Hemicellulose Extraction from South African *Eucalyptus grandis* using Green Liquor and its Impact on Kraft Pulping Efficiency and Paper Making Properties

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The feasibility of enhancing the efficiency of the kraft pulping operations while at the same time evolving the process into a biorefinery, and thus producing hemicelluloses together with paper products, was studied. Hardwood chips (*Eucalyptus grandis)* were pre-treated with green liquor prior to pulp production. At optimal pre-treatment conditions, the pH of the resulting extract was 7.8, the wood weight loss was 14%, and the hemicellulose extracted was almost 40 kg/ton of woodchips. In the subsequent kraft pulping, the resulting data revealed that the woodchips from which hemicellulose had been pre-extracted could be pulped much faster than woodchips pulped without hemicellulose extraction. As a result, to maintain the target kappa number, a 20% reduction in pulping chemicals was achievable. Hemicellulose pre-extraction led to a 10% reduction in black liquor solid contents. Moreover, the strength properties of the pulps produced with and without hemicellulose extraction were comparable. Industrial acceptance of this concept, however, still requires a more accurate understanding of the effect of specific mill operating conditions on mill energy balance. Careful economic assessment of the options for handling the calcium carbonate scale problem will also be required before the technology can be considered for implementation.

Keywords: Biorefinery; Eucalyptus grandis; Green liquor pre-treatment; Hemicellulose pre-extraction; Kraft cooking; Black liquor properties; Pulp quality; Paper Strength properties

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INTRODUCTION

The South African pulp and paper industry seeks to increase revenues and improve the environmental performance of its pulp and paper operations. One promising approach to achieving this goal is enhancing the efficiency of the pulping operations, whilst at the same time evolving into forest biorefineries. The production of new value-added materials together with traditional paper products has significant potential to provide additional income and mitigate some environmental impacts (Van Heiningen 2006).

Kraft pulp mills are primary candidates for consideration of the integration of biorefinery concepts, as the hemicellulose that is traditionally wasted in the pulping process could be extracted prior to pulping. The key reason for extracting hemicelluloses prior to pulp production has to do with the fact that during kraft pulping, hemicelluloses, together with lignin, are degraded and partly end up in the spent liquor, which is referred to as “black liquor” (Suckling *et al*. 2001; Van Heiningen *et al*. 2003). In current mill practices, the black liquor is combusted in the recovery boiler in order to regenerate pulping chemicals and to produce energy. Lignin and hemicelluloses present in the black liquor are the main source of energy. However, the contribution of hemicelluloses to the overall black liquor heat value has been found to be insignificant (Van Heiningen 2006). This has made it necessary to find optimal economical ways of utilizing the hemicelluloses wasted during kraft pulping.

Hemicelluloses could be used as a feedstock for the production of value-added chemicals such as furfural, acetic acid, xylitol, and additives for improving pulp yield and paper strength (Ladisch *et al*. 2005; Van Heiningen 2006). Hemicelluloses could also be used as a feedstock for the production of biofuels such as ethanol (Hamelinck *et al*. 2005; Van Heiningen 2006).

In order to create a processing stream for the hemicelluloses, woodchips must be pre-treated prior to the pulp production so that the hemicelluloses may be extracted. The amount of hemicelluloses extracted depends on the severity of the pre-treatment conditions. Since, in pulp production, hemicelluloses play a vital role in determining the pulp yield and the pulp quality (Christensen 1998; Gullichsen and Fogelholm 1999), the economic limitation related to yield loss and/or poor pulp quality must be avoided. Furthermore, to maintain the energy and the inorganic balances in the chemical recovery cycle at the mill (Pendse *et al*. 2009), the lignin and the organic salts must be recovered from the hemicelluloses processing streams and sent to the recovery boiler. Lignins are recovered from the hemicellulose extract through acidic precipitation or ultrafiltration and/or the combination of the two. The filtrate is rich in hemicelluloses and can be concentrated or directly processed to yield the desired products.

The dissolution of hemicelluloses involves the hydrolysis of ester and ether bonds that link the hemicelluloses to lignin (Cheng *et al*. 2010; Zheng *et al*. 2009). As a result of this dissolution, the removal of lignin is facilitated in the subsequent pulping process. This can lead either to a greater retention of pulping chemicals or to a reduction in the pulping time. Such changes are critical in achieving cost reduction and improvements in the environmental performance of kraft pulp mills.

