Beneficiation of sawdust waste in the context of an integrated forest bio-refinery mill: Kraft and pre-hydrolysis Kraft pulping properties

Jerome E. Andrew[1], Jonas Johakimu[1], Prabashni Lekha[1], Magdi E. Gibril[1,2], Bruce B. Sitholé[1,2]

[1]CSIR, Forestry and Forest Products Research Centre, P O Box 17001, Congella, Durban, 4013, South Africa; [2]University of KwaZulu-Natal, Discipline of Chemical Engineering, Durban, South Africa

Corresponding author: Jerome E. Andrew (jandrew@csir.co.za)

ABSTRACT

As part of a broader objective to extract cellulose from sawdust waste material for the production of nano-crystalline cellulose, conventional industrially available processes such as the Kraft and pre-hydrolysis Kraft (PHK) processes were investigated for delignification of sawdust produced from *Eucalyptus grandis* wood. In the context of the integrated forest biorefinery, it was felt that it may be useful to provide South African papermakers with preliminary data on the Kraft and PHK pulping properties of sawdust as none appeared to be available in the country. The results showed that *E. grandis* sawdust Kraft pulps with acceptable yields (48 %) and fibre morphologies comparable to conventional Kraft pulps, produced from wood chips, could be produced in the laboratory using typical Kraft pulping conditions. As expected, the exception was pulp strength properties such as burst, tear and tensile strengths which were 50-70 % lower than conventional pulps. During the pre-hydrolysis stage of the PHK process, up to 24 $g.l^{-1}$ xylose could be removed from sawdust with minimal removal of lignin (0.1 $g.l^{-1}$) and cellulose (2.5 $g.l^{-1}$). Pulping of the pre-hydrolysed sawdust resulted in a pulp yield of ca. 35 %. Preliminary characteristics measured

on the unbleached PHK sawdust pulp such as pentosan content (3-4 %), brightness (41 %) and viscosity (760 – 850 $ml.g^{-1}$) alluded to its potential for the production of dissolving pulp.

Keywords: biorefinery, sawdust, Kraft pulp, pre-hydrolysis Kraft, nano-crystalline cellulose

1. INTRODUCTION

The Forestry, timber, pulp and paper (FTPP) sector plays an important role in the economy of South Africa and is a major contributor to job creation, directly employing over 170,000 people (Godsmark 2014). The sector, however, like many others in the country, is facing severe challenges related to soaring energy costs and water shortages, some of which have a direct influence on production costs and its international competitiveness. In addition, there is an ever-increasing pressure on the sector to make changes, improvements and/or adaptations to their processes in order to achieve cleaner production technologies that are more environmentally friendly. The disposal of waste in an economically and environmentally acceptable manner is another critical issue facing the sector. This is mainly due to increased difficulties in locating disposal facilities and complying with stringent environmental quality requirements imposed by waste management and disposal legislation.

A case in point is disposal of sawdust waste generated when wood is chipped, screened, sawed, turned, drilled or sanded. Sawmills are major producers of sawdust waste, but other typical industries that produce sawdust include pulp mills and furniture manufacturers. It is estimated that South Africa may have close to 400 sawmills of varying capacities countrywide (Timberwatch 2000). Data on the amount of sawdust produced in the country is difficult to come by, and where available, is severely outdated or vary significantly

depending on the source. Based on figures obtained from *Forestry South Africa* (Godsmark 2014), the total amount of wood processed in the country during 2011/2012 was around 18.8 mil tonnes, of which sawmills accounted for 20% or 3.76 mil tonnes of this consumption. Olufemi *et al*. (2012) estimated that only 56% of a log processed in a sawmill is recovered as sawn timber, while 44% is left as wood residues in the form of wood slab (34%) and sawdust (10%). Then assuming that the amount of sawdust generated from sawn timber averages around 10%, it can be estimated that the amount of sawdust produced by South African sawmills was around 376,000 tonnes in 2012. These figures are conservative and exclude wood chips, offcuts, and shavings, and additional sawdust generated from pulp mills and other smaller informal sawmills. Estimates obtained from *Timberwatch* (2000) showed that at one stage, the forestry and wood processing industries in South Africa generated as much as 4-6 mil tonnes of wood waste per year. According to one local sawmilling company, 90% of its revenue is obtained from only 40% of a tree (Herbst 2013). This means that the remaining 60% of the tree may be discarded as waste products in the form of sawdust, chips, offcuts and shavings, or used to heat kilns to dry timber. Some are also sold to composting companies and board manufacturers. However, there still appears to an excess of sawdust that is either stockpiled onsite and allowed to biodegrade due to lack of disposal options or are sometimes landfilled. According to environmental regulations (e.g. Act 39 of 2004), these practices are being curtailed as they are environmental hazards that generate greenhouse gases and possible leaching of toxic chemicals into surrounding ground and water sources when stock-piled. In the case of landfilling as a means of waste disposal, significant costs are incurred by transporting waste to landfill sites, and maintaining and establishing new landfill sites.

Within the context of an integrated forest bio-refinery (IFBR), there is therefore a need to find new and innovative uses to beneficiate the sawdust waste. A bio-refinery is a facility that

integrates biomass conversion processes and equipment to produce fuels, power, heat and other value added chemicals, in addition to traditional products (Van Heiningen 2006). The biorefinery concept is analogous to petroleum refineries that produce multiple fuels and speciality and commodity chemicals from petroleum. For the FTPP sector, producing "green" bio-energy, bio-chemicals and new bio-materials, in addition to traditional wood products, may therefore lead to competitive synergies, new markets and increased product flexibility for the sector, whilst at the same time, mitigating some of its environmental impacts (Van Heiningen 2006; Mäkinen 2011). Within this context, the overall objective of the study was to investigate alternative options for beneficiation of sawdust into high value products. One option being explored by our Research Group is to produce nano-crystalline cellulose (NCC) from sawdust. Nano-crystalline cellulose are nano-sized cellulose particles that are extracted from cellulose. They have impressive mechanical properties that are comparable with stainless steel and Kevlar (George 2013), and thus have the potential to serve as the reinforcing (or load-bearing) components in composite materials. Due to their superior properties, they also offer promising opportunities for applications in several areas such as construction, automotive, medical and environmental (Shatkin *et al.* 2014). However, because of the heterogeneity and low crystallinity of wood, NCC cannot be produced directly from it. A pre-requisite is that the cellulose contained in the wood must first be fractionated and isolated from the remaining wood components such as lignin and the hemicelluloses (Abraham *et al.* 2011). In this study, as part of the pre-treatment process to extract cellulose, the sawdust was delignified using a conventional industrial pulping process called the *Kraft* process. Although Kraft pulp from sawdust may be of poor quality with possibly low strength, it was felt that it may be useful to provide South African papermakers with preliminary data on the Kraft pulping properties of sawdust as none appeared to be available in the country. Some possible uses of sawdust Kraft pulp include the production of tissue

