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Research

Mechanical and thermal properties of composite carbonized briquettes developed from cassava (*Manihot esculenta*) rhizomes and groundnut (*Arachis hypogea*. *L*.) stalks with jackfruit (*Artocarpus heterophyllus*) waste as binder

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Abstract

Composite briquettes from agricultural residues are a potential sustainable domestic solid fuel resource. This study aimed to develop and characterize composite briquettes developed from cassava rhizomes and groundnut stalks with jackfruit waste binder as an alternative sustainable fuel for domestic cooking applications. Cassava rhizomes and groundnuts stalks feedstock were carbonized in a step-down kiln under slow pyrolysis conditions at temperatures between 400 and 500 °C. Thermogravimetric analysis was used to determine the proximate and thermal properties of the developed composite briquettes. Bomb calorimetry was used to determine their heating values. Relaxed density, drop strength and compressive strength results were used to determine the mechanical properties of the developed briquettes. Design of Experiments (Box Behnken design) was used to evaluate the effect of factors (biochar amount, jackfruit waste binder amount, and amount of water) on the mechanical and thermal properties of the developed composite briquettes. The Coats-Redfern kinetic model was used to determine the activation energy for the developed briquettes. Calorific values and drop strength of developed composite briquettes ranged from 18.1 to 24.0 MJ/kg and 92–99%, respectively. Combustion performance results indicated that ignition temperature increased from 155.1 to 184 °C, when heating rate was increased from 10 to 15 °C/min. However, burnout temperature decreased from 618.1 to 453 °C/min with a similar corresponding increase in heating rate. Optimum biochar amount, amount of water, and jackfruit waste binder amount for optimal mechanical and thermal properties were 89.3%, 893.0 ml, and 29.5 g, respectively. Composite briquettes developed from cassava rhizomes and groundnut stalks with jackfruit waste as binder are suitable potential domestic cooking fuels.

Highlights

- Cassava rhizome and groundnut stalks agricultural residues were carbonized using slow pyrolysis at temperatures between 400°C 500°C.
- Jackfruit waste was used as binding material in producing composite briquettes from the carbonized agricultural residues

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Carbonized cassava rhizome and groundnut stalk composite briquettes had adequate properties for use as domestic cooking fuels.

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Keywords Cassava rhizomes · Composite briquettes · Groundnut stalks · Jackfruit waste · Thermogravimetric analysis

1 Introduction

Biomass energy accounts for approximately 94% of Uganda's energy mix [1]. Approximately 90% of Uganda's population relies on biomass fuel for cooking and heating applications, with firewood, charcoal, and agricultural waste accounting for 70, 16, and 4% of this distribution, respectively, [2]. However, the continued use of firewood and charcoal for cooking and heating applications leads to indoor pollution, forest depletion through deforestation, health problems, and global warming [3]. A promising solution to the limitations of traditional biomass conversion methods is the adoption of briquetting. Briquetting is the compaction of loose materials into solid fuels with high energy content and that have lower pollution levels relative to firewood and charcoal [4–9]. Low-pressure briquetting techniques are commonly used in developing countries due to their relative production simplicity at economically viable production costs. This normally includes a combination of carbonization of biomass-based raw materials followed by the briquetting process under low pressure using a binding agent (< 7 MPa) [10-12].

Uganda, like most countries in sub-Saharan Africa, is an agricultural country. Over 19 million metric tons of agricultural waste are generated annually. However, disposal of these wastes continues to be a major environmental and ecological hazard due to the approach of open burning currently being used to deal with them. These wastes are a potential energy resource vital for ensuring a sustainable energy matrix [13]. Cassava (Manihot esculenta) and groundnut (Arachis hypogea. L.) crops are staple foods grown in the Bukedea, Kumi, Pakwach, Arua, and Zombo districts of Uganda, generating approximately 1.157 mt of cassava waste and 513 kt of groundnut waste annually [14, 15]. Jackfruit (Artocarpus heterophyllus) farming is abundant in the central, eastern, and western regions of the country resulting in large volumes of jackfruit waste which is known for its very sticky texture when handled with un-oiled hands [16]. This implies that these wastes are readily available and are a potential sustainable resource for sustainable production of briquettes from them.

The development of composite briquettes is gaining momentum because they increase the raw material options that can be used in briquetting. Composite briquettes provide an added benefit of combining raw materials with distinct positive properties to counteract the negative properties in any single material of the composite [9]. This results in the development of briquettes with tailor-made properties including higher heating value, lower ash content, and improved mechanical strength compared to briquettes made with single agricultural residues [9, 17, 18]. Composite briquettes made from rice straw and banana peel exhibited a high heating value ranging from 20.98 to 21.26 MJ/kg [19]. Vegetable market waste and sawdust composite briquettes were reported to have heating values ranging from 14.002 to 15.721 MJ/ kg [20]. Coffee and rice husks biochar composite briquettes were shown to have heating values between 16.6 and 22 MJ/ kg [9]. An increase in higher heating value (HHV) from 27.4 to 28.8 MJ/kg was observed when the proportion of maize cob biochar in maize cob and bean straw briquettes was increased from 25 to 75% [21, 22]. Charred briquettes made from a combination of sawdust, rice, and coconut husks were recorded to have a heating value of 24.69 MJ/kg [23]. The gross calorific value of fecal char-sawdust blended briquettes was reported to be 19.8 MJ/kg, which was lower than the 25.7 MJ/kg value for charcoal [24]. Additionally, the corncob and oil palm trunk bark composite briquettes exhibited fuel burning rates of 0.69 kg/h and 0.70 kg/h [25]. An improvement in bulk density of up to 1.1939 g/cm³, corresponding to a compressive strength of at least 5.12 kgf/mm² was observed when co-briquetting sugarcane bagasse and rice bran [26]. Briquettes made from paper pulp and Mesua ferrea mixtures had heating values ranging from 15.77 to 18.99 MJ/ kg [27]. Sawdust-charcoal composite briquettes showed high shattered indices or drop strengths, with cassava starch gel and orange waste recording values of 98.21 and 96.71%, respectively, at a size of 0.2 mm [28]. Combustion characteristics of composite briquettes developed from onion peels and tamarind shells with cassava starch binder showed higher calorific values ranging between 18.24 and 21.05 MJ/kg for the composite briquettes [29]. Composite briquettes were developed from Gloriosa superba and turmeric leave wastes using cassava starch as binder. The calorific value of the composite briquettes ranged from 11.66 to 15.64 MJ/kg [30].

