Delignification of *L. leucocephala* and *C. equisetifolia* through kraft pulping and Mitigation of Vessel Picking

Poonam Maan,* Ashish Kadam, and Dharm Dutt

*Leucaena leucocephala* and *Casuarina equisetifolia* are two fast-growing deciduous tropical hardwoods that were characterized for their morphological and chemical characteristics to assess their suitability for pulp production. The effects of kraft pulping sulfidity, cooking time, and cooking temperature on screened pulp yield and Kappa number were studied. Handsheets made from these pulps showed a vessel picking problem during printing that was reduced by treating the pulp with 0.1% cellulase and beating the pulp at high consistency.

**Keywords:** *Leucaena leucocephala; Casuarina equisetifolia; Chemical composition; Kraft pulp; Cellulase; Vessel picking*

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**INTRODUCTION**

The pulp and paper industry plays an important role in the socio-economic development of a country. Currently, this industry faces severe wood shortage as a raw fiber source. In view of the wood-fiber crisis, increasing attention is currently being directed towards fast-growing wood species that can grow on wasteland to make a sustainable supply of wood fibers. Many fast-growing annual and perennial plants of higher biomass have been investigated to access their suitability for pulp and paper production. These include non-woody plants such as *C. sativa, I. carnea* (Dutt and Tyagi 2010), *H. cannabinus, H. sabdariffa* (Upadhyaya *et al.* 2008), *S. aculeata,* and *S. sesban* (Dutt *et al.* 2004, 2005). Agricultural residues including sugarcane bagasse and wheat straw (Agnihotri *et al.* 2010; Singh *et al.* 2011), fast-growing hardwoods such as *C. equisetifolia* (Maan *et al.* 2018) and *L. leucocephala* (Poonam and Dutt 2014; Maan and Dutt 2017), and waste papers have also been investigated. *L. leucocephala* and *C. equisetifolia* are two fast-growing hardwoods that belong to the families of Fabaceae and Casuarinaceae, respectively. These plants can vigorously grow on barren and polluted sites, can increase soil fertility due to their nitrogen-fixing ability, and produce a high pulp yield (Lopez *et al.* 2008). During offset printing on the uncoated fine sheets of paper made from hardwood pulp, vessel picking is a general problem and is characterized by the appearance of small white spots in the print area (Dutt *et al.* 2007b). With this background, the goal of this study is to assess *L. leucocephala* and *C. equisetifolia* as a raw fiber source for the production of bleached kraft pulp. This study also examines how to minimize vessel element picking at the paper surface during the printing process.
EXPERIMENTAL

Materials
Fiber morphology

The fiber lengths of *L. leucocephala* and *C. equisetifolia* were determined by macerating small wood slices in 10 mL of 67% HNO₃ at 100 ± 2 °C for 10 min (Ogbonnaya et al. 1997). The softened slices were washed and then placed in a small flask containing 50 mL distilled water; the fiber bundles were disintegrated into individual fibers using a small motorized mixer with a plastic end. The macerated fiber suspension was placed onto a standard microscope glass slide by means of a graduated pipette. The graduated pipette was used to deliver 0.5 mL suspension. All of the fiber samples were viewed under a calibrated microscope; a total of 100 randomly chosen fibers were measured. Kraft pulp samples of *L. leucocephala* and *C. equisetifolia* were also taken for morphological examination. The Kraft fiber suspensions (0.1% consistency) of *L. leucocephala* and *C. equisetifolia* were characterized in terms of fiber width, fines, number of kinks, kink angle, and kink index; measurements were made using a fiber tester (Model: 912; L&W, Kista, Sweden). The fiber suspensions of 0.05% consistency were used for studying anatomical features that included the fiber lumen diameter, wall thickness, vessel length and diameter, and parenchyma cell length and diameter. The slides were observed under a motorized research microscope (Olympus BX 61; Olympus Instruments, Waltham, MA, USA). A total number of 100 fibers, 25 vessels, and 25 parenchyma cells were randomly selected for measurements. The derived fiber properties of slenderness ratio (fibre length/fiber diameter) (Varghese et al. 1995), flexibility coefficient (100× lumen diameter/fiber diameter), and Runkel ratio (2× fiber wall thickness/lumen diameter) (Runkel 1949) were calculated; the results were compared to *Eucalyptus tereticornis* (Anonymous 2004).

