

Original Research Article

Proximate and Ultimate Analyses of Biocoal Briquettes of Nigerian's Ogboyaga and Okaba Sub-bituminous Coal

Abstract

Proximate and Ultimate analyses of biocoal briquettes were undertaken with the aim of presenting the analytical results and ascertaining the optimum biomass composition for use as composite domestic fuel coal samples from 2 coal mines and sites of Ogboyaga and Okaba in Kogi state of Nigeria were collected. The samples were pulverized and blended with sawdust at various constituent ratios of 0:100, 10:90, 20:80, 30:70, 40:60, 50:50 and 100:0. Cassava starch was used as binding agent while calcium hydroxide was used as a desulphurizing agent for the briquettes. Briquettes of various blends were produced. Proximate and ultimate analyses were carried out to ascertain the elemental composition of the raw materials and the biocoal briquettes. Experimental tests, which involved the determination of calorific value was also determined. All the 50/50% biocoal briquettes compositions have better characteristics than other blends while Ogboyaga, OG_{90/10} biocoal briquette exhibits the best quality with the highest calorific value of 29.55MJ/kg.

1.0 Introduction

Coal is one of the most abundant fossil fuels in Nigeria; it is also one of the leading commodities in terms of industrial importance. There are many coal deposits in Nigeria whose fuel characteristics are unknown. Coals of different varieties and their characterization are very important in deciding their suitable applications. The global concern for new source of energy has restored interest in coal and how it can be utilized without the environmental consequences and health hazards associated with the use of raw coal. Densification of various ranks of coal for the purpose of making solid fuels has been a technology widely used in many countries [4], [3] and [11]. However, recently, it has been shown that blending coal and biomass gives rise to briquettes with better properties and environmentally friendly compared to the conventional coal briquettes [3]. This type of briquette could be known as biocoal briquette. Most of the coal deposits in Nigeria have not been utilized well due to availability of petroleum, some of these coals are now being investigated and densifying with biomass to produce biocoal briquettes [6].

Biocoal briquetting is a new kind of solid fuel made up of coal, biomass and sulphur retention agent; it is prepared by compacting pulverized coal, biomass, binder, and sulphur fixation agent [7]. The high pressure involved in the process ensures that the coal and the biomass particles are sandwiched and adhered together, as a result do not separate during transportation, storage and combustion. Biocoal briquette technology combines irrenewable fossil energy and renewable biomass, embodying both functions of synthetic utilization of energy and reduction of air pollution. Furthermore, the presence of sulphur fixation agent otherwise known as desulphurizing agent ensures that most of the sulphur content of the coal is fixed into the ash instead of being liberated into the atmosphere as sulphur dioxide [9]. The desulphurizing agent in the briquette reacts with the sulphur content of coal to fix about 60-80% into ash [9]. This implies that, by this technology, the pollution problems associated

with burning of coal is to a great extent eliminated. Nigeria has potential for utilizing biocoal technology as a measure to addressing its energy problem associated with rural household energy demands and means of utilizing the large deposits of coal as well as means of managing agro - wastes thereby creating avenues for substitutes for excessive use of fuel wood. Sawdust is one of the agro wastes that are available in abundance locally as waste material from saw mills across the country [1].

The present research is aimed at investigating the properties of biocoal briquettes as concentration of sawdust varies with the hope of determining the optimum composition using Nigeria's Ogboyaga and Okaba coal deposits and in comparison with the properties of 100% coal briquettes.

2.0 Materials and Methods

2.1 Sources and Preparation of Materials

Coal samples were sourced from identified and accessed coal mine sites of Ogboyoga - Odu and Okaba in Kogi State in North Central Nigeria. Sawdust was sourced from a saw mill in Akure, South-west Nigeria while starch used as binder was gotten from an open market Calcium hydroxide (98% purity) was bought and used as desulphurizing agent. The samples were dried and the coal samples were pulverized and sieved to pass through 0.20mm mesh.

2.2 Proximate and Ultimate Analysis of Materials

Proximate and ultimate analyses of the coal, sawdust and biocoal briquettes were conducted in accordance with American Society of Testing and Materials (ASTM). The calorific value was determined using Oxygen Gallenkamp Ballistic Bomb Calorimeter of model CBB- 330.

2.3 Preparation of the Briquette Samples

The two milled coal samples were prepared for briquetting with appropriate labelling while the sawdust sample was screened of impurities like sand, metallic objects and chips of wood. Six samples each from the two coal samples were blended with sawdust at various concentrations of 0%, 10%, 20%, 30%, 40% and 50% while 100% sawdust was also prepared for comparison. For each of the concentration excluding 100% sawdust, 5% $\text{Ca}(\text{OH})_2$ based on the mass of the coal was added for desulphurization and 10% cassava starch gel based on the entire mass of the mixture was used as binder for all the samples as adopted by [6]. The samples were weighed using digital weighing balance type HZ- K600EB with maximum load of 600g and accuracy of 0.1g. The different concentrations were loaded into the mould compartment of the manually operated hydraulic briquetting machine. A maximum of 16 briquettes were obtained at each operation of the machine under a total load of 57.4N. Biocoal briquettes of different concentrations as well as coal and sawdust briquettes were produced under this condition while maintaining the pressure at 6.89MPa throughout production.

