



## CHARACTERIZATION OF ENERGY VALUE OF LIGNIN EXTRACTED FROM MILL WOOD RESIDUES OF *GMELINA ARBOREA* AND *TECTONA GRANDIS*

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**ABSTRACT:** Lignin is of great interest due to the existence of large scale manufacturing processes dependent on retrieving the polysaccharide component of plants. In this study, lignin extracted through acid and alkaline hydrolysis was characterized in order to quantitatively determine the energy value of lignin in mill-wood residues. The calorific, mineral elements, chemical and functional groups of compounds present in the extracted lignin was determined using standard methods. The acid insoluble lignin content ranged from 28.0 to 31.70% while alkaline soluble lignin ranged from 24.57 to 31.77%. The volatile matter, fixed carbon and heating value showed that lignin is a major energy bearing compound in the mill-wood residues with value range of 27.6 – 35.31%, 53.32 – 68.57% and 30.13 – 32.79 KJ/Kg respectively. The ash fraction predominantly contained Aluminum but low in iron, magnesium potassium, calcium, manganese, lead, zinc and copper. The values of the mineral elements in the milled-wood residue lignin are below the range of fuel causing fouling problem during combustion, hence the fuel from these mill-wood residues are not expected to cause fouling problem. Furthermore, Fourier Transform Infrared (FT-IR) analysis revealed the presence of Alkanol (O-H), Amine (N-H), Phosphine (P-H), Carboxyl (C=O), Nitroso (N=O), Nitro (N-O) and Alkane (CH, CH<sub>2</sub>, and CH<sub>3</sub>) compounds at various concentration and frequency.

**Keywords:** Mill-wood residue, Lignin, chemical composition, calorific value, Fourier Transform Infrared analysis

### 1. INTRODUCTION

Wood conversion process in many developing countries are largely ineffective and generate various quantities of energy-rich biomass as wastes, depending on technological level and wood quality. According to Ogunwusi (2014), most of the wood processing outfits in Nigeria are usually without facilities for process integration of waste, thus, making it very inefficient in terms of wood conversion. The waste generated is very enormous and the wood processing units lack the facilities for their utilization. A close look at the wood based industry in Nigeria showed that average percentage volume recovery is getting lower while waste generation is on the increase. Ajayi (2004), revealed that only about half of the original wood volume harvested becomes

marketable after processing in sawmills and plywood mills in Nigeria. However, despite enormous volumes of biomass waste generated, developing countries, Nigeria inclusive still have inefficient way of utilizing biomass energy for cooking, lighting and heating with characteristic negative impact on people's health as well as on the environment. Large volume of residues generated are burnt on daily basis, thus constituting a major environmental problem (Adegeye *et al.* 2009). With energy demand still a problem in many developing countries and expected 50% increase in world in consumption of plant resources for food and fuel by 2050 (Alexandratos and Bruinsma 2012), disposal of wood residues for landfill and open air burning are becoming less acceptable. To reduce emission as a result of such activity, there is need to embrace Clean Development

Mechanism (CDM) which is part of Kyoto protocol agreement. Energy recovery from wood wastes is an acceptable alternative to their disposal or incineration. Waste-to-energy is gaining more and more attention as landfill costs and environmental concern increase and, at the same time, space available for landfilling waste is diminishing, especially in densely populated areas (Gavrilescu 2008). One way to make efficient use of CDM and waste-to-energy is to make efficient use of technical lignin which has been adjudged to be the main energy bearing component of wood biomass.

