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Determination of energy content and heavy metals in briquettes produced from some agricultural wastes

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Abstract
The decreasing availability of domestic fuel like wood, charcoal and the ever-rising of kerosene and cooking gas in Nigeria, has drawn the attention to the need to consider alternative sources of energy for domestic use. This research was carried out to analyze some properties of some bio-briquettes (Rice husk, coconut shell, sheanut shell and millet stalk) prepared at moderate pressure and die temperature using a simple extruder briquetting machine. different briquette samples were produced by blending varying percentage of the biomass materials in the ratio of 100:0, 80:20, 70:30,60:40, 50:50,and 0:100. The results of the combustion characteristic revealed that the groundnut shell briquettes has a shorter ignition time (0.8mm/s) and will catch fire easily while the sheanut shell briquettes had the longest ignition time (4.3mm/s). The coconut shell briquettes had the highest after glowtime of 82sec while sheanut shell and millet stalk blend briquettes at ratio 70:30 had the lowest afterglow time of 13 sec. It took the coconut shell briquettes 16 mins to boil two litres of water just like kerosene (control) with the same quantity of water while it took the ground nut shell briquettes 24mins to boil the same quantity of water. The heavy metals analyses revealed that Pb, Ni, Se and Cd were not detected in the ashes of the fuel briquettes hile high values of Fe and Mn were obtained from rice husk and coconut shell briquettes. All values fell below the WHO/FAO and the DPR (2002) target and intervention values. An affordable and efficient source of energy to firewood which is environmentally friendly has been obtained from these agricultural wastes.

Keywords: Ignition time, renewable energy, heavy metals, densification

Introduction
Densification involved compacting of biomass residue into product of high density than the original raw material (Erickson and Prior, 1990). Densification of biomass is mostly called briquetting when utilized for energy production, pelleting or cubing when used for animal feed (Mani *et al*., 2003) [13]. A gain of 2 to 10 times calorific values can be expected when biomass are densified. The lowest bulk densities are around 40 kg/mg3 for loose straw and bagasse, the highest levels are around 250 kg/mg3 for some wood residue (Demirbas, 2001) [5]. In order to understand the suitability of biomass for density desification, it is essential to know the physical and chemical properties of the biomass, which includes its behavior as a fuel. These process variable determine the density, stability and durability of the product in most cases (Mani *et al*., 2006) [14]. The chemical properties include the heating value and ultimate analysis (Kenny *et al*., 1990). Biomass have a limited degree of elasticity. They have the tendency to spring back or even fall apart when compression is released (Bruhn, 1989) [3]. In order to reduce its springness and maintain bulk density, binder or stabilizing agent may be introduced. Most biomass contain wax-like adhesives like protein in grass and forage, lignin in wood residues. Under high pressure these constituents are squeezed out of the stem and leaf walls and are responsible for bonding in briquetting (Srivastava *et al*., 1981 and Reece, 1990) [21]. In the production of soft pellet by product of sugar industry and paper industry may be incorporated as binders. Water is also a suitable binding agent (Bruhn, 1989) [3]. Most widely used binder are calcium lingo-sulphone, colloids, bentonite starches, protein and calcium hydroxide (Mishra *et al*., 2008) [16]. The choice of a stabilizing agent of courage is highly dependent on the ultimate use of the product and the chemical compatibility of the materials and the binder (Mani *et al*., 2003) [13].

Materials and Methods
Sample Collection
Samples of corn cob, rice husk, groundnut shells, shea nut shell, millet stalk and coconut shell were collected from Maga, Danko Wasagu Local government while cassava starch was purchased at Zuru Central Market.

Sample Preparation
The collected samples were sun-dried for four days and pulverized and sieved with 8 mesh to obtain fine particle size. The sample were kept in a polythene bags until required for briquettes preparation.

Preparartion of Briquettes
A cylindrical mould of 16cm in length and 2.5 cm internal diameter was constructed. A metal bar of 2.5 cm diameter was used in pushing the formed briquettes out of the moulding cylinder. Blend of a pair of wastes biomass were prepared in the ratio of 80:20; 70:30; 60:40; 50:50. Each blend was thoroughly mixed with the slurry of the starch (the binder) in the mass ratio of 6:1. Each blend was then loaded into the cylinder mould and compressed with a screw presser and kept for 30 mins. The densified briquette was

pushed out of the mould with the aid of a metal bar. The same procedure was repeated for the other ratio. The produced briquettes were air dried for three weeks (Kyari, 2000) [12].

