Chemical Structure And Glass Transition Temperature Of *Ricinodendron Heudelotii* Wood For Its Pulp Production Potential

Bolade M. Ogunleye

Abstract: The chemical structure and glass transition temperature of *Ricinodendron heudelotii* wood were studied using Attenuated total reflectance Fourier transform infrared (FTIR) spectroscopy and dynamic mechanical analysis (DMA), respectively. The thermal characteristic of *R. heudelotii* was conducted on N-methyl-2-pyrolidone saturated specimens while submerged under the same solvent at a temperature range from 130 to 0°C at 3°C/min, multi-frequencies of 0.1-10 Hz using DMA. 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 correlate well with lowering softening temperature. The findings in this research reveals 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 and radial positions, respectively where wood were collected. Also, outerwood favour pulp production compared to middlewood and corewood because of the high holocellulose content.

Keywords: glass transition temperature, lignin, *Ricinodendron heudelotii,* syringyl to guaiacyl

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1 INTRODUCTION

Wood being a naturally occurring polymeric composite composed of cellulose, hemicelluloses, lignin, and extractives (Plomley *et al*.,1976). These chemical components contribute immensely to the physical and chemical properties exhibited by wood and wood products. For example, cellulose content dictates the strength of any wood fibre because of its high degree of polymerization and crystallinity (Yildiz and Gümüşkaya, 2007). Hemicelluloses (xylan and mannan), serves as a matrix for the cellulose; it also link the fibrous cellulose and amorphous lignin (Pandey 1999). Lignin, a polyphenolic compound, acts as a cementing material for wood fibres (Pandey, 1999). Therefore, understanding the chemical structure especially of the lignin could be a screening approach to recommend a wood or lignocellulosic material for pulp production. In a previous study, del Río *et al*. (2005) investigated the effect of lignin composition of eucalypt on paper pulp yield using Py-GC/MS. However, this present study sought to use Infrared (IR) spectroscopy to screen a selected wood species for its pulp and paper production potential. IR spectroscopy has been used extensively to study wood. The majority of the work published on IR spectroscopy of wood or wood components has focused upon the pulp and paper industry, where the main uses are quantitative determination of lignin within the pulp (Faix 1988; Saad *et al*. 1990), structural studies of lignin (Obst, 1982; Schultz and Glasser, 1986) and monitoring progress of the pulping process (Faix 1988; Michell, 1988; Schultz *et al*. 1985). The use of Fourier transform infrared (FTIR) spectroscopy has been reported for surface chemical characterization and qualitative estimation of the lignin and carbohydrate contents in wood, various lignocellulosics and wood plastic composites (Pandey and Theagarjan, 1997; Fabiyi and McDonald, 2010).

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Fabiyi and Ogunleye (2015) used IR spectroscopy and dynamic mechanical analysis to monitor the chemical structure and rheological property of the heat-treated *Triplochiton scleroxylon* wood, respectively. Fourier Transform Infrared spectroscopy (FTIR) has advantages over conventional chemical analysis (chemical extraction techniques). It requires less specimen preparation and very fast in running a test, small solid/powder sample is accommodated, it does not result in concomitant polymer degradation. Infrared spectroscopy is a very useful tool for obtaining fast, useful information on the structure of wood chemical. Based on these facts, FTIR would be a rapid screening of wood for its pulp production. The aim of this study was to investigate the chemical structure and glass transition temperature of *R. heudelotii* wood for its potential as pulp production fibrous material.

Materials and Method

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. The ages of these trees could not be ascertained because they were felled from a natural forest and also their growth ring boundaries are either absent or indistinctive. Bolts of about 70 cm were cut from the felled trees at three different merchantable height levels of 10% (base), 50% (middle), and 90% (top). 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. Attenuated total reflectance Fourier transform infrared (FTIR) spectroscopy was used to determine the chemical structure (compositional analysis) of *R. heudelotii* wood. Infrared measurements were performed at room temperature with a Thermo-Nicolet Avatar 370 FTIR spectrometer (with SmartPerformer, ZnSe crystal of 2 mm diameter sampling area ATR) following the method developed by Fabiyi *et al*. (2011) and Fabiyi and Ogunleye (2015) without any modification. Baseline correction was carried out between 2000 and 1800 cm^{-1} following the approach adopted by Zavarin *et al*. (1990). For the glass transition temperature of *R. heudelotii* wood determination, 8 mm diameter and 5 mm thick cylindrical discs specimens were cut. The specimens were saturated in N-methyl-2-pyrolidone prior testing; then they were submerged under the same solvent at a temperature range from 130 to 0°C at 3°C/min,

