

Characterization of Lignocellulose Wood Waste from Hardwood, Softwood, and Mixed Sawdust for Thermochemical Conversion into Gaseous Fuel

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Abstract: A comprehensive study of eight wood waste samples as feedstock for thermochemical conversion such as gasification was done. Three softwood (*Antiaris africana*, (SW1); *Terminalia superba*, (SW2); *Cieba pentandra*, (SW3)), four hardwood (*Pterygota macrocarpa* (HW1); *Celtis africana* (HW2); *Celtis zenkeri* (HW3); *Cordia millenii* (HW4)) and mixed sawdust (MW) was used for the study. The samples were characterised for proximate composition (volatile matter, fixed carbon and ash content) and bulk density. Ultimate (C, H, N and O) analysis was done using CHN analyzer. Percentages of chemical structural components were evaluated. Crystallinity was examined using X-ray diffractometer (XRD). The functional groups were determined using Raman Spectroscopy. Thermal decomposition behaviour of these samples was studied using thermo gravimetric analyzer TGA (DTG). Results showed that wood species are different even within the same class of lignin. Relatively high volatile matter, carbon content, higher heating value (HHV) and, low ash and nitrogen content was observed in most of the samples. However, sample SW2 and HW1 has high ash content, and oxygen content with low carbon content and ultimately low HHV. Hard wood had significantly higher cellulose and hemicelluloses unlike the softwood which has more lignin content.

Keywords: Softwood, Hardwood, Thermal conversion, Gasification, Pyrolysis, Lignocellulose

1. INTRODUCTION

The use of Lignocellulose wood waste as an alternative source of energy is highly promising. With an increasing energy demand in Nigeria where agriculture is the economic mainstay, conversion of these agricultural waste materials will help to avoid issues such as deforestation and environmental concerns [1, 2]. Nigeria is blessed with woody biomass and like most countries, woody biomass account for more than 50% of the Lignocellulose biomass feedstock for conversion as a renewable source of energy [1,3]. Sawmill industry in Nigeria accounts for 93.32% of the total wood based industries [4] and the “waste” wood residue generated in the form of sawdust, wood bark, slabs, abounded felling and so on come in Large volumes. As reported by Ajobo in 2014 sawmill industry appears to be the most active of all wood based industry.

The thermochemical conversion technologies available for the conversion of these wood residue “waste” to useful raw material for energy production are fast or slow pyrolysis and gasification [1,3 ,6]. These processes are all thermal decomposition, for pyrolysis it happens in the absence of oxygen and has bio char, bio oil as its major product [7, 8,9] with non condensable gases. Gasification happens in the presence of oxidative substances (medium) such as air, oxygen and water with gaseous fuel as its major product and bio oil and char as by-products or residue. [10,11,12, 13]. The conversion of this lignocellulose feedstock into gaseous fuel gives a wider range of technologies for innovative end usage [11,14]. These technologies include heat and electricity generation for small to large-scale applications, transportation fuels such as synthetic diesel or hydrogen, methanol, biomethane (12, 15), decentralized power generation, production of hot water and steam in small industries, drying of a variety of agricultural and industrial products. [30]

These thermochemical technologies provide more environmentally friendly methods for conversion than the traditional combustion of “waste” or wood residues. [6, 9]. The thermochemical conversion of these lignocellulose materials is largely influenced by the basic operating conditions of the operation and the properties of the feedstock [9]. To apply any of these thermochemical conversion technologies for the conversion of sawdust (wood residue) [1, 3,8,11] or any other biomass waste like palm kernel shell [6], Rice husk [13], bamboo [9], bagasse [2], a comprehensive characterisation of their physical and chemical properties must be studied [1,6, 9]. These properties will affect greatly the process design

and product of gasification, thus the need to characterise first before gasification or any other conversion method so as to predict the composition, yield, the product and possible co-products.

Woody biomass, can be classified as softwood or hardwood depending on its lignocellulosic composition (hemicellulose, cellulose, lignin and extractives), shape (coniferal plant and broad leaves), colour (red and white), distribution and location. Various characterisation studies have been done on both softwood and hardwood biomass sourced from different countries for different conversion methods. Koukouzas *et al.*, 2008 characterized sawdust pellets from Oak wood and sorghum for gasification purposes. Ojolo *et al.*, 2012 studied sawdust (no name) and palm kernel shell as a feed stock for an updraft gasification work. Wander *et al.*, 2004 studied *Pinus eliottii* sawdust an exotic species of wood in south Brazil. Wenja *et al.*, 2013 studied two hardwood species, red oak and yellow poplar to understand the pyrolysis kinetic of the wood components. He considered the bark, sapwood and heartwood components. Wan Azlina *et al.*, 2014 studied rubber wood sawdust (*Heveabrsiliensis*) to understand the stability of biochar that will be produced from it through pyrolysis.

Mazlan *et al.*, 2015 characterized sawdust from Meranti wood found in Malaysia for the production of biochar through fast pyrolysis. He recommended that a further study which will consider varieties of wood species is of essence for there to be a clearer understanding of the process of conversion, the product, the yield and the characterization of the feedstock. In 2016, Kim *et al.*, characterised two soft wood (*Pinus (P) densiflora & P. koraiensis*), two hardwood (*Quercus acutissima and Liriodendron tulipifera*) and the nut shell of one of the soft wood (*P koraiensis*) which are wood species found in Korea.