2.4 Proximate Analysis

The proximate analysis which involved the determination of moisture content, volatile matter and ash were determined based on the American Society of Testing and Materials (ASTM) D3173, D3175, and D3174 standards. The fixed carbon was obtained by subtracting the percentage of ash, moisture content and volatile matter from 100.

2.5 Calorific Value Determination

The Gallenkamp Ballistic Bomb Calorimeter was first calibrated using a standard sample of benzoic acid whose known calorific value is 6.32kCal/g. A known mass of sample of small quantity, 0.5g of the different samples were placed in the crucibles. One end of a cotton thread strand of length 50mm was inserted between the coil of ignition wire and the other end dipped into the centre of the sample in the crucible. The thread enhances the combustion of the sample inside the crucible. The bomb body was placed and tightly screwed in position. The thermocouple wire was plugged into the hole on top of the bomb body. The pressure release valve was closed and oxygen was admitted into the bomb until the pressure rose to 25bars. The light spot index was set to zero using the galvanometer zero knob ensuring a stable temperature before the firing knob was depressed and released to fire the bomb. Heat was released and the maximum deflection of galvanometer scale was recorded after which the burnt gases were released from the apparatus with the aid of the pressure release valve. The maximum deflection obtained in the galvanometer was converted to energy value of the sample material by comparing the rise in galvanometer deflection with that obtained when a sample of known calorific value of benzoic acid is combusted as shown in equation:

Heat released from sample, $Q = \frac{G \cdot \text{meter deflection} \times \text{calibration}}{\text{Original weight of sample}}$ which is equal to:

$$Q = \frac{(\theta_3 - \theta_1) \gamma}{Z} \text{ kcal/g} \quad (1)$$

The whole experiment was repeated for all the different samples of coal, biocoal and sawdust briquette samples.

2.6 Ultimate Analysis

Ultimate analysis which involves the determination of carbon and hydrogen, nitrogen, sulphur and ash were also determined based on the American Society of Testing and Materials (ASTM) D3178, D3179, and D3177 standards. The oxygen was obtained by subtracting the percentage of ash, carbon, hydrogen, nitrogen and sulphur from 100.

2.7 Determination of Carbon and Hydrogen by Liebig Method

The carbon and hydrogen contents value were determined based on American Society for Testing and Materials standards (ASTM- D3178) standard. The equipment used consists of two parts; a combustion unit and an absorption train. The combustion unit is made up of three separate electrically heated furnace and combustion tube. 2g of sample was placed in a platinum crucible and inserted into the combustion tube under the first furnace where the sample is burned in oxygen at a temperature of 1300°C. The combustion product was allowed to flow over a heated copper oxide and lead chromate and into the absorption train. The copper oxide ensures complete combustion of the carbon and hydrogen in the coal, whereas the lead chromate absorbs the oxides of sulphur. The pre weighed absorbers in the absorption train absorb water and carbon dioxide, and the percentage of carbon and hydrogen in the sample was calculated from the gain in weight of absorbers. The carbon as carbon dioxide and hydrogen as water were calculated from the increase in weight of the absorbents used to collect the water and carbon dioxide. An oxide of sulphur which was released in significant amount

was removed from the combustion gases by passage over silver at about 600°C while nitrogen dioxide is removed by lead chromate.

2.8 *Determination of Nitrogen Content by Kjeldahl method*

The determination of nitrogen content was determined using ASTM- D3179 standard. 2g of sample was weighed into a Kjeldahl digestion flask. 20ml sulphuric acid and 1g each of copper sulphate and potassium sulphate as catalysts were added into the flask. The flask was tilted to 45°, heated gently until effervescence stopped and then brought to boil. The mixture was then diluted with 100ml of distilled water and allowed to cool. Thereafter, the flask was connected to the Kjeldahl distillation apparatus and excess of 50% of sodium hydroxide solution was added to the mixture and then brought to boil. The ammonia gas was condensed into the receiving flask containing 2% boric acid. Bromocresol green and methyl red indicators were added dropwise and alkaline distillate was titrated against 0.1M hydrochloric acid. The same procedure was repeated for the 13 samples and the percentage of nitrogen was calculated using the formula shown in equation below:

$$\text{Percentage nitrogen, N (\%)} = \frac{V_2 - V_1 \times 0.1 \times 14}{\text{Weight of sample (g)}} \times 100 \quad (2)$$

Where: N = Nitrogen, v_1 and v_2 are the volume of the Hydrochloric acid used in the sample and the blank respectively, 14 is the relative atomic mass of nitrogen.