Methods
Proximate chemical analysis

Wood chips (100 g) of *L. leucocephala* and *C. equisetifolia* were ground into a powder using a laboratory Wiley mill. The powder fractions of each that passed through a -48-mesh screen but retained on +80-mesh screen were collected for chemical analysis. The screen wood meals were analyzed for alcohol-benzene solubility according to TAPPI T204 cm-97 (1997), cold and hot water solubility according to TAPPI T207 cm-99 (1999), and 1% NaOH solubility according to TAPPI T212 om-02 (2002).

Wood meals of *C. equisetifolia* and *L. leucocephala* were then extracted with ethanol-toluene (1:2, v/v) for 6 h in a Soxhlet apparatus to remove wood extractives as per TAPPI T264 cm-97 (1997). The extractive-free samples were used for the determination of lignin according to TAPPI T222 om-02 (2006), pentosans (TAPPI T223 cm-01 (2001)), holocellulose (TAPPI T249 cm-85 (2009)), α-cellulose, β-cellulose, γ-cellulose, and ash content (TAPPI T203 cm-09 (2009)).

The holocellulose extraction of the wood meals was performed by the modified chlorite method of Erickson (1962). The results of the proximate chemical analysis were compared to *E. tereticornis* (Dutt and Tyagi 2011) and to *Trema orientalis* (Jahan and Mun 2003).
Kraft pulping

Kraft pulping of *L. leucocephala* and *C. equisetifolia* was performed in an electrically heated rotary digester (0.02 m$^3$ capacity; L&W, Kista, Sweden) containing four bombs each of 1-L volume. The wood chips and the white liquor were introduced into the bombs; the bombs were sealed and placed into the digester for cooking at different conditions as prescribed by a given experiment. At the end of cooking, the pulps were separated from the spent liquors by washing the pulps on a flat stationary screen (300-mesh size bottom).

After washing, the total pulp yields were determined. The washed pulps were disintegrated for 3 min at 2500 rpm and then screened with a WEVERK vibratory flat screen (L&W, Kista, Sweden) (0.15-mm slot size) to remove the rejects. The screened pulps were then analyzed for screened pulp yield and for Kappa number according to TAPPI T236 om-13 (2013).

Enzymatic treatment

Unbleached kraft pulps (100 g) of *L. leucocephala* and *C. equisetifolia* were treated with a crude enzyme mixture with a cellulase activity of 6.5 IU/mL at a dose of 0.1% (on oven-dry pulp basis) prior to refining. The crude cellulase enzyme mixture was obtained from the fungus *Coprinopsis cinerea* RM-1 NFCCI-3086, which was isolated in the authors’ laboratory (Maan et al. 2016).

The enzyme treatment conditions were: reaction time 120 ± 5 min, reaction temperature 55 ± 2 °C, and pH 6.0 ± 0.1. After cellulase treatment, the pulp samples were filtered through a four-layered cheese cloth. The control was examined similarly, except using phosphate buffer instead of enzyme. The pulp samples were washed with 1 L of tap water and squeezed.

Preparation, evaluation, and microscopic observations of laboratory handsheets

The unbleached pulps of *L. leucocephala* and *C. equisetifolia* were refined at different levels in a PFI mill according to TAPPI T200 sp-96 (1996). Laboratory handsheets of 60 g/m$^2$ grammage were prepared using a British handsheet former according to TAPPI T205 sp-02 (2002).

