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Characterization Of Selected Nigerian Indigenous Biomass Wastes For Their Suitability In Biofuel Production.

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Abstract: *This work investigated the properties of ten selected Nigerian indigenous biomass wastes. The biomass wastes investigated were bambaranut shell (BS), bush mango nut shell (BMS), cassava stalk (CS), cocoyam peel (CP), detar shell (DS), empty fruit bunch (EFB), maize stalk (MS), mango seed shell (MSS), sugarcane bagasse (SB), and wild cassava peel (WCP). For comparison, the properties of coal were investigated, and the results obtained compared to those of the biomass wastes. The metal contents of the coal and biomasses were determined using an Atomic Absorption Spectrometer and total sulphur content determined using gravimetric method. Proximate analyses were done using ASTM methods. Calorific value was determined using an Oxygen Bomb calorimeter and Scanning Electron Microscope (SEM) was used to observe the morphology of the coal and the different biomasses. The AAS analyses showed that coal contained higher concentration of metals, Ca (115mg/kg), Fe (63.37mg/kg), Mg (21.15mg/kg), Na (12.64mg/kg), Zn (18.25mg/kg), K (8.10mg/kg), than the biomasses, Ca (21.27mg/kg to 95.56mg/kg), Fe (26.18mg/kg to 46.72mg/kg), Mg (1.47mg/kg to 20.00mg/kg), Na (3.11mg/kg to 9.22mg/kg), Zn (2.75mg/kg to 16.50mg/kg), and K (0.40mg/kg to 1.90mg/kg). Total sulphur content analysis showed 0.6% for coal, and BDL to 0.01% for the biomasses. SEM analyses showed different lignocellulosic structures. Proximate analyses of the materials showed that the moisture content of the biomasses ranged from 6.21 ± 0.13% to 8.81 ± 0.23%, and that of coal 7.76 ± 0.12%, while the ash content of the biomasses ranged from 4.16 ± 0.02% to 6.11 ± 0.00%, and that of coal was 18.06 ± 0.03%. The calorific value of coal was 24.30 ± 0.10MJ/kg, and ranged from 16.73 ± 0.05MJ/kg to 18.90 ± 0.20 MJ/kg for the biomasses. The low sulphur, and ash content, as well as low concentration of the metals in the biomasses presented them as a better fuel than coal, and hence, suitable feedstock for bio-fuel production. The results obtained in this work could be useful to understand the biomass combustion related issues, and also help in finding appropriate energy conversion technologies to effectively utilize the biomass feedstock.*

Keywords: *Biomass, coal, proximate analysis, scanning electron microscope.*

I. Introduction

In line with the annual increase in demand for energy globally, the environmental impacts of the use of fossil fuels and the need for alternative sources of energy supply, there is interest in the use of renewable source of energy to sustain economic development. Biomass is one of the most common and easily accessible renewable energy resources and can serve as a feedstock for bioenergy production. Biomass covers approximately 10% of the global energy supply, of which two-thirds is used in developing countries for cooking and heating (Schill, 2013). Biomass (agricultural residues) is defined as the non product output of production and processing of agricultural products that may contain materials that can benefit man, but whose economic values are less than the cost of collection, transportation and processing for beneficial use (Obi et al., 2016). They are comprised of animal waste (manure, animal droppings, feather, bones, e.t.c), food processing and crop wastes (maize cob, sugarcane bagasse, prunnings, etc). Biomass is considered as playing an important role in mitigating global warming and security fuel supply, as it does not add carbon (iv) oxide to the atmosphere, rather, it absorbs it in growing (Patel and Gami, 2012). Biomass provides liquid fuels (e.g. ethanol and biodiesel) and solid fuels (including charcoal, pellets and briquettes), hence, it can be utilized in different kinds of boilers as well as power generation systems. Presently, the compaction of biomass for use as a source of energy (briquette) is increasing in developing countries. The energy consumption and the quality of final product depend on both the properties (chemical and physical) of the biomass and the briquetting processes employed. Bioenergy, if carefully managed could provide:

a. An even larger contribution to global primary energy supply,
b. Significant reductions in green house gas emissions, and potentially other environmental benefits,
c. Improvements in energy security and trade balances, by substituting imported fuels with domestic biomass,
d. Opportunities for economic and social development in rural communities, and
e. Scope for using waste and residues, reducing waste disposal problems and making better use of resources (Bauen et al., 2016)