The choice of the hemicelluloses extraction process is critical and depends on its efficiency, selectivity, and compatibility with the existing pulp production process. Usually, mild alkaline treatment favors higher solubility of hemicelluloses with less degradation to furfural (Cheng *et al*. 2010; Carvalheiro *et al*. 2008). Such a pre-treatment process has the potential to allow the evolution of a kraft pulp mill into a forest biorefinery. For example, in the case of a kraft pulp mill integrated with an ethanol production facility, a pre-treatment process that results in a formation of extract which is too acidic limits the recovery of the solubilized hemicelluloses (Hamelinck *et al*. 2005). This is because under acidic conditions, the monomeric sugars in the extracts are further solubilized to degradable products such as furfural and hydroxymethylfurfural (5-HMF). These compounds are referred to as “inhibitors”, and extracts having high concentrations of inhibitors are difficult to process and may lead to an increase in downstream operational costs. For example, this may include the requirement of detoxification process stages or higher enzyme and yeast dosages during enzymatic hydrolysis and the fermentation process, respectively (Hamelinck *et al*. 2005). Hence, a pre-treatment method that minimizes the formation of degraded products has the potential to also minimize downstream operational costs (Ladisch *et al*. 2005). At the same time, during pulp production, pre-treated woodchips that form an acidic extract may also require washing or pH adjustments, which inevitably will require additional investment and operational costs. Furthermore, the pulping of pre-treated woodchips produced under acidic conditions has been shown to produce pulp with inferior yield and strength properties (Helmerius *et al*. 2010; Yoon *et al*. 2011).

Hemicelluloses obtained from different wood resources are not the same. The dominant hemicelluloses in hardwoods are acetylated 4-O-methyl glucuronoxylan (xylan), while in softwoods the dominant hemicelluloses are glucomannan (Christensen 1998; Van Heiningen 2006). De-acetylated, solubilized oligomeric xylans are stable in hot alkaline solutions due to their 4-O-methyl glucuronic acid side chains (Van Heiningen 2006; Helmerius *et al*. 2010). In contrast, the alkaline peeling reaction degrades glucomannans severely under alkaline conditions (Helmerius *et al*. 2010; Van Heiningen 2006). This suggests that the nature of the wood resource is an important factor governing the choice of the pre-treatment method. For instance, alkaline solutions are more suitable for hemicellulose extraction from hardwoods than from softwoods.

Hemicellulose pre-extraction from hardwood chips using various alkaline solutions combined with pulp production has been investigated previously (Helmerius *et al*. 2010; Sixta and Schild 2009; Yoon and Van Heiningen 2010; Jin *et al*. 2010). However, considering a number of factors such as investment and operational costs and compatibility with the existing kraft process, applications of some of the alkaline solutions are limited. Generally, alkaline solutions that are directly accessible at the kraft pulp mills are more economically attractive to the industry. Therefore, much attention has been focused on green liquor and kraft pulping liquor (white liquor). Helmerius *et al*. (2010) reported hemicellulose extraction from North America hardwoods using white liquor. Although the pulp produced from the pre-extracted hardwood chips met the requirements for paper making properties, the hemicellulose yield was quite low. Presumably, the low yield of hemicellulose was observed because white liquor is a strongly alkaline solution, and consequently the solubilized hemicelluloses were severely degraded.

In order to maximize the hemicellulose yield (in a pure polymeric form) with minimal wood yield loss, a pre-treatment process resulting in a near-neutral pH has been proposed (Ladisch *et al*. 2005; Yoon and Van Heiningen 2010; Zheng *et al*. 2009). Maintaining a near-neutral pH prevents excessive carbohydrate hydrolysis (Ladisch *et al*. 2005; Mao *et al*. 2008). Furthermore, a near-neutral pH preserves dissolved hemicelluloses as oligomers, which minimize the formation of sugar degradation products (Hamelinck *et al*. 2005; Zheng *et al*. 2009). Mao *et al*. (2008) reported an extract with a near-neutral pH when performing the extraction of hemicelluloses from North American mixed hardwoods using green liquor. When the hemicellulose extraction was limited to 45 kg/ton of wood chips, the pulp quality was comparable to that of the pulp produced without hemicellulose extraction. Additionally, the extracted hemicelluloses could be used as yield improvement additives because they are rich in hemicellulose oligomers. This can be explained by the fact that green liquor is a mild alkaline solution rich in sodium carbonate salts, which provides a buffering effect that prevents the pH from dropping to acidic levels.

In previous studies it has been claimed that green liquor hemicellulose extraction could be integrated with pulp production. It was thought that it would be very interesting to see how South African-grown wood resources respond to the green liquor hemicelluloses extraction process. The emphasis of this study was thus on acquiring data on hemicellulose yield, adjusted kraft pulping conditions, pulp quality, and black properties that will enable the South African pulp and paper industry to integrate this technology in their mills.

Additionally, in order to determine the extent to which this concept would help to reduce the amount of HexAs prior to bleaching, *Eucalyptus grandis*, a wood species that is known for the formation of a large amount of hexenuronic acids (HexAs) during standard kraft cooking, was chosen for the study. The effect of the pre-treatment conditions on wood loss, pH of the resulting extract, and the dissolution of hemicelluloses were evaluated and optimized. Furthermore, the impact of hemicellulose extraction on subsequent kraft pulping efficiency, pulp quality, and black liquor properties were also studied. The kraft pulping efficiency was defined as how much faster lignin could be removed after the hemicelluloses extraction.

