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Comparative Assessment of Proximate and Thermal Properties of Selected Biomass, Composite, and Fossil Fuels for Sustainable Cement Production

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Abstract

Waste is usually produced from man's activities and Nigeria is ranked among the top producers of waste globally, which is mostly from food and agriculture. This study evaluates the suitability of several agricultural wastes (sugarcane bagasse, coconut husk, groundnut shell, sawdust, palm kernel shell and corncobs) a composite blend (equal weight fraction of sugarcane bagasse, coconut husk, groundnut shell, sawdust, palm kernel shell and corncobs agricultural waste biomass were blended), and conventional fossil fuels (coal, LPFO) as alternative fuels for cement production. Using proximate and thermogravimetric analysis, the research determines properties like gross calorific value (GCV), ash content and volatile matter. The findings indicate that certain biomass fuels, particularly coconut husk and palm kernel shell, possess high energy content, high volatile matter, and low ash, positioning them as viable, sustainable alternatives to fossil fuels in cement manufacturing. Gross calorific value (GCV), ash content, volatile, and moisture content were determined using a bomb calorimeter, laboratory muffle furnace and laboratory oven, while thermo gravimetric analysis (TGA) was determined using a thermo gravimetric analyzer. GCV obtained was between (3732.67 ± 8.51 - 10992.34 ± 6.43 Kcal/Kg), LPFO showed the highest GCV while coal showed significantly high ash content (28.85% ± 0.1%) compared to biomass fuels, which exhibited lower ash contents (1.77% - 6.24%). Coconut shell and palm kernel shell exhibited the highest calorific values of the biomass samples (4585 and 4188 Kcal/Kg), an indication of their good renewable energy potential. Biomass fuels displayed higher volatile matter, with corncobs (82.58% ± 0.09%) and sawdust (82.01% ± 0.08%) outperforming coal fossil fuels. Thermo gravimetric analysis (TGA) corroborated this, showing that fuels like coconut husk

underwent 80.9% of their mass loss in the volatile release phase (110˚C - 400˚C), confirming their rapid volatilization and combustion readiness.

Subject Areas

Analytical Chemistry, Environmental Chemistry

Keywords

Biomass Fuels, Cement Production, Proximate Analysis, Thermo Gravimetric Analysis, Sustainable Energy, Alternative Fuels

1. Introduction

Cement is considered the world's second most consumed material after water [1]. The cement manufacturing process consumes high energy with exhaustion of non-renewable fuel sources and significant contributions to carbon emissions and degradation [2] [3]. Cement manufacture contributes about 8% of the global anthropogenic CO_2 emission [4] [5]. About 80% - 90% of these emissions take place during calcination and burning processes [6].

One possible means to reduce fuel cost is to introduce alternative fuels [7]. Use of different types of alternative fuels in the cement industry is a practice that is in existence worldwide and expected to grow as the cement kiln is a good incinerator due to its alkaline nature and as it operates at high temperature and counter-current flow of gas with raw meal [8].

Disposal of agricultural wastes constitute difficulties for farmers as they are usually in large sizes and on the increase [9] [10] due to increasing growth in population and are poorly managed and underutilized as sources of energy in Nigeria [11] as about 56.9 ± 3.3 metric tons of agricultural food waste are wasted annually which could meet a third of Nigeria's bioenergy potential [12]. Agricultural waste is rich in organic matter making it an essential as good sources of energy recovery [13] [14]. If not properly managed, agricultural wastes can cause a noteworthy challenge and increase environmental pollution [15] [16].

Changing alternative fuels presents some challenges as they have diverse physicochemical and emission characteristics compared to the conventional fuels [3] which are critical to determining their workability and environmental benefits. A readily available group of alternative fuels are biomass [17] changing or co-processing of biomass offers the potential of reducing greenhouse gas emissions and promoting sustainable cement production [1]. This study investigates and compares the proximate and thermal properties of selected biomass, composite biomass blends, and conventional fossil fuels to evaluate their suitability for use in cement kilns.

2. Materials and Methods

2.1. Sample Collection

Two samples each were collected from farms and markets in the three senatorial

zones of Benue State, Nigeria as shown in the map in Figure 1.

