Green liquor impregnation and Kraft pulping of South African *Pinus Patula* – "A practical approach to provide cost savings in a Kraft mill's pulping operation"

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Abstract

The effect of green liquor pre-treatment (GLP) on Kraft pulping of *Pinus Patula* has been investigated. Wood chips were pre-treated with green liquor, and subsequently subjected to Kraft pulping to achieve a target Kappa number of 65-70.

The results here in have revealed that GLP has the potential to substantially improve the delignification rate during Kraft pulping. Compared to regular Kraft pulping; the H-Factor can be reduced by almost 52% when GLP is applied. In addition, if the H-Factor is maintained at the same level as was used during regular Kraft pulping, the liquor charge can be reduced by 33%. GLP followed by Kraft pulping produced pulp samples with superior strength properties to those produced by regular Kraft pulping.

The potential benefits of GLP technology to the Kraft pulping industry are; providing cost savings, increased digester productivity, and mitigation of some of environmental impacts. Depending on the process economics of the pulping process of a Kraft pulp mill, GLP can be used to shortening of the digester pulping time or down sizing the limekiln requirements.

Key words: Green liquor, Kraft pulping, H-Factor, pulping liquor, Kappa number, strength properties

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Introduction

The Kraft pulping industry accounts for almost 80% of the South African (SA) pulp and paper industry. In recent years the industry has been under pressure to address the increasing production costs and environmental issues. These issues negatively affect the competiveness of the industry. The long-term impact for the South African economy could be the closing of pulp mills or downsizing of operations. Therefore, maximizing the capital effectiveness of a mill's pulping operations is a key priority for the industry.

In order to address such concerns requires the development of a cost effective and cleaner technology which improves the efficiency of the Kraft pulping process. A promising practical way of achieving this goal is to target advancement in Kraft pulping delignification rate and selectivity [12-14]. An increase in the Kraft pulping delignification rate ensures: a reduction in digester pulping energy, increase in digester throughput and reduction in pulping chemicals. This provides an opportunity for cost savings and mitigation of some environmental impacts at the Kraft pulp mills. On the other hand, an improvement in the selectivity of the Kraft pulping process maximizes retention of carbohydrates which is essential for pulp yield improvement [3, 7]. An increase in pulp yield maximizes profits by decreasing wood consumption in the pulping process, whose cost accounts almost 70% of the total production costs.

Despite the development of various technologies for improving Kraft pulping efficiency i.e. pulping additives, polysulphide, split sulphidity liquor charge [3, 7], their applications have been limited. This is due to capital constraint and increases in operational costs [12-14].

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On the other hand, the Kraft pulping efficiency can be improved through using a cheap delignification enhancing reagent. The reagent can be accessed at the Kraft mills in the form of hydrosulphide rich liquor “black and green liquor”. However, since black liquor is characterised by relatively low levels of hydrosulphide and contains a high organic load [3, 12-14], its application to enhance pulping efficiency is limited.

It is well understood that the active components of the Kraft pulping chemicals are hydroxide and hydrosulphide ions. The roles of hydrosulphide ions are to stabilise carbohydrates against degradation and also enhance the delignification rate [2, 3, 14]. More importantly, the concentration of hydrosulphide ions at the beginning of the pulping has a critical effect on the delignification efficiency [2, 3, 14]. According to literature [1, 2, 12-14], lower concentrations of hydrosulphide ions at the initial stages of the pulping lead to the formation of enol ether structures which are resistant to delignification. This is a common phenomenon in regular Kraft pulping.

Therefore, the key driver behind hydrosulphide rich liquor pre-treatment research has been to achieve selective Kraft pulping i.e. removing lignin efficiently with limited attack on the carbohydrates. In the present study the effect of green liquor on the Kraft pulping efficiency was studied. South African grown *Pinus Patula* woodchips was directly pre-treated with green liquor prior to Kraft pulping. Kraft pulping conditions for high yield Kraft pulp were evaluated to determine the potential of the technology.

