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Preliminary Studies on Biofuel Potentials of Shea Nut Cakes in Niger State, Nigeria

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Shea nut cake is produced in large quantity as a by-product by the local communities across Niger state. Three samples were obtained and analysis for proximate, ultimate and mineral analysis using the standard methods. The Proximate analysis results indicated that the shea nut cake had average 8.36% crude proteins, 44.96% carbohydrates, 11.60% crude fat. ash content, 6.27% moisture and 2.17% crude fibre. The average ultimate analysis result obtained in the three samples were volatile matter (79.36%), fixed carbon (22.20), carbon content (75.07%),, nitrogen 8.43%), oxygen (36.76%), Sulphur (0.70%). The average mineral analysis obtained were sodium (247.50 mg/g) potassium (201.50 mg/g), magnesium (381.0 mg/g), calcium (49.05 mg/g), phosphorus (201.5 mg/g) and iron (36.34mg/g) respectively. This study highlights the potential of the shea nut cake, the cakes biomass feedstock can be thermally be converted to potential energy product such as the animal feed, fertilizer and energy generation biochar, bio-oil and gaseous which are sources of biochemical especially phenol and their derivative.

Keywords: Shea nut cake, proximate, crude oil Mineral composition.

1. Introduction

The Nigerian economy is purely driven by the availability of petroleum crude oil. In the year 2011 the country was regarded as the 14th largest producer of crude oil in the world and account for approximately 3% of the global crude oil production (EIA, 2012). It is however pathetic that almost all Nigerian crude oil are been refined outside the shores of the country because the nation refineries are presently operating at a low capacity due to inadequate maintenance, sabotage, and fire disaster (Iye and Bilsborrow, 2013). As a result, the country is currently importing most of its refined petroleum products which together with subsidized consumption is costing the Nigerian government $3–4 billion per year (IEA, 2012). The rapid depletion of world fossil fuel reserves, concern for climate changes and ever soaring price of petroleum derived fuels are among the drivers for alternative sources of energy (Rahman *et al.,* 2014). Conversely, the interest in renewable energy and specifically energy from biomass energy as alternative sources of sustainable energy has received a great deal of concern (Akowuah *et al*., 2012)

Among many of the available sources of bioenergy, biomass is the most common and readily available making it a potential sources of feedstock for bioenergy generation. The sources of biomass includes (cakes from seed and fruit), wood wastes, forest residue, paper waste and energy crop grown on short rotation perennials. Energy derived from biomass can be utilized in generating electricity, and order forms of bioenergy (Wan Azlina *et al*., 2014).

Nigeria is challenge with the twin problems of solid waste management and insufficient power generation. The seeming lack of inadequate waste disposal management system has contributed to the disposal wool wastes along road sides and rivers or openly combusted. These practices negatively impact humans in addition to the loss of useful energy sources. Since the generation of waste by man cannot be prevented, a waste disposal plan has to be in place for proper collection of generated waste. These wastes if properly managed however can be reprocessed to serve as a source of renewable energy (Rupinderjit *et al*., 2012)

The shea butter tree (*Vitellaria paradoxa*) tree is a local fruit. The shea fruit is a green epicarp, a fleshy mesocarp (pulp) and a relatively hard shell (endocarp) which encloses the shea kernel. The shea nuts contain from 25% up to 55% edible fat. The Shea fruit according to Moore (2008) produces more solid shea butter as compared to other oil bearing fruits as it contains more stearic acid. The kernel, according to Axtell *et al*. (1993) contains about 65% edible fat (shea butter) and the remaining product from which the butter is removed (shea cake), is an excellent ingredient for animal feed production. Niger state is on the average of becoming the main hub for shea butter in Nigeria. Currently, the state claims of having the largest collection of shea trees in the world, controlling about 54% of the trees in Nigeria and of the vaunted 32,000 metric tonnes of shea nut and butter exported from Nigeria. It is a known fact that vital research has been showed into the phenology of the shea tree, its usage and that of the uses of the shea butter extracted from the nuts of the shea fruit in Nigeria, however, no or very little research has been done in expanding the benefits and adding value particularly to the by-product of the shea industry. Therefore, this study seeks to add value to Shea nut cake by converting it to a useful product.

