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Pre-Extraction of Hemicelluloses from Hardwood Chips Using an Alkaline Wood Pulping Solution Followed by Kraft Pulping of the Extracted Wood Chips

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Mixed southern hardwood chips were extracted with an alkaline wood pulping solution called kraft green liquor. This aqueous solution containing mainly sodium carbonate and sodium sulfide was applied at different alkali charges (expressed as Na₂O) of 0, 2, 4, and 6% on dry wood weight. The extractions were performed at 160 °C for effective times ranging from about 1–2 h to determine the effect of extraction severity on pulp yield and composition of the extracted liquor. The severity of hemicellulose extraction time and alkaline charge controls the concentration of acetic acid and monosaccharide sugars available for downstream processing, the accumulation of degradation products such as organic acids and furans in the extract, and the pulp yield attainable for the extracted wood chips. As the alkali charge was increased, the amount of acetate side chains on the hemicelluloses and the dissolved lignin in the extract increased but the carbohydrate and sugars in the extract decreased appreciably. Water extraction (0% alkali addition) released the greatest amount of carbohydrates, up to 30 g/L measured as component sugars, but resulted in the greatest decrease in pulp yield, dropping from 47% to 35%. Extraction with 2% green liquor increased the pulp yield to 51% while greatly reducing the component sugars to 8 g/L. Data obtained in this work will allow selection of optimum hemicellulose extraction conditions for integrating the extraction operation into the Kraft pulping process.

Introduction

Why a Biorefinery? Woody biomass is an abundant and renewable material with potential to replace the feed-stocks of many fuels and chemicals currently made from fossil fuels.¹ The concept of an integrated forest products biorefinery draws on the technology and infrastructure already present in the pulp and paper industry to generate new products in addition to the existing core business. A biorefinery would utilize all components of the biomass to make a range of products including fuels, chemicals, heat, and power in proportions that maximize economic returns.² During Kraft pulping, cellulose in the wood remains nearly undegraded, whereas the majority of hemicellulose and lignin are dissolved into the pulping liquor and burned with the spent liquor in the chemical recovery process to generate energy.^{3,4} Cellulose presently has a higher commercial value by manufacture into pulp and paper products than can be derived by hydrolyzing it into glucose for conversion to liquid biofuels.⁵ The combustion of lignin, which has a higher heating value (HHV) of 25 ± 1.5 MJ/kg, provides the bulk of the energy generated in the recovery furnace.^{2,6} Hemicelluloses have a significantly lower HHV of 18.6 MJ/kg and are not presently utilized to their maximum potential.^{6,7} Many micro-organisms are capable of fermenting the sugars of hemicellulose into products such as bioethanol, butanol, or lactic acid, which could achieve higher economic returns than the current combustion process.^{8–10}

Undesirable Side Reactions. During Kraft pulping, the major fraction of hemicelluloses are degraded mostly into low-value hydroxy acids.¹¹ However, extracting the hemicellulose under acidic or mild alkaline conditions prior to pulping allows utilization of the hemicelluloses in higher value oligomeric or monomeric form.^{2,12,13} The most important reactions responsible for degradation of polysaccharides and reduction in chain length are the alkaline peeling and alkaline hydrolysis reactions.^{14,15}

Alkaline peeling begins by an enolization of the end carbonyl group, followed by isomerization to a β -alkoxy-carbonyl, which undergoes rapid decomposition, splitting off the end unit, which rearranges to hydroxyl acids. The new end unit on the remaining chain again has an aldehyde end unit, which in turn can be split off.¹⁶ Peeling continues until a stopping reaction occurs, usually in the order of 100 monomers from each starting point, when an alkali-stable conformation is reached.¹⁶ Possible end products of peeling include gluco-isosaccharinic acid in the case of glucomannan, xylo-isosaccharinic acid in the case of xylan, and glycolic acid, lactic acid, formic acid, 2-hydroxy-butanoic acid, and 2,5-dihydropentanoic acid for both types of hemicelluloses.¹⁴ Xylans are more stable than glucomannans because the 4-O-methylglucuronic side groups in xylan provide stability against the peeling reactions. As a result, xylans are peeled off slowly compared to glucomannans, and dissolve partly in the solution as polymers. Alkaline hydrolysis is also responsible for cleaving acetyl groups from the hemicellulose chain.¹⁶ These reactions that occur during pulping will also impact the alkaline extraction process.

Anthraquinone is used as a pulping catalyst and stabilizes polysaccharides against alkaline peeling by causing oxidation of aldehyde end groups on the carbohydrates to stable aldonic acids.¹⁴ A well-known redox mechanism has been proposed where anthraquinone is reduced to anthrahydroquinone by reaction with the aldehyde end groups on the carbohydrates and then reoxidized by reaction with lignin thus accelerating the delignification reactions.¹⁷

Advantages and Disadvantages of the Hemicellulose Extraction Process. Hemicellulose extraction prior to Kraft pulping is anticipated to improve pulp mill operations by reducing Kraft cooking times and increasing production capacity for pulp mills, which are limited by the recovery-furnace throughput.⁵ The recovery boiler and lime kiln may be off-loaded by about 20%, allowing higher throughput in mills where these operations are the bottleneck.¹⁸ Pre-extraction of wood