Nigeria is a well recognized producer of agricultural and food products. Nigeria's diverse climate, from the tropical areas of the coast to the arid zone of the north made it possible to produce virtually all agricultural products that can be grown in the tropical areas of the world. In Nigeria, millions of tones of various categories of biomasses are generated annually. They are either left to litter the environment or burnt ineffectively in their loose forms, causing environmental pollution. The conversion of the biomass into energy is a good measure to curtail environmental pollution. The price of fossil fuel is also high in Nigeria. These factors may encourage industries to use biomass as fuel. But, large amount of impurities in various biomasses made lot of nuisance to boiler operation. A major problem observed was due to fouling and corrosion of boiler heat exchange surface by deposits (Patel & Gami, 2012). This prevents proper air distribution and lowers combustion efficiency. The deposits stick to the boiler surfaces and cause damages. They also attract expenses due to cost incurred in removing them. Therefore, for effective utilization of biomass fuel for energy production, the knowledge of their characterization is essential. This provides information on concentration and speciation of some elements which are useful for energy and environmental issues, e.g., concentration and speciation of alkali will help to better design biomass power generation system or of heavy metal to assess the potential environmental impacts (Savitri et al., 2006). Information obtained would also help in finding for the biomass suitable and appropriate energy conversion technologies to effectively use biomass feedstock.

In this study, selected Nigerian indigenous biomasses were characterized in order to ascertain their suitability as biomass feedstock. For comparison, coal was characterized as well, and its properties compared to that of the biomass samples. The need to determine the properties of biomass materials available in Nigeria for their effective utilization in bioenergy production necessitated this work.

II. Methodology

Sample collection and preparation:

Onyeama coal (sub-bituminous) was sourced from Nigerian Coal Corporation, Enugu. The biomasses (empty fruit bunch, maize stalk, bush mango nut shell, wild cassava peel, mango seed shell, cocoyam peel, detar shell, cassava stalk, sugarcane bagasse, and bambaranut shell) were obtained from different farming / local communities where they are produced in large quantities, and from different dumpsites at Abakaliki, Ebonyi state. They were oven dried at 70^{o}C for 24hours. The empty fruit bunch, maize stalk, cassava stalk, mango seed shell, and detar shell were cut into very small sizes using a cutlass. This is to enable them to be fed into the milling machine. The biomass wastes were milled using the electrically operated hammer milling machine and the particles sieved using a standard sieve to obtain particles of size 3mm.The coal was broken into smaller pieces using a hammer, and then crushed to fine particles using the electrically operated hammer milling machine. The coal fines obtained were sieved using a standard sieve to obtain coal particles of size 1mm. Plate 1 shows the biomass waste materials.


Bambara groundnut shells.


Bush mango nut shells.


Cassava stalks


Detar shells


Empty fruit bunches


Cocoyam peels

Mangoseed shells Sugarcane bagasse Maize stalks Wild cassava peel.

Plate 1: The biomass materials.

Determination of the metal content of the samples:

Digestion of the samples: The materials were digested following the procedures of Jackson, (2008). Each of the ground samples (2.0g) were weighed into different teflon crucibles. Aqua regia, 10ml (prepared by mixing HCl and HNO_3 in a ratio of 3:1), 10ml of water and 5ml of hydrofluoric acid were added into each crucible. The whole mixture was thoroughly stirred using a spatula. The mixture was put into an oven set at 100^0C for 2hrs, after which the samples got digested. This was transferred into a 200ml volumetric flask and made up to mark.

The digested samples were analyzed for Ca, Fe, Mg, Na, Zn, K, Pb, Cr, P, and Si, using Atomic Absorption spectrophotometer (AAS) Instrument, Buck Scientific Model 210VGP in air acetylene flame type (for all except Al) and nitrous oxide acetylene flame type (for Al) at flame temperature of 2000k.

Determination of total sulphur content of the samples:

The total sulphur content was determined following the procedures of Jackson, (2008). 25ml of the digested sample was measured into a 250ml conical flask. 1ml of concentrated HCl was added, and the mixture shaken thoroughly. The mixture was heated to boil and 20ml of 25% $BaCl_2$ was gradually added into the solution. A precipitate was formed showing the presence of sulphate ions. The solution formed was filtered using a filter paper. The filter paper was rinsed with distilled water and stuffed into a muffle furnace at 700^oC for 30mins, after which the weight of the precipitate was determined. The percentage sulphur in the precipitate was calculated from the expression:

$$\text{Sulphur content (\%)} = \frac{\text{weight of precipitate x 0.137 x 100}}{\text{weight of sample.}}$$

0.137 = gravimetric factor.

