Production and Characterization of Agricultural-Based Composite Biomass Briquettes Using a Novel Heterogeneous Catalyst

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***Abstract*: Reliance on conventional energy sources, such as wood and coal, has had a detrimental impact on the environment, resulting in air pollution and greenhouse gas emissions. Biomass briquettes offer a sustainable and renewable alternative to traditional energy sources. However, optimizing the quality of briquettes using biowaste materials remains a significant research gap. The study aims to optimize the physicochemical properties of composite briquettes using calcined turtle shell as a heterogeneous catalyst in a blend of 20% palm kernel shell, 30% plantain peel, and 50% cocoa pods biowaste, as per Optimal Custom Design (OCD) DoE 13.0. A maximum yield of heating value 18.14 MJ/kg and a minimum ash content of 6.01% was obtained. The study shows that the heterogeneous catalyst can effectively substitute CaO, advancing the viability of biomass briquettes as a sustainable, cost-effective alternative fuel source.**

***Keywords*: Biowaste, Calcined turtle shell, Palm kernel Shell, Plantain Peel, Cocoa Pod.**

1. Introduction

Human progress relies on energy generation and utilization (FOA, 2017). The combustion of conventional fossil fuels enormously contributes to greenhouse gas emissions and environmental degradation (Bukkarapu and Krishnasamy, 2022). The adoption of fossil fuels has impacted the economy, necessitating an urgent need for secure, sustainable, and environmentally friendly energy sources. Biomass sourced from agricultural byproducts offers an ecologically balanced energy (Ahmad et al. 2018). However, the burning effects and improper disposal of these agricultural residues create environmental concern and public health risks. Biomass briquetting is a sustainable material that converts organic wastes into compact, lightweight, energy-dense briquettes, providing an eco-friendly alternative to heating and cooling appliances (Gilvari et al. 2019). The inherent variability of raw materials such as palm kernel shell, plantain peel, and cocoa pod is an underlying issue in the production of high-quality, homogeneous composite briquettes with reduced mechanical strength and low combustion efficiency (Alabi et al. 2024; Elehinafe and Okedere, 2023).

The energy transition from non-renewable (fossil fuels) to renewable energy sources (wind and solar) is essential for urban development and sustainability (Alchalil-Setiawan and Juwaini, 2021). Biomass derived from agricultural waste is an integral part of this transition. Over the years, the briquetting densification process has gained significant attention, with modern techniques involving mechanical presses and pre-treatment processes like torrefaction to improve efficiency (Chomini et al. 2022). Palm kernel shells, plantain peels, and cocoa pods were chosen due to their low cost and availability. Previous studies have shown that this biomass has a high volatile matter content, making it suitable for briquetting production, while cocoa pod husks offer high calorific value (Łaska and Ige, 2023; Banerjee, 2023). Hybrid biomass residues are known to enhance the calorific value, the physical, and some mechanical properties of the resulting briquettes. Moreover, an approach was developed, utilizing the turtle shell as a precursor for a heterogeneous catalyst. This study, therefore, aims to optimize the physicochemical properties of composite briquettes made from agricultural residues (palm kernel shell, plantain peel, and cocoa pods) using turtle shell as a catalyst (David et al. 2011). Specifically, to prepare and characterize turtle shell as a heterogeneous catalyst and optimize the processing parameters for the composite briquette using the OCD method in Design of Expert 13.0.

2. Materials and Methods

A. Materials

The raw materials used for this experiment include palm kernel shells, plantain peels, and cocoa pods obtained from Oku Village, Akinlalu town, Osun State, Nigeria. turtle shells

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sourced from Ojo market, Ibadan, Oyo State, were used as a heterogeneous catalyst. Figure 1 shows the samples of palm kernel shells (a), plantain peels (b), cocoa pods (c), and turtle shells (d).

(a) Palm kernel shells

(b) Plantain peels

(c) Cocoa pods

(d) Turtle shells

(e) Samples of fuel briquettes produced

Fig. 1. Raw materials used for briquette production (a-d) and briquette samples (e)

B. *Methods*

About 2000 kg each of palm kernel shells, plantain peels, and cocoa pods were used as the base materials. Each constituent was cut into pieces, washed, sundried for 7 days to remove moisture and extrinsic content, and ground in a ball mill. It was subsequently sieved to obtain particle sizes of 425 µm. Turtle shells were subjected to calcination in a laboratory furnace (HTF model) at 900^{o}C for 4 h (Łaska and Ige, 2023), to produce the heterogeneous catalyst. A 320 µm particle size of the calcinated Turtle shell was used. 350 g of soluble starch (CAS Lab. Supplies, China) is first dissolved in 0.5 L of water, and gelatinized at 90°C before being mixed with the constituents. The prepared samples were weighed as per Table 1, and mixed in a planetary mixer at a speed of 250 rpm for 5 min. Briquette samples of length 90 mm by 60 mm diameter were produced, as shown in Figure 1e. The densification process was done in a screw jack following the experimental procedure of Kaur et al. (2017). Briquette production parameters were then optimized using the Optimal Custom Design (OCD) Method available in the Design Expert 13.0 software. The varied factors of the mixture design were the biomass blend ratio, binder concentration, and compaction.