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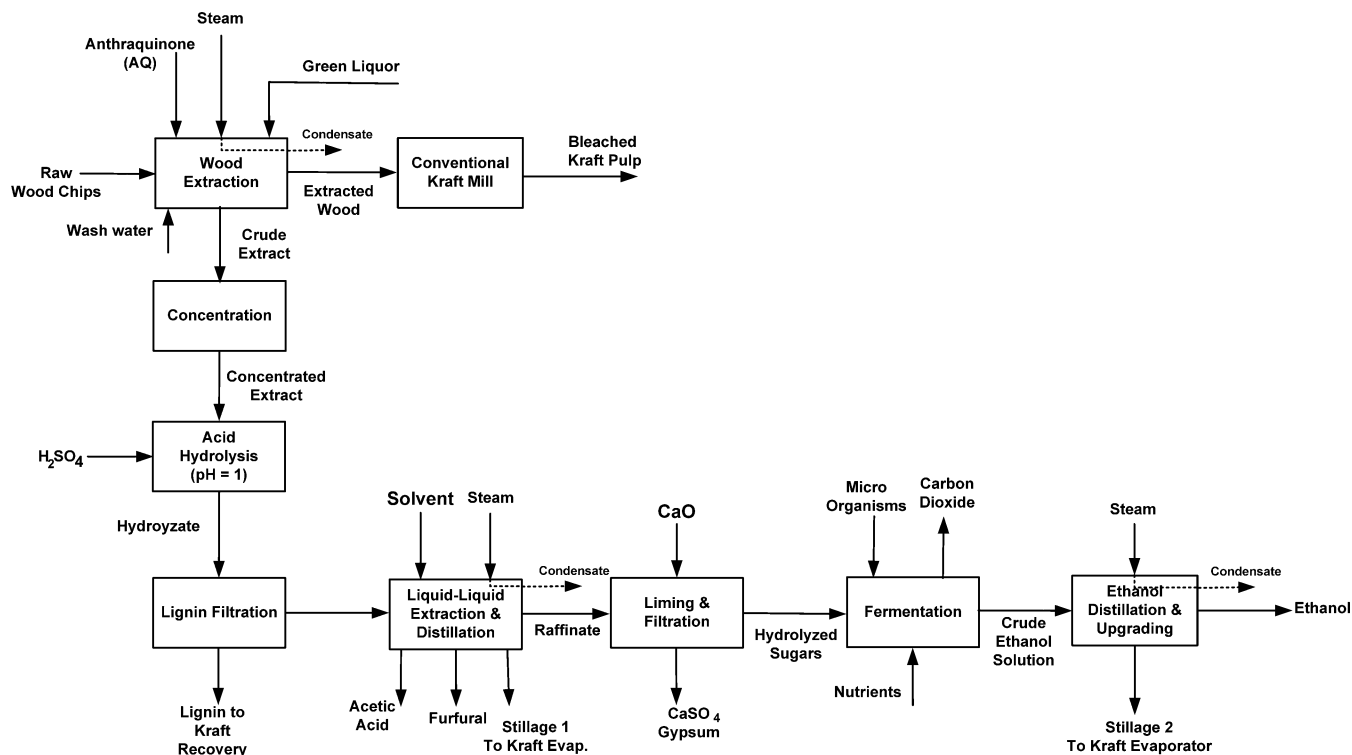


Figure 1. Schematic of proposed near-neutral hemicellulose extraction process.

chips using water/steam as the only solvent has been investigated because it is cheap and environmentally friendly and results in simpler downstream processes compared to dilute acid and alkaline prehydrolysis. Water pre-extraction is also called autohydrolysis because the hydrolysis and subsequent dissolution of the wood is catalyzed by acetic acid released from O-acetyl groups in the polysaccharides, which lowers the pH of the extract to 3–4.¹⁹ Autohydrolysis in combination with kraft pulping to produce coproducts such as ethanol besides pulp has been reported by several research groups.^{20,21} However, as a result of the acidic conditions, high-temperature pre-extraction with water leads to a significant loss in pulp yield and paper strength in the subsequent pulping step.^{12,22,23} Pre-extraction of poplar wood chips at strong alkaline conditions (1–2 Molar NaOH at L/W of 4 kg/L) and relatively low temperatures (50–90 °C) was recently reported.^{13,23} At these conditions, about 40–50 kg (per metric tonne of oven dry original wood) of hemicellulose oligomeric sugars could be extracted without detrimental effect on overall pulp yield when the extracted wood was subjected to modified kraft pulping. In the present study, mixed northern hardwood chips were extracted with alkaline solutions at much lower alkali chemical charges (0–6% as Na₂O on wood) and much higher temperatures (160 °C) so that the pH of the extract obtained was near neutral. A disadvantage of this so-called near-neutral hemicellulose extraction process is that less steam is produced in the recovery boiler because some of the energy content in the wood is contained in the extract and steam is required in the processing of the extract. In addition, a considerable amount of sulfuric acid is required for the hydrolysis step in the process and lime is required for neutralization of the hydrolyzed extract. This gives rise to gypsum, which must be removed and most likely results in a waste disposal problem.

The practice of pre-extracting hemicelluloses is already employed in the manufacture of dissolving grades of pulps, which produce high-purity cellulose for products such as rayon,

cellophane, and cellulose acetate.² In this so-called prehydrolysis-kraft process, the chips are first exposed to high-temperature steam, which results in autohydrolysis of the hemicelluloses. Then, without removing the dissolved hemicelluloses, the chips are delignified using the kraft process.