Material and Methods

Woodchips: The *Pinus patula* wood logs were sampled from one of the local plantation. The logs were debarked and thereafter were chipped in a pilot scale chipper “(Precision husky type” at the CSIR – Forestry and Forest Products Research Centre Laboratory). The woodchips were screened using a vibrating screen to remove both undersized and oversized chips. Wood chips with an average chip thickness of 3-8 mm were collected for the subsequent experiments [3]. All the wood chips were allowed to air dry for two weeks to reach moisture content equilibrium [3, 7]. Woodchips moisture content was determined according to TAPPI test method T258om-94. The pulping trials were carried out at the North Calorina State University (NCSU), Department of Wood Science Laboratory.

Green liquor: The green liquor used in the experiments was prepared in the laboratory. The liquor specifications were similar to those attained in industrial generated green liquor [3]: sodium sulphide (35 g/lℓ as Na_2O), sodium hydroxide (10 g/lℓ as Na_2O) and sodium carbonate (154 g/lℓ as Na_2O). TAPPI method TM 624 cm-85 was used to analyse the green liquor quality.

Pulping equipment: The pulping experiments were conducted using a 7-liter M&K Digester. The pulping temperature profile was controlled by a computer. The ramping time was 90 minutes at a ramp rate of 1.2 ^{O}C/minute.

Pulping procedures: Green liquor pre-treatment modified Kraft pulping experiments were carried out in a two stage process**.** Firstly, a green liquor pre-treatment was performed in which woodchips were pre-treated with green liquor at dosage of 35% (GL/GL+H_2O). The pre-treatment time was 30 minutes at a temperature of 130 ^{O}C. After pre-treatment, the free spent liquor was drained out. Secondly, a Kraft pulping stage was performed in which a regular Kraft pulping liquor was added to the digester and the Kraft pulping was performed at a pulping temperature 170 ^{O}C, sulphidity 30%, and a liquor to wood ratio of 4.5: 1.

In order to gain a better understanding of the influence of GLP on Kraft pulping efficiency and the resultant pulp quality, three batches of experiments were conducted. Firstly, the pulping conditions for the regular Kraft pulping (without GLP) to obtain the target Kappa number of 65-70 was determined. The Kraft pulping liquor charge was varied between 16-14% while pulping time was maintained constant to give an H-Factor of 1300.

Secondly, the effect of GLP on the delignification rate during Kraft pulping was determined. Wood chips were pre-treated with green liquor, and thereafter free spent green liquor was drained out. This was followed by Kraft pulping using the same pulping conditions as defined in the regular Kraft pulping studies. The Kappa number was evaluated and compared to the one achieved during the regular Kraft pulping.

Thirdly, the most effective way of utilising GLP in high yield Kraft pulping operations was determined. Potential savings in terms pulping time (H-Factor) and/or pulping chemicals in a combined GLP+Kraft pulping process were examined. The GLP conditions were maintained constant while the conditions during Kraft pulping were varied. The pulping conditions were varied as follows: 1) H-Factor was varied between 600-1300 while maintaining the liquor charge at 15% and, 2) Liquor charge was varied between 10-15% while H-Factor was maintained at 1300. In each case the Kraft pulping conditions required to obtain the target Kappa number of 65-70 were established.

After pulping each pulp sample was defibrated, screened and washed thoroughly. Screened and spin dried pulp samples were stored in the fridge at 4ºC for pulp quality tests i.e.Kappa number and strength properties.

Pulp quality evaluation: The total pulp yield (TPY) for each pulp sample was evaluated as a percentage of the mass of oven dried defibrated pulp relative to the mass of oven dried wood chips charged into the digester. While screened pulp yield (SPY) was evaluated as a percentage of the mass of oven dried (defibrated pulp minus shives) relative to the mass of oven dried wood chips charged into digester. The Kappa number was determined according to TAPPI Test Method T236 om-85. The amounts of rejects present in the pulp mass were defined as the pulp fraction retained on the screen plates with 0.15 mm slots [8].