Methods

Calorific Value: The calorific value for the briquette was determined using a fulton, XRY-IB oxygen bomb calorimeter (ASTM, 1990) [1]. The sample (1g) was placed in the mould of the bomb. Two ends of a chromium firing wire of 10cm length were fixed on two electrode poles and then kept in good contact with the moulded sample. The calorimeter was filled with 10cm3 distilled water and the cover was screwed down. The bomb was filled oxygen at a pressure of 2.8-3.0 MPa. The wires of the bomb calorimeter connected and temperature sensor was put into the canister. The water was stirred until the temperature reading stabilized. The temperature reading was noted as (T_0). The combustion was started after about 31 mins and the final temperature was noted (T_f).

The length of the unburnt firing wire was measured and recorded. The inner linings of the oxygen and crucible was then washed with distilled water and poured into a conical flask. 2 drops of methyl red indicator was added and titrated with 0.7 M sodium carbonate. Titre value was recorded.

The heating value of the sample was calculated using the equation below.

$$W = \frac{E \triangle T - \emptyset - V}{M}$$

Where:
W= heat of combustion of Sample,
M= mass of sample combusted
E= Energy equivalent of the calorimeter per degree Celsius
$\triangle$T= temperature change, (i.e. TF-T0)
Ø= correction for heat of combustion of firing wire= length of burnt wire ×specific heat capacity of chromium (2.3)
V= volume of alkali solution used

Flame Propagation: This was determined as described by Oladeji (2010) [17]. A piece of the briquette was graduated in centimeters, ignited at one end and allowed to burn until it extinguished itself. The flame propagation rate was estimated by dividing the distance burnt by the time taken in seconds.

Afterglow Time: The afterglow time was determined to estimate how long the briquettes will burn before restocking when used I cooking and heating. A piece of oven-dried briquette was ignited and after a consistent flame was established the flame was blown out. The time, in seconds, within which the glow was perceptible was recorded (Oladeji, 2010) [17].

Porosity Index: The method of (Ilochi, 2010) [9] was used to determine the parameter. The porosity test determines the cell opening of the briquettes. It was carried out by weighing an equal dimension of the various briquettes samples. The samples were then immersed in 100cm3 of water for 3 minutes. The excess water was allowed to drain out. The volume of water drained out, the volume of water retained in the briquette samples and the weight of the briquette after immensing in water was recorded. The value obtained was used to calculate the porosity index

$$\text{Porosity Index} = \frac{\text{Mass of Water Absorsed}}{\text{Mass of the Sample}}$$

Specific Power Output: The specific power output was determined using the following equation

Heat given out (Q) = mc$\triangle$T

Where: m= Mass of water (2kg, c= Heat capacity of water (4184J/kg), $\triangle$T = T2-T1= initial Temp and final Temp.

$$\text{Power} = \frac{Q}{t}$$

Where: t= time taken in seconds

$$\text{Spesific Power} = \frac{\text{Power output}}{\text{Mass of briquette}}$$

Combustibility: 2kg of a briquette was stacked into a stove and ignited after application of 1cm3 absolute ethanol to ease ignition. The fire was allowed to assume a steady combustion. An aluminium pot containing 1litre of water, whose initial temperature was recorded, was placed on the stove after a steady combustion was assumed and a stop watch was started and the temperature reading was taken after two minutes with a mercury –in-glass thermometer until the water started to boil as reported by (Onuegbu *et al*., 2012) [20]. The time taken for the briquettes to boil 1 liter of water was recorded. A similar procedure was repeated on a kerosene stove to serve as control (Etonihu *et al*., 2008) [8]

Determination of Heavy Metals by AAS

The principle of the method is based on nebulizing a sample solution into an air-acetylene flame where it is vaporized. Element ions are atomized and the atoms formed absorbs radiation of the characteristic wavelength from a hollow-cathode lamp. The absorbance measured is proportional to the amount in the sample solution.

Heavy metals comprising of Cu, Zn, Cr, Ni, Fe Co, Pb, As, and Mn were determined as reported by (Shahidi *et al*., 1999) [22]. The ash sample of a briquette was sieved and 4g of the ash was treated with 10cm3 of HNO_3/H_2O_2 (1:1) and heated gently on a hot plate until brown fume disappeared. 5cm^3 of deionized water was then added and heated until a colorless solution was obtained The solution was filtered into a 100cm3 volumetric flask with Whatman No.1 filter paper and volume made to the mark with deionized water. The solution was used for the heavy metal analysis by flame atomic absorption spectrophotometry (FAAS).

Results

Table 1: Combustion characteristic of rice husk and corn cob briquettes and their blends.