Most studies on low-pressure briquette development have focused on cassava starch as a binder, highlighting its widespread use and potential [31-33]. However, the use of cassava starch as binding material, even in exceedingly small



quantities, is facing significant backlash because cassava starch is a staple food crop for millions of people. Therefore, there is an urgent need to explore the potential of using alternative non-edible binder options for the purpose of lowpressure briquette development. Briquettes produced from sawdust residue and paper pulp and clay soil binder had reasonable fuel quality, offering an alternative energy source and waste management option [34]. Wastepaper pulp as a binder was used in the development of briquettes with Mesua ferrea mixtures [27]. Biomass briquettes were developed using corn starch as a binding agent in developing briquettes using grass and tree leaves biomass further demonstrating the diversification of binder materials beyond cassava starch and the exploration of alternative options in briquette development [35]. The effect of different binders including cassava starch and tree gum, on the physical properties of onion leaves briquettes resulted in variations in compressed density, dimensional stability, and relaxation ratio [36]. Rice waste was used as binding agent in the production of briquettes from waste potato skins and yam skins [37]. Tapoica starch was used as binder in the development of composite briquettes from Senna auriculata and Ricinus communis. The results showed that spontaneous burning characteristics due to the irregular surface characterized by lumps, cavities, and few deposits of carbon [38]. Nano-clay as a binder was used in the development of composite briquettes from turmeric and onion wastes. The calorific values of the developed briquettes ranged from 11.66 to 15.64 MJ/kg [39]. Another potential non-edible waste that can be considered as a binder in low-pressure briquette production is jackfruit (Artocarpus heterophyllus). Studies have explored the potential of jackfruit waste in various applications, including briquette production [40]. However, studies on the use of jackfruit waste as a binder in briquette development are extremely limited in literature. Jackfruit waste as binding material is of particular interest because it contains pectin, cellulose and latex components which are naturally occurring binding agents and have been used in other industrial applications [40–42].

Therefore, while cassava starch has been the primary focus of binder research in briquette development, the potential of other binders, including jackfruit waste, in the development of composite carbonized briquettes needs to be explored. This study therefore aimed to develop composite briquettes from carbonized cassava rhizomes and groundnut stalks using jackfruit waste as the binding agent. Very few studies exist in the literature on the development of similar composite briquettes using jackfruit waste as binder. The mechanical and thermal properties of the developed composite briquettes were also determined.

2 Experimental

2.1 Material processing

60 kg of Cassava rhizomes (NAROCASS 1) and 30 kg of groundnut stalks (Serenut 5R) were obtained from Namulonge (0°31′32.192″ N; 32 ° 36′49.305″ E), Wakiso district in Uganda. 20 kg of jackfruit wastes were obtained from Kalerwe market (0°21′3.94″ N; 32 ° 34′19.965″ E) in Kampala, Uganda. Figure 1 shows typical cassava rhizomes, groundnut stalks and jackfruit wastes that were used in this study. All the raw materials were manually sorted to remove all impurities. Before further processing the raw material, feedstocks were cut into 10 cm lengths to increase surface area for moisture evaporation. Cassava rhizomes, groundnut stalks and jackfruit waste were sun-dried for 5 days until the moisture content of the feedstocks was less than 15%, which is the recommended moisture content of biomass for briquetting [43].

Fig. 1 Agricultural waste raw materials: cassava rhizomes (**a**); groundnut stalks (**b**) before carbonization, jackfruit waste (**c**); carbonized cassava rhizomes (**d**); and carbonized groundnut stalks (**e**)





Cassava rhizomes and groundnuts stalks feedstock were carbonized in a step-down kiln by placing in saggers of 80 L capacity and 0.77 m height. During slow pyrolysis, the saggars were covered with flat ceramic covers and the edges were further sealed with clay to prevent oxygen supply during the combustion process. The saggars were then arranged in the kiln carbonizer. Slow-pyrolysis was conducted for a residence time of 4 h at temperatures between 400 and 500 °C [12]. Figure 1d, e show the resulting biochar developed from carbonized cassava rhizomes and groundnut stalks. Bio-char size reduction was done initially using a motor and pestle after which further size reduction was done using a blender until ground biochar of < 600 μ m was attained after sieving. Jackfruit wastes were initially reduced to 1 cm length before sun drying for seven days. The dried jackfruit wastes were then milled and until they attained particle sized of < 600 μ m [28]. In developing the jackfruit waste binder, jackfruit waste powder was mixed with water and heated to 80 °C when boiling commenced so that starch gelatinization could occur, which is necessary to affect the binding action in briquette development [44].

2.2 Design of experiments and briquette development

Box-Behnken design (BBD) was used to determine the effects of biochar amount (groundnut stalks and cassava rhizomes–60–90%), amount of water (600–900 ml), and binder amount (jackfruit waste–10–30 g) on briquette performance parameters, including heating value, compressive strength, and drop strength. The respective levels in the BBD design for these factors are shown in Table 1. The percentage of biochar, water and jackfruit waste binder amount have been demonstrated as critical factors in the development of composite briquettes [45]. In the BBD, the minimum level for cassava rhizome biochar automatically corresponds to the maximum level of the groundnut stalk biochar in the composite matrix and, similarly, the maximum level of cassava rhizome biochar corresponds to the minimum level of groundnut stalk biochar in the composite matrix. Therefore, according to the BBD, 17 randomized experimental runs were determined as adequate to achieve statistical significant effects of the selected factors on the desired responses due to the fact that the numerical factors are represented at three levels (minimum, mean and maximum) as well as at 5 replicated center points, which cover the entire design space [46].

The development of the composite briquettes followed the BBD (See Table 2). 340 g of biochar (mixture of cassava rhizome and graoundnut stalk biochar) was weighted using an electronic weighing balance (accuracy 0.1 g). The jackfruit waste starch

Table 1 BBD experimental design used in briquette production for the factors of cassava rhizomes biochar (%), amount of water (ml) and Jackfruit waste binder amount (g)

	Factors	Responses				
Run	Amount of biochar (% Cassava rhizomes)	Amount of water (ml)	Binder amount (g)	Heating value (MJ/ kg)	Drop strength (%)	Compressive strength (N/ mm)
1	90	750	30	23.671	97	0.194
4	75	600	10	20.7405	92	0.157
7	60	900	20	18.694	95	0.178
2	75	750	20	20.3129	94.9	0.117
6	75	750	20	20.158	97.96	0.207
3	75	600	30	20.678	95.75	0.137
9	75	750	20	20.2978	94.38	0.152
13	75	750	20	20.3951	92	0.156
11	90	900	20	24.0157	99	0.219
16	60	600	20	18.073	92.69	0.087
5	75	900	10	20.549	98.52	0.172
17	90	600	20	22.4165	98.34	0.185
8	90	750	10	22.7956	97.56	0.167
12	60	750	30	18.579	94.87	0.079
10	75	750	20	20.3215	97.63	0.183
14	75	900	30	20.1539	98.71	0.212
15	60	750	10	18.398	95.7	0.103