multi-frequencies of 0.1-10 Hz using DMA following the procudre of Chowdhury *et al*., (2010). In this study, sample preparation, testing procedure and analysis strictly followed the previously conducted study by Fabiyi and Ogunleye (2015).

Results and Discussion

The overall infrared spectra of *Ricinodendron heudelotii* wood using Fourier transform infrared (FTIR) spectroscopy is shown in Figure 1. While the summary of infrared bands observed in *R. heudelotii* wood with their peak assignments and structural polymers is 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 direction of *R. heudelotii* with few exceptions. For clarity, the spectra at 1750-600 cm^{-1} were considered. The peak intensity depicts 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} (Fabiyi and Ogunleye 2015). 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, there is no difference in the xylan (1736 cm^{-1}) content along the longitudinal position. 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 1).
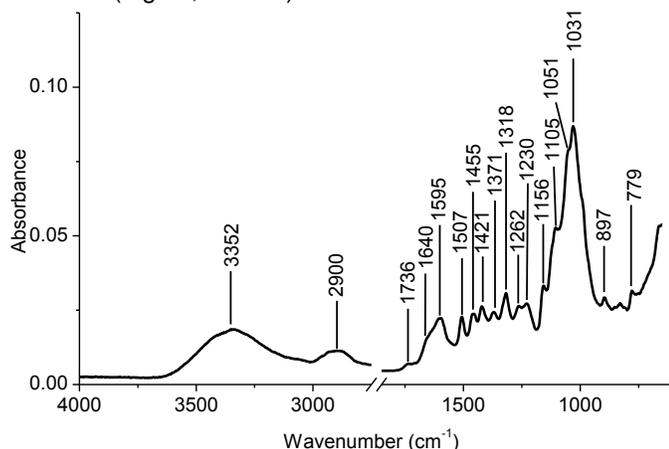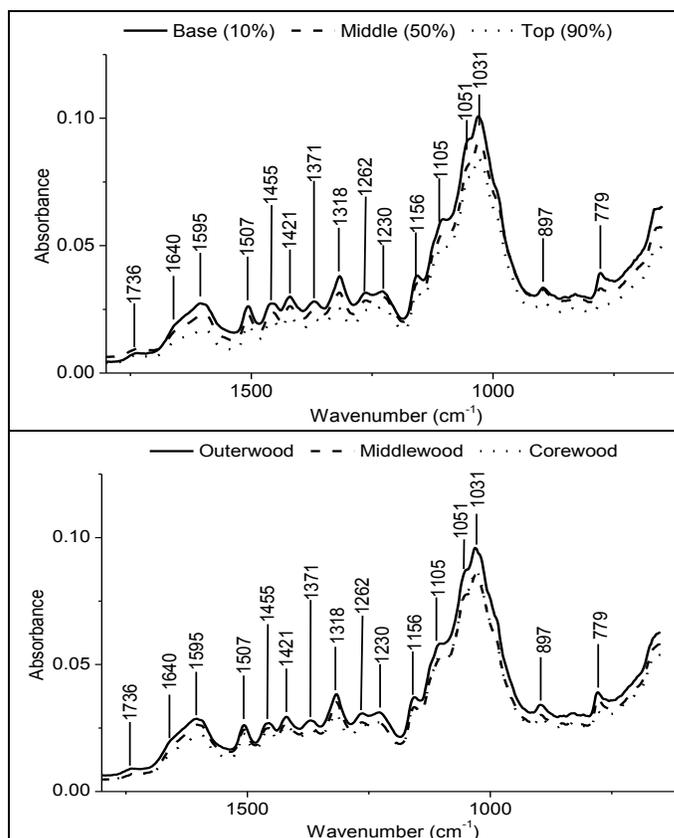