1.1 The State of Shea Cake in Niger Shea Butter

The use of the shea nut cake has not changed in Niger state over the last decade. It has been reported that the residual meal (the first extraction cake), as in the case with shea butter, is also used as a waterproofing agent to repair and mend cracks in the exterior walls of mud huts, windows, doors and traditional beehives. The sticky black residue (the second extraction cake), which remains after the clarification of the butter, is used for filling cracks in hut walls (Marchand, 1988) and Ofosu (2009), claims that the shea waste, the shea nut cake, is a biodegradable organic material with high volatile solids content and has shown to have the potential to produce biogas with high methane content (Ofosu, 2009). The study indicated that fermentation of the shea waste with cattle manure was found to be the feasible anaerobic digestion option in the generation of up to 61.4% of methane and the treatment of shea waste prior to disposal in an effort to reduce its pollution potential on the environment. The study concluded that the production of biogas from anaerobic digestion of shea waste provides an important energy potential, which should be of value in improving the economics of shea processing.

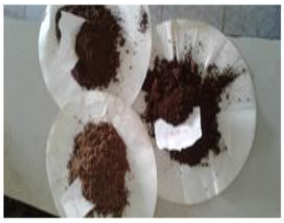

Plate 1: Shea butter tree Plate 2: Shea nut cake in 3 samples

2. Materials and Methods

2.1 Sample collection

The sample cakes from shea butter nut were collected from three Local Government Areas, one from each senatorial zones of Niger State. The cakes were ground into powder using a household grinder, before use so as to minimize voids inside the reactor, as well as to fill maximum amount of the cake in the reactor.

2.2 Proximate and Ultimate Analyses

The proximate analysis provides information on moisture, ash, volatile matter and fixed carbon of shea cakes. Moisture content was determined according to AOAC (2000) at 105 ^oC. The percentage moisture content was calculated using the equation:

$$\text{Moisture (\%)} = \frac{\text{initial oven dry weight}}{\text{initial weight}} \times 100$$

2.3 Ash content

The Ash content was determined by weighing a known amount of dried sample cakes in to a pre weighed 25cm^3 silica crucibles, then the crucible containing the samples were heated in a muffle furnace at 575 ^0C for 3 hours and cooled in a dessicator.

$$\text{Ash (\%)} = \frac{\text{weight ash}}{\text{weight of sample}} \times 100$$

2.4 Volatile Matter

The volatile matter of the cakes was determined by placing known amount of sample into a pre-weighed crucible. The crucible containing the samples was heated in a muffle at 950 ^oC for 3 minutes then cooled in a desiccator. The percentage weight loss of the sample was calculated using equation:

$$\text{Volatile matter} = \frac{\text{weight loss of dry sample}}{\text{weight of dry sampl}} \times 100$$

2.5 Fixed Carbon

Fixed carbon was determined using equation

Fixed carbon (%) =100-[volatile matter %+ ash (%)].

2.6 Net Calorific Values

The Net calorific values (NCV) was calculated using equation

$$NCV = GCV \times \left[1 - \frac{w}{100}\right] - 2.44 \times \left[\frac{H}{100}\right] \times [8.936 \times [1 - \frac{w}{100}]; \left[\frac{Mj}{Kg} wb\right]$$

Where 2.44 is the enthalpy difference between gaseous and liquid water at 25 ^{0}C, 8.936= MH_2O/MH_2 (i.e. molecular mass ratio of water and hydrogen, w is the moisture content (%) and GCV is the gross calorific value and H is the concentration of H_2 (%) in the samples.

2.7 Crude Protein

Total protein was determined by the Kjeldahl method as modified by Pousga *et al*. (2007). The analysis of protein content in a compound by Kjeldahl method is based upon the determination of the amount of reduced nitrogen present. 30 g of each sample was weighed into a filter paper and put into a Kjedahl flask, 15 tablets of Na_2SO_4 were added with 1 g of $CuSO_4$ respectively. Twenty millilitres (20ml) of concentrated H_2SO_4 were added and then digested in a fume cupboard until the solution became colourless. It was cooled overnight and transferred into a 500 ml flask with 200 cm^3 of deionised water. it was then cooled with the aid of packs of ice block. About 62 to 72 ml of 40% of NaOH were poured into the conical flask which was used as the receiver with 60 ml of 5% boric acid using methyl red as indicator. The ammonia gas was then distilled into the receiver until the whole gas evaporated. Titration was done in the receiver with 0.1 N H_2SO_4 until the solution became colourless. The following formula was used:

$$\text{Crude protein } (\%) = \frac{Vs - Vb \times Nacid}{\text{original weight of sample used}} \times 100\%$$