EXPERIMENTAL

Materials

Eucalyptus grandis woodchips obtained from a kraft pulp mill in South Africa were used in this study. The woodchip samples were screened using a vibrating screen to remove under- and over-sized chips, knots, and bark. Air-dried chips with an average thickness of 3 to 8 mm were collected and stored in plastic bags for the subsequent experiments. Chip moisture contents were determined according to TAPPI method T258 om-94. For wood chemical characterization, chips were ground into sawdust in the range of 40 to 60 mesh using a Wiley mill. Klason lignin was determined according to TAPPI method T222 om-88. The determination of sugars was done using high-performance liquid chromatography (HPLC). Samples of the wood sawdust were first hydrolyzed in two steps. Thereafter, the extracts were diluted and filtered through a 0.22 µm syringe filter and analyzed using HPLC. The sugars measured were arabinose, galactose, glucose, xylose, and mannose, which were then corrected for arabinan, galactan, glucan, xylan, and mannan, respectively.

Pre-extraction of Hemicelluloses

Key variables that could lead to process constraints and thus limit the integration of hemicellulose extraction with pulp production were studied. These variables were: the pH of the resulting extract, the wood loss, and the concentration of hemicelluloses in the extract. The solution used for extracting the hemicelluloses was green liquor. Green liquor was prepared by mixing sodium hydroxide, sodium carbonate, and sodium sulphide. The liquor specifications were kept similar to those attained in industrially generated green liquor (Christensen 1998; Gullichsen and Fogelholm 1999): sodium sulphide (40 g/L as Na_2O), sodium hydroxide (12 g/L as Na_2O), and sodium carbonate (95 g/L as Na_2O). The green liquor dosages were varied between 0% and 3% at a constant liquor-to-wood ratio of 3:1.

In all of the pre-treatment experiments, the hardwood chips were pre-treated at 170 ^oC in a 7-liter rotating digester, and the reaction times were varied between 15 and 90 min. At the end of each pre-treatment, a portion of the spent liquor was collected and stored in the cold room at 4 ^oC for a pH and chemical composition analysis. The wood loss was evaluated gravimetrically; solid residue obtained after performing the pre-treatment was expressed as percentage of the wood mass charged into the digester (on an oven dry basis). The determination of sugars in the extract was performed using HPLC. The extract pH was first adjusted to a pH of 5 to 6 using 6 mol/L of HCl, and then the sugars were hydrolyzed via heating with 4% H_2SO_4 at 121 ^oC for 1 h. The filtration and dilution steps were also done before injection into the HPLC. For sugar yield calculations, the HPLC analysis data for arabinose, galactose, glucose, xylose, and mannose were corrected for arabinan, galactan, glucan, xylan, and mannan (Janson 1974; Yoon *et al*. 2011).

All of the pre-treated woodchips were defiberized using a disk refiner equipped with defiberation plates. Defiberized pulp samples were spin-dried to remove excess water, weighed, and stored in plastic bags at 4 ^{o}C for yield and/or wood loss determination. Following the screening of the effects of pre-treatment conditions on key variables that could lead to process constraints at a kraft pulp mill, the pre-treatment conditions that resulted in relatively high hemicellulose yields at a minimal wood loss were selected for subsequent kraft pulping studies.

Kraft Pulping of Hemicellulose Pre-Extracted Woodchips

Control kraft cooks (without hemicellulose extraction) were performed using the following pulping conditions: 18% active alkali (as Na_2O), liquor-to-wood ratio 4.5:1, 90 min ramp time to 170 ^{o}C, and the time to reach 170 ^{o}C was varied until a desired target kappa number of 20 was achieved. In kraft pulping of hemicellulose-extracted wood chips, pre-treatments were performed in the same manner as described previously and in the same rotating digester that was used for the pre-treatment stage. The only exception was that the free spent liquor from each pre-treatment was drained out prior to pulping using the same conditions as described for the control. After pulping, the pulp samples were thoroughly washed with hot water to remove residual liquor. Next, the pulp samples were screened and stored in plastic bags at 4 ^{o}C until further use. The screened pulp yield (SPY) was evaluated gravimetrically, and screened pulp obtained after pulping of hemicellulose-extracted wood chips was expressed as a percentage of the wood mass that was charged into the digester before hemicelluloses extraction (on an oven dry basis). The portion of the spent liquor samples, *i.e.*, “black liquor”, was collected and stored at 4 ^{o}C for further analysis.

Evaluation of Pulp Properties

Pulps produced with and without pre-treatments at the desired target kappa number were characterized. The kappa number, pulp yield, and viscosity were measured according to standard testing methods. The hexenuronic acid content in pulps was measured according to TAPPI standard method T282 pm-07. Pulps were refined in a PFI mill, and handsheets were prepared according to TAPPI standard method T205 sp-95. Strength properties, including sheet density, tensile index, tear index, and burst index, were tested using TAPPI standard methods T494 cm-01, T403 om-02, and T414 om-04, respectively. Pulp polysaccharides were characterized using high performance liquid chromatography (HPLC). For statistical purposes, all data reported were the mean of 3 independent measurements.

