

Comparative Analyses of Lean Grade Coal and Carbonized *Antiaris toxicaria* for Energy Generation

Adekunle A. Adeleke¹, Peter P. Ikubanni^{2,4*}, Ayokunle O. Balogun², Jude A. Okolie³, Chiebuka T. Christopher⁵, Ayobami O. Olawale², Joseph C. Okonkwo²

¹ Department of Mechanical Engineering, Nile University of Nigeria, Abuja, Nigeria

² Department of Mechanical Engineering, Landmark University, Omu-Aran, Kwara State, Nigeria.

³ Department of Chemical and Biological Engineering, Sakatoon Saskatchewan University, Canada

⁴ Landmark University SDG-9 (Industry, Innovation and Infrastructure Research Group), Omu-Aran, Kwara State, Nigeria

⁵ Department of Mechatronics Engineering, Bowen University, Iwo, Osun State, Nigeria

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Abstract

The current study focused on characterizing lean grade coal and carbonized biomass (at 400°C) for energy generation. Samples were pulverized using a ball mill and then mixed with a mechanical mixer at two mixing ratios. Proximate, ultimate and calorific value analyses were carried out on the samples using different ASTM standards and some available linear regression models. Lean grade coal has the highest ash content (79.58%) while raw biomass has the least (2.29%). Carbonized biomass samples have the highest heating value (9.49 MJ/kg). The O/C and H/C atomic ratios shows that carbonized biomass is the best fuel compared to coal and blended samples. The FTIR spectra of coal and blended samples shows peaks representing Si-O-Si while C-H bonds were the predominant ones in raw and carbonized samples. Lean grade coal and blended samples contain silicon as displayed by the EDX spectra. The coal and blended samples have grey-like silica and carbide microstructure. The coal and blended samples are not good for energy generation but may serve well as raw material for silicon recovery. Carbonized biomass has good fuel properties that can be useful in existing coal-fired plants.

Keywords: Lean grade coal; *Antiaris toxicaria*; Carbonization; FTIR spectroscopy; Energy.

1. Introduction

Energy generation plays a significant role in a nation whether under-developed, developing or developed [1-2]. Access to various energy sources in order to generate electricity has become a dynamic force for economic or social development [3-4]. There are several sources of renewable and non-renewable sources of energy spread across the country [5-8]. Coal and biomass materials are two key examples of these materials. Nigeria has large coal deposits and abundance biomass wastes. Nigeria has a widespread of coal supply with proven reserve of millions of tons [9]. The Electricity Company of Nigeria (ECN) and the Nigerian Cement Company (NCC) at Nkalagu use coal for their electricity generation. Coal plays major role in the power sectors. However, there are critical issues with coal usage all over the world. The continuous release of greenhouse gases into the atmosphere and environmental pollution has become a major barrier to its application [10-12]. Thus, the need for its partial or total replacement [13]. Biomass as an ancient energy source that is considered as carbon neutral has become an enviable material for this purpose [2,14]. Biomass has been found useful in so many other applications [1, 15-21]. Its usefulness is predominantly for energy generation [22-23]. However, biomass has some limitations when it comes to its application as fuel in coal-fired plants. These include low energy content, high moisture content, poor grindability and fast combustion [24-25]. Biomass must have certain properties like coal for it to be effective in partially replacing it in a coal-fired plant. Some coal-fired plants work with pulverized coal/coal fines.

Thus, biomass must be easy to grind, have improved energy content and be void of unbounded moisture for effectiveness. Thus, the need for initial pretreatment before use. Previously, researcher have adopted several treatment methods for biomass upgrade. These include torrefaction [26-27], pyrolysis [28], and carbonization [29]. This thermochemical conversion process improves the energy content and upgrade the grindability property of biomass. Adeleke *et al.* [23] improved the energetic properties of melina wood using torrefaction technology. The higher heating value of the biomass increased from 18.39 MJ/kg to 22.07 MJ/kg based on different parametric settings. Similar effort by Odusote *et al.* [26] on torrefaction of *Tectonas grandis* at 240 - 300°C yielded an improved heating value, lower moisture content and improved structural content which was ultimately reported to affect grindability in positive direction. Torrefaction, carbonization and other methods have been tested and approved as good approach for upgrading biomass. Thus, the need for selecting one of those processes in this study. This process is carbonization. It helps in carbonaceous residue generation via thermal decomposition (as well as distillate removal) from biomass materials [30]. Pulverized coal and upgraded biomass will serve as good source of fuel in coal-fired plant. This is because there will be reduction in deleterious effluents which affects the global climatic sphere. Meanwhile, there are limited information on the various coal from different mines available at the Nigerian coal market. Thus, further effort is brought to forward by the current study. The biomass (Babu wood) used in this study is one of the common woods at the sawmill in Nigeria for several furniture works. Hence, it contributes to the huge deposit of wastes at the sawmill. Therefore, the present study focuses on comparing carbonized Babu wood wastes and lean grade coal obtained from market. This is to ascertain their properties singly and when combined for use in an existing coal-fired plant.

