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Research Article

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Physicochemical Assessment, Pyrolysis and Thermal Characterization of Albizia Zygia Tree Sawdust

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Abstract
Standard methods were used to obtain proximate and ultimate parameters of Albizia zygia tree sawdust. The HHV of 16.01 MJ/Kg, H/C of 0.127, O/C of 0.96, high volatile matter of 87.85 wt.% and low ash content of 1.55 wt.% Albizia zygia sawdust makes it a good biofuel. Its empirical formula from elemental ratios combination is $CH_{0.127}O_{0.96}N_{0.057}$. There were insignificant volumes of oxides of nitrogen and sulphur produced during its pyrolysis since %N & %S are relatively low (2.63 & 0) wt.% respectively. Its TG/DTG profile showed devolatilization of sawdust began at 230 °C and the pyrolysis temperature was in the range of 420-600 °C. Its fixed bed pyrolysis recorded maximum value of bio-oil at 450 °C. FTIR analysis confirmed the presence of oxygenated compounds in the sawdust and its crude bio-oil. The analysis of the obtained bio-oil using GC-FID showed that significant quantity of -OH compounds were produced from the sawdust through pyrolysis though the obtained quantity is not economical. Sintering and slagging-fouling indicators such as; $[Na_2O + K_2O] / [SiO_2]= 0.0695$ showed (unlikely sintering inclination); Base/Acid=0.438 (low ash deposition tendency); $[SiO_2]/([Al_2O_3]=5.44$ & $[Fe_2O_3] / [CaO]=0.28$ (low ash deposition tendencies respectively); slagging viscosity index= 68.58 (low slagging tendency); $\%(SiO_2)=55.18$ (high); Babcock (Rs)= $4.38x\ 10^{-5}$ & Fouling indices (Fu)= $1.68x10^{-2}$ (low deposition tendencies); Total alkalis (TA) =0.0097 (Low fouling tendency). It can be projected that improvement on pyrolysis process parameters and pre-treatment of sawdust can be used to achieve higher yield of bio-oil then consequently leading to higher quantity of alcohol compounds.

Keywords: Biomass, Fossil Fuel, Adsorbent, Pyrolysis, Bio-Oil, Biochar

Introduction
The global future demand of energy might become difficult to meet due to the depletion of known fossil fuel reserves with use. Fossil fuel has actually made this modern world possible with its lots of gains but the environmental challenges and political issues associated with its use becomes worrisome as each day passes by. The unstable electricity supply in Nigeria has made her dwellers relied on burning of fossil fuel to power automobiles and generator used in homes and industries which had created a trend of continuous release of greenhouse gases detrimental to the environmental through its impacts [1]. These environmental challenges have called for policies and protocols formulation with the aim to reducing its damaging effect as indicated in climate submission of The United Nation on projected reduction in greenhouse gas emission by 50-80% by 2050 [2]. To actualize this set target, there is an urgent need to shift focus from the use of fossil fuel in energy generation to other renewable energy sources with zero or insignificant environmental consequences.

Albizia zygia belongs to the family Fabaceae, a common deciduous tree in Nigeria with about 9-30m tall with a spreading crown and a well-defined architectural form. Due to its inherent properties and availability in Yoruba land, the wood has made itself a material being used as timber suitable for construction of carpentry, joinery or for reconversion for manufacturing purposes. Wastes from wood milling i.e. sawdust are produced in million tons yearly and are continuously been burnt to reduce land space it occupies and used for domestic cooking through direct combustion. Hence, exploring this waste material for energy generation is preferable to environmental nuisance it constituted. An estimated volume of sawdust generated yearly in Nigeria was about 1.8 Metric Tons [3]. Also, bio-oil can be obtained through pyrolysis of biomass wastes [4]. Bio-oil are rich in oxygenated compounds e.g. ethanol, phenol, methanol etc. Using low molecular weight methanol CH_3OH as fuel in motor-powered vehicle can drastically reduce carbon emission by 81% and adoption of methanol fuel cell for electricity generation can reduce carbon emission t by 32% [5]. Methanol can be assumed to be the most essential component of pyrolytic oil due to its higher heating value suitable as a good alternative to gasoline or diesel fuel. Another well used fuel (C_2H_5OH) Ethanol are obtainable from the pyrolysis of biomass [6]. Kamarudin *et al.*, obtained methanol and ethanol from sawdust root, paddy dregs, rice husk, sugarcane bagasse, cornstalk, peanut skin, treek trunk, bark waste etc [5]. In the study 5.93, 4.36 and 4.22 wt% of methanol were generated from sugarcane bagasse, roots and sawdust respectively. The pyrolytic oil with highest amount of C_2H_5OH 18.44 wt.% is tree trunk waste, bark waste has 9.59 wt.% and corn stalk has 6.07 wt.% of ethanol. Bu et al., used activated carbon as catalyst in the microwave pyrolysis of lignocellulosic Douglas fir to produce phenol (38.9%, phenolic compounds (66.9%) and other alcohols due to significant degradation of lignin which could serve as substitute to fossil fuel in automobile engines [7]. Ogunkanmi et al., pyrolyzed palm kernel shell to obtain bio-oil at varied process parameters with peak area of 38.44% and 17.34% for C_6H_5OH and 2-methoxyphenol, respectively [8]. The percentage of C_6H_5OH, its methoxyl and its derivative are significantly high indicating its suitability to be used as biofuel and could also be deoxygenated to obtain higher-grade biofuel. Zuhdy *et al.*, investigated slow pyrolysis of Tectona Grandis and Albizia Chinensis sawdust with TGA. The research obtained pyrolysis characteristics, including devolatilization profiles and kinetic energy of the biomasses. The results of the study indicated that the mixture of Tectona Grandis and Albizia Chinensis has the highest activation energy value of all pyrolysis samples with 80.79 kJ/mol.

