Effect of Integrating Xylan Extraction from *E. grandis* into the Kraft Pulping Process on Pulp Yield and Chemical Balance

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Kraft mills have the potential to pre-extract hemicellulose from wood as another value added product. The impacts of pre-extracting xylan on pulp and handsheet properties, sodium and sulfur balances, and chemical make-ups in the kraft pulping process of *Eucalyptus grandis* were assessed. Xylan extractions using white liquor, green liquor, and NaOH were done under varying extraction times, temperatures, and alkaline concentrations; residues were subsequently pulped at 170 °C for 45 min. The highest xylan yield (15.15% w/w) was obtained with 2 M NaOH, at 120 °C for 90 min followed by white liquor (13.27% w/w), utilizing 20% AA at 140 °C for 90 min. Green liquor extraction with 2% total titratable alkali (TTA), at 160 °C and an H-factor of 800 produced the lowest yield (7.83% w/w). However, the green liquor extractions were the most practical for integration into the kraft process due to their limited effect on pulp yield and properties of handsheets produced from the pre-extracted woodchips and the sulfur and sodium make-up increase. White liquor extractions would favour high pulp yield with low kappa number and reduced chemical charge and cooking time. These results are important for technical-economic assessment of integrated kraft pulp biorefineries.

Keywords: Hemicellulose; Xylan pre-extraction; Kraft cooking; Green liquor extraction; White liquor extraction; NaOH extraction; Sodium balance; Sulfur balance

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INTRODUCTION

Pulp mills are facing increased environmental and economic pressures. Consequently, it is important that mills maximize the economic value derived from woody biomass that they process. Establishing integrated biorefineries (IFBRs) where additional value added products can be produced instead of pulp alone, entails important economic benefits (Ragauskas *et al.* 2006). Kraft pulp mills are especially well suited for conversion into IFBRs as they already have the required infrastructure, support networks, and specialized manpower (van Heiningen 2006; Mateos-Espejel *et al*. 2011).

A promising concept towards establishing IFBRs is the extraction of hemicelluloses prior to the pulping process (van Heiningen 2006; Tunc *et al*. 2010). Hemicelluloses have a wide variety of potential industrial uses, including not only the pulp and paper industry itself, but also the food and pharmaceutical industries. In the standard kraft pulping process, half of the hemicellulose, equivalent to about 15% of the wood weight, and almost all of the lignin present in woodchips raw material, is dissolved into the black liquor (Christopher 2013).

The fairly high heating value of lignin, 26.9 MJ/kg, makes it cost-effective to recycle it back to the reboiler for combustion. The heating value of hemicellulose, on the other hand, is about 13.6 MJ/kg, thus causing it to be underutilized when it is incinerated in the reboiler, as it provides only about a quarter of the energy recovery (Christopher 2013). It is more valuable to extract hemicellulose prior to the pulping process to generate an additional stream of high value products (Um and van Walsum 2010). Any hemicellulose pre-extraction method needs to be compatible with the existing kraft mill processes, while ensuring that the pulp and resulting paper qualities, obtained after hemicellulose pre-extraction, are still within the required industry standard. Importantly, the quantity of xylan extracted also needs to be sufficient to ensure that the pre-extraction process is viable, but without compromising subsequent pulp production.

A number of hemicellulose pre-extraction methods have been investigated by researchers, ranging from hot water extraction, to more “mild” extraction methods using alkaline chemicals. The recovery of the hemicellulose, in particular xylan, can vary considerably during alkali extraction (Al-Dajani and Tschirner 2008; Jun *et al*. 2012). Relatively higher xylan yields of approximately 25% of the original xylan fraction in the aspen hardwood chips were reported by Al-Dajani and Tschirner (2008) and Jun *et al.* (2012) when using white liquor and NaOH, respectively.

Although water and acid methods for hemicellulose extraction may achieve high hemicellulose yields, the severity of such extraction methods reduces the final pulp yield and paper quality obtained by pulping of solid residues from hemicellulose extraction (Mendes *et al*. 2010; Vena *et al*. 2013). These are key concerns of pulp and paper manufacturers (Jun *et al*. 2012).

Alkaline extraction methods alleviate some of these concerns, as they have minimal effect on pulp yield reduction when compared to other extraction methods, such as acid and water extraction methods (Vena *et al.* 2013). Moreover, acid-based methods for hemicellulose pre-extraction will neutralize pulping chemicals in subsequent process steps, resulting in inefficient use of these chemicals. The water and acidic extraction methods are also more prone to degradation of extracted xylan biopolymers to oligosaccharides and monomers when compared to that of alkaline extraction methods, thus impeding the potential to produce high value biopolymers (Fiserova and Opalena 2012).

The qualities of paper produced from solid residues of woods from xylan pre-extraction using alkaline methods such as NaOH, green liquor as well as white liquor, have been comparable with those obtained by pulping of non-extracted woodchips. In some instances, the qualities have improved properties (Helmerius *et al*. 2010; Walton *et al*. 2010; Jun *et al*. 2012; Vena *et al*. 2013). In striving for commercial feasibility, increased attention is being directed towards using pre-existing alkaline chemicals within kraft mills for hemicellulose pre-extraction (Johakim and Andrew 2013).

Eucalyptus grandis species is one of the most important sources of fiber in the pulp and paper industry (Magaton *et al.* 2009) and is widely used by South African mills due to its high pulping yield and low production costs. The aim of this study was to determine the impact of the xylan pre-extraction by green liquor, white liquor, and NaOH on pulp yields and paper properties from kraft process of *E. grandis* at a South African pulp mill. Furthermore, the study assessed the impact on the sodium and sulfur balances of the kraft mills, and the requirement for make-up chemicals to the kraft pulping cycle.

EXPERIMENTAL

Green liquor, white liquor, and NaOH were used to extract xylan from *E. grandis* woodchips prior to kraft pulping. Pre-extracted woodchips from selected extraction conditions were subjected to varying pulping conditions, to compare pulp yields and properties with those obtained from untreated *E. grandis* chips with conventional pulping. Handsheets were also made from the pulps produced under the highest pulp yield conditions, and these were tested for pulp quality properties. Furthermore, mass balances were performed to gauge the impact that hemicellulose pre-extraction would have using green liquor, white liquor, and NaOH on the sodium and sulfur balances of the mill. The most feasible method for hemicellulose (xylan) pre-extraction in an existing kraft process could thus be identified.

Feedstock Utilized

Experiments were performed using wood chips obtained from an 11-year-old *E. grandis* plantation grown in Tzaneen in South Africa. The wood was chipped and the resulting wood chips were screened for size fractions ranging between 4 to 8 mm. The screening was done by a six-component chip screen driven by an electric motor. Before use, the wood chips were conditioned in a conditioning room allowing for constant temperature of 23 °C coupled with 55% relative humidity.

Compositional Analysis of *E. grandis* and Solid Residue from Alkaline Pre-Extraction

The *E. grandis* chips were sub-sampled as prescribed by British Standards DD CEN/TS 14780 (2005). *E. grandis* chips were milled to a particle size below 625 μm with the use of a Condux-Werk mill (Netzsch, Germany) as well as in a Retsch ZM 200 mill (Retsch GmbH, Germany). The particles produced were then sieved using a Retsch AS200 vibratory shaker (Retsch GmbH, Germany), with the 425 μm and 625 μm size fractions being utilized for further analysis.

