Infrared Spectroscopy Studies of *Ricinodendron heudelotii* Wood for its Pulp and Paper Production Potential

Bolade M. Ogunleye 1*, James S. Fabiyi 2, Joseph A. Fuwape 2, Armando G. McDonald 3

1Department of Wood and Paper Technology, Federal College of Forestry, Jericho, Ibadan, Oyo State, Nigeria
2Department of Forestry and Wood Technology, Federal University Technology, PMB 704, Akure, Ondo State, Nigeria
3Renewable Materials Program; Dept. of Forest, Rangeland, and Fire Sciences, University of Idaho, Moscow, ID 84843

*Corresponding Author: mercysteve2003@gmail.com

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Abstract. The high demand for paper production due to its various uses, but the dwindling of forest trees as a result of deforestation and forest exploitation necessitate the investigation of *Ricinodendron heudelotii*, a lesser utilised tree species for its pulp and paper production potential. In addition, any technique for such investigation that would give reliable but fast information is encouraged. Therefore, infrared spectroscopy was employed to study the chemical components of *R. heudelotii* wood since chemical component. Ratios of syringyl to guaiacyl associated bands along the longitudinal and radial positions of the wood differ significantly. Higher syringyl/guaiacyl ratio of the corewood than middlewood was observed. The practical implication of this finding is that more chemical would be required to pulp *R. heudelotii* wood obtained from the base (10% of the merchantable height) and outerwood, because of the presence of high lignin content compared to the other longitudinal (middle, 50% and top, 90% of the merchantable height) and radial (corewood and middlewood) positions where wood were collected. Also, outerwood favour pulp production compared to middlewood and corewood, because of the high holocellulose content.

Keywords: lignin; polymers; *Ricinodendron heudelotii*, syringyl to guaiacyl

1. INTRODUCTION

Wood is one of the most important naturally, renewable resources and has been an object of research for many years (du Plessis, 2012). The demand for timber and other forest products increases will keep on escalating as the economy of the world keeps growing (du Plessis, 2012). Wood has multipurpose applications such as timber for building and construction, biofuel and energy, pulp and paper, and so on. World paper consumption was about 300 million tons in 1996/1997 (Hurter and Riccio, 1998). It was estimated to grow from 300 million tonnes to over 490 million tonnes by the year 2020 with an average growth rate of 2.8 % per annum (John 2006).

In Nigeria, the first paper industry established in 1969 made use of admixtures of sixteen different hardwood species as sources of fibrous raw materials (Oluwadare and Egbewole, 2008). Unfortunately, the high cost of importation of pulp into the country was one of the main challenges that led to the closure of that first paper mill (Osadare, 2001). The shortage of suitable fibrous raw materials for pulp production contributes to the setback that pulp and paper industries is facing according to the report of the Central Bank of Nigeria (2005). In fact, only 27,000 MT (megatonnes) of paper and paperboards was produced in 2005.

In order to increase the production of pulp and paper and at the same time lower the cost of production, more indigenous hardwood species are needed to be investigated so as to classify them as suitable or unsuitable potential fibrous materials for pulp production. However, a challenge with such approach is that over-exploitation of natural forest trees, especially the prime economic timber species is alarming. One of the best possible approaches to mitigate against the use of such economic timbers is to search for lesser-used species. Among the numerous lesser-used species in the natural forest of Nigeria, *Ricinodendron heudelotii* was selected for this study. It is a fast-growing tree and normally reaches up to 50 m in height and 2.7 m in girth (Orwa et al., 2009; Assanvo et al., 2015). It has bole straight with short buttress.

The rule of thumb is that before recommending any wood species for pulp production, preliminary screening of its chemical, morphological and
rheological properties is required. The outcomes of such screening will provide information that could help project how its properties will affect its pulp and paper properties.

The scope of this study is within the investigation of wood chemical structure derived from the wood chemical components. Wood is a naturally occurring polymeric composite, which is made up of cellulose, hemicelluloses, lignin, and extractives. These constituent polymers are responsible for most of the physico-chemical properties exhibited by wood, especially the pulp and paper properties (Pandey, 1999; Yildiz and Gümüşkaya, 2007). Lignin consists of three phenylpropanoid monomers: coniferyl (p-hydroxyphenyl, H), synapyl (guaiacyl, G) and p-coumaryl (syringyl, S) alcohols, which serve as important parameter in pulp production in terms of delignification rates, chemical consumption and pulp yields (Rodrigues et al., 1999). During pulping, the ease of delignification of hardwoods has been attributed significantly to the S/G ratio. The S/G ratio was a dominant processing variable in oxygen delignification and chlorine dioxide bleaching of hardwood kraft pulps (Colodette and Gomes, 2014; Ventorim et al., 2014).