paper or addition to recycled paper pulps. With the inclusion of a preceding hydrolysis stage prior to Kraft pulping, *i.e*. pre-hydrolysis Kraft (PHK) process, the process may also be used to produce dissolving pulps (Kautto *et al*. 2010). Dissolving pulps are high grade cellulose pulps with low amounts of hemicelluloses, lignin and degraded cellulose. They are used to manufacture several cellulose derived products such as cellulose acetate, viscose, microcrystalline cellulose, rayon, *etc*. (Sjöström 1981). In addition, the pre-hydrolysate from the PHK pulping process is rich in hemicelluloses and may provide a valuable source of raw material for the production of additional products such as ethanol, acetic acid and various polymers. The objective of this study was therefore to investigate the Kraft and pre-hydrolysis Kraft pulping properties of sawdust and to provide South African papermakers with preliminary data on the potential use of sawdust waste for Kraft and dissolving pulp applications.

2. BACKGROUND

During Kraft pulping, a uniform distribution of pulping chemicals throughout the wood chips is important for uniform delignification, which in turn produces pulps of high yield and quality (Zanuttini *et al*. 2005). The penetration and diffusion of pulping chemicals throughout the wood chips is strongly affected by chip dimensions such as length, width and thickness, with chip thickness being the principle dimension of concern (Jimenez *et al*. 1990). Wood chips thicker than the ideal chip thickness of 2-8 mm can lead to increased rejects, whilst smaller chips can have a detrimental effect on pulp yield (MacLeod 2007). With a surface area 30 times that of conventional wood chips, the major challenge when pulping sawdust particles is the non-uniform wetting of these particles with cooking chemicals that lead to uneven penetration and diffusion of the pulping chemicals. In turn, this can lead to low pulp

yield and strength properties (Winstead 1972). To overcome this challenge, the conventional method of pulping sawdust involves pre-steaming, cooking and discharging of the sawdust pulp using specialised digesters of the Messing-Durkee (M&D) or Kamyr types (Luthe *et al*. 2004; Korpinen *et al*. 2006). When cooked in conventional wood chip digesters, sawdust is often added to wood chips in controlled amounts and co-cooked with the wood chips (Korpinen *et al*. 2006). Although not practiced in South Africa, sawdust pulping is common to many parts of the world, and has been practised since the early 1960's in the United States of America and Canada (Winstead 1972; Korpinen & Fardim 2009). Sawdust pulp yields can range between 43-45 % for bleachable grades and 46-48 % for unbleached pulps (Winstead 1972). However, it has been found that sawdust pulp strength is significantly lower than that produced from wood chips (Winstead 1972). This is presumably due to the shorter fibres obtained from the small sized sawdust particles. Despite this, sawdust pulps have found use in several papermaking applications. Korpinen & Fardim (2009) used sawdust Kraft pulp to reinforce thermomechanical (TMP) and pressurised ground-wood (PWG) pulps for use in uncoated super-calendered (SC) and light-weight coated (LWC) papers. They found that up to 30 % of sawdust Kraft pulp could be added to TMP and PGW pulps, without negatively impacting any of its properties. Winstead (1972) also reported that up to 20 % sawdust pulp could be added to fine papers without any detrimental effect on strength properties; and that 50-70 % of sawdust pulp may be blended to produce towelling and tissue papers.

With the addition of a preceding hydrolysis stage prior to Kraft pulping, the Kraft process can also be used to produce dissolving pulp *i.e.,* the pre-hydrolysis Kraft (PHK) process (Kautto *et al*. 2010). Pre-hydrolysis of wood chips with dilute acids (Saukkonen *et al*. 2012), bases (Um & van Walsum 2009; Johakimu & Andrew 2013), hot water (Sixta *et al*. 2013) and

steam (Leschinsky *et al*. 2009) enable the extraction and recovery of the hemicelluloses traditionally burned with lignin in the black liquor.

3. EXPERIMENTAL

Sampling and sample preparation

One-and-half metre bottom billets were taken from each of five 11 year old *Eucalyptus grandis* trees sampled from a single site (site index 24). The billets were chipped and sawdust was generated by passing the chips first through a hammer mill and then a Wiley mill. The sawdust was collected in a plastic bag and stored at room temperature until required.

Kraft pulping

Pulping was carried out in an electrically heated rotating digester (Regmed, Brazil) using the Kraft process. The digester consisted of a 25 L stainless steel main boiler vessel that housed four intermediate 1.5 L boiler vessels which were independent of the main boiler vessel and from each other. One hundred-and-fifty grams oven dried (OD) equivalent sawdust samples were pulped at 170 °C for 20, 40 50, and 60 mins. The ramp time to maximum temperature was 90 mins. The sulphidity of the cooking liquor was kept constant at 27%, and the active alkali charge (%AA as Na_2O) was varied at 3 levels (14, 16, and 18 %). During pulping, the moisture content of the sawdust was taken into account in order to maintain a constant liquor-to-wood (L:W) ratio, which was varied at 2 levels (4.5:1 and 7.5:1). After pulping, the cooked sawdust pulp was disintegrated for 5 mins using a standard laboratory pulp disintegrator before washing under vacuum on a Büchner flask and funnel using tap water. The pulp was then screened on a 0.15 mm slotted screen to separate uncooked sawdust material (rejects) from the pulp.