Moisture content was determined using the NREL-TP 510-42621 (Sluiter *et al.* 2008a) method, with the extractives content being determined by a two-step extraction process, where both water and ethanol/cyclohexane extractives were quantified as described by the NREL-TP 510-42619 method. Klason lignin as well as carbohydrate composition of both the feedstock and the residue from alkaline pre-extraction were determined using NREL-TP 510-42618 (Sluiter *et al.* 2007), whereas the ash contents were determined *via* NREL-TP 510-42622 (Sluiter *et al.* 2008b).

Following xylan pre-extraction, the remaining solid residue was air-dried and conditioned at constant temperature of 23 °C coupled with 55% relative humidity. Moisture content of the residue was determined subsequently using infrared drying. The wood chips were subjected to two consecutive size reduction processes of the Condux-Werk mill and Retsch ZM 200 mill for characterization and determination of ash content. The subsequent wood weight loss of the pre-extracted chips was determined using Eq. 1 on ash free and dry weight bases,

$$\%\,Wood\ weight\ loss = \left(\frac{W_{IO} - W_{EO(1-Ash_E)}}{W_{IO}}\right) \times 100 \tag{1}$$

where W_{IO} = the oven dry weight of the initial sample subjected to pre-extraction; W_{EO} = the oven dry weight of the remaining residue after pre-extraction; and Ash_E = the ash fraction of the remaining residue after pre-extraction.

Composition Analysis of Liquor Fraction Obtained after Alkaline Pre-Extraction

The liquor fractions from NaOH and white liquor extractions (pH > 13), were neutralized using 37% HCl to pH 7. Subsequently, the samples were frozen at -4 °C until they were prepared for HPLC analyses. Liquid fractions obtained from green liquor extractions, with pH between pH 5 and pH 7, depending on the initial alkali charge, were frozen at -4 °C without neutralization, before high performance liquid performance (HPLC) analysis. The sugars (glucose, xylose, galactose, and arabinose) and acetate composition were analyzed using HPLC according to the method described by the NREL-TP 510-42623 (Sluiter *et al.* 2008c). The HPLC system used consisted of a Thermo Separations Spectra P 2000, which was equipped with both an Aminex HPX-87H column, operating at 65 °C, and an IG cation H guard column, with a Shodex RI-101 refractive index detector. The mobile phase was 5 mM H_2SO_4 at a flow rate of 0.6 mL min^{-1}, with the IG cation H guard column. Furthermore, the liquor samples were subjected to FT-IR analysis using a Thermo Nicolet Nexus 870 Fourier transform infrared (FT-IR) system *via* the attenuated total reflection (ATR) Golden Gate measurement device. The data analysis was done with the use of Omnic 7 software which was subsequently exported to Microsoft Excel.

Alkaline Pre-Extraction of Xylan from *E. grandis*

White liquor xylan extractions were performed at both mild as well as more severe extraction conditions. The mild extraction experiments were performed *via* a face centered central composite design with temperatures from 50 °C to 90 °C coupled with active alkali (AA) charges ranging from 16% to 20%. Extractions were performed by mixing 50 g (over dry weight, O.D.W.) *E. grandis* chips with white liquor (4:1 liquor to wood ratio) in 500 mL Schott bottles and subsequently placing them in a shaking hot water bath. Xylan content in the liquor fraction was considered a response of the central composite design with data interpreted using Stat Soft® Statistica 9.0. Table 1 shows both the extraction conditions as well as the corresponding results.

E. grandis chips were also subjected to green liquor, white liquor, and NaOH at liquor to wood ratio of 4:1 at extractions exceeding 100 °C, through the use of a pressurized oscillating digester. Extractions were carried out using batches of 50 g (O.D.W.) of *E. grandis*. During the extraction cycles the digester oscillated through 45° in order to ensure sufficient liquid contact with the wood chips. The temperature and pressure of the digester were monitored with a thermocouple and pressure gauge fitted to the lid of the digester. A programmable logic computer (PLC) was used to control the entire extraction cycle. Pressure in the digester was liberated through the use of a blow valve, with operating pressure during pulping being around 8 bar and that of the extractions varying between 2 and 7 bar.

The white liquor extractions were carried out at a temperature range from 100 °C to 140 °C using AA charges of 16% and 20% for a period of 90 min at each given temperature interval. The NaOH extractions were performed at temperatures of 100 °C, 110 °C, 120 °C, and 130 °C and at molar concentrations of 1 M and 2 M for 90 min.

The green liquor extractions were carried out at 160 °C with H-factors between 200 and 800. The total titratable alkali (TTA) charges that were investigated included 2% and 6% for extractions performed using green liquor. For the green liquor extractions that were performed, a charge of 0.05% of anthraquinone (based on oven dry weight of wood chips) was added (Walton *et al*. 2010). The extraction conditions that were used are summarized in Table 1.

Micro-Pulping of Pre-Extracted Residues

As a benchmark, non xylan-extracted *E. grandis* was subjected to pulping by simulating batch cooking conditions. Pulping conditions included a liquor to wood ratio of 4.5:1, 170 °C pulping temperature, 18% AA coupled with 25% sulfidity. Cooking conditions were based on suggested pulping conditions of South African *E. grandis* (Myburgh 1967). Pulping time at 170 °C was set to 45 min to achieve a kappa number of 20.

After pre-extraction, the wood chips residues were removed from the micro-bombs and the resulting liquor was drained from the chips through a 100 mesh screen. The solid residue (unwashed) from the extractions was placed in micro-bombs for further pulping.

Table 1. Process Conditions for Extraction of Xylan at Temperatures Exceeding 100 °C using Green Liquor, White Liquor, and NaOH

Solvent	Extraction temperature (°C)	Alkaline Concentrations	Extraction time
NaOH	100,110,120,130	1 M, 2 M	90 min
White Liquor	100,110,120,130,140	16%, 20%*	90 min
Green Liquor	160	2%, 6%**	200,400,600,800 (H-factor)***

* % Active Alkali (AA) based on oven dry wood.

**% Total Titratable Alkali (TTA) based on oven dry wood.

***Extraction carried out at 160 °C with equivalent length of time to result in given H-factor.

Testing of Physical Properties of Handsheets

Pulp fibers were separated from the pulping black liquor by washing it through a 10 mesh screen with running water until all the pulp had passed through with the uncooked fibers (rejects) retained on the screen. Thereafter, the pulp was screened with a packer slotted laboratory screen. Excess water from the pulp was removed through spin drying, to a moisture content of approximately 70%. The pulp yield was determined as the percentage of the original oven dry mass of the *E. grandis* chips *using* Eq. 2 (Vena *et al*. 2013).

$$\text{Pulp Yield (\%)} = \frac{Oven\ dry\ Mass\ of\ Pulp \times 100}{Initial\ Oven\ dry\ Mass\ of\ wood\ chips.} \qquad (2)$$

The kappa number of the pulps was determined using the method that is outlined by ISO 302:2004. The unbeaten pulps, which were comparable in pulp yields to that of non-extracted chips, were subsequently formed into handsheets according to TAPPI T 205 om-88 method.