The formed handsheets were then air-dried. The sheets were printed with a laboratory printer (Model: AIC2-5; IGT Testing Systems, Almere, Netherlands) using a commercial sheet-fed offset printing ink (IGT medium viscosity oil). The following conditions were maintained during the printing process: 2.5 m/s printing speed; 125 N/cm printing force; 8 µm amount of ink; and 25 ± 5 °C inking roll and room temperature. The ink kneading time was 2 min.

Ink was transferred to the ink roll in 30 min, and before printing, the printing roll was kept at rest for 1 min. Pick marks were collected from the blanket with adhesive tapes. The tapes were analyzed with a microscanner (Model: LAD094; Paprican, Pointe-Claire, Canada) to determine the picking tendency.
RESULTS AND DISCUSSION

Fiber Morphology
The morphological characterizations of *L. leucocephala* and *C. equisetifolia* are presented in Table 1. The fiber lengths of *L. leucocephala* and *C. equisetifolia* were 0.78 and 0.74 mm, respectively; this was comparable to 0.65 mm for *E. tereticornis*. The average fiber widths of *L. leucocephala* and *C. equisetifolia* were 18.3 and 16.9 µm, respectively, versus 14.2 µm for *E. tereticornis*. Fiber width provides the surface contact area for bonding in papermaking, which affects the tear, tensile, and burst strength of the resulting paper. The lumens of *C. equisetifolia* fibers (4.70 µm) were narrow compared to *L. leucocephala* fibers (7.98 µm), but wider than that of *E. tereticornis* fibers (3.40 µm). The sizes of the lumens influenced the beating, collapsibility, and conformability of the fiber. Fibers with larger lumen diameters exhibited better beating and collapsibility, and provided increased fiber surface area for bonding. The cell wall thicknesses of *L. leucocephala* (5.2 µm) and *E. tereticornis* (5.4 µm) fibers were nearly identical, but were somewhat thinner than those of *C. equisetifolia* (6.10 µm).

Table 1. Morphological Characterization of *L. leucocephala* and *C. equisetifolia*

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameter</th>
<th><em>L. leucocephala</em></th>
<th><em>C. equisetifolia</em></th>
<th><em>E. tereticornis</em> (Anonymous 2004)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fiber length, L (mm)</td>
<td>0.78 ± 0.00</td>
<td>0.74 ± 0.00</td>
<td>0.65</td>
</tr>
<tr>
<td>2</td>
<td>Fiber diameter, D (µm)</td>
<td>18.30 ± 0.14</td>
<td>16.90 ± 0.00</td>
<td>14.2</td>
</tr>
<tr>
<td>3</td>
<td>Lumen diameter, d (µm)</td>
<td>7.98</td>
<td>4.70</td>
<td>3.40</td>
</tr>
<tr>
<td>4</td>
<td>Wall thickness, w (µm)</td>
<td>5.16 ± 0.10</td>
<td>6.10 ± 0.11</td>
<td>5.4</td>
</tr>
<tr>
<td>5</td>
<td>Slenderness ratio (L/D)</td>
<td>42.62</td>
<td>43.79</td>
<td>45.77</td>
</tr>
<tr>
<td>6</td>
<td>Flexibility coefficient (d/DX100)</td>
<td>43.61</td>
<td>27.81</td>
<td>23.94</td>
</tr>
<tr>
<td>7</td>
<td>Runkel ratio (2w/d)</td>
<td>1.29</td>
<td>2.59</td>
<td>3.18</td>
</tr>
<tr>
<td>8</td>
<td>Vessel length (µm)</td>
<td>480.55 ± 26.93</td>
<td>431.24 ± 19.7</td>
<td>360</td>
</tr>
<tr>
<td>9</td>
<td>Vessel diameter (µm)</td>
<td>48.31 ± 1.98</td>
<td>109.76 ± 4.36</td>
<td>140</td>
</tr>
<tr>
<td>10</td>
<td>Parenchyma cell length (µm)</td>
<td>128.98 ± 10.93</td>
<td>116.22 ± 7.60</td>
<td>69.0</td>
</tr>
<tr>
<td>11</td>
<td>Parenchyma cell width (µm)</td>
<td>27.50 ± 2.13</td>
<td>18.11 ± 1.10</td>
<td>23.0</td>
</tr>
<tr>
<td>12</td>
<td>Vessels per 10000 fibers</td>
<td>102.50 ± 3.54</td>
<td>154 ± 1.41</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>Fines mass basis (%)</td>
<td>3.90 ± 0.00</td>
<td>3.15 ± 0.07</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>Number of kinks per mm</td>
<td>0.73 ± 0.00</td>
<td>0.83 ± 0.00</td>
<td>0.98</td>
</tr>
<tr>
<td>15</td>
<td>Mean kink angle (°)</td>
<td>47.72 ± 0.16</td>
<td>48.11 ± 0.18</td>
<td>29.93</td>
</tr>
<tr>
<td>16</td>
<td>Mean kink index</td>
<td>1.71 ± 0.00</td>
<td>1.95 ± 0.01</td>
<td>2.15</td>
</tr>
<tr>
<td>17</td>
<td>Number of fibers/mg</td>
<td>15000</td>
<td>11000</td>
<td>-</td>
</tr>
</tbody>
</table>