2. Methodology

2.1. Raw materials

In this study, the Okpara mines coal samples purchased from Okpara coal sellers in Nigeria were characterized. The coals were said to be obtained from Okpara mines, Nigeria. Three days (5 h/day) sun-drying was done on the coal samples to eliminate the residual external moistness. A ball mill was used in crushing the coal samples and later were screened to acquire particle size lower than 0.5 mm. The coal samples were then reserved in zip-locked bag for further characterization and utilization. The woody biomass utilized in this study was sawdust of Babu wood, which was gotten from Al-Barka Sawmill, Omu-Aran, Nigeria. The sawdust was sun-dried for three days in Engineering Building in Landmark University to remove surface and residual moisture. It was further milled to a particle size lower than 2 mm.

2.2. Carbonization of Babu wood dust

The carbonization process was done using a muffle furnace. The muffle furnace has constant supply of lean oxygen from outside through a metallic duct. Pulverized biomass (200 g) was placed in a crucible. The crucible was then placed in the muffle furnace, while the furnace was set to 400°C. The sample was kept for 30 minutes after the furnace reached 400°C [31]. The sample was removed and placed in a desiccator. The carbonized sample was milled and screened to a particle size less than 0.5 mm for easy mixing with coal for further analyses. Carbonized biomass (CB) and lean grade coal were thoroughly mixed using a mechanical mixer at two different ratios; 50: 50 and 40: 60, respectively.

2.3. Proximate and higher heating value analyses

The IS:1350-1(1984) [32] standards for coal and coke was utilized to determine the proximate analyses of the coal samples. Moisture content (MC) analyses was evaluated by measuring the mass of the blank crucible (M_1) by utilizing an Electronic Analytical and Precision Balance (Sartorius BSA Series: BSA 224S-CW). Each sample of mass (1 g) was placed into the crucible before weighing to obtain mass (M_2). The sample in the crucible was positioned into an oven (Model No: OF-22G, JESO TECH, Korea) at 105°C and drying time of 1 h was

used. The oven dried sample in the crucible was ejected from the oven and cooled in a desiccator, which was later measured as M_3 . Equation (1) was utilized to evaluate the moisture content.

$$MC = \frac{M_2 - M_3}{M_2 - M_1} \times 100\% \quad (1)$$

Volatile matter (VM): The mass of alumina crucible was obtained through the usage of an Electronic Analytical and Precision Balance (Sartorius BSA Series: BSA 224S-CW) and recorded as M_0 . Sample of 1 g was placed in the crucible and lid covered, to disallow the blasting and combustion of the sample. The mass of the sample with the covered crucible was taken to be M_a . The samples with the covered crucible were placed in a muffle furnace (Model No: CBFL518C, USA) for 7 mins after the furnace has been initially heated to 950°C. The crucible was then removed and cooled in a desiccator. The obtained mass after measurement was recorded as M_f . Equation (2) was used for the volatile matter determination.

$$VM = \frac{M_a - M_f}{M_a - M_0} \times 100\% \quad (2)$$

Ash content (AC): The mass of silica crucible was obtained through Electronic Analytical and Precision Balance (Sartorius BSA Series: BSA 224S-CW) and noted as M_c . Using muffle furnace (Model No: CBFL518C, USA), 1 g of each sample was placed into the crucible and values noted as M_s , and placed in the furnace at 815°C. Soaking was done for 1 h in the furnace and later cooled in a desiccator. The furnace-dried sample with the crucible were taken as M_f . The ash content calculation was by Equation (3).

$$AC = \frac{M_f - M_c}{M_s - M_c} \times 100\% \quad (3)$$

Equation (4) was utilized to determine the fixed carbon (FC) of the sample by finding the difference 100 and when MC, AC, and VM are summed. Equation (5) was used to determine the higher heating value (calorific values) of the sample [33].