Lignin is the second most abundant natural substance in the world after cellulose (Rastogi and Dwivedi 2007) and about  $5 \times 10^6$  metric tons of lignin is produced by industry annually (Mai *et al.* 200). It has been estimated that Kraft process alone produced about 95% of the world quantity of lignin per year and the 55 million tons of lignin co-produced per year are only used as energy source for combustion application (Gosselink *et al.* 2004). Joffres *et al.* (2013) opined that significant part of the Kraft-lignin ( $8 \text{ to } 11 \text{ Mt.y}^{-1}$ ) could be valorized in other applications without weakening the industry economy. Also, with industrial production of bio-ethanol from lignocellulosic materials, it can be planned that more and more lignin will be available as by-product of bio-ethanol production in the near future (Soccol *et al.* 2011). As a consequence, and considering the depletion of the fossil fuels, lignin appears as an interesting alternative raw material for sustainable fuel production (Thring *et al.* 2000).

Apart from its availability and its prospect for liquid fuel and biochemicals, it is also the major energy-bearing compound in wood. It has a higher heating value ( $22.3 - 26.6 \text{ MJ/kg}$ ) when compared to cellulose ( $16.1 - 19.0 \text{ MJ/kg}$ ) or hemicellulose ( $14.7 - 18.2 \text{ MJ/kg}$ ) (Sheng and Azevedo 2005; Telmo and Lousada 2011) and therefore a target index when screening a biomass material for fuel energy production. According to Gavrilescu (2008), pulp and paper mills generate more than half of their energy needs from industrial lignin rich biomass fuels recovered from solid waste and process streams. Based on this, Pulp and paper industry, though energy-intensive, are still regarded as energy efficient industry.

Energy-rich biomass, derived from black liquor, wood chips, bark, sawdust, rejects, sludge, is the result of atmospheric carbon dioxide amassed by trees during growth and transformed into organic carbon substances. This present study centered on the characterization of lignin extracted from mill-wood residues of *Gmelina arborea* and *Tectona grandis*. This is with the aim of determining its energy value and provide a clean fuel alternative for both domestic and industrial use.

## 2. MATERIALS AND METHODS

The raw materials used for this study were the sawdust termed, Mill-Wood Residue (MWR) generated from conversion of matured stems of Teak (*Tectona grandis*) and Gmelina (*Gmelina arborea*) at the Sawmill of Forestry Research Institute of Nigeria, Ibadan. The residues obtained from Teak, Gmelina and their mixture respectively were oven dried at  $105 \pm 3^\circ\text{C}$  to constant moisture content for 2 hours using Pietarinen *et al.* (2006) method. Each sample was milled, screened to about 0.4 mm particle size and extracted with 95% ethanol using ASTM designation D1107-56 (1972) followed by lignin, calorific, elemental and functional group analysis.

### 2.1 Lignin content quantification

The lignin content of the MWR was quantified using acid hydrolysis (Klason lignin) and alkaline hydrolysis. The Klason lignin was determined based on the acid hydrolysis of the water-insoluble fraction of the MWR samples. 2 g of extract-free sawdust was conditioned in 120-mL polyethylene screw capped bottles. Fifteen millilitres (15 ml) of 12 M H<sub>2</sub>SO<sub>4</sub> was added to the sample and stirred with a glass rod. The bottles were kept in a water bath at  $30^\circ\text{C}$  for 30 min. Subsequently, 80 mL of distilled water was added to each bottle, and the bottles were then sealed and autoclaved at  $105^\circ\text{C}$  for 1 h. After autoclaving, while the contents were still warm, the insoluble material was quantitatively vacuum-transferred to filter crucibles and then washed with hot water and dried at  $105^\circ\text{C}$  for 16 h. Subsequently, the crucibles were heated in the muffle furnace at  $500^\circ\text{C}$  for 3 h. The weight after incineration was subtracted from the weight of the residue insoluble in sulfuric acid to calculate the lignin content.

