Correlates of the yield of chemical pulp, lignin and the extractive materials of tropical hardwoods

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The aim of this investigation is to correlate the percentage yields of pulp of twenty tropical hardwood species with their lignin and extractive contents. The hardwoods studied include Abura (*Hallea ciliata*), Afara (*Terminalia superba*), Agba (*Entada gigas*), Akomu (*Pycnanthus angolensis*), Eki-Eki (*Lophira alata*), Erimado (*Ricindendron heudelotii*), Erun-obo (*Erythropleum suaveolens*), Iroko (*Milicia exelsa*), Itako (*Strombosia pustulata*), Itara (*Sacoglottis gabonensis*), Mahogany (*Khaya ivorensis*), Masonia (*Masonia altissima*), Obeche (*Triplochiton scleroxylon*), Odoko (*Ipomoea asarifolia*), Ofun (*Avicennia germinans*), Okilolo (*Symphona globulifera*), Opepe (*Nauclea diderrichii*), Oporoporo (*Pterygota macrocarpa*) and Some (*Ceiba pentadra*). Hardwood species such as *H. ciliata*, *T. superba* and *S. globulifera* that gave pulp yield of 50% were found to have the lowest lignin contents in the range of 19.0 to 28.4% and extractives contents of 4.8 to 6.0%. The results obtained showed that there is significant negative correlation (p < 0.01 and r = -0.84) between the percentage pulp yield and the lignin contents as well as between percentage pulp yield and contents of extractive materials (p < 0.01, r = -0.811). However, a significant positive correlation (p < 0.01, r = 0.649) between the percentage lignin contents and the extractive components of the wood samples was observed. The chemical integrity of the pulp, lignin and extractive contents of the wood samples was confirmed by infra-red (i.r.) spectroscopic studies.

**Key words:** Tropical hardwood species, pulp yield, lignin content, extractives.

INTRODUCTION

Wood is a complex of natural organic polymer substances that include cellulose, hemicelluloses and lignin. Cellulose is a structural polysaccharide and consists of long chains of D-glucose units linked by β-1,4 glycosidic bonds. Hemicelluloses are built up from a relatively limited number of sugar residues that include D-xylose, D-mannose, D-glucose, D-galactose, L-arabinose, 4-O methyl-D-glucuronic acid, D-galacturonic acid, D-glucuronic acid and to a lesser extent, L-rhamnose, L-fructose and various O-methylated neutral sugars (Sjostrom, 1993). Lignin is made up of three primary precursors which include trans-coniferyl, trans-sinapyl and trans-p-coumaryl alcohols (Argyropoulos et al., 2002; Froass et al., 1996). Lack of enzymic control during lignin polymerization results in an almost random series of bonding and a very complex structure (Jung and Fahey, 1983). The existence of strong carbon-carbon (C-C) and ether (C-O-C) linkages in the lignin affects its susceptibility to chemical disruption (Karhunen et al., 1999). The non-structural components of wood include extractives which consist of triglycerides, fatty acids, waxes, fatty alcohols, sterols and steryl esters (Fengel and Wegener, 1989; USDA, 1999). The various polymer substances present in wood are not uniformly distributed within the cell wall and their concentrations change from one morphological region to the other (Saka, 2001). Various studies have shown that the chemical composition of hardwoods of temperate zones is different from those of tropical regions (Hon and Shiraishi, 2001). In many cases, the latter contain higher percentages of extraneous substances and lignin. This fact is not
unconnected with the difficulty encountered in pulping of most tropical hardwoods (Sykes and Prentice, 1996; Poke and Raymond, 2006).

Studies on hardwoods from the temperate zone are well documented in literature (Foster et al., 1996; Kreyling, 2010; Pijut et al., 2011) but very little information exist on wood species from the tropical forest of Africa and its sub-region, despite the quantum of foreign exchange earnings and the increasing potential for wealth creation obtainable from this sector (Odeyemi, 1986). Few West African hardwood species have been studied (Lai and Iwamida, 1993) and sufficient details about the levels and composition of lignin and extraneous materials contents of these hardwoods have received little attention. This formed the basis for the present studies in the determination of amount of lignin, extraneous materials and the pulp yield obtainable from twenty tropical hardwood species sourced from Nigeria.