The physical properties of handsheets formed from the pulps that were produced were also analyzed. These properties included the burst, tear, as well as the tensile indices of the handsheets produced. Methods used for the determination of the physical properties of the handsheets are presented in Table 2.

Table 2. Analytical Standard Methods Used to Determine Physical Properties of Handsheets Formed.

Physical Property	**Control Handsheet**	**References for Analytical Standards**
Burst Index (kPa.m^2.g^{-1})	0.924 ± 0.029	TAPPI T 220 om-88/TAPPI T 403 om-08 (2008)
Tear Index (mN.m^2.g^{-1})	3.365 ± 0.366	TAPPI T 220 om-88/TAPPI T414 om-98 (1998)
Tensile Strength (N.m^{-1}.g^{-1})	18.106 ± 1.706	TAPPI T 220 om-88/TAPPI T 494 om-96 (1996)
Basis weight (g.m^{-2})	60.615	TAPPI T 220 om-88/TAP PI T 410 om-08 (2008)

Sodium and Sulfur Mass Balance for the Kraft Process

To investigate the effect the pre-extraction conditions would have on the make-up of chemicals required in the kraft mill, sodium and sulfur mass balances were calculated for the modified kraft processes. The sodium and sulfur mass balances were done using extraction conditions selected for pulping of wood chips to form handsheets. The estimated kraft chemical recovery cycle in the conventional process was assumed to be 97% (Tran and Vakkilainannen 2012). The amount of sodium and sulfur (kg) used for each specific hemicellulose extraction condition, per ton of air dried pulp produced, was calculated with Eqs. 3 to 6.

$$Na_{Na2S} = ((M_{Na2S} \text{ x } 2 \text{ x } (23/78.1)) \text{ x } \frac{1000}{0.085 \text{ x } Y x (1+P_M)} \tag{3}$$

$$Na_{NaOH} = ((M_{NaOH} \text{ x } (23/40)) \text{ x } \frac{1000}{0.085 \text{ x } Y x (1+P_M)} \tag{4}$$

$$Na_{Na2CO3} = ((M_{Na2CO3} \text{ x } 2 \text{ x } (23/106)) \text{ x } \frac{1000}{0.085 \text{ x } Y x (1+P_M)} \tag{5}$$

$$S_{Na2S} = ((M_{Na2S} \text{ x } 2 \text{ x } (32/78.1)) \text{ x } \frac{1000}{0.085 \text{ x } Y x (1+P_M)} \tag{6}$$

Na_{Na2S}, Na_{NaOH}, and Na_{Na2CO3} represent the mass (kg) of sodium, if one ton of air dried pulp is to be produced, from Na_2S, NaOH, and Na_2CO_3 respectively. S_{Na2S} represents the mass (kg) of sulfur used during hemicellulose extraction, if a ton of air dried pulp is to be produced, from Na_2S. In order to calculate the total amount of sodium used during white liquor extraction, the sodium used from Na_2S and NaOH was added together, while, as green liquor consists of all three Na_2S, NaOH, and Na_2CO_3, the Na from all these components were added together. With NaOH extraction, only the Na from the NaOH was used for the calculation. The only component containing sulfur was Na_2S, which is found only in white and green liquor. The values 23, 32, 78.1, 40, and 106 are the molecular weights (g/mole) of sodium, sulfur, Na_2S, NaOH, and Na_2CO_3, respectively. The value 0.085 is the oven dry mass (kg) of the wood chips used during extraction, while Y represents the pulp yield as a fraction. P_M is the moisture fraction for air dried pulp which was assumed to be 10%.

RESULTS AND DISCUSSION

Compositional Analysis of the *E. grandis* Feedstock

The chemical composition of the *E. grandis* feedstock for combined hemicellulose extraction and pulping is shown in Table 3. The cellulose fraction is expressed in terms of the glucose content, while the hemicellulose content is expressed as monomeric xylose and arabinose contents.

Table 3. Chemical Composition of *E. grandis* Utilized

Component	Average
Xylose (wt. %)	15.79 ±0.73
Glucose (wt. %)	48.44 ±0.48
Arabinose (wt. %)	0.66 ±0.04
Klason Lignin (wt. %)	23.44 ±1.92
Acid Insoluble Lignin (wt. %)	4.32 ±1
Total Extractives (wt. %)	4.53 ±0.45
Summative Analysis (wt. %)	97.17 ±4.05

The contents of xylan and cellulose, which were polymers of particular interest in this study, were typical for *E. grandis.* Previous reports show xylan contents between 11.5% and 21%, and cellulose contents between 43% and 53% (Magaton *et al*. 2009; Vena *et al*. 2013).

The lignin content for the species was typical of *E. grandis* with reported values between 21% and 30% (Cotteril and Macrae *et al*. 1997; Vena *et al*. 2013). Low lignin content is especially desirable for pulping purposes due to easier delignification. Moreover, lignin can also hinder the release of sugars during hemicellulose pre-extraction (Studer *et al*. 2011). The extractives content was higher than those reported in previous reports of 2.9% to 4.2% for *E. grandis* (Emmel *et al*. 2003; Magaton *et al*. 2009).

Yield of Xylan from Alkaline Pre-Extraction of *E. grandis* with Green Liquor, White Liquor, and NaOH

The xylan yield was influenced more by level of alkalinity than temperature. Higher xylan yields were obtained with alkaline extraction from *E. grandis* at temperatures above 100 °C. The highest yield of 15.5% was obtained with NaOH (2M) extraction at 120 °C for 90 min, followed by white liquor, 13.27% obtained at 20% AA, 140 °C for the same duration (Fig. 1). The green liquor extraction, which had lowest alkalinity (Table 1), yielded the lowest xylan (7.83%), despite using higher extraction temperatures of 160 °C than the other two methods. This indicated that the higher alkali charges used during the white liquor and NaOH extractions had a more significant impact on xylan yield than the higher extraction temperature utilized by the green liquor extraction.

The specific *E. grandis* used in this study showed recalcitrance in releasing xylan at lower temperatures. At temperatures ranging from 50 to 90 °C, the maximum recovery of xylose was 5.63% (5.41% predicted by the model) from white liquor extractions (Table 4), which was lower than that of nearly 25% from aspen under similar conditions (Jun *et al.* 2012).

Table 4. Central Composite Design Output of White Liquor Xylan Extraction from *E. Grandis* at Temperatures Lower than 100 °C.