Near Neutral Hemicellulose Extraction Process. Alternative pre-extraction methods using alkaline chemicals to maintain the pH of the final extraction liquor at near-neutral pH have been reported.^{18,24} A schematic diagram of the proposed near-neutral hemicellulose extraction process using green liquor as the solvent is shown in Figure 1. In the process, extracted wood chips serve as the feed to the conventional Kraft pulp mill, whereas the extracted liquor undergoes concentration by evaporation or ultrafiltration, hydrolysis using sulfuric acid, separation of lignin, acetic acid recovery, neutralization of acids using lime, separation of precipitated calcium sulfate, fermentation into ethanol or other biofuels such as butanol, and lastly alcohol recovery by distillation and product purification. In the scheme shown in Figure 1, acetic acid is also recovered as a valuable coproduct using liquid/liquid extraction followed by stripping and distillation. Alternatively, Jin et al. proposed a green liquor pretreatment of woodchips for repurposed kraft mills, which would produce ethanol instead of pulp and utilize enzymatic hydrolysis along with mechanical refining to generate fermentable sugars from the fiber.²⁵

Objective and Scope. The objective of this work was to assess the composition of hemicellulose extracts made under a variety of conditions and determine which were best suited to the biorefinery operation. The hemicellulose extraction conditions tested in this work, i.e., green liquor charged at 0–6% Total Titratable Alkali (TTA as Na₂O) and 160 °C, dissolves a portion of the hemicellulose and lignin in a manner similar to black liquor, but maintains the pH of the extract at near-neutral conditions so that oligosaccharides are not fully degraded into hydroxy acids. This solution was hydrolyzed using sulfuric acid and fermented to determine its effect on micro-organisms that

produce ethanol and other chemicals. The extracted wood chips then underwent Kraft cooking to determine if the resulting pulp yield was greater than or equal to a control pulp produced using raw chips. The optimum process will generate an aqueous hemicellulose extract solution containing the highest possible concentration of oligosaccharides while preserving or increasing the pulp yield.

Materials and Methods

Chips Used in Experiments. Mixed southern hardwood chips were used in the extraction and Kraft pulping experiments. Raw chips were obtained from a southern Kraft pulp mill following chip screening at the mill. Because the chip sample had been previously screened no additional screening was performed in the laboratory to exclude oversize chips. This procedure was followed to achieve a chip size distribution representative of industrial Kraft processing. Because the chips were not re-screened, it would be expected that the mill chips had a broader chip size distribution than conventional laboratory screened chips. The chip size distribution in laboratory-screened chips often is quite narrow and tightly controlled. As such, the mill chips used in the experiments reported here would be expected to contain a higher percentage of thick oversized chips, leading to higher rejects during pulping.

Hemicellulose Extraction Experiments. Wood chips were extracted with 0% (water), 2%, 4%, and 6% TTA of either sodium carbonate or green liquor in a custom-built rotating digester at the University of Maine Process Development Center. The reactor system consists of 4 stainless steel digesters of 68 L each placed in a single rotating frame. The maximum rated pressure and temperature of the digesters are 15 bar and 205 °C respectively, which are monitored wirelessly by Honeywell XYR 5000 transducers. A Honeywell Experion distributed control system allows simultaneous, independent computer control of the digesters. After extraction or cooking, the liquor is cooled by recirculation through a heat exchanger. Then the liquor is removed by drainage through a ball valve. In each batch, 7 kg of wood (on an oven-dry basis) was added to the digester at liquor to wood ratio of 4:1 kg/kg. The liquor to wood ratio is defined as the mass of extraction liquor (M_L) added to the extraction vessel plus the water in the wood (M_w) divided by the dry mass of wood, (M_{wood})

$$r_{L/W} = \frac{M_L + M_w}{M_{\text{DryWood}}}$$

The wood chips contained 48% moisture (wet basis). All cooks also contained 0.05% anthraquinone (AQ), which has been shown to increase pulp yield and delignification.²⁶ As an example of digester loading, for 2% green liquor the required chemical addition was 15 g NaOH (97% purity), 75 g Na₂S (61.5%), 150 g Na₂CO₃ (100%), and 6.75 g AQ (51.9%). The extraction was performed at a top temperature of 160 °C for target H-factors of 400, 600, and 800 h at each chemical loading. The H-factor is a kinetic model applicable to alkaline pulping that expresses cooking time and temperature as a single variable. It was developed to predict the temperature or cooking time needed to obtain a given lignin content in the pulp, when measured in terms of the Kappa number. The H-factor is given by the expression

$$H = \int_{t_0}^t e^{[43.19 - (\frac{16,113}{T})]} dt$$

where time (t) is in hours and the temperature (T) is given in degrees Kelvin.²⁷ The numerical constants in the expression are related to the activation energy of 134 kJ/mol for delignification during kraft cooking. The H-factors tested correspond to effective cooking times of about 1–2 h. The extracted wood-chips then underwent Kraft pulping. In total, 21 different extraction cooking conditions were tested and compared to the unextracted control Kraft cooks. Water extraction at the 800 h H-factor was performed in triplicate and the standard deviations for each component are used as the basis for error bars of all other conditions presented in the figures.

Kraft Pulping Experiment. Control pulping using raw chips was done in the digesters described above at 16% effective alkali (EA)²⁷ to a target H-factor of 1350 h. Extracted woodchips were pulped after draining the extraction liquor and adding cooking liquor such that the total combined H-factor of the extraction step and Kraft pulping step was maintained at 1350 h. Therefore, the H-factor targets in the Kraft pulping were 950, 750, and 550 h and corresponded to H-factors during the extraction step with 400, 600, and 800 h H-factors, respectively. The target Kappa number for all pulps was 17, which is equivalent to a total lignin content of about 2.55% in the brownstock pulp. Because it is extremely difficult to reach the target Kappa number without performing multiple experiments, pulps with experimental values ranging between 15 and 19 were deemed to have reached the target lignin content. EA was the only parameter that was varied to control the Kappa number of the pulp if the initial Kraft cook did not meet the Kappa target.