2.8 Crude fibre

Crude fibre content was determined according to methods adopted by Pousga *et al.,* (2007). 25 g of each shea nut cake (SNC) samples were defatted separately with Diethyl ether for 9 hours and boiled under reflux for exactly 35 min with 200 ml of 1.25% H_2SO_4, and then filtered through cheese cloth on a fluted funnel. This was later washed with boiling water to completely remove the acid. The residue was then boiled in a round bottomed flask with 200 ml of 1.35% NaOH for another 35 min and filtered through formerly weighed couch crucible. The crucible was then dried with samples in an oven at 105°C, and was left to cool in a desiccator.it was then weighed after cooling. This was later cremated in a muffle furnace at 605°C for 2 to 4 hours and later allowed to cool in a desiccator and weighed. The following formula was used:

$$\text{Crude fibre } (\%) = \frac{\text{weight of fibre (g)}}{\text{dry weight of original sample (g)}} \text{ x } 100\ \%$$

2.9 Crude Fat

The method employed was the Soxhlet extraction technique adopted by in which 20g of the samples were weighed and carefully placed inside a fat free thimble. This was covered with cotton wool to avoid loss of the sample. The loaded thimble was put in the Soxhlet extractor and about 200 cm^3 of petroleum ether poured into a weighed fat free soxhlet flask with the flask attached to the extractor. The flask was placed on a heating mantle such that the petroleum ether in the flask refluxed. Cooling was achieved by a running tap connected to the extractor for about 8 hours after which the solvent was completely tapped into the flask. Rotary vacuum evaporator was used to evaporate the solvent leaving behind the extracted lipids in the soxhlet. The flask was removed from the evaporator and dried to a constant weight in the oven at 65°C. The flask was then cooled in a desiccator and weighed. Each determination was done in triplicate. The amount of fat extracted was calculated by the following formula presented below:

$$\text{Crude fat } (\%) = \frac{\text{weight of extracted lipids (g)}}{\text{weight of dry sample (g)}} \text{ x } 100\ \%$$

2.10 Ultimate Analysis of Shea Butter Cake

Oxygen, nitrogen, and Sulphur content of Cake were found out under the ultimate analysis. The ultimate analysis Calculating heat balances in any process in which coal cake was use, Using the values of proximate done theoretically by using the various formulas.

Calculation y of O, N and S from the proximate analysis: These values were carried out through the following steps:

2.11 Oxygen Content

Oxygen content of the sample was calculated theoretically by difference on the basis of the following formula.

$$O_2 = 100 - \%\ of\ (C + H + N + Ash)\%$$

2.12 Mineral Analysis

The AOAC (1990) procedure was used for the determination of mineral contents present in the different shea nut cake samples. Each sample of the shea nut cake was digested in a di-acid mixture (HNO_3:$HClO_4$) in the ratio (7:3) on hot plate at 185 ^oC for about 2 hours. The contents were diluted to volume of 105 ml with deionised water. The mineral contents (Na, K, Ca, Mg, P, and Fe) in the digested samples were estimated separately using Atomic Absorption Spectrophotometer. (AAS) method as described in the AOAC (2000) methods of analysis of heavy metals.

3. Results and Discussion

Results of analysis of shea nut cakes are presented in Tables 1, 2 and 3.