C. *Preliminary Analysis*

Proximate analysis on the briquette samples were carried out to determine percentage volatile matter, percentage moisture content, percentage ash content and percentage fixed carbon.

(a) Percentage volatile matter of the dried sample: The percentage volatile matter (PVM) was determined using the standard method CEN/TS 15148. Two grams of the briquette samples were pulverized and oven-dried at 105^{o}C until their weight was constant. The sample was then heated at 550^{o}C for 10 min and weighed after cooling. The percentage volatile matter was calculated using the expression (Karunanithy et al.,2012):

$$PVM = \left(A - {}^{B}/_{A}\right) \times 100 \qquad (1)$$

where PVM is the percentage volatile matter, A is the weight of the oven-dried briquette sample, and B is the weight of the briquette sample after 10 min in the furnace at 550^{o}C.

(b) Percentage moisture content on dried sample: The percentage moisture content (PMC) of the briquette samples

was determined using standard CEN/TS 14774. Three grams of the briquette samples were oven dried at 105 ± 2^{o}Cuntil a constant mass was obtained. The weight change (W) after 16 – 24 h was then used to determine the percentage moisture content of each sample following Equation 2 (Adetunji et al. 2015):

$$PMC = \left({}^{W}/_{M}\right) \times 100 \quad (2)$$

where PMC is the percentage moisture content, W is the change in dried weight of the briquette sample, and M is the initial weight before drying.

(c) Percentage ash content of the dried sample: The percentage ash content (PAC) of the briquette samples was determined using standard CEN/TS 14775. Two grams of the briquette were heated in a furnace at 450^{o}C for 1 h and weighed after cooling to get the weight of the ash (W_c). The percentage ash content was determined using (Karunanithy et al. 2012):

$$PAC = \left({}^{W_c}/_{M_d}\right) \times 100 \quad (3)$$

where PAC is the percentage ash content, W_c is the weight after cooling, and M_d is the weight of the oven-dried sample

(d) Percentage fixed carbon of the dried sample: The percentage fixed carbon (PFC) of the briquette samples was computed by subtracting the sum of PVM, PAC, and PMC from 100.

$$Fixed\ Carbon = 100\% - (PVM + PAC + PMC) \quad (4)$$

(d) Calorific Value of the dried sample: The calorific value of the briquette samples was determined by using a Parr Oxygen bomb calorimeter in accordance with CEN/TS 14918 Standard Method (Karunanithy et al. 2012; Rahaman and Salam 2017). The calorific values of the briquette samples were calculated by the Equation:

$$Q_v = \frac{C\ (G_{d1} - G_{d2})}{M_b}$$

where Q_v = Heating/Calorific Value (kJ/kg), C = Calibration of constant for biomass acid (0.6188), G_{d1} = Galvanometer deflection without sample, G_{d2} = Galvanometer deflection due to the test sample, and M_b = Weight of briquette sample.

D. Briquette Characterization

The crystalline structure of the catalytic material was characterized using X-ray diffraction (XRD) analysis. The physicochemical properties, including the percentage moisture content, volatile matter, ash content, fixed carbon, and calorific value (higher and lower heating value) of the composite briquettes produced were evaluated, and the analysis of variance (ANOVA) was performed.

Table 1
Optimal custom design method for briquette mixture matrix

Variable constituent	LI	LII
Palm kernel shells (wt.%)	20	30
Plantain peels (wt.%)	54	72
Cocoa pads (wt.%)	72	82
Content constituent		
Tortoise shells (wt.%)	40	
Starch (wt.%)	50	
Compaction (MPa)	6.85	

3. Results and Discussion

The quality indicators of the briquette samples are high fixed carbon, high calorific value, low moisture, low ash, and low sulfur content. Presented in Table 2 are the characterization equivalent values of the raw biomass briquettes produced. The addition of palm kernel shows a low ash value of 2.41 and higher combustion efficiency, resulting in a caloric heating value of 13.38%. The reduced sulfur values (0.184) indicate lower emissions and minimize energy loss during combustion. Cocoa pod shows volatile matter of 65%, a higher fixed carbon value of 11.3%, and the highest energy per caloric value of 21.25%, indicating a faster burning process. This is in agreement with the work of Ofori and Akotoz (2020), where the characterisation of briquettes from carbonised cocoa pod husk and sawdust results in briquette calorific value (23.6 MJ/Kg). Furthermore, the addition of plantain peels gives a fixed carbon value of 36.8% indicating long-lasting heat output, reduced burning effect, and improves combustion stability. This result corroborates with the reported of Mitan and Muhammad (2019) on the effects of temperature distribution on densification of banana peels where 20.59 to 30.03% ash content, 2.00 to 3.80% fixed carbon and volatile content 6 1.91% to 70.15% were obtained. The plantain peels show the lowest SO_2 emission, indicating adequate indoor or domestic briquette usage. The effect on temperature on densification of banana peels briquette by Mitan and Muhammad, (2019).