The characterisation of these in-situ chemical components of wood prior pulping could be a screening approach to determine any fibrous raw material for its pulping and paper production potential. The appropriate tool for this task is Fourier transform infrared (FTIR) spectroscopy. FTIR spectroscopy is a cost effective, time and labour saving technique for surface chemical characterisation. It requires less specimen preparation and very fast in running a test; also a small solid or powder sample is required. Infrared (IR) spectroscopy has been used extensively to study wood. Most of the studies published on IR spectroscopy of wood or wood components focused on the quantitative determination of lignin within the pulp (Xiao et al., 2001; Jaaskelainen et al., 2003), structural properties of lignin (Antonović et al., 2008; Shi et al., 2012) and paper quality, aging and/or origin (Lojew ska et al., 2006; Calvini et al., 2006; Eriksson et al., 2006; Polovka et al., 2006).

Therefore, the aim of this study is to use FTIR spectroscopy technique as a rapid screening tool to investigate R. heudelotii for its fibrous raw material potential in the production of pulp and paper via its chemical structure properties.

2. MATERIALS AND METHOD

2.1 Tree selection and samples preparation

Trees of R. heudelotii were obtained from a free forest at Ilaramokin, located between 7.321°N 5.145°E and 7.389°N 5.097°E of Ondo state, Nigeria. Three trees (unknown ages because they were felled from a natural forest and also their growth ring boundaries are either absent or indistinctive) were randomly selected and used for destructive sampling procedures. Bolts of about 70 cm were cut from the felled trees at three different merchantable height levels of 10%, 50%, and 90%. The bolts were sawn through the pith into four parts while three radial positions from each part: core-wood, middle-wood and outer-wood were obtained prior to samples preparation.

2.2. Analytical methods

The chemical structure (compositional analysis) of R. heudelotii wood was determined using Attenuated total reflectance Fourier transform infrared (FTIR) spectroscopy. Infrared measurements were performed at room temperature with a Thermo-Nicolet Avatar 370 FTIR spectrometer operating in the attenuated total reflection (ATR) mode (SmartPerformer, ZnSe crystal with 2 mm diameter sampling area). Detail description of the method was reported by Fabiyi and Ogunleye (2015). Six spectra per wood specimen (totaling 30 spectra per wood sample) were collected and averaged to one spectrum, which was thereafter ATR and baseline corrected following spectra analysis procedure from Omnic software v 7.3. The spectra were shifted parallel to the wave number-axis so that the minimum between 2000 and 1800 cm⁻¹ was equal to zero, as suggested by Zavarin et al. (1990). Spectra used for the calculation of the compositional analysis were baseline-corrected using the rubber-band method whereby more than two reference points were used (Fabiyi and Ogunleye, 2015).

3. RESULTS AND DISCUSSIONS

The average infrared spectra of the outerwood of Ricinodendron heudelotii using Fourier transform infrared (FTIR) spectroscopy is shown in Figure 1. The summary of infrared bands observed in R. heudelotii wood with their peak assignments and structural polymers are presented in Table 1. The positions of most bands and their intensities in the fingerprint region are similar both along the longitudinal and across the radial directions of R. heudelotii with few exceptions. For clarity, the spectra at 1750-600 cm⁻¹ were considered. The peak intensity shows the level of concentration of each of
the functional groups representing a macromolecule, for example, cellulose at 896 and 1455 cm\(^{-1}\), lignin at 1230, 1262, 1318, 1421 and 1507 cm\(^{-1}\), xylan in hemicelluloses at 1736 cm\(^{-1}\) and holocellulose at 1031, 1051, 1156 and 1371 cm\(^{-1}\).

The spectra obtained for the longitudinal and radial positions of the wood sample are shown in Figure 2. Along the longitudinal position, little or no variation was observed in cellulose at 897 cm\(^{-1}\) as shown in Fig. 2, top. Arabinogalactan (779 cm\(^{-1}\)) at the base was greater than at the middle or top. Holocellulose at base is greater than at the middle or top at 1031, 1051 and 1156 cm\(^{-1}\). Syringyl (1230 cm\(^{-1}\)) and guaiacyl (1262, 1507, 1595 cm\(^{-1}\)) of lignin at the base is greater than middle or top. Cellulose (1455 cm\(^{-1}\)) at the base is less than that of the middle or top, however, xylan (1736 cm\(^{-1}\)) content is similar along the longitudinal position.