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

$$HHV(\text{MJ/kg}) = 0.2949C + 0.825H \quad (5)$$

2.4. FTIR and SEM-EDX

The functional groups of the samples were characterized using the Fourier Transform Infrared spectrophotometry (FTIR) spectrophotometry. The samples were appropriately prepared and placed in discs for analysis in the FTIR, while 4000 – 450 cm^{-1} is the range of the spectra having a resolution of 4 cm^{-1} . The micrographs as well as the elemental studies of the samples was done on a scanning electron microscope (SEM) equipped with EDX (energy dispersive x-ray spectroscopy).

3. Results and discussion

3.1. Proximate, ultimate and calorific values analyses

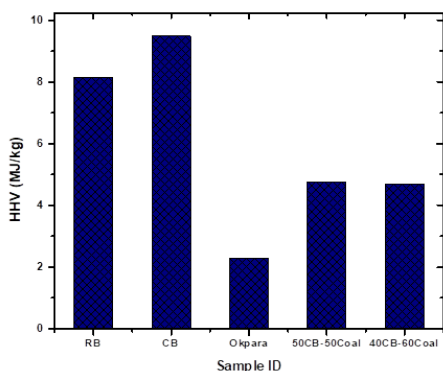


Figure 1. Calorific values of the samples

Table 1 presents the ultimate and proximate contents of the samples while the calorific values are displayed in Figure 1. Based on the proximate analysis for the samples, the moisture content of coal (2.16%) and carbonized biomass (2.20%) were lower than that sawdust (4.60%). Carbonized biomass (CB) had a moisture content of 2.20%. Carbonization has driven off some OH bonds from the sawdust [4]. Similarly, coal and carbonized biomass are now in range based on moisture content. It has been proposed that good fuel should have moisture content lower than 15% [34].

System capacity is lowered while operational cost is increased as a result of high moisture content of fuel. This is disadvantageous. As expected, the Babu wood sawdust (biomass) displayed a higher moisture content compared to coal. This is because the moistness in coal has been eliminated during the coal formation process. The coal-CB mixture 50:50, 60:40 had a moisture content of 3.24% and 2.34%, respectively. The moisture content of the coal-CB blend increased with increased biomass content, which reveals that more volume of moisture was retained by biomass material than coal. The coal's ash content is extremely higher than that of raw biomass and carbonized. This has huge implication on its usage as fuel in a boiler or for energy generation. High ash content of the coal makes the coal very lean grade coal that may be peat family [35].

Table 1. Proximate and ultimate analyses of the samples

Proximate					
Sample	MC (%)	AC (%)	VM (%)	FC (%)	
RB	4.60	2.26	84.74	8.40	
CB	2.20	2.27	70.33	25.20	
Okpara Coal	2.16	79.58	14.22	2.29	
50%CB-50%Coal	3.24	67.24	20.12	9.40	
40%CB-60%Coal	2.34	68.83	20.03	8.80	
Ultimate					
	C (%)	H (%)	N (%)	S (%)	O (%)
RB	23.70	1.40	1.72	0.02	4.48
CB	28.75	1.22	1.20	0.02	1.75
Okpara Coal	5.24	0.90	0.39	1.88	0.27
50%CB-50%Coal	12.59	1.30	0.41	1.83	0.81
40%CB-60%Coal	11.71	1.50	0.57	1.82	0.49