Proximate analysis of the samples:

The proximate analysis to measure the moisture, volatile matter, fixed carbon and ash content was performed using ASTM methods as follows:

Moisture content: Moisture content of the materials was determined following the procedures of ASTM E1871-82, (2006). Each 2g sample was carefully measured into different crucibles of known weight and kept in an oven at 105^oC for 2 hours to enable the sample to dry (to constant weight). The beakers were transferred to a desiccator, allowed to cool to room temperature and weighed. The moisture content was calculated using the following formula:

$$Mc\ (\%) = \frac{W_1 - W_2}{W_1} \times 100$$

Mc = moisture content, W_1 = weight of original sample, W_2 = weight of the sample after drying.

Volatile matter: The volatile matter content was determined following the procedures of ASTM E872-82, (2006). The residual dry samples from moisture content determination were weighed and heated at 400^oC in a furnace for 2hrs. The samples were removed from the furnace, cooled and re-weighed. The volatile matter was calculated using:

$$Vm\ (\%) = \frac{W_1 - W_2}{W_2} \times 100$$

W_1 = Weight of the residual dry sample, W_2 = Weight of the sample after cooling.

Ash content: The ash content was determined following the procedures of ASTM E1755- 01,(2007). Each 2.0g dry sample was measured into different crucibles of known weight. The crucibles and their contents were placed in a furnace and heated at 590^oC for 3hrs. The crucibles and their contents were put in a desiccator to cool and then weighed. The ash content was calculated using:

$$Ac\ (\%) = \frac{W_1}{W_2} \times 100$$

Where W_1 = weight of ash.

W_2 = initial weight of the dry sample.

Fixed carbon: The fixed carbon content was determined using the data previously obtained from proximate analysis and according to Garcia et al., (2012), using the formula:

%Fc = 100 – (% Ac + %Vm + % Mc)

Where Ac= ash content, Vm= volatile matter, Mc= moisture content.

Calorific value: The calorific values of the samples were determined using an Oxygen Bomb calorimeter, Model XRY-1A.

Scanning Electron Microscope (SEM) Analysis:

Scanning electron microscope was used to observe the morphology of the materials. The SEM analysis was carried out using Phenom pro X Scanning Electron Microscope, at a voltage of 10kV and magnification of 100µm.

III. Results And Discussion

Metal content concentration of the samples:

Table 1 and Figure 1 showed the metal concentration of the samples.

Table 1: Metal content concentration of the materials.

Metals	Materials										
(mg/kg)	**Coal**	**BS**	**BMS**	**CS**	**CP**	**DS**	**EFB**	**MS**	**MSS**	**SB**	**WCP**
Ca	115	39.04	21.2 7	69.19	31.42	34.63	66.18	95.56	31.72	52.19	61.78
Fe	63.37	45.19	33.24	40.17	31 .15	31.09	34.43	46.72	31.97	26.18	25.76
Mg	21.15	17.15	10.00	18.51	11.15	1.47	20.00	12.12	9.42	10.17	19.14
Na	12.61	3.66	3.11	9.20	3.33	4.31	7.30	7.03	4.64	4.12	9.22
Zn	18.25	7.50	7.75	10.25	13.00	15.11	3.75	16.50	10.50	2.75	12.75
K	8.10	1.03	0.40	1.40	0.74	0.51	1.90	1.46	0.62	1.00	1.40
Pb	0.38	0.01	ND	ND	ND	ND	ND	0.01	ND	ND	ND
Cr	0.30	0.05	ND	ND	ND	0.01	0.01	0.01	0.01	0.01	ND
P	0.59	0.01	0.02	0.01	0.01	0.05	0.00	0.04	0.01	0.01	0.00
Si	5.42	1.51	1.01	2.20	2.01	1.03	2.13	2.03	1.44	1.90	2.20

NB: BS= Bambara groundnut Shell, BMS= Bush Mango nut Shell, CS= Cassava Stalk, CP= Cocoyam Peel, DS= Detar nut Shell, EFB= Empty Fruit Bunch, MS= Maize Stalk, MSS=Mango Seed Shell, SB= Sugarcane Bagasse, WCP= Wild Cassava Peel, ND=Not Detected.