Run	Charge (%)	Temperature (°C)*	Time (min)	% Xylose Recovery (actual)	% Xylose Recovery (Predicted)	% Xylose Residual
1	16	50	60	**3.54**	3.70	-0.16
2	16	50	240	**3.79**	3.40	0.40
3	16	90	60	**4.88**	4.49	0.39
4	16	90	240	**5.09**	5.30	-0.21
5	20	50	60	**4.18**	4.06	0.12
6	20	50	240	**3.79**	4.14	-0.35
7	20	90	60	**3.72**	4.23	-0.51
8	20	90	240	**5.63**	5.41	0.22
9	16	70	150	**3.93**	4.34	-0.41
10	20	70	150	**5.03**	4.52	0.51
11	18	50	150	**3.47**	3.48	-0.01
12	18	90	150	**4.44**	4.33	0.11
13	18	70	60	**4.13**	3.98	0.16
14	18	70	240	**4.36**	4.42	-0.06
15	18	70	150	**3.90**	4.10	-0.20
16	18	70	150	**3.99**	4.10	-0.11
17	18	70	150	**4.20**	4.10	0.10

* Significant linear effect (p = 0.007, F = 13.96; MS = 2.54; R^2 = 0.78)

Under mild alkali conditions of 1 M NaOH at 90 °C, Vena *et al.* (2013) extracted 12.4% of the xylan present in *E. grandis* feedstock that had lower lignin content (21.1%). The low yield may be attributed to the high extractives content (4.3%) and lignin in the *E. grandis* (Table 3).

Some of the extractives are hydrophobic and can aggregate on the surface of the fiber, blocking both the penetration of chemicals and the diffusion of lignin from the fiber wall (Dai *et al.* 2004), thus affecting the xylan yield. Feedstock with low lignin is particularly amenable to xylan release, during alkali extraction (Studer *et al.* 2011). The *E. grandis* in the present study had a higher lignin (Table 3) than one Vena *et al.* (2013) used. The decrease with increasing lignin content is possibly due to the presence of lignin-carbohydrate complexes (Jeffries 1990).

White liquor pre-extraction performed at temperatures below 100 °C had a significant effect ($p<0.5$) on xylose recovery. However, alkaline charge in the range of 16% and 20% for the same temperature range (< 100 °C), had no significant effect ($p>0.5$) on the xylose recovery. Therefore, the effect alkali charge on xylan extraction is temperature dependent (Liu *et al.* 2011). The R-squared value of 0.78 of the model itself implies reasonable predictability of xylose recovery.

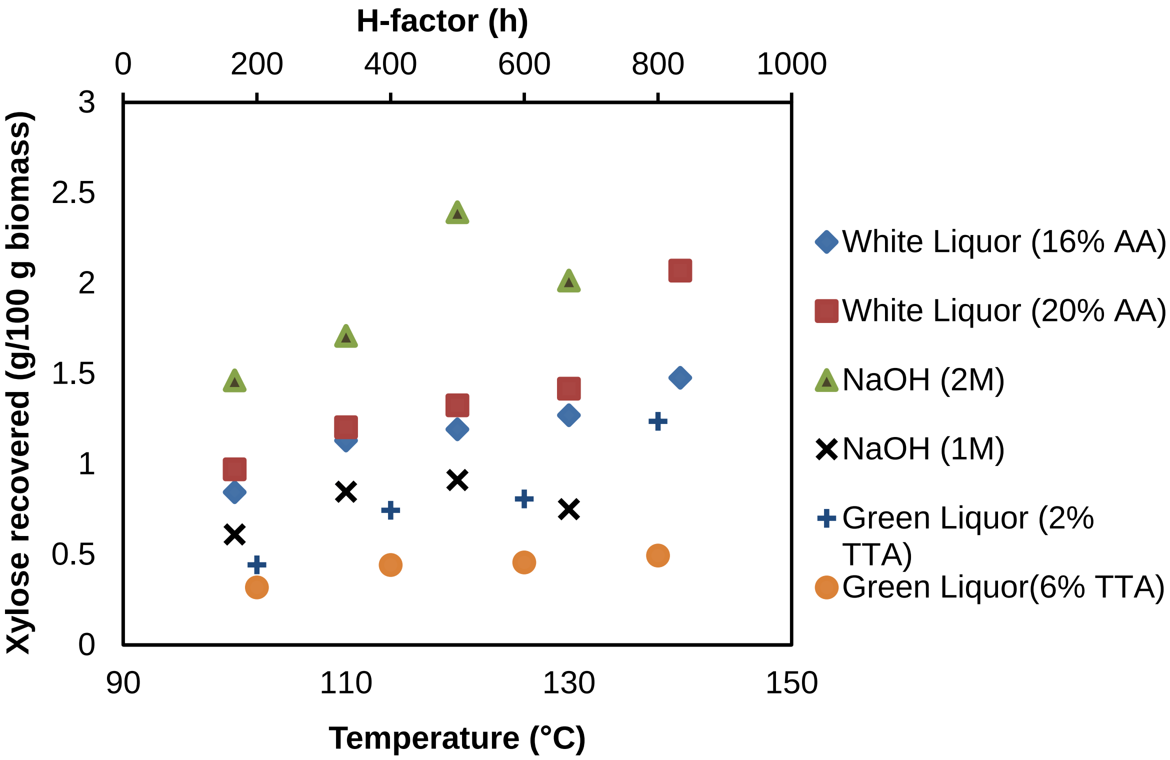

Fig. 1. Mass of solubilized sugars recovered in extraction liquor per 100 grams of *E. grandis* feedstock. Temperature on the bottom x-axis is for white liquor and NaOH extractions, while H-factor on the top x-axis is for the green liquor extractions that were performed**.**

The lower quantities of xylan recovered from the green liquor liquid phase, compared to white liquor and NaOH, reflect the lower xylan solubilisation and release from the residue (Fig. 1), which corresponded to the maximum wood weight losses of 7.67% for green liquor extractions compared to 20.67% and 16.44% for white liquor and NaOH, respectively (Fig. 2).

The xylan was extracted by green liquor with relatively higher purity than when utilizing white liquor and NaOH, as reflected by the presence of lower content of lignin derivatives than those extracted by the latter two methods (Fig. 3). The FTIR spectra for xylan from white liquor and NaOH extractions displayed peaks at 1193/1192 cm^{-1}, associated with C_{aryl}-O (Collier *et al*. 1992) as well as at 1052 cm^{-1}, which depicts the deformation of C-O coupled with the deformation of aromatic C-H associated with lignin (Collier *et al*. 1992; Akerholm *et al*. 2005).

In contrast, peaks at the aforementioned bands were absent in the spectra for green liquor extracted xylan (Fig. 3). Notably, the green liquor extraction conditions were less severe (lower alkalinity) than those of white liquor and NaOH, which may have limited the co-release of lignin and xylan. Depending on the application, a purer xylan may offset cost of purification and lower yield, thus making green liquor pre-extraction more practical for integration in the kraft process.