The quality of any fuel is better when the fuel has lower ash content [36]. Solid fuel ash content is germane to its combustion characteristics. Coal-CB blend 60:40 had ash content of 68.83% higher than that of 50:50 mixtures at 67.24%. The more the biomass content of the blend, the lower is the coal-CB blend's ash content. The ash content of the samples and blend are non-fuel components of the blends, thus, undesirable as fuel. Studies have shown that typical biomass possesses lower ash content with composition depending on the plant's chemical components acquired during growth compared to coal, which have mineralogical composition [37]. The volatile matter of CB (70.33%) and raw biomass (84.74%) were higher than that of coal (14.22%). Biomass contains high volatile matter (70 – 85%). Hence, it is extremely reactive as a fuel with a faster rate of combustion [38]. There is slight increment in the volatile matter of the coal-CB blends between 20.03% (60:40) and 20.12% (50:50). The Babu wood sawdust contains the highest volatile matter in the blends than the coal. During combustion, many pollutants such as smoke from the fuel are due to volatile matter. It is quite challenging to naturally utilize biomass residues as fuel owing to their small bulk density, little heat release as well as the excessive amounts of smoke they generate [1,39]. The carbonized sample has the highest fixed carbon (FC) content (25.20%), while raw biomass has 8.40% and lean grade coal has 2.29% fixed carbon. The most paramount fuel property is the fixed carbon, which have direct relations with the calorific/heating value [23]. The result of the FC of the coal-CB blend revealed that CS-50:50 had 9.40% and went on a downward trend with 60:40 being 8.80%. The FC percentage is important having direct influence on the calorific value. This implied that the coal is extremely poor as fuel source. It contains high amounts of impurities that impair its fuel properties. Calorific value results (Figure 1) revealed that coal had 2.29 MJ/Kg, carbonized biomass and raw biomass had a calorific value of 9.49 MJ/Kg and 8.15 MJ/Kg, respectively. The major influencers of the calorific value of a fuel are the volatile

matter and fixed carbon content. There is relative closeness between the raw and the carbonized sawdust fixed carbon content and volatile matter, which could have resulted in their heating values closeness. Oxygen diffusion and transfer of heat to the fuel surface during char combustion is significantly influenced by ash [1,34,40]. The coal sample utilized in this study is a doubt as fuel in any application. Carbonized biomass is to be used at 100% for any boiler/heat generation. The incombustibility of the ash makes it to reduce the solid fuels' calorific value. The result of the ultimate analysis is shown in Table 1. Biomass samples had higher carbon contents compared to the hydrogen, nitrogen, sulphur and oxygen contents. Coal had a carbon content of 5.24%, carbonized while carbonized biomass had 28.75% carbon content and raw sawdust had 23.70% carbon content. The carbon content of the coal-CB blends is 12.59% and 11.71% in 50:50 and 60:40, respectively. The hydrogen content of the saw dust is 1.40%, coal sample is 0.90%, and carbonized biomass 1.22%. Biomass such as sawdust contain hydrogen obtainable from water (H_2O) as well as other volatile and tars (CH_4 , C_6H_6). The content of hydrogen present in the coal- CB blends is 1.30% and 1.50% in 50:50 and 60:40, respectively.

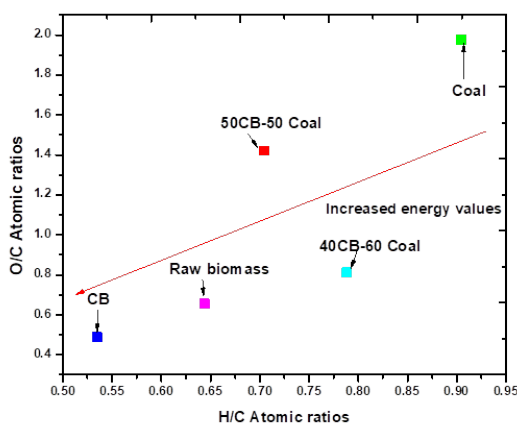


Figure 2. O/C and H/C atomic ratios for the samples

The amount of carbon and hydrogen present in the Babu wood sawdust are closely in agreement with values reported by Odusote *et al.* [26]. The effect is evidently displayed in the O/H and C/O atomic ratios shown in Figure 2. Figure 2 shows the rank of the samples as the energy content improves. Carbonized biomass is the best fuel compared with other. Carbonization has been reported to lower the oxygen and hydrogen contents of biomass, while it increases the stable aromatic carbon content that give room for better calorific value [38,40]. The nitrogen and sulphur contents of the coal samples are respectively 0.39% and 1.88%.

Carbonized biomass and sawdust contain 1.72% and 1.20% of nitrogen, respectively. The sulfur content (0.02%) is the same for raw and carbonized biomass. When solid fuels containing nitrogen and sulphur are combusted, they potentially pollute the environment and affects man's health. The extremely reduced amount of sulphur in biomass is advantageous. The aggregate sulphur content can be reduced when biomass are blended with other solid fuel. The nitrogen and sulphur contents of the coal- CB blends are 0.41% and 1.83%, and 0.57% and 1.82% in 50:50 and 60:40, respectively. The proximate, ultimate and calorific value estimation of the fuel show that the properties blend of carbonized biomass with the lean grade coal used in this study is inadequate as fuel materials.