Hydrolysis of Extraction Liquor. Samples were hydrolyzed at pH 1.0 with sulfuric acid in an autoclave (Hirayama, Japan). Depending upon the final pH and the carbohydrate content of the extract, the hydrolysis time and temperature were varied in accordance with the data of Garrote and co-workers.²⁸ The mildest hydrolysis conditions were used with the extracts produced using hot water extraction since the low pH conditions in the extraction experiments produced carbohydrates that had been partially hydrolyzed. The liquid extracts produced by increasing the alkali application rate using green liquor (2%, 4%, and 6%) require higher severity hydrolysis conditions. The optimum hydrolysis condition for the water extracted samples was 120 °C for 30 min, whereas alkaline extracts were hydrolyzed at 130 °C for 30 to 60 min depending upon the green liquor application rate in the extraction step. These conditions are in agreement with more recent studies of the hydrolysis of extracts as reported by Mittal et al.^{29,30}

Neutralization, Filtration, and Sample Storage. After hydrolysis, the solutions were filtered through a glass microfiber filter to remove Klason or acid-insoluble lignin. The solution pH was then raised to neutral conditions by careful addition of solid calcium hydroxide and then filtered through glass microfiber filters to remove the precipitated gypsum. The neutralized extracts were then refrigerated for future use in fermentation experiments conducted using several micro-organisms, including *Escherichia coli* K011, *Pichia stipitis* CBS-6054, and *Bacillus coagulans* MXL-9.

Chemical Analyses. Component sugars, organic acids, and furans were analyzed by high-performance liquid chromatography (HPLC) equipped with refractive index and UV detection (Shimadzu, Columbia, MD), using the Aminex HPX-87H column (Bio-Rad, Hercules, CA). The column was operated with a 5 mM sulfuric acid mobile phase at a flow rate of 0.6 mL/min and oven temperature of 60 °C. Samples were filtered through 0.22 µm syringe filters prior to injection. Xylose, mannose, and galactose (XMG) coelute on this column at the

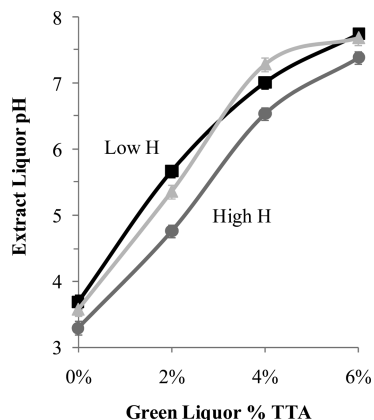


Figure 2. Hemicellulose extraction liquor final pH as a function of alkaline charge and H-factor. Data showed for green liquor closely matches that of carbonate. Low (400 h) H-factor (—■—), medium (600 h) H-factor (—▲—), high (800 h) H-factor (□).

approximate distribution of 85% xylose, 12% galactose, and 3% mannose for hardwood hemicellulose extracts. The distribution of component sugars was found using an Aminex HPX-87P column with a water mobile phase at a flow rate of 0.6 mL/min and oven temperature of 80 °C. Klason lignin content was determined by filtration and gravimetric measurement of the acid hydrolyzed samples. Acid soluble lignin was measured by absorbance at 205 nm using a Thermo-Electron Corp. spectrophotometer following Tappi Useful Method 250.³¹ Sodium analysis was performed by the University of Maine Soil Testing Laboratory using ICP-AES, method EPA 200.7.

Results and Discussion

Hemicellulose Extract Properties. The hemicellulose pre-extraction experiments resulted in liquid solutions containing dilute oligosaccharides, acetic acid liberated from the hemicellulose polymers, lignin, organic acid degradation products, and residual salts from the alkaline chemicals used. The proportions of the various components are determined by the alkalinity (% TTA), and cooking severity (H-factor) in the extraction stage of the process. The two different alkaline chemicals tested — green liquor and sodium carbonate — did not result in significantly different extract solutions or properties of the resulting pulp. The ensuing figures give representative trends only for green liquor.

Figure 2 shows the pH of the extracted liquor as a function of alkalinity and H-factor for the green liquor extraction experiments. For water extractions at 0% TTA, the pH of the final extraction liquor drops to 3.5. Addition of 2% green liquor or carbonate at 400 h H-factor maintained the extract liquor pH near 5.7, but higher H-factors decrease the pH further, indicating more complete consumption of the added alkaline chemicals followed by an increase in acetic acid release. Addition of 4% green liquor or carbonate for H-factors of 400 and 600 h maintained the pH slightly above 7 in the final extract liquor, but at the highest H-factor of 800 h the pH fell below neutral.

All extracts prepared with 6% green liquor or pure sodium carbonate maintained the pH above neutral conditions, indicating incomplete consumption of the alkali. During subsequent acid hydrolysis, any extract with unconsumed alkali, as indicated by a pH above 7, released CO₂ gas upon addition of sulfuric acid, causing the liquid to foam. For processing, the formation of foam required a vessel to have at least 50% headspace to prevent overflow. Foam formation was particularly high in the

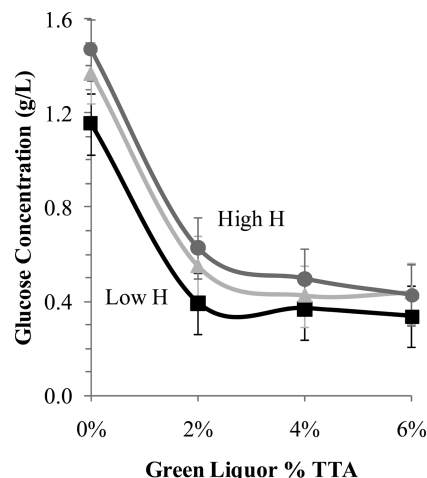


Figure 3. Glucose concentration in hemicellulose extraction liquor as a function of green liquor charge and H-factor. Low (400 h) H-factor (—■—), medium (600 h) H-factor (—▲—), high (800 h) H-factor (□).

