NaOH was used for the extraction performed at 50° C. Furthermore, the overall rates of dissolution of glucan, other hemicelluloses (galactan and mannan) and Klason lignin were clearly higher at 90° C. The term "Others" in Table II refers to acid-soluble lignin, extractives, ash, acetyl and uronic acid groups. The increase in extraction temperature resulted in more dissolution for these components as well.

In contrast to pre-extraction of hemicellulose under acidic conditions (autohydrolysis or dilute-acid treatments), the xylans extracted under alkaline conditions exhibit longer chain polymers due to stability in alkaline media with very slow end-wise peeling [16]. In order to verify this, we isolated the xylan fractions from the liquors, according to the protocol described by Zinbo and Timell [17] with some modifications. The extraction liquor was poured with stirring into ethanol-acetic acid mixture (9:1 v/v). The precipitate, which is the xylan-rich fraction, was recovered and purified by centrifugation and successive washing with ethanol-water mixture (9:1).

When we analyzed the fractions extracted at 50° and 90° C , xylan was clearly the major constituent in both cases, at ~ 63%. We prepared solutions of the xylan fractions, xylose (MW=150 g/mol) and polyethylene glycol standard

	Extraction at 50°C, 2.08 M NaOH			Extraction at 90°C, 1.67 M NaOH		
	Wet Wood residue (to pulping)		Liquor (extracted matter),kg	Wood Residue (to pulping)		Liquor (extracted matter), kg
	In Solids kg	In Liquid kg		In Solids kg	In Liquid kg	
Glucan	445.0	0.0	0.0	438.8	2.7	3.5
Xylan	133.1	18.6	25.3	124.2	22.7	30.1
Galactan	10.4	1.1	1.5	6.5	2.8	3.7
Arabinan	5.0	0.0	0.0	4.8	0.1	0.1
Mannan	16.5	0.2	0.3	5.6	4.9	6.5
Klason lignin	187.1	10.1	13.8	178.3	14.1	18.6
Others[α]	72.9	25.0	34.1	48.5	35.9	47.6
Total	**870.0**	**55.0**	**75.0**	**806.7**	**83.2**	**110.1**

II. Mass balances over alkaline extraction of aspen chips at 50°C (2.08 M NaOH) and 90°C (1.67 M NaOH). [α] ***Includes acid-soluble lignin, extractives, ash, acetyl and uronic acid groups.***

Note: Pre-extracted wood chips still contain significant amounts of liquid (water and dissolved organic material and NaOH). In this table "In Solids" refers to the composition of the pre-extracted chips after removal of the liquid phase. "In Liquid" is the composition of the material present in the liquid phase in the chips. This material will be transported into the subsequent pulping process. Liquor (extracted matter) is the material drained from chips and used for hemicellulose recovery.

	No extraction	Extraction at 50°C 2.08 M NaOH	Extraction at 90°C 1.67 M NaOH
Extraction with NaOH: L:W ratio 4:1, time 4 h			
Chips, kg	1000	1000	1000
NaOH charge, kg	-	333.3	266.7
NaOH in residue, kg	-	105.6	73.0
NaOH in drained liquor, kg	-	144.4	93.3
NaOH extraction uptake, kg	-	83.3	100.4
Kraft Pulping: 1-hour-impregnation at room temperature. 30°C, 3.5°C/min to 170°C			
Cook	Kraft	Kraft-50	Kraft-90
Time at 170°C, min	35	25	25
H-Factor	614	461	461
Chips/residue O.D., kg	1000	870.0	806.7
Effective alkali, % NaOH	21.0	15.1	12.0
Active alkali, % Na_2O	18.6	14.1	11.6
NaOH in chips/residue, kg	180.0	105.6	73.0
NaOH from Na_2S, kg	30.0	26.0	24.1
NaOH total in cook, kg	210.0	131.6	97.1
Initial [HO^-]	1.31	0.95	0.75
Residual [HO^-]	0.33	0.45	0.37
NaOH pulping uptake, kg	156.8	69.6	49.0
Total NaOH consumed (extraction + pulping), kg	156.8	152.9	149.4
Sulfidity, %	25.0	33.0	39.8
NaSH charge, kg	42.0	36.4	33.8
NaSH uptake, kg	20.7	19.9	20.2