± Refers standard deviation from the mean

The slenderness ratio (L/D) was 42.62 for *L. leucocephala* and 43.79 for *C. equisetifolia* versus 45.77 for *E. tereticornis*. The slenderness ratio was directly proportional to the length of the fiber. Fibers with a low slenderness ratio had a high degree of collapsibility and conformability. The handsheets made from such fibers have higher density with lower tear but higher tensile, burst, and double fold (Reddy and Yang 2005). The flexibility coefficients of *L. leucocephala* and *C. equisetifolia* were 43.6 and 27.8, respectively, versus 23.9 for *E. tereticornis*. Fibers that have low flexibility...
coefficients are rigid and retain their tubular structure upon pressing; such fibers do not collapse to a double-walled ribbon structure, which results in lower contact area for fiber-to-fiber bonding. The handsheets made from such fibers are bulky and have higher opacity with higher tear strength (Rydholm 1965). The Runkel ratio values of *C. equisetifolia* and *E. tereticornis* were two and two and a half times greater than that of *L. leucocephala*. Fibers with a Runkel ratio greater than 1.0 are lignified and thick-walled. Paper conformability and pulp yield are also affected by the Runkel ratio (Ona et al. 2001). *Leucaena leucocephala* had large-sized vessel elements with narrow diameters. The vessel elements of *C. equisetifolia* were also larger with smaller diameter in comparison to *E. tereticornis*. The lengths and widths of the parenchyma cells of *L. leucocephala* (128.98 and 27.50 μm, respectively) were higher than those of *C. equisetifolia* (116.22 and 18.11 μm, respectively). The average vessel elements per 100000 of fibers in *L. leucocephala* were 102.5 versus 154.0 in *C. equisetifolia*. Due to their large dimensions, the vessel elements acted as a filler and bonded loosely with the fibers, and were easily picked-out from the paper surface during the printing process and during the sheet drying process. Vessel picking is related to the vessel element width, length, and number per unit weight. Figure 1 shows the fiber, parenchyma cell and vessel cell present in kraft pulp of *L. leucocephala*. The vessel cells of *C. equisetifolia* have longer tapering end and large diameter (Fig. 2).