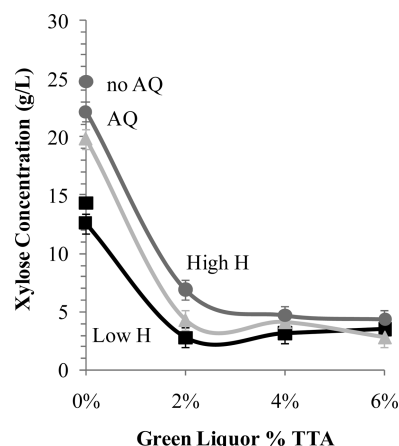


Figure 4. Xylose (XMG) concentration in hydrolyzed extraction liquor as a function of green liquor charge and H-factor. Low (400 h) H-factor (—■—), medium (600 h) H-factor (—▲—), high (800 h) H-factor (□).

6% alkali extracts. For the process to be run efficiently, the residual alkali must be such that excessive foaming does not occur.

The conductivity of the extract was measured for future control purposes with the objective to quickly obtain a measure of the content of inorganic salts in the extract so that the total solids content could be corrected for the inorganic salts. The conductivity increased with alkalinity, ranging from 1 mS/cm in water extracts to 18 mS/cm in 6% carbonate extracts or 14 mS/cm in 6% green liquor extracts. Total solids in the extract were lowest in 2% alkaline extracts at low H-factor (1.9% solids). Solids increased with increasing H-factor as more lignocellulosic material was dissolved and went into solution. Water extracts ranged from 2.2% solids at low H-factor to 3.9% solids at high H-factor. The highest solids levels (5.3%) were present in 6% alkaline extracts at high H-factor.

Sugar Content of Hemicellulose Extract. The concentration of dissolved component sugars that are detected in the extraction liquor following hydrolysis decreases with increasing green liquor addition. This is illustrated in Figure 3 for glucose and Figure 4 for xylose. It can be seen in Figure 3 that glucose is released at low levels for all extraction conditions, ranging from 0.2 to 0.6 g/L in alkaline extractions, and 1.1 to 1.9 g/L in water extractions depending upon the extraction severity.

Table 1. Typical Wood Chemical Distribution for Southern Hardwood Mixture

chemical component (%)	amount (% by wt)	chemical component (%)	amount (% by wt)
arabinan	0.49 ± 0.04	uronic acid	2.30 ± 0.10
galactan	1.28 ± 0.04	klason lignin	26.80 ± 0.30
glucan	46.58 ± 0.05	acid soluble lignin	2.64 ± 0.05
xylan	17.40 ± 0.05	acetyl	2.85 ± 0.10
mannan	2.19 ± 0.05	ash	0.34 ± 0.07

There are several reasons why the glucose concentration is higher in water extractions than in alkaline extractions. First, the acid conditions due to the release of acetyl groups from hemicellulose during water extraction leads to more extensive hydrolysis and dissolution of glucomannan. The amount of glucan in glucomannan in the present mixture of southern hardwoods (Table 1 for overall composition) is estimated as 1.4% (on oven dry original wood) based on a glucose to mannose molar ratio of 1.6 for hardwoods.³² Also at very severe water extraction conditions leading to a pH level of about 3.5, amorphous cellulose is hydrolyzed sufficiently so that low degree of polymerization (DP) fragments may be formed that are soluble in water. The DP must be less than 8 to allow any significant dissolution of cellulose oligomers.³³ Another contribution to the glucose detected after extract hydrolysis is starch. The presence of starch in beech sapwood and the heartwood was earlier reported.³⁴ We recently verified this using the classical iodine test for the autohydrolysate of mixed hardwoods.³⁵ It is known that the solubility of starch in water is high. Because the dissolved glucan during autohydrolysis of hardwoods has a DP of about 75, this supports that a significant part of the glucose detected after alkaline or mild water extract hydrolysis is derived from starch, which is stored in wood as food. Finally, the alkaline green liquor promotes alkaline degradation of the dissolved glucomannan and glucan or starch, and thus reduces the amount of glucose detected in the alkaline extractions.

Arabinose is a minor constituent of hardwood hemicellulose, which is dissolved into the extract solution. Arabinose removal was found to have a maximum of 1.3 g/L, which was achieved in water extracts at all H-factors tested. It was inferred from these results that all of the available arabinose most likely had been removed at the lowest H-factor. Alkali extractions had even lower concentrations of arabinose because arabinose is easily degraded by alkaline peeling reactions.