2.9 *Determination of Sulphur by the Eschka Method*

Sulphur content was determined using ASTM-D3177 standard. 1.00g of coal sample was weighed into a 30ml porcelain crucible and mixed with 3.00 g of Eschka mixture which is a combination of two parts by weight of light calcined magnesium oxide with one part of anhydrous sodium carbonate. The mixture was again covered with 1.00 g of Eschka mixture. The blank and standard samples were also prepared in a similar manner. The crucibles were then placed in a cold muffle furnace and gradually heated to 800°C for 60 minutes. The crucibles were then emptied into 400 ml beakers containing 100 ml of hot water. Digestion was carried out for 45 minutes with occasional stirring. The solution in each beaker was then decanted through a no. 540 watman filter paper into a 400 ml beaker. Three drops of methyl orange indicator were added dropwise until colour turned just neutral. Then, 1ml of hydrochloric acid was added, after which 25 ml of potassium sulphate solution was also added. The sample was thereafter heated to boiling and 10 ml of 10% barium chloride solution was slowly added with stirring (to ensure good precipitation). The solution was boiled for 30 min and allowed to cool down to ambient temperature. The solution was then filtered with no. 42 watman filter paper and the trapped residue was washed thoroughly with hot water. The filter paper with the residue was thereafter placed into a crucible and smoked off gradually, avoiding burning. The temperature was raised gradually to 800°C and maintained for 60 minutes. The crucible was then cooled in a desiccator and the weight of barium sulphate was determined. The total sulphur content was calculated using the formula shown in equation below:

Total sulphur

$$S_t = \frac{A - B \times 137.3}{C} \quad (3)$$

where:

S_t = the total sulphur

A = the mass of barium sulphate from the sample

B = the mass of barium sulphate from the blank
 C = the mass of sample
 137.3 = relative atomic mass of barium

2.10 Determination of Oxygen Content

In practice, in the expression of the ultimate analysis, it is customary to deduct from hundred the sum of the percentages of ash, carbon, hydrogen, nitrogen, and sulphur, hence, the oxygen was determined by the difference as shown in equation below:

Percentage oxygen

$$\text{Percentage, O}_2 = 100 - (\text{Carbon} + \text{Hydrogen} + \text{Nitrogen} + \text{Sulphur})\% \quad (4)$$