MATERIALS AND METHODS

Wood samples

The tropical hardwood species chosen for this study are Abura (Hallea ciliata), Afara (Terminalia superba), Agba (Entada gigas), Akomu (Pycnanthus angolensis), Akun (Uapaca guineensis), Eki-Eki (Lophira alata), Erimado (Ricindendron Heutol), Erun-obo (Erythropleum suaveolens), Iwo (Milicia excelsa), Ita (Strombosia pustulata), Itara (Sacoglottis gabonensis), Mahogany (Khaya ivorensis), Masonia (Masonia altissima), Obeche (Triplochiton scleroxylon), Odogo (Ipomoea asarifolia), Ofun (Avicennia germinans), Opiolo (Symphonia globulifera), Opepe (Nauclea diderrichii), Opopo (Pterygota macrocarpa) and Some (Ceiba pentandra). The species were chosen based on their availability in the region of study. The samples were obtained from Forestry Research Institute of Niger (FRIN) between August and November, 2006.

Pulping process

The Kraft process was employed in the pulping investigations using 2 kg each of the wood sample in sawdust form in a stainless steel rotary digester. The white liquor was made of 28.5% sulphidity, 2 kg each of the wood sample in sawdust form in a stainless steel apparatus and extractions were carried out in triplicates and the mean values of pulp, lignin and extractive contents of each wood sample recorded. The infra-red analysis of the pulp, lignin and the extractive components of the tropical hardwoods was carried out on a Perkin-Elmer spectrometer FT-IR 2000 model in a KB window.

RESULTS AND DISCUSSION

The results showing the mean percentage yield of pulp, lignin, extractive materials and moisture content of the twenty tropical hard wood species selected for this study are shown in Table 1. The results showed that five samples, namely Akon (U. guineensis), Eki-Eki (L. alata), Iwo (M. excelsa), Masonia (M. altissima) and Ofun (A. germinans) gave the lowest yield of pulp and were in the range of 35.0 to 39.0%. A moderate yield of pulp (40.0 to 43.3%) were observed for Agba (E. gigas), Mahogany (K. ivorensis), Ita (S. pustulata) and Itara (S. gabonensis) while relatively high yield (45.0-50.0 %) of pulp were observed for eleven samples namely Abura (H. ciliata), Afara (T. superba), Akomu (P. angolensis), Erimado (R. heudelotii), Erun obu (E. Suaveolens), Obeche (T. scleroxylon), Odogo (I. asarifolia), Okilolo (S. globulifera), Opepe (N. diderrichii), Opopo (P. macrocarpa) and Some (C. Pentadra).

The lignin contents of the wood samples were determined using soxhlet extractor in accordance with standard Tappi T204 om-88 test method (TAPPI, 1988). A solvent mixture consisting of benzene and ethanol (2:1 v/v) was used in the extraction of the extraneous materials. 1g of air-dried wood sample from each of the hardwoods investigated was placed in a 28 x 100 mm thimble obtained from Toyo Roshi Kaisha, Ltd. Japan. The extraction thimble containing the specimen was then placed in the soxhlet apparatus and extracted with 200 cm³ ethanol-benzene mixture for 4 to 6 h. The solvent obtained at the end of each extraction process was evaporated at reduced pressure to obtain the extractive content of the wood sample. The weight of the dried extract was expressed as a percentage of the moisture-free sample.

Determination of lignin

The lignin contents of the wood samples were determined on the extractive free wood. A weighed amount of the wood sample (1.00 g) was placed in a 50 cm³ beaker containing 15 cm³ of 72% H₂SO₄ and allowed to stand at 25°C for 2 h. The contents of the beaker were later transferred into a 1 L Erlenmeyer flask and the volume adjusted to 575 cm³ with distilled water and thereafter refluxed for 4 h in a round-bottomed flask. The mixture was allowed to cool down to room temperature and filtered through a previously weighed Gooch crucible of porosity 4. The residue was washed with distilled water before drying to a constant weight at 105°C in an oven. The lignin content was expressed as a percentage of the extracted oven-dried wood. All determinations were carried out in triplicates and the mean values of pulp, lignin and extractive contents of each wood sample recorded. The infra-red analysis of the pulp, lignin and the extractive components of the tropical hardwoods was carried out on a Perkin-Elmer spectrometer FT-IR 2000 model in a KBr beam splitter and DTG detector in the region 4000 to 400 cm⁻¹. They were run as mulls in Nujol in KBr windows.