### Table 1: Summary of infrared spectra bands observed in Ricinodendron heudelotii wood

<table>
<thead>
<tr>
<th>Position (cm(^{-1}))</th>
<th>Peak assignment</th>
<th>Structural polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>779</td>
<td></td>
<td>Arabinogalactan</td>
</tr>
<tr>
<td>897</td>
<td>CH out of plane associated with the syringyl nuclei</td>
<td>Lignin (Syringyl)</td>
</tr>
<tr>
<td>896</td>
<td>C1-H deformation of glucose ring</td>
<td>Cellulose</td>
</tr>
<tr>
<td>1031</td>
<td>C-O stretch</td>
<td>Cellulose and hemicelluloses</td>
</tr>
<tr>
<td>1051</td>
<td>C-O stretch</td>
<td>Cellulose and hemicelluloses</td>
</tr>
<tr>
<td>1105</td>
<td>aromatic skeletal and C-O stretch</td>
<td>Polysaccharides and Lignin</td>
</tr>
<tr>
<td>1156</td>
<td>C-O-C vibration</td>
<td>Cellulose and hemicelluloses</td>
</tr>
<tr>
<td>1230</td>
<td>C-O of syringyl ring</td>
<td>Lignin</td>
</tr>
<tr>
<td>1262</td>
<td>C-O of guaiacyl ring</td>
<td>Lignin</td>
</tr>
<tr>
<td>1318</td>
<td>C1-O vibration</td>
<td>Syringyl</td>
</tr>
<tr>
<td>1371</td>
<td>C-H deformation</td>
<td>Cellulose and hemicelluloses</td>
</tr>
<tr>
<td>1421</td>
<td>C-H in-plane deformation with aromatic ring</td>
<td>Lignin</td>
</tr>
<tr>
<td>1455</td>
<td>CH deformation, asymmetry in CH(_3) and CH(_2)</td>
<td>Cellulose</td>
</tr>
<tr>
<td>1507</td>
<td>aromatic skeletal vibration (C=C), guaiacyl &gt; 5</td>
<td>Lignin</td>
</tr>
<tr>
<td>1595</td>
<td>aromatic skeletal vibration (C=C)</td>
<td>Tannin</td>
</tr>
<tr>
<td>1736</td>
<td>Conjugated C=O</td>
<td>Xylan in hemicelluloses</td>
</tr>
<tr>
<td>2900</td>
<td>C-H stretching</td>
<td></td>
</tr>
<tr>
<td>3352</td>
<td>OH stretching from cellulose</td>
<td>Cellulose</td>
</tr>
</tbody>
</table>

Source: Fabiyi et al. (2011)
Table 2: Variation in the ratios of the peak absorbance of syringyl to guaiacyl associated bands of *Ricinodendron heudelotii* wood

<table>
<thead>
<tr>
<th>Longitudinal position</th>
<th>Radial position</th>
<th>$A_{1230}/A_{1262}$</th>
<th>$A_{1230}/A_{1595}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base (10%)</td>
<td>Corewood</td>
<td>1.03±0.00</td>
<td>1.27±0.11</td>
</tr>
<tr>
<td></td>
<td>Middlewood</td>
<td>1.01±0.02</td>
<td>1.13±0.09</td>
</tr>
<tr>
<td></td>
<td>Outerwood</td>
<td>1.03±0.27</td>
<td>1.27±0.21</td>
</tr>
<tr>
<td>Middle (50%)</td>
<td>Corewood</td>
<td>1.03±0.05</td>
<td>1.36±0.18</td>
</tr>
<tr>
<td></td>
<td>Middlewood</td>
<td>1.04±0.2</td>
<td>1.27±0.04</td>
</tr>
<tr>
<td></td>
<td>Outerwood</td>
<td>1.04±0.01</td>
<td>1.37±0.16</td>
</tr>
<tr>
<td>Top (90%)</td>
<td>Corewood</td>
<td>1.06±0.29</td>
<td>1.30±0.07</td>
</tr>
<tr>
<td></td>
<td>Middlewood</td>
<td>1.04±0.03</td>
<td>1.28±0.12</td>
</tr>
<tr>
<td></td>
<td>Outerwood</td>
<td>1.05±0.01</td>
<td>1.44±0.11</td>
</tr>
</tbody>
</table>