3.0 Results and Discussion

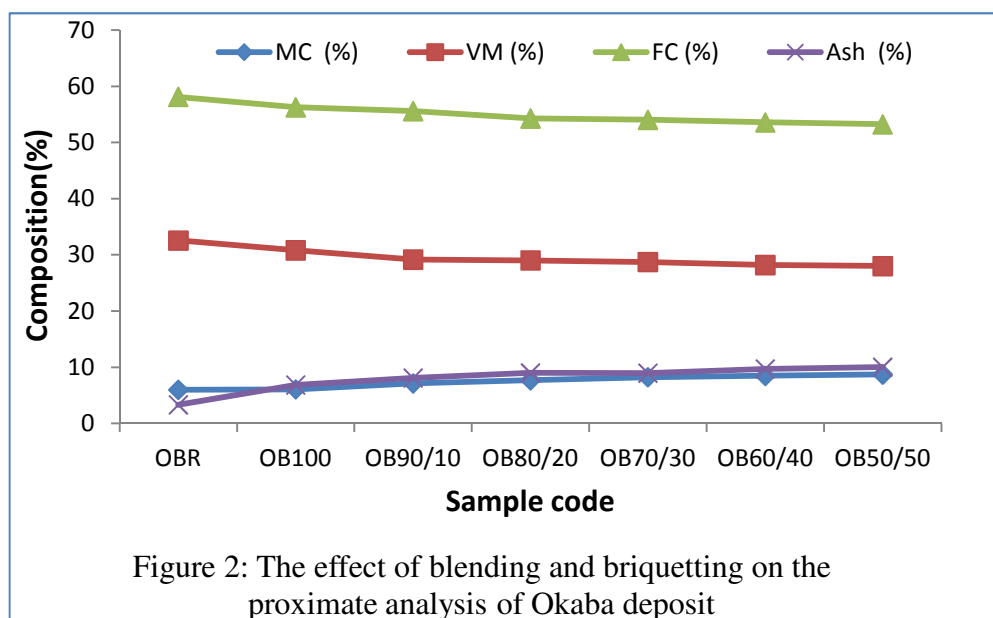
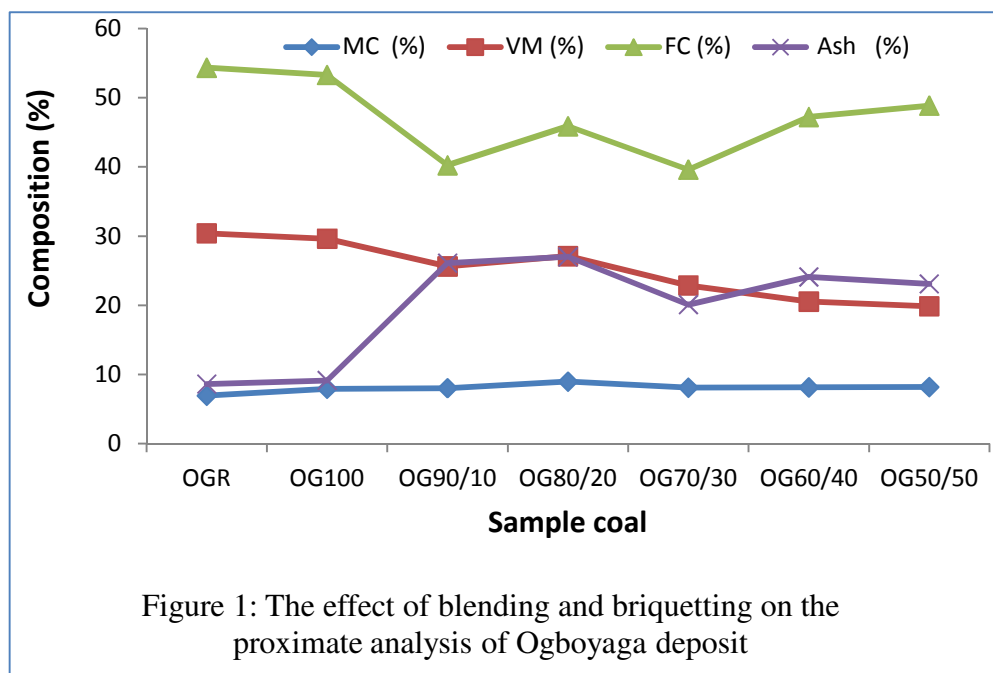
The results obtained from the proximate and ultimate analyses of the raw materials are presented in Table 1 and 2. Figures 1 and 2 show the effect of blending and briquetting on the proximate analysis of coal and biocoal briquettes respectively. Figure 3 shows the effect of briquetting on the sawdust and Figures 4 and 5 show the effect of blending and briquetting on the ultimate analysis of raw coal and the biocoal of Ogboyaga and Okaba coal deposits. Figure 6 shows the effect of briquetting on the sawdust, Figure 7 and 8 show the effect of blending and briquetting on the calorific value of coal and biocoal briquettes.

Table 1: Data from Proximate Analysis of the Raw Materials

Samples	Moisture Content (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash Content (%)	Calorific Value (%)	Coal Rank
Ogboyaga(Odu) Coal	6.93	30.41	54.33	8.63	32.51	Sub-bituminous
Okaba Coal	5.99	32.56	58.13	3.32	32.93	Sub-bituminous
Sawdust	8.26	70.1	21.03	0.68	16.68	N/A

Table 2: Data from Ultimate Analysis of the Raw Materials

Samples	Hydrogen (%)	Carbon (%)	Nitrogen (%)	Oxygen (%)	Sulphur (%)	Ash (%)
Ogboyaga - Odu Coal	4.1	78.9	1.2	6.6	0.6	8.63
Okaba Coal	4.3	82.8	2.4	7.3	0.6	3.32
Sawdust	2.13	1.48	13.2	82.51	0	0.68



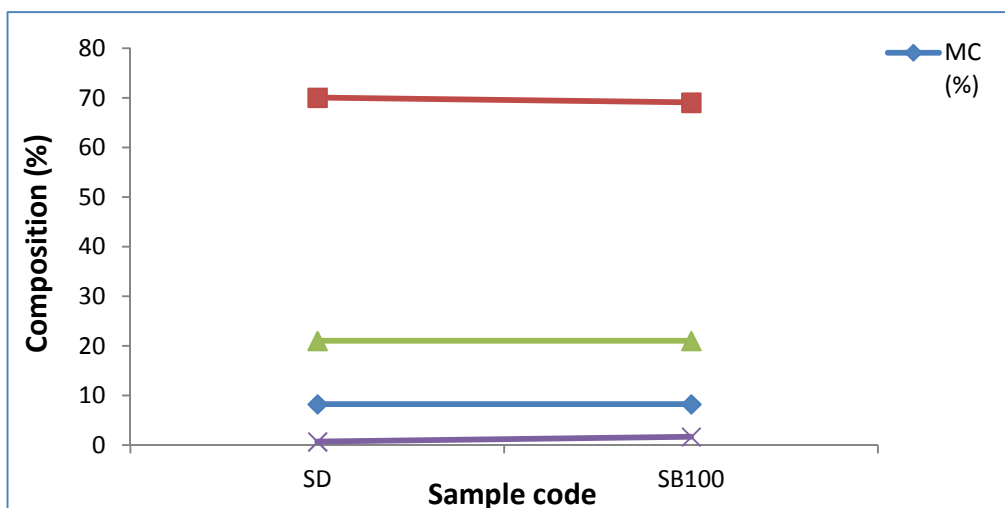


Figure 3: The effect of blending and briquetting on the proximate analysis of sawdust