Statistical analysis

Pearson’s correlation and regression analyses were used to test for significant correlation and relationship between the investigated parameters at 0.01 levels. The analysis was performed using computer software SPSS 10.0 for windows.
### Table 1. The mean percentage yield of pulp, lignin and extractive contents of tropical hardwood samples.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Common names (Yoruba)</th>
<th>Botanical names</th>
<th>Mean % yield of pulp at 28.55% sulphidity</th>
<th>Mean % lignin content (Klason lignin)</th>
<th>Mean % extractive content (benzene ethanol extract)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Abura</td>
<td><em>H. ciliata</em></td>
<td>50.00 ± 1.00&lt;sup&gt;E&lt;/sup&gt;</td>
<td>19.00 ± 1.00&lt;sup&gt;A&lt;/sup&gt;</td>
<td>6.00 ± 0.26&lt;sup&gt;B&lt;/sup&gt;</td>
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<tr>
<td>2</td>
<td>Afara</td>
<td><em>T. superba</em></td>
<td>50.00 ± 1.00&lt;sup&gt;E&lt;/sup&gt;</td>
<td>20.10 ± 0.95&lt;sup&gt;A&lt;/sup&gt;</td>
<td>5.33 ± 0.76&lt;sup&gt;C&lt;/sup&gt;</td>
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<tr>
<td>3</td>
<td>Agba</td>
<td><em>E. gigas</em></td>
<td>43.33 ± 8.39&lt;sup&gt;C&lt;/sup&gt;</td>
<td>32.30 ± 1.25&lt;sup&gt;C&lt;/sup&gt;</td>
<td>7.17 ± 0.90&lt;sup&gt;C&lt;/sup&gt;</td>
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<tr>
<td>4</td>
<td>Akomu</td>
<td><em>P. angolensis</em></td>
<td>49.00 ± 1.00&lt;sup&gt;E&lt;/sup&gt;</td>
<td>28.35 ± 0.44&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.00 ± 0.50&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>5</td>
<td>Akun</td>
<td><em>U. guineensis</em></td>
<td>38.33 ± 2.52&lt;sup&gt;B&lt;/sup&gt;</td>
<td>34.40 ± 0.66&lt;sup&gt;d&lt;/sup&gt;</td>
<td>11.87 ± 0.86&lt;sup&gt;d&lt;/sup&gt;</td>
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<tr>
<td>6</td>
<td>Araba</td>
<td><em>C. pentadra</em></td>
<td>49.00 ± 2.00&lt;sup&gt;E&lt;/sup&gt;</td>
<td>28.44 ± 0.51&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.80 ± 0.26&lt;sup&gt;A&lt;/sup&gt;</td>
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<tr>
<td>7</td>
<td>Eki-Eki</td>
<td><em>L. alata</em></td>
<td>38.00 ± 1.00&lt;sup&gt;B&lt;/sup&gt;</td>
<td>33.47 ± 0.55&lt;sup&gt;C&lt;/sup&gt;</td>
<td>11.23 ± 0.31&lt;sup&gt;D&lt;/sup&gt;</td>
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<tr>
<td>8</td>
<td>Erimado</td>
<td><em>R. heudelotti</em></td>
<td>46.00 ± 1.00&lt;sup&gt;D&lt;/sup&gt;</td>
<td>29.00 ± 0.87&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.80 ± 0.26&lt;sup&gt;A&lt;/sup&gt;</td>
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<td>9</td>
<td>Erun-obo</td>
<td><em>E. suaveolens</em></td>
<td>47.00 ± 3.00&lt;sup&gt;D&lt;/sup&gt;</td>
<td>29.33 ± 0.76&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.60 ± 0.52&lt;sup&gt;A&lt;/sup&gt;</td>
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<td>10</td>
<td>Iroko</td>
<td><em>M. exelsa</em></td>
<td>35.00 ± 1.00&lt;sup&gt;A&lt;/sup&gt;</td>
<td>35.17 ± 1.26&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10.57 ± 0.61&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>11</td>
<td>Itako</td>
<td><em>S. pustulata</em></td>
<td>40.00 ± 1.00&lt;sup&gt;B&lt;/sup&gt;</td>
<td>32.10 ± 2.05&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7.33 ± 0.90&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
<td>12</td>
<td>Itara</td>
<td><em>S. gabonensis</em></td>
<td>40.00 ± 1.00&lt;sup&gt;B&lt;/sup&gt;</td>
<td>30.10 ± 0.90&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.33 ± 0.76&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>13</td>
<td>Mahogany</td>
<td><em>K. ivorensis</em></td>
<td>40.00 ± 2.00&lt;sup&gt;B&lt;/sup&gt;</td>
<td>31.40 ± 1.25&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7.47 ± 0.76&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
<td>14</td>
<td>Masonia</td>
<td><em>M. altissima</em></td>
<td>39.00 ± 1.73&lt;sup&gt;D&lt;/sup&gt;</td>
<td>33.40 ± 0.79&lt;sup&gt;C&lt;/sup&gt;</td>
<td>8.10 ± 0.95&lt;sup&gt;C&lt;/sup&gt;</td>
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<tr>
<td>15</td>
<td>Obeche</td>
<td><em>T. scleroxylon</em></td>
<td>49.00 ± 2.00&lt;sup&gt;E&lt;/sup&gt;</td>
<td>28.57 ± 0.86&lt;sup&gt;B&lt;/sup&gt;</td>
<td>5.57 ± 0.75&lt;sup&gt;B&lt;/sup&gt;</td>
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<tr>
<td>16</td>
<td>Odoko</td>
<td><em>L. asarifolia</em></td>
<td>45.00 ± 2.00&lt;sup&gt;D&lt;/sup&gt;</td>
<td>30.07 ± 0.90&lt;sup&gt;B&lt;/sup&gt;</td>
<td>6.07 ± 0.32&lt;sup&gt;B&lt;/sup&gt;</td>
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<tr>
<td>17</td>
<td>Ofun</td>
<td><em>A. germinans</em></td>
<td>38.00 ± 2.65&lt;sup&gt;B&lt;/sup&gt;</td>
<td>34.17 ± 1.04&lt;sup&gt;D&lt;/sup&gt;</td>
<td>11.50 ± 0.50&lt;sup&gt;D&lt;/sup&gt;</td>
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<td>18</td>
<td>Okilolo</td>
<td><em>S. globulifera</em></td>
<td>50 ± 2.00&lt;sup&gt;E&lt;/sup&gt;</td>
<td>28.44 ± 0.51&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.80 ± 0.26&lt;sup&gt;A&lt;/sup&gt;</td>
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<tr>
<td>19</td>
<td>Opepe</td>
<td><em>N. diderrichii</em></td>
<td>48.00 ± 2.00&lt;sup&gt;D&lt;/sup&gt;</td>
<td>29.07 ± 0.81&lt;sup&gt;B&lt;/sup&gt;</td>
<td>6.06 ± 0.21&lt;sup&gt;B&lt;/sup&gt;</td>
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<tr>
<td>20</td>
<td>Oporoporo</td>
<td><em>P. macrocarpa</em></td>
<td>46.00 ± 3.61&lt;sup&gt;D&lt;/sup&gt;</td>
<td>29.00 ± 0.67&lt;sup&gt;B&lt;/sup&gt;</td>
<td>4.57 ± 0.51&lt;sup&gt;A&lt;/sup&gt;</td>
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Means with different letters in a column are significantly different in the Duncan’s multiple range test at p = 0.05.
Figure 1. The correlation between % pulp yield and the % lignin contents of the wood samples.