This current study, provided a broader physiochemical analysis and thermal study of Albizia zygia sawdust.

Methodology

Samples Preparation

Albizia zygia sawdust was obtained from a local saw mill in Oye, Ekiti state, Nigeria. The sawdust particle size used in the study was < 100 µm. Sawdust was dried in an oven at 70^0C for 7 days.

Sample Analyses

Proximate and Ultimate Analyses

Moisture content was done in accordance to ASTM E949-88 in an oven at 110 °C for 30 min using approximately 3 g of sawdust [9]. Volatile matter was determined according to ASTM E897-88 [10]. The oven temperature was set and maintained at 950 °C . The ash content was determined according to ASTM E830- 87 [11]. The percentage of fixed carbon was calculated according to ASTM D5681-98a [12]

$$FC=100-(MC+VM+AC)\ \% \qquad (1)$$

Where MC, VM and AC are; moisture content, volatile matter and ash content respectively.

The percentage of (C, H, N, S) and Oxygen present in the sawdust was determined by a LECO CHNS 932 elemental analyzer by placing 1- 2mg of the sample into a silver capsule and then analyzed it. The furnace temperature of the elemental analyzer was maintained at 800 °C, oxygen concentrations was obtained by difference as follows

$$\%O_2 = 100 - (\%C + \%H + \%N + \%S) \qquad (2)$$

Gross and Net heating value (HHV and LHV) were determined using Parr 6400 bomb calorimeter.

An approximately 0.3-0.5g of the sawdust was weighed and placed in a crucible. A cotton thread attached to an ignition wire ignited inside the decomposition chamber where combustion will take place.

Working Principle of the Fixed-Bed Pyrolyzer

This typical biomass pyrolyzer parts is as labelled in Fig 1. etc. The thermal reactor consists of heating chamber where the pyrolysis of Albizia zygia saw dust was carried out. It is surrounded with clay as its refractory material and encased in a steel frame work. It is equipped with a temperature controller and thermocouple for varying and measuring the temperature within the chamber [13]. The condensing unit is the heat exchanger where volatiles generated from the heating chamber is cooled in order to capture the condensable liquid (Bio-oil). It consists of a water reservoir, connecting hoses and a water pump for increasing the water flow rate so as to increase the cooling rate of the condenser. The bio-oil collector is a transparent glass used for the collection of the bio oil produced during the pyrolysis process. It is attached to the exit pipe of the condensing unit which passes through an air tight rubber cork used as its cover. Vacuum pump works to evacuate air and moisture from the gas collectors before each experiment for easy flow of the bio gas. It is equipped with manifold gauges and hose.

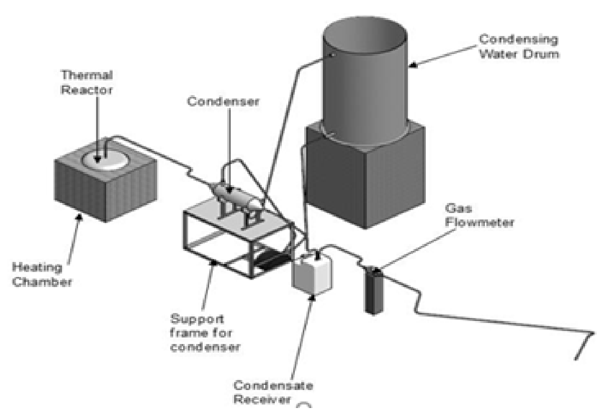

Figure 1: Schematic Representation of Fixed Bed Pyrolyzer

Thermogravimetric Analysis

Pyrolysis characteristics of the sawdust was investigated by TGA in N_2 environment. The instrument used for this purpose was TGA 4000- PERKIN ELMER using Nitrogen as the purge gas (20 mL/min) at 10oC min^{-1} heating rate. TGA recorded initial weight continuously as a function of temperature and time. The derivative (DTG) curve showed the weight loss of sample per unit time against temperature and the exact temperature where an event takes place.

XRF Analysis
X-Thermo ARL Advant XP XRF was used to analyze sawdust ash prepared for XRF analysis by creating a fusion at 1200 °C in a fused glass discs which consisted of 0.5 g of size <106 µm, 5.0 g of flux and 0.05 g LiBr.