Briquettes	Ignition time (mm/s)	After glow (s)	Calorific value KJ/Kg)	Combu stability (min)	Specific power Output (w/kg)	Efficiency (%)
Rh	1.70±0.01	20±0.12	7.20±0.10	22	430.45	71.99
Cc	0.50±0.01	82± 1.0	6.80±0.20	20	488.13	81.63
80:20	1.60±0.03	61±0.2	7.60±0.20	20	485.34	81.17
70:30	1.40±0.02	45±1.0	8.20±0.10	18	542.45	90.72
60:40	1.10±0.01	35±0.7	8.15±0.03	18	532.22	89.01
50:50	1.00±0.03	30± 1.0	6.70±0.28	22	443.88	74.23
Kerosene		-	-	16	597.96	100.00

Table 2: Combustion characteristic of shea nut shell and millet stalk briquettes

Briquettes	Ignition Time (mm/s)	Afterglow Time (s)	Calorific Value (MJ/kg)	Combustion Test (min)	Specific Power Output (w/kg	Efficiency (%)
S/nut shell	4.30±0.02	20±1.20	7.50±0.90	30	480.46	80.35
Millet stalk	1.70±0.01	47±0.50	6.88±0.08	22	435.52	75.83
80:20	3.40±0.02	16±0.75	7.95±0.03	18	532.30	89.02
70:30	2.60±0.02	13±0.25	6.70±0.07	22	441.22	73.79
60:40	2.00±0.01	38±1.30	7.82±0.08	18	532.30	89.02
50:50	1.70±0.03	38±0.85	6.75±0.18	22	439.95	73.58
Kerosene	-	-		16	597.96	100.00

Table 3: Combustion characteristic of ground nut shell and coconut shell briquettes and their blends.

Briquettes	Ignition Time(mm/s)	Afterglow Time (s)	Calorific Value (MJ/kg)	Combustion Test (min)	Specific Power output (W/kg)	Efficiency (%)
G/nut Shell	0.80±0.01	20±0.50	5.85±0.02	24	399.80	66.86
C/nut shell	1.70±0.02	50±1.20	8.40±0.04	16	587.50	98.25
80:20	0.70±0.01	40±0.78	6.61±0.08	22	445.83	75.06
70:30	1.00±0.02	42±1.00	7.70±0.12	20	468.61	78.37
60:40	1.30±0.03	46±1.80	8.10±0.08	18	524.55	87.72
50:50	1.60±0.02	60±2.00	8.00±0.41	18	552.23	92.35
Kerosene	-	-	-	16	597.96	100.00

Table 4: Results of the heavy metal concentration of fuel briquettes

Cations (ppm)	Rh	Cc	Gs	Cs
Fe	112±02	43.15±0.03	43.48±0.01	37.10±0.01
Cu	2.0±0.01	5.65±0.002	8.35±0.002	9.35±0.02
Zn	2.50±0.01	ND	0.60±0.002	3.25±0.02
Mn	125.0±0.15	ND	19.85±0.001	125.95±0.01
Pb	ND	10.60±0.02	ND	ND
Ni	ND	13.15±0.03	ND	ND
Cr	15.80±0.03	2.85±0.04	11.08±0.026	21.45±0.001
Se	ND	ND	ND	ND
Cd	3.3±0.01	ND	ND	ND

Discussion

The flame propagation results ranged from 0.08mm/s (groundnut shell) to 4.30 mm/s sheanut shell). The biomass briquettes have short ignition time and will catch fire easily. As the proportion of biomass ratios reduces, the ignition time also reduces. A direct proportion relationship was established between campaction and ignition time at ($P \leq 0.0001$). This observation is in agreement with Davies and Abolude (2013) [4] who stated that increased in density of briquettes, result in delayed in ignition time of the briquettes. This might be linked to the fact that course particle sizes could have more pore spaces in betwwen the particles than finer particle sizes thus increase in the porosity index of the briquettes which might cause reduction in time taken for the briquettes to be ignited (Davies and Abolude, 2013 [4] than finer particle sizes. This will increase the porosity index of the briquettes which might cause reduction in the time taken for the briquettes to be ignited (Davies and Abolude, 2013) [4].

The results of the afterglow time ranged from 13 sec (Sn/Ms at 70:30) to 82 sec (corn cob). The low value of afterglow time in the Sn/Mn blends at ratio 70:30 could be attributed to its high density which resulted in reduced porosity. Reduction in air content within the matrix of the briquettes has inhibited flame propagation due to low thermal conductivity is influenced by density due to reduced porosity which tends to hamper the rate of infiltration of oxidant and outflow of the combustion products during burning. The higher value of the corn cob briquettes attributed to the coarse nature of the particle size which allows for free infiltration of oxygen into the briquettes leading to increase in burning time. This is in agreement with the findings of Oladeji (2010) [17] who reported that corncob will ignite more easily and burn with intensity for a long time than rice husk briquettes.