**Fig. 1.** *L. leucocephala* showing fibers, parenchyma cells and vessel (4X) (A); fiber and vessel showing bordered pits (10X) (B)

**Fig. 2.** *C. equisetifolia* showing fibers, parenchyma cells and vessel (4X) (A); fiber and vessel (10X) (B)
Table 2. Chemical Characterization of *L. leucocephala* and *C. equisetifolia*

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Characteristic Component (%)</th>
<th><em>L. leucocephala</em></th>
<th><em>C. equisetifolia</em></th>
<th><em>E. tereticornis</em> (Anonymous 2004)</th>
<th><em>T. orientalis</em> (Jahan and Mun 2003)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cold water solubility</td>
<td>1.75 ± 0.08</td>
<td>0.57 ± 0.03</td>
<td>2.38</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>Hot water solubility</td>
<td>3.70 ± 0.18</td>
<td>2.1 ± 0.10</td>
<td>4.31</td>
<td>5.1</td>
</tr>
<tr>
<td>3</td>
<td>0.1 N NaOH solubility</td>
<td>17.72 ± 0.23</td>
<td>14.27 ± 0.08</td>
<td>16.83</td>
<td>21.9</td>
</tr>
<tr>
<td>4</td>
<td>Alcohol-benzene solubility</td>
<td>4.02 ± 0.21</td>
<td>2.53 ± 0.17</td>
<td>3.00</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Holocellulose</td>
<td>75.31 ± 0.83</td>
<td>74.73 ± 0.60</td>
<td>70.3</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>α-cellulose</td>
<td>42.88 ± 0.21</td>
<td>43.9 ± 0.60</td>
<td>42.6</td>
<td>49.7</td>
</tr>
<tr>
<td>7</td>
<td>β-cellulose</td>
<td>17.68 ± 0.79</td>
<td>17.23 ± 0.32</td>
<td>16.22</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>γ-cellulose</td>
<td>14.59 ± 0.52</td>
<td>13.3 ± 0.49</td>
<td>11.48</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Pentosans</td>
<td>14.72 ± 0.22</td>
<td>15.88 ± 0.32</td>
<td>11.07</td>
<td>23.4</td>
</tr>
<tr>
<td>10</td>
<td>Total lignin</td>
<td>21.65</td>
<td>23.05</td>
<td>28.5</td>
<td>22.9</td>
</tr>
<tr>
<td>11</td>
<td>Klason lignin (acid insoluble)</td>
<td>20.83 ± 0.16</td>
<td>22.41 ± 0.41</td>
<td>27.9</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Acid soluble lignin</td>
<td>0.82 ± 0.01</td>
<td>0.64 ± 0.03</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>Ash</td>
<td>1.20 ± 0.06</td>
<td>0.87 ± 0.03</td>
<td>0.66</td>
<td>1.0</td>
</tr>
</tbody>
</table>

± Refers standard deviation from the mean

The mean kink indices for *L. leucocephala* and *C. equisetifolia* were 1.71 and 1.95, respectively, which were lower than the 2.15 obtained for *E. tereticornis*. A high kink index value for fibers indicates that the resulting paper has high tensile, burst, and double fold values, but low tear (Sharma et al. 2011). The kink angles for *L. leucocephala* and *C. equisetifolia* were 47.72° and 48.11°, respectively, versus 29.93° for *E. tereticornis*. A high angle value leads to low tensile strength, but higher stretch and tear for paper than paper made from straight fibers. The values for kink per mm for *L. leucocephala* and *C. equisetifolia* were similar, and both were smaller than the value for of *E. tereticornis*. However, laboratory beaters are very effective in removing kinks from pulp fibers (Seth 1988). Based on the morphological characteristics for both raw materials (*L. leucocephala* and *C. equisetifolia*), these characteristics were comparable to those of *E. tereticornis* and *T. orientalis*.