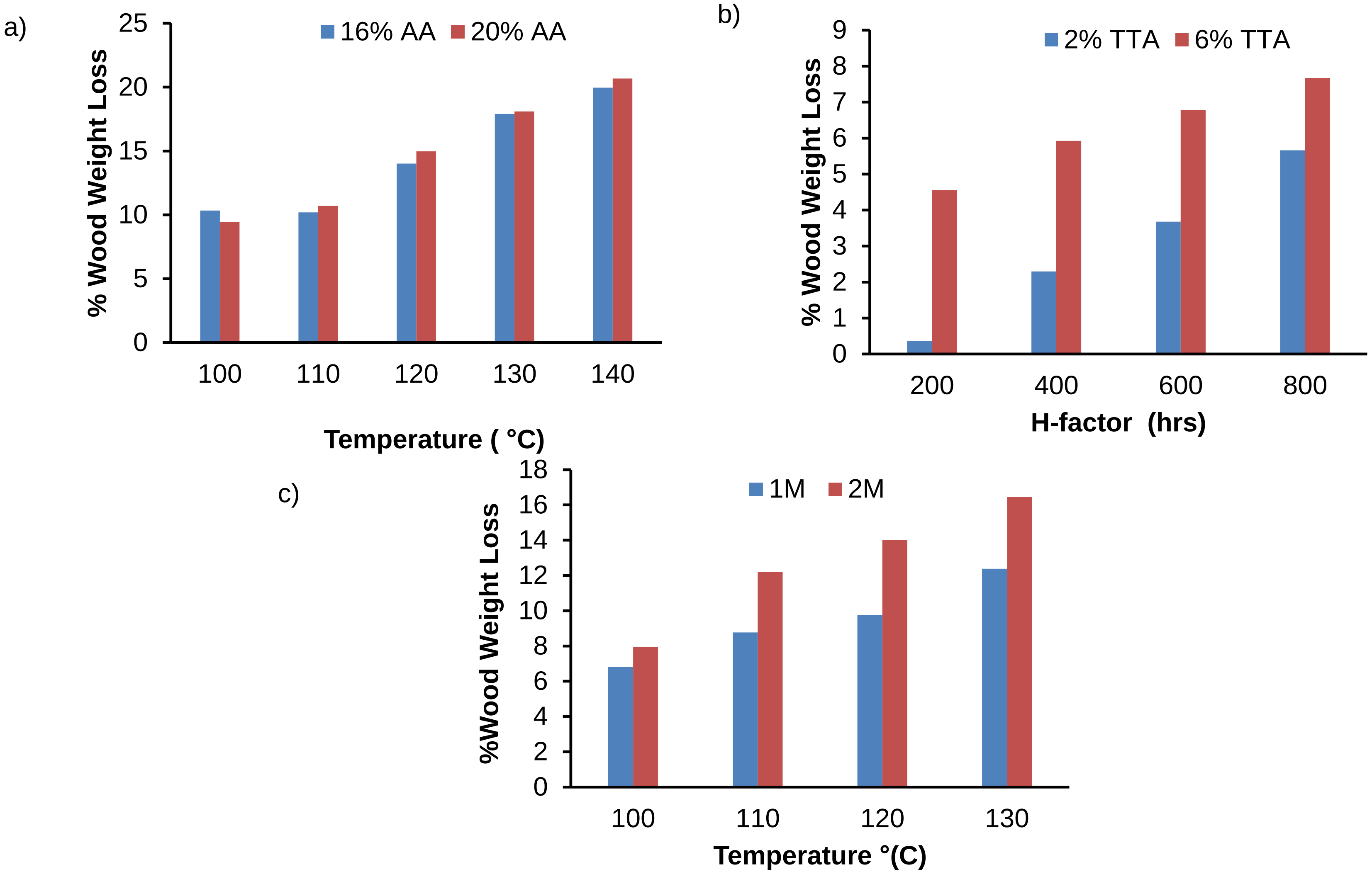

Fig. 2. Wood weight losses obtained using three different extraction methods. (a) White liquor extraction for 16% and 20% Active Alkali. (b) Green liquor extraction using 2% and 6% TTA. (c) NaOH extraction for 1M and 2M.

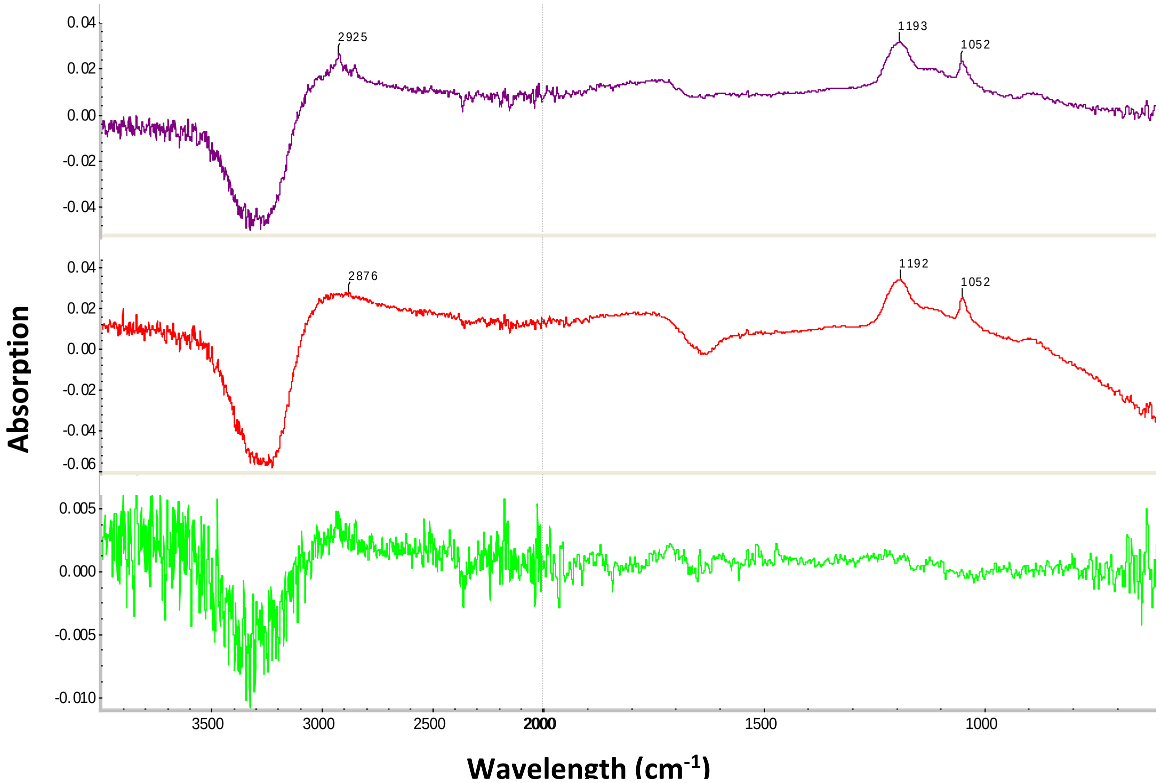

Fig. 3. FT-IR spectra of xylan extract from different extraction methods: (Top) White Liquor (Middle) NaOH, and (Bottom) Green liquor

Yield of Pulp and Properties of Handsheets Made from the Solid Residues from Green Liquor, White Liquor, and NaOH of Xylan Extraction

The final selection of the most feasible extraction method, for integrating with kraft pulp production would have to be based on the subsequent properties such as tensile, tear, burst indices of the pulp, and paper products as well as the make-up chemicals required. Green liquor had a pulp yield of 43.19%, which corresponded to a kappa number of 18.70 (Table 5). The pulp yield of the non-extracted chips was 41.67% with a corresponding kappa number of 20.3, indicating that green liquor pre-extraction benefited the subsequent pulping processes in yield and kappa number. The average pulp yield of 41.67% from the non-extracted chips (Table 5) was on the lower side when compared to industrial process yields of above 50% (Vena *et al*. 2013). Significant variations in wood properties between *E. grandis* trees, even with trees that grow within the same location, are known to occur (Malan 1988), making the deviation of pulp yield of this particular feedstock not particularly exceptional. The higher extractives content than normal (Table 3) for this *E. grandis* species might have lowered the pulp yield by preventing chemical penetration during pulping. Therefore, it is desirable that the extractives content should be as low as possible for efficient pulping (Macleod 2007).