Hand sheet strength properties: The Canadian Standard of Freeness (ml CSF) measurement was performed according to TAPPI test method T227 om-94. Handsheets were made in accordance with TAPPI method T205 sp-95. The prepared hand sheets were left in a conditioned room 23 °C ± 0.5 °C and relative humidity 50% ± 1 for 24 hours prior to testing. Strength properties were tested using TAPPI methods [3, 7].

Results and discussion

Regular Kraft pulping (RKP) conditions to obtain the target Kappa number

Kappa number is an indirect measurement of the residual lignin in the pulp mass " i.e. the wood fibre cementing material". Its presence in the pulp mass hinders the bonding potential of the fibres [3, 7]. Thus each paper grade has a defined Kappa number range. The Kraft pulping conditions required to obtain the target Kappa number of 65-70 suitable for the sack paper (a reference paper product) were determined. Pulping was conducted at 170 °C using an H-Factor of 1300 while the liquor charge was varied between 14-16%. Pulp yield and Kappa number were determined. The results are shown Table 1 confirmed that liquor charge of 15% gave the desired Kappa number (68).

Table 1: Kraft pulping liquor charge required to achieve the target Kappa (65-70), pulping temperature 170 °C at H-Factor of 1300

Liquor charge (% dried mass of wood)	Kappa number	Total pulp yield
14	80	54
15	**68**	**52**
16	57	51

Effect of GLP on Kraft pulping delignification rate

The efficiency of any pulping operation is based on how fast the lignin can be removed during pulping. An increase in the Kraft pulping delignification rate provides an opportunity for cost savings [1, 2, 12-14]. The digester pulping energy could be reduced due to the reduction in pulping time. In addition, an increase in digester through put and savings in pulping chemicals could also be realised.

Therefore, the key driver behind the introduction of GLP was to promote the more efficient removal of lignin during Kraft pulping. The effect of GLP on Kraft pulping is illustrated in Figure 1. Green liquor pre-treatment followed by Kraft pulping (GLP + KP) produced pulp samples with a much lower Kappa number (41%) than RKP pulp samples. It has been speculated that an increase in the delignification is due to the formation of thiolignin [13, 14]. Thiolignin is more soluble in the Kraft pulping liquor and as a result, it is removed faster than the natural lignin normally removed during regular Kraft pulping ‘‘without GLP’’.