Results and Discussion
Proximate and Ultimate Analyses

Table 1: Ultimate and Proximate Analyses of The Sawdust (wt% on air dry basis)

Ultimate Analysis(%)	C	H	N	S	O_2 (by difference) =100%-(%C+%H+%N+S)	O/C <0.6	H/C 1.5-2.0	C/N >30	N/C
	46.48	5.94	2.63	0	44.95	0.96	0.127	17.67	0.0566
Proximate Analysis	MC(%)	VM(%)	FC(%)	AC(%)	HHV(MJ/Kg)				
	7.62	87.85	2.98	1.55	16.01				

Presentations of results of the proximate and ultimate composition of sawdust was on Table 1 which showed high carbon content of 46.48 wt%. High carbon content resulted via de-volatilization process to form biochar and high hydrocarbons. While H value is 5.94 wt%. C and H are major contributors to organic material heating values. Zuhdy *et al.*, reported similar H and C values for Albizia chinensis. The wt% of N is 2.63. Zero Sulphur content was reported for sawdust. Values of % N is not too high although biofuel of low nitrogen (< 2.0%) and sulfur (< 0.2%) is desirable as substitute for fossil fuel because it will pose little or insignificant risk associated with the emission of their toxic oxides during pyrolysis or combustion [14]. The low % (N &S) causes insignificant volume of NO_x and SO_x production during pyrolysis which supports this sawdust material as a potential feedstock. The zero sulphur content mitigates the fear of acid rain from biomass sample pyrolysis or combustion. The ratio H⁄C of 0.127, O/C of 0.967 fall within the range 1.5–2.0 and < 0.6 respectively thereby making the biomass a good alternative to fossil fuel [15]. The H/C of 0.127 sawdust makes this biomass sample good alternatives to fossil fuel. The ratio C/N of sawdust was 17.67 which is less than 30 but C/N ratios exceeding the value of 30 is preferred for thermochemical conversion. Based on the atomic ratios (H/C, N/C and O/C) empirical formulae of albizia zygia sawdust is $CH_{0.127}O_{0.96}N_{0.057.}$

The moisture content of biomass sample used in this study was 7.62 wt.% which is far lesser than 30 wt.% needed to achieve adequate ignition and satisfactory calorific value from the biomass [16]. The volatile matter and ash content were 87.85 wt.% and 1.55 wt.% respectively. Value of ash content reported in this study is similar to Misra *et al.*, Wu *et al.*, and Hussain *et al.*, values of ash content in wood-based and marine-based biomass within the ranges of 0.43–1.82% and 6.46–27.2% respectively [17-19]. High volatile matter and low ash content assist pyrolysis and gasification process to be operated at a lower temperature range of (600-750)^{o}C [20]. Low ash content is a vital parameter in selecting biomass feedstock to avoid slagging, fouling and agglomeration problems. Using the selected biomass sample will not encourage the need to install ash removing system for the pyrolysis system and hence saves capital cost. These high values of volatile matter (87.85 wt.%) and low ash (1.55wt.%) will enhances thermochemical conversion (pyrolysis & gasification) at a lower temperature range of 600–750^{o}C [20]. Higher heating value (HHV) is a measure of stored energy (chemical) in the sawdust. The HHV or the gross calorific value of biomass samples presented in Table 1 was 16.01 MJ/Kg close to reports in studies [21-23]. The range of HHV for different agroforestry species and bio-based industry residues is 14.3 - 25.4 MJ/kg.

Pyrolysis Products Distribution

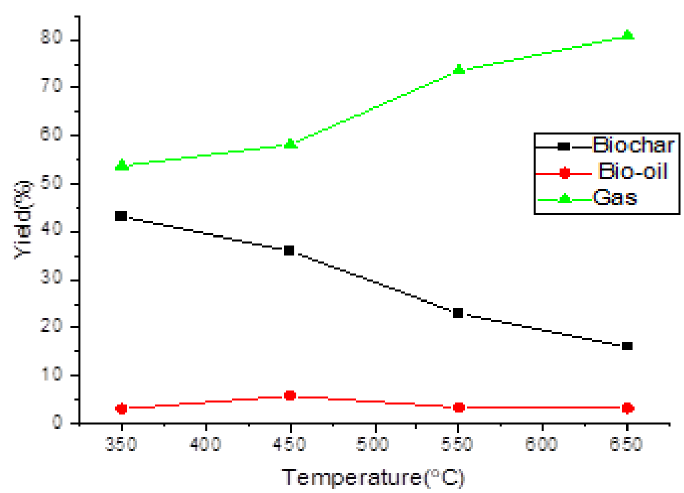

Figure 2: Percentage Yield of Biochar, Bio-Oil and Gas

The lowest temperature chosen for the pyrolysis study was (350 °C), sawdust decomposition was slow due to incomplete carbonization and low devolatilization of raw sawdust with char as the major product. But as the temperature increased from 350 to 450 °C, the amount of bio-oil increased significantly from 3.1-5.84%. Sawdust recorded its maximum value of bio-oil at 450°C. At higher pyrolysis temperatures from 550 °C- 650°C, the bio-oil yield decreased significantly for sawdust similar to results in literature (Hossain et al., 2014 and Uddin et al., 2012).