Pre-hydrolysis Kraft (PHK) pulping

Water was used for the pre-hydrolysis treatment. The conditions employed was a temperature of 170 °C, ramp time to maximum temperature of 60 mins, and the time at maximum temperature was varied between 15-60 mins. After pre-treatment, the sawdust material was removed from the reactor and filtered and washed under vacuum on a Büchner flask with deionised water. Prior to washing, an aliquot of the pre-hydrolysate was taken for chemical analysis. After washing, the pre-extracted sawdust was weighed and the moisture content measured to calculate the yield and to maintain an accurate L:W ratio during the subsequent pulping. Fresh white liquor was then added to the pre-hydrolysed sawdust and conventional Kraft pulping was carried out as described above.

Chemical characterisation

The polysaccharide content of the wood or pulp was determined by acid hydrolysis (TAPPI T249 cm-85) followed by separation using high performance anion exchange chromatography, coupled with pulsed ampherometric detection (Wright & Wallis 1996; Wallis *et al*. 1996). Acid insoluble lignin was determined by quantitatively filtering the hydrolysate from the acid hydrolysis step through a 0.45 μm filter paper. The material remaining on the filter paper was defined as Klason lignin. The acid soluble lignin was determined by measuring the UV absorbance of the filtrate or decantate at 205 nm using a Cary spectrophotometer (Varian, USA). The acid soluble lignin and monosaccharides in the pre-hydrolysate was measured by first acidifying the extract with 1 ml of 72 % sulphuric acid followed by hydrolysis in an autoclave with 4 % H_2SO_4 at 121 ºC (103 kPa) for 1 hour prior to analysis. Cellulose was determined according to the Siefert method (Fengel & Wegener 1984). Ash content and Kappa number were measured using TAPPI standard methods T211 om-93 and T236 cm-85, respectively. The intrinsic viscosity of pulps was measured using the

Scandinavian method SCAN-CM 15:88 (1988), and for the PHK pulps, the pentosan content was measured using a method based on TAPPI T450 os-44.

Fibre morphology and paper properties

Fibre morphological properties were measured using a Morfi Compact fibre analyser (Techpap, France). Pulp properties were assessed by preparing and testing handsheets. Handsheets with a basis weight of 60 $g.m^{-2}$ were prepared on a Rapid Köthen sheet forming machine. Pre-conditioned handsheets (23 °C, 50 % RH) were tested for burst (TAPPI T403 om-02), tear (T414 om-98), tensile (T494 om-01), tensile energy absorption (T494 om-01), breaking length (T494 om-01), sheet density (T411 om-97), stiffness (T489 om-08), porosity (ISO 5636-3), water absorptiveness (T441 om-98) and brightness (T452 om-02).

4. RESULTS AND DISCUSSION

Sawdust Kraft pulping properties

Screened pulp yield (SPY) generally increased with increasing cooking times (Figure 1A). Using a constant AA charge (*i.e*. varying L:W ratio), optimum SPY was obtained using 7.5:1 L:W ratio at 60 mins cooking time. This was expected as a higher liquid volume ensured a more efficient wetting of the material. Subsequently, this ensured uniform distribution of the cooking liquor and as a result, a more uniform pulp (Winstead, 1972). At constant cooking time of 60 mins and 7.5:1 L:W ratio, SPY increased with increasing AA. This was consistent with findings by MacLeod & Kingsland (1990). Optimum SPY (48.4%) was achieved using 60 mins cooking time, 7.5:1 L:W ratio and 18% AA. This yield fell within the typical range (45-55 %) for bleachable grade hardwood Kraft pulps (Macleod 2007), and was only a few

percentage points below that obtained for other South African *E. grandis* Kraft pulps produced from woodchips (Sefara *et al*. 2000; Megown *et al*. 2000; Andrew *et al*. 2014).

The reject content (Figure 1B) decreased sharply as cooking time increased. At shorter cooking times, below 40 mins, the sawdust material pulped using 4.5:1 L:W ratio showed lower reject contents compared to that pulped using the 7.5:1 L:W ratio. Presumably, at the shorter pulping times, the lower rejects content may be attributed to the higher concentration of pulping chemicals in contact with the sawdust material when a lower L:W ratio is used. As the pulping time was increased when using 7.5:1 L:W ratio, the more uniform pulping achieved was related to a better wetting of the sawdust material due to a higher amount of free liquid available. At constant cooking time of 60 mins and 7.5:1 L:W ratio, as expected, the reject content increased as the AA decreased. This may be due to insufficient chemicals available for delignification.

The kappa number is a measure of the residual lignin in the pulp and is usually used to estimate the amount of chemicals required during bleaching. For hardwood bleachable grade pulps, as in the case of Eucalypt pulps, the kappa number target during pulping is typically around 16-18, but can be as low as 12 in some instances. For the sawdust pulps, the kappa number decreased as cooking time increased (Figure 1C). Lower kappa numbers were achieved when pulping at the higher L:W ratio of 7.5:1. This may be an indication of a more uniform cook at the higher L:W ratio. At constant cooking time of 60 mins and 7.5:1 L:W ratio, delignification was reduced as AA dosage decreased, as shown by the higher kappa numbers obtained.