With all these great works, wood species that are found in Nigeria are lacking. There is need for a detailed characterisation of soft wood & hardwood species locally found in Nigeria. In this study, wood waste (sawdust) from representative wood species found locally in Nigeria were characterised for thermochemical conversion through gasification. The aim of this study is to characterise various sawdust from hardwood, softwood and mixture to establish the fact that wood species are different and determine the properties of the lignocellulose wood residue that will help select the best specie for thermochemical conversion into gaseous fuel.

2. MATERIALS AND METHODS

2.1 Raw Materials

The sawdust samples from eight different wood species were sourced locally from sawmills industries in Akure, Ondo State, Nigeria. These woods include *Pterygota macrocapa* commonly known as Oporoporo, *Cetis africana* (Ita white), *Cetis zenkeri* (Ita red), *Cordia milleini* (Omo Sheda), *Antriaris africana* (Oroi), *Terminalia superba* (Afara), *Cieba pentandra* (Araba) and a Mixed sawdust. The samples were air dried and sieved using octagon digital sieve shaker and particles sizes 850 μ m and 600 μ m retained were packed in an air tight Ziploc plastic bag for further studies.

2.2 Analysis of Raw Materials

Moisture and Ash content of the sample were determined on dry basis using methods described by AOAC [1990] and the volatile matter was determined using ASTM E872 [2013], while the fixed carbon was done by difference as described by Omoniyi and Olorunisola (2014). The bulk density was determined using a method adopted from ASTM D1895 B. The ash composition (mineral analysis) was determined as described by Osodi [1992] and Omoniyi and Olorunisola [2014]. The determinations were carried out in triplicates and data were subjected to statistical analysis. The elemental (Ultimate) analysis was done using a Perkin Elmer 2400 series II CHN analyzer for carbon, hydrogen, and nitrogen content, the percentage of oxygen was estimated by difference. The feedstock was dried completely before the ultimate analysis so as to exclusively determine the structural hydrogen of the biomass. The higher heating value (HHV) was determined from the ultimate composition using an empirical correlation - Dulong – Berthelot Equation described by Basu 2013 and Wenjia *et al.*, 2013.

The structural composition of the lignocelluloses samples was studied according to the work done by Ayeni *et al.*, 2015, for the determination of percentages of cellulose, hemicelluloses, Lignin and extractive present in the sample.

The nature of the chemical compound and the functional groups were determined by Raman spectroscopy (Pro Raman-L-785-B15, Enware Optronics) with 500mW laser power from 4000 cm^{-1} to 400 cm^{-1} .

The crystalline structure present in each sample was identified using PAN analytical Xpert Pro X-ray diffractometer (XRD) with monochromatic $\text{CuK}\alpha$ radiation ($\lambda=1.5418\text{\AA}$) using acceleration voltage. The diffraction angle was scanned from $0^\circ - 100^\circ 2\theta$ at a step size of 0.167 and a rate of 5.00 $^\circ/\text{min}$.

The thermal decomposition behaviour of the polymer component was studied using TGA model Q500 V20.10 build 36machine. The sample of about 3mg was steadily heated in the presence of nitrogen gas flow at 50ml/min from room temperature to 1000 $^\circ\text{C}$ at a heating rate of 50 $^\circ\text{C}/\text{min}$.

2. RESULT AND DISCUSSION

3.1 Proximate Analysis

Table 1. shows the result of the proximate analysis determined experimentally on a dry basis. It revealed that there is narrow difference between the proximate of the softwood and hardwood samples.

| Sample | Moisture Content (dry basis) db% | Ash Content % | Volatile Matter % | Fixed Carbon % | Bulk Density kg/m ³ |
|--------|----------------------------------|-------------------------|--------------------------|--------------------------|--------------------------------|
| HW1 | 35.96 ^c ±0.04 | 4.47 ^f ±0.40 | 86.10 ^b ±0.00 | 9.20 ^b ±0.00 | 148.00 ^d ±11.00 |
| HW2 | 18.62 ^a ±0.02 | 1.93 ^d ±0.15 | 88.37 ^e ±0.06 | 9.70 ^c ±0.17 | 234.00 ^f ±3.00 |
| HW3 | 18.57 ^a ±0.06 | 1.30 ^a ±0.10 | 88.80 ^f ±0.10 | 9.90 ^c ±0.17 | 269.70 ^g ±1.50 |
| HW4 | 25.89 ^c ±0.23 | 1.33 ^b ±0.23 | 88.17 ^d ±0.15 | 10.50 ^d ±0.30 | 199.70 ^e ±1.50 |
| SW1 | 20.62 ^b ±0.60 | 2.77 ^e ±0.15 | 87.57 ^c ±0.06 | 9.67 ^c ±0.15 | 129.70 ^c ±0.60 |
| SW2 | 27.87 ^d ±0.49 | 9.07 ^g ±0.12 | 89.50 ^g ±0.00 | 1.43 ^a ±0.12 | 63.33 ^a ±0.58 |
| SW3 | 20.48 ^b ±0.32 | 1.93 ^d ±0.21 | 85.60 ^a ±0.00 | 12.47 ^e ±0.21 | 101.00 ^b ±1.00 |
| MW | 26.10 ^c ±0.00 | 1.53 ^c ±0.32 | 88.70 ^f ±0.10 | 9.78 ^c ±0.35 | 163.70 ^d ±24.50 |