III. Pulping conditions and results.

(Mp=21,030 g/mol) and their corresponding SEC-chromatograms are shown in **Fig. 3**. Evidently, both xylan-50° C and xylan-90° C fractions have much higher molecular weights than xylose and the PEG-standard. Noteworthy is that both the xylan fractions were only partially soluble in water. Therefore, the chromatograms shown in Fig. 3 for xylan-50° C and xylan-90° C represent only the soluble parts.

For this process to be industrially feasible, it is important to recover all the NaOH in the hydrolysate and reuse it either to extract a new batch of chips or in subsequent pulping. For this purpose, ultrafiltration using commercial thin-film polymeric membranes is currently being tested to purify the xylan-rich fractions.

Pulping

The residues after alkaline extraction were used for subsequent kraft pulping. Three different pulps having a similar degree of delignification (kappa number ~ 23) were prepared as follows (**Table III**):

- **Kraft**: Control pulp produced without NaOH extraction
- **Kraft 50**: Pulp produced by first extracting chips with 2.08 M NaOH at 50° C
- **Kraft 90**: Pulp produced by first extracting chips with 1.67 M NaOH at 90° C

We calculated NaOH consumption during the extraction as ($NaOH_{charge} - NaOH_{in\ residue} - NaOH_{in\ drained\ liquor}$). Similarly, NaOH consumption during the cook was calculated as ($NaOH_{charge} - NaOH_{residual}$). The total NaOH consumption (extraction + pulping) is, therefore, the summation of the two values.

We did no washing of the extracted chips residue before the pulping stage. We chose the alkali charge for the extraction stage so that a sufficient amount of NaOH would remain in the chips residue and no make-up NaOH would be needed during subsequent pulping, other than the amount coming from the added Na_2S.

As compared to the control run, we applied higher charges of NaOH for experiments with chips extraction (333.3 and 266.7 kg NaOH for extractions at 50° and 90° C, respectively, vs. 210.0 kg NaOH for a control cook.) Provided that all the NaOH in the drained liquor is recovered, then the total NaOH consumption during both extraction and pulping stages to produce the pulps kraft-50 and kraft-90 would actually be slightly lower than that consumed to afford the control kraft

	No extraction		Extraction at 50 °C 2.08 M NaOH		Extraction at 90 °C 1.67 M NaOH	
Cook	Kraft		Kraft-50		Kraft-90	
Pulp, kg	526.9		522.9		533.1	
Shives, kg	8.9		7.4		6.5	
Kappa number	23.1		23.0		23.3	
Viscosity, cp	48.1		43.0		46.6	
Brightness, % ISO	30.6		32.0		32.0	
Fiber length L_{ww}, mm	1.1		1.1		1.1	
Glucan/xylan ratio	4.3		5.0		5.0	
Tensile index, kNm/kg	33.3		30.3		28.9	
Chemical composition	(%)	(kg)	(%)	(kg)	(%)	(kg)
Glucan	76.5	403.1	79.3	414.7	79.4	423.3
Xylan	17.8	93.8	16.0	83.7	16.0	85.3
Galactan	0.8	4.2	0.8	4.2	0.8	4.3
Arabinan	0.0	0.0	0.0	0.0	0.0	0.0
Mannan	0.4	2.1	0.8	4.2	0.5	2.7
Klason Lignin	2.5	13.2	2.5	13.1	2.7	14.4
Total	**98.0**	**516.4**	**99.4**	**519.9**	**99.4**	**530.0**

IV. Properties and composition of pulps.

pulp (152.9 and 149.4 kg NaOH for the modified pulps vs. 156.8 kg NaOH for the control), as shown in Table III. In a traditional kraft cook, some NaOH is consumed for the degradation reactions of hemicelluloses. Therefore, lower consumption of alkali is expected during the pulping of "low-hemicellulose-content" extracted wood residues.