RESULTS AND DISCUSSION

Pre-extraction of Hemicelluloses

Effects of pre-treatment conditions on extract pH and wood loss

The effects of pre-treatment conditions on the extract pH and wood loss are presented in Table 1. The data showed that the pH of the extracts was strongly influenced by the green liquor dosage across the entire range of pre-treatment conditions. The pH values of the extracts were in the range of 3 to 3.2, 4 to 5, and 5 to 9 for the green liquor dosages of 0%, 1%, and 3%, respectively. The results indicated that when the pre-treatments were performed without green liquor (0%), the resulting extract pH was extremely acidic, *i.e.*, pH<4. As reported by Helmerius *et al.* (2010) and Yoon *et al.* (2011), hot water pre-treatments are characterized by the hydrolysis of acetyl groups in hemicelluloses. The hydrolysis of acetyl groups leads to the formation of acetic acid, which causes the pH of the resulting extract to drop to acidic levels.

In contrast, when the green liquor was applied at 1% and 3% dosage levels, increases in the pH of the extracts were observed at the higher dosage. This may be because at a high dosage, there is a sufficient concentration of sodium carbonate to provide an effective pH buffering effect. Furthermore, it can also be seen that the extract attained a near-neutral pH when the pre-treatment time of 45 to 60 min was applied at a 3% dosage (highlighted in Table 2).

Table 1. Effects of Pre-treatment Conditions on Extract pH and Preserved Wood Yield

Green liquor dosage (%)	Time (min)	Yield (%)*	Extract pH**
0 (water)	15	84.3±0.0	3.2±0.0
	45	76.1±1.0	3.1±0.0
	60	74.8±0.2	3.0±1.4
	90	72.9±0.9	3.0±0.02
1	15	95.0±0.3	5.3±0.0
	45	91.1±0.3	5.0±0.2
	60	88.4±0.2	4.8±0.0
	90	79.1±0.3	4.4±0.0
3	15	87.7±1.7	9.2±0.8
	45	**86.1±1.1**	**7.8±0.2**
	60	**84.0±0.5**	**6.8±0.1**
	90	81.6±0.0	5.6±0.1

* Yield data are expressed as % of original woodchip weight, oven dried weight basis (ODW), charged in the digester

** The spent liquor pH was collected and measured after performing the extraction.

Pulp yield is a primary concern for pulp mills that seek to evolve into biorefineries. The effectiveness of the chosen pre-treatment process in preserving the wood yield is important during the pre-treatment stage. It was, therefore, necessary that the effects of the pre-treatment conditions be screened and that the optimal conditions be identified. This helps to avoid excessive wood loss, which has a detrimental effect on pulp production. As expected, increases in both green liquor dosage and pre-treatment time had an adverse effect on wood yield. The effects were much more pronounced at a lower dosage: for example, at 0% the wood loss was in the range of 16% to 27%. However, when pre-treatments were performed at a higher green liquor dosage, such as 3%, more wood was preserved (at a dosage of 3%, wood losses were in the region of only 12% to 18%). The higher wood loss at a lower dosage may be caused by the induced effects of hot-water-like pre-treatments, which lead to the excessive dissolution of carbohydrates (Yoon *et al.* 2010; Tunc *et al.* 2010; Tunc and Van Heiningen 2008a). On other hand, pre-treating wood chips with green liquor prior to kraft pulping has been shown to stabilize carbohydrates towards the peeling reaction (Ban *et al*. 2003b; Olm *et al.* 1996), thus reducing yield loss in the subsequent pulping process.

Effects of pre-treatment conditions on the solubilization of the carbohydrates

Having established the effects of pre-treatment conditions on extract pH and wood loss, it was clear that a near-neutral pH could be obtained by using a green liquor dosage of 3%. As a result, the amount of carbohydrates solubilized in the extract only at this green liquor dosage was determined. The resulting data are presented in Fig. 1. The total sugars (carbohydrates) are the summation of the hemicelluloses and cellulose present in the extract. When considering both wood loss data (Table 1) and carbohydrate dissolution data (Fig. 1), it can be seen that most of the wood weight loss was contributed by hemicelluloses. Over the entire range of pre-treatment conditions investigated, the highest amount of cellulose in the extract was 0.5%. These results indicated that the green liquor pre-treatment was more selective, and that as a result, degradation of the cellulose was minimal.