For alkaline hydrolysis, 2 g extractive-free mill-wood sample was hydrolyzed with 1.25M of NaOH at  $80^\circ\text{C}$  for 5hrs. The hydrolysate was then filtered with a glass filter and washed with water ( $3 \times 10 \text{ ml}$ ), followed by ethanol ( $2 \times 10 \text{ ml}$ ), and acetone ( $1 \times 10 \text{ ml}$ ) in turns. The pH of the filtrate was reduced to 5.5 by addition of 6M of HCl. After filtration with a glass filter, the precipitated material (i.e. hemicelluloses) was washed with 70% ethanol and allowed to air dry. Ethanol was evaporated from the filtrate, and the alkali soluble lignin was obtained from the filtrate by precipitation at pH of 1.5 by addition of 6 M of HCl. The alkali soluble lignin was washed with acidified water (pH 2), centrifuged and freeze dried. The extracted was then calculated as the percentage of extractive-free sawdust sample.

## 2.2 Calorific test

The calorific properties which include volatile matter, ash and fixed carbon contents of lignin extracted from Gmelina, Teak and their mixture were determined based on ASTM Standard E711-87 (2004), while the heating value was determined by the Gouthal formula. For volatile matter determination, 1g of the sample was placed in a crucible of known mass and oven-dried to constant mass, after which it was heated in the furnace at temperature of 600°C for 10 min. The volatile matter was then expressed as the percentage loss in mass to the oven dried mass of the sample. The percentage ash content followed the same procedure as volatile matter, except that the sample was heated in the furnace for 3 h. The percentage fixed carbon was calculated using the equation below:

$$C = 100 - (V + A) \dots \text{Eq. 1}$$

Where, C is percentage of fixed carbon, V is percentage of volatile matter and A is percentage of ash content, while the heating value ( $HV$ ) ( $\text{MJ kg}^{-1}$ ) was calculated by using the equation stated below:

$$HV = 2.326(147.6FC + 144V) \dots \text{Eq. 2}$$

### *2.3 Elemental and Functional Group Composition Analysis*

The concentrations of Mg, Ca, Al, Fe, Mn, Cu, Zn and Pb present in the extracted lignin of mill-wood residues were measured by PERKIN ELMER 200 Flame Atomic Absorption Spectrophotometer (AAS) method. Potassium concentration was measured using JENWAY pfp7 elemental analyzer. Lastly, functional group composition of sawdust and extracted lignin of the samples were determined using PERKIN ELMER 1600.

### 3. RESULTS AND DISCUSSION

### *3.1 Lignin content*

The lignin yields of the Milled-Wood Residues (MWR) differ with respect to wood sources and extraction methods. Except in Teak MWR, acid insoluble lignin was generally higher than alkaline soluble lignin. Nevertheless, Teak MWR yielded the highest lignin averaged 31.77 and 31.70% in both alkaline and acid hydrolysis respectively compared to 28.0 and 24.57% for Gmelina MWR and 28.57 and 27.0% for Mixed MWR acid insoluble and alkaline soluble lignin respectively (Table 1). The generally higher yield of acid insoluble lignin in both Gmelina and Mixed MWRs could be due to either non lignin components within the wall of the wood residue that are oxidize or dissolved by alkaline solution or due to the presence of some compounds in the MWRs that are not completely hydrolysed by acid. In

line with this, Van Soest (1994) opined that the use of Klason (acid insoluble) lignin with no adjustment to quantify lignin content could be exaggerated because of the significant presence of nitrogenous compounds in the insoluble residue that could be incorrectly classified as lignin. Nevertheless, the lignin content of the mill-wood residues extracted with the two methods compared well to 26.1% lignin in *Gmelina* stem (Chow and Lucas 1988), 23.4-34.5% in *Eucalyptus* globules (Anttonen *et al.* 2002) but higher than 19.8% in Teak stem (Chow and Lucas 1988).