Fig. 2: Infrared spectra of *Ricinodendron heudelotii* wood showing variation along the longitudinal position (top) and across the radial position (bottom)
The spectra variation across the radial position is shown in Fig. 2, bottom. There was little or no variation in the arabinogalactan and cellulose contents at 779 and 897 cm\(^{-1}\), respectively. Holocellulose at outerwood is slightly greater than at the middlewood or corewood at 1031, 1051 and 1156 cm\(^{-1}\). For lignin content, syringyl (1230 cm\(^{-1}\)) and guaiacyl (1262, 1507, 1595 cm\(^{-1}\)) are higher in outerwood than middlewood or corewood. Cellulose (1455 cm\(^{-1}\)) is lower in corewood than middlewood or outerwood. For the hemicelluloses, xylan (1736 cm\(^{-1}\)) content is similar across radial position. The ratios of syringyl to guaiacyl slightly increased from base to top, but no distinctive variation was observed from corewood to outerwood (Fig. 3, Table 2). Hardwood species exhibit varied S/G between trees: 0.74 for *Terminalia brassii* and 1.6 for *Eucalyptus deglupta* (Wallis et al. 1996). The S/G ratio varied within *E. tereticornis* from 0.68 to 2.22 and in *E. camaldulensis* from 1.37 to 2.01 (Kawamura and Bland 1967). Ona et al. (1997) reported that the stem inner part and higher stem regions of *E. camaldulensis* had higher and decreased S/G ratios, respectively. In term of bleaching, the eucalyptus pulp with S/G ~1.7 consumed ~4.5% equiv. Cl\(_2\) (from ClO\(_2\)) to achieve 90% ISO brightness while the Acacia pulp with S/G ~0.6 consumed ~7.4% equiv. Cl\(_2\) (Evtuguin and Pascoal, 2007). Based on the findings in this study, *R. heudelotii* pulp would consumes more chlorine in relatively the same amount of the Cl\(_2\) during bleaching with ClO\(_2\) with eucalyptus and less than Acacia.
The practical implication of the findings is that more chemical would be required to pulp R. heudelotii wood obtained from the base (10% of the merchantable height) and outerwood because of the present of high lignin content compared to the other longitudinal and radial positions where wood were collected. Also, outerwood favour pulp production compared to middlewood and corewood because of the high holocellulose content.

Pulp yield increased as the S/G ratio of a wood increases (del Río et al. 2005). This is due to the fact that the S units are mainly linked by more labile ether bonds (at the C4 position of the aromatic rings) whereas C–C linkages (at the free C5 position) also exist between the G units, as described in lignin structural models (Lu et al., 2010). Higher proportions of S-lignin units allow their easier removal during kraft pulping, which results in lower alkali consumption during pulping, less degradation of cellulose and, consequently, higher pulp yields. Higher S/G ratio of the corewood than middlewood could result in a lower softening temperature (Table 2 and Fig. 3 bottom), as explained by Fabiyi et al. (2011) that higher S/G ratio caused lower softening temperature.

4. CONCLUSION

This research has provided fundamental information on the chemical structure of Ricinodendron heudelotii wood using infrared spectroscopy. Fourier transform infrared spectroscopy (FTIR) was used to investigate the concentration dominance of wood chemical composition and to elucidate the estimate the ratio of syringyl to guaiacyl. Higher syringyl/guaiacyl ratio of the corewood was estimated than middlewood. The practical implication of this study is that more chemical would be required to pulp R. heudelotii wood obtained from the base (10% of the merchantable height) and outerwood because of the present of high lignin content compared to the other longitudinal and radial positions where wood were collected. Also, outerwood favour pulp production compared to middlewood and corewood because of the high holocellulose content.

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Bolade Mercy Ogunleye is a Senior Lecturer at the Federal College of Forestry, Ibadan, Nigeria. She had her Ph.D in Wood Products Technology (Pulp and Paper Technology) from the Department of Forestry and Wood Technology, Federal University of Technology Akure (FUTA). She joined the Department of Wood and Paper Technology, Federal College of Forestry, Jericho, Ibadan, Oyo State, Nigeria, in the year 2001.

James Sunday Fabiyi currently serves as the Director of the PRS Innovation and Educational Services, Surrey, British Columbia, Canada. He holds B.SC. and M.Sc. degrees from the Federal University of Technology, Akure (FUTA) and a Ph.D degree from the University of Idaho, Moscow, USA. He worked as a Lecturer at the Federal University of Technology Akure for 14 years and as a Research Associate at Virginia Tech, Virginia, USA. He has published over 65 scientific publications, which are well cited internationally.

Professor Joseph Adeola Fuwape currently serves as the Vice-Chancellor of Salem University, Lokoja, Kogi State, Nigeria. Prior to his appointment as Vice-Chancellor, he had worked at the Federal University of Technology, Akure (FUTA) for about 30 years. At the Federal University of Technology Akure, he served as Head of the Department of Forestry and Wood Technology for 7 years, Dean, School of Agriculture and Agricultural Technology for 4 years and member of the University Governing Council for eight years.

Armando G. McDonald is a professor of Biomaterial Chemistry at Dept. of Forest, Rangeland, and Fire Sciences, University of Idaho, Moscow, USA. He had his Ph.D in Chemistry at York University, Toronto, Ontario, Canada in 1993. His research programs include Carbohydrate chemistry and biochemistry, Wood materials chemistry and wood science, Biopolymer and Biomaterials science, and Natural products chemistry. He has published many articles in reputable international Journals and supervised many postgraduate students from various countries.