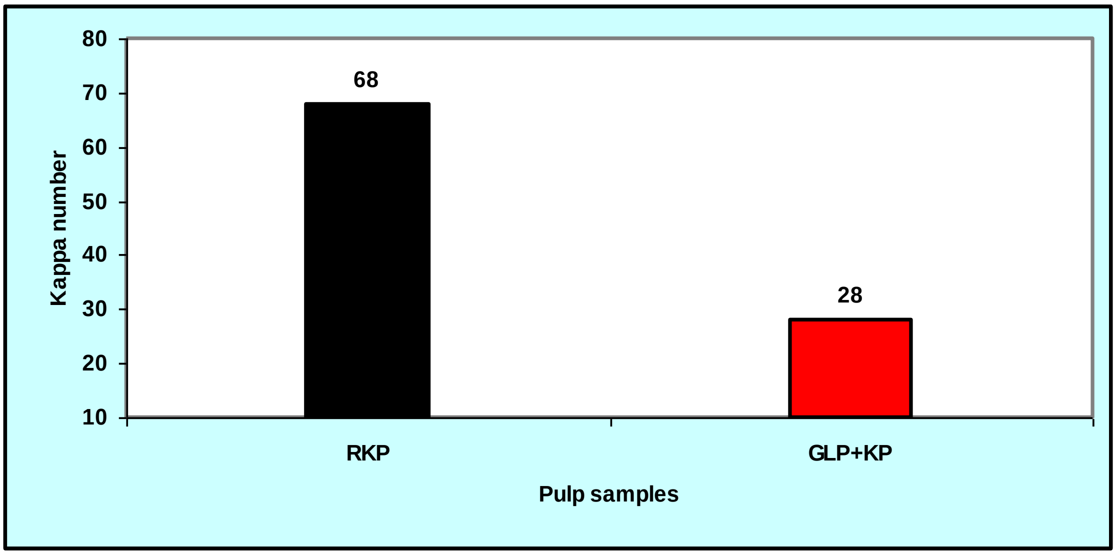

Figure 1: Comparison between regular Kraft pulping (RKP) and green liquor pre-treatment modified Kraft pulping (GLP+KP). Note RKP pulp samples were produced using regular Kraft pulping method using 15% liquor change, 170°C at H-Factor of 1300. While the GLP+KP pulp samples were produced after GLP followed up with regular Kraft pulping method using 15% liquor change, 170°C at H-Factor of 1300

Effect of GLP on Kraft pulping stage conditions

Both pulping liquor charge and pulping time (H-Factor) have a significant impact on the economics of the pulping process [13]. Therefore, it is essential and critical to establish the extent which the pulping time and/or pulping liquor can be reduced. The result shown in Figure 2 indicate that if the liquor charge in the Kraft pulping stage could be maintained at the same level used for as in the RKP, is possible to reduce the H-Factor in GLP+KP by 52% (i.e. from 1300 to 628).

Alternatively, if the H-Factor is maintained at the same level as used in RKP (Figure 3), the liquor charge could be reduced in GLP+KP by almost 33% (i.e. from 15 to 10%). More importantly, the Kappa number achieved in both cases was within the target range (65-70).

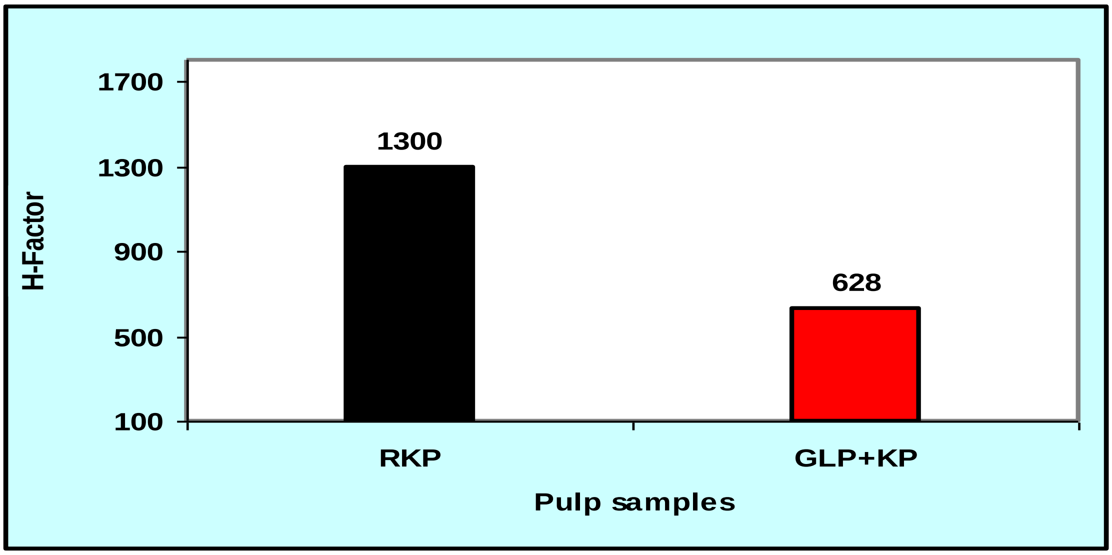

Figure 2: Comparison between regular Kraft pulping (RKP) and green liquor pre-treatment modified Kraft pulping (GLP+KP) on H-Factor required to produce pulp samples at a target Kappa number. Note RKP was performed using 15% liquor change, 170°C at H-Factor of 1300. While the GLP+KP was conducted using 15% liquor change, 170°C and the H-Factor was varied in the Kraft pulping stage until the target Kappa same as in RKP was obtained

