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Evaluations of Mixed Wood Sawdust from Igbinedion Sawmill, Okada, Edo State, as Potential Feedstock in Biomass Pyrolysis

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ABTRACT

Sawdust (or wood dust) is a by-product in the wood processing industries. Sawdust can cause environmental pollution concern, though it is not without practical uses. For modern interest, biomass (sawdust) is converted to clean fuels which curbs environmental pollution. Its possible use as feed in thermochemical process solves waste management concerns and simultaneously improves the country's energy-mix. The characteristics of the biomass affect the conversion of biomass into bio-energy. Biomass analyses result can improve our understanding of the economics and environmental impact of biomass conversion process. Proximate analysis gave the moisture, ash, volatile matter and fixed carbon contents as, 6.93, 2.03, 38.5 and 52.54 wt %, respectively. Ultimate analysis gave the carbon, oxygen, nitrogen, and hydrogen and sulphur contents as, 61.5, 29.52, 0.67, 7.68 and 0.63 wt %, respectively. While chemical analysis gave the cellulose, hemicellulose and lignin contents as, 68.7, 27.3 and 4.0 wt %, respectively. The higher heating value and lower heating value of the mixed wood sawdust sample are about 25.58 MJ/kg and 24.53 MJ/kg, respectively. Furthermore, the physiochemical analysis of mixed wood sawdust sample revealed the presence of twenty two elements. The organic compounds functional groups present in the mixed wood sawdust sample include aldehydes, alkanes, amines, anhydrides, carboxylic acids, nitro-compounds and primary amines.

Keywords: *Sawdust, Biomass, Thermochemical process, Energy, Environment*

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INTRODUCTION

Existing global supply of energy depends on non-renewable fuels such as crude oil, gas and coal formed naturally beneath the earth's crust. However, the amount of fossil fuel is depleting fast due to the growing population of the world; the consumption of energy per capital also, is increasing rapidly (IEA, 2023). Thus, the necessity for finding alternative sources of energy is evident. In addition, the use of petroleum fuel affects the environment by generating large amounts of carbon dioxide (CO_2) emission and other pollutants such as nitrogen oxides (NO_X) and sulphur oxides (SO_X) (Hu & Gholizadeh, 2019). Biomass meets such requirement, because biomass is carbon-neutral and its use produces less SO_X and NO_X, due to its much lower content of nitrogen and sulphur. Biomass has proven to be an important option for several applications including energy and chemicals production, because it is economically viable and environmentally acceptable (Makepa et al., 2024). For thermochemical conversions (like gasification, pyrolysis and torrefaction), chemical (polymeric) parameters, proximate parameters and ultimate (elemental) parameters are used to evaluate its suitability as feedstock in biomass pyrolysis (Aboelela et al., 2023). Biomass is an organic matter derived from living things.

They include wood, forest residue, and waste from food crops, horticulture, food processing, animal farming and processing, sewage among others (Farhad et al., 2024). Biomass can be changed into a clean fuel by a variety of technologies. In addition to producing clean fuels, these technologies can lead to significant reductions in the total amount of biomass waste requiring final disposal which can be better managed by safe controlled disposal while meeting pollution control standards. Sawdust (or wood dust) is a by-product in the wood processing industries. Sawdust can cause environmental pollution concern, though it is not without practical uses (Onochie et al., 2018), such as producing fuel briquettes or pellets for cooking and other heating purposes. It is also used to make particle board and for wood pulp. For modern interest, biomass (sawdust) is converted to clean fuels which curbs environmental pollution. Its possible use as feed in thermochemical process solves waste management concerns and simultaneously improves the country's energy-mix. In the literature (Vuppaladadiyam et al., 2019; Ali et al., 2020) the values for these parameters vary (probably due to the source and type of the sawdust). The sawdust at a saw mill is mixed-wood sawdust, and it is the most abundant form of sawdust.