Table 1: Proximate Analysis of Sawdust samples

Wet basis = *wb* , Dry basis = *db*

Means following the same superscript are not significantly different $p \leq 0.05$

The moisture content (MC%) of wood sample on a dry basis db% is ranged between 18.57 – 35.96wt%. The highest value was obtained in HW1 as 35.96wt% . There appear to be significant differences in the moisture content of the samples except for HW4 and MW Mixed sawdust, SW1 and SW3, and then HW2, and HW3 . The moisture content for the eight wood samples fell within the acceptable moisture content (40%) for conversion using a downdraft gasifier [10, 12]. It plays an important role in reacting with the volatiles and char converting them to the desired gas. It is also essential for water – gas shift reaction needed to favour hydrogen content of the gaseous fuel [12, 21] but lowers greatly the calorific value of the fuel especially when it exceeds the accepted limit [21, 22].

For the ash content, HW1 and SW2 has higher ash content (4.47%) and (9.07%) respectively as compared to the other six wood samples ranged between (1.30-2.77%). There are significant differences in the ash content except that of sample HW2 and SW3. Ash content in a biomass is desired to be low while the ash fusion temperature is desired to be high to avoid the problem of slagging or clinker formation in the reactor especially in a down draft reactor [14, 22].

Volatile Matter ranges between (85.60- 89.50 %) with SW2 having the highest value. There are significant differences in the volatile matter content for the entire 8 samples.

For the fixed carbon of range between (1.43 – 10.50) %, with HW4 having the highest value and SW2 has least value. There are significant differences in the fixed carbon content of the samples except for HW2, SW1 and MW (Mixed sawdust)

Bulk density of the samples are ranged between 269.7kg/m³ - 63.33kg/m³ with SW2 having the least value compare to other seven samples. By observation, SW2 has more particles per volume. There are significant difference in the bulk density of the various samples except HW1 and MW.

3.2 Ultimate Analysis

The ultimate (elemental) analysis in Table 2 was determined using CHN analyzer generally agrees with the work reported in [7, 8]). The CHN-O percentages were used for the determination of various other parameters needed for the gasifier design and the selection of the best sawdust species.

Table 2: Ultimate Analysis (wt % dry basis)

| Sample code | C | H | N | O* | H/C Atomic ratio | O/C Atomic ratio | HHV (MJ/Kg) | Calorific Value (kWh per kg) |
|-------------|-------|------|------|-------|------------------|------------------|-------------|------------------------------|
| HW1 | 43.71 | 4.01 | 0.91 | 51.37 | 0.092 | 1.175 | 14.56 | 4.05 |
| HW2 | 44.51 | 4.56 | 1.06 | 49.87 | 0.102 | 1.120 | 15.70 | 4.36 |
| HW3 | 45.74 | 4.77 | 0.84 | 48.65 | 0.104 | 1.064 | 16.52 | 4.59 |
| HW4 | 47.10 | 4.64 | 0.82 | 47.44 | 0.099 | 1.007 | 16.96 | 4.71 |
| SW1 | 45.55 | 4.84 | 1.13 | 48.48 | 0.106 | 1.064 | 16.67 | 4.63 |
| SW2 | 41.36 | 5.06 | 1.05 | 52.53 | 0.122 | 1.270 | 15.18 | 4.22 |
| SW3 | 46.52 | 5.72 | 1.04 | 46.72 | 0.123 | 1.004 | 18.21 | 5.06 |
| MW | 45.77 | 5.69 | 0.98 | 47.56 | 0.124 | 1.039 | 17.82 | 4.95 |

*Oxygen is by difference

Elements like nitrogen (N) and ash content have direct effect on the harmful emissions produced during gasification and as such required in low percentage [22]. HW1 and SW2 has lower carbon content (43.71% and 41.36% respectively) and higher oxygen content (51.37%, 52.53% respectively) as compare to other six samples. This invariable gave HW1 and SW2 lower heating value as compared to other samples. HW1 is a hardwood yet it has lower heating value due to its high ash content, low carbon and higher oxygen content when compare to other hardwood species. High oxygen content tend to lower the heating value of the fuel [1, 6,10].

From the relative abundance (C%, N%, O %) (Table 2) and the relative atomic mass of each element, the molecular composition for each was calculated. HW1 had 1.13 mols of Carbon and 1.25 mols of hydrogen for every mole of oxygen. This gave a molecular composition for as $C_{1.14}H_{1.33}O_1$. Similarly, molecular composition for the other seven sawdust sample are; $C_{1.19}H_{1.46}O_1$, $C_{1.23}H_{1.57}O_1$, $C_{1.32}H_{1.56}O_1$, $C_{1.24}H_{1.60}O_1$, $C_{1.05}H_{1.54}O_1$, $C_{1.33}H_{1.96}O_1$, $C_{1.28}H_{1.92}O_1$ for HW2, HW3, HW4, SW1, SW2, SW3, MW Mixture respectively. This can be compared with result given in [3].