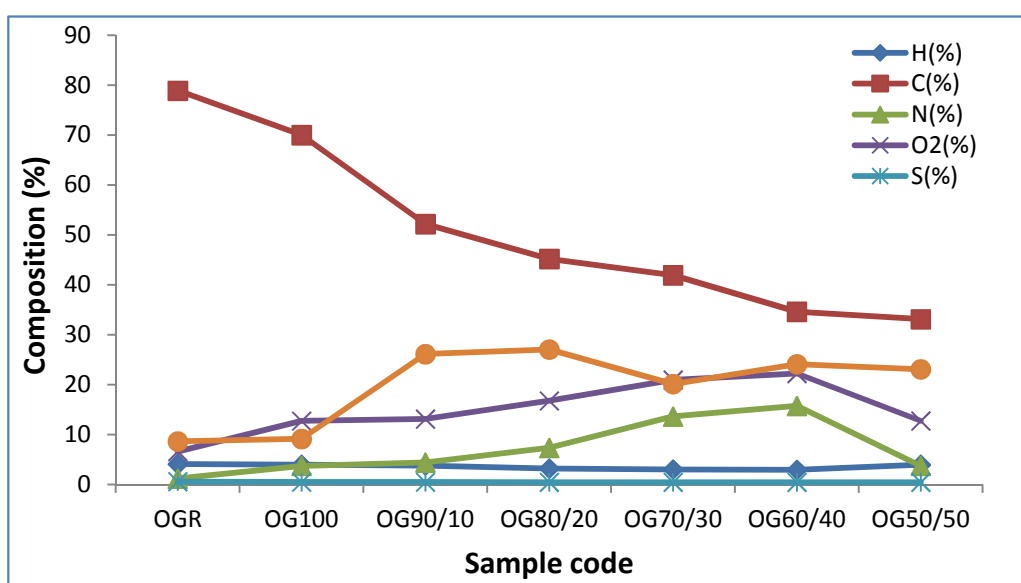


Figure 4: The effect of blending and briquetting on the ultimate analysis of Ogboyaga(Odu) deposit

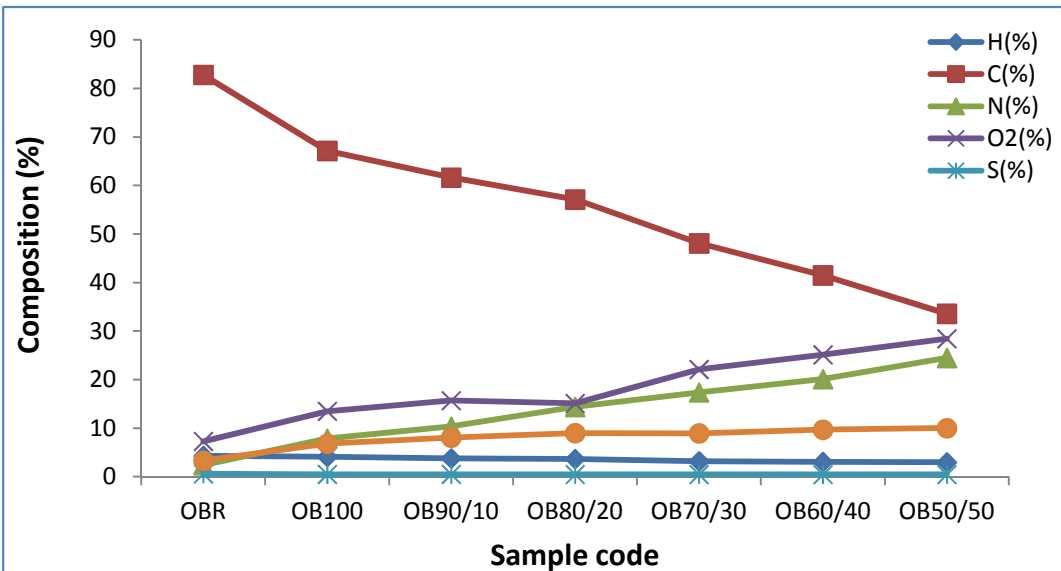


Figure 5: The effect of blending/briquetting on the ultimate analysis of Okaba deposit