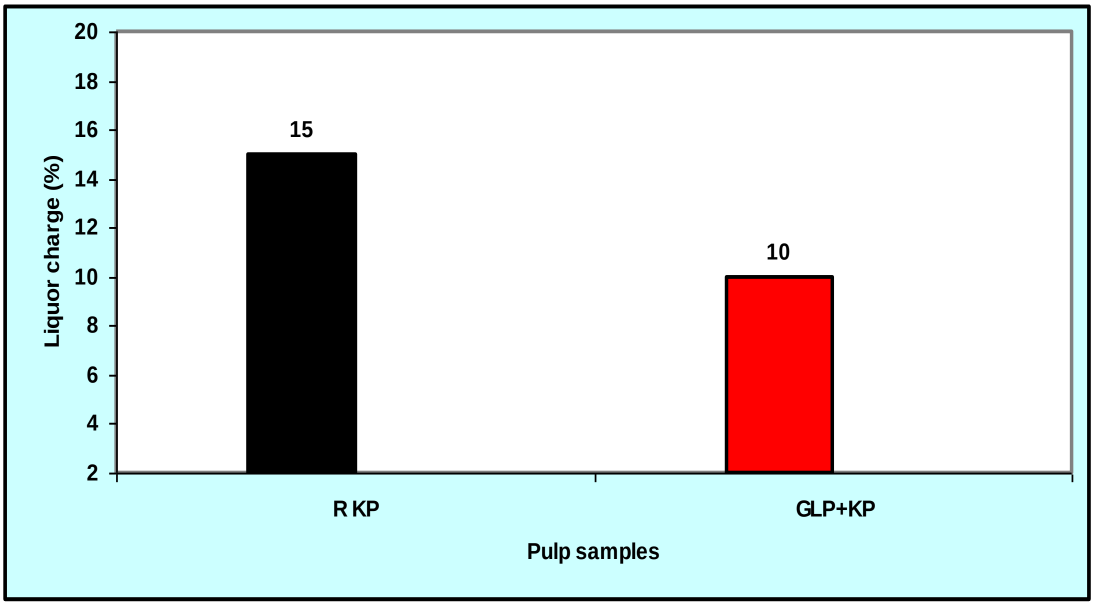

Figure 3: Comparison between regular Kraft pulping (RKP) and green liquor pre-treatment modified Kraft pulping (GLP+KP) on liquor charge required to produce pulp samples at a target Kappa number. Note RKP was performed using 15% liquor change, 170°C at H-Factor of 1300. While the GLP+KP was conducted using H-Factor of 1300 at 170°C and the liquor charge was varied in the Kraft pulping stage until the target Kappa same as in RKP was obtained

However, reductions in both liquor charge and H-factor following GLP did not provide pulp with the desired Kappa number. The Kappa was 47 units higher than the baseline Kappa number of 68 (Figure 4). The results suggest that this approach is not an option for a GLP Kraft pulping strategy.