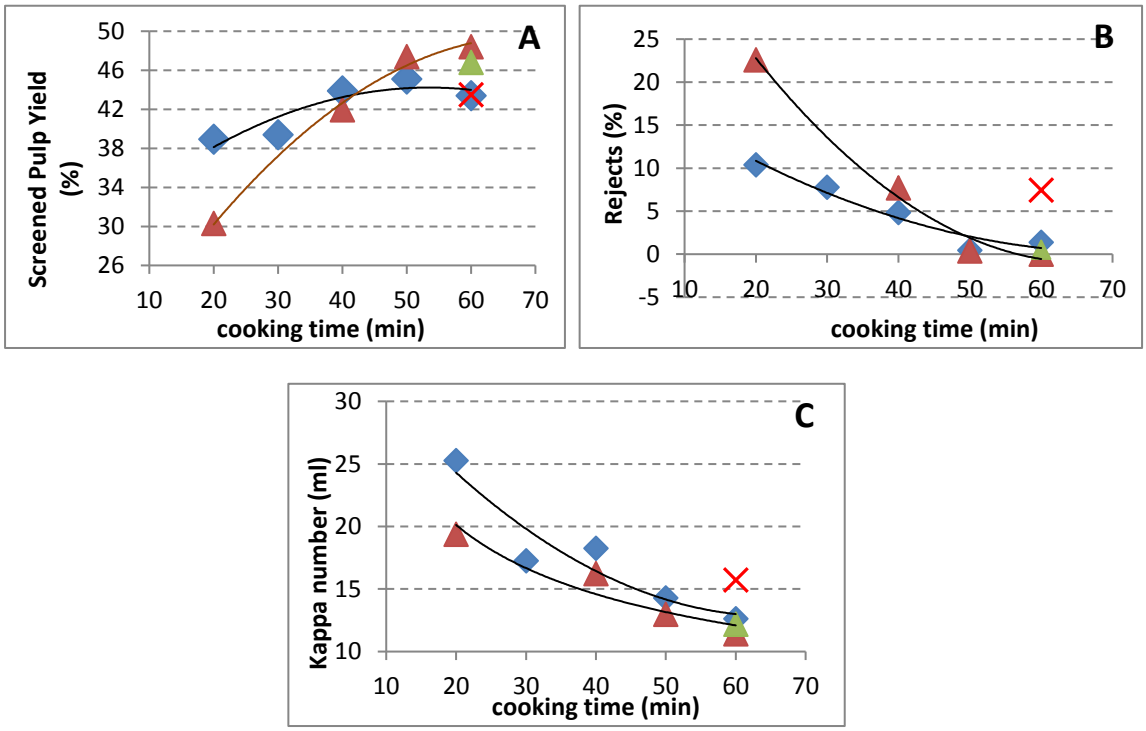

Figure 1. Kraft pulping properties of sawdust waste material: 4.5L:W-18%AA (♦); 7.5L:W-18% AA (▲); 7.5L:W-16%AA (▲) and 7.5L:W-14%AA (x).

Sawdust Kraft pulp fibre morphology

The fibre content of the sawdust pulps averaged 26.8 mil fibres.g^{-1} and appeared to be in a similar range as Eucalyptus Kraft pulps produced from wood chips (Table 1). Neiva *et al.* (2015) reported 24-26 mil fibres.g^{-1} for *E. grandis, E. saligna, E. globulus, E. propinqua and E. botryoides* pulps. However, they found that the fibre content of Eucalypt pulps produced from chips can vary significantly. They reported values as low as 18 mil fibres.g^{-1} in the case of *E. maculata* and as high as 41 mil fibres.g^{-1} for *E. viminalis.* Fibre length is an important property because a minimum length is required for inter-fibre bonding during papermaking (Paavilainen 1993). It is generally accepted that pulp strength is strongly correlated to fibre length. The sawdust pulp fibres exhibited an average length-weighted fibre length of ca. 0.65 mm which is within the acceptable range (0.6-0.85 mm) for Eucalypt pulps produced from

wood chips (Foelkel 2007), and higher than that reported for *E. camaldulensis* (0.57 mm), *E. sideroxylan* (0.57 mm), *E. viminalis* (0.6 mm), *E. ovata* (0.61 mm), *E. rudis* (0.63 mm) and *E. resinifera* (0.63 mm) pulps produced from wood chips (Neiva *et al*. 2015). Only a few Eucalypt species such as *E. saligna*, *E. botryoides*, *E. globulus*, *E. maculata* and *E. grandis* were reported with higher length-weighted pulp fibre lengths of 0.71 mm, 0.72 mm, 0.73 mm, 0.75 mm and 0.76 mm, respectively (Neiva *et al*. 2015). Fibre coarseness is an important papermaking property and is strongly related to sheet structure and formation, which in turn, affects the strength properties, sheet density and porosity of paper (Ramezani & Nazhad 2004). A higher coarseness value is indicative of fibres with thicker cell walls that are stiffer and less collapsible (Ramezani & Nazhad 2004). Sawdust pulp fibres exhibited fibre coarseness values that were in a similar range as conventional *Eucalyptus* Kraft pulp fibres produced from wood chips. Neiva *et al*. (2015) reported typical values for coarseness for several Eucalyptus Kraft pulp species that ranged between 4.6–8.4 mg.100m^{-1}. They reported an overall average coarseness value of 6.4 mg.100m^{-1} for these Eucalypts, and that of *E. grandis* pulps in particular was 6.1 mg.100m^{-1}. Similar to findings of other researchers, the coarseness of sawdust Kraft pulps increased with increasing fibre length, and as expected, it correlated with the fibre content of the sawdust pulps, in that the number of fibres per gram of pulp increased with decreasing fibre coarseness. Fibre deformations such as kinks and curls may contribute to reduced fibre strength. According to Foelkel (2007) a typical range for conventional Eucalyptus Kraft pulp kinks is between 0.4 -1.5 kinks, with kink angles greater than 30°. For fibre curliness, the range given by Foelkel (2007) was between 5-15%.

Table 1. Sawdust Kraft pulp fibre morphology.