The principal monosaccharide in the extracts from hardwood was xylose. Xylose extraction, seen in Figure 4, was significantly higher in water extracts than with any amount of alkali. In water extracts, xylose concentration showed a strong correlation to H-factor but the alkaline extracts did not show as strong a correlation. Liquid extracts produced using 2% carbonate or 2% green liquor at higher H-factors begin to exhibit higher xylose concentrations, where there is a corresponding drop in pH. The greatest concentration of xylose, 25 g/L, was generated in water extracts at 800 h H-factor, which did not have AQ added (Figure 4). AQ addition to water extractions lowered the xylose concentration by 2–3 g/L compared to the same H-factor extraction experiment performed without AQ. The highest xylose concentration reached in any of the alkaline extractions was 8 g/L at 2% TTA and occurred at an H-factor of 800 h. The xylose degradation product furfural was not generated in significant quantities for any hemicellulose extracts. Before acid hydrolysis, only water extracts contained measurable quantities of furfural generated during the extraction itself – up to 0.9 g/L at the highest H-factor. Furfural levels in the hydrolyzed

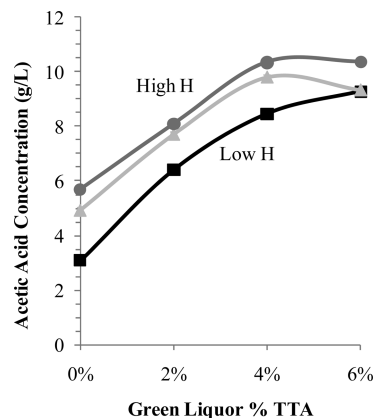


Figure 5. Acetic acid concentration in hydrolyzed extraction liquor as a function of green liquor charge and H-factor. Low (400 h) H-factor (—■—), medium (600 h) H-factor (—▲—), high (800 h) H-factor (—○—).

extract can be minimized if the hydrolysis severity is tailored to the individual feedstock. Alkaline extracts did not generate more than 0.2 g/L of furfural in any case tested at the optimum acid hydrolysis condition.

By-Products of the Hemicellulose Extract Process. When evaluating optimum extraction conditions there are several important considerations. Impact on pulp yield is critical, but effect on downstream fermentation operations is also of great importance, as many byproduct of the extraction process have inhibitory effects on growth of microorganisms.³⁶ Compounds with the potential to accumulate to inhibitory concentrations include sodium, furfural, lignin, formic acid, and acetic acid. The alkali charge determines how much sodium will remain in the final liquor. The measured concentration of sodium in the extract liquor varied from 3 g/L to 9 g/L depending upon the TTA application rate; 2–6% TTA based on wood. To minimize sodium inhibition the extraction should be done with the minimal amount of alkali needed to protect the pulp quality.

Acetic Acid. Acetic acid is an important byproduct of the hemicellulose extraction process. Acetyl groups are liberated from the hemicellulose in the form of acetate when the pH is above the pK_a of acetic acid (4.8). At lower pH, the acetyl groups lead to the formation of acetic acid. In the extract, the amount of acetyl groups removed from the hemicelluloses and the split between the acetate and the acid form will depend upon pH of the extraction liquor. Figure 5 shows the concentration of acetic acid in hydrolyzed green liquor extracts as a function of alkaline charge and H-factor. Acetic acid content increases with both increasing H-factor and increasing alkalinity and reaches a maximum of 10.5 g/L at the highest alkaline charge and H-factor (Figure 5). However, once the maxima is reached no further increase in acetyl groups is observed and this suggests that no additional acetyl groups are removed from hemicellulose polymers in the fiber wall. In alkaline extracts, the acetyl groups are cleaved entirely from the hemicellulose chain during the extraction process and subsequent acid hydrolysis does not result in an increase in acetic acid. However, in water extracts more than half of the acetyl groups remain bound to the hemicellulose prior to acid hydrolysis. Concentration of acetic acid in low H-factor water extracts increases from 1.3 g/L before hydrolysis to 3.5 g/L after hydrolysis, 2 g/L to 5 g/L at medium H-factor, and 3 g/L to 7 g/L at the highest H-factor. Acetic acid is both a valuable coproduct and an inhibitor to downstream fermentation. Acetic acid can be removed by liquid–liquid extraction before fermentation, as described in Figure 1, and purified by distillation for sale as a byproduct.

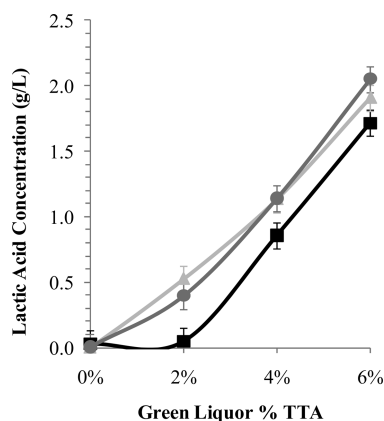


Figure 6. Lactic acid concentration in hydrolyzed extraction liquor as a function of green liquor charge and H-factor. Low (400 h) H-factor (—■—), medium (600 h) H-factor (—▲—), high (800 h) H-factor (□).

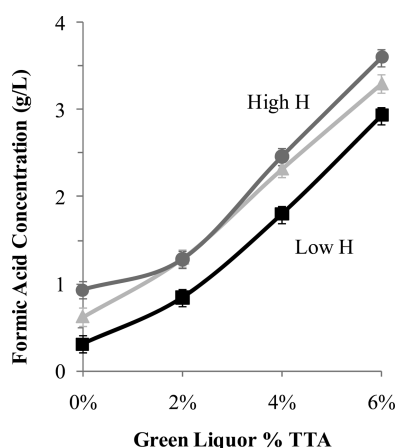


Figure 7. Formic acid concentration in hydrolyzed extraction liquor as a function of green liquor charge and H-factor. Low (400 h) H-factor (—■—), medium (600 h) H-factor (—▲—), high (800 h) H-factor (□).