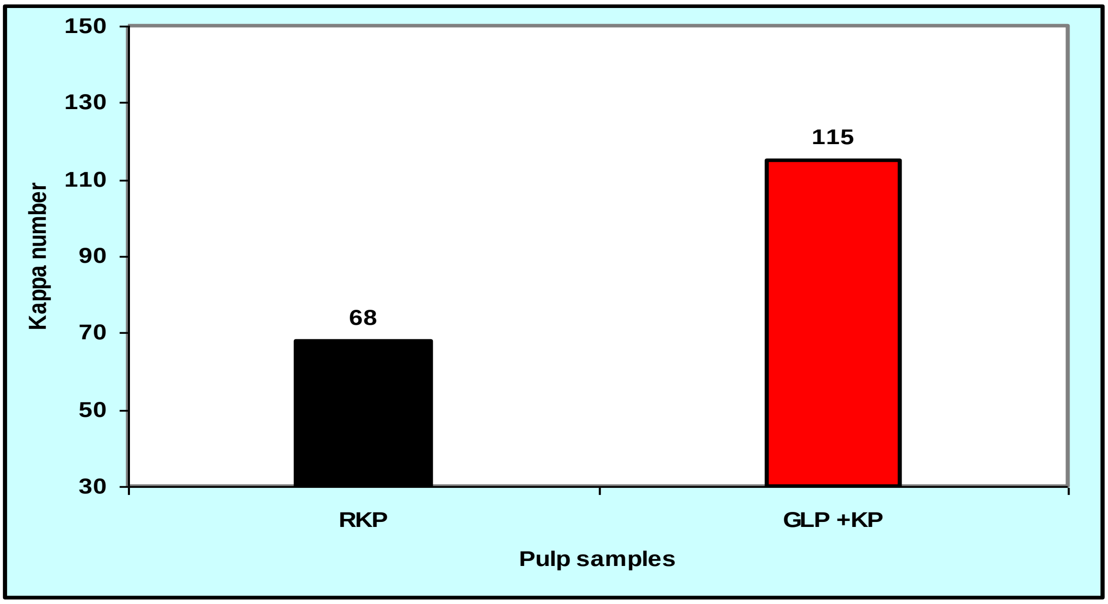

Figure 4: Effect of reducing both liquor charge and H-Factor on Kappa number in GLP +KP. Note RKP was performed using 15% liquor change, 170°C at H-Factor of 1300 . While the GLP+KP was conducted using 10%, 170°C at H-Factor of 628

Effect of GLP on Kraft pulping stage - pulp quality

Figure 5 shows the Kappa number and corresponding screened pulp yield (SPY) obtained for RKP and GLP +KP under different Kraft pulping conditions. It can be seen that both GLP strategies produced pulp samples with Kappa number comparable to RKP. However, the GLP followed by pulping using10% liquor charge at an H-factor of 1300, gave slightly a lower Kappa number and SPY. To maintain the Kappa as well as SPY at the same level obtained during RKP, it is presumed that the H-Factor must be slightly lower than 1300.

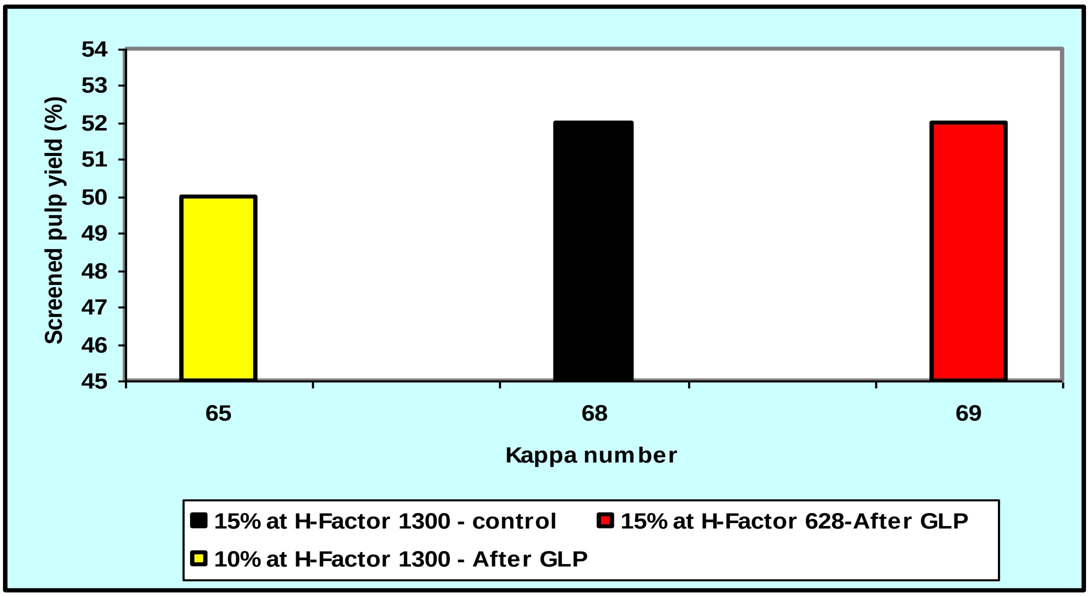

Figure 5: Illustration of Kappa number and the corresponding screened pulp yield (SPY) obtained for the control and GLP+ KP under different Kraft pulping stage conditions