3.3 Heating Value

The heating value also generated from C, H, S, O, N and ash content varied with narrow intervals with softwood (15.18 MJ/kg – 18.21 MJ/kg) having higher values than hardwood (14.86MJ/kg – 16.96 MJ/kg) and mixed sawdust (17.82 MJ/kg) this agrees with [23]. According to Basu [2013], higher heating value (HHV) correlate well with oxygen –to-carbon (O/C) ratio, as O/C ratio increases from 0.86 to 1.03, HHV reduces from 20.5 to about 15MJ/kg and as hydrogen-to-carbon ratio (H/C) increases, effective heating value of fuel reduces. This can be seen from the result obtained from the eight samples, SW3 has the lowest oxygen-to-carbon ratio (O/C) ratio and thus have highest HHV (18.21MJ/kg) [8, 24].

Wan Azlina et al., 2014, determined the (H/C) and (O/C) (mass/mass) for the biochar produced and not for the raw rubber wood sawdust. He gave low values for the (O/C) and H/C ratio as the temperature increased with increase carbon content and hence calorific values when compared with the raw rubber sawdust which has 18.3 MJ/kg as calorific value. Mohammed et al., 2015, characterised and studied Napier grass leaf, stem and Napier grass leaf and stem and he gave O/C (atomic ratio) and H/C (atomic ratio) for the samples with Napier grass stem having lowest value thus producing a highest (HHV) of 18.11MJ/kg when compared to the other two samples.

3.4 Mineral Analysis

Table 3: Mineral Analysis of sawdust samples

| Sample | Na | K | Ca | Cu | Fe | Cd | Mg | Zn | Mn |
|--------|--------------------------|---------------------------|---------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| HW1 | 44.30 ^b ±0.36 | 74.57 ^b ±0.31 | 27.83 ^s ±0.35 | 0.26 ^d ±0.00 | 0.44 ^c ±0.00 | 0.03 ^d ±0.00 | 6.99 ^b ±0.01 | 0.38 ^c ±0.01 | 0.51 ^c ±0.01 |
| HW2 | 10.40 ^s ±0.26 | 10.80 ^s ±0.10 | 131.77 ^a ±0.31 | 0.19 ^f ±0.00 | 0.30 ^e ±0.01 | 0.01 ^f ±0.01 | 5.16 ^e ±0.01 | 0.29 ^e ±0.00 | 0.48 ^e ±0.01 |
| HW3 | 12.47 ^f ±0.35 | 16.97 ^f ±0.35 | 86.67 ^d ±0.11 | 0.29 ^c ±0.00 | 0.31 ^d ±0.00 | 0.02 ^e ±0.00 | 5.10 ^f ±0.00 | 0.31 ^d ±0.00 | 0.49 ^d ±0.01 |
| HW4 | 13.00 ^f ±0.95 | 10.47 ^s ±0.2 | 12.47 ^h ±0.21 | 0.20 ^e ±0.00 | 0.44 ^c ±0.00 | 0.00 ^e ±0.00 | 5.19 ^e ±0.01 | 0.24 ^f ±0.01 | 0.48 ^e ±0.02 |
| SW1 | 30.40 ^c ±0.56 | 51.70 ^c ±0.98 | 92.47 ^c ±0.15 | 0.39 ^b ±0.01 | 0.51 ^b ±0.00 | 0.02 ^e ±0.03 | 6.71 ^c ±0.00 | 0.43 ^b ±0.00 | 0.57 ^b ±0.01 |
| SW2 | 62.87 ^a ±1.09 | 102.73 ^a ±2.41 | 120.07 ^b ±1.21 | 1.42 ^a ±0.00 | 2.35 ^a ±0.04 | 1.07 ^a ±0.01 | 7.34 ^a ±0.01 | 2.12 ^a ±0.01 | 2.32 ^a ±0.00 |
| SW3 | 23.80 ^d ±0.82 | 30.53 ^e ±0.45 | 52.70 ^f ±0.40 | 0.19 ^f ±0.00 | 0.32 ^d ±0.00 | 0.22 ^b ±0.00 | 6.71 ^c ±0.05 | 0.30 ^d ±0.00 | 0.49 ^d ±0.02 |
| MW | 18.50 ^e ±0.62 | 33.17 ^d ±1.97 | 65.60 ^e ±0.17 | 0.17 ^s ±0.00 | 0.28 ^e ±0.01 | 0.06 ^c ±0.02 | 6.50 ^c ±0.01 | 0.31 ^d ±0.01 | 0.45 ^f ±0.00 |

Means following the same superscript are not significantly different $p \leq 0.05$

Table (3) gave the mineral analysis of the ash in the various wood species. The Sodium (Na) concentration ranged between 10.40 and 62.87. The highest value was obtained in SW2. However there was significant difference in the concentration of the Na in the sample except of sample HW3 and HW4. Potassium (K) concentration ranged between 10.47 and 102.73 with SW2 also having the highest value. There was significant difference in the concentration of K generally except in HW2 and HW4. Calcium (Ca) concentration is ranged between 12.47 and 131.77. The highest value was obtained in HW2. However there was significant difference in the concentration of Ca. Copper (Cu) ranged between 0.17 and 1.42 with SW2 having the highest value. There is significant difference in the concentration of Cu except for HW2 and SW3.