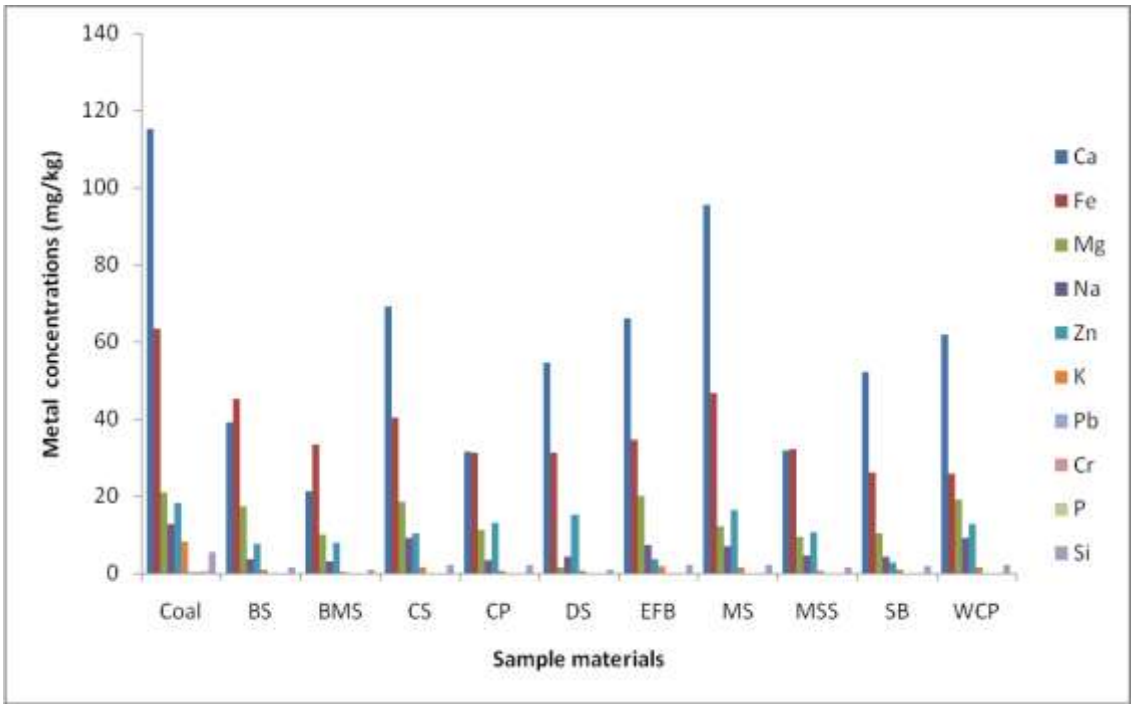

Figure 1: Metal concentrations of the materials.

The results obtained showed that the concentration of Ca for coal was 115mg/kg, while it ranged from 21.27mg/kg (BMS) to 95.56mg/kg (MS) for the biomasses. Fe concentration for coal was 63.37mg/kg, and it ranged from 25.76mg/kg (WCP) to 46.72mg/kg (MS) for the biomasses. The concentration of Mg was

21.15mg/kg for coal, and ranged from 1.47mg/kg (DS) to 20.00mg/kg (EFB) for the biomasses. Na concentration for coal was 12.61mg/kg and ranged from 3.11mg/kg (BMS) to 9.22mg/kg (WCP) for the biomasses. The concentration of Zn was 18.25mg/kg for coal, and ranged from 2.75mg/kg (SB) to 16.50mg/kg (MS) for the biomasses. The concentration of K was 8.10mg/kg for coal, and ranged from 0.40mg/kg (BMS) to 1.90mg/kg (EFB) for the biomasses. The concentration of Pb was 0.38mg/kg for coal, 0.01 for BS and MS, and was not detected in the other biomasses. The concentration of Cr was 0.30mg/kg for coal, 0.01mg/kg for DS, EFB, MS, MSS, SB, 0.05mg/kg for BS and was not detected in the other biomasses. P concentration was 0.59mg/kg for coal, and ranged from 0.01mg/kg to 0.50mg/kg for the biomasses. The concentration of Si was 5.42mg/kg for coal, and ranged from 0.01mg/kg (BMS) to 2.20mg/kg (WCP) for the biomasses.

The concentration of the metals in coal was higher than the concentration of the metals in the biomasses, including the ash forming elements (Si, Ca, K, Fe, Mg, Na, K, and P). During combustion, the ash forming elements would be deposited as ash, since they are not combustible (Maciejewska *et al*., 2006; Patel & Gami, 2012). It is expected that coal would have higher ash content values than the biomasses, since it had higher concentration of these elements.