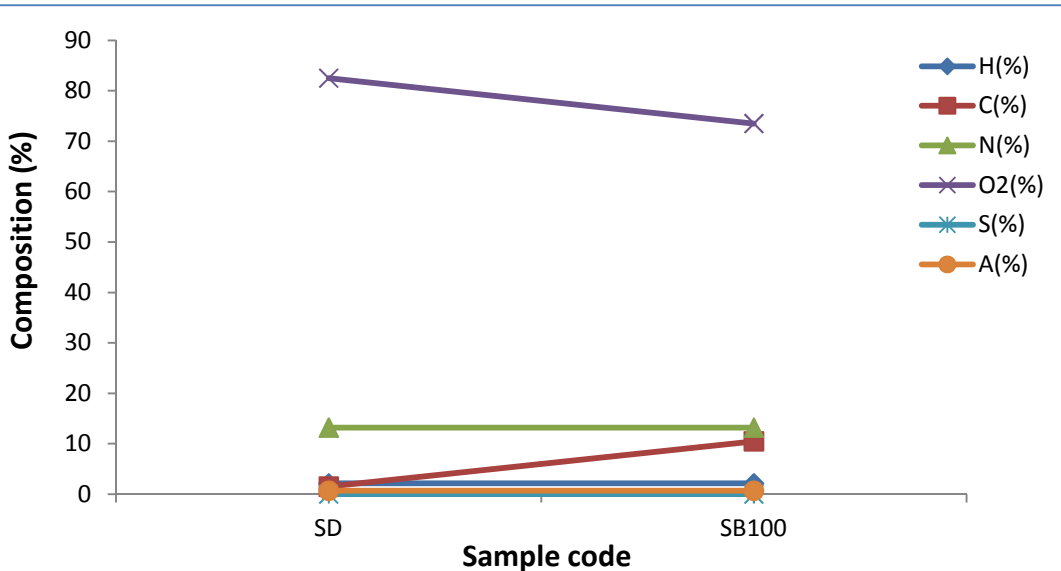
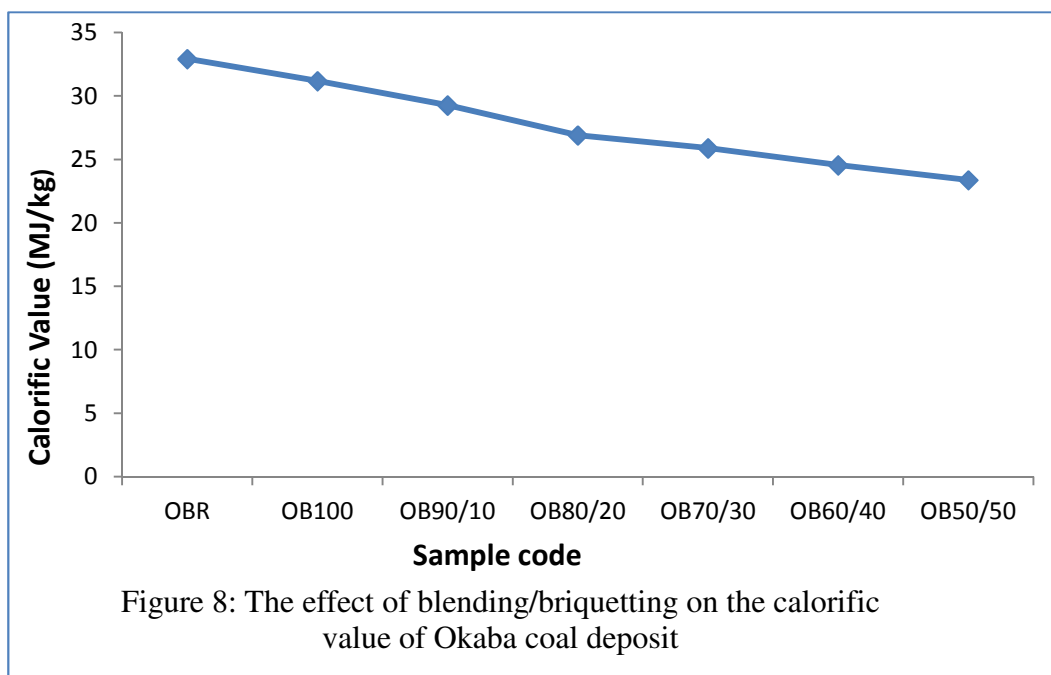
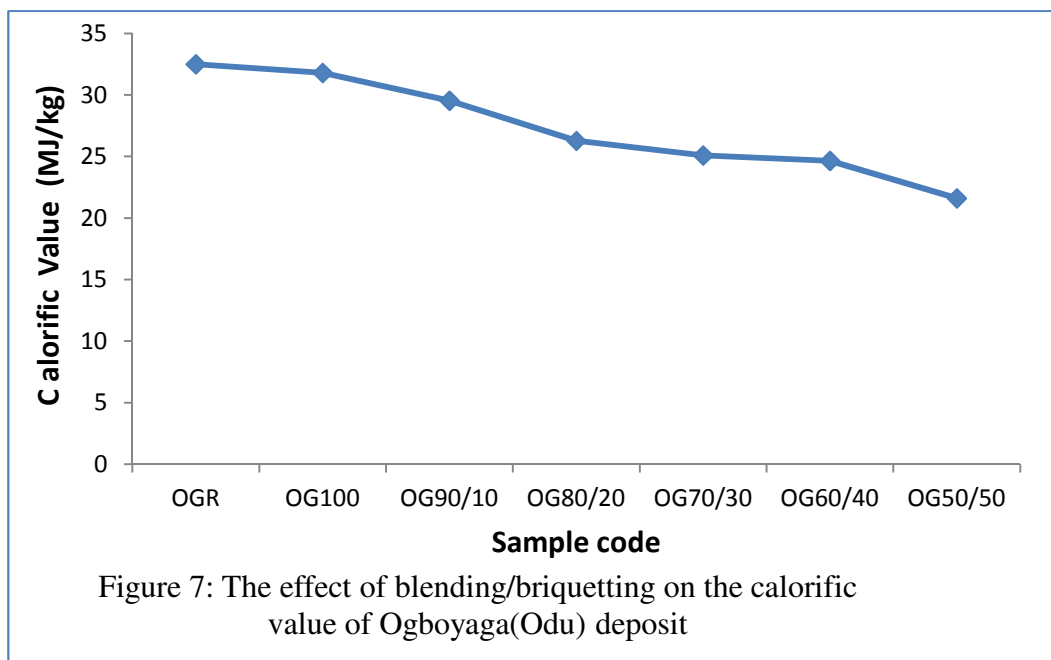