Table 3 shows the output parameters of the experimental runs. The OCD method successfully determined the blend ratio that maximized energy output with optimal heating value of 18.14 MJ/kg, and minimized ash content with 6.01% at composition 20% palm kernel shell, 30% plantain peel, and 50% cocoa pod. The synergistic effect of combining the three agricultural residues meets the requirement for sustainable

Table 2
Characterization of the raw biomass briquettes production

Physicochemical Property	Component 1	Component 2	Component 3
	Palm Kernel	Plantain Peel	Cocoa Pod
Ash	2.41	6.15	8.7
Moisture Content	5.725	8.66	10.15
% Volatile Matter	51.06	40.8	65
Carbon	48.63	38.6	44.8
Fixed carbon	24.2	36.8	11.3
Sulphur	0.184	0.022	0.165
Calorific Value	13.38	16.1	21.25

Table 3
Response from experimental design of composite biomass briquette

Components				**Responses**	
Run	**A: Palm kernel**	**B: Plantain Peel**	**C: Cocoa Pod**	**Ash Content (%)**	**Calorific Value (MJ/Kg)**
1	24	33	43	6.40	17.73
2	20	37	43	6.17	17.76
3	22	38	40	6.41	17.60
4	25	30	45	6.43	17.76
5	30	30	40	6.85	17.38
6	27	32	41	6.70	17.50
7	20	35	45	6.16	17.89
8	20	30	50	6.01	18.14
9	20	40	40	6.23	17.58
10	22	30	46	6.52	17.86

Table 4
Calcined turtle shell at 900^{o}C

Compound Name	**Scale Factor**	**Chemical Formula**
Calcium Oxide	0.125	CaO
Zincite	0.118	ZnO
Potassium Molybdenum Oxide	0.221	$K_{0.33}MoO_3$
Potassium Oxide	0.238	K_2O
Potassium Magnesium Molybdenum Oxide	0.162	$K_2Mg(MoO_4)_2$
Zinc Molybdenum Oxide	0.112	$Zn_3Mo_3O_8$
Molybdenum Oxide	0.155	MoO_3
Potassium Zinc Molybdenum Oxide	0.195	$K_4Zn(MoO_4)_3$
Calcium Zinc	0.325	$Ca_{6.67}Zn_{20.26}$
Magnesium Zinc	0.144	Mg_4Zn_7

development goals (SDG 7 and 13), resulting in a composite briquette with fuel characteristics suitable for energy application and reduced deforestation.

XRD analysis of the calcinated turtle shell is shown in Table 4. The reported scale factors are semi-quantitative indicators of phase abundance of the calcinated turtle shell obtained from the Rietveld X-pert high-score fit. It is dominated by inorganic oxides CaO, ZnO, K_2O, MoO_3-related phases, and mixed K–Zn–Mg–Mo phases. Few inorganic crystalline oxides like Ca–Zn phase (0.325), K_2O (0.238), and several K–Mo/Zn–Mg molybdate phases (0.221, 0.195, 0.162) were present. Furthermore, analysis showed that the heterogeneous catalyst derived from waste turtle shell could effectively substitute commercial CaO, highlighting a crucial economic and environmental benefit. The XRD shows many stable metallic oxides and complex inorganic phases (CaO, ZnO, MoO_3, K_2O, mixed Ca–Zn and Mg–Zn phases). This could result in the presence of large non-combustible residue. The low heating value of a briquette composite can be attributed to the presence of combustible organic components (C, H, some volatile matter). The crystalline metallic oxides are thermodynamically stable, and non-combustible solids.

4. Conclusion

This study examined the production of biomass composite briquettes using a novel 425 µm turtle shell heterogeneous catalyst. It was characterization for the presence of metallic crystalline oxide after calcinated at 900°C for 4 h. High heating value of 18.14 MJ/kg and low ash content of 6.1% was obtained for composite briquette blend ratio of 20% palm kernel shell, 30% plantain peel, and 50% cocoa pod, paving way for their large-scale production as an alternative, renewable energy source for domestic and industrial applications.

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