By extracting the hemicellulose prior to pulping, a shorter time in the digester at the maximum cooking temperature was needed: 25 min for kraft-50 and kraft-90 vs. 35 min for the control kraft pulp (Table III). Furthermore, the total sulfur charge, expressed as kg NaSH, was ~13% lower for kraft-50 and ~20% lower for kraft-90 as compared to the control pulp. Since NaSH uptake was almost similar for all the three cases, lower amounts of sulfur would consequently be recovered for processes kraft-50 and kraft-90.

Adjusting the chemical charge and cooking time to a lower level after the alkaline extraction gave very encouraging pulping results. There was no pulp yield loss for the extracted wood residues in subsequent pulping after both extractions (**Table IV**). In addition, pulp viscosities were also comparable. Pulp kraft-50 had somewhat lower viscosity than the control pulp kraft, probably because the former had a higher residual alkali concentration, 0.45 vs. 0.33 M (Table III). Several studies have emphasized the importance of hemicellulose for the strength properties of pulp fibers. Due to hemicellulose extraction, pulps kraft-50 and kraft-90 had higher cellulose/hemicellulose ratios (or simply glucan/xylan) than the control kraft (Table IV). Molin and Teder [18] showed that fibers with higher cellulose/hemicellulose ratio had lower tensile stiffness and tensile index (which is in agreement with the present tensile index values shown in Table IV), and higher tear index, fracture toughness and folding endurance. Moss and Pere [19] have recently shown that fiber swelling properties are severely reduced by partial removal of xylan, and that fibers with reduced xylan content collapsed on drying and swelled very little on rewetting. Hence, the removal of hemicellulose prior to kraft pulping should be optimized so that the strength of the final paper sheet is not adversely affected.

CONCLUSIONS

This study has demonstrated that it is possible to extract hemicelluloses from aspen chips without detrimentally affecting the quality of the final fiber product during subsequent pulping. When compared to a control kraft pulp produced conventionally without any extraction, the benefits obtained from extracting some of the hemicelluloses from aspen chips before kraft pulping include the isolation of 40-50 kg hemicellulose per tonne of wood chips while maintaining the same pulp yield. By modifying the pulping conditions for the extracted material, a 10-minute-shorter residence time at maximum cooking temperature is made possible, as well as a saving of ~ 5.5-8.0 kg of NaSH per ton of chips. NaOH charge is slightly higher for the modified process, but total NaOH consumption is similar or slightly lower as compared to a control cook. Although hemicellulose extraction can have some impact on pulp properties, optimizing the extraction and pulping conditions allows full control over the cellulose/hemicellulose ratio and, consequently, provides a pulp with retained fiber properties. **TJ**