Table 1: Average yield (%) of acid insoluble and alkaline soluble lignin

Raw materials	Acid insoluble lignin	Alkaline hydrolysis
Gmelina MWR	28.00±1.11	24.57±6.25
Teak MWR	31.70±0.89	31.77±9.75
Mixed MWR	28.57±0.46	27.00±1.50

$\pm$ Standard deviation

### 3.2 Calorific properties

The heating value of the extracted lignin from the MWRs were determined as a function of the volatile matter, ash and carbon contents. Extracted lignin from Gmelina MWR had the lowest volatile matter and ash content averaged 27.60 and 3.48% respectively, but yielded the highest fixed carbon (68.57%) and heating value (32.79 KJ.kg<sup>-1</sup>) compared with lower fixed carbon (53.32 vs 57.91 %) and heating values (30.13 vs 31.70 KJ/Kg) obtained in lignin extracted from Teak and Mixed MWRs, respectively (Table 3). Therefore, it could be inferred that the lower the volatile matter and ash content of a biomass material, the higher would be the fixed carbon and by extension the heating value. High percentage fixed carbon and heating values of lignin extracted from the residues attest to the fact that lignin is a major energy bearing compound in wood and can be used to predict the energy value of wood (Zhou *et al.* 2011). Also, the closeness of the heating values of extracted lignin from the mill-wood residues, is an indication that incurring extra cost for separation of the residues according to the wood source is not economically rational (Macfarlane *et al.* 2009).

Table 3: Combustion Properties of Extracted Lignin from the MWRs

Combustion properties	Teak	Gmelina	Mixed
% Volatile matter	27.6	35.31	35.29
% Ash	3.48	11.37	6.80
% Fixed Carbon	68.57	53.32	57.91
Heating Value (KJ/Kg)	32.79	30.13	31.70

### 3.3 Elemental Analysis of the Mill-Wood Residue (MWR) Lignin

The mineral element and their contents in MWR lignin are presented in Figure 1. Generally, Mixed MWR lignin had the highest mineral element concentration. In all the lignin extracted from the MWRs, aluminum had the highest concentration with average values of 57.86 mg/L in Mixed MWR, 49.96 mg/L in Teak MWR and 31.53 mg/L in Gmelina MWR. This is followed by iron (10.62 – 6.60 mg/L), magnesium (6.68 - 8.47 mg/L) and potassium (4.40 – 4.90 mg/L). The high contents of monovalent potassium, divalent magnesium and trivalent aluminum in fuels are responsible for the lower organic volatile yield and may promote dehydration of holocellulose and demethoxylation of lignin units during pyrolysis (Fahmi *et al.* 2007; Bridgwater 2012;

Akinrinola *et al.* 2014). At industrial level, high alkali content in fuels causes severe slagging on the boiler grate or in the bed and because of its volatility, also results in fouling of convection heat transfer surfaces (Jenkins *et al.* 1998). However, one major deduction from this result is that the proportion of mineral element in extracted lignin is not dependent on those in the original wood residue. The reason for this could be attributed to substantial loss of mineral nutrient to both alkaline and acid hydrolysis subject to lignin extraction. Therefore, the mill-wood residues and their lignin are expected to have different ash melting behavior. In this study the mineral matter obtained from the ash of the mill-wood residues are much lower than those in major energy crops (Akinrinola *et al.* 2014) and are therefore not expected to cause fouling problems.