The concentration of Iron (Fe) ranged between 0.28 -2.35 with the highest values obtained in SW2. There appear to be less significant difference in Fe concentration as HW1 and HW4, HW2 and MW and finally HW3 and SW3 have same concentration respectively. Cadmium (Cd) concentration ranges between 0.01- 1.07 with SW2 having the highest concentration. However there is significant difference in the concentration of Cd except for HW2 and HW4; HW3 and SW1. For Magnesium (Mg) concentration, it ranges from 5.10 to 7.34 with SW2 having the highest concentration. There is significant difference in the concentration of Mg except for HW2 and HW; SW1 and SW3. Zinc (Zn) concentration ranges between 0.24 and 2.12 with SW2 having the highest concentration. However, there is significant difference in the concentration of Zn except for HW3, SW3 and MW (Mixed wood). Manganese (Mn) concentration ranges between 0.45 – 2.32 with the highest occurring at SW2, The concentration is same for HW3 and SW3; HW2 and HW4; others having significant difference. Generally, the result followed the trend of biomass ash analysis [2,11,24]. It has calcium, magnesium, potassium and sodium as the major elements found in higher proportions and others like copper, zinc, iron, and manganese in trace amount. The proportion of major elements came in the order $K > Ca > Na > Mg$ with few exceptions and that of the minor elements as $Mn > Fe > Cu > Cd$.

3.5 Structural Analysis

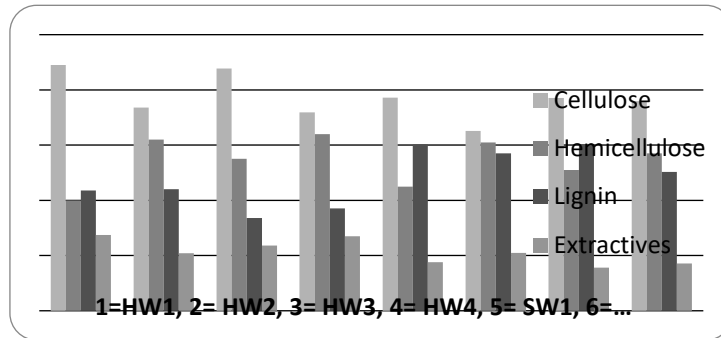


Figure 1: Structural Composition for the Lignocellulose samples

The result of the structural analysis as presented in Figure 1 showed for the eight sample that cellulose has a range of 32.22% - 44.51%, hemicelluloses has 20.00% - 32.00% and lignin has 16.79% - 30.15%. A typical hardwood HW2, showed cellulose content (36.80%), hemicellulose (31.00%), Lignin (22.00%) and extractive (10.40%). A typical softwood SW1 (38.58%, 22.50%, 30.15% and 8.78%) respectively. Generally, there is a slight significance difference ($p \leq 0.05$) in the concentration of cellulose, hemicelluloses, lignin and the extractives within the eight samples with large percentage of cellulose and hemicelluloses in all samples except in the softwood samples which have more percentage of lignin concentration. This relative high cellulose and hemicellulose content will have a positive effect on the decomposition and energy conversion of the biomass [2;14] and a greater volume of expected gaseous products [1;14]. Large lignin concentration will favour bio-char production through fast pyrolysis as proposed by [6].