The phrase "*mixed-wood*" which qualifies this type of sawdust needs brief explanation. The operations at a saw mill include splitting logs of wood into smaller pieces and planning a piece of wood to a desired shape or size (Oony-Iye et al., 2024). These operations produce sawdust, as by-product. But a saw mill processes wood from a variety of trees, so the sawdust at a saw mill is mixed (not by conscious design but as a consequence of its mode of operation). Cellulose, hemicelluloses and lignin are the three main components of lignocellulosic biomass (to which mixed wood sawdust belongs). Furthermore, biomass also contains other organic compounds, called extractives (which are non-structural compounds), including paraffin, fat, resin, tannin, starch, pigments, etc. (Chen et al., 2012).

There are also a number of inorganic metal salts, consisting mainly of alkali and alkaline earth metals. The physical and chemical properties of biomass are closely related to the composition and relative content of cellulose, hemicellulose and lignin, as well as extractives and inorganic salts. Cellulose is a linear polysaccharide (that is, a complex carbohydrate), consisting of 3000 or more glucose unit linked together by β (1→4) glucosidic bonds. Hemicelluloses are branched heterpolymers with monomers units that include pentose (arabinose and xylose), hexose (glucose, galactose, mannose, rhamnose and fructose) and uronic acids (galacturonic, glucuronic and methylglucuronic) (Partiama, 2018; Cheng, 2010). Lignins are amorphous, complex, aromatic polymers of phenylpropane units (Rowell, 2005). The building blocks of lignin biosynthesis are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Extractives are a group of low-molecular-weight organic compounds that do not constitute cell walls or layers (Wang & Luo, 2017).

The inorganic content of a wood is usually referred to as its ash content, which is an approximate measure of mineral salts and other inorganic matter in the ash of biomass, whose content and composition vary with the type of biomass. The characteristics of the biomass affect the conversion of biomass into bio-energy. It is important to know the characteristics of biomass, to maximise its value in the bio-energy field. Biomass analyses results can improve our understanding of the economics and environmental impact of biomass conversion processes. Proximate analysis gives the gross composition of lignocellulosic biomass in terms of gross components, namely, moisture content (MC), volatile matter (VM), ash (ASH) and fixed carbon (FC) (Basu, 2013). The ultimate analysis of biomass gives the basic elements present in the organic component of the biomass in terms of carbon (C), oxygen (O), hydrogen (H), nitrogen (N) and sulphur (S) (Basu, 2013). (Ash content may also be determined.) With the per centages of carbon, hydrogen and oxygen in a biomass we can calculate the hydrogen-to-carbon (H/C) ratio and oxygen-to-carbon (O/C) ratio. These atomic ratios help us understand the heating value of the biomass. Chemical analysis (also called polymeric analysis) gives the per centages (or fractions) of extractives, cellulose, hemicelluloses and lignin in a biomass sample (Basu, 2013). The behaviour of a biomass during pyrolysis can be predicted using knowledge of the ratios (cellulose-to-lignin and hemicellulose-to-lignin) of the lignocellulose biomass components. Heating value represents the heat released during the complete combustion of a biomass, determined by burning the sample in a controlled environment. Heating value is expressed in KJ/kg (or MJ/kg) and may be referred to the wet basis, dry basis or ash-free basis (Zhao et al., 2024). Heating value is classified as higher heating value (HHV) or lower heating value (LHV) depending on whether the water from the combustion process is considered in liquid or vapour phase. Heating value is a basic parameter that indicates the energy potential of a biomass. For FTIR analysis, the commonly used wavenumber region for infrared absorption spectroscopy is 4000 to 400 cm^{-1} because the absorption radiation of most organic compounds, inorganic compounds and ions is within this region (Smith, 1996). X-ray fluorescence is a non-destructive method for the elemental analysis of solids and liquids. The sample is irradiated by an intense x-ray beam, which causes the emission of fluorescent x-rays. The wavelengths of the emitted x-rays are used to identify elements present in the sample while the concentrations of the elements are determined by the intensity of the x-rays (Kazuhiko, 2023). The aim of the study is to evaluate the potential of sawdust from Igbinedion University sawmill as biomass pyrolysis feedstock.