Effect of GLP on Kraft pulping stage - strength properties

The freeness vs. PFI beating relationship for the pulp samples produced by RKP and GLP+KP is illustrated in Figure 6. At all PFI beating levels, the pulp samples produced using GLP +KP gave higher average values of freenesses. When compared to the RKP samples, the pulp samples produced using GLP followed by Kraft pulping with a 15% liquor charge at H-Factor of 628 gave the freeness values that were higher by 14%, 14%, 30% and 33% for 4000, 6000, 8000 and 10000 rpm respectively. While the pulp samples produced using GLP followed by Kraft pulping with a 10% liquor charge at H-Factor of 1300 gave the freeness values that were higher by 18%, 16%, 11% and 21% for 4000, 6000, 8000 and 10000 rpm respectively.

Presumably, the fibres of the pulp samples after GLP are less collapsible. Pulp fibres with less collapsibility during refining/beating retains high proportional of long fibres resulting in better dewatering characterists [3]. Pulp with better dewatering characterists enhances the paper machine runnability [3], and thus increase the paper machine productivity i.e. avoids web breakage as the result of poor drainage.

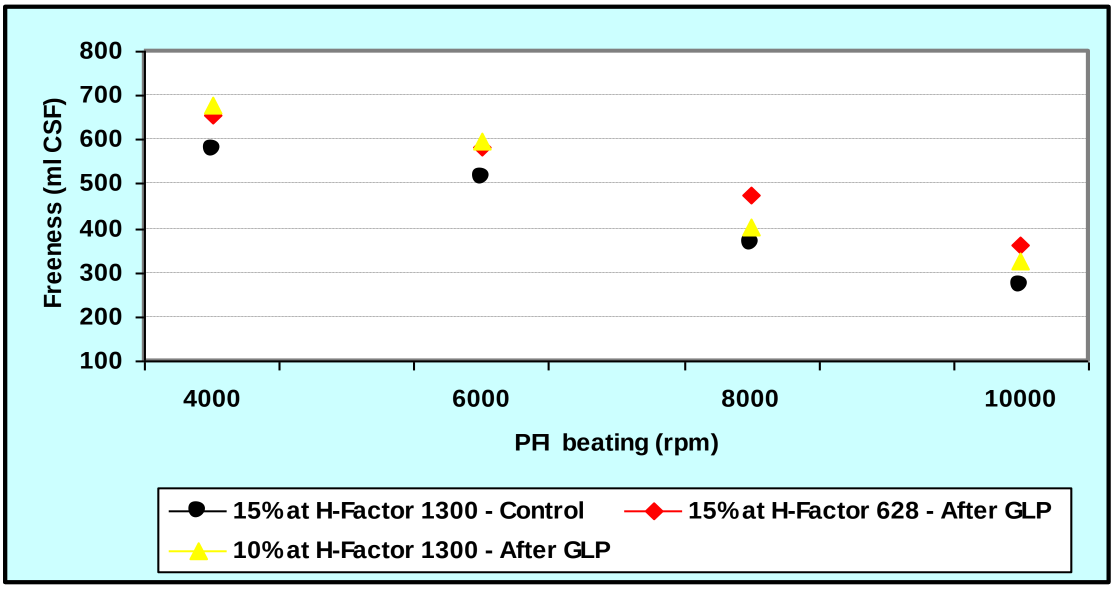

Figure 6: Freeness vs. beating relationships for the control and GLP+ KP under different Kraft pulping stage pulping conditions

To determine the effect of GLP on the resultant pulp properties, the strength properties were evaluated at the same PFI beating level of 6000 rpm. At this beating level of the freeness were 514, 595 and 598 ml CSF for RKP, 15% liquor charge at an H-Factor of 628 and 10% liquor charge at an H-Factor of 1300 GLP +KP pulp samples respectively. The results are presented in Table 2. Despite the GLP pulp samples exhibiting higher average freeness values (see Figure 6), they had superior strength properties when compared to RKP pulp samples. The following improvements in strength properties were achieved: Tensile index (2-3%), Tear Index (10-14%), TEA index (2%), short dry span failure load (15%) and breaking length (14%).