In general, CS, EFB, MS, and WCP had higher concentration of the metals. It is expected that their ash content would be higher than that of the other biomasses. As reported by Savitri *et al*., (2006), high contents of alkali are known to cause critical technical problems when the biomass is used as feedstock for thermal power production, since they contribute to slagging, fouling, and sintering formation. The biomasses displayed low concentration in Na, Mg, Si, P, and more especially, K, compared to that reported by Savitri *et al*., (2006) . The low concentration of these metals in the biomasses has therefore presented them as suitable feedstock for thermal power production.

Total sulphur content of the samples:

Table 2: Results of total sulphur content of the samples:

Sample materials	Coal	BS	BMS	CS	CP	DS	EFB	MS	MSS	SB	WCP
				Materials							
Sulphur (%)	0.60	0.01	BDL	0.01	BDL	BDL	BDL	BDL	0.01	0.01	0.01

BDL = Below Detection Limit.

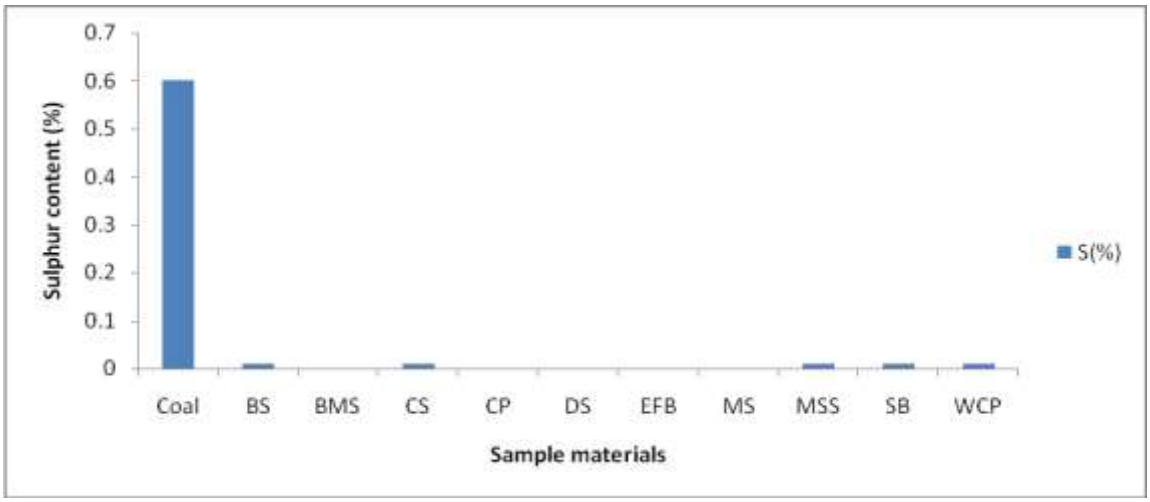

Figure 2: Total sulphur content analysis results.

Table 2 and Figure 2 showed that the total sulphur content of the biomass materials was lower than that of coal. Total sulphur content of the biomasses ranged from BDL to 0.01%, while that of coal was 0.6%. Sulphur in fuels is undesirable because it produces acids of sulphur dioxide and sulphur trioxide which corrodes combustion equipment and also causes environmental pollution. The sulphur content of the biomass is low. This also presents the biomasses as suitable feedstock for bioenergy production. The values obtained for the biomasses are lower than that obtained by Jekayinfa & Omisakin, (2005), 1.06% (palm oil effluent) to 4.86% (mango peel), while that obtained for coal is the same as that obtained by Adekunle et al., (2015), 0.6% for Ogboyaga and Okaba sub-bituminous coal.

Proximate analyses of the materials:

The results of proximate analyses of the materials are shown in Table 3 and Figure 3.

Table 3: Mean proximate analyses results of the materials.