Table 2 Proximate properties of cassava rhizomes and groundnut stalks raw materials

	Composition	Cassava rhizomes	Groundnut stalks
Proximate (TGA heating rate:	Moisture content	12.50	12.4
10°C/min)	Volatile matter	75.4	75.1
	Fixed carbon	16.4	13.1
	Ash content	4.6	8.4
Proximate (TGA heating rate:	Moisture content	13.6	12.7
15 °C/min)	Volatile matter	74.3	74.2
	Fixed carbon	17.5	13.3
	Ash content	4.0	8.1

binder was mixed with water (according to the BBD and brought to a boil in order to form the starchy mixture, which was added to the biochar mixture and mixed thouroughly. A hollow cylindrical mold of height 54 mm, inner diameter of 16 mm, outer diameter of 44.7 mm, with wall thickness of 2.65 mm. Internal surfaces of the mold were smoothened to reduce friction during densification of the composite mixture. The composite mixture was filled into the hollow mould and then compressed for a minimum of 120 s dwelling time. The force applied to compact and densify the briquettes was that of a human arm which is equivalent to \leq 7 MPa. The developed briquettes were then allowed to sun-dry for 7 days [5, 8, 47]. Optimization studies were conducted with the objective of developing composite briquettes with maximum heating value, maximum drop strength and maximum compressive strength for optimal briquette development factors namely: biochar amount, amount of water and jackfruit waste binder amount), using the numerical optimization method in Design Expert software.

2.3 Proximate and ultimate analysis

Proximate analyses to determine moisture content, ash content, fixed carbon and volatile matter were done using an Eltra Thermostep Thermogravimetric analyzer (TGA). Prior to proximate analyses, crucibles and TGA chamber were initially cleaned with high pressure compressed air. 1.1 g of sample of developed composite briquette was loaded into the chamber and heated from room temperature (27 °C) at 2 different heating rates of 10 °C/min and 15 °C/min. Initial heating was done to approximately 105 °C so that inherent initial moisture content in the composite briquette samples could be adequately expelled. Once a constant weight was attained, then the samples were further heated to 920 °C. After attaining 920 °C, the samples were heated for 7 min in the presence of nitrogen gas to ensure that all volatile matter had escaped. Nitrogen gas was supplied at a flowrate of 1 L/minute. The temperature was lowered to 750 °C, and nitrogen gas flow cut off and replaced with oxygen gas to ensure complete combustion of the fixed carbon so that the ash content could be determined [7–9, 12].

The fixed carbon, volatile matter and ash content results from the proximate analyses determined from TGA, were then used to determine the elemental constituents of the composite briquettes using numerical models postulated by Shen et al. [48] (See Eq. 1a–1c) and Parikh (2007) (See Eq. 2a–2c), where C is the carbon content, H is the hydrogen content, O is the oxygen content, FC is fixed carbon, VM is volatile matter, and AC is ash content [48, 49].

$$C(\%) = 0.635FC + 0.460VM - 0.095AC$$
 (1a)

$$H(\%) = 0.059FC + 0.060VM + 0.010AC$$
 (1b)

$$O(\%) = 0.340FC + 0.469VM - 0.023AC$$
 (1c)

$$C(\%) = 0.637FC + 0.455VM$$
 (2a)

$$H(\%) = 0.052FC + 0.062VM$$
 (2b)

$$O(\%) = 0.304FC + 0.476VM$$
 (2c)



2.4 Calorific value determination

An IKA 1C 2000 oxygen bomb calorimeter was used to investigate the higher heating value of the developed composite briquettes according to ASTM D5865-13 standards. Approximately 1 g of composite briquette sample was placed in a nickel crucible and fired inside the bomb calorimeter using an ignition wire in the presence of oxygen. The experiment was performed in triplicate [7, 9]. The experimental results for calorific value were further compared to the mathematical models postulated by García et al. [50] (See Eq. 3) and Nhuchhen & Afzal, [51] (See Eq. 4) [50, 51].

$$HHV = 17300 - 117.51AC + 165.55FC - 232.69MC$$
 (3)

$$HHV = 0.1846VM + 0.0352FC \tag{4}$$

2.5 Kinetic modeling

The Coats-Redfern model was used to determine the combustion kinetics, such as activation energy and preexponential factors, of optimized briquettes. Coats-Redfern remains commonly used because it is economical as it determines conservative, but useful kinetic parameters using a single heating rate [52]. The kinetic study was conducted at two fixed heating rates of 10 and 15 °C/min. The rate of briquette decomposition is described by Eq. 5 [12, 53, 54].

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{5}$$

where, α , k, t, T, and f (α) represent the rate of conversion during thermal decomposition, the rate of constant of the rection, the time taken to decompose given weight of the briquettes, the absolute temperature, and the reaction model, respectively.

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \tag{6}$$

where $m_{i_r}m_t$ and m_f represent the initial weight of the biomass at the beginning of the experiment, the weight of the biomass at any given time and the final weight at the end of combustion, correspondingly.

$$f(\alpha) = (1 - \alpha)^n \tag{7}$$

n is a represent the order of reaction. According to Arrhenius equation:

$$k(T) = Ae^{\frac{-E}{RT}} \tag{8}$$

Here, A, E, and R represent the pre-exponential factor (min^{-1}), the activation energy and gas constant, respectively. From Eq. 5, k(T) can be rearranged as the subject of the equation, resulting in Eq. (9).

$$\frac{d\alpha}{dtf(\alpha)} = k(T) \tag{9}$$

From Eqs. (8), (9) can be re-written to obtain Eq. (10) as:

$$\frac{d\alpha}{dt f(\alpha)} = Ae^{\frac{-E}{RT}}$$
 (10)

Making $\frac{d\alpha}{dt}$ the subject of equation.

$$\frac{d\alpha}{dt} = Ae^{\frac{-E}{RT}}f(\alpha) = Ae^{\frac{-E}{RT}}(1-\alpha)^{n}$$
(11)



However, the heating rate,

$$\beta = \frac{dT}{dt} \tag{12}$$

For a non-isothermal reaction:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} * \frac{dt}{dT} \tag{13}$$

Substituting Eqs. (11) and (12) into Eq. (13) further simplifies into Eq. (14)

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$$\frac{d\alpha}{dT} = Ae^{\frac{-E}{RT}} (1 - \alpha)^n * \frac{1}{\beta}$$
 (14)

Re-arranging Eq. (14)