However, GLP pulp samples gave lower air flow resistance (decreased by 10-23% when compared to RKP pulp samples, indicating improvement in porosity. Since porosity determines the level of fibre collapsibility in the hand sheet [3], an increase in porosity supports the freeness trend reported earlier. High levels of fibre collapsibility result in a higher air flow resistance (poor porosity). As the fibres conforms and consolidates in the sheet leaving no voidage for air to escape. Thus, if pulp samples at higher freeness develop strength properties similar to the pulp sample at lower freeness, this indicates the potential of better pulp drainage characteristics [3].

Table 2: Hand sheet pulp strength properties at constant PFI beating of 6000 rpm

	15% at H-Factor 1300 RKP	15% at H-Factor 628 After GLP	10% at H-Factor 1300 After GLP
	Kappa 68	**Kappa 69**	**Kappa 65**
Freeness (ml CSF)	514	585	598
Tensile Index (N.m/g)	94	96	95
Tear Index ($mN.m^2/g$)	14	16	15
Burst Index ($Kpa.m^2/g$)	8.1	7.7	8.1
TEA Index (kJ/g)	1.6	1.7	1.7
Air flow resistance (Gurley sec/100 ml)	5.2	4	4.7
Tensile breaking length (km)	9.5	9.7	9.7
Failure load (kg/15 mm) at 0.2 span	14	16	16
Breaking length (km) at 0.2 span	15	17	17

Summary

- The potential of the efficiency of the Kraft pulping operation through GLP prior to Kraft pulping has been demonstrated. Depending on the Kraft pulp mill process economics, there are two strategies in which the GLP technology can be utilised at the Kraft pulp mills. These are namely, an shortening of pulping time or reducing pulping chemicals. This due to an increase of delignification rate of green liquor pre-treated woodchips during Kraft pulping.

- Pulping time (H-Factor) could be reduced by almost 52% when GLP was applied. An Increase in the digester throughput and savings in pulping energy in terms of steam are potential benefits that can be realised. From an environmental point of view, a reduction in the steam consumption of the digester implies less coal or furnace oil will be fired in the power boiler resulting in lower green gas emissions.

- Alternatively, if the H-Factor is maintained at the same level as used in the RKP, liquor charge can be reduced by 33%. Liquor charge reduction minimises the requirement of the lime kiln. Since the lime kiln is an energy intensive operation [3, 15], this will result in substantial savings in operation costs and a reduction in environmental impacts associated by the lime kiln operations.

- Despite reducing pulping chemicals or pulping time, GLP technology also improves the pulp strength properties. The observed improvements in strength properties can provide savings in the amount of pulp required to manufacture the final paper products. Thus, more pulp could be available without necessarily increasing mill capacity or increasing wood inputs in the pulping process.

- However, for green liquor pre-treatment technology (GLP) to be success at a mill scale requires: 1) modelling the pulping liquor balance based on mill data. This will help to define the optimal green liquor charge that could be spared on GLP without compromising the chemical balance in the chemical recovery system and, 2) Knowledge of handling the spent green liquor and the inorganics/organic flow to the recovery boiler. Further research works are being carried to address the mentioned issues above.

Acknowledgement

The authors wish to acknowledge the CSIR for providing financial support which enabled the conduction of this research work. We would like to thank the technical staff at the Department of wood science laboratory at NCSU for providing support on conducting the experiments. We are especially indebted to Prof Hasan Jameel (Department of wood science - NCSU) for his valuable discussions regarding to the potential of this GLP technology and for handling of the trials.

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