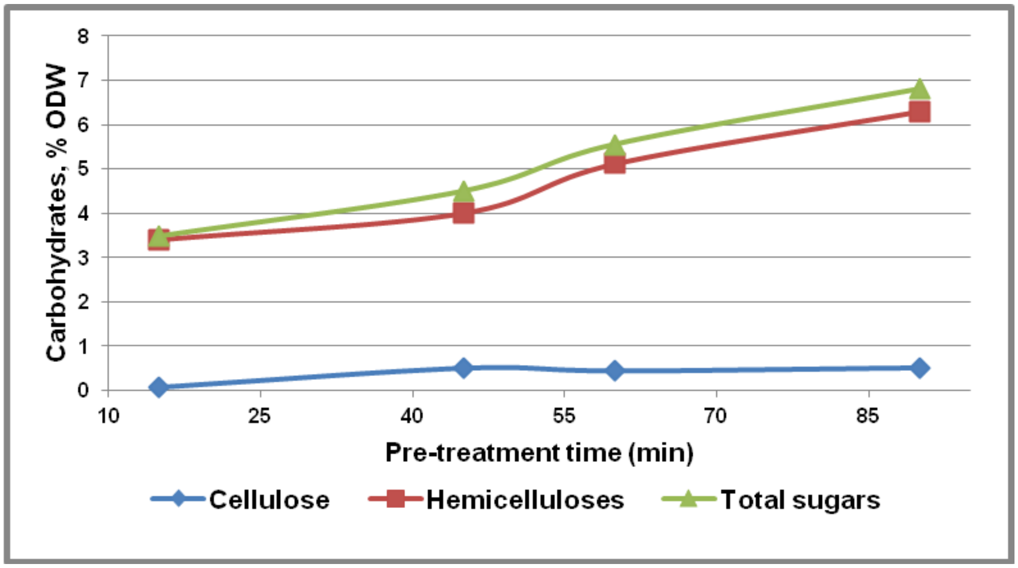

Fig. 1. Effects of pre-treatment conditions on the dissolution of wood carbohydrates. Carbohydrate data are expressed as a percentage of the original wood weight (oven dried weight basis).

Presumably, maintaining a near-neutral pH minimizes random hydrolysis of carbohydrates (Ladisch *et al*. 2005; Mao *et al*. 2008), resulting in a higher retention of cellulose. Referring to wood losses and carbohydrate yield data in Table 1 and Fig. 1, respectively, it can also be seen that there was a tradeoff between preserved wood yield and carbohydrate yield, *i.e.*, a higher carbohydrate yield could be obtained at the expense of a higher wood loss. For instance, at a pre-treatment time of 90 min, the carbohydrate yield was 6.3% of the original wood weight (on ODW basis), and the corresponding wood loss was 18.4%. On the other hand, when using a pre-treatment time of 45 min, the carbohydrate yield was 4% and the corresponding wood loss was 14%.

The optimal pre-treatment conditions were identified as being a pre-treatment time of 45 min and a green liquor dosage of 3% at 170 ^{o}C. Using these conditions, the wood loss was 14%, the pH of the resulting extract pH was 7.8, and the hemicellulose yield was 4%. As mentioned previously, the pulp yield is an important issue in the pulp and paper industry, and it therefore seemed unreasonable to gain a sugar yield of 1% whilst having a wood loss of 2% at a longer pre-treatment time (60 min).

In the industrial process, appropriate process controls are required to maintain the target hemicellulose yield and at the same time avoid pulp yield loss in the subsequent pulping process. This requires identification of key control parameters to be used to predict wood loss as well as hemicellulose yields. A plot of wood loss as a function of extract pH (Fig. 2) showed a strong correlation ($R^2 = 0.98$). Similarly, a plot of wood loss as a function of sugars yield (Fig. 3) showed an even stronger correlation ($R^2 = 0.99$). These results tended to suggest that the pH of the extract may be used to predict the wood loss and the sugars yield during pre-treatments.

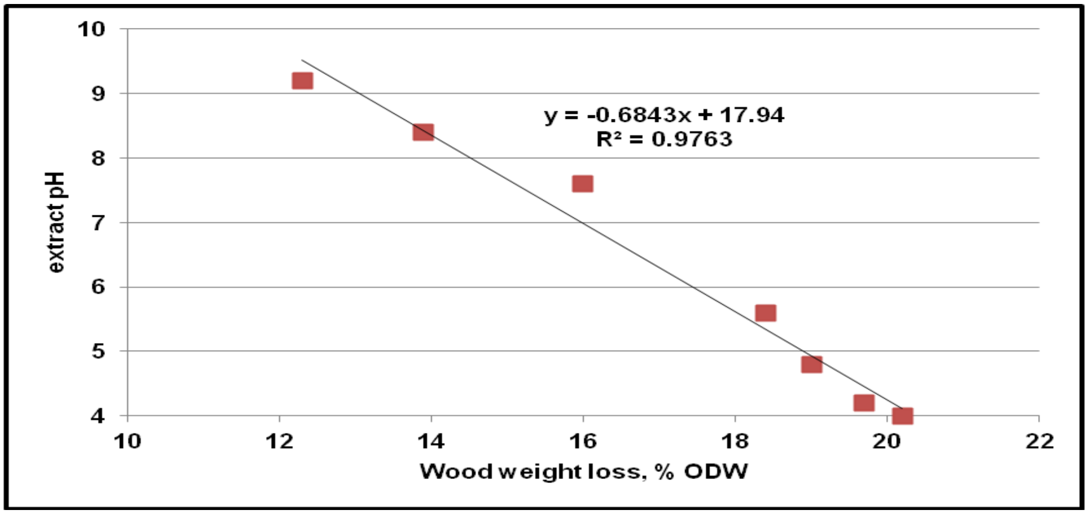

Fig. 2. Correlation of pH of the resulting extract and wood loss during pre-treatments