3.2. FTIR spectroscopy

Figure 3 (a-b) display the FTIR spectra of the samples. The spectra revealed strong sharp peak in the range of $3600 - 3000\text{ cm}^{-1}$ in the coal sample. This is the assigned to O-H stretching and indicative of moisture forming bonds presence [18,26]. Similar peaks at 1095 and 1011 cm^{-1} , 1000 and 1420 cm^{-1} , and 1092 and 1041 cm^{-1} depicting OH associations and OH bending are obtained in raw biomass, carbonized and other samples, respectively [18,26]. The peaks between 900 and 700 cm^{-1} revealed the high tendency of the presence of C-H and C-O bonding [41]. At peaks $1200-1050\text{ cm}^{-1}$, Si-O-Si presence is also eminent in the samples. Si-O presence has been reported to be prominent for peaks below 500 cm^{-1} [18]. The peaks 691 cm^{-1} , 635 cm^{-1} , and 691 cm^{-1} peaks indicate the presence of $-Si(CH_3)_3$ [35,42]. The result of the FTIR analysis explains the excessive ash content of the Okpara coal. It could be concluded that the FTIR analyses show significant C-H bonds for raw biomass, aromatic functional group for carbonized biomass and, Si-O-Si, C-O stretching and C-O deformation for the coal sample. The Si-based

functional group dominated the spectra of the coal sample. By implication, the coal formation has been extremely linked to peat family, which is not useful for energy generation but may be effective for recovering of silicon and some other metals [43].

3.3. SEM-EDX of the samples

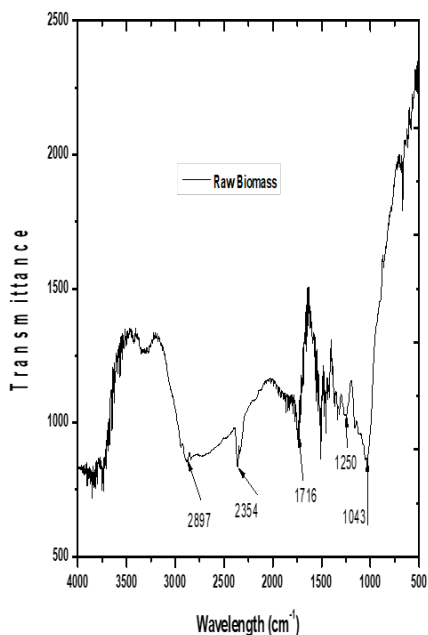


Figure 3a. FTIR spectrum of the raw biomass

Figures 4a - 8a show the micrographs of the raw biomass, carbonized biomass, coal and the blends. Figures 4b—8b are the EDX-spectra for the samples. The micrograph of raw biomass shows spongy like structure (Figure 4a). This has been reported in previous literature that biomass has spongy structure that makes it hydrophilic in nature [23]. This factor necessitated its carbonization. The micrograph of the carbonized samples was extremely different with breakaways. It depicts some disintegration of the spongy nature in the raw biomass (Figure 5a). Thermochemical treatment causes loss of volatiles and thus weakened bonds and pores that may eventually lead to breakaways in biomass structure [44].