Fibre Characteristics	4.5L:W-18%AA	7.5L:W-18%AA	7.5L:W-16%AA	7.5L:W-14%AA	Conventional pulps
Number of fibres	5106	5113	5099	5086	-
Fibre content ($x10^6.g^{-1}$)	27.3	30.0	25.0	24.7	24-26[a]
Length-weighted length (μm)	644	644	654	676	600-850[b]
Fibre coarseness ($mg.100m^{-1}$)	5.9	6.4	6.9	7.0	4.6–8.4[a]
Kink number	1.2	1.3	1.2	1.2	0.4 -1.5[b]
Kink angle (°)	132.3	130.7	132.0	131.0	>30.0[b]
Fibre curl (%)	5.0	6.6	5.4	5.7	5-15%[b]

[a]Neiva *et al*. 2015
[b]Foelkel 2007

Sawdust Kraft pulp and paper properties

The sawdust Kraft pulp handsheets properties at constant freeness of 400 ml are listed in Table 2, and where available, they were compared to conventional South African *E. grandis* Kraft pulps produced from wood chips. Whilst an extensive set of paper properties is provided for information purposes, only a few pertinent properties related to paper strength are discussed. Sheet density is an important property that affects most mechanical and physical properties of paper. The density of the handsheets produced from sawdust Kraft pulps were about 35 % lower than the average sheet densities listed for conventional Kraft pulps in Table 2. Generally, a higher sheet density is indicative of better bonding in a paper sheet. Sheet density usually increases with beating due to improved flexibility of the beaten fibres that conform easily to one another in the sheet. This results in an increased bonded area and more densely packed fibres in the paper sheet (Law *et al*. 1999; Gulsoy *et al*. 2013). To reach 400 ml CSF, as reported in Table 2, the sawdust Kraft pulp required minimal beating

(650 beating revolutions). This was 60 % lower than that required by conventional Kraft pulps produced from wood chips. The increased degree of beating of conventional pulps therefore resulted in a more compact sheet and higher sheet density for the conventional Kraft pulps.

Table 2. Handsheet properties of sawdust Kraft pulps compared at constant freeness of 400 ml CSF to Kraft pulps produced from wood chips.

	sawdust pulp	wood chip pulp
Beatings to reach 400 ml CSF (revs)	650	1750[a]
Sheet density ($kg.m^{-3}$)	498 (±10)	792[a] 76[b] 740[c]
Tensile Index ($kNm.kg^{-1}$)	51.5 (±2.3)	92[a] 102[b] 105[c]
Burst Index ($MN.kg^{-1}$)	2.1 (±0.3)	7.3[b] 7.0[c]
Tear Index ($Nm^2.kg^{-1}$)	4.7 (±0.1)	9.6[a] 8.6[b] 9.0
Tensile Energy of Adsorption ($J.m^{-2}$)	38.7 (±2.1)	Na
Water absorptiveness at 45 secs ($g.m^{-2}$)	132 (±8)	Na
Stiffness (mN)	737 (±65)	na
Porosity ($ml.min^{-1}$)	1585 (±129)	1250[d]
Brightness (%ISO)	40.3 (±0.7)	na
Unbeaten pulp brightness, (%ISO)	42.4 (±0.7)	na

na – not available
[a]Azeez, Andrew & Sithole, 2015
[b]Megown *et al*. (2000)
[c]Grzeskowiak *et al*. (2000)
[d]Neiva *et al*. (2015) and reported at ~550 ml CSF

Directly related to this is tensile strength, which in addition to being dependant on the bonding area (O' Neil *et al*. 1999), is also dependant on fibre length (O' Neill *et al*. 1999), fibre strength (Gulsoy *et al*. 2013) and bonding strength (Twimasi *et al*. 1996). The tensile strength of the handsheets produced from sawdust pulps were found to be ca. 50 % lower than handsheets produced from conventional Kraft pulps. Similar findings were observed for bursting and tearing strengths, which were 70 % and 50 % lower than conventional Kraft pulps, respectively. Lower bursting strength is attributed to weaker fibre-to-fibre bonding, and as a result, a more bulky sheet (Smook 1992); whilst a decrease in tearing strength is related to a lower fibre strength and shorter fibres (Muneri 1994).

Chemical characterisation of the pre-hydrolysate during PHK pulping

In hardwoods, the hemicelluloses account for 25-35 % of the wood. However, during pulping, a majority of the hemicelluloses are removed from the wood and collect in the black liquor where it is burned together with lignin. In recent times, there has been increasing interest in the valorisation of these sugars since their contribution to the calorific value of the black liquor is not significant (van Heiningen 2006). Within the context of resource optimisation and a biorefinery mill, the attractiveness of the PHK process is due to the availability of the hemicellulose rich stream for beneficiation into a range of additional products (Kautto *et al*. 2010). Table 3 shows the chemical composition of the pre-hydrolysate extract prior to pulping. Maximum arabinoses and rhamnoses were removed early during pre-hydrolysis, and their concentrations in the pre-hyrolysate remained relatively constant thereafter over the entire duration of the pre-hydrolysis stage. The amount of the galactoses removed also appeared relatively stable early in the pre-hydrolysis stage between 15-45 mins, and then increased marginally around 60 mins. In the case of glucose, ca. 2 $g.l^{-1}$ was removed

early in the pre-hydrolysis stage, and this increased marginally as the pre-hydrolysis time increased, peaking at ca. 2.5 $g.l^{-1}$ after 60 mins in the pre-hydrolysate. Xylose was the dominant monosaccharide removed during pre-hydrolysis. At 15 mins pre-hydrolysis time, up to 17 $g.l^{-1}$ was found in the pre-hydrolysate, and this increased to just over 24 $g.l^{-1}$ after 60 mins pre-hydrolysis time. The removal of lignin was also marginal, with the amount removed remaining fairly constant at ca. 0.1 $g.l^{-1}$ over the entire duration of the pre-hydrolysis stage. Similar to other studies (Tunc *et al*. 2008), the pH of the extract varied between 2-3. The high acidity of the extract was attributed to the hydrolysis of the acetyl groups attached to the hemicelluloses that result in the formation of acetic acid, hence lowering the pH of the pre-hydrolysate extract (Pu *et al*. 2011).

TABLE 3. Chemical characterisation of the pre-hydrolysate liquors prior to PHK pulping.