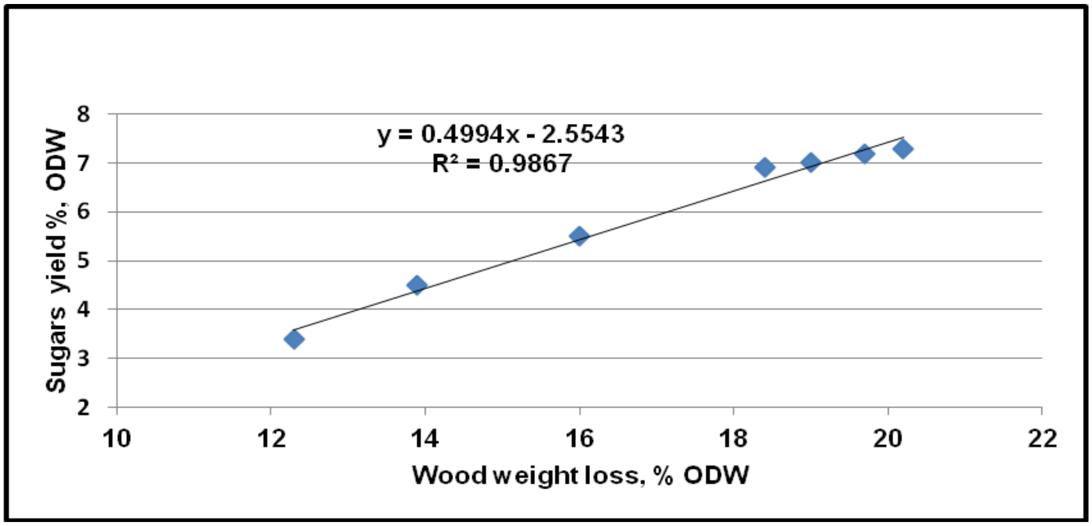

Fig. 3. Correlation of sugars yield and wood loss during pre-treatments

These findings on the effect of pre-treatment on the pH of the resulting extract, wood loss, and the dissolution of carbohydrates are in line with findings reported in previous studies. Mao *et al*. (2008) reported a wood loss of about 10% at a near-neutral pH of the resulting extract. These wood loss data are slightly lower than that observed in the present study, due to the different pre-treatment temperature and raw material used. However, the trend of carbohydrate yield was also found to be influenced more strongly by hemicellulose than cellulose, as was the case in this study. Similar results were also reported by Yoon *et al*. (2011), in which wood weight loss was found to be an important control parameter that could be used to predict the sugars yield in the course of pre-treatments, despite the fact that hot water was used to extract hemicelluloses from softwood.

Kraft Pulping of Hemicelluloses Pre-extracted Woodchips

Following the screening of the effects of pre-treatment conditions on wood loss, the pH of the resulting extract, and the hemicellulose yields, the pre-treatment conditions leading to a wood loss of 14% and a hemicellulose yield of 4% were selected for the subsequent pulping studies. The effects of the hemicellulose extraction on the kraft pulping delignification rate were studied. Furthermore, pulping conditions were optimized so as to produce pulp at the same kappa number as that of the cooks performed without hemicellulose extraction (control cooks). This was achieved by reducing the pulping liquor dosage. A reduction in the pulping liquor was preferred because this approach enables the downsizing of the lime kiln, which results in saving the recausticing operation costs and mitigating the environmental impacts associated with lime kiln operation (Ban *et al*. 2004; Johakimu *et al*. 2011). Four levels of pulping liquor dosages, 17.1%, 16.2%, 15.3%, and 14.4% AA, which translated to a pulping liquor reduction of 5% to 20%, were investigated. The paper making properties of the pulp produced at the target kappa with or without hemicellulose extraction were evaluated and compared. Similarly, the black liquor solid properties were also studied.

Effects of pre-extraction of hemicelluloses on subsequent kraft pulping

As reported earlier, the pre-treatment of woodchips prior to pulp production serves not only for the purpose of hemicellulose extraction, but also leads to the disruption of the cell wall and/or modification of lignin, which promotes a more efficient removal of lignin during kraft pulping. When hemicellulose pre-extracted woodchips were pulped using the same liquor charge as the control, the pulps produced had lower kappa numbers than the controls, indicating that the removal of the lignins from the hemicellulose-extracted wood chips was much faster. The kappa and the corresponding screened pulp yield (SPY) are illustrated in Table 2. These results suggested that to maintain the same kappa number as the control pulps, a reduction in pulping chemicals was required.