Fig. 2: *Infrared spectra of Ricinodendron heudelotii wood showing variation along the longitudinal position (top) and across the radial position (bottom).*

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

Position (cm^{-1})	Peak assignment	Structural polymer
779	-	Arabinogalactan
897	CH out of plane associated with the syringyl nuclei	Lignin (Syringyl)
896	C1-H deformation of glucose ring	Cellulose
1031	C–O stretch	Cellulose and hemicelluloses
1051	C–O stretch	Cellulose and hemicelluloses
1105	aromatic skeletal and C–O stretch	Polysaccharides and Lignin
1156	C–O–C vibration	Cellulose and hemicelluloses
1230	C–O of syringyl ring	Lignin
1262	C–O of guaiacyl ring	Lignin
1318	C$_1$–O vibration	Syringyl
1371	C–H deformation	Cellulose and hemicelluloses
1421	C-H in-plane deformation with aromatic ring stretching	Lignin
1455	CH deformation, asymmetry in CH$_3$ and CH$_2$	Cellulose
1507	aromatic skeletal vibration (C=C), guaiacyl > 5	Lignin
1595	aromatic skeletal vibration (C=C)	Tannin
1736	Conjugated C=O	Xylan in hemicelluloses
2900	C-H stretching	
3352	OH stretching from cellulose	Cellulose

Source: *Fabiyi et al (2011)*

Fig. 1: *Infrared spectra of Ricinodedron heudelotii wood*

Table 2: *Variation in the ratios of the peak absorbance of syringyl to guaiacyl associated bands of Ricinodendron heudelotii wood*

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

A huge S/G variability between hardwood species is well established; 0.51 for *Acer macrophyllum* (Chang and Sarkanen 1973), 0.74 for *Terminalia brassii* and 1.6 for *E. deglupta* (Wallis *et al.* 1996). Variability has also been found for species within the same genera. Concerning eucalypts, an S/G ratio of 5.2 was found for *Eucalyptus maculata* and *Eucalyptus diversicolor* (Bland *et al.* 1950) and 0.7 for *E. tereticornis* (Kawamura and Bland 1967). The S/G ratio varied within *E. tereticornis* from 0.68 to 2.22 and in *E. camaldulensis* from 1.37 to 2.01. The S/G ratios of *Acer negundo* and *A. rubrum* were 0.4 and 3.3, respectively (Towers and Gibbs, 1953; Creighton *et al.*, 1994), which showed a wide variation in the S:G ratio of Aceraceae family. Additionally, variability in the S/G ratio was observed in the radial and axial direction of *E. globulus* and *E. camaldulensis* Ona *et al.* (1997). The inner part of the stem had higher S/G ratios for both species, however S/G contents of *E. camaldulensis* decreased at higher stem regions. The practical implication of the observed S/G ratio in 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. According to del Río *et al.* (2005), an increase in the S/G ratio of a wood caused an increase in the pulp yield because the high quantity of S-lignin units results in uncomplicated delignification during kraft pulping thereby resulting in less consumption of alkali and less cellulose degradation. The higher syringyl/guaiacyl ratio of the corewood than middlewood could results in a lower softening temperature (Figures 3 and 5). This is based on the explanation given by Fabiyi *et al.* (2011) that higher syringyl/guaiacyl ratio caused lower softening temperature.