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} e^{\frac{-E}{RT}} dT \tag{15}$$

Integrating Eq. (15)

$$\int_{1}^{0} \frac{d\alpha}{(1-\alpha)^{n}} = \int_{0}^{T} \frac{A}{\beta} e^{\frac{-E}{RT}} dT \tag{16}$$

Applying the limits of the integrals and further computation simplifies to Eq. (17).

$$\left(\frac{-(1-\alpha)^{1-n}}{1-n} - \frac{-1}{1-n}\right) = \frac{ART^2}{\beta E} \left[1 - \frac{2RT^2}{\beta E} e^{\left(\frac{-E}{RT}\right)}\right]$$
(17)

Introducing natural logarithms to Eq. (17):

$$\ln\left(\frac{-(1-\alpha)^{1-n}}{1-n} - \frac{-1}{1-n}\right) = \ln\left(\frac{ART^2}{\beta E} \left[1 - \frac{2RT^2}{\beta E}e^{\left(\frac{-E}{RT}\right)}\right]\right) \tag{18}$$

Evaluation of Eq. (18)

$$\ln\left(\frac{1-(1-\alpha)^{1-\alpha}}{T^2(1-n)}\right) = \ln\left[\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right]\right] - \frac{E}{RT}for(n \neq 1)$$
(19)

If $\frac{2RT}{F} \ll 1$ therefore Eq. (19) becomes:

$$\ln\left(\frac{1-\left(1-\alpha^{1-n}\right)}{T^2(1-n)}\right) = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT}for(n \neq 1)$$
(20)

Assuming an order of reaction corresponding to unity [55]. Therefore, results in a simplified model for Coats-Redfern that was used in this study.

$$\ln\left(-\frac{\ln(1-\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \tag{21}$$

A plot of $\ln\left(-\frac{\ln(1-\alpha)}{T^2}\right)$ against $\frac{1}{T}$ resulted in a straight line, whose slope was easily determined from an equation of a straight line y = mx + C. This implies that the slope (m) is $\frac{-E}{R}$ and the y-intercept (C) is $\ln\left(\frac{AR}{\beta E}\right)$. β , T, R, α , A and E represent the heating rate, temperature, gas constant, conversion rate, pre-exponential factor, and activation energy, respectively.



2.6 Thermal and combustion characteristics

TGA of the optimized developed composite briquettes were done at heating rates of 10 °C/minute and 15 °C/minute in the ELTRA THERMOSTEP TGA, as previously described (See Sect. 2.3). Using TGA, weight loss vs. temperature was determined for the optimized composite briquettes [7–9, 12, 54]. The DTG (differential thermogravimetric analysis), and peak temperatures attainable by the developed composite briquettes were also determined.

Following the Tangent line method, both the ignition temperature and burnout temperatures were determined for the developed optimized composite briquettes at each heating rate [54]. The ignition temperature, T_i , is a measure of difficulty to generate a thermal reaction on a fuel and the burnout temperature, T_i , corresponds to final temperature of the combustible parts of the fuel. Both T_i and T_f are particularly important parameters in determining the combustion characteristic index (See Eq. (22)) and the flammability index (See Eq. (23)) of the developed optimized composite briquettes.

$$S_{N} = \frac{\left(\frac{d\alpha}{dt}\right)_{max} \cdot \left(\frac{d\alpha}{dt}\right)_{mean}}{T_{i}^{2} T_{f}}$$
 (22)

$$C = \frac{\left(\frac{dy}{dx}\right)_{max}}{T_i} \tag{23}$$

where: $\left(\frac{d\alpha}{dt}\right)_{max}$, $\left(\frac{d\alpha}{dt}\right)_{mean}$, represent the maximum burning rate and average burning rate for the composite carbonized briquettes. Maximum burning rate was obtained from the DTGA curve. The average burning rate was calculated using Eq. (24).

$$\left(\frac{d\alpha}{dt}\right)_{mean} = \beta \left(\frac{\alpha_i - \alpha_f}{T_f - T_i}\right) \tag{24}$$

where: β , α_i and α_f represent heating rate, percentage of the biomass remaining after ignition temperature and percentage of the biomass remaining after burnout temperature, respectively [54].

Water boiling test (Version 4.2.3) was used to determine water boiling time, ignition time, specific fuel consumption and burning rate for the developed composite briquettes. For each test, 113 g of briquette, including the kindler, was weighed. An aluminum cooking pot had 500 ml of water placed in it and temperature measurements of water and composite briquettes were recorded using a DT-8865 non-contract infrared thermometer gun. A combustion flame was then started. The time taken for the fuel to ignite was recorded. Upon ignition, the pot was brought to a boil, and the time, temperature, and amount of briquette consumed during boiling were recorded [12]. The burning rate and specific fuel (composite briquette) consumption were determined as follows:

Burning rate =
$$\frac{\text{Mass of fuel consumed (g)}}{\text{Total time taken to burn (min)}}$$
 (25)

Specific Fuel Consumption =
$$\frac{\text{Total mass of fuel consumed (g)}}{\text{Volume of water boiled (litre)}}$$
 (26)

2.7 Mechanical characterization

Mechanical characterization of the developed composite briquettes was determined from the particle density, drop strength, and compressive strength. Briquette density was determined as the ratio of the mass of the briquette to its volume. In determining the briquette volume, the cross-sectional area, taking into consideration the inner diameter and outer diameter of the briquette, corresponding to the mold for briquette development process. The drop strength of the composite was done by raising the briquettes to a height of 2 m and dropping them on a thick steel plate.



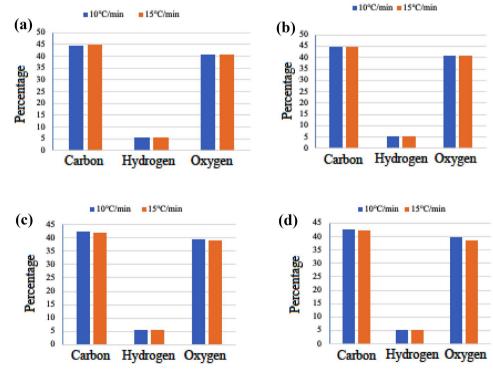
Drop strength is determined as a percentage of the final weight of the composite briquette to its initial weight [7–9, 56]. Compressive strength testing was done using a Universal Testing Machine. The developed composite briquettes were placed between the platens of the machine and then adjusted to touch the sample firmly. Compression was done at a loading rate of 10.00 mm/min with a load of 300 kN until the sample fractured. The load at fracture was then recorded and the corresponding compressive strength was determined as the ratio of the load at fracture to the cross-sectional area of the briquette under direct load.