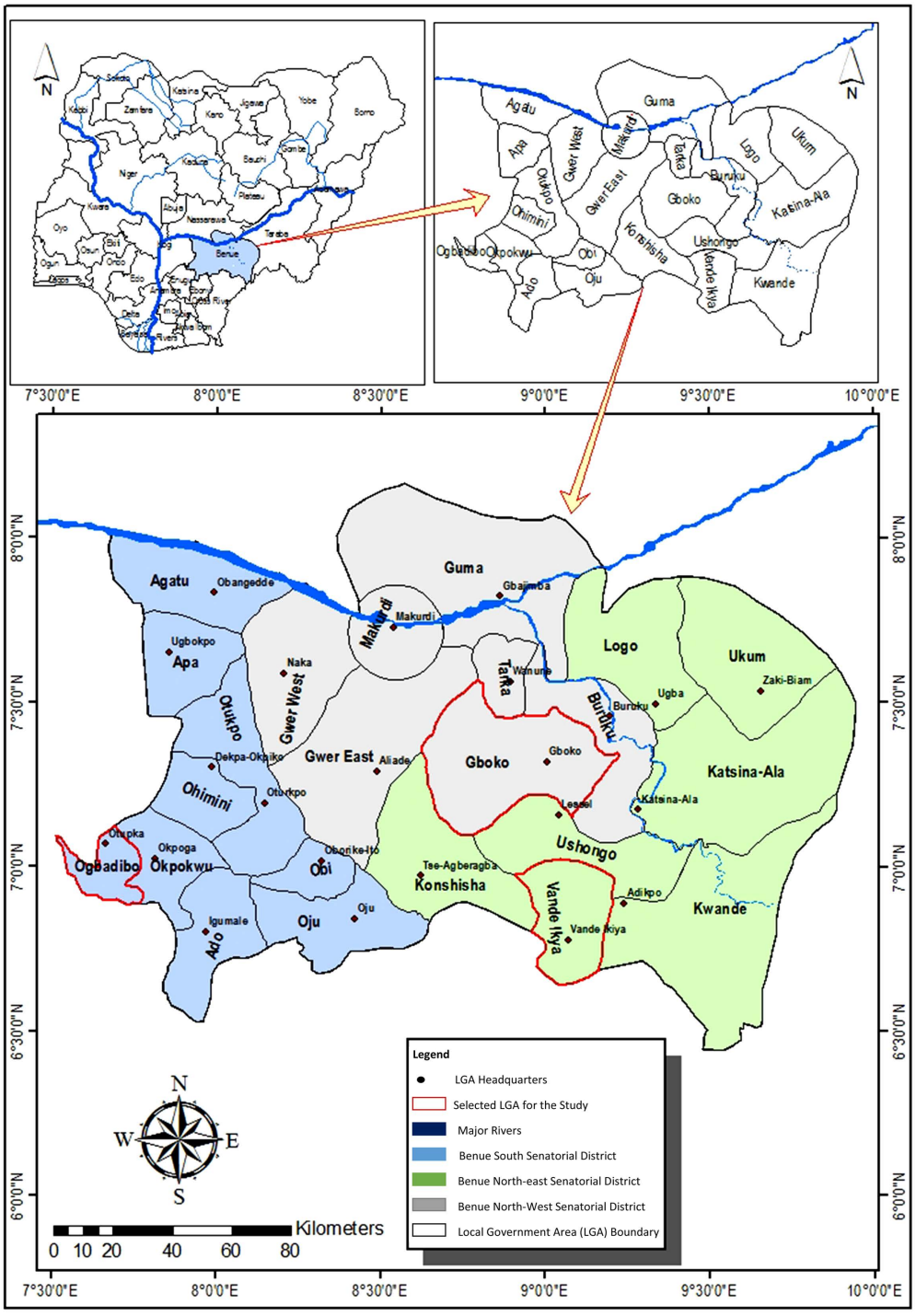


Figure 1. Map of Benue state shows the sampling areas.

2.2. Sample Drying and Moisture Determination

Moisture content is expressed as percentage of wet weight

$$M = (w - d)/w * 100 \quad (1)$$

where M= moisture content (%), w = initial waste sample as delivered (kg) and d = weight of sample after drying at 105˚C [18].