MATERIALS AND METHODS

The sawdust was taken from Igbinedion Sawmill Okada,

Edo State using a 10kg bag. The collected sawdust was sun-dried by spreading it on a nylon sheet 7 hours a day, for 5 days. This procedure exposes the sawdust to air and sun to remove moisture. 1kg of the sundried was ground and sieved through a 500µm sieve. Samples of the fine sawdust powder were then analysed following approved methods (methods of the American Society for Testing and Materials (ASTM), the International Organization for Standard (ISO) and others) for its physiochemical characteristics.

Proximate analysis procedure

The following procedures have been performed on the samples for proximate analysis. These procedures are as given in Basu (2013).

Moisture content

Moisture content was determined in an air-tight oven. A quantity of the powdered sample was placed in an evaporating dish and was subjected to a temperature of 105 − 110˚ C for 3 hours in the absence of air, until a constant weight was attained. The weight per cent of moisture content (MC) was estimated thus:

$$MC = \frac{M_i - M_f}{M_i} \times 100 \quad (1)$$

Where M_i is the initial mass and M_f is the final mass.

Volatile matter content

Volatile matter is the material that is driven off when biomass is heated to a high temperature in the absence of air under specified conditions. A quantity of powdered sample of the sawdust was weighed and covered in a 50 ml platinum crucible. The sample was subjected to a temperature of 500˚C in a muffle furnace for 7 minutes. The weight per cent of volatile matter (VM) content was estimated thus:

$$VM = \frac{M_i - M_f}{M_i} \times 100 \quad (2)$$

Where M_f is the mass after volatile matter is removed, and M_i is the initial mass of sample.

Ash content

A quantity of powdered sample was weighed into a platinum crucible and subjected to a temperature of 600˚C in a muffle furnace for about 2 hours. The furnace was then switched off and the sample was left inside for about 60 minutes for the temperature to drop, it was then Removed and placed in a desiccator where the was allowed to drop to ambient temperature. The weight per cent of ash content (ASH) was estimated thus:

$$ASH = \frac{Mass\ of\ Ash}{Mass\ of\ Sample} \times 100 \quad (3)$$

Fixed carbon content

The fixed carbon content of a sample is the carbon found in the sample after volatile materials are driven off. This differs from the ultimate (or total) carbon content of a sample because some carbon is lost in hydrocarbons with the volatiles. The weight per cent of fixed carbon content (FC) was estimated thus:

$$FC = 100 - (MC + VM + ASH) \quad (4)$$

where *MC* is the moisture content, *VM* is the volatile matter and *ASH* is the ash content, in weight per cents. After the weight per cent of fixed carbon content has been calculated, it is necessary to cross check the sum of *ASH, FC, MC* and *VM* if it will total 100.

Ultimate analysis procedure

The following procedures have been performed on the sample for ultimate analysis. These procedures are as given in Onochie et al., (2018).

Hydrogen content

A quantity of powdered sample was measured, put into a 100 ml evaporating dish, placed in an air-tight oven and heated. The weight of moisture driven off was noted. The weight per cent of hydrogen content was estimated thus:

$$Hydrogen\ \ content = \frac{weight\ of\ H_2O \times 0.1111 \times 100}{mass\ of\ sample} \quad (5)$$

Nitrogen content

Nitrogen content was determined by Kjeldahi method. A quantity of powdered sample was measured and turned into a 250 ml conical flask and 5 g of copper (II) sulphate ($CuSO_4$) added as catalyst with 20 ml of hydrogen (II) tetraoxosulphate (VI) acid (H_2SO_4). The mixture was swirled gently, placed on a hot plate and warmed for several minutes until a clear solution was obtained. It was cooled and diluted with 100 ml of distilled water. The content was stirred with a glass rod and transferred into a 500 ml flat bottom flask and connected to a distillation unit and a conical flask containing 25 ml of 4 % boric acid solution was attached to the condenser outlet. 50 ml of 40 % sodium hydroxide (NaOH) was carefully dispensed

into the flask containing the sample and distillation was carried out for 10 minutes. The ammonium borate solution formed was titrated with 0.1 M of hydrochloric (HCl) acid solution to get a purplish-grey end point using methyl red indicator. The weight per cent of nitrogen content was estimated thus:

$$Nitogen\ content = \frac{(S-B)\times N\times 1.4007}{w} \quad (6)$$

where N is the normality of acid, S is the titre value of sample, B is the titre value of blank, and w is the mass of sample digested.