3 Results and discussion

3.1 Proximate and ultimate results for raw materials

Results for the proximate analyses for the raw material feedstock i.e., cassava rhizomes and groundnut stalks, which were used in this study are shown in Table 2 for two different heating rates of 10 and 15 °C/min. The results for the elemental analysis using both the Shen et al. [48] and Parikh [49] models are shown in Fig. 2. When the heating rate was increased from 10 to 15 °C/min, a slightly marginal increase was observed for both the moisture content and fixed carbon, while volatile matter and ash content results for cassava rhizome and groundnut stalk feedstock showed a reduction. Proximate analysis results for cassava rhizomes and groundnut stalks in this study were similar to those presented in other studies [5, 47, 57–61]. Moisture content was within the 10–15% range, which is critical for thermochemical conversion of biomass feedstock into briquettes [43]. Fixed carbon content was higher in cassava rhizomes (16.4 and 17.5% compared to groundnut stalks (13.1 and 13.3%) at heating rates of 10 and 15 °C/min. However, the significant amounts of fixed carbon present in the feedstock implies the potential for thermochemical conversion into biochar for development into briquettes [57]. Both cassava rhizome and groundnut stalks feedstocks had volatile matter content > 70% which indicates suitability for thermochemical conversion using pyrolysis and biochar formation by condensation processes during pyrolysis [62]. Cassava rhizomes had lower ash content of 4.6 and 4.0% compared to 8.4 and 8.1% recorded for groundnut stalks at different heating rates of 10 and 15 °C/min. Higher ash content is associated with the formation of slag during combustion of biomass fuels limiting overall thermal efficiency and calorific value of the combustion equipment and briquette fuel developed [63]. Chemical compositions for hydrogen, oxygen and carbon content for cassava rhizomes and groundnut stalks are shown in Fig. 2 using the commonly used Shen [48] and Parikh [49] models. These results are

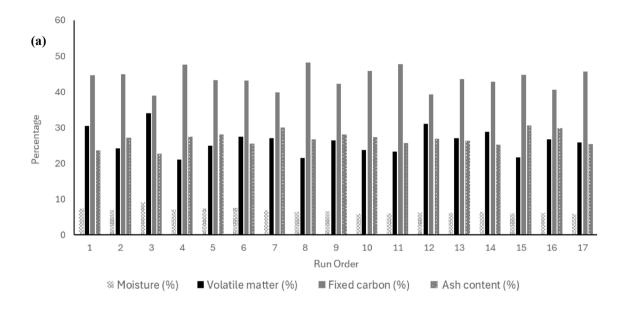
Fig. 2 Elemental (Carbon, Hydrogen and Oxygen) composition of Cassava rhizomes (a, b) and Groundnut shells (c, d) using the Shen et al. [48] (a, c) and Parikh [49] (b, d) models at heating rates of 10 and 15 °C/min



consistent with those reported by other studies [61, 64]. Varying heating rates did not have any impact on the chemical elements of either cassava rhizome or groundnut stalks. Carbon content for both cassava rhizome and groundnut stalks were > 40%, which implies that briquettes developed from these feedstock materials will have higher heating values due to reduced capacity for additional oxygenation [65]. However, groundnut stalks had lower hydrogen and oxygen content of 5.34 and 39.14% respectively compared to cassava rhizomes which had 5.53 and 40.69%, respectively.

3.2 Proximate analysis for developed composite briquettes

Proximate analysis results for the developed composite briquettes are shown in Fig. 3 for heating rates of 10 °C/min (See Fig. 3a) and 15 °C/min (See Fig. 3b). Moisture content ranged between 5.9 and 9.1 and 6.4 and 7.7% for heating rates of 10 °C/min. and 15 °C/min., respectively. For volatile matter, the range at these heating rates was 21.1 to 34% and 22.6 to 36.2%, respectively. Fixed carbon content ranged from approximately 39% to 47.8% at 10 °C/min and 35–47.4% at 15 °C/min., respectively. At heating rates of 10 °C/min and 15 °C/min. ash content ranged from 22.6 to 30.6% and 23.9 to 32.4%, respectively. Generally, the results showed a reduction in moisture content and volatile matter and a



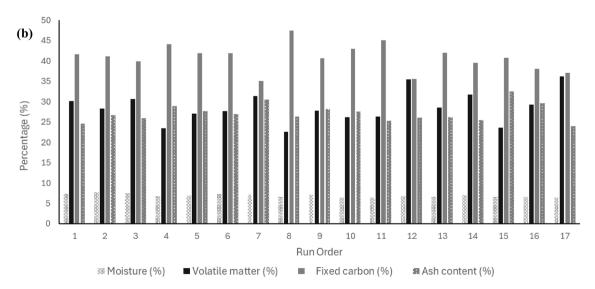


Fig. 3 Proximate analysis results for the developed composite briquettes at heating rates of (a) 10 °C/min. and (b) 15 °C/min



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corresponding increase in fixed carbon and ash content in the developed composite briquettes when compared to the proximate analysis results of the raw materials. This is attributed to the carbonization process of the cassava rhizomes and groundnut stalks [7, 8]. Moisture content results were in the range between 8 and 10%, which range is recommended for briquettes to be used for domestic cooking applications [66]. Moisture content levels should not be high in briquettes so that minimal energy due to latent heat of vaporization is lost, thus reducing the effective energy available from that solid fuel, which will enhance heat transfer across the internal structure of the briquette during combustion. Furthermore, high moisture content is responsible for reducing adiabatic flame temperature during combustion. This explains why briquettes with low moisture content require less time for ignition [7, 8].

3.3 Calorific values for raw materials and composite briquettes

Calorific value results shown in Table 3, clearly show that there was no significant difference between the analytical and experimental results. Experimental heating value of the cassava rhizome was 16 MJ/kg compared to 12.6 MJ/kg for groundnut stalks. These results are explained by the higher carbon content and lower ash content in cassava rhizomes compared to groundnut stalks (See Table 2). Calorific values for the developed composite briquettes ranged from 18.1 to 24 MJ/kg (See Fig. 4). Highest calorific values were observed for composite briquettes with the highest percentages of cassava rhizome in the matrix compared to briquettes that had more groundnut stalks in the composite matrix (See Table 1). This implies that composite briquettes had higher calorific values than that recorded for individual raw material cassava rhizomes and groundnut stalks separately. This is due to the carbonization process that increases the fixed carbon and reduces the volatile matter content in the developed composite briquettes. Carbonization results in reduced oxygenation because of breaking weak O–H bonds and developing stronger C=C bonds [67].