Proximate Chemical Analysis

Table 2 lists the proximate chemical analysis of *L. leucocephala* and *C. equisetifolia*. The cold and hot water soluble fractions in *L. leucocephala* were higher when compared to *C. equisetifolia*; both species contained lower water-soluble fractions when compared to *E. tereticornis* and *T. orientalis*. This may have been due to a lower amount of inorganic compounds, in addition to tannin, gums, and sugars. The low water solubility indicated that less pulping chemicals were required to produce a high pulp yield with a low Kappa number. The value of 1% NaOH solubility can be used as an estimate of the dissolution of low molecular weight carbohydrates. The value of 1% NaOH solubility of wood estimates the degradation of carbohydrates by light, solar radiation, oxidation, and fungal attack when stacked in the log yard. *Casuarina equisetifolia* had a lower value of alkali soluble compounds when compared to *L. leucocephala*. *E. tereticornis* had an alkali solubility value similar to *L. leucocephala*, whereas *T. orientalis* had the highest value. These observations indicate that *C.*
C. equisetifolia may be stacked for longer time periods in the wood yard, whereas L. leucocephala and E. tereticornis should be stored for a short time period. Alcohol-benzene solubility represents the extractives that contribute to pulp pitch deposits, such as waxes, terpenes, fatty acids, resins, alcohols, aldehydes, and phenolics. These compounds have an adverse effect on pulping process (Sari et al. 2010). The holocellulose content was higher in L. leucocephala (75.31%) when compared to C. equisetifolia (74.73%) and E. tereticornis (70.3%). The total pulp yield and overall paper strength depend on holocellulose content, which includes high degree of polymerization (DP) cellulose, as well as low molecular weight and branched hemicelluloses. α-Cellulose is the high molecular weight fraction of cellulose that does not dissolve in 17.5% NaOH. α-Cellulose contents in L. leucocephala and C. equisetifolia were 42.9% and 43.9%, respectively; these values were higher than that of E. tereticornis (42.6%) but lower than that of T. orientalis (49.7%). According to the rating system, plant materials with α-cellulose greater than 34% are considered promising for chemical pulping and papermaking (Nieschlag et al. 1961). High α-cellulose content is related to high fiber and paper strength and longevity of the paper. β-Cellulose is the fraction that is soluble in 17.5% NaOH. For L. leucocephala and C. equisetifolia, the β-cellulose contents were similar to one another, but they were higher than that of E. tereticornis. The γ-cellulose content was higher in L. leucocephala (14.59%) when compared to C. equisetifolia (13.3%) and E. tereticornis (11.48%). Consequently, L. leucocephala fibers required less beating for fibrillation to develop better physical strength properties of the pulp when made into paper. The pentosans in C. equisetifolia were slightly higher than those of L. leucocephala, but were lower than those of E. tereticornis. T. orientalis had the highest pentosans. Pentosans promote the fibrillation of fibers during beating. The lignin content of L. leucocephala (21.65%) was lower than that of C. equisetifolia (23.05%), which was similar to the value found in T. orientalis (22.9%) but lower than that found in E. tereticornis (28.5%). The bleachability, hardness, fiber stiffness, and color of the pulp are related to the lignin content (Erickson 1962; Anonymous 2007). Therefore, C. equisetifolia required more pulping chemicals and longer cooking time to pulp. Moreover, the pulp of C. equisetifolia may be darker and may require more chemicals to bleach. The Klason lignin of L. leucocephala (20.83%) was lower when compared to C. equisetifolia (22.41%), but both were lower than that of E. tereticornis (27.9%). The acid soluble lignin was less than 1% in both of the hardwoods examined. The ash content of C. equisetifolia was lower when compared to T. orientalis but higher than that of E. tereticornis. Alternatively, the ash content in L. leucocephala was higher than those of E. tereticornis and T. orientalis. The ash content is undesirable because trace transitional metal ions interfere bleaching with H2O2 and O2, and a high silica content damages wood chippers and other mill equipment.
Pulping