Table 2. Effects of Pre-extraction of Hemicelluloses on Subsequent Kraft Pulping Delignification Rates

Pulp samples	Kappa number	SPY (%)
Control pulps	19.6±1.7	50±0.35
HE+Kraft pulps	16±0.6	47±1.1

Note: control pulp was produced without hemicellulose extraction and HE+ kraft pulps; refer to kraft-pulped pulp produced from pre-extracted wood chips.

This reduction of pulping chemicals is important for improving the economics of kraft pulp mills. Increases in the delignification rate are caused by the partial removal of lignin as well as the formation of thiolignin (Ban *et al*. 2003b). Thiolignin is more soluble in the kraft pulping liquor, and as a result, it is removed faster than the natural lignin that is normally removed during regular kraft pulping without green liquor pre-treatments.

Optimizing kraft pulping conditions to produce pulp at target kappa number

As discussed earlier, a reduction in the pulping liquor dosage was necessary to maintain the target kappa number and the desired pulp yield. It can be seen in Table 3 that when the pulping liquor dosage was reduced by almost 20%, *i.e*., to 14.4% instead of 18%, the target kappa number was achieved. The properties of the pulp produced with and without hemicellulose extraction at the desired target kappa number are illustrated in Table 4. Pulp produced from pre-extracted woodchips exhibited superior viscosity, indicating minimal degradation of the carbohydrates (Christensen 1998).

Table 3. Effects of Cooking Liquor Dosage on Kappa Number of Hemicelluloses Pre-Extracted Hardwood Chips during Kraft Cooking

No	Types of Cooks	Liquor dosage (%)	Reduction in cooking liquor (%)	Kappa number
1	Control cooks	18	0	**19.6**
2	HE+ Kraft cooks	18	0	15.3
3	HE+ Kraft cooks	17.1	5	16.4
4	HE+ Kraft cooks	15.3	15	17.8
5	HE+ Kraft cooks	**14.4**	**20**	**19.6**

Note: control cooks were performed without hemicelluloses extraction and HE+ Kraft cooks; refer to kraft-pulped pulp produced from pre-extracted woodchips.

Eucalyptus grandis pulps are known for releasing a large quantity of HexAs (Andrew *et al.* 2009a). The presence of hexenuronic acid groups in pulp leads to a higher bleaching chemical consumption and may affect bleached pulp properties such as brightness reversion (Andrew *et al.* 2009b; Chai *et al*. 2001), effects that need to be avoided. In current mill practices, the pulps are either treated in acid hydrolysis or hot chlorine dioxide prior to bleaching (Andrew *et al.* 2009b). Therefore, removing the HexAs during pulping could eliminate the need for a HexA removal stage. Additionally, removal of HexAs during pulping could decrease the loss of bleaching chemicals. As is evident in Table 4, green liquor hemicellulose extracted pulp had 38% less HexAs when compared to control pulps. This result tended to suggest that pulp produced from green-liquor-extracted woodchips has the potential to improve the bleachability of the pulp.

Table 4. Pulp Properties of Pulp Produced With and Without Hemicelluloses Extraction at the Same Desired Target Kappa Number

	Liquor dosage (%)	Kappa number	SPY (%)	Viscosity (ml/g)	HexA (µmol/g)
Control cooks	18	19.6	50	1133	83
HE + Kraft cooks	14.4	19.6	50	1286	50

Lucia *et al*. (2008) have also observed that at the same kappa number level, conventional kraft pulp has more HexAs than do green-liquor-modified kraft pulps. It is worthwhile to note that in this study, a pinewood species was used that has a relatively lower quantity of HexAs than do hard wood species such as *Eucalyptus.* Although a different wood species was used, this study's findings support the novelty of this technology in reducing HexAs during the pulping process. An examination of bleaching was beyond the scope of this study and will be reported elsewhere (the paper is still in preparation).

Table 5 displays the results of black liquor properties for the cooks performed with and without hemicellulose extraction to produce pulp at the desired target kappa number. Despite reducing the pulping liquor charge by almost 20%, the residual AA measured in the black liquor of hemicellulose pre-extracted cooks was more than that found in control cooks. Presumably, the partial removal of lignin during hemicellulose extraction reduces the demand for AA in the subsequent kraft pulping (Cheng *et al*. 2010).