Hydrolysis time at 170°C (min)	pH	Arab ($mg.l^{-1}$)	Gal ($mg.l^{-1}$)	Rham ($mg.l^{-1}$)	Glu ($mg.l^{-1}$)	Xyl ($mg.l^{-1}$)	Man ($mg.l^{-1}$)	Acid soluble lignin ($mg.l^{-1}$)
15	3.08	503	1406	665	1828	17511	608	98
30	3.11	405	1497	756	2309	20465	512	103
45	2.39	237	1471	748	2357	21936	710	106
60	1.94	451	1714	813	2476	23453	463	110

Chemical characterisation of the pre-hydrolysed sawdust during PHK pulping

The sawdust yield remaining after pre-hydrolysis decreased with increasing pre-hydrolysis time (Table 4). At 15 mins, the yield loss was already ca. 20 %. After 60 mins, this loss extended to 28 %. Similar results were obtained by other researchers when hydrolysing wood chips at 170 °C (Pu *et al*. 2011). The measured cellulose content in the pre-hydrolysed

sawdust remained stable during pre-hydrolysis and averaged ca. 62 %. More than 50 % of the original xyloses in the wood were lost early in the pre-hydrolysis stage (after 15 mins). Beyond this time, the xylose concentration steadily decreased to ca. 2.5 % after 60 mins. Maximum removal of the arabinoses and galactoses occurred early in the pre-hydrolysis stage, and their residual concentrations were negligible in the pre-extracted wood. Beyond 30 mins pre-hydrolysis time, virtually all the rhamnoses were removed and none were detected in the pre-extracted wood after 45 mins. Mannose appeared to be more resistant to pre-hydrolysis, and after 60 mins, 0.3 % remained in the pre-extracted wood. Interestingly, not all the soluble lignin was removed, and around 3 % remained in the wood after pre-hydrolysis. The Klason lignin fell 1 % to 35 % after 60 mins. The increase in glucose in the pre-extracted sawdust was due to the removal of the other sugars and some lignin. After 60 mins pre-hydrolysis, the glucose concentration in the pre-hydrolysed wood reached 57 %.

TABLE 4. Chemical characterisation of pre-hydrolysed sawdust prior to PHK pulping.

Hydrolysis time at 170°C (min)	Sawdust yield (%)	Cell (%)	Arab (%)	Gal (%)	Rham (%)	Glu (%)	Xyl (%)	Man (%)	Acid soluble lignin (%)	Klason lignin (%)
15	80.4	61.4	0.02	0.15	0.07	54.0	4.42	0.45	3.70	36.5
30	75.0	62.4	0.01	0.06	0.04	55.6	3.01	0.37	3.31	37.0
45	73.0	62.8	0.02	0.02	0.00	56.0	2.99	0.34	3.13	36.9
60	72.1	62.2	0.02	0.03	0.00	56.9	2.49	0.30	3.13	35.4

Expressed as a percentage of the original wood, Figure 2 shows that the rhamnoses were removed completely from the wood during the pre-hydrolysis stage (*i.e.* 100 % removal). This was followed closely by the galactoses (97 % removal), arabinoses (88 %), xyloses (80 %), and to a lesser extent, the mannoses (36 %), and finally the glucose, with around 12 % removed. Besides the glucoses, the two other main monosaccharides remaining in the wood

after pre-extraction were the xyloses, at 1.8% residual concentration and the mannoses at 0.2%.

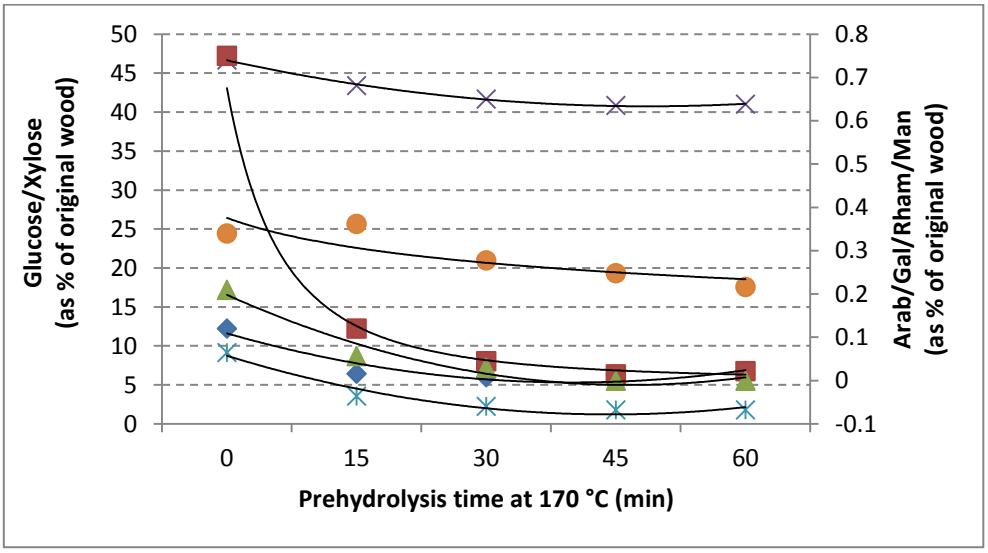

Figure 2. Residual hemicelluloses content in pre-hydrolysed sawdust material prior to PHK pulping: glucose (×), arabinose (♦), mannose (●), galactose (■), xylose (ж) and rhamnose (▲).

Kraft pulping of pre-hydrolysed sawdust

The optimum Kraft pulping conditions obtained for pulping the un-hydrolysed sawdust (*i.e.* conventional Kraft pulping process) was 18 % AA, 7.5:1 LW and 60 mins pulping time. These optimum conditions were then used to pulp the pre-hydrolysed sawdust material. The resulting Kraft pulping properties of the pre-hydrolysed sawdust material is shown in Table 5. The screened pulp yield varied by about 1 % around 42-43 % for all pre-hydrolysis treatments. As a percentage of the original sawdust material, this equated to an overall Kraft pulp yield of ca. 35 % for the sawdust pre-hydrolysed between 15-45 mins. Extending the pre-hydrolysis beyond these times resulted in a further 2 % drop in pulp yield to 33 %. No uncooked sawdust material was detected after screening. It can be seen from the lower kappa

numbers that the rate of delignification was significantly higher for the pre-hydrolysed sawdust compared to conventional Kraft pulping. Similar results have been reported previously, in that lignin removal is enhanced during Kraft pulping of pre-hydrolysed wood (Kautto *et al*. 2010; Duarte *et al*. 2011; Johakimu & Andrew 2013).