The plots of sulfidity versus screened pulp yield indicate that the yield increased with increasing sulfidity levels up to 25% for *L. leucocephala* and up to 20% for *C. equisetifolia* at each temperature investigated. Beyond that, sulfidity did not result in a remarkable increase in the yield (Fig. 3). Additionally, the screened pulp yield increased as the white liquor sulfidity increased at cooking temperatures from 160 to 170 °C; there was a sharp decrease in screened pulp yield as the cooking temperature was raised above 170°C. The screened rejects decreased with increasing cooking temperature from 160 to 170 °C, whereas higher cooking temperatures beyond 170 °C did not affect reject levels (i.e., they remained constant) (Fig. 4). The relationship of sulfidity to brown stock Kappa number (Fig. 5) can roughly be approximated by two straight lines for a given pulping temperature that was examined. For sulfidity levels between 15% to 25% for *L. leucocephala* and 15% to 20% for *C. equisetifolia* the slope value was steep. This was related to a rapid decrease in the Kappa number and the curves with a gentler slope, beyond a sulfidity level of 20%, indicated a slow decrease in Kappa number. Hence, beyond 20% sulfidity, there was no improvement in the screened yield and a reduction in the Kappa number. Figure 5 shows that the curves plotted at 160 °C were quite separated from the curves plotted at 170 and 180 °C, which almost impose on each other. This observation indicated that the Kappa number decreased sharply over the temperature range of 160 to 170 °C; at temperatures above 170 °C, the reduction in Kappa number was inconsequential. It was concluded that the optimum pulping sulfidity favorably affected the screened pulp yield and reduced screen rejects. The improvement in pulp yield was due to selective delignification and reduced screening rejects.

![Fig. 3. Screened pulp yields vs. white liquor sulfidities at various kraft pulping temperatures: L. leucocephala (A) and C. equisetifolia (B) ](image)
Further, the screened pulp yield sharply decreased as the pulping temperature increased from 170 to 180 °C. This may have been attributed to the degradation of the cellulose and hemicelluloses by depolymerization at the reducing ends (i.e., alkaline peeling reactions); this resulted in decreasing pulp yields and in creating new reducing ends, from which further degradation reactions can occur (secondary peeling) (Norden and Teder 1979). The Kappa numbers were also higher at the lower sulfidity values, which may have been attributed to the slower rate of delignification at low concentrations of HS⁻ ions. The rate of delignification is accelerated in the presence of HS⁻ ions, and the
high concentration of HS$^-$ is essential for selective delignification with minimum carbohydrate degradation (Gierer and Wannstrom 1984). Furthermore, lignin-carbohydrate complexes (LCC) are speculated to be formed during kraft pulping (Lawoko 2005); these linkages are alkali stable and resistant to delignification. The HS$^-$ ions inhibited or reduced the formation of LCC linkages while it facilitated lignin fragmentation via sulfidolytic cleavage of the $\beta$-aryl ether linkages. In addition, a high sulfidity prevents the coupling reactions of reactive intermediates (e.g., oxirane type) with carbohydrates, which reduces further yield loses (Rakkolainen et al. 2009).

Fig. 6. Screen pulp yields vs. different cooking times at various kraft pulping active alkali levels: L. leucocephala (A) and C. equisetifolia (B)

Fig. 7. Kappa numbers vs. different cooking times at various kraft pulping active alkali levels: L. leucocephala (A) and C. equisetifolia (B)
Figure 6 shows the screened pulp yields varied at different cooking time and active alkali doses (14% to 20% as Na₂O on pulp) while at a pulping temperature 170 °C. The screened pulp yield increased with increased cooking time for each active alkali dose examined. The trends indicated that beyond a cooking time of 90 min, the screened pulp yield started to decrease. Furthermore, the trends at 17% active alkali were higher than the trends at 20% active alkali at different cooking times. This observation indicated excessive active alkali charges that remained unconsumed during the course of pulping, which adversely affected the pulp yield instead of increased lignin removal. Similarly, the trends among Kappa numbers and cooking times at different active alkali doses (14% to 20% as Na₂O on pulp) (Fig. 7) showed that the Kappa number decreased with increased cooking time up to 90 min. Beyond a cooking time of 90 min, the decrease in Kappa number was inconsequential for each active alkali dose examined. The trends for 17% and 20% active alkali coincided with one another, particularly after 90 min. This observation indicated that it was not advisable to pulp with active alkali doses at or greater than 20%. Hence, a 25% sulfidity level for L. leucocephala and 20% sulfidity level for C. equisetifolia were ideal when using a cooking time of 90 min at 170 °C and an active alkali dose of 17% (as Na₂O on pulp).