Sulphur content

6 ml of bromine water was added to a quantity of the sample in a 500 ml capped beaker. After 10 minutes of heating, 15 cc of concentrated nitric acid was added. The mixture was heated slowly and then boiled to remove bromine and nitric acid after the strong reaction. After adding 2.5 g of sodium chloride (NaCl) to prevent sulphuric acid loss, the mixture was evaporated to half its content. Evaporation was repeated three times; after each evaporation 5 ml of strong hydrochloric (HCl) acid was added, allowed to dry and heated gradually. The residue was taken up with 5 ml of weak hydrochloric acid and 10 ml of water, and the insoluble residue was filtered using a Whatman filter and washed on filter paper with hot water. In a 500 ml volumetric flask, the filtrate was diluted and mixed. 100 ml of aliquot was measured and poured into a beaker, heated to boiling point, then 100 ml of barium chloride ($BaCl_2$) solution was added drop-by-drop with steady stirring. After stirring, the solution was filtered and calcined at 700˚C in a crucible with a muffle furnace. The residue (barium sulphate, $BaSO_4$) was washed clean of chlorides with boiling water, dried and weighed. The weight per cent of sulphur content was estimated thus:

$$Sulphur\ content = \frac{0.1374\times M_1}{M}\times 100 \quad (7)$$

where M_1 is the mass of barium sulphate insoluble residue, and M is the initial mass of the sample.

Carbon content

Carbonisation method was used to determine the carbon content of the powdered sample. A quantity of powdered sample was weighed and turned into a 100 ml crucible and placed into a muffle furnace set to heat at 400˚C and allowed to carbonize for 60 minutes. The crucible was placed in a desiccator until the temperature reduced to ambient temperature. Then the mass of the residue was weighed and recorded. The weight per cent of carbon content was estimated thus;

$$Carbon\ content = \frac{M_s - M_c}{M_s}\times 100 \quad (8)$$

where M_s is the initial mass and M_c is the final mass.

Oxygen content

Oxygen content was estimated by difference using the equation:

$$Oxygen\ content = 100 - (C + H + N + S + ASH) \quad (9)$$

where C is the carbon content, H is the hydrogen content, N is the nitrogen content, S is the sulphur content, and ASH is the ash content in weight per cents. After the per centage of the oxygen has been calculated, it is necessary to check that the sum of *ASH, C, H, N, O* and *S* is 100.

Chemical analysis procedure

The following procedure has been performed on the sample for chemical analysis. The procedure is as given in Carrier et al., (2011). To remove the hemicellulose content, a quantity of mixed wood sawdust sample was heated at 100˚C with 500ml of 0.5M sodium hydroxide (NaOH) solution for 2 hours and the residue which is the cellulose and lignin content was filtered and washed with plenty amount of distilled water until pH 7 was obtained. The residue was dried in an oven at 105˚C to completely remove water and weighed. The mass of hemicelluloses is obtained by difference. The lignin content was removed from the dried residue by boiling the residue in 250ml 0.1M hydrogen (II) tetraoxosulphate (VI) solution (H_2SO_4) for 2 hours under reflux and allowed to remain soaked for 24 hours at ambient temperature. The un-dissolved residue (cellulose) was washed with plenty amount of water until pH 7 was attained. The residue was dried at 90˚C for 4 hours, cooled in a desiccator and weighed. The mass of lignin is obtained by difference.
The mass of cellulose was estimated thus:

$$C_m = B_m - H_m - L_m \quad (10)$$

where C_m is the mass of cellulose, B_m is the mass of biomass, L_m is the mass of lignin, and H_m is the mass of hemicellulose. The masses of hemicellulose and lignin were estimated, sequentially, by weight difference.