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LITERATURE CITED

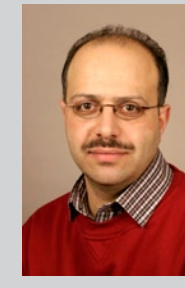
1. Ebringerova, A., Hromadova, Z., Kaucurakova, M., and Antal, M., "Quaternized xylans: synthesis and structural characterization". Carbohydrate Polymers, 24, 301-308 (1994).
2. Gabrielii, I., Gatenholm, P., Glasser, W. G., Jain, R. K., and Kenne, L., "Separation, characterization and hydrogel-formation of hemicellulose from aspen wood". Carbohydrate Polymers. 43, 367- 374 (2000).
3. Jain, R. K., Sjostedt, M., and Glasser, W. G., "Thermoplastic xylan derivatives with propylene oxide". Cellulose –andover-, 7(4), 319-336 (2000).
4. Niu, W., Molefe, M. N., and Frost, J. W., "Microbial synthesis of the energetic material precursor 1,2,4-Butanetriol". J. Am. Chem. Soc.125:12998 (2003).
5. Lora, J. H., and Wayman, M., "Delignification of hardwoods by autohydrolysis and extraction". Tappi J. 61: 47-50 (1978).
6. Kubikova, J., Zemann, A., Krkoska, P., and Bobleter, O., "Hydrothermal pretreatment of wheat straw for the production of pulp and paper". Tappi J. 79: 163-169 (1996).
7. Heitz, M., Carrasco, F., Rubio, M., Chauvette, G., Chornet, E., Julian, L., and Overend, R. P., "Generalised correlations for the aqueous liquefaction of lignocellulosics". Can. J. Chem. Eng. 64, 647-650 (1986).
8. Lundqvist, J., Jacobs, A., Palm, M., Zacchi, G., Dahlman, O., and Stålbrand, H., "Characterization of galactoglucomannan extracted from spruce (Picea abies) by heat-fractionation at different conditions". Carbohyd Polym 51(2), 203-211 (2002).
9. Palm, M., and Zacchi, G., "Extraction of hemicellulosic oligosaccharides from spruce using microwave oven or steam treatment". Biomacromolecules 4(3), 617-623 (2003).
10. Hashimoto, T., and Hashimoto, K., "Studies on the utilization of xylan and glucomannan in woods. I. Purification and separation". Yakugaku Zasshi, 95(10) 1239-1244 (1975).
11. Cunningham, R. L., Carr, M. E., and Bagby, M. O., "Hemicellulose isolation of annual plants". Biotechnol. Bioeng. Symposium, no 17, Sump. Biotechnol. for fuels and chemicals (Gatlinburg) 8th: 159-168 (May 13-16, 1986).
12. Scott, R. W., "Influence of cations and borate on the alkali extraction of xylan and glucomannan from pine pulps". J Appl Polymer Sci, 38(5), 907-914 (1989).
13. Ragauskas, A. J., Nagy, M., Kim, D. H., Eckert, C. A., Hallett, J. P., and Liotta, C. L., "From wood to fuels: integrating biofuels and pulp production". Indus. Biotech. 2(1): 55-65 (2006).
14. Van Heiningen, A., "Converting a kraft pulp mill into an integrated biorefinery". Pulp Pap. Can. 107(6): T141-T146 (2006).
15. Timell, T. E., "Recent progress in the chemistry of wood hemicelluloses". Wood Sci Technol. 1: 45-70 (1967).
16. Laver, M. L., and Zerrudo, J. V., "Alkaline peeling reaction of a xylan". Fourth Canadian Wood Chemistry Symposium, Quebec, Canada. Extended Abstracts: 61-62 (1973).
17. Zinbo, M. and Timell, T. E., "The degree of branching of hardwood xylans". Svensk Papperstidn. 68(19): 647-662 (1965).
18. Molin, U., and Teder, A., "Importance of cellulose/hemicellulose-ratio for pulp strength". Nordic Pulp Paper Res. J. 17(1), 14-19, 28 (2002).
19. Moss, P. A., and Pere, J., "Microscopical study on the effects of partial removal of xylan on the swelling properties of birch kraft pulp fibres". Nordic Pulp Paper Res. J. 21(1), 8-12 (2006).

INSIGHTS FROM THE AUTHORS

Most of the recent research in this area has been focused on autohydrolysis. While this method results in more complete extraction of hemicellulose, it also tends to have a negative effect on pulp properties and yield. To maintain yield and preserve fiber properties, extraction must be optimized carefully.

We found that alkaline hemicellulose extraction significantly reduced required pulping times. In addition, we were surprised to find that, with careful optimization, it was possible to maintain the original pulp yield even after the extraction.

Additional optimization experiments are underway. Specifically, a number of separation methods for the removal of larger quantities of hemicellulose are being explored.



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