Pentosans in dissolving pulps are considered as contaminants for the production of cellulose derivatives. Their residual concentration in the unbleached PHK sawdust pulps ranged between 3-4 %, and showed a decreasing trend as the severity of the pre-hydrolysis stage was increased. A similar trend was observed for viscosity, which decreased from 848 $ml.g^{-1}$ to 759 $ml.g^{-1}$, when the pre-hydrolysis time was increased from 15 to 60 mins. Brightness on the other hand, increased with increasing severity of the pre-hydrolysis stage. Maximum brightness of 41.4 % was achieved after 60 mins pre-hydrolysis time. Sixta and Schild (2009) reported similar results for pulp yield, kappa number, brightness and pentosan content of unbleached PHK pulps produced from *E. globulus* wood chips. However, the viscosity they reported was about 25 % higher than that reported in this study for sawdust PHK pulps.

TABLE 5. Kraft pulping properties of pre-hydrolysed sawdust.

Pre-hydrolysis time at 170°C (min)	Screen pulp yield (%)	Screen pulp yield (as % of original sawdust)	Rejects content (%)	Total pulp yield (%)	Kappa number (ml)	Viscosity (ml/g)	Pentosan content (%)	Brightness (ISO)
15	42.5	35.2	0.0	42.5	5.3	848	3.77	33.5
30	42.8	35.3	0.0	42.8	3.1	791	3.50	34.0
45	43.3	35.2	0.0	43.3	3.0	759	3.45	37.5
60	42.3	32.7	0.0	42.3	2.6	759	3.08	41.4

5. CONCLUSION AND WAY FORWARD

As part of a broader objective to isolate cellulose from sawdust waste material for the production of nano-crystalline cellulose, conventional industrially available processes such as the Kraft and pre-hydrolysis Kraft (PHK) processes were investigated for delignification of sawdust produced from *E. grandis* wood. Sawdust Kraft pulp yields (48 %) and fibre morphologies were within acceptable ranges and comparable to conventional Kraft pulps produced from wood chips. The exception was the pulp strength properties such as burst, tear and tensile strengths which were 50-70 % lower than conventional pulps. Possible applications of this pulp could be addition or replacement of thermomechanical pulps and/or chemical pulps during newsprint manufacture, or other recycled paper applications such as tissue paper. During the pre-hydrolysis stage of the PHK process, up to 24 $g.l^{-1}$ xylose could be removed from sawdust with minimal removal of lignin (0.1 $g.l^{-1}$) and cellulose (2.5 $g.l^{-1}$). Wood yield after the pre-hydrolysis stage ranged between 70-80 %, and pulping of the pre-hydrolysed sawdust resulted in pulp yield ca. 35 %. Preliminary properties measured on the unbleached PHK sawdust pulps such as pentosan content (3-4 %), brightness (41 %) and viscosity (760 – 850 $ml.g^{-1}$) alluded to its potential for the production of dissolving pulps. Future work in this area may include bleaching and full characterisation of pulps, and may be extended to include techno-economic studies for beneficiation of the hemicelluloses, lignin and cellulose fractionated from sawdust. Co-cooking of sawdust with wood chips is another option to explore.

6. ACKNOWLEDGEMENTS

Special thanks to SAPPI for assistance with measurement of pentosan content in PHK pulps. Thanks and appreciation to CSIR technical staff for assistance with remaining analyses.

7. REFERENCES

Abraham, E., Deepa, B., Pothan, L.A., *et al*. (2011). Extraction of nanocellulose fibrils from loignocellulosic fibres: a novel approach. *Carbohydrate Polymers 86:1468-1475*.

Andrew, J.E., Johakimu, J. and Ngema, N.E. (2013). Ozone bleaching of South African *Eucalyptus grandis* Kraft pulps containing high levels of hexenuronic acids. *TAPPI Journal 12(8):7-14.*

Andrew, J.E., Johakimu, J. and Sithole, B.B. (2014*).* Bleaching of Kraft pulps produced from green liquor pre-hydrolyzed South African *Eucalyptus grandis* wood chips. *Nordic Pulp & Paper Research Journal 29(3):383-391.*

Azeez, M.A., Andrew, J.E. and Sithole, B.B. (2016). A Preliminary Investigation of Nigerian Gmelina arborea and Bambusa vulgaris for pulp and paper production. *Maderas-Ciencia Tecnología 18(1):65-78.*

Duarte, G.V., Ramarao, B.V., Amidon, T.E. and Ferreira, P.T. (2011). Effects of hot water extraction on hardwood Kraft pulp fibres (*Acer saccharum*, Sugar Maple). *Ind. Eng. Chem. Res. 50:9949-9959.*

Fengel, D. and Wegener, G. (1984). Wood: Chemistry, ultrastructure, reactions. *Walter de Gruyter & Co., Berlin pp 6-25*.

Foelkel, C. (2007). The Eucalyptus fibers and the Kraft pulp quality requirements for paper manufacturing. Eucalyptus Online Book and Newsletter: http://www.eucalyptus.com.br/capitulos/ENG03_fibers.pdf (last accessed 23 September 2015).

George, A. (2013). New wood pulp concoction stronger than kevlar, carbon fiber: http://www.wired.com/2012/09/wood-pulp-material/ (last accessed: 12 July 2016).

Godsmark, R. (2014). The South African industry's perspective on Forestry & forest products statistics – 2014: http://www.forestry.co.za/statistical-data/ (last accessed 5 October 2015).

Gulsoy, S.K., Kustas, S. and Erenturk, S. (2013). The effect of old corrugated container (OCC) pulp addition on the properties of paper made with virgin softwood Kraft pulps. *Bioresources 8(4):5842-5849.*

Grzeskowiak, V., Turner, P. and Megown, R.A. (2000). The use of densitometry and image analysis techniques to predict pulp strength properties in Eucalyptus plantations. *TAPPSA Conference "African Paper Week 2000 and Beyond", Durban, South Africa, 17-20 October.*

Herbst, S. (2013). Forestry group moves ahead plan to integrate Sabie site, extract more value: http://www.engineeringnews.co.za/article/forestry-group-moves-ahead-plan-integrate-sabie-site-extract-more-value-2013-05-10 (last accessed 5 October 2015).