Lactic and Formic Acids. The alkaline peeling reactions lead to formation of lactic acid and formic acid through degradation of the extracted carbohydrates. The concentration of lactic acid in the hydrolyzed extracts is shown in Figure 6. Lactic acid is not formed at all during water extractions, indicating that it is only formed through alkaline peeling. Formic acid, seen in Figure 7, is formed during water extraction to a small extent, indicating that acid hydrolysis caused by the cleaved acetyl groups may also be a formation mechanism. Both the lactic and formic acid concentrations increase steadily with increasing alkalinity and also to a lesser extent with increasing H-factor. The maximum lactic acid concentration was 2 g/L and the maximum formic acid was 3.6 g/L; both were reached at 6% TTA green liquor and an H-factor of 800 h.

Lignin Degradation Products. Lignin degraded phenolics are potential inhibitors to the downstream fermentation operation. Insoluble lignin can be removed by filtration prior to fermentation but acid soluble lignin remains. Acid soluble lignin concentrations were slightly higher in green liquor extracts than carbonate extracts because sulfide aids in delignification. The highest concentration of acid soluble lignin, 9 g/L, was achieved at an H-factor of 800 h and 6% green liquor, whereas 6% carbonate at the same severity only produced 6 g/L of acid soluble lignin. Figure 8 shows the concentrations of soluble lignin in green liquor extractions following hydrolysis. All of the curves shown in Figure 8 resulted from experiments in which

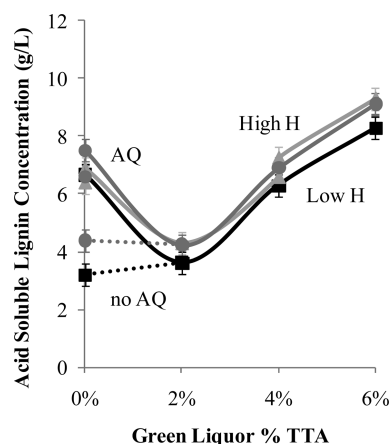


Figure 8. Acid soluble lignin concentration in hydrolyzed extraction liquor as a function of green liquor charge and H-factor. Low (400 h) H-factor (—■—), medium (600 h) H-factor (—▲—), high (800 h) H-factor (□).

0.05% anthraquinone (AQ) was added to the extraction step to aid in pulping the partially macerated chips following extraction. The water extraction experiments included in Figure 8 were also conducted with AQ for consistency. Water extraction experiments performed without AQ had much lower concentrations of acid soluble lignin, which are indicated with dotted lines. AQ is added during pulping to increase delignification, so this result was anticipated. Water extracts without AQ contained approximately 3 g/L acid soluble lignin, compared to 7 g/L in water extracts that did contain 0.05% AQ. Acid soluble lignin can be removed by ion exchange methods if it would inhibit fermentation but would of course add to the complexity and capital and operating cost of the process.

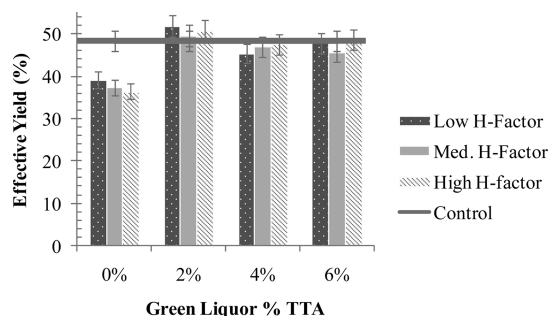
Kraft Pulping of Hemicellulose Extracted Wood Chips. Typically almost half of the xylan and mannan polymers are lost during Kraft pulping.¹⁵ It is the objective here to recover these polymers as component sugars while maintaining the composition of the pulp similar to that obtained during conventional Kraft pulping with equal pulp yield and physical properties.

Kraft pulping of extracted wood chips is affected by many variables. Consequently, it is difficult to compare pulp qualities and yields on a uniform basis for the combined processes of pre-extraction and Kraft cooking. The H-factor and white liquor charge of Kraft pulping for extracted woodchips were adjusted to the pre-extraction H-factor and alkali charge so that the combined operations would represent uniform cooking severity. For an accurate direct comparison of pulp yields between varying pre-extraction conditions, all pulps should have had a uniform Kappa number of 17. The final Kappa number of the unbleached pulp varied between 15 and 19 because it proved difficult to hit the target kappa number 17 exactly.

Effective Pulp Yield. Rejects in a Kraft pulp mill are often repulped to recover additional wood pulp. Rejects result from oversized chips as well as knots and reaction wood, which have high lignin content. Because screened mill chips were used that had a greater proportion of oversized chips compared to laboratory chips, the pulp rejects were high in this experiment (Table 2). In a mill situation, screened rejects would be repulped by recycling them back to the digester. Because mill chips were used in the current experiments the effective pulp yield was used as the indicator for pulp obtainable from the process. Figure 9 shows the effective pulp yield achieved at each pre-extraction condition, in comparison to the unextracted control. The effective pulp yield (Y_{eff}) was estimated as the mass of screened