Vessel Cells Picking

Figure 8 illustrates the effect of pulp freeness level (5% to 20%) during an enzymatic refining treatment on the vessel pick counts of L. leucocephala and C. equisetifolia, respectively, at different beating levels (20 to 50 °SR). Vessel pick counts decreased with increased pulp beating level up to 40 °SR freeness; higher °SR values did not appreciably affect the pick counts. It was observed that vessel pick counts decreased as the refining consistency increased from 5% to 20%. The maximum reduction in vessel pick counts was observed at 15% consistency. The gap between the trends of 15% and 20% consistency at different beating levels was inconsequential. Hence, a pulp refining consistency of 15% and a beating level 40 °SR were taken as optimum for the reduction of vessel pick counts. The sliding wad under mechanical pressure at a fixed refiner clearance caused the friction among fibers and vessels and resulted into the breaking of vessels or parenchyma cells. The repeated mechanical action caused the rupture of vessel elements and the fibrillation of fibers entrapped the broken vessel elements. Therefore, the tendency of parenchyma or vessel cells to be picked out by the printing ink or at the dryer drums at the paper machine was lessened (Fig. 8). The parenchyma cells and vessel elements had no appreciable bonding effect, and were too large to function as fillers. Their deposition may have occurred as an invisible thin film on dryer drums that caused sheet picking and fiber rising on the paper sheet, whereas visible deposits on the dryer cylinders impeded heat transfer. Reductions in dryer heat transfer resulted in an uneven paper reel moisture profile, as well as reduced paper machine productivity. Vessel elements on the surface of the base sheet inhibited the penetration of coating chemicals. If vessel elements are not bonded well to the base sheet, then a pick out could occur during offset printing (Colley 1975). The pulps of L. leucocephala and C. equisetifolia treated with an enzyme dose of 0.1% (v/w) and then beaten at 40 °SR freeness at a pulp consistency of 15%, reduced vessel pick counts 90% and 82.8%, respectively, when compared to their respective controls.
Fig. 8. Vessel element pick counts vs. different refining levels (°SR) at different pulp refining consistencies: (A) *L. leucocephala* and and (B) *C. equisetifolia*
The enzyme treatment weakened the vessel walls by breaking the saccharide ring structures and glycolytic ester linkages. This promotes the bonding strength of vessels and fibers and reduces press picking problems (Sari et al. 2010). High consistency refining destroyed the vessel elements and considerably reduced the number of large-sized vessel elements (Sari et al. 2010). These investigators observed that the number of vessel picks in *Eucalyptus globulus* was reduced 91.5% (from 27.0 picks/cm² to 2.3 picks/cm²) for 10% consistency in pulp beaten at 2000 PFI revolutions.

**CONCLUSIONS**

1. Proximate chemical analysis of *L. leucocephala* and *C. equisetifolia* indicated that these raw materials were comparable to *E. tereticornis* and *T. orientalis*, and they could be used as a raw fiber source for the production of pulp and paper.

2. The optimum kraft pulping conditions were at 170 °C for 90 min and 17% active alkali when using a sulfidity level of 25% for *L. leucocephala* and 20% for *C. equisetifolia*.

3. The enzymatically treated pulp beaten at 40 °SR at pulp consistency of 15% reduced vessel element pick counts by 90% and 82.8% in *L. leucocephala* and *C. equisetifolia*, compared to their respective controls.

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