Figure 6: The effect of briquetting on the ultimate analysis of sawdust



3.1 *Effect of Proximate Analysis on the Samples*

The result of the proximate analysis of the raw materials is shown in Table 1. It can be seen that Okaba coal has higher fixed carbon content of 58.13% as compared with Ogboyaga at 54.33%. In Figures 1 and 2, the fixed carbon decreased progressively from 100% coal briquettes compositions to 50/50% biocoal briquettes in the two deposits; these are substantially higher than that of sawdust briquette at 21% in Figure 3. This may be due to the addition of biomass material which is lower in fixed carbon compared to the coal. Fixed carbon 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 coke that will be obtained on carbonization[2]. The fixed carbon content of all the biocoal briquettes are higher than that of sawdust briquette which make them better as solid fuel for domestic heat applications.

As for the moisture content, Okaba has lower moisture content (5.99%) as compared to Ogboyaga (6.93%) while sawdust has the highest at 8.28% compared to the two samples. In Figures 1 and 2, the moisture contents range between 6.07 and 8.73% with marginal increment amongst the blends which progressed from the 100% coal briquettes to 50/50% biocoal in all the compositions. This may be due to the blending of biomass and addition of starch as a binder which added to the moisture content of the biocoal briquettes. Moisture content is undesirable constituent because it reduces calorific value and its weight adds to the transportation cost of solid fuel. However, the percentages present in these biocoal briquettes are low enough not to have serious negative impact on the combustibility of the samples when used for domestic heat applications.

Table 1 shows Ogboyaga coal has higher ash content of 8.63% than Okaba with 3.32%. In Figures 1 and 2 it is observed that the ash content increased from the 100% coal briquettes to the 50/50% biocoal briquettes. The progressive increase may be due to the addition of biomass, binder and desulphurizer which fixed some of the sulphur to ash. It may also be due to the loss of water from the carbonate mineral and oxidation of iron pyrite to oxides [10], a fuel with low ash is desirable as in these biocoal briquette samples.

Okaba has higher volatile matter of 32.56% as compared to Ogboyaga put at 30.41%. In Figure 1, the volatile matter decreased progressively from the 100% coal briquettes to 50/50% biocoal briquettes in the two deposits. The amount of volatile matter indicates whether the coal will burn with a short or long flame and whether it will tend to produce smoke. The more volatile in the coal, the more it will smoke. Hence, the biocoal briquettes are all expected to generate less smoke and burn with high flame since they have less volatile matters than 100% coal briquettes.

3.2 *Effect of Ultimate Analysis on the Samples*

Table 2 shows the ultimate analysis of the raw materials. It shows that the carbon content is substantially high in all the two deposits with Okaba having higher carbon of 82.8% while Ogboyaga has 78.9% while sawdust has 1.48%. This is in agreement with [5] that a good coal sample should have high amount of carbon. The higher the carbon content, the higher is the calorific value and the better is the quality of the coal. In Figures 4 and 5, the carbon content decreased relatively from 100% coal briquettes to 50/50% biocoal in the samples of sawdust in Figure 6 put at 10.5%. Since carbon is one of the major combustible constituents of coal, it then follows that the biocoal briquettes have higher combustible carbon constituents than sawdust briquette although lower in comparison to coal

briquettes. The carbon contents of the biocoal briquettes are high enough to be a good fuel for domestic heat applications.