Table 3 Comparison of experimental heating values with numerical heating values calculated using the models of Nhuchhen and Afzal, [51]; and Garcia et al. 2014 [50, 51]

Raw material	Heating rate (°C/ min)	Numerical HHV	Experimental HHV	
		Nhuchhen & Afzal [51]	Garcia et al. 2014	
Cassava rhizomes	10	14.5	16.58	16.0
	15	14.33	16.56	
Groundnut stalks	10	14.33	15.62	12.6
	15	14.16	15.44	

Fig. 4 Calorific values for the developed composite briquettes developed with different jackfruit waste binder amounts





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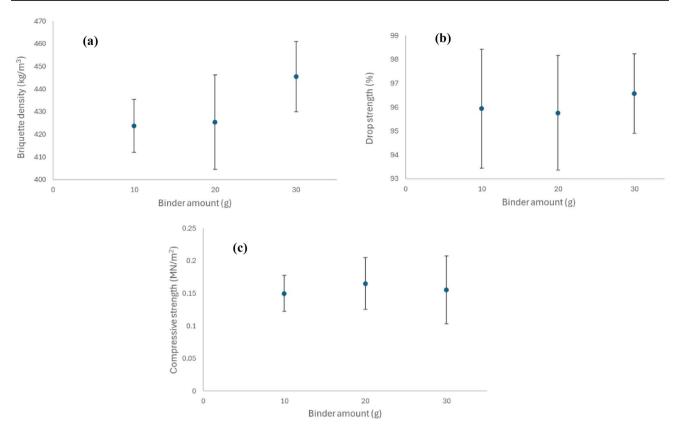


Fig. 5 Effect of different Jackfruit waste binder amounts on briquette density (a), drop strength (b) and compressive strength (c) for the developed composite briquettes

3.4 Mechanical properties of composite briquettes

The density of the developed briquettes ranged from 397.1 to 458.7 kg/m^3 . An increase in jackfruit waste binder resulted in an increase in briquette density (See Fig. 5a). This is explained by increased adhesive surface area for additional bonding because of increased pore sizes due to carbonization and the impact of naturally occurring binding agents in Jackfruit waste binder in the formation of the composite briquettes [9, 40, 41]. Sen et al. [60] developed briquettes from cassava rhizomes and recorded briquette densities ranging from 400 to 900 kg/m³ [60]. The developed composite briquettes had drop strength results between 92 and 99% (See Fig. 5b) which was generally in the range for carbonized briquettes [4, 5, 7-9, 12, 45]. Drop strength is an indicator that measures the handling and transportation integrity of the developed composite briquettes to determine whether they will retain their structure for a given period without disintegration, which would affect their ability to function as solid fuels for domestic cooking applications. An increase on jackfruit waste binder resulted in an overall average increase in drop strength results for the composite briquettes due to its naturally occurring binding agents [41, 42]. However, from Table 1 it is also clear that an increase in cassava rhizome biochar in the overall composite matrix resulted in higher drop strength results for the developed composite briquettes. The variation of compressive strength results for different amounts of jackfruit waste binder are shown in Fig. 5c. Results for compressive strength of the briquettes are shown in Table 1. Variation of compressive strength results with different amounts of jackfruit waste binder are shown in Fig. 5c. Compressive strength values for the developed briquettes ranged between 0.079 and 0.219 MN/m². Highest values of compressive strength corresponded very well with results for composite briquettes with the highest drop strength.

3.5 Optimization results

Response surface methodology was used to determine the optimal briquetting processing parameters to attain the optimal calorific value, drop strength and compressive strength of the developed carbonized briquettes. Analysis of



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Table 4 Variance analysis of responses for calorific (heating) value, drop strength and compressive strength

Source	Sum of squares	df	Mean square	F-value	P-value	Significance
Response 1: Heating value						
Model	46.19	3	15.40	74.27	< 0.0001	Significant
A-biochar amount (CR%)	45.86	1	45.86	221.23	< 0.0001	
B-Amount of water	0.2830	1	0.2830	1.36	0.2637	
C-binder amount(g)	0.0448	1	0.0448	0.2162	0.6496	
Residual	2.70	13	0.2073			
Lack of fit	2.67	9	0.2961	39.75	0.0015	
Pure error	0.0298	4	0.0074			
Cor total	48.89	16				
Response 2: Drop strength						
Model	43.44	3	14.48	4.29	0.0260	Significant
A-biochar amount (CR%)	23.26	1	23.26	6.89	0.0210	
B-Amount of water	19.38	1	19.38	5.74	0.0323	
C- binder amount (g)	0.8128	1	0.8128	0.2408	0.6318	
Residual	43.88	13	3.38			
Lack of fit	19.50	9	2.17	0.3557	0.9089	
Pure error	24.37	4	6.09			
Cor total	87.32	16				
Response 3: Compressive st	rength					
Model	0.0185	3	0.0062	7.75	0.0032	Significant
A-biochar amount (CR%)	0.0126	1	0.0126	15.91	0.0015	
B-Amount of water	0.0058	1	0.0058	7.27	0.0183	
C- binder amount (g)	0.0001	1	0.0001	0.0832	0.7775	
Residual	0.0103	13	0.0008			
Lack of fit	0.0057	9	0.0006	0.5488	0.7912	
Pure error	0.0046	4	0.0012			
Cor total	0.0288	16				

variance (ANOVA) was used to evaluate the variance of responses for heating value, drop strength and compressive strength for variation in the independent factors including proportion of biochar (i.e. in the briquette matrix the percentage of carbonized cassava rhizome is indicated which means the other proportion consists of groundnut stalks), binder amount (jackfruit waste) and the amount of water used in processing the binder. Variance analysis from Table 4, showed that the statistical models for heating value, drop strength and compressive strength were significant as p-values were less than 0.05. The model F-values of 74.27, 4.29 and 7.75 for heating value, drop strength and compressive strength, respectively, indicated that the models were significant at 0.01, 2.60 and 0.32% significance levels, respectively, implying that the F—values were large due to noise. The lack of fit for the models being insignificant implied that the predictive models generated were sufficient to numerically predict the calorific (heating) value, drop strength and compressive strength properties of the developed composite briquettes (See Eqs. 27-29).

The model equations for the factors used to predict about responses are given by;

Heating value =
$$20.60 + 2.39A + 0.1881B + 0.0749C$$
 (27)

Drop strength =
$$96 + 1.71A + 1.56B + 0.3187C$$
 (28)

Compressive strength =
$$0.1591 + 0.0398A + 0.0269B + 0.0029C$$
 (29)

A is the carbonized cassava rhizome and groundnut stalk rhizome biochar in the composite matrix, B is the amount of water, and C is the jackfruit waste binder amount. The 2D plots for the effect of these factors on the responses of compressive strength (a), drop strength (b) and heating (calorific) value (c) are shown in Fig. 6.