Materials	Mc (%)	Vm (%)	Ac (%)	Fc (%)	Cv (MJ/kg)
Coal	7.76 ± 0.12	43.56 ± 0.38	18.06 ± 0.03	30.65 ± 0.41	24.30 ± 0.10
BS	6.42 ± 0.23	69.31 ± 0.30	4.25 ± 0.05	20.02 ± 0.58	18.90 ± 0.20
BMS	7.22 ± 0.36	70.81 ± 0.23	4.92 ± 0.05	17.05 ± 0.24	17.00 ± 0.34
CS	8.11 ± 0.12	69.87 ± 0.01	5.22 ± 0.26	16.80 ± 0.12	17.00 ± 0.13
CP	6.85 ± 0.19	70.94 ± 0.07	5.71 ± 0.06	17.20 ± 0.13	16.85 ± 0.03
DS	7.12 ± 0.30	68.00 ± 0.00	5.04 ± 0.01	19.84 ± 0.29	17.94 ± 0.03
EFB	6.38 ± 0.61	68.79 ± 0.01	6.11 ± 0.00	18.72 ± 0.61	16.73 ± 0.05
MS	6.91 ± 0.03	68.30 ± 0.02	5.89 ± 0.02	18.90 ± 0.06	17.74 ± 0.05
MSS	7.00 ± 0.05	71.59 ± 0.05	5.11 ± 0.05	17.30 ± 0.05	18.04 ± 0.03
SB	8.81 ± 0.23	70.69 ± 0.04	4.16 ± 0.02	16.34 ± 0.66	17.09 ± 0.31
WCP	6.21 ± 0.13	71.66 ± 0.05	5.20 ± 0.02	16.93 ± 0.14	16.90 ± 0.01

NB: Mc= Moisture content, Vm= Volatile matter, Ac= Ash content, Fc= Fixed carbon, Cv= Calorific value.

BS= Bambara groundnut Shell, BMS= Bush Mangonut Shell, CS= Cassava Stalk, CP= Cocoyam Peel, DS= Detax nut Shell, EFB= Empty Fruit Bunch, MS= Maize Stalk, MSS =Mango Seed Shell, SB= Sugarcane Bagasse, WCP= Wild Cassava Peel.

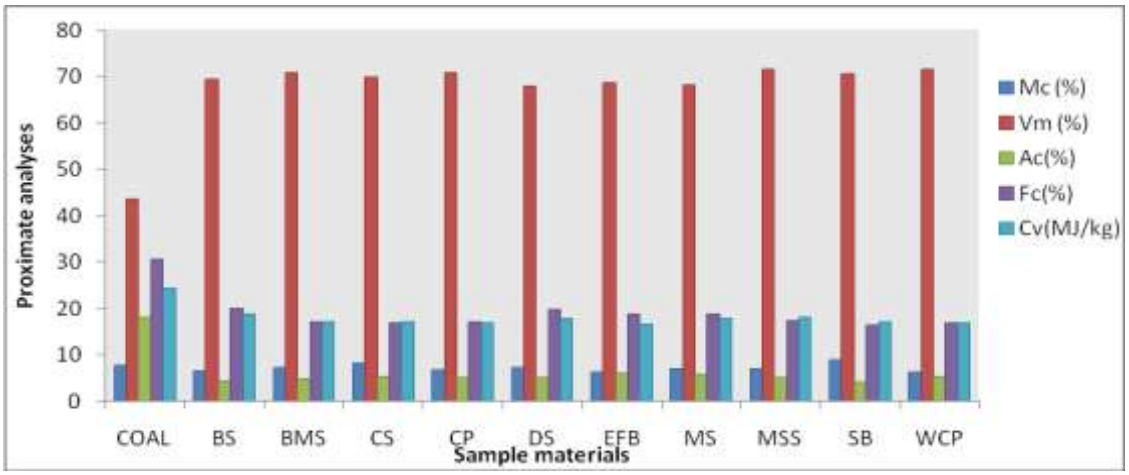

Fig 3: Proximate analyses of the materials.

From Table 3 and Fig 3, for the biomasses, WCP had the lowest moisture content value (6.21%), followed by EFB (6.38%), BS (6.42%), CP (6.85%), MS (6.91%), MSS (7.00%), DS (7.12%), BMS (7.22%), CS (8.11%), and SB (8.81%). The moisture content of coal was 7.76%. Moisture content is undesirable constituent because it reduces calorific value of fuels. However, the values obtained for these biomasses are low enough that they will not pose negative impact on the combustibility of the samples when used for domestic heat applications. This implied that they are good for solid fuel (e.g. briquettes and pellets) production, as it is good for storability and combustibility of the briquettes as recommended by Mills (1998), and Karunanithy *et al*., (2012). Sundip & Rabindra (2013) also noted that high moisture content above 10% will pose problems in grinding. The biomasses had high volatile matter content, with that of WCP (71.66%) being the highest, followed by MSS (71.59%), CP (70.94%), BMS (70.81%), SB (70.69%), CS (69.87%), BS (69.31%), EFB (68.79%), MS (68.30%), DS (68.00%). The volatile matter content of coal was 43.53%. As reported by Akowuah *et al*., (2012), and Sotannde *et al*., (2010), high volatile matter content is a characteristic of good biomass material for solid fuel production since it enables easy ignition and complete combustion.