In Table 2, the hydrogen content of the Okaba is put at 4.3% while that of Ogboyaga is 4.1%. In Figures 4 and 5, it is shown that hydrogen decreased in all the biocoal briquettes as compared to 100% coal briquettes with OG_{60/40} having the lowest at 3.80% while OG_{90/10} have the highest at 3.81% and sawdust briquettes put at 2.13%. Hydrogen is mostly associated with volatile matter, and hence, it affects the use to which the coal would be put [8]. A good coal sample should have low amount of hydrogen as in the case of these biocoal briquettes, hence, the available low hydrogen in the right proportion will enhance the combustibility of the samples, this makes the biocoal briquettes a good fuel.

The nitrogen content of Okabacoal is put at 2.4% while that of Ogboyaga is at 1.3% and Figures 4 and 5 show that the nitrogen content increased relatively in the all biocoal briquettes while the OB_{50/50} biocoal briquette has the highest nitrogen content of 25% while the OG₁₀₀ and OG_{50/50} have 3.74% each. The slight increase in nitrogen content may be due to the biomass blend which contains more plant materials that have plant alkaloids, chlorophyll and other porphyrins containing nitrogen in cyclic structures. It can be said that it also draws nitrogen from the air in which it burns during combustion [10]. [5] affirmed that nitrogen has no calorific value but low nitrogen is required in coal because it reduces oxidation, hence the low nitrogen in the biocoal as compared to 100% coal briquettes will reduce oxidation.

Table 2 shows that the two coal deposits have low oxygen content with Ogboyaga having 6.6 % while Okaba has 7.30% while that of sawdust is put at 82.5%. In Figures 4 and 5, it is shown that the oxygen content increased progressively in 100% coal briquettes to 50/50% biocoal briquettes in all the compositions with increase in sawdust concentration. The oxygen content of 28.45% for OB_{50/50} coal briquette is the highest as compared with that of OG_{50/50} biocoal briquettes put at 12.72%. The increase may be due to the blend of sawdust which is a plant material that has higher oxygen content than coal. This is significant because the more oxygen a solid fuel contains, the easier is its ignition [5]. Hence, the biocoal will be easier to burn than coal briquettes.

In Table 2, the sulphur content Ogboyaga and Okaba coal are put at 0.6% each. In Figures 4 and 5, it can be seen that the sulphur content decreased relatively with increase in sawdust concentration in all the compositions. The addition of calcium hydroxide used as a desulphurizing agent further reduced the sulphur content in all the coal and biocoal briquettes in Figures 4 and 5 to between 0.47 and 0.48 in this other, Ogboyaga, 0.6% to 0.46% and Okaba, 0.6% to 0.47%. Sulphur is one of the major undesirable elements in coal even though it contributes to the heating value, on combustion, it produces acids of sulphur dioxide and sulphur trioxide which corrode combustion equipment and also cause atmospheric pollution. Since the sulphur in the biocoal briquettes are low in sulphur content as compared to the raw coal and coal briquettes, it will be better as fuel because it will emit less sulphur dioxide to the atmosphere.

3.3 Effect of blending and briquetting on the calorific values of biocoal briquettes

Table 1 show that Okaba has calorific value of 32.93MJ/kg while Ogboyaga has 32.51MJ/kg. Figures 7 and 8 show the effect of blending and briquetting on the calorific values on the biocoal briquettes. It can be observed that the calorific value decreased with increase in sawdust concentration from 100% coal briquettes to 50/50% biocoal briquettes in the two samples. OG_{90/10} biocoal has the highest calorific value of 29.55MJ/kg while OG_{50/50} has the lowest of 21.61MJ/kg among the

compositions. Even though the calorific value of the biocoal decreased with increase in sawdust concentration, they are still substantially higher than sawdust briquette, SB₁₀₀ with 17.68 MJ/kg and comparable with net calorific value of kerosene put at 37 MJ/kg and wood at 14.6 MJ/kg [1] used for domestic heat applications. The decrease in calorific value may be attributed to the blending of biomass and the addition of calcium hydroxide, a non-combustible substance and the starch used as binder which does not contribute to the total heat value released.

4.0 Conclusion

This study revealed that biocoal briquettes from Okaba and Ogboyaga raw coal are suitable for the production of environmentally solid fuel that can be used for domestic heat applications. It showed further that all the 50/50% coal and sawdust blend of the two coal samples are good as fuel while Ogboyaga with 90/10% coal and sawdust blend may be better in term of having the highest calorific value.

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