Table 2. Effect of Hemicellulose Extraction on Pulp Quality and Yield

extract H-factor (hrs)	extract % TTA	total yield on OD wood (%)	screened yield on OD wood (%)	rejects on OD wood (%)	effective yield (%)	Kraft EA (%)	residual EA (g/L)	black liquor solids (g/L)	Kappa # (mL)	viscosity (cps)	fiber strength factor (psi) ^a	Canadian Standard Freeness (mL) ^a	wet zero-span breaking length (m) ^a	brightness (%ISO) ^a
Kraft Control		49.5	46.4	3.1	48.3	15.6	4.2	167.1	17.4	36.6	32.8	503	13.6	23.6
400	0	42.7	33.8	8.9	39.2	12.0	0.3	130.2	17.3	74.2	32.0	592	13.3	23.3
400	2	53.5	49.4	4.1	51.9	14.2	5.1	151.3	16.5	36.2	34.2	528	14.2	26.4
400	4	46.4	43.8	2.5	45.3	13.9	7.3	146.8	15.9	37.7	33.5	482	13.9	26.7
400	6	49.4	45.2	4.2	47.7	10.5	3.0	126.5	18.8	55.8	33.2	502	13.8	25.0
600	0	42.2	30.2	12.1	37.4	12.0	0.1	122.7	17.8	87.2	30.3	623	12.5	23.4
600	2	51.3	47.2	4.1	49.6	15.3	8.5	160.7	17.4	41.1	33.7	499	13.9	27.4
600	4	48.3	44.6	3.7	46.8	13.9	10.4	159.3	16.1	38.7	35.3	506	14.6	26.4
600	6	46.8	43.7	3.1	45.6	11.9	7.2	135.7	17.9	49.0	35.5	496	14.7	24.7
800	0	40.3	30.5	9.8	36.4	12.0	0.5	130.2	17.6	77.2	27.6	612	11.5	24.1
800	2	56.0	42.9	13.0	50.8	14.8	1.4	126.1	17.7	91.2	34.3	516	14.2	22.5
800	4	49.5	44.8	4.7	47.6	13.3	7.3	144.0	18.8	53.9	34.5	501	14.3	25.6
800	6	51.4	44.7	6.6	48.7	11.3	6.0	126.6	18.6	62.4	34.1	489	14.1	25.5

^a At 4000 PFI revolutions.**Figure 9.** Effective pulp yield for green liquor extracted woodchips.

pulp (M_S) plus 60% of the mass of the screened rejects (M_R) divided by the initial mass of dry wood sent to the extraction vessel ($M_{Dry\ Wood}$).

$$Y_{Eff} = \left[\frac{M_S + 0.6 \cdot M_R}{M_{Dry\ Wood}} \right]$$

The factor of 60% is the industrially observed efficiency for repulping screened rejects. For green liquor extraction, 2% alkali charge may achieve as high as 50% effective pulp yield, an increase of 3% over the control. Water extraction however shows a clear drop in pulp yield, averaging as much as 12 percentage points lower than the control for the experiments in which AQ was added as a pulping additive. Green liquor addition at 4% and 6% were slightly below or equal to the control pulp yield within the accuracy of the experiments.

Pulp Physical Properties. Measurement of pulp yield is a strong indicator of whether hemicellulose extraction has impacted the cellulose fiber quality and process economics, but it is certainly not the only consideration. For a successful extraction process, the physical properties of the resulting pulp must not be negatively impacted. Selected testing of pulp properties at all hemicellulose extraction conditions was performed. The results are summarized in Table 2. Nearly all extracted pulps experienced an increase in viscosity. For hot water extraction, the viscosity in all cases was more than doubled. Green liquor extracted pulps all had higher viscosity than carbonate extraction at the corresponding charge and H-factor. The least impact on viscosity was observed at low H-factor and 2% or 4% alkaline charge.

Physical strength properties such as fiber strength factor and wet zero-span breaking length were measured after beating the pulps at 4000 revolutions in a PFI mill are listed in Table 2.

The data show that green liquor extracted kraft pulp fibers are stronger than the control kraft pulp irrespective of green liquor extraction conditions. On the other hand, the strength properties of the water-extracted kraft pulps are lower than that of the control especially at high H-factor extractions. Thus, it appears that the strength properties of the pulps produced by the three different processes (green liquor extracted kraft, water-extracted kraft, and control kraft) correlate roughly with total pulp yield and thus hemicellulose content. The positive correlation between hemicellulose content and fiber strength was earlier noticed by Duchesne et al. (2001) for different softwood kraft pulps.³⁷ They explained that in fibers with low hemicellulose content the fibrils aggregate to form larger macrofibrils resulting in a much more compact cell wall ultrastructure. The increased size of the macrofibrils may explain the decreased ability to take up and transfer load and thus explain the decreased mechanical properties of the water-extracted kraft fibers.

Pulp drainage as measured by Canadian Standard Freeness after beating the pulps at 4000 revolutions in a PFI mill was highest for water-extracted kraft pulps as can be seen in Table 2. This agrees with well-known experience that low hemicellulose content pulps are difficult to beat. The green liquor pre-extracted kraft pulps had about the same beating behavior as the kraft control fibers. The optical brightness of the green liquor pre-extracted kraft pulps is generally higher than that of the kraft control, whereas the water extracted kraft pulps have the same brightness as the kraft control.

Conclusions

Extraction of woodchips prior to Kraft pulping has the potential to remove hemicellulose selectively without degrading the cellulose fiber. Addition of 2% green liquor maintains the pH of the final extract at near-neutral conditions and prevents acetic acid from causing autohydrolysis of the cellulose. Water extraction releases the highest amount of oligosaccharides but does so at the expense of pulp yield. The highest concentration of sugars was 30 g/L in water extracts at high H-factor, but the corresponding pulp yield was only 35%. Control Kraft pulping experiments conducted with mill chips showed an effective pulp yield value of 47%, whereas pulping green liquor extracted woodchips led to similar pulp yields. For the 2% green liquor extraction experiment conducted at an H-factor of 400 h, effective pulp yields were about 50% (Table 2). Carbonate and green liquor extraction resulted in similar aqueous extract composition and pulp yields. The hemicellulose extraction process can be tailored to optimize the economic trade-off

between oligosaccharide concentration and pulp yield based on the data presented in this work. Recovery of acetic acid is possible and would represent a valuable byproduct.

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