Predicting heating values

Empirical correlation equations exist for predicting heating values of a fuel. These empirical equations use

proximate analysis data, or ultimate analysis data. The heating values are estimated using any of the correlation equations below (Asadieraghi, 2016; Basu, 2013; Parikah et al., 2005; Silva et al, 2020; Oyebanji et al., 2022):

$$HHV_1 = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211ASH \quad (11)$$

$$HHV_2 = -1.3675 + 0.3137C + 0.7009H + 0.318O \quad (12)$$

$$HHV_3 = 0.3536FC + 0.1559VM - 0.0078ASH \quad (13)$$

$$HHV_4 = 0.6042FC + 0.4083VM + 0.2442ASH + 0.4107MC - 25.20 \quad (14)$$

$$LHV = HHV_4 - \left(\frac{2.442 \times 8.936 \times H}{100}\right) \quad (15)$$

Where *C, H, O, N, S* are weight per cents from ultimate analysis, *MC* is moisture content weight per cent from proximate analysis and *HHV* and *LHV* are, respectively, higher heating value and lower heating value measured in MJ/kg.

FTIR analysis

FTIR analysis of mixed wood sawdust sample was performed using Fourier Transform Infrared (FTIR) Cray 630 Spectroscopy, Agilent Scientific Technologies, CA, USA. The analysis was performed by scanning the sample (that is, mixed wood sawdust) through a wave-number range of 4000 to 400 cm^{-1} to obtain its spectra. The spectra was analysed to identify the organic functional groups in the sample.

XRF analysis

XRF analysis of mixed wood sawdust sample was performed using Energy Dispersive X-Ray Fluorescence ARL QUANT'X EDXRF, Thermo Fisher Scientific, USA. We analysed the graph of energy versus intensity from the XRF experiment to obtain the quantitative and qualitative data on elements present in the sample.

RESULTS AND DISCUSSION

Proximate analysis

Proximate analysis is used to explore fuel quality and is a good indicator of the burning and heating properties of solid biomass (Varma & Mondal, 2016). The proximate analysis of the mixed wood sawdust sample is shown in (Table 1). Elehinafe et al. (2019) report the result on proximate analysis of a hundred Nigerian woods.

Table 1 Proximate analysis of mixed wood sawdust

ASH	MC	FC	VM
2.03	6.93	52.54	38.50

Their study gives the range for values of ash, moisture, fixed carbon and volatile matter to be 0.08 – 5.09, 7.92 – 15.96, 77.51 – 93.59 and 9.58 – 18.44, wt %, respectively. A significant observation from their report is that for all the 100 Nigerian woods they studied, the weight per cent of fixed carbon is greater than that of volatile matter. We note that the proximate analysis result in this study, also, shows this feature. Also, our values for ash (2.03 wt %) and moisture (6.93 wt %) lie within the range given by Elehinafe et al. (2019).

However, it is important to mention that the observation of the weight per cent of fixed carbon being greater than that of volatile matter may be a feature of Nigerian woods, only. Sharma and Mohanty (2021) working in India report proximate analysis data of mango (*Mangifera indica*) wood with the weight per cent of the fixed carbon less than that of volatile matter, while for the same wood Elehinafe et al. (2019) report the opposite.

The mixed wood sawdust sample shows high volatile matter content (38.50 wt %), which indicates the suitability of sawdust to be devolatilized and to give high bio-oil yield (Ali et al., 2020). Volatile matter represents the constituents of hydrogen, oxygen and carbon present in a solid biomass that when heated changes to vapour, usually a mixtures of hydrocarbons (Chaney, 2010). Volatile matter content affects the thermal characteristic of solid fuels (Van & Koppejan, 2008) and influences the structure and bond within the solid fuel.

Ash content of 2.03 wt % is low, and this is favourable for pyrolysis process. Low ash content in biomass favours thermochemical conversion processes and reduces slag formation problems, fouling and corrosion in pyrolysis reactors (Ali et al., 2020; Czajczynska et al., 2017). Moisture content of 6.93 wt % is low, and within the range of 7.92-15.96 wt % reported by Elehinafe et al. (2019). Aina et al. (2009) reports that low moisture content implies a high calorific value, which is a major parameter that determines solid bio-fuel quality. Moisture content affects the internal temperature history and total energy that is needed to bring the solid up to the pyrolytic temperature (Zaror & Pyle, 1982). Low moisture content means that water in biomass can be removed with small energy expenditure during a thermochemical process.