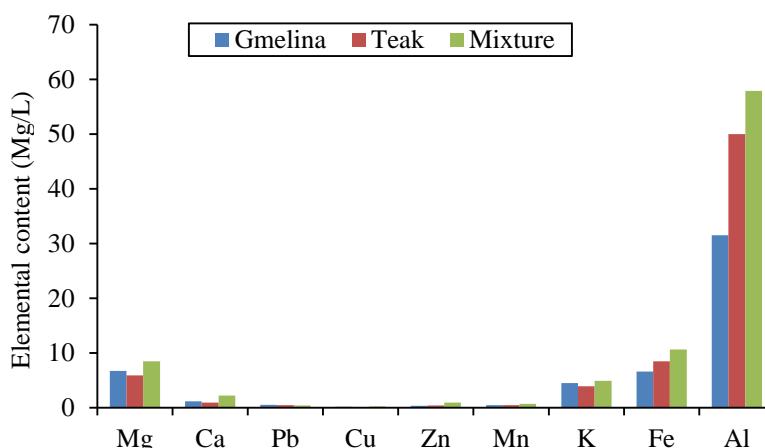


Figure 1: Elemental content of extracted lignin in mill-wood residue

### 3.4 Compositional Analysis (FT-IR)

FTIR spectra analysis was carried out to identify chemical compounds influencing the energy content of lignin extracted from the mill-wood residues. Generally, alkanols (O-H), Amide/Amine (N-H), Phosphine (P-H), carboxyl (C=O), Nitroso (N=O) and Nitro (N-O) and Alkanes (C-H, CH<sub>2</sub> and CH<sub>3</sub>) compounds were detected at various concentration (Fig. 3) and frequencies (Fig. 4). The concentration of these compounds increased from 2.5 cm<sup>2</sup> in alkanols to 72.5 cm<sup>2</sup> in Amide/Amine obtained from Gmelina MWR lignin while it increased from 6.3 cm<sup>2</sup> in Nitro to 172.5 cm<sup>2</sup> in Amide/Amine obtained from mixed MWR lignin. However, the concentration of compounds in Teak MWR lignin did not follow a particular order with alkanes, carboxylic, amide/amine and nitro compounds having significant concentrations of 20.0, 25.0, 20 and 27.5 cm<sup>2</sup>, respectively while the alkanols had the least averaged, 7.5 cm<sup>2</sup> (Fig. 3). The high concentration of amine in both the milled wood

residues and lignin attest to the high energy value of the wood samples. This is because, wood with high calorific values tend to favour high rate of pyrolysis. Also, the variation in concentration of compound in MWR lignin could be attributed to the differential response of the wood residues to alkaline and acid hydrolysis during extraction process and by extension the difference in energy content of their lignin.

Meanwhile, the concentration each of the compound detected in the MWR lignin had little to do with the wave number region of absorption of the compound. The functional group with high concentration were detected at lower wavenumber regions while it took high frequency number to detect lower concentration functional group (Fig. 4). For example, the O-H group of Alkanols were generally detected at high frequency band of 3469 cm<sup>-1</sup> in Gmelina MWR lignin, 3525.0 cm<sup>-1</sup> in Teak MWR lignin and 3429.0 cm<sup>-1</sup> in mixed MWR (Fig. 5) compared to the lowest frequency band of 1461

$\text{cm}^{-1}$  and  $1456.0 \text{ cm}^{-1}$  where  $\text{CH}_2$  and  $\text{CH}_3$  of alkanes were detected in Gmelina and Teak MWRs lignin and  $1339 \text{ cm}^{-1}$  where N-O of amine were detected in mixed MWR lignin (Fig.4). The distribution of functional groups in Gmelina and Teak MWR lignins is a bit different from FTIR band range of  $3365\text{-}3350 \text{ cm}^{-1}$  for OH,  $2932\text{-}2930 \text{ cm}^{-1}$  for C-H and  $1690 \text{ cm}^{-1}$  for conjugated carbonyl Kraft and klason lignin structure obtained from pine

(Ghatak 2008). This could be attributed to the fact that the lignin structure of both soft wood and hard wood were different in their chemical structure (Li 2011). The implication of this is that the presence of these functional groups at each wave number region could play a big role in determining the energy characteristics of the wood samples.