3.6 Raman spectroscopy

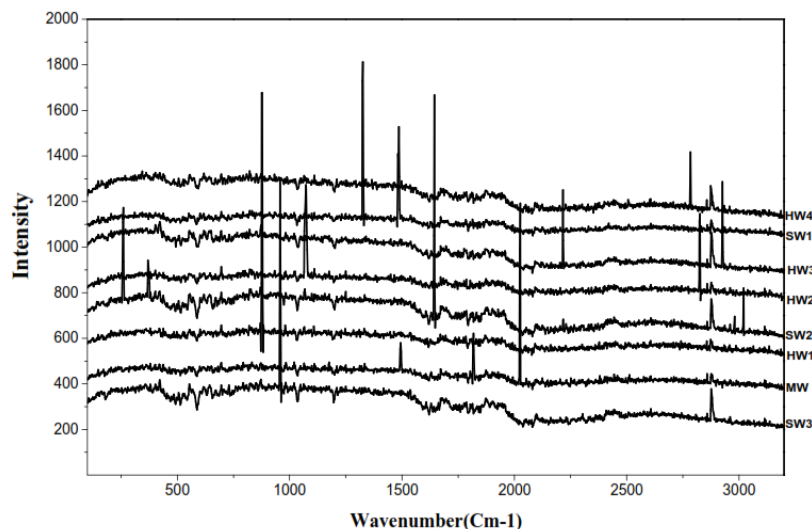


Figure 2: Raman Spectra for the Lignocellulose samples

Figure 2. Present the result of the chemical composition and functional group using Raman spectroscopy. Raman features seen in the spectra are majorly due to lignin. Amorphous hemicellulose and cellulose which are present in small quantities and their contributions is expected to be negligible [25], but can be observed clearly when FT-IR spectrophotometer is employed [26]. In figure 2, the eight wood species has band positions which appear to be similar with some distinct deviations observed, confirming that all wood species are not the same even within same class of lignin; softwood sawdust and hardwood sawdust. All hardwood sawdust are not also the same as can be seen, HW 2 (*Cetis africana*) and HW3 (*Cetis zenkeri*) are hardwood sawdust from the same family, having different colour and of the family of the Cannabis containing Canabinoids which according to literature is a natural occurring phenol [27] yet have their lignin appearing at different bands and intensity. There appear to be regions of bands common to almost all the species appearing within 2500 -3500 cm^{-1} region. Here all wood species confirmed the presence of lignin appearing both as aliphatic and aromatic C-H stretches [25]. In all eight cases lignin bands appeared approximately at 2776 cm^{-1} , 2786 cm^{-1} , 2826 cm^{-1} , 2920 cm^{-1} and 3100 cm^{-1} . The band at

3100 cm^{-1} is due to the aromatic stretching [25,28] seen in only one specie SW2 of softwood, while the bands at 2776 cm^{-1} , 2786 cm^{-1} , 2826 cm^{-1} , 2920 cm^{-1} are contributions from aliphatic C-H stretching mode with some attached to the aromatic units of the aliphatic C-H stretching in lignin.

The 2826 cm^{-1} band is common to all both hardwood, softwood and the mixed sawdust with the hardwood showing peaks that are sharper and more intense when compared with the softwood. The bands at 2776 cm^{-1} , 2786 cm^{-1} and 2920 cm^{-1} are seen prominently in the hardwood sawdust. The 2920 cm^{-1} band appeared only in one specie HW3 of the hardwood sawdust. This confirms the presence of aromatic methoxy group in the form of syringyl units which is in higher amounts in hardwood lignin [25]. The common and most prominent spectra of all lignin band appeared at 2940 cm^{-1} .

There are concentration of bands also appearing between 1400 cm^{-1} to 2250 cm^{-1} (1486 cm^{-1} , 1644 cm^{-1} , 1818 cm^{-1} , 2026 cm^{-1} , 2216 cm^{-1}), which are due to aromatic ring, ring conjugated ethylene C=C bonds in coniferyl alcohol units and y - C=O in Coniferaldehyde units in lignin with likely overlapping of CH₃, CH₂ and CH bending mode [25,28]. The aromatic ring at 1486 cm^{-1} appeared prominently in softwood sawdust SW2 (*Terminlia superba*) and mixed sawdust MW. 1644 cm^{-1} , 1818 cm^{-1} , 2026 cm^{-1} , 2216 cm^{-1} are strong bands assigned to ethylene C=C bond in coniferyl alcohol units and coniferaldehyde units in lignin. Most of the bands observed at this stage except for 2216 cm^{-1} which appeared in hardwood HW3 (*Cetis zenkeri*), appeared sharply in the softwood (1486 cm^{-1} in SW1 (*Antiaris toxicaria*), 1644 cm^{-1} in SW2 (*Terminlia superba*)) and others in the mixed sawdust (1486 cm^{-1} , 1644 cm^{-1} , 1818 cm^{-1} , 2026 cm^{-1}). The coniferaldehyde /sinapaldehyde and coniferyl sinapyl alcohol which are present at this stage have molecular structures that have aromatic conjugated bonds such conjugation is known to affect the intensity of 1486 cm^{-1} , 1644 cm^{-1} , 1818 cm^{-1} , 2026 cm^{-1} , 2216 cm^{-1} in the softwood sawdust. Also, unconjugated carbonyl groups have low sensitivity in Raman spectroscopy and therefore their contributions remain undetected [25].

The last region of concentration appeared so sharp and prominent in both softwood and hardwood with no band appearing in the mixed sawdust. The bands appeared at 260 cm^{-1} , 384 cm^{-1} , 888 cm^{-1} , 958 cm^{-1} , 1077 cm^{-1} , and 1326 cm^{-1} . The bands at this range are from aliphatic chains, aliphatic OH bend and C-C, C=O and C-C-O stretching of phenol C-O-C glucosidic band vibration [25]. Softwood sawdust SW2) unlike any other softwood has two bands at 260 cm^{-1} and 384 cm^{-1} , both of which are aliphatic chains, and a third band of high intensity at 1326 cm^{-1} , of aliphatic bend. SW3 has a strong prominent band of high intensity at 958 cm^{-1} of C-O-C glucosidic band vibrations [28, 29].

For the hardwood, HW1 has a strong band of very high intensity at 888 cm^{-1} , HW2 has a band at 1077 cm^{-1} , of moderate intensity which is visibly absent from HW3 of the same family.