The unbeaten handsheets from pulps obtained from green liquor extracted chips, had tensile, tear, and burst indices of 18.2 $N.m^{-1}.g^{-1}$, 3.2 $mN.m^{2}.g^{-1}$, and 0.924 $kPa.m^{2}.g^{-1}$, respectively. These values were almost identical to that of the reference pulp (Fig. 5). The inherent high alkalinity of the white liquor extractions allowed for a greater reduction in chemical charge during the subsequent pulping of the pre-extracted residue when compared to that of green liquor extraction. The resulting pulp yield of 41.60% was comparable with that of the reference pulp of 41.67% (Table 5) but with a lower kappa number of 12.86 compared to kappa number of 20.3 of pulp produced from non-extracted *E. grandis* (Table 5). Maintaining the pulp yield with a lower kappa number indicates that the white liquor extractions reduced both the cooking time and chemical charge and had selective dissolution of lignin, thus increasing pulping efficiency. There was no statistical significance observed in terms of burst, tear, and tensile indices of handsheets produced from white liquor pre-extracted residues when compared to those of the non-extracted *E. grandis* (Fig. 4). However, beating could potentially result in more significant deviations being exhibited in the properties of handsheets produced from pulps of non-extracted *E. grandis* chips.

The *E. grandis* chips that were subjected to NaOH pre-extraction had a pulp yield of 40% (Table 5) with a corresponding kappa number of 18.85. The resulting yield was lower than the yields of 43.19% and 41.67% (Fig. 4) for pulps resulting from green liquor and white liquor pre-extraction, respectively. Furthermore, disparities were observed in terms of both the tear and burst indices of pulps resulting from NaOH pre-extracted chips when compared to that of the non-extracted chips (Fig. 4). An increase of 28% was observed for the tear index of pulps derived from NaOH extracted chips; however, a reduced burst index of 9.6% was also observed (Fig. 4). This indicates that the quantity of xylan removed from the NaOH pre-extracted chips was significant enough to start impacting the pulp fibers and subsequently the paper properties. The increase in tear strength becomes apparent when there is significant reduction in flexible inter-fibre bonding that is enhanced by presence of hemicelluloses (Wan *et al.* 2010). The effects of decreased flexibility of inter-fibre bonding on the tear strength properties of the paper have been discussed before (Helmerius *et al.* 2010) and are attributable to the contribution of hemicelluloses to the electrostatic character of pulp fibres. As hemicellulose content of pulp is reduced there is reduction in accessible fibril surfaces for water molecules, which results in dried pulps being less conducive to swelling when soaked in water as a result of fiber separation. The effect becomes more challenging for fibre bonding because it provides less contact area with water (Wan *et al.* 2010; Reyes *et al*. 2015).

Effect of Pre-Extraction of *E. grandis* Utilizing Green Liquor, White Liquor, and NaOH on Kraft Chemicals Balance

Pre-extraction of *E. grandis* with the green liquor reduced the chemicals requirement for subsequent pulping of the solid residues, without compromising the pulp yield or quality. A reduced chemical charge of 35% was obtained with improvements in both the yield and kappa numbers of pulps, which indicates that extraction of hemicellulose preserved the cellulose fiber quality, which in turn is an indicator of how the integration process economics would be affected (Walton *et al*. 2010). The reduction in chemicals obtained is much higher than the 20% reduction in pulping chemicals for a kappa number of 20 (Johakim and Andrew 2013). A pulp yield of 41.67% obtained from pulping of pre-extracted residues from xylan extraction by white liquor at 120 °C and 20% AA for 90 min, resulted in a 50% reduction in chemical charge and 15 min reduction in cooking time, relative to the standard cooking conditions of non-extracted chips (Table 5).

Table 5. Pulp Yields and Corresponding Kappa Numbers of Pre-Extracted Chips

	Extraction Conditions			Pulping Conditions			
Solvent	**Alkali Charge (% on O.D.W)**	**Temp (°C)**	**H-factor (H-F)/ Time (min)**	**Chemical Charge**	**Time at 170° C (min)**	**Screened Pulp yield (%)**	**Kappa**
Control				18% AA	45	41.67±0.02	20.3±2.2
Green Liquor	2% TTA	160	800 H-F	10% Reduction*	45	37.2	12.86
	2% TTA	160	800 H-F	20% Reduction*	45	40.6	16.01
	2% TTA	160	800H-F	35% Reduction*	45	43.19	18.76 [e]
White Liquor	20%AA	120	90 min	10% Reduction*	30	37.4	ND
	20% AA	120	90 min	50% Reduction*	30	41.6	12.68 [e]
	20% AA	120	90 min	85% Reduction*	30	Uncooked**	–
	20% AA	140	90 min	40% Reduction*	25	34	10.83
	20% AA	140	90 min	60% Reduction*	25	37	15.92
NaOH	2M	120	90 min	No chemicals added[a]	30	Uncooked**	–
	2M	120	90 min	0.5 std Na_2S[b]	30	Uncooked**	–
	2M	120	90 min	Std Na_2S[c]	30	**Uncooked****	–
	2M	120	90 min	Std Na_2S[c]	45	**Significant amount of rejects****	–
	2M	120	90 min	Std Na_2S & 25% Std NaOH[d]	45	40	18.85 [e]

[a] *No additional chemicals were added to chips after extraction.*

[b] *Only half the amount of Na_2S required for 85 g (O.D.W.) of non-extracted chips was added. No NaOH added.*

[c] *Same amount of Na_2S as is required for 85 g (O.D.W.) of non-extracted chips was added. No NaOH added.*

[d] *Same amount of Na_2S and 25% of NaOH as is required for 85 g (O.D.W.) of non-extracted chips added.*

[e] *Extraction and pulping combinations selected for handsheet formation.*

**Represents percentage reduction of Na_2S and NaOH relative to Na_2S and NaOH required for 85 g (O.D.W.) of non-extracted chips.*