The fixed carbon content of 52.54 wt %, is high compared to that of some (Nigerian) coal species which range between 20.0 − 46.3 wt% (Ugwu, 2012; Obernberger et al., 2018). The fixed carbon content of a fuel is the per centage of carbon available for char formation (Elehinafe et al., 2019). From this study, we can say that the mixed wood sawdust sample stores chemical energy more in form of fixed carbon than volatile matter. The value for fixed carbon gives a rough estimate of the

heating value of fuel. Also, fuels of with high fixed carbon content are more reactive and much easier to ignite and burn (Lewandowski & Kicherer, 2010).

Ultimate analysis

Table 2 Ultimate analysis of mixed wood sawdust

C	H	N	S	O
61.5	4.80	0.67	0.63	30.37

The ultimate analysis of the mixed wood sawdust sample is shown in (Table 2). It is observed that the values are of same order of magnitude, though our value for elemental carbon (61.5%) is slightly higher (which is consistent with the high fixed carbon content).The results show that nitrogen (0.67 wt %) and sulphur (0.63 wt %) contents are low. So the mixed wood sawdust sample contains low amount of sulphur oxides (SO_X) and nitrogen oxides (NO_X) which corresponds to low pollutant effect of the biomass (Ali et al., 2020). Though our biomass sample is mixed wood sawdust, we include an empirical formula for it. To do this we calculate the atomic ratios H/C, O/C, and N/C using ultimate analysis data, obtaining approximately 0.494, 0.078, and 0.011, respectively, for O/C, H/C, and N/C. Thus, the empirical formula for our mixed wood sawdust may be written as $CH_{0.078}O_{0.494}N_{0.011}$.

Chemical analysis

Table 3 Chemical analysis of mixed wood sawdust

Hemicelluloses	Lignin	Cellulose	Extractives
27.3	4.0	68.7	-

The chemical analysis result of the mixed wood sawdust sample is shown in (Table 3). The result from this study replicates the common trend in the relative values, in wt %, of various lignocellulosic components: cellulose > hemicelluloses > lignin (Vuppaladadiyam et al., 2019; Guida et al., 2019; Sharma & Mohanty, 2021). The result from this study show a slightly higher amount of cellulose and a much lower amount of lignin, compared to published results in the literature (though, it should be remembered that this study used mixed wood sawdust). Ordinarily, one expects the extractives fraction to be included in the result. Guida et al. (2019) and Zanzi (2001) report a similar polymeric components distribution (with nil for extractives).

Table 4 Heating values from correlation (in MJ/kg)

HHV_1	HHV_2	HHV_3	HHV_4	LHV
23.99	22.25	24.55	25.58	24.53

Predicted heating values

The heating values calculated using correlation equations (3.10) to (3.14) for higher heating value (HHV) and lower heating value (LHV) are given in (Table 4). Overall, the predicted values for higher heating value from the different correlation equations are of same order of magnitude, and can be said to give an acceptable estimate of an average higher heating value 24.09 MJ/kg for our mixed wood sawdust sample. Though, we note that the higher heating values predicted by equations that use proximate analysis data (HHV_3 and HHV_4) are slightly greater than those predicted by equations that use ultimate analysis data (HHV_1 and HHV_2). Experimental results of higher heating values of wood sawdust reported in the published literature range from 14.89 – 21.051 MJ/kg (Tillman, 1978; Nyombi et al., 2018; Ali et al., 2020; Silva et al., 2020; Tabal et al., 2021; Sharma & Mohanty, 2021). We observe that the predicated average higher heating value (24.09 MJ/kg) in this study is greater than most of the experimental values reported in the literature.