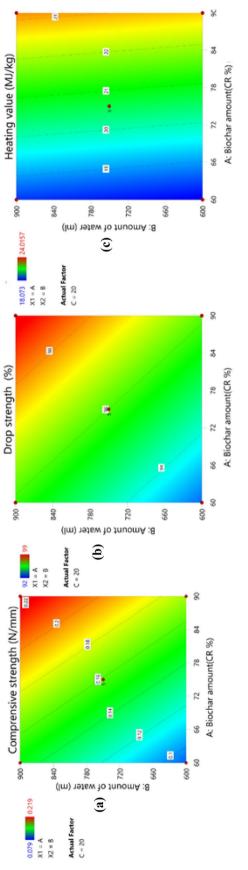


Fig. 6. 2D plots for the effects of factors on biochar amount and amount of water on responses of compressive strength (a), drop strength (b) and heating value (c)



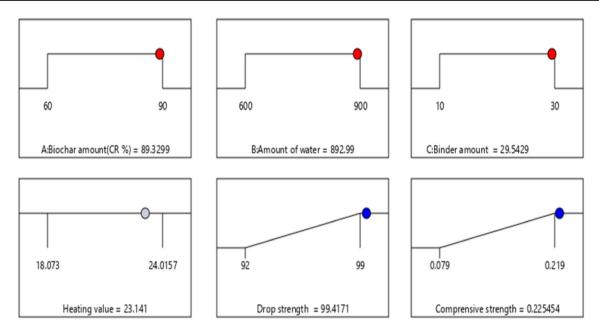


Fig. 7 Optimum processing parameters for biochar amount (cassava rhizome % in composite matrix), amount of water and jackfruit waste binder amount and resulting optimal responses for heating/calorific value, drop strength and compressive strength

The optimum processing parameters (to achieve a desirability of 1.0) for biochar ratio (cassava rhizomes: ground-nut stalks), amount of water and jackfruit waste binder amount (% of biochar) were determined as 89.3:10.7; 893 ml and 29.5g, respectively, resulting in heating/calorific values of 23.141 MJ/kg, drop strength of 99.42% and compressive strength of 0.225 MN/m², respectively (See Fig. 7). Based on the selected best-fit solution, it was concluded that the factors had a significant influence on the heating value and mechanical strength of the briquettes.

3.6 Combustion characteristics of the developed composite briquettes

Ignition time, water boiling time, burning rate and specific fuel consumption for the developed composite briquettes are shown in Fig. 8. Ignition time for the composite briquettes ranged from 3 to 6 min. The average ignition time shows an increasing trend as jackfruit waste binder is increased from 10 to 30 g. Time to boil 1 L of water ranged from 18 to 37 min, respectively. These results are similar to results from other studies [68]. Burning rates and specific fuel consumption values ranged from 2 to 4 g/min and 91–180 g/liter, respectively. Average specific fuel consumption results showed an increasing trend as jackfruit waste binder amount was increased. Burning rates are influenced by volatile matter percentages in the developed composite briquettes. Composite briquettes with higher volatile matter also have high specific fuel consumption due to the need for energy for devolatilization, which reduces the actual energy available for domestic cooking applications. Additionally, carbon bonds in the developed composite briquettes require significant amounts of energy to thermally decompose the C-C and C=C bonds, which lowers the overall burning rate and specific fuel consumption [54, 67]. This is particularly true for composite briquettes with high fixed carbon percentages, despite the positive benefit of higher heating value/ calorific results for these composite briquettes. Therefore, the combustion characteristic results for the developed composite briquettes are directly correlated with the physical properties of the developed composite briquettes [69]. Composites briquettes developed with higher amounts of jackfruit waste binder had reduced internal porosity which limited oxygen flow and affected ignition capability [69]. These results are especially important because they imply that the developed composite briquettes achieve the necessary combustion properties required to function as solid fuels for domestic applications. It further supports transition to a sustainable resource for development of these briquettes using cassava rhizomes and groundnut stalks with jackfruit waste as binder.



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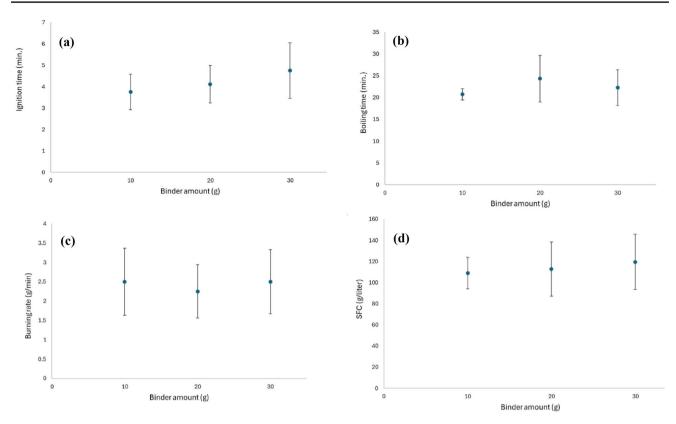


Fig. 8 Effect of jackfruit waste binder amount on ignition time (a), boiling time (b), boiling rate (c), and specific fuel consumption (d) for the developed composite briquettes

3.7 Thermal degradation and kinetic characteristics for optimized composite briquettes

The thermal degradation behavior, in terms of both thermogravimetric and derivative thermogravimetry, for the composite briquettes developed using optimal processing conditions described in Sect. 3.5, are shown in Fig. 9 for heating rates of 10 °C/min and 15 °C/min. The first stage of thermal degradation is characterized by evaporation and drying of the composite briquettes from room temperature to about 105 °C, resulting in a weight loss of 6.5%. Devolatilization took place between 152 and 364 °C for 10 °C/min and between 182 and 435 °C for the 15 °C/min,

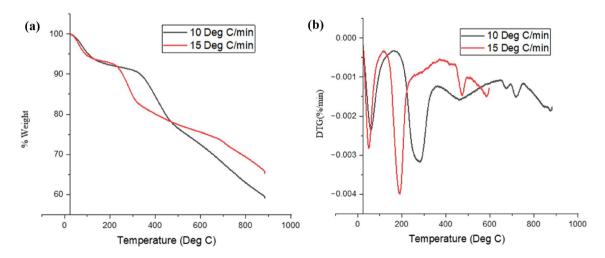


Fig. 9 TGA (a) and DTG (b) curves for the thermal degradation of optimized composite briquettes at heating rates of 10 and 15 °C/min