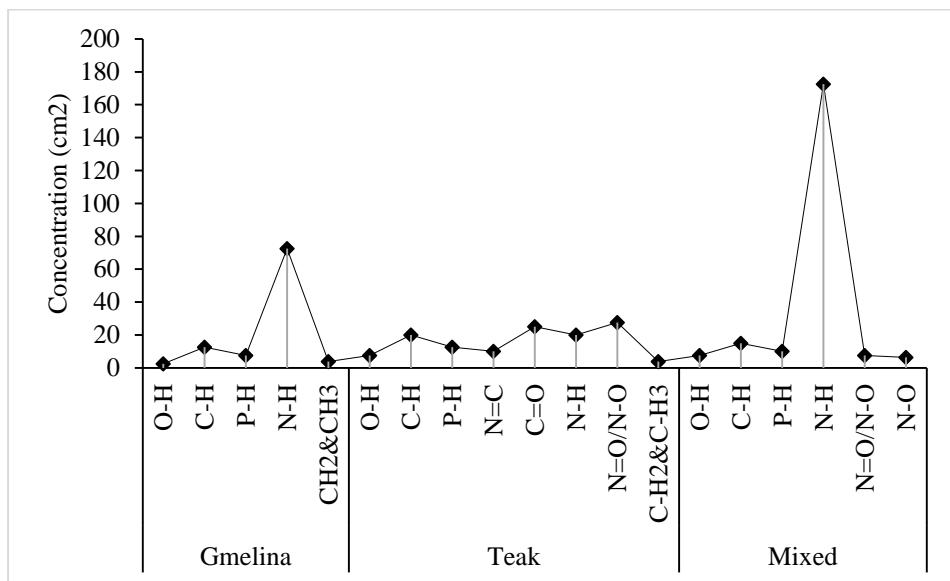


Figure 1: Concentrations of compound detected in lignin extracted from the mill wood residues

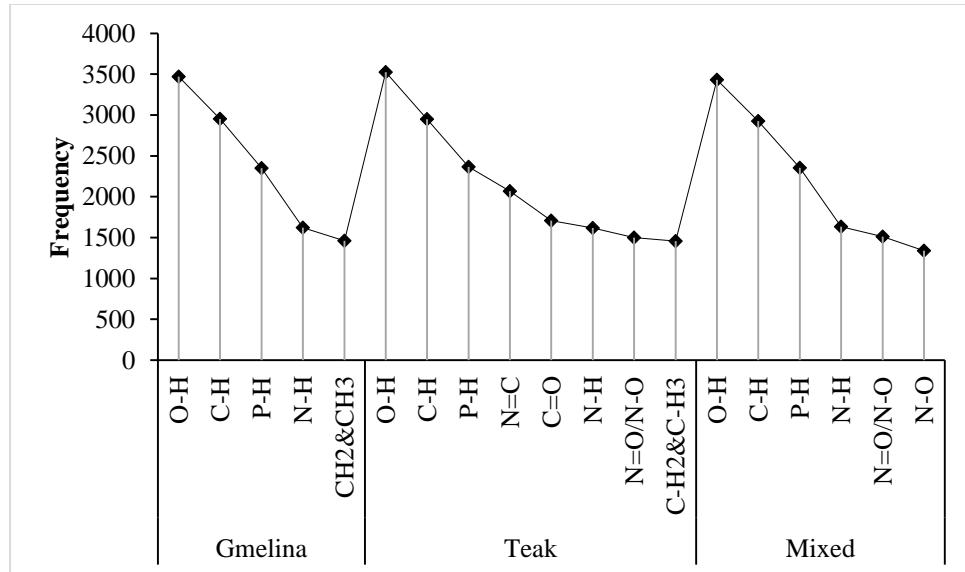


Figure 2: Frequency of functional groups detected in lignin extracted from the mill-wood residues

#### 4. CONCLUSION

The present study investigates the energy value of lignin extracted from mill-wood residues of *Gmelina arborea*

and *Tectona grandis*. From the study, the following conclusions are drawn:

1. Teak mill-wood residue was higher in lignin content than *Gmelina* mill-wood residue, but variation exist with extraction methods.
2. The high fixed carbon content and corresponding heating values of extracted lignin showed that lignin is a major energy bearing compound in the mill-wood residues.
3. The ash fractions of extracted lignin from the mill-wood residues contained predominantly aluminum, iron, magnesium, potassium and traces of calcium, lead copper, zinc and manganese. The compositions are relatively low and predicted not to cause fouling problems during combustion.
4. There is a strong relationship between lignin content of wood residues and their energy content.

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