The results of the combustibility test to compare the cooking efficiency of the briquettes. It measured the time taken for each set of briquettes to boil an equal volume of water under similar conditions. Ccoconut shell briquettes took 16 minutes to boil 2 litres of water, while it took the ground nut shell briquettes 24 minutes to boil the same quantity of water. It was observed that bleding the agro- wastes with each other actually reduced the time taken to boil, the same quantity of water while improving the residence time for the briquettes to undergo complete combustion. This agreed with the findings of Onuegbu *et al*., (2011) [19], who observed that the cooking efficiency of briquettes increase with the increase in biomass concentration (within the biomass range of 0% to 15%) and sometime beyond this range, the cooking efficiency wiil start to drop. They burn and boil water faster and less quantity of them were required to produce 1 litre of boiled water than the other briquettes which are not blended. The discrepancy noticed in this study are the cases of rice husk/corncob blends at (50:50) and sheanut shell/ millet stalk blends at (60:40) ratios which took 22 minutes to boil the same quantity of water. This could be as the result of their high ash content and stress value which could impede combustion (Olorunnisola, 1998) [18].

The specific power output varied from 399.80w/kg (groundnut shell) to 587.50w/kg (coconut shell). The low value for groundnut shell briquette could be attributed to the low propagation time and high density while the high value for coconut shell could be as a result of low density and high propagation (David *et al*., 2013) [4].

The efficiency of the fuel briquettes when compared to kerosene varied from 66.86% (groundnut shell) to 98.25% (coconut shell). It was observed that blending this biomass samples has actually increased the fuel efficiency. As the blend ratio increases, the efficiency of the fuel briquettes also increases except at 50:50 where there was a slight drop.

The computed calorific values of the briquettes varied from 5.8 MJ/kg (groundnut shell) to 8.40 MJ/kg (coconut shell). It was noticed that blending this residues improved the calorific value of the samples except at ratio 50:50 which showed a slight decrease. The values obtained are less than those obtained from literatures, for soybeans 12.9MJ/kg (Enweremadu *et al*., 2004) [6], 12.6 MJ/kg (Kaliyan and Morey, 2009) [10] ground nut shell briquettes. These values are significantly different at ($P \leq 0.0001$). It was observed that the coconut shell has a high bulk density and the energy value of the briquettes are influenced by their density.

The results of the heavy metals analysis is shown in Table 3. Heavy metals are the heavy, dense metallic elements that occur in trace levels but are toxic and tend to accumulate, hence commonly referred to as trace metals. The major anthropogenic sources of heavy metals are the industrial waste water and surface run-offs. Many of these trace metals are highly toxic to human such as Hg, Pb, Ni, Cd, As and Sn. Their presence in surface and underground water at above background concentration is undesirable (Bhatia, 2001) [2]. Some have also been identified as deleterious to aquatic ecosystem and human health (Bhatia, 2001) [2]. The level of heavy metals in the ashes of the burnt briquettes samples. The concentrations ranged from 1.0ppm for Zn in the millet stalk briquettes to 125.0ppm for Mn in the rice husk briquettes. The highest value obtained were 112.0ppm for Fe and 125.0ppm for Mn both from rice husk briquette. The study revealed that Pb, Ni, Se, and Cd were not detected (ND) in the briquette ash samples or were below detection limit (BDL) except for the rice husk briquettes ash which showed traces of Cr and Cd.

It was observed that the different briquette sample differ in their metal content and metal concentrations. This could be attributed to the different sampling locations where they were collected sine plant materials absorb these metals from the soil (Bhatia, 2001) [2]. Also, the values recorded from the ashes of these burnt briquettes fell below the recommended levels by WHO/FAO and DPR (2002). This implies the ashes of these briquettes pose no environmental threat and therefore can be used in farmlands as manure or neutralize soil acidity thereby enhancing plant growth and food productivity.

Conclusion

In view of this, the production of agricultural by – products briquettes can greatly provide alternative energy sources for domestic cooking in Nigeria and also serve as a measure in curbing the environmental hazard posed by poor methods of agricultural wastes disposal in addition to reduce the popular use of fire-wood which has and adverse effect on our environment such as desert encroachment, soil and gully erosion and climate change in general.

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