Figure 2. The correlation between % pulp yield and % extractive contents of the hardwood samples.

with the lowest lignin content was one of the samples that gave the highest yield of pulp. However, the percentage pulp yield did not correlate well with the extractive contents of the wood shown in Figure 2. Statistical analysis of the results using Pearson’s correlation test showed a negative significant correlation between the mean percentage pulp yield and the lignin content, \( r = -0.84 \) (p < 0.01), as well as between mean percentage pulp yield and extractives, \( r = -0.811 \) (p < 0.01). There was, however, a positive correlation, \( r = 0.649 \) (p < 0.01), between the % lignin content and the extractive component of the wood samples studied as shown in
Figure 3. The Pearson’s correlation is used to find a correlation between at least two continuous variables. The value for a Pearson’s can fall between 0.00 (no correlation) and 1.00 (perfect correlation). P < 0.01 is the probability that the Pearson’s correlation between % pulp yield and the lignin content; % pulp yield and extractives and the % lignin and extractives contents of the wood samples studied is less than 0.01.

The chemical integrity of the pulp, lignin and extractive components of the wood samples was confirmed from infra-red (i.r) spectroscopic studies shown in Figures 4 and 5 for lignin and extractives respectively. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. The i.r studies carried out on the pulp showed that the OH absorption occurred between 3150 and 3400 cm$^{-1}$ while the C-C bonds were observed in the region of 550 to 1300 cm$^{-1}$. These absorptions are typical of the OH and C-C bonds found in cellulose (Ndukwe et al., 2009).

Figure 4. The i.r. spectra of lignin obtained from T. superba.
The absorption band at 1500 to 1510 cm\(^{-1}\) in Figure 4 is assigned to aromatic vibrations found in lignin, while the region ranging from 1485 to 1495 cm\(^{-1}\) is associated with the phenyl propane units, a major constituent of lignin molecule. The phenolic hydroxyl group is observed at 1340 to 1380 cm\(^{-1}\). These groups play important role in the chemistry of lignin. In Figure 5 while the absorption at 500 to 700 cm\(^{-1}\) and 1300 to 1500 cm\(^{-1}\) are characteristics of alkaloids, phenols and triglycerides that are present in wood extractives (Fengel and Wegener, 1989; Malan et al., 1996).

Conclusion

The results obtained from this study showed that many of the tropical hardwood samples investigated such as A. germinans, U. guineensis, M. altissima, L. alata and M. exelsa have high contents of lignin and extractive materials and will not be suitable for pulp and paper production.

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