FTIR analysis

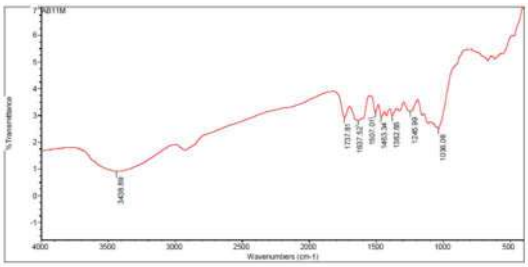


Figure 1 The FTIR analysis of mixed wood sawdust

The Fourier transform infrared (FTIR) analysis is used to identify the organic compound functional groups and chemical bonds present in the mixed wood sawdust sample. Figure 1 shows the FTIR wave number versus transmittance plot from the analysis of the mixed wood sawdust sample, including the wavenumber peaks.

Table 5: Wavenumber bands, wavenumber peaks, vibrations and function groups

Wavenumber band (cm^{-1})	Wavenumber peak (cm^{-1})	Vibration	Functional group
3500 – 3400	3438.89	N – H (stretch)	Primary Amine
1740 – 1720	1737.81	C = O (stretch)	Aldehyde
1760	1637.52	C = O (stretch)	Carboxylic acid
1550 - 1500	1507.01	N – O (stretch)	Nitro compounds
1465	1463.34	C – H (bend)	Alkane
1385 – 1380	1382.65	C – H (bend)	Alkane
1250 – 1020	1245.99	C – N (stretch)	Amine
1050 – 1040	1036.08	CO – O – CO (stretch)	Anhydride

Table 5 lists the functional groups identified as aldehyde, alkane, amine, primary amine, anhydride, carboxylic acid, nitro-compounds, and possibly alcohol. Some of these groups were also identified by Ali et al. (2020) in a mixed wood sawdust sample.

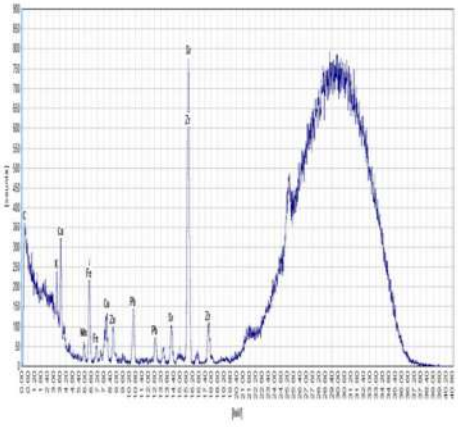


Figure 2 The XRF analysis of mixed wood sawdust

Table 6 Elements identified in sample and their concentrations

Element	Concentration (%)
Iron (Fe)	0.02293
Copper (Cu)	0.000503
Nickel (Ni)	0.00496
Zinc (Zn)	0.003261
Aluminium (Al)	0.02198
Magnesium (Mg)	0.02149
Sodium (Na)	0.00762
Sulphur (S)	0.08036
Phosphorus (P)	0.08377
Calcium (Ca)	0.5934
Potassium (K)	0.28334
Manganese (Mn)	0.008679
Rubidium (Rb)	0.000598
Strontium (Sr)	0.001164
Bromine (Br)	0.00017
Chlorine (Cl)	0.01526
Chromium (Cr)	0.000502
Tungsten (W)	0.0307
Tin (Sn)	0.34
Niobium (Nb)	0.0140
Tantalum (Ta)	0.00867
Lead (Pb)	0.720