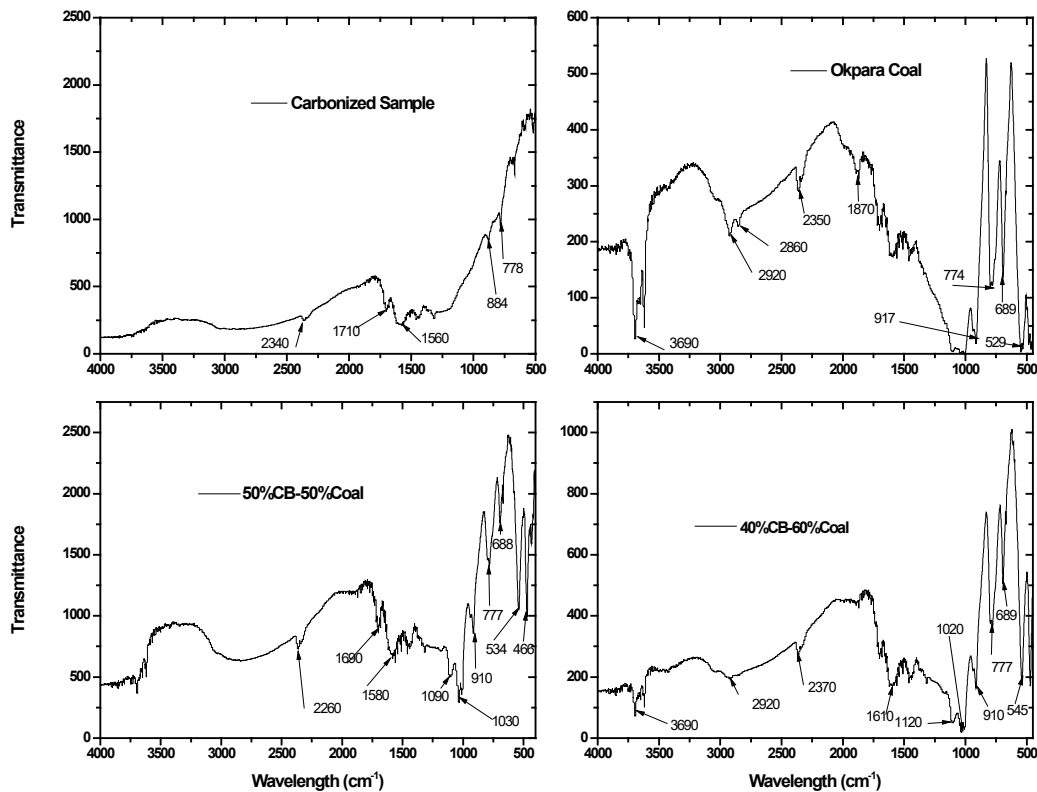


Figure 3b. FTIR of carbonized biomass, lean grade coal and mixed samples

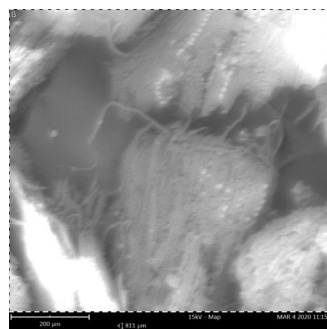


Figure 4a. Micrograph of raw biomass

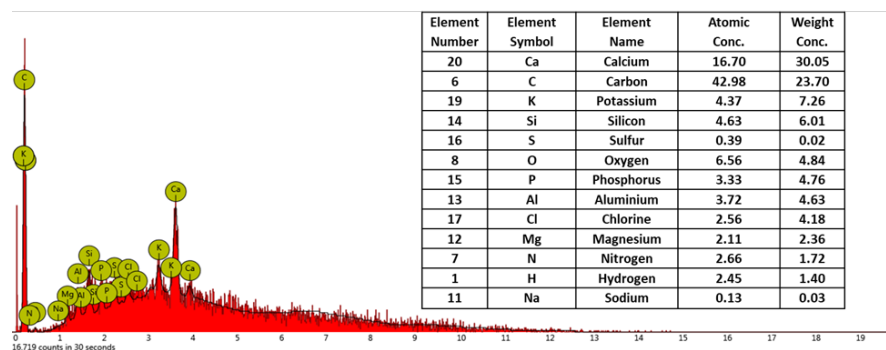


Figure 4b. EDX spectra and elemental presence of raw biomass

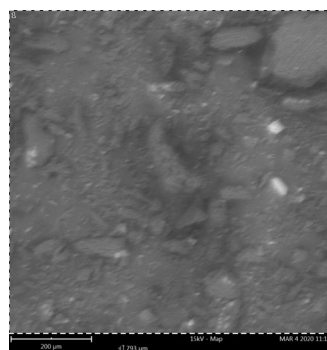


Figure 5a. Micrograph of carbonized biomass

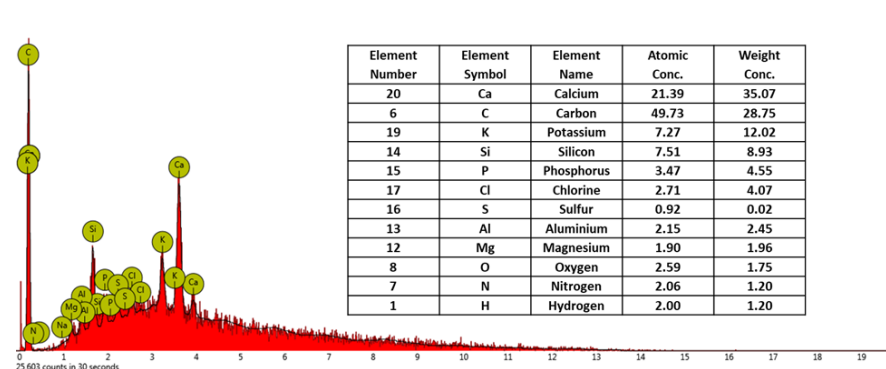


Figure 5b. EDX and elemental presence of carbonized biomass

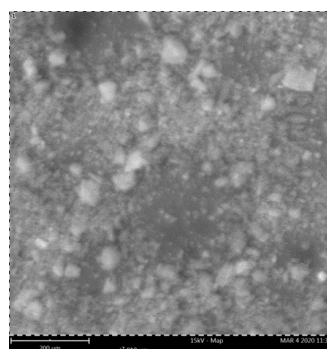


Figure 6a. Micrograph of Okpara coal sample

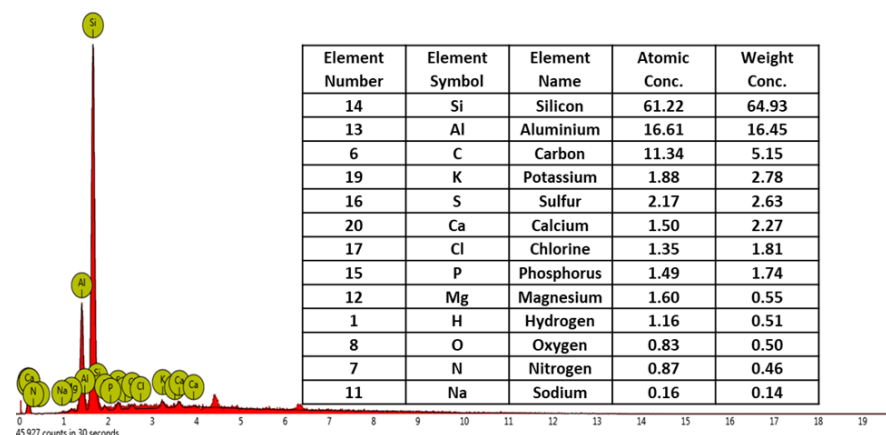


Figure 6b. EDX and elemental presence of Okpara coal

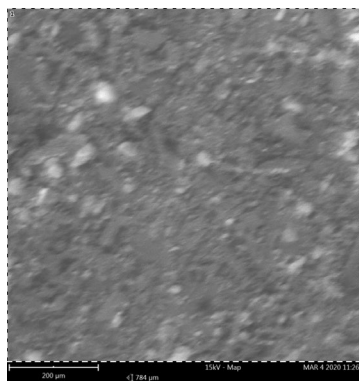


Figure 7a. Micrograph of 50%carbonized biomass and 50% coal

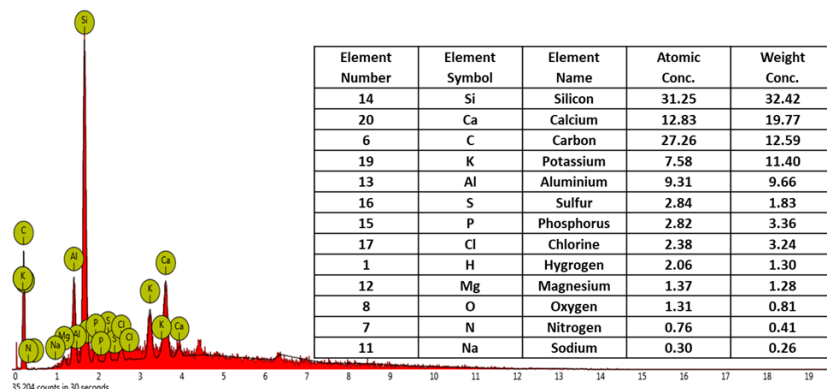


Figure 7d. EDX and elemental presence of 50%carbonized biomass and 50%coal

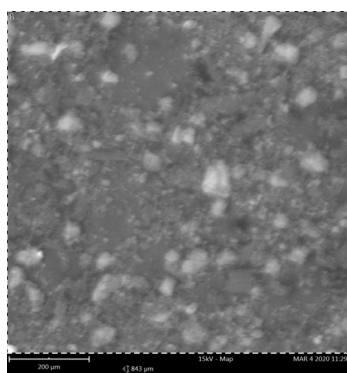


Figure 8a. Micrograph of 40%carbonized biomass and 60%coal sample

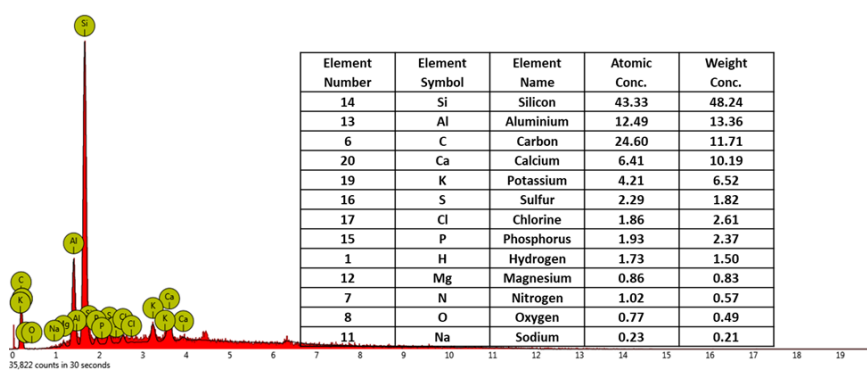


Figure 8b. EDX and elemental presence of 40%carbonized biomass and 60%coal sample

The micrographs of coal and the blends (Figures 6 -8) generally revealed cluster of silica and carbide. Dominant grey-like structures are dispersed in the micrograph of the samples. This is in agreement with the FTIR and ash results