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Fig. 10 Coats Redfern plot for optimized cassava rhizome and groundnut stalks composite briquettes at heating rates of 10 and 15 °C/min

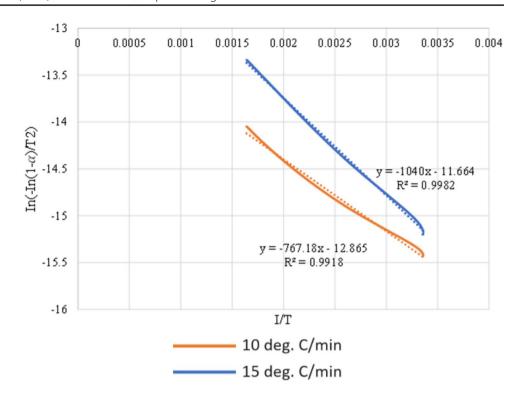


Table 5 Combustion performance parameters of optimized briquettes

Combustion parameters	Heating rate			
	10 °C/min	15 °C/min		
Ignition temperature (°C)	155.12	184		
Burnout temperature (°C)	618.14	453		
Maximum burning rate (%/min)	0.3175	0.3585		
Average burning rate (%/min)	0.07343	0.2031		
Flammability index (%/min°C ²)	2.047×10^{-3}	2.1658×10^{-3}		
Combustion characteristics index % ² /min ² /°C ³	1.567×10^{-9}	2.0285×10^{-10}		

resulting in weight losses of between 18 and 10%, respectively. Char formation, which is characterized by partial and complete degradation of cellulose initially and then lignin (at higher temperatures) occurred between 365.3 °C and 881.8 °C for heating rate of 10 °C/min. and between 460.3 °C and 883.5 °C for 15 °C/min heating rate. The weak peak on the left of the DTG curve (See Fig. 9b) corresponds to the dehydration during evaporation and moisture content reduction. During the dehydration stage mass loss rate was 2.4%/min for a heating rate of 10 °C/min. and 2.8%/min for a heating rate of 15 °C/min. The mass loss rate shown by the second peak of the DTG curve corresponds to the devolatilization stage at which maximum weight loss occurs at 270 °C and 283.2 °C for heating rates of 10 °C/min and 15 °C/min. respectively, with corresponding mass loss rates of 0.3175%/min and 0.3985%/min, respectively. From this discussion, increasing the heating rate will increase the rate of devolatilization due to higher kinetic energy available for molecules to impinge onto one another and contribute to significant combustion properties of the developed composite briquettes [12, 54]. Weak peaks on the right side of the maximum peaks (See Fig. 9b) corresponded to lignin decomposition and char formation regions. From this analysis it can be noted that the highest mass loss rate was observed for the devolatilization stage, which mass loss rates are least during char formation. The reduction of volatiles results in results in reduced ignitability thus promoting char formation [70–72].

The Coats Redfern model (See Eqs. 5–21) was used to determine the kinetic parameters including the activation energy and pre-exponential factor. Whereas the Coats Redfern model is inadequate for a complete kinetic study given the use of



one heating rate, it has a major advantage of providing conservative and reliable results for the kinetic parameters [12]. From Eqs. 5–21 and from the thermal degradation results already presented (See Fig. 9), the Coats Redfern plots for the optimized composite briquettes at different heating rates of 10 °C/min and 15 °C/min. were plotted (See Fig. 10). The activation energies for the optimized composite briquettes were 6376.84 J/mol and 8646.56 J/mol, while the pre-exponential factors were 0.73 and 0.88 for heating rates of 10 °C/min and 15 °C/min, respectively. These results indicate the obvious that combustion at higher heating rates proceeds faster than at lower heating rates. However, at higher heating rates more energy is required to initiate the combustion process as a result of higher kinetic mobility of molecules [12, 54].

Combustion performance indices for the optimized composites briquettes are summarized in Table 5. Ignition temperature, burn out temperature, flammability, and combustion characteristic indices for the developed optimized composite briquette at heating rates of 10 °C/min and 15 °C/min have been shown. For optimized composite briquettes thermally degraded at 10 °C/min the ignition temperature and burnout temperature were 155.1 °C and 618.1 °C, respectively, whereas at 15 °C/min, the ignition and burnout temperatures were 184°C and 453°C, respectively. The trends in these results are consistent with the results for the combustion properties for the non-optimized composite briquettes discussed in Sect. 3.6. The burning rate, flammability index and combustion characteristic index for the optimized composite briquettes combusted at 15 °C/min were higher than those of 10 °C/min heating rate. This was attributed to the higher concentration of heat which increased kinetic energy and mobility of the molecules [5, 9, 12].

4 Conclusion

This research developed briquettes using cassava rhizomes and groundnut stalks agricultural residues, and jackfruit waste as a binder. The feedstocks' properties were characterized, including elemental, physical, and thermal properties. Optimization of the briquettes' development involved varying biochar amount, water, and jackfruit binder amounts. The briquettes were then characterized, and optimal conditions determined based on heating value and drop strength. Cassava rhizomes had 12.20% moisture and 74.28% volatile matter, while groundnut stalks had 12.28% moisture and 74.22% volatile matter. Groundnut stalks had higher ash content (8.75%) than cassava rhizomes (4.86%), but cassava rhizomes had higher fixed carbon content (17.49%) compared with groundnut stalks (13.27%). Cassava rhizomes also had higher lignin and cellulose content. The mechanical and thermal properties of the carbonized composite briquettes were influenced by the amount of biochar, water, and jackfruit waste binder. Optimization studies revealed the ideal ratios of biochar, water, and jackfruit waste binder (89.33:10.67%, 893 ml, and 29.54 g) to achieve desired heating value, drop strength, and compressive strength. The briquettes' properties included moisture content (5.87–9.11%), volatile matter (21–36%), fixed carbon content (35–47%), ash content (22–32%), calorific values (18.07–24.02 MJ/kg), apparent density, drop strength, compressive strength, ignition time, time to boil, burning rate, and specific fuel consumption. Further research should focus on techno-economic and environmental analyses for composite briquette production. The developed composite briquettes achieve the necessary combustion properties required to function as solid fuels for domestic applications.

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Author contribution C.A.O and M.L conceptualized, performed experiments, wrote the main manuscript and reviewed the manuscript; V.A.Y wrote the main manuscript, supervised research and reviewed the manuscript; F.W. and O.B. and J.S. wrote the manuscript and reviewed the manuscript.

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Data availability Data will be made available upon reasonable request to the corresponding author

Declarations

Ethics approval and consent to participate All raw materials used in this study were agricultural residues or wastes. No plants were culitvated or uprooted by the researchers during the course of the study.

Competing interests None.



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