TG/DTG Analysis

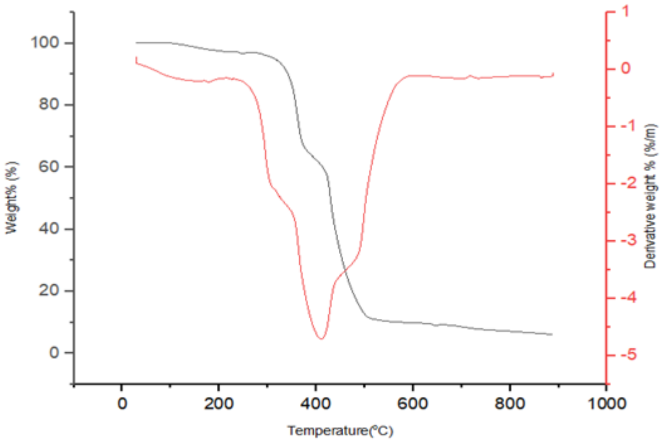

Figure 3: TG/DTG CURVE

Thermal decomposition of sawdust was investigated using nitrogen gas purged TGA 4000- Perkin elmer at a flow rate of 20 mLmin^{-1} and heating rate of 10 °C min^{-1}. Thermogram shown in Fig. 3 is a combined TG/DTG profiles of thermal degradation characteristics of sawdust at the heating rate of 10°C min-1. There are three regions in the pyrolysis of lignocellulosic biomass i.e. at < 120°C marks the removal light volatile materials and bound moisture; the three major components of biomass hemicellulose, cellulose and lignin thermal degradation takes place at (220–315°C); (315–400 °C) and >450°C respectively [24-25]. The decomposition of lignin takes place over a wide temperature region 180–900°C [26]. Fast devolatilization stages were the first two stages which resulted into a large proportion of weight-loss of sawdust as shown in the derivative thermogravimetry (DTG) then the slow lignin degradation was the third stage. The removal of moisture and light volatile matters is followed by second stage which is devolatilization of sawdust at 230°C. The DTG curve of the sawdust during the devolatilization stage showed one distinct peaks. In the evaporation-dehydration stage, the percentage of weight loss was 5.3%. The second stage of weight loss, rapid thermal decomposition, occurred from 120 to 420°C. In the slow thermal decomposition stage (230–500°C), the percentage of weight loss was from 10.0 to 95.0%. The pyrolysis temperature for albizia zygia sawdust is in the range of 420-600°C. Bamboo, sawdust, softwood (average) and hardwood (average) undergone pyrolysis at 400-700°C, 450-600°C, 470-770°C and 470-770°C, respectively [4, 27].