where silica-based bands, and ash contents were vehemently dominant. The EDX spectra of raw and carbonized biomass (Figures 4-5b) showed that carbon was the predominant elements, while the EDX spectra of coal and blended samples in Figures (6 - 8b) displayed silicon to have the highest intensity. This affirms silica as the principal content of the coal and blended samples. Aluminum (Al) noticeably appears in the lean grade coal and blended samples. This depicts the alumina's presence. Coal sample (Figure 6) has high amount of calcium (Ca), Al and Si were the dominants in the samples. This helps to classify the coal samples into clay/sedimentary rock family. It implied that is not coal but clayish peat. Other trace elements present in the samples include potassium, magnesium, calcium, sulphur, sodium, and so on, as shown in Figures 4-8. It is expected that coal should have carbon as the major element with the trace elements in abysmal quantity [35]. However, the biomass samples (raw and carbonized) have a carbon content ranging from 42.98 - 49.73% of the atomic concentration. By implication, biomass is extremely better as raw and carbonized samples than the characterized coal. The coals sample is indeed a lean grade coal or a sedimentary rock, which is not recommended in any form for energy generation [43].

4. Conclusion

Comparative analyses of lean grade coal and carbonized biomass has been carried out in this study. The samples were blended and characterized. The lean grade coal contains 79.58% ash and 2.29% fixed carbon. Carbonization improved the fixed carbon of biomass sample from 8.4% to 25.20%. The blended sample have poor proximate and ultimate content. Carbonized biomass has the highest heating value (9.49 MJ/kg), while coal has the least (2.29 MJ/kg). The C-H band is predominant in the FTIR spectra of raw and carbonized biomass while Si-O-Si and Si-C bands are predominant in the coal and blended samples. The microstructure of raw biomass is spongy while that of carbonized biomass display disintegrated sponges. The microstructure of lean grade coal and blended samples is grey-like of silica and carbide. The EDX of the coal and blended samples have silicon as the dominant element. Carbonization improves biomass. However, the product should not be blend with coal of these characteristics. The lean grade coal is not a material for energy generation as it is dominated by silica. Thus, it is recommended as raw materials for silicon recovery.

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To whom correspondence should be addressed: Dr. Peter P. Ikubanni, Department of Mechanical Engineering, Landmark University, Omu-Aran, Kwara State, Nigeria, E-mail: ikubanni.peter@lmu.edu.ng