Glass Transition Temperature
Temperature dependencies of the softening of the saturated *R. heudelotii* wood specimen at 0.1, 1 and 10 Hz with cooling rate of 3 °C/min are shown in Figure 4. The higher the frequency, the higher the glass transition temperature (Tg). The effect of the radial position (where wood specimen were collected) on the tan δ maximum (the point where transition

between the glassy to rubbery state occurs) is shown in Figure 5. The Tgs of the corewood are lower than that of the middlewood irrespective of the frequency used in this study. The interpretation of this data in relation to the Syrngyl - Guaiacyl ratio from the IR spectroscopy results reveals that S-G ratio contribute to the trend of the Tgs observed in this study (Figures 3 and 5). It has been reported that guaiacyl-rich lignin has a more branched structure and a higher degree of polymerization than syringyl-rich lignin (Sterwart *et al.* 2009). Therefore, it was speculated that syringyl-rich lignin may have a lower softening point and is more easily relocated to the surface than guaiacyl-rich lignin. This phenomenon therefore leads to easy pulping of the corwood than the middlewood.
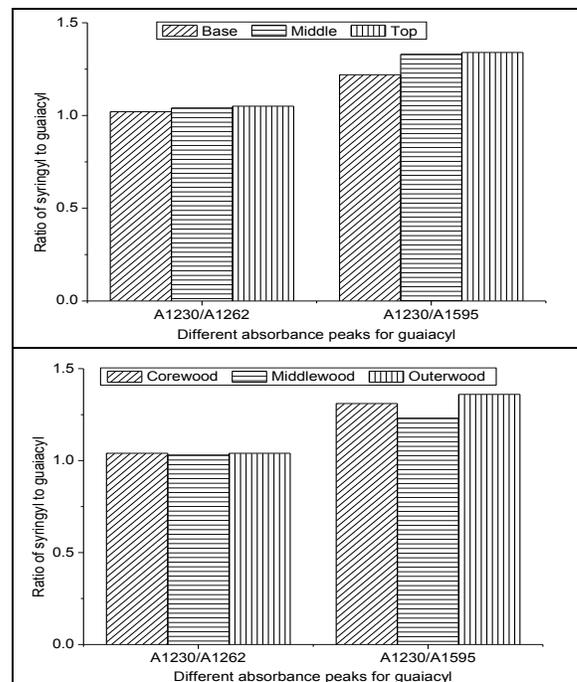

Fig. 3: Ratios of syringyl to guaiacyl associated bands along the longitudinal (top) and radial (bottom) positions of *Ricinodendron heudelotii* wood.
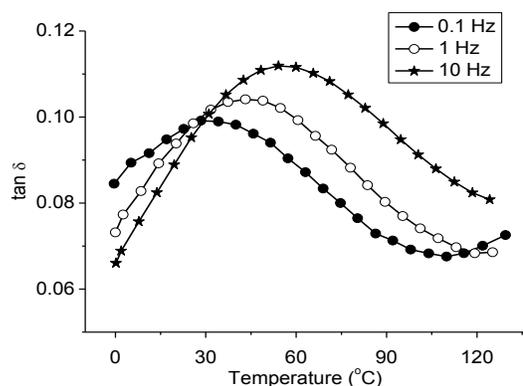

Fig. 4: *DMA cooling scans (3 ◦C/min) for Ricinodendron heudelotii wood showing glass transition temperature for every frequency.*
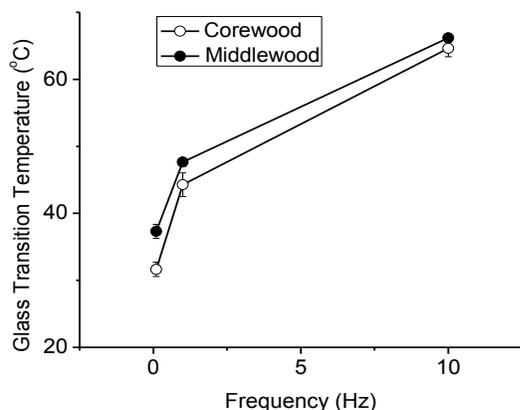
Fig. 5: *Glass transition temperature of Ricinodendron heudelotii wood showing for every frequency.*

4 CONCLUSION

Fourier transform infrared spectroscopy (FTIR) and dynamic mechanical analysis were used to elucidate the influence of the ratio of syringyl to guaiacyl on the lignin softening temperature. For example, higher syringyl/guaiacyl ratio of the corewood than middlewood results in a lower softening temperature. Other chemical components were studied to help understand the chemistry of *Ricinodendron heudelotii* wood using the FTIR. The practical implication of this section 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.

Acknowledgements

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