Jimenez, G., Chian, D.S., McKean, W.T. and Gustafson, R.R. (1990). Experimental and theoretical studies to improve pulp uniformity. *Proceeding of the 1990 TAPPI Pulping Conference, Toronto, Canada: 49-53.*

Johakimu, J and Andrew, J.E. (2013). Hemicellulose extraction from South African *Eucalyptus grandis* using green liquor and its impact on Kraft pulp efficiency and paper making properties. *Bioresources 8(3):3490-3504.*

Kautto, J., Saukkonen, E. and Henricson, K. (2010). Digestability and paper-making properties of prehydrolyzed softwood chips. *Bioresources 5(4):2502-2519.*

Korpinen, R., Hultholm, T., Lönnberg, B. and Achrén, S. (2006). Development of sawdust cooking. *Appita Journal 59(5):406-411.*

Korpinen, R.I. and Fardim, P.E. (2009). Reinforcement potential of bleached sawdust Kraft pulp in different mechanical pulp furnishes. *Bioresources 4(4):1572-1585.*

Leschinsky, M., Sixta, H. and Patt, R. (2009). Detailed mass balances of the autohydrolysis of *Eucalyptus globulus* at 170°C. *Bioresources 4(2):687-703.*

Luthe, C., Berry, R. and Li, J. (2004). Polysulphide for yield enhancement in sawdust pulping: Does it work? *Pulp and Paper Canada 105(1):32-37.*

MacLeod, J.M. and Kingsland, K.A. (1990). Kraft-AQ pulping of sawdust. *TAPPI Journal – January 1990:191-193.*

MacLeod, M. (2007). The top ten factors in Kraft pulp yield. *Paperi ja Puu – Paper and Timber 89(4):1-7*.

Mäkinen, T. (2011). Biorefineries in pulp and paper industry. *Central European Biomass Conference, 26-29 January, Graz, Austria.*

Megown, K.A., Turner, P., Male J.R. and Retief, J. (2000). The impact of site index and age on the wood, pulp and pulping properties of a Eucalyptus grandis clone (Tag 5). *IUFRO Conference, 8-13 October, Durban, South Africa.*

Neiva, D.M., Fernandes, L., Araújo, S., Lourenço, A., Gominho, J., Simões, R. and Pereira H. (2015). Pulping potential of young eucalypts: a comparative study of wood and pulp properties of 12 eucalypt species. *7th International Colloquium on Eucalyptus Pulp, 26-29 May, Vitória, Espirito Santo, Brazil.*

Olufemi, B., Akindeni, J.O. and Olaniran, S.O. (2012). Lumber recovery efficiency among selected sawmills in Akure, Nigeria. *Drvna Industrija 63(1):15-18.*

Paavilainen, L. (1993). Importance of cross-dimensional fibre properties and coarseness for characterization of softwood sulphate pulp. *Paperi ja Puu 75(5):343-351.*

Pu, Y., Treasure, T., Gonzalez, R., Venditti, R. and Jameel, H. (2011). Autohydrolysis pretreatment of mixed hardwoods to extract value prior to combustion. *Bioresources 6(4):4856-4870.*

Ramezani, O. and Nazhad, M.M. (2004). The effect of coarseness on paper formation. *African Pulp and Paper Week, 12-15 October, Durban, South Africa.*

Saukkonen, E., Kautto, J., Irina, R. and Backfolk, K. (2012). Characteristics of prehydrolysis-Kraft pulp fibers from Scots pine. *Holzforschung 66(7):801–808.*

Sefara, N.L. Conradie, D. and Turner, P. (2000). Progress in the use of near-infrared absorption spectroscopy as a tool for the rapid determination of pulp yield in plantation eucalypts. *TAPPSA Journal November:15-17.*

Shatkin, J.A., Wegner, T.H. Bilek, E.M. and Cowie, J. (2014). Market projections of cellulose nanomaterial-enabled products – Part 1: Applications. *TAPPI Journal 13(5):9-16.*

Sixta, H. and Schild G. (2009). A new generation Kraft process. *Lenzinger Berichte 87:26-37.*

Sixta, H., Iakovlev, M., Testova, L., Roselli, A. *et al*. (2013). Novel concepts of dissolving pulp production. *Cellulose 20(4):1547-1561.*

Sjöström, E. (1981). Wood chemistry: fundamentals and applications, Academic Press, Inc., New York, 169-189.

Smook, G.A. (2002). Handbank for pulp and paper technologists. Angus Wilde Publications Inc.

Timberwatch (2000). The state of forestry in South Africa today: *http://www.timberwatch.org/old_site/archives/2000807stateofforrestry.htm* (last accessed 15 October 2015).

Tunc, M.S. and Heiningen, A.R.P. (2008). Hemicellulose extraction of mixed southern hardwood with water at 150°C: effect of time. *Industrial & Engineering Chemistry Research 47:7031-7037.*

Um, B-H. and van Walsum, G.P. (2009). Acid hydrolysis of hemicellulose in green liquor pre-pulping extract of mixed northern hardwoods. *Applied Biochemistry and Biotechnology 153:127-138.*

Van Heiningen, A. (2006). Converting a Kraft pulp mill into an integrated forest biorefinery, *Pulp & Paper Canada 107(6):38-43.*

Wallis, A.F.A., Wearne, R.H. and Wright, P.J. (1996). Chemical analysis of polysaccharides in plantation eucalypt woods and pulps. *Appita Journal 49(4):258-262.*

Winstead, T.E. (1972). Rapid Kraft pulping of sawdust and other small wood particles. *Paper Trade Journal 156(43):52-53.*

Wright, P.J. and Wallis, A.F.A. (1996). Rapid determination of carbohydrates in hardwoods. *Holzforschung 50:518-524.*

Zanuttini, M., Citroni, M., Marzocchi, V. and Inalbon, C. (2005). Alkali impregnation of hardwood chips. *TAPPI Journal 4(2):28-30.*