Table 1: Proximate Analysis of Various Shea Nut Cakes

Samples Description	Dry matter (%)	Moisture content (%)	Ash (%)	Crude fat (%)	Crude protein (%)	Crude fibre (%)	CHO (%)
Sample A	89.56	10.44	6.18	1.60	8.36	2.17	44.96
Sample B	89.56	6.27	8.67	1.33	10.19	1.83	42.31
Sample C	93.73	7.25	9.23	1.31	8.23	1.73	23.42

Table 2. Ultimate Composition of Shea Nut Cakes

Sample description	Volatile matter (%)	Fixed carbon (%)	Energy Value (%)	Nitrogen (%)	Oxygen (%)	Sulphur (%)
Sample A	79.36	14.39	23.56	7.04	36.76	0.70
Sample B	69.12	22.20	17.32	5.62	46.85	0.45
Sample C	58,94	19.02	19.48	8.43	47.71	0.33

Table 3 Mineral Analysis of Shea Nut Cakes

Sample description	Sodium (mg/g)	Potassium (mg/g)	Calcium (mg/g)	Magnesium (mg/g)	Phosphorus (mg/g)	Iron (mg/g)
Sample A	247.50	201.50	49.05	381.00	201.50	36.34
Sample B	230.00	386.00	55.60	327.00	386.00	43.12
Sample C	210.00	166.25	102.50	325.50	166.25	27.23

3.1 Proximate Analysis

Dry Matter Content

Table 1 above shows different values of dry matter content in the samples A 89.56%, B 89.56%, C 93.73%, from the values it shows that sample C 93.73% has the highest value than sample A and B sample. Also the values obtained from these sample were higher than what was reported (68.03 %) by Abdul-Mumeen *et al.* (2013)

Moisture Content

The biomass conversion technologies are influenced by the moisture content of the feedstock and low moisture favored thermal conversion technique (Mckendry, 2002).The moisture content of the sample cakes as shown in Table 1. They ranged from (6.27-10.44%) with sample A cake (10.44%) had the highest value followed BY sample C cake (7.25%) and sample B (6.25%) respectively. The values obtained from the work shows that sample B and C are within the standard value of (6.50%) while sample A had values above those of cowpea (9.4%) and green pea (7.8%) obtained by Iqbal *et al* (2006). The relative low moisture content of the cakes leads to high efficiency during combustion and increase in heating rate.

Ash Content

Ash is a parameter that directly affects the heating value, high ash content of biomass make it less desirable as fuel (Demirbas, 2007) as it might stickled to heating plate thereby reducing the heat transfer and increase the risk of reactor slagging. Sample C had the highest ash content value (9.23%), followed by sample B (8.67%)

and lastly sample A (6.18%) .The low values obtained from the cakes indicated that the cakes contained less impurity that will attack furnace component on strong heating.

Crude Fat

The crude fat obtained from the shea cakes are shown in Table 1, the highest value was found in sample A cake (1.60%) followed by sample B cake(1.33%) and lastly sample C cake (1.31%), the values obtained are lower than what was reported for calabash seed cake (3.30%) reported by (Abdullahi *et al.,*2013). Low values from the cakes lead to low soluble material, high biodegradability and hence high biogas production, the differences in fat levels of the Shea trees due to their genetic disparities or probably due to their different geographical and ecological zones.

Crude Protein

Crude protein measures the total nitrogen of a product. Samples with low crude protein is associated with low nitrogen content, which increase the activates of microbes during fermentation biogas produced the crude protein content of cakes are presented in Table 1. The values range from (8.23-10.98%) with sample B cake (10.19%) had the highest value, followed by sample A with (8.36%) and sample C (8.23%) the values are lower than 16. 48 and 29.90 % for calabash and soy bean respectively (Sani, 2011).

Crude Fibre

Crude fibre It refers to the indigestible carbohydrate components that is present in plant (biomass), the values obtained shows that sample A cake had the highest value (2.17%) followed by sample B cake (1.83%) and lastly sample C cake (1.73%). The values obtained from the cakes are low which favoured the action of microorganisms during biogas production.

Carbohydrate The carbohydrate content in the sample cake are shown in Table 1, it range (23.42-44.96%) the highest value was recorded in sample A cake (44.96%) followed by sample B cake (42.31%) and the lowest from the value was sample C cake (23.42%) the differences between the sample cakes indicated the distribution of carbohydrate, since the cake in sample A tend to be more higher when compare with other samples cakes. The result is lower than 78% and 89% reported for Ludai and Gyandama cakes (Sani, 2011). The result from the sample cakes by percentage of carbohydrate will serves as a substrate for bioethanol and biogas production.