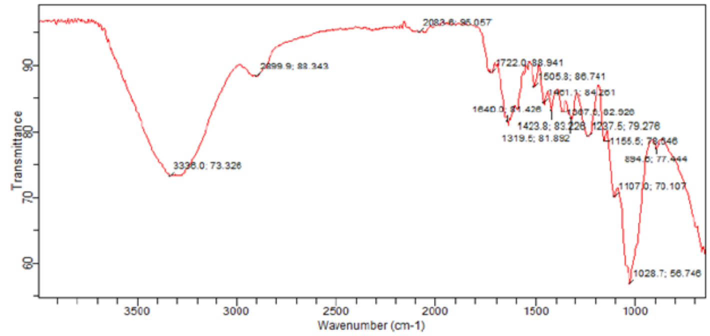

Figure 4a: FTIR Spectra of Sawdust

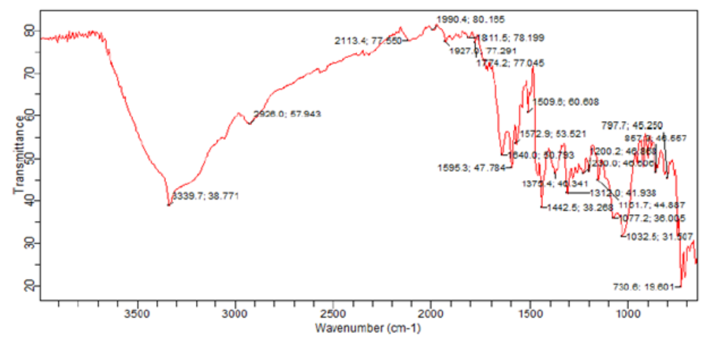

Figure 4b: FTIR Spectra of Sawdust Bio-Oil

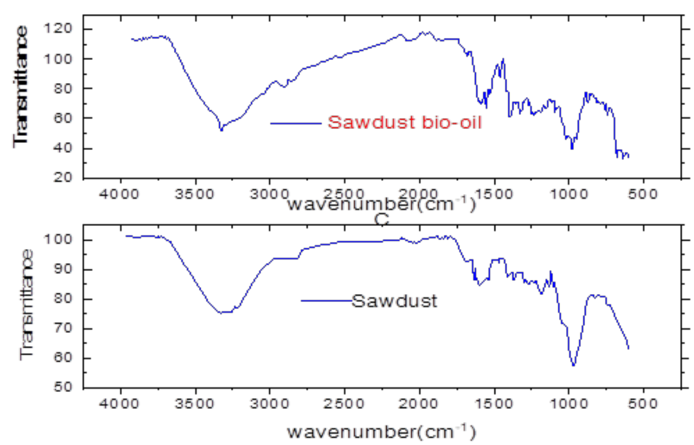

Figure 4c: Spectrum of Sawdust Bio-Oil and Sawdust

Scanning of sawdust bio-oil between 4000-650 cm^{-1} using FTIR spectrometer was done to identify the functional groups present in the sawdust and its bio-oil. The FTIR peaks in sawdust and its bio-oil are almost the same as shown in Fig. 4 a & 4b.

Table 2: FTIR Peaks Analysis of Sawdust Bio-Oil

Sawdust crude bio-oil	Description
857.9	C-H alkynes bends
730.6, 797.7	C-H alkynes bends, C-H phenyl ring substitution bands
1077.2, 1032.5, 1151.7,	C-O-C symmetric stretching
1210, 1200.2	Aromatic C-O stretching
1595.3; 1572	NO_2 Aromatic
1442.5; 1461.1; 1375.4, 1312.0	Aliphatic C-H stretching, alkanes C-H scissoring and bending
1640.0	Aromatic C-C ring stretching, N-H amines
1774.2	Ester C=O stretch
2926.0;	Alkanes/aliphatic C-H stretching
2079.9;2113.4	C≡C alkynes stretching
3339.7	–OH stretching

The GC-FID

A Carle 400 gas chromatograph (GC) with a flame ionization detector (GC-FID) was used to evaluate the bio-oil using $0.5\mu L$ of it and calibrated particularly for -OH compounds.

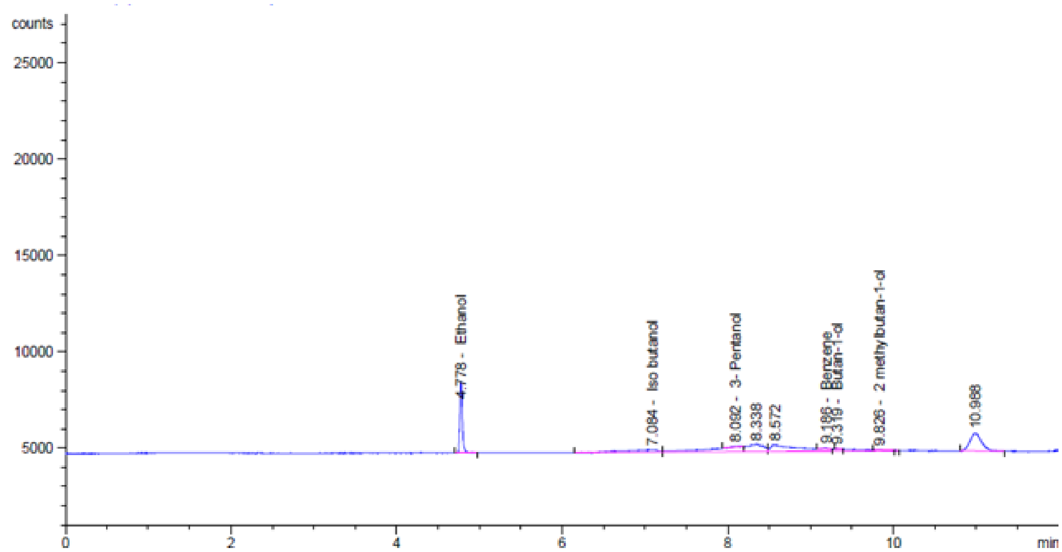

Figure 5: Chromatogram of Bio-Oil

Table 3: GC-FID Data

RetTime (min)	Type	Area Counts*s	Amt/Area	Amount(ppm)	Name
2.200	-	-	-	-	Ethanal
3.107	-	-	-	-	Ethylacetate
3.906	-	-	-	-	propan-2 ol
4.174	-	-	-	-	Methanol
4.778	PB	7958.87354	1.48632e-4	1.18294	Ethanol
5.756	-	-	-	-	Butan-2-ol
6.187	-	-	-	-	Propan-1-ol
7.084	PV	3986.33667	5.33936e-3	21.28448	Iso butanol
8.092	VV f	331.10297	8.68247e-3	2.87479	3-Pentanol
9.186	VV b	187.31616	0.00000	0.00000	Benzene
9.319	VV b	19.79819	1.50014	29.70000	Butan-1-ol
9.826	VV b	96.59114	5.97664e-1	57.72908	2 methylbutan-1-ol
10.118	-	-	-	-	3 methyl butan-1-olol
Total				112.77130	