Wet samples were dried at temperatures below 100˚C for twenty-four hours.

2.3. Determination of Gross Calorific Value

Gross calorific value was determined according to ISO standard (ISO 1928:2020) where 1g of the given fuel was taken in nickel crucible supported over a ring inside the steel bomb which is connected with two electrodes. The bomb lid was tightly screwed and filled with oxygen up to 25 atmosphere pressure. The bomb was then lowered into the copper calorimeter containing known mass of water. The water was stirred with the help of mechanical stirrer and the initial temperature (t_1) recorded. The electrodes were then connected to electricity and the circuit completed. The sample burned and the heat liberated. Uniform stirring of water was continued and the maximum temperature (t_2) attained was recorded.

$$\text{Gross Calorific values} = \frac{H \times \Delta T}{xg} \tag{2}$$

where,

Weight of the fuel sample taken = x g;

Temperature difference = $\Delta T = t_2$˚C − t_1˚C;

Heat capacity of Calorimeter = H.

2.4. Determination of Ash

Ash is the non-combustible residue formed from the inorganic or mineral components of the sample. Ash was determined according to [19]. Where an empty silica crucible was taken and cleaned by heating it in furnace for 850˚C and allowed to cool and weighed. 1 g of sample was taken of −212 μ size. Sample and crucible were weighed together and placed inside a muffle furnace maintained at temperature 850˚C for 1 hour. After which the crucible was removed and allowed to cool in a desiccator and weighed again.

The calculation was by following formula,

Where,

X = weight of empty crucible in grams;

Y = weight of coal sample + crucible in grams (Before heating);

Z = weight of coal sample + crucible in grams (After heating);

$$Y - X = \text{weight of coal sample, g} \tag{3}$$

$$Z - X = \text{weight of ash, g} \tag{4}$$

2.5. Determination of Volatile Matter

It is the weight loss obtained on heating 1 g of sample of −212 μ size at 950˚C in a muffle furnace for 7 minutes in the absence of air, after which the crucible is removed and allowed to cool in air, then in a desiccator and weighed again [19].

Total weight loss of a moist sample = weight loss due to volatile matter + moisture.

Weight loss due to VM= total weight loss – moisture.

If sample is dry. Then weight loss is due to volatile matter only:

$$\% \text{ Volatile matter} = (\text{weight loss due to VM/weight of sample}) \times 100 \quad (5)$$

2.6. Thermogravimetric Analysis

A test used to decide the change in a material mass over time as its temperature usually increases. It involves heating the sample in a controlled atmosphere and measuring its weight loss or gain to estimate its thermal stability, rate of decomposition, moisture content and compositional analysis.

3. Results

The results of the proximate analysis for the selected biomass fuels, composite biomass blend and conventional fossil fuels are presented in Table 1. The data reveal clear variations in the proximate properties analyzed. Among the fossil fuels, LPFO exhibited the highest Gross Calorific Value (GCV), while coal had considerably higher ash content compared to the biomass fuels. Notably, all biomass fuels basically showed higher volatile matter content compared to coal.

Table 2 summarizes the thermogravimetric Analysis (TGA) results showing the percentage mass loss of each fuel sample across critical temperature ranges that correspond to different stages of thermal decomposition (loss in moisture, active pyrolysis of volatiles and combustion of fixed carbon). The data indicate that biomass fuels like coconut husk undergo the majority of their mass loss (80.9%) in the volatile release phase (110˚C - 400˚C), a confirmation of their high reactivity. However, fine coal fuel showed different mass loss profiles and having the highest proportion of residual char.

The thermal decomposition behavior is further illustrated in Figure 2, which presents the Derivative thermogravimetry (DTG) and Differential Thermal Analysis (DTA) curves for all fuels. The DTG peaks indicate the rate of mass loss, with distinct profiles for different fuel types. For instance, the similar DTG peak shapes for the composite blend and sawdust suggest comparable chemical compositions, particularly as regards cellulose and hemicellulose content. All DTA curves confirm an exothermic combustion reaction for each fuel sample.

Table 1. Proximate analysis of biomass, composite blend and fossil fuels including gross calorific value, ash content, volatile matter and moisture content.