3.2 Ultimate Composition of Shea Butter Cakes

Volatile Matter

The volatile matter of the cakes ranges from 58.94-79.36%, sampe A (79.3) has the highest value, follow by sample B (69.12) and lastly sample C (58.94), these values are nearer to the value reported by (Ankit *et* al., 2011) for groundnut cake (83%).The volatile matter and fixed carbon content measure the ease at which biomass can ignite and gasified. High volatile matter is advantageous in biomass usage as fuel and can cause instance ignition.

The fixed carbon range from (14.39-22.20%) with sample B cake had the highest value (22.20%) followed by sample C (19.02%) and lastly sample A (14.39%) respectively

Energy value of material measures the energy or heat value it releases when burnt in air, it is also used to assess the competitiveness of a processes fuel in a given market (Veeresh *et al.,* 2012). The energy value obtained in this study ranged from (17.32-23.56 MJ mol^{-1}) with sample A cake having the highest value of (23.56) followed by sample C cake (19.48) and lastly sample B cake having the lowest value of (17.32 MJ mol^{-1}) the result obtained are similar to 20.81 reported by Basak and Ersan (2006) for cotton cake. From the result obtained for HHV it shows the cakes could be a good energy carrier for generation of heat.

Table 2 shows that nitrogen ranges from 6.5-8.43% with sample C cake having the highest value of 8.43 followed by sample A cake 7.04 and lastly B cake (6.24). These values are similar to value reported for groundnut cakes (6.80%) (Ankit *et al*., 2011). The oxygen range from (36.76-46.85). These values are similar to what was reported for linseed and groundnut cakes Ankit *et al* (2011). The findings of this study shows that cake heating values are within the acceptable heating values with high content of volatile matter, oxygen and low sulphur content.

3.3 Mineral Analysis

Results of mineral content in shea nut cakes are presented in Table 3

Sodium Content

The sodium content in shea nut cakes from three samples in Niger ranges from 120.00mg/g to 247.50 mg/g, the sodium content varies across the three samples. Sample A has the highest sodium content, follow by sample B (230.00 mg/g) and sample C has the lowest sodium content with 210.00mg/g. The result obtained is lower than the 345 .10mg/g reported by Abdul-Mumeen *el al*. (2013).

Potassium Content

Table 3 shows the potassium content which ranged from 166.25 mg/g for sample C, follow by 201.50 mg/g for sample A and 386.00mg/g for sample B which has the highest value. The Potassium content obtained across the three samples is lower than the 410.00 mg/g reported by Abdul-Mumeen *et al*. (2013).

Calcium content

Results of calcium analysis of the three samples of shea nut cake are presented in Table 3. Sample C had the highest calcium content with (102.50 mg/g) follow by sample C (55.60 mg/g) and sample A has the lowest calcium content (49.05 mg/g).

Magnesium Content

It can be observed from Table 3 that magnesium was significantly different across the three samples. Sample A has the highest magnesium content (381.00 mg/g), values of sample B and C were 327.00 mg/g and 325.50 mg/g respectively. These values obtain are lower than 997.57 mg/g reported by Abdul-Mumeen *et al.* (2013). Magnesium is generally required for healthy bones and muscles and the functioning of many enzymes in living systems. The results reveal that Shea nut cake has high magnesium content.

Phosphorus Content

Table3. Shows the Phosphorus content (P) of the three shea nut cakes significantly differ across the three zones, with sample B has the highest Phosphorus content (386.00mg/g), follow by sample A (201.50 mg/g) and sample C has the lowest phosphorus content (166.25 mg/g), the value obtain are high than what was reported by (Abdul-Mumeen *et al*., 2013).

4. Conclusion

The findings of this study shows that cake heating values are within the acceptable heating values with high content of volatile matter, carbon and low sulphur content. Since the elemental constituents in biomass and their ratios are important in selection of energy conversion process. Crude fibre values obtained from the cakes are low which favored the action of microorganisms during biogas production. The high percentage of carbohydrate in all the seed cakes makes them suitable to serves as substrate for Bioethanol and biogas production. In general the seed cakes are good source of protein for industry of biodegradable material and also used as biofertilizer.

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Conflict of interest

The authors declare no conflict of interest.

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