At different retention time, the following –OH compounds were identified using GC-FID; ethanol, isobutanol, 3-Pentanol, Butan-1-ol, 2-mthylbutan-1-ol and 3-methylbutan-1-olol. Summation of concentration of –OH compounds is 112.77130 ppm. So, in an 0.5µL of the bio-oil, the total concentration of alcohol compounds is 112.77130 ppm. Terakado *et al.*, pyrolysed woody biomass to obtain methanol (0.17–0.61 wt.%), Gullu and Demirbas, pyrolyzed soft and hard wood to obtain (1.0–1.7 wt.%) CH_3OH and and Ni *et al.*, obtained bio-oil of 2–5 wt.% CH_3OH from wood [4, 28, 29]. Galindo and Badr, obtained 1.2 kg methanol/kg of dry forestry biomass and Nakagawa *et al.*, reported 36–55% of methanol via gasification of agricultural wastes [30, 31]. Although the concentration of –OH compounds produced in this current study was at low value, it can be projected that improvement on pyrolysis process parameters and pre-treatment of sawdust can be used to achieve higher yield of alcohol.

XRF Analysis

Table 4: X-Ray Fluorescence Analysis (XRF) of Biomass Ash

Compounds	Sawdust (%)
SiO_2	55.18
Al_2O_3	10.13
Fe_2O_3	5.17
CaO	17.96
MgO	2.15
SO_3	0.41
K_2O	3.75
Na_2O	0.09
Mn_2O_5	0.20
P_2O_5	1.86
TiO_2	1.17
LOI	0.44
TOTAL	**98.51**

The chemical composition of the ash was as represented in Table 4 above. The result showed percentage of elements in their oxides form. The ash contains mainly SiO_2 55.18 wt%. Decreasing order of percentage of oxide is given as: SiO_2>CaO > Al_2O_3> Fe_2O_3> K_2O >MgO>P_20_5 > TiO_2> > SO_3> Mn_2O_5> Na_2O which is similar to report (Sieng-Huat et al., 2019; Garcia-Maraver *et al*., 2017). Chlorine was not detected in the sawdust ash thereby eliminating formation of dioxin and furan emissions during pyrolysis. Sulphur expressed in SO_3 is 0.41 wt% which is not a threatening value.

Table 5: Sintering, Slagging and Fouling Indices

Index	Standard	Sawdust	Ref.
Sintering index = $[Na_2O+ K_2O] / [SiO_2]$	>1 Sintering inclination	0.0695 Sintering inclination unlikely	Sutton *et al.,* 2001 [34].
Sintering index= $[Na_2O + K_2O] / [HHV]$	>0.34 Sintering inclination	0.239 Sintering inclination unlikely	Sutton *et al.,* 2001 [34].
B⁄A=%[MgO+CaO+Na_2 O+ K_2 O+Fe_2 O_3] /%[SiO_2+TiO_2 +Al_2 O_3]	<0.5 Low; 0.5-1 Medium; 1-1.75 High; >1.75 Extremely high	0.438 low deposition tendency	Munir, 2010 [35].
[SiO_2]/[Al_2 O_3]	<0.31 or >3 Low; 0.31-3 High	5.44 low deposition tendency	Carpenter, 1998 [36].
[Fe_2 O_3]/[CaO]	<0.31 or >3 Low; 0.31-3 High	0.28 low deposition tendency	Carpenter, 1998 [36].
Bed Agglomeration index=[Fe_2 O_3]/[Na_2 O+ K_2 O]	<0.15 High	1.34 deposit formation Unlikely	Vamvuka & Zografos, 2004. [37].
Fouling index (Fu) =[OH⁄H^+] .[Na_2 O+ K_2 O]	<0.6 Low; 0.6-40 Medium;>40 High.	1.68×10^{-2}	Bryers, 1996; Pronobis 2005. [38,39].
Slagging viscosity index (Sr) =%[SiO_2] /%[SiO_2+Fe_2 O_3+-CaO+MgO] x 100	>72 Low; 65-72 Medium;<65 High	68.58 High Sr means Low slagging tendency	Pronobis, 2005 [39].
%[SiO_2]	<20 low; 20-25 Medium; >25 High	55.18 High slagging inclination	Ohman *et al.,* 2004 [40].
Babcock index (Rs) =[B⁄A] . S^d	<0.6 Low; 0.6-2 Medium; 2.0-2.6 High	4.38x 10-5 Low deposition tendency	Bryers, 1996; Pronobis 2005; [38, 39].
Total alkalis TA=Na_2 O+ K_2 O	<0.3 Low 0.3<TA <0.4 Medium T_A>0.4 High	0.0097 Low fouling tendency	Carpenter, 1998 [36].