XRF analysis

X-ray fluorescence (XRF) is a non-destructive analytical method that uses x-ray to identify the elemental composition of a material (including biomass). The fluorescence emitted from the excited material produces a unique 'fingerprint' that can be used to analyse the chemical composition of the material (Revenko & Pashkova, 2023). From the XRF analysis two data sets were generated, a qualitative data which shows the elements present in the mixed wood sawdust sample and a quantitative data which not only shows the elements present but also their quantities (concentrations). Figure 2 is the graphical output from the XRF analysis, and (Table 6) lists the elements identified and their concentrations. From the XRF analysis of the mixed wood sawdust sample, twenty two (22) elements where identified, namely; Iron (Fe), Copper (Cu), Calcium (Ca), Potassium (K), Zinc (Zn), Nickel (Ni), Aluminium (Al), Magnesium (Mg), Sodium (Na), Sulphur (S), Phosphorus (P), Manganese (Mn), Rubidium (Rb), Strontium (Sr), Bromine (Br), Chlorine (Cl), Chromium (Cr), Tungsten (W), Tin (Sn), , Niobium (Nb), Tantalum (Ta), and Lead (Pb). The elements identified in the mixed wood sawdust sample may be grouped as major (concentration ≥ 0.01 %), minor (concentration between 0.01 – 0.001 %) and trace (concentration < 0.001 %) based on their concentrations. From the concentration ranges, we found the following: trace elements (Br, Cr, Cu); minor elements (Ta, Ni, Zn, Na, Mn, Rb, Sr); and major elements (Fe, Al, Mg, S, P, Ca, K, Cl, W, Sn, Nb, Pd). The elements can be grouped as: Transition metals (Fe, Cu, Ni, Zn, Mn, Cr, Ta, W, Nb); Alkaline earth metals (Mg, Ca, Sr); Alkali metals (Na, K, Rb); Other metals (Al, Pb, Sn); Halogens (Br, Cl); and Non-metals (S, P,) in light of the groupings in the periodic table. The elements shown in the XRF analysis of the mixed wood sawdust sample are the inorganic content, and are indicative of the mineral salts and inorganic matter present. The mineral salts and inorganic matter constitute the ash fraction of the mixed wood sawdust (Oony-Iye et al., 2024). Their total concentration is about 2.27 %, which compares well with ash content (2.03 wt %) in proximate analysis, in this study. These mineral salts probably exist in the wood as oxalates, carbonates, sulphates, phosphates, chlorides and bromides or bound to carboxyl groups in pectic materials (Hon & Shirashi, 1991).

Calcium, magnesium, potassium and lead make up about 71% of the inorganic matter (in the mixed wood sawdust sample) which compares well with the 80% contribution of calcium, magnesium and potassium in ash of wood given in Rowell (2005). The concentration of lead (0.72%) in this study is significantly high and about 31.7% of the total inorganic content. This maybe likely connected to the prevalence of crude oil related human activities in the Niger Delta Region of Nigeria.

Some of these elements are essential for wood growth. Inorganic ions are absorbed into the tree through the roots and transported throughout the tree. Young & Guinn (1966) determined the distribution of 12 inorganic elements in various parts of a tree (roots, bark, wood, and leaves) and concluded that the total inorganic content and concentration of each element varied widely both within and between species. The inorganic content varies depending on the environmental conditions in which a tree lives.

Conclusion

The mixed wood sawdust sample has cellulose, hemicellulose and lignin weight per cents 68.7, 27.3 and 4.0, respectively. The weight per cents of carbon, hydrogen, oxygen, nitrogen and sulphur are, respectively, 61.5, 7.68, 29.52, 0.67 and 0.63. While its ash content, fixed carbon, moisture content and volatile matter content are, respectively, 2.03, 52.54, 6.93 and 38.5 weight per cents. The mixed wood sawdust sample has fixed carbon

content greater than its volatile matter content. This finding corroborates the result on 100 Nigerian woods, and seems to be a feature peculiar to Nigerian woods. The higher heating value and lower heating value of the mixed wood sawdust sample are about 25.58 MJ/kg and 24.53 MJ/kg, respectively. Furthermore, the physiochemical analysis of mixed wood sawdust sample revealed the presence of twenty two elements, with iron, magnesium, aluminium, calcium, potassium, tungsten, tin, niobium, lead, chlorine, sulphur, and phosphorus in significant concentrations. The concentration of lead (0.72 %) is much higher than expected. The organic compounds functional groups present in the mixed wood sawdust sample include aldehydes, alkanes, amines, anhydrides, carboxylic acids, nitro-compounds and primary amines. A relatively high concentration of lead in the mixed wood sawdust sample. This may be connected with the prevalence of petroleum industries in the Niger Delta Region, and it is indicative of soil pollution by petroleum industry activities.

The mixed wood sawdust sample has fixed carbon content greater than its volatile matter content. This finding corroborates the result on 100 Nigerian woods, and seems to be a feature peculiar to Nigerian woods.

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