3.7 X-ray Diffraction

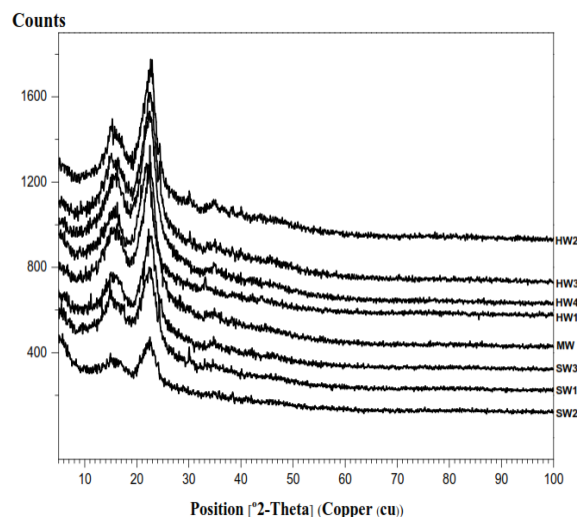


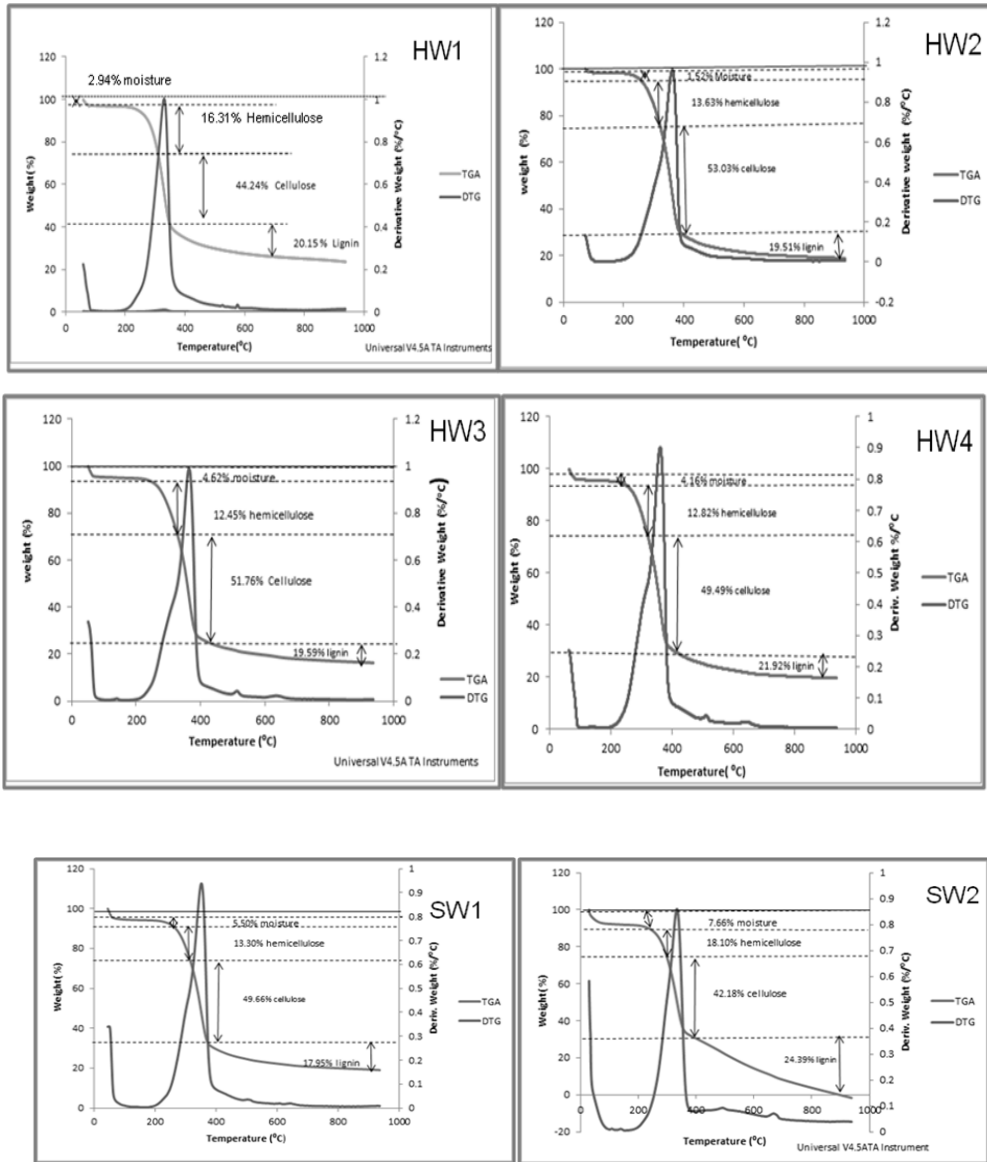
Figure 3: XRD Patterns for the Eight Sawdust Samples

The XRD patterns for the sawdust samples shown in figure 5 appeared similar for all eight with peaks at 2θ have approximate values as 22.5° (main peak), 15.5° and 35°. This is a reflection of the crystalline form of the biomass as can be seen in a typical diffraction pattern for native cellulose [27]. Narrow bands or sharp diffraction peaks show crystalline samples while broad band stands for amorphous systems in a sample [26].