Conclusion

This study demonstrated the potential of albizygia tree sawdust as a source of biofuel. The proximate and ultimate parameters of the sawdust was assessed using standard methods. The HHV of 16.01 MJ/Kg, H/C of 0.127 and O/C of 0.96 make the material a good biofuel. Also, the low % N &S causes insignificant volume of NOx and SOx production during pyrolysis which supports this sawdust material as a potential alternative to fossil fuel. TGA showed three stages of decomposition evaporation-dehydration to remove water and some volatiles molecules, fast thermal decomposition experienced by majorly hemicellulose and cellulose and slow thermal decomposition associated with lignin. The pyrolysis temperature for albizia zygia sawdust is in the range of 420-600°C.

Fixed bed pyrolysis of sawdust recorded its maximum value of bio-oil at 450°C. The FTIR confirmed present of oxygenated compounds in sawdust and its bio-oil. The analysis of bio-oil using GC-FID showed significant quantity of alcohol compound was produced from albizygia tree sawdust termed waste through pyrolysis though the obtained quantity is not economical.

Sintering and slagging-fouling indicators such as; [Na_2 O+ K_2 O]/[SiO_2]=0.0695 showed (unlikely sintering inclination); Base/Acid=0.438 (low ash deposition tendency); [SiO_2]/[Al_2 O_3])=5.44 & [Fe_2 O_3]/[CaO]=0.28 (low ash deposition tendencies respectively); slagging viscosity index= 68.58 (low slagging tendency); %(SiO_2)=55.18 (high); Babcock (Rs)= 4.38×10^{-5} & Fouling indices (Fu)= 1.68x10-2 (low deposition tendencies); Total alkalis (T_A) =0.0097 (Low fouling tendency). It can be projected that improvement on pyrolysis process parameters and pre-treatment of sawdust can be used to achieve higher yield of bio-oil then consequently leading to higher quantity of alcohol compounds.

References

1. Adeoye, A. O., Quadri, R. O., & Lawal, O. S. (2020). Pyrolysis of Biomass as A Suitable Alternative to Fossil Fuel Energy in Nigeria: An Overview. Journal of Wastes and Biomass Management (JWBM), 3(1), 27-30.
2. Bogner, J., Pipatti, R., Hashimoto, S., Diaz, C., Mareckova, K., Diaz, L., ... & Gregory, R. (2008). Mitigation of global