***Wood chips after pulping were not in pulp form as they weren't sufficiently pulped.*

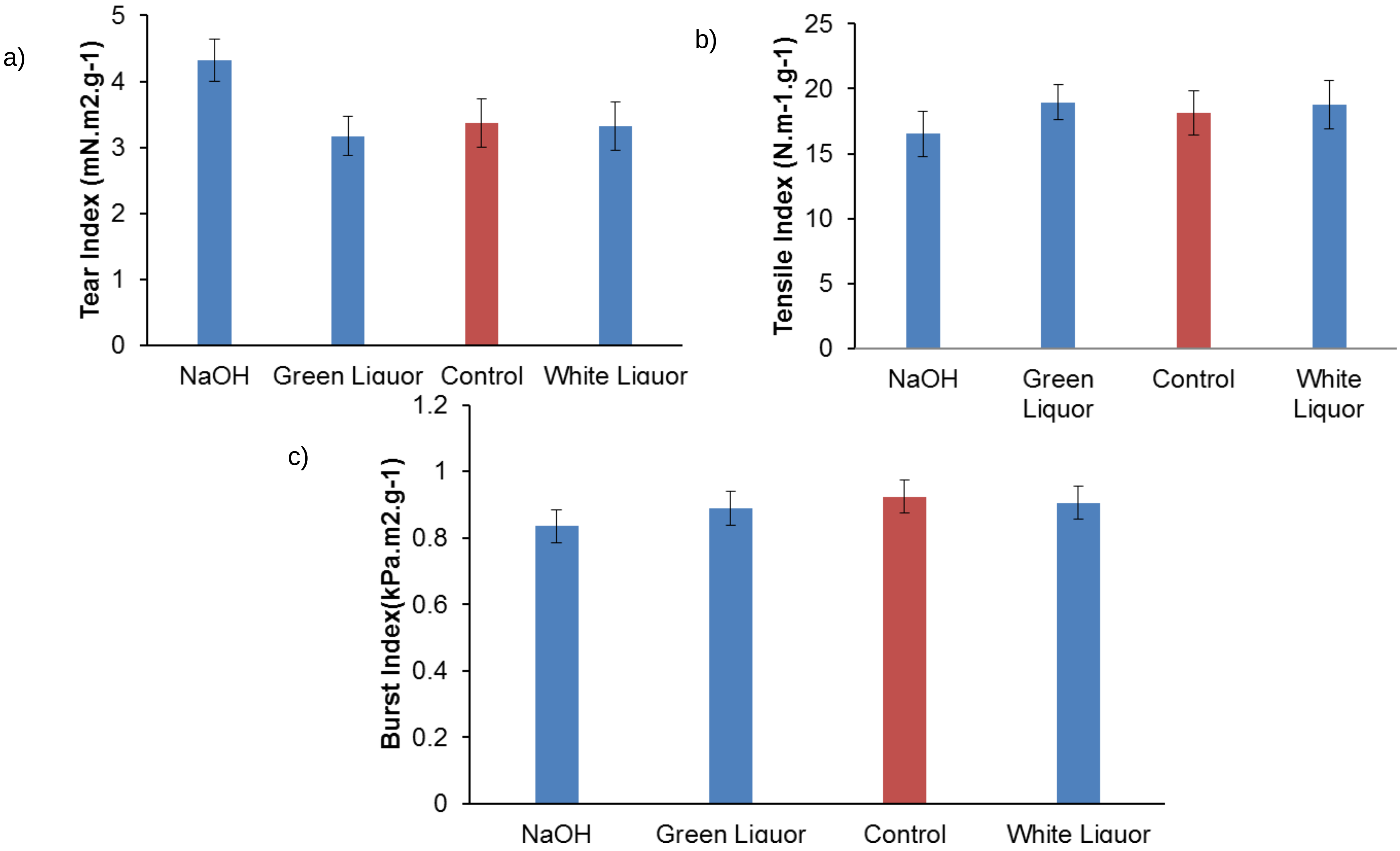

Fig. 4. Properties of handsheets made from xylan pre-extracted residues (a) Tear, (b) Tensile, and (c) Burst indices

Such an effect was reported earlier by Johakim and Andrew (2013). The *E. grandis* chips that were subjected to NaOH pre-extraction produced the best pulp properties with a 25% reduction in the quantity of NaOH requirement relative to that of the standard pulping conditions when the residues were pulped with the same amount of Na_2S as that of the non-extracted chips for 45 min (Table 5).

The practicality of hemicellulose extraction integrated in the kraft pulp process lies both in the extraction technology and the chemical recovery technologies. About half of all the technical equipment in the kraft process is physically used for pulping, with the remaining used for chemical recovery from the spent liquor. About 97% of the alkaline chemicals are recovered (Blechschmidt *et al*. 2013) to reduce operating costs. In hemicellulose extraction streams the recovery was 90%. The chemical balance assessments to evaluate the losses of sodium and sulfur during hemicellulose pre-extraction against the amount of Na_2SO_4 and NaOH needed to compensate for the lost sodium and sulfur per ton of pulp produced are depicted in vector diagrams for white liquor (Fig. 5b), and for NaOH and green liquor extractions (Figs 6,a and b, respectively) . When compared with a kraft process without hemicellulose extraction (Fig. 5 a), the sodium and sulfur exiting with the hemicellulose stream in white liquor extraction represented 4.46 and 5.08 times increase in make-up of sodium and sulfur (Fig.5 b). In NaOH extraction the increase in chemical make-up, thus sodium make up was found to be increased 4.96 times (Fig. 6 a). On the other hand, the loss of sodium and sulfur from the green liquor extraction for the same chemical recovery led to 1.73 and 1.29 times increases in the make-up for sodium and sulfur, respectively (Fig. 6 b), which is attributed to the low alkali concentration used during the initial extraction process. The results imply that sodium and sulfur balances in NaOH and white liquor xylan extractions can be closer to those of standard pulping if there is close to 100% recovery of chemicals used in the-extraction-of-the-hemicellulose. This information is important for techno-economic assessment of establishing integrated forest biorefineries.