These characteristic peaks are comparable to the work of Mohammed et al., 2015; sabiha-Hanim and Aziatul-Akuma, 2013. Classifying the sawdust species into hardwood, softwood sawdust and mixed sawdust and comparing the diffraction patterns of the XRD study, we observe slight differences. The hardwood sample HW1, HW2, HW3 and HW

all have sharp marrow bands of high intensity (counts) as compared with the softwood sample SW1, SW2 and SW3 which have broader bands. The mixed Sawdust also has narrow band. Cellulose is the major part of wood that is crystalline, other parts like hemicellulose , lignin and extractives are amorphous [24] thus the XRD diffraction validates the presence of cellulose in the sample and it is commonly used in determining the degree of cellulose crystallinity [26].

3.7 TG /DTG Analysis



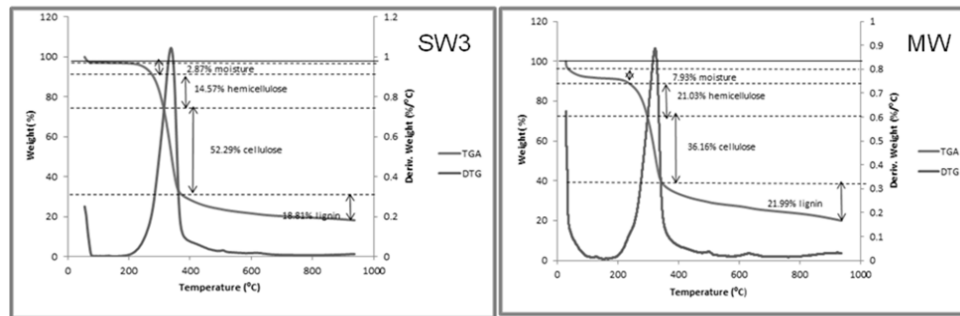


Figure 4: TGA and DTG of Lignocellulose Samples

The thermogravimetry TG (in wt.%) and the differential thermogravimetry DTG (in wt.%/°C) plot of the different sawdust samples is presented in figure 4. Decomposition of the Lignocellulose wood waste starts with dehydration at a temperature below 100°C, next is the decomposing of hemicellulose occurring at a temperature range between 100°C to 300°C. This followed by decomposition of cellulose at a temperature range of 300 °C to 380 °C and then lignin at a wider range of 250 °C and 500 °C.

This shows that hemicellulose decomposes faster than cellulose and lignin due to their individual chemical nature. Similar result were reported in literature [3,6,7, 14]. Hemicellulose is an amorphous polysaccharide structure rich in varied sugar branches. Cellulose is made up of straight chain polymer of glucose. Lignin which has a wide range of temperature for its decomposition is the most complex consisting of highly branched 3-D polymer structure of phenylpropane units. Cellulose and lignin are the major component of a typical biomass material and they both decompose at a higher temperature.

4 CONCLUSION

Three softwood sawdust sample, four hardwood sample and a mixed sawdust sample were investigated. The proximate and ultimate analysis showed that lignocellulose wood waste (sawdust) generally has high volatile matter content, higher heating value, high carbon content and low moisture, ash, nitrogen and sulphur content with slight difference for each sample. The ultimate analysis revealed that the molecular composition for each wood sample is different; the atomic ratio for hydrogen-to-carbon ratio (H/C) and oxygen-to-carbon ratio (O/C) (mass/mass) for each wood sample is slightly different. The ash content and inevitably the heating value for each wood species are different. The structural analysis confirmed the presence of the lignocelluloses materials (cellulose, hemicellulose, lignin and extractives) each of which are different for all samples. This study has give room for better understanding of the product of the conversion process and characteristic of the feedstock having handled eight different samples using standard methods.

It showed a relative high cellulose and hemicellulose content that will favour the conversion of the sawdust into gaseous fuel. The crystallinity of the samples was confirmed by the XRD. The lignin content of softwood is high compared to hardwood samples as was confirmed from the percentage composition of the structural constituents and the functional groups identified using Raman spectrometer. Some unique lignin groups were also identified in some hardwood. The mineral analysis for the ash gave high value of elements such as potassium. The thermal decomposition behaviour of the samples showed that cellulose, hemicellulose, lignin and the extractive decomposition occur at different temperatures

Wood species are entirely different and the thermochemical conversion of the samples is greatly influenced by the lignocelluloses compositions present and the ash content thus the need for this comprehensive characterisation of samples to determine which lignocellulose sample (wood) that will be better for a desired goal (biogas, bio oil or biochar) and which conversion process (gasification, slow pyrolysis or fast pyrolysis) will give the desired product and yield. Softwood will be better for bio-oil and biochar production through fast pyrolysis while hardwood will be better for gaseous fuel through gasification with exceptions such as *pterygota marcapa* (HW1) commonly known as Oporoporo , due to its high ash content and probably due to its strong lignin band of very high intensity at 888 cm⁻¹ which is a skeletal deformation that is out of phase. It is yet very crystalline showing that it is actually a hardwood but with some softwood qualities. This goes to confirm the conclusions of Ohagwu and Ugwuishiwu, 2011 that the classification of wood into hardwood and softwood is relative. According to the field study conducted prior to this characterisation, *pterygota marcapa* (Oporoporo) i commonly used for lodging in building construction.

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