greenhouse gas emissions from waste: conclusions and strategies from the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report. Working Group III (Mitigation). Waste Management & Research, 26(1), 11-32.
3. Sambo, A. S. (2009, October). The place of renewable energy in the Nigerian energy sector. In world future council workshop on renewable energy policies (Vol. 10).
4. Güllü, D., & Demirbaş, A. (2001). Biomass to methanol via pyrolysis process. Energy Conversion and Management, 42(11), 1349-1356.
5. Kamarudin, S. K., Shamsul, N. S., Ghani, J. A., Chia, S. K., Liew, H. S., & Samsudin, A. S. (2013). Production of methanol from biomass waste via pyrolysis. Bioresource technology, 129, 463-468.
6. Hasegawa, F., Yokoyama, S., & Imou, K. (2010). Methanol or ethanol produced from woody biomass: which is more advantageous?. Bioresource Technology, 101(1), S109-S111.
7. Bu, Q., Lei, H., Ren, S., Wang, L., Zhang, Q., Tang, J., & Ruan, R. (2012). Production of phenols and biofuels by catalytic microwave pyrolysis of lignocellulosic biomass. Bioresource technology, 108, 274-279.
8. Ogunkanmi, J. O., Kulla, D. M., Omisanya, N. O., Sumaila, M., Obada, D. O., & Dodoo-Arhin, D. J. C. S. I. T. E. (2018). Extraction of bio-oil during pyrolysis of locally sourced palm kernel shells: Effect of process parameters. Case studies in thermal Engineering, 12, 711-716.
9. ASTM, E. (2003). 989-88, E 790-87 and E897-88. Standard Test Method for Total Moisture in a Refuse-Derived Fuel Laboratory Sample.
10. ASTM, S. (2004). Standard test method for volatile matter in the analysis sample of refuse-derived fuel.
11. ASTM, S. (2004). Standard test method for ash in the analysis sample of refuse-derived fuel.
12. ASTM D5681-98a, 2004. Standard Terminology for Waste and Waste Management.
13. Akinola, A. O., & Vol, T. (2016). Evaluation of the efficiency of a thermochemical reactor for wood pyrolysis. European Journal of Engineering and Technology Vol, 4(4).
14. Ye, G., Luo, H., Ren, Z., Ahmad, M. S., Liu, C. G., Tawab, A., ... & Mehmood, M. A. (2018). Evaluating the bioenergy potential of Chinese Liquor-industry waste through pyrolysis, thermogravimetric, kinetics and evolved gas analyses. Energy Conversion and Management, 163, 13-21.
15. Capunitan, J. A., & Capareda, S. C. (2012). Assessing the potential for biofuel production of corn stover pyrolysis using a pressurized batch reactor. Fuel, 95, 563-572.
16. McKendry, P. (2002). Energy production from biomass (part 3): gasification technologies. Bioresource technology, 83(1), 55-63.
17. Misra, M. K., Ragland, K. W., & Baker, A. J. (1993). Wood ash composition as a function of furnace temperature. Biomass and Bioenergy, 4(2), 103-116.
18. Wu, K., Liu, J., Wu, Y., Chen, Y., Li, Q., Xiao, X., & Yang, M. (2014). Pyrolysis characteristics and kinetics of aquatic biomass using thermogravimetric analyzer. Bioresource technology, 163, 18-25.
19. Hussain, M., Tufa, L. D., Azlan, R. N. A. B. R., Yusup, S., & Zabiri, H. (2016). Steady state simulation studies of gasification system using palm kernel shell. Procedia engineering, 148, 1015-1021.
20. Khan, Z., Yusup, S., Ahmad, M. M., & Rashidi, N. A. (2014). Integrated catalytic adsorption (ICA) steam gasification system for enhanced hydrogen production using palm kernel shell. international journal of hydrogen energy, 39(7), 3286-3293.
21. Okoroigwe, E. C., Saffron, C. M., & Kamdem, P. D. (2014). Characterization of palm kernel shell for materials reinforcement and water treatment. Journal of Chemical Engineering and Materials Science, 5(1), 1-6.
22. Muhammad S., Suzana Y., Angga P., Abrar I., David O.P., Muhammad A. (2016). Parametric Study and Optimization of Methane Production in Biomass Gasification in the Presence of Coal Bottom Ash. Procedia Engineering. 148: 409 – 416
23. Rashid, S. R. M., Saleh, S., & Samad, N. A. F. A. (2017). Proximate analysis and calorific value prediction using linear correlation model for torrefied palm oil wastes. In MATEC Web of Conferences (Vol. 131, p. 04002). EDP Sciences.
24. Sanchez-Silva, L., López-González, D., Villaseñor, J., Sánchez, P., & Valverde, J. L. (2012). Thermogravimetric–mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. Bioresource Technology, 109, 163-172.
25. Yang, H., Yan, R., Chen, H., Lee, D. H., & Zheng, C. (2007). Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel, 86(12-13), 1781-1788.
26. Knoetze, J. H., & Görgens, J. F. (2010). Thomas Johannes Hugo, Pyrolysis of sugarcane bagasse, Department of Process Engineering at the University of Stellenbosch (Doctoral dissertation, Msc Thesis).
27. Güllü, D., & Demirbaş, A. (2001). Biomass to methanol via pyrolysis process. Energy Conversion and Management, 42(11), 1349-1356.
28. Terakado, O., Amano, A., & Hirasawa, M. (2009). Explosive degradation of woody biomass under the presence of metal nitrates. Journal of Analytical and Applied Pyrolysis, 85(1-2), 231-236.
29. Ni, M. J., Xiao, G., Chi, Y., Yan, J. H., Miao, Q., Zhu, W. L., & Cen, K. F. (2006). Study on pyrolysis and gasification of wood in MSW. Journal of Environmental Sciences, 18(2), 407-415.
30. Cifre, P. G., & Badr, O. (2007). Renewable hydrogen utilisation for the production of methanol. Energy conversion and management, 48(2), 519-527.
31. Nakagawa, H., Harada, T., Ichinose, T., Takeno, K., Matsumoto, S., Kobayashi, M., & Sakai, M. (2007). Biomethanol production and CO2 emission reduction from forage grasses, trees, and crop residues. Japan Agricultural Research Quarterly: JARQ, 41(2), 173-180.
32. ieng-Huat, K., Soh Kheang L., Robert, T. B., Haryati, Z., Kah, Y.C. (2019). Palm kernel shell biochar production, char-

acteristics and carbon sequestration potential. Journal of Oil Palm Research https://doi.org/10.21894/jopr.2019.0041
33. Garcia-Maraver, A., Mata-Sanchez, J., Carpio, M., & Perez-Jimenez, J. A. (2017). Critical review of predictive coefficients for biomass ash deposition tendency. Journal of the Energy Institute, 214-228.
34. Sutton, D., Kelleher, B., & Ross, J. R. (2001). Review of literature on catalysts for biomass gasification. Fuel processing technology, 73(3), 155-173.
35. MUNIR, S. (2010). Potential slagging and fouling problems associated with biomass-coal blends in coal-fired boilers. Journal of the Pakistan Institute of Chemical Engineers, 38(1), 1-11.
36. Carpenter, A. M. (1998). Switching to cheaper coals for power generation.
37. Vamvuka, D., & Zografos, D. (2004). Predicting the behaviour of ash from agricultural wastes during combustion. Fuel, 83(14-15), 2051-2057.
38. Bryers, R. W. (1996). Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels. Progress in energy and combustion science, 22(1), 29-120.
39. Pronobis, M. (2005). Evaluation of the influence of biomass co-combustion on boiler furnace slagging by means of fusibility correlations. Biomass and bioenergy, 28(4), 375-383.
40. Öhman, M., Nordin, A., Hedman, H., & Jirjis, R. (2004). Reasons for slagging during stemwood pellet combustion and some measures for prevention. Biomass and bioenergy, 27(6), 597-605.