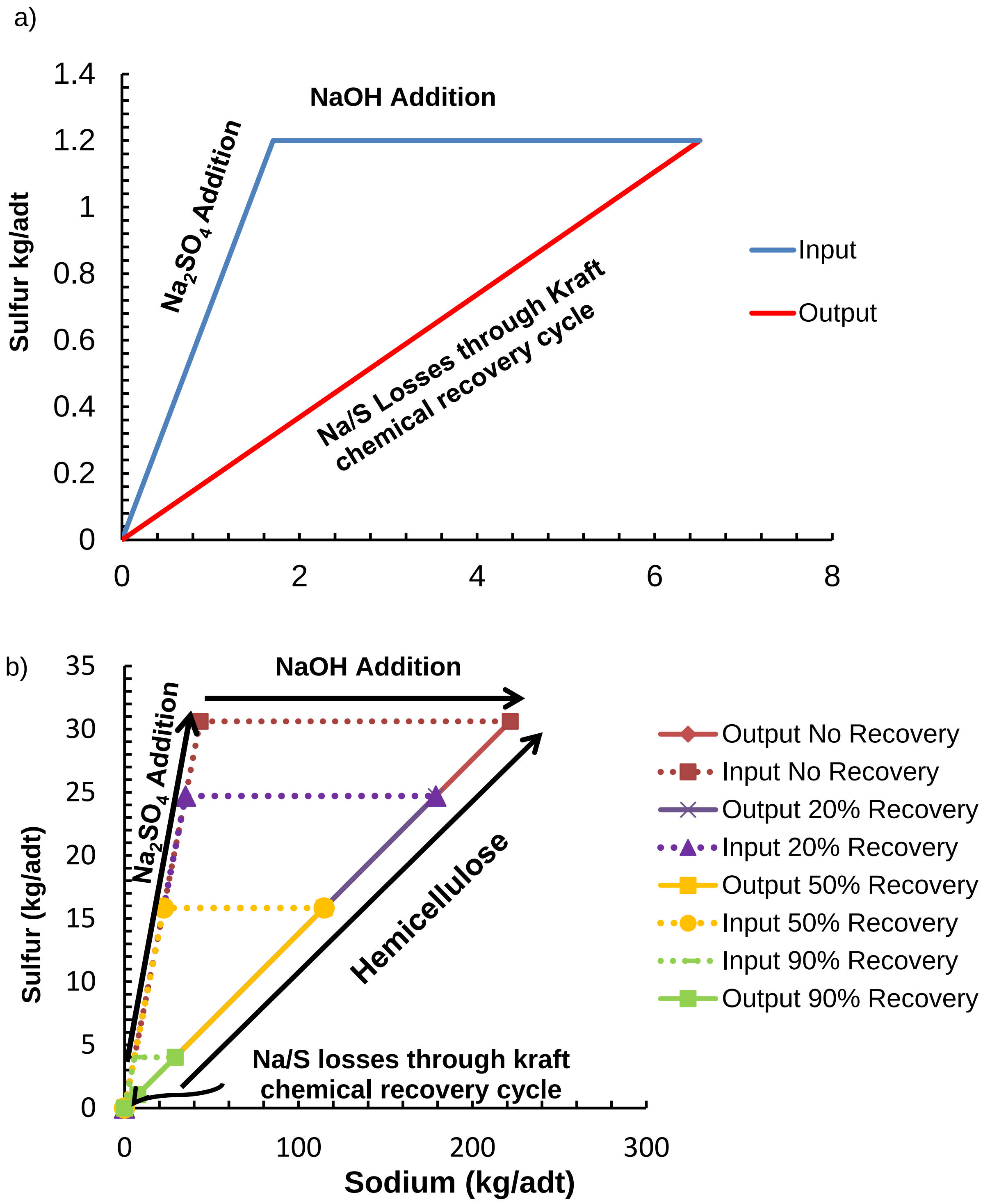

Fig. 5 Sodium and Sulfur balance in kraft mill: (a) Without hemicellulose extraction (b) during hemicelluloses extraction with white liquor

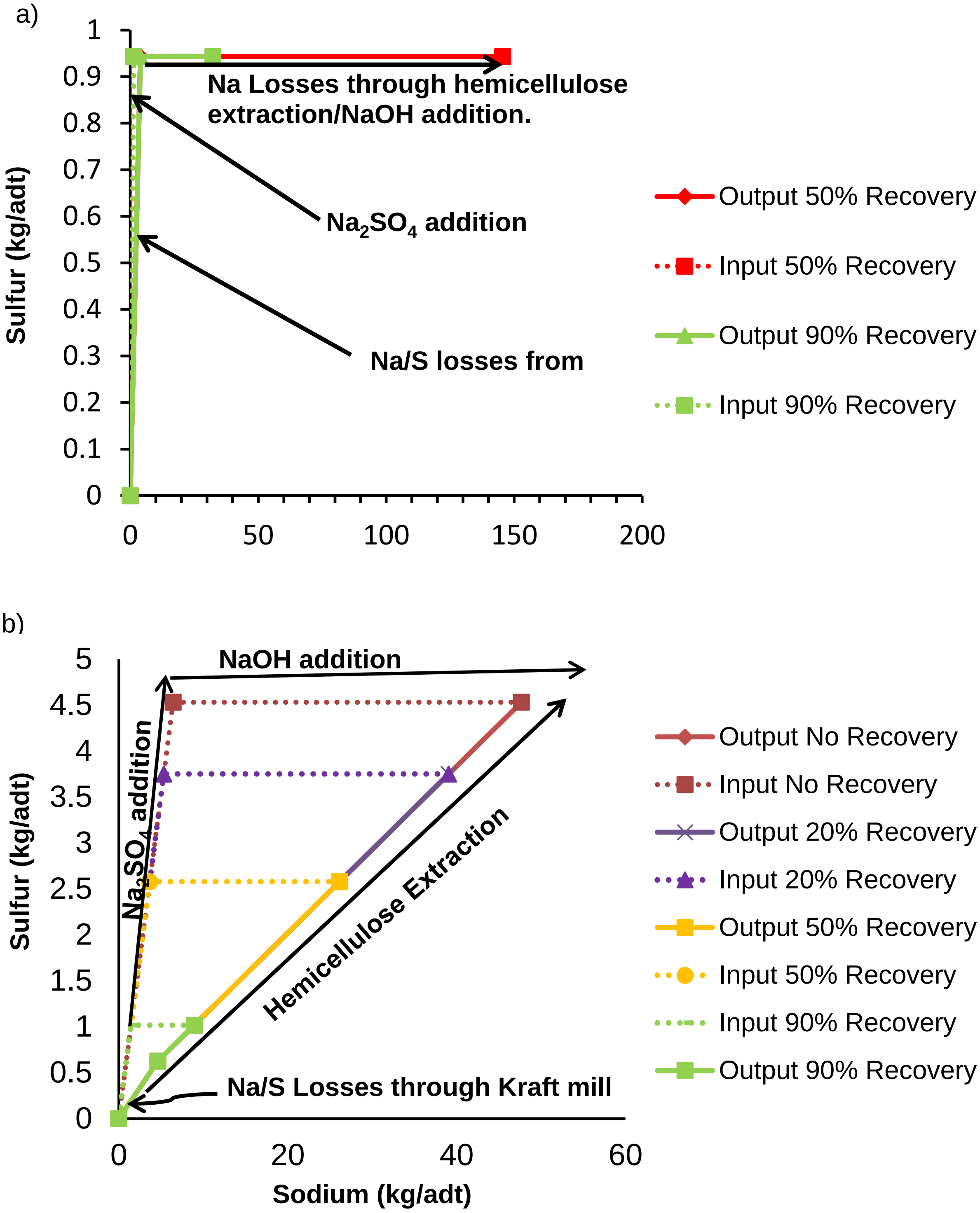

Fig. 6 Sodium and sulfur balance in kraft mill during hemicelluloses extraction with (a) NaOH and (b) green liquor

CONCLUSIONS

1. Green liquor was found to be the most feasible pre-extraction method to be integrated into the kraft pulp cycle compared to the white liquor and NaOH extraction methods.
2. The green liquor extraction demonstrated a better sodium and sulfur balance as reflected in the reduced increase in the make-up chemicals of the kraft process.
3. Green liquor was selective for xylan release and preserved the pulp fibers, thus giving xylan with greater purity and increased pulp yield relative to the pulps obtained from xylan non-extracted wood chips.
4. Green liquor xylan pre-extraction maintained the burst, tear, and tensile properties of handsheets derived from unbeaten pulp.
5. About 100% recovery of chemicals from the hemicellulose extract is necessary in white liquor and NaOH xylan pre-extraction to minimize the impact of hemicellulose pre-extraction on the kraft cycle chemical balance.
6. The white liquor extractions allowed for a greater reduction in chemical charge during the subsequent pulping of the pre-extracted residue and can be used to obtain high pulp yield and low kappa number with reduced cooking time.
7. Chemical balance and effect of xylan pre-extraction were demonstrated to be important parameters for techno-economic assessment of integrated forest biorefineries based on kraft mills.

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