Table 5. Black Liquor Properties of Cooks Performed With and Without Hemicelluloses Extraction to Produce Pulp at the Same Target Kappa Number

	Total dissolved solids %	**Inorganics %**	**Organic %**	**Inorganics: organics ratio**	**Residual AA (g/L)**
Control cooks	16.9	11.8	5.1	2.3:1	4.5
HE + Kraft cooks	15.2	10.2	5.0	2.0:1	9.4

The significance of maintaining a high residual alkali in the black liquor during kraft pulping is two-fold. Firstly, a high residual alkali concentration prevents lignin dissolved in the spent liquor from precipitating back onto the fibers. Precipitated (or condensed) lignin is hard to remove during pulping and bleaching (Christensen 1998). Secondly, a high residual alkali concentration in the black liquor improves the removal of calcium salts during the soap skimming process (Christensen 1998). Therefore, calcium salts scale problems in the evaporation process can be controlled upfront. This is more important for kraft pulp mills that use hardwood species (Christensen 1998).

The solid contents in the black liquor of the hemicellulose pre-extracted cooks were 10% less than those found in cooks performed without hemicellulose pre-extraction. The reduction in black liquor solid contents implied that a lower load of black liquor solids could be sent to the chemical recovery. This suggested that a controlled hemicellulose extraction could also improve the recovery boiler capacity, thus improving productivity at kraft pulp mills that have a limited recovery boiler capacity (Christensen 1998).

Pulp chemical composition at desired kappa number

The chemical composition of raw wood and pulp produced with and without hemicellulose extraction is shown in Table 6. The arabinan, galactan, and mannan were not detected with HPLC in either pulp sample, indicating that these polysaccharides were completely dissolved in the black liquor.

Table 6. Chemical Composition of Wood and Pulps, % of Original Wood (ODW)

	Carbohydrate (%)					**Klason Lignin (%)**
	Arabinan	Galactan	Glucan	Xylan	Mannan	
Wood	0.2	1.1	47	11.2	1.7	28.5
Control - pulps	0.0	0.0	35.6	7.2	0.0	2.8
HE + Kraft - pulps	0.0	0.0	40	6.2	0.0	2.6

When compared to the initial wood content, the cellulose retained in hemicellulose pre-extracted pulps was about 85%, whereas in control pulps the cellulose retained was 76%. These results confirmed that the green liquor pre-treatment during hemicellulose extraction could also improve the selectivity in the subsequent kraft pulping process (Ban *et al*. 2003a; Olm *et al*. 1996), as the degradation of cellulose was minimal in hemicellulose pre-extracted pulps compared to control pulps. Traditionally, regular kraft pulping is characterized by the degradation of carbohydrates, which is due to induced effects of the peeling reaction (Christensen 1998; Olm *et al*. 1996). As expected, hemicellulose pre-extracted pulps had relatively lower xylan. The residual lignin concentrations were similar for both pulps.

Handsheet Physical Strength Properties

Effects on development of strength properties

Refining is performed to enhance the pulp fiber's paper making properties through increased fiber fibrillation, fiber swelling, and fiber flexibility. These properties are critical in rendering fibers with good bonding ability that contribute to improved paper strength properties. In order to assess the effects of hemicellulose pre-extraction on paper making properties, pulps produced with and without hemicellulose extraction were compared. Both pulp samples were subjected to refining/beating using a PFI mill. Strength properties were evaluated at the same PFI beating level of 3000 rpm, which gave the desired freeness range of 300 to 350 mL CSF for lower kappa number pulps (Christensen 1998; Gullichsen and Fogelholm 1999). The results are presented in Table 7.

Table 7. Effect of Hemicellulose Pre-Extraction on Handsheet Pulp Strength Properties

	Control pulps	**HE+Kraft pulps**
AA dosage (%)	18	14.4
Kappa number	19.6	19.6
PFI beatings (rpm)	3000	3000
Freeness (mL CSF)	307	309
Tensile Index (N.m/g)	101	85
Burst Index (Kpa.m^2/g)	6.3	6.1
Tear Index (mN.m^2/g)	9.1	9.7
Density (g/cm^3)	1.2	1.1

Except for the tensile index, the strength properties of the control pulps were similar to those of the hemicellulose pre-extracted pulps. The decrease in tensile index (-16%) can be explained by the lower amount of xylan reported earlier in Table 6. Tensile strength depends on the level of fiber-to-fiber bonding during the paper making process (Christensen 1998), which is negatively affected by the lower hemicellulose content in extracted pulps (Van Heiningen *et al*. 2003; Tunc *et al*. 2010).

CONCLUSIONS

1. Hemicellulose extraction with green liquor was shown to provide multiple benefits for kraft pulp mills. These include improvement in the kraft pulping efficiency, removal of HexAs during pulping, and reduction of black liquor solids, which would lead to increased productivity (as the recovery boiler capacity is often limited at mills), and the creation of an additional economic stream for hemicelluloses.
2. Industrial acceptance of this concept, meanwhile, will require a more accurate understanding of the effects of specific mill operating conditions on mill energy balance. Careful economic assessment of the options for handling calcium carbonate scale problems, *e.g.*, in impregnation vessels and associated systems, will also be required before the technology can be considered for implementation.

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