The ash content (Ac) of the biomasses was relatively low. SB had the lowest value (4.16%), followed by BS (4.25%), BMS (4.92%), CP (5.01%), DS (5.04%), MSS (5.11%), WCP (5.20%), CS (5.22%), MS (5.89%), and then, EFB (6.11%). The ash content of coal was 18.06%, and this was as expected, since it contained high percentage of ash forming elements compared to the biomasses. The ash content values obtained for the biomasses were low, implying a better thermal utilization as reported by Akowuah *et al*., (2012), and Sotannde *et al*., (2010). It was also observed that the biomasses WCP, CS, MS, EFB, with ash content higher than the other biomasses had higher percentage of ash forming elements – Ca, Na, Fe, Si, Mg, K. (Table1) than

the other biomasses. The fixed carbon content (Fc) values obtained for the biomasses were SB (16.34%), CS (16.80%), WCP (16.93%), BMS (17.05%), CP (17.20%), MSS (17.30%), EFB (18.72%), MS (18.90%), DS (19.84%), and BS (20.02%). The fixed carbon content of coal was 30.65%. This showed that coal contained high percentage of carbon, compared to the other biomasses. Fixed carbon content is a measure of the solid combustible material in solid fuel after the expulsion of volatile matter. Its content is used as an estimate of the amount of carbon that will be obtained on carbonization. High fixed carbon content of a material implied high calorific value. This means that coal would have higher calorific value compared to the biomasses as reported by Onuegbu *et al*., (2012). The calorific values of the biomasses were EFB (16.73MJ/kg), CP (16.85MJ/kg), WCP (16.90MJ/kg), CS (17.00MJ/kg), BMS (17.00MJ/kg), SB (17.09MJ/kg),MS (17.74MJ/kg), DS (17.94MJ/kg), MSS (18.04MJ/kg), and BS (18.90MJ/kg). The calorific values of the biomasses were high, implying that they are suitable biomass feedstock for the production of briquettes as reported by Maciejewska *et al*., (2006). Calorific value is the most important fuel property. The energy values can produce enough heat required for household cooking and small scale industrial cottage applications (Akowuah *et al*., (2012). As expected, coal had the highest calorific value (24.30MJ/kg) (due to its high fixed carbon content). It was also observed that biomasses with low ash content had high calorific value (e.g. BS, BMS, SB, DS, etc) and vice versa. This was in line with the findings of Sotannde *et al.*, (2010). The values obtained are comparable to those obtained by Adekunle et al., (2015), 16.68MJ/kg for sawdust, Veeresh & Narayana, (2012), 17.55 MJ/kg (sawdust), 19.07 MJ/kg (groundnut shell), and 15.06 MJ/kg (press dug), etc.The values obtained for coal is lower than that reported by Adekunle et al., (2015), 32.51MJ/kg and 32.93MJ/kg for Ogboyaba and Okaba coal respectively.

Scanning electron microscope analysis of the sample

Plate 2 shows the SEM images of the coal and the biomass samples.

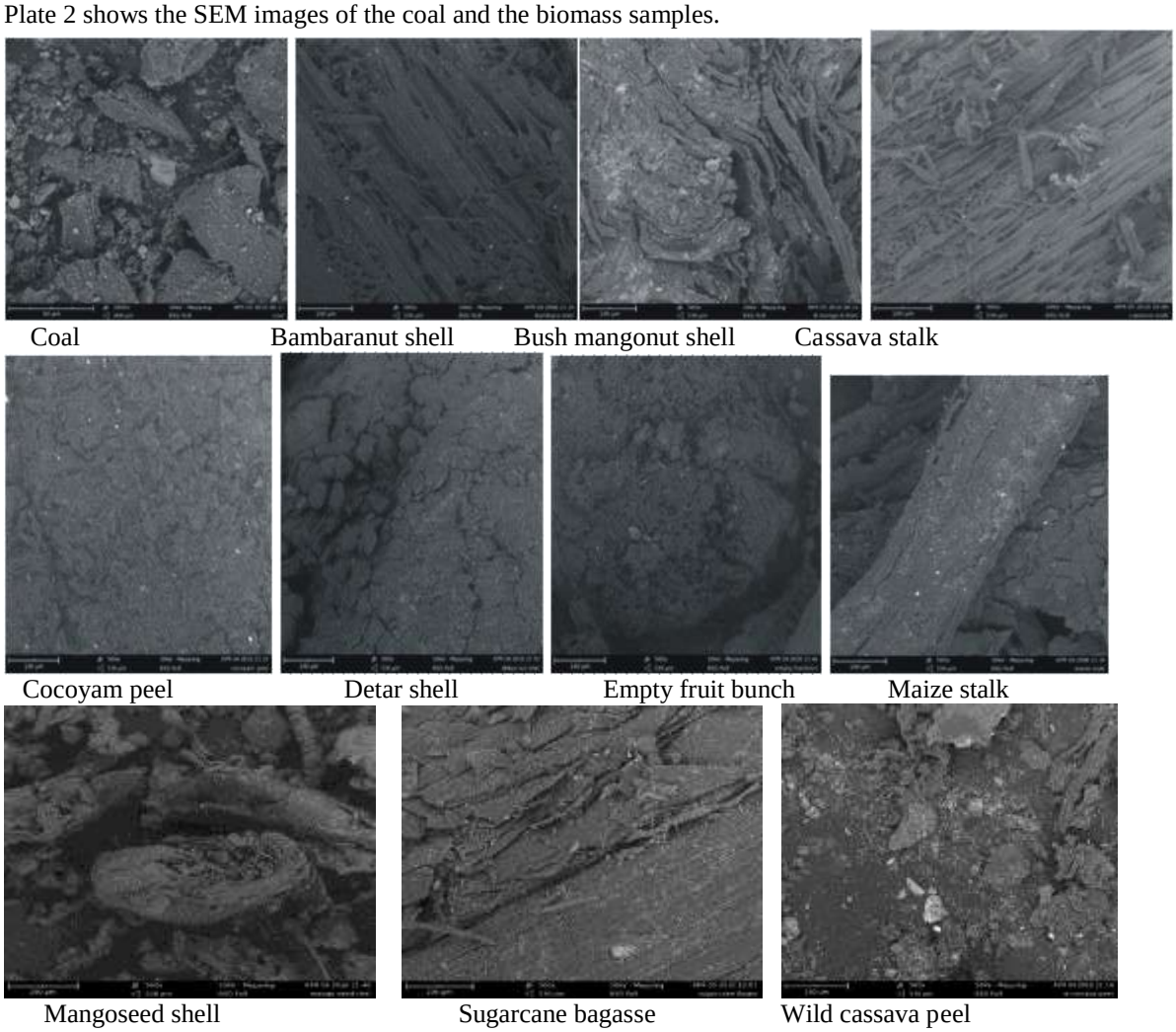

Plate 2: SEM images of coal and the biomasses.

The morphological structure of coal showed short granular structures, indicating typical mineral structure. The morphological structures of bambaranut shell, sugarcane bagasse and cassava stalk showed long uniform fibrous ligno-cellulosic structures. Bush mangonut shell, cocoyam peel and mango seed shell images showed thick, large and dense structures. The images of detar shell and empty fruit bunch showed spongy lignocellulosic structures. Maize stalk showed long, dense and fibrous uniform lignocellulosic structures. The image of wild cassava peel showed large and small granulated structures.The morphology structure of the material studies help to predict their agglomeration properties. Blesa *et al*., (2003) reported that typical fibrous texture of biomasses could favour the coal-biomass agglomeration and as a consequence, it would increase the compression strength of the final solid fuel. The SEM images obtained for the biomasses are similar to those reported by Avila and Lester (2012) for Miscanthus, corn, wheat, and rapeseed residues, and Raju *et al*., (2014) for coco peat, almond leaves and sawdust residues. The SEM image obtained for coal is similar to that obtained by Adebimpe *et al*., (2004)

IV. Conclusion

The present study examined the properties of ten selected Nigerian indigenous biomass wastes. The results obtained showed that the metal content of the biomass samples contributed to their ash content. CS, WCP, EFB, MS which had high percentage of ash forming elements had high ash content compared to the other biomasses. The total sulphur content result proved that the biomass materials are environmental friendly compared to coal. The biomasses also had appreciably high calorific value and volatile matter content. Therefore, they can be used as feedstock for bio-fuel production.

Prior knowledge of biomass properties would help in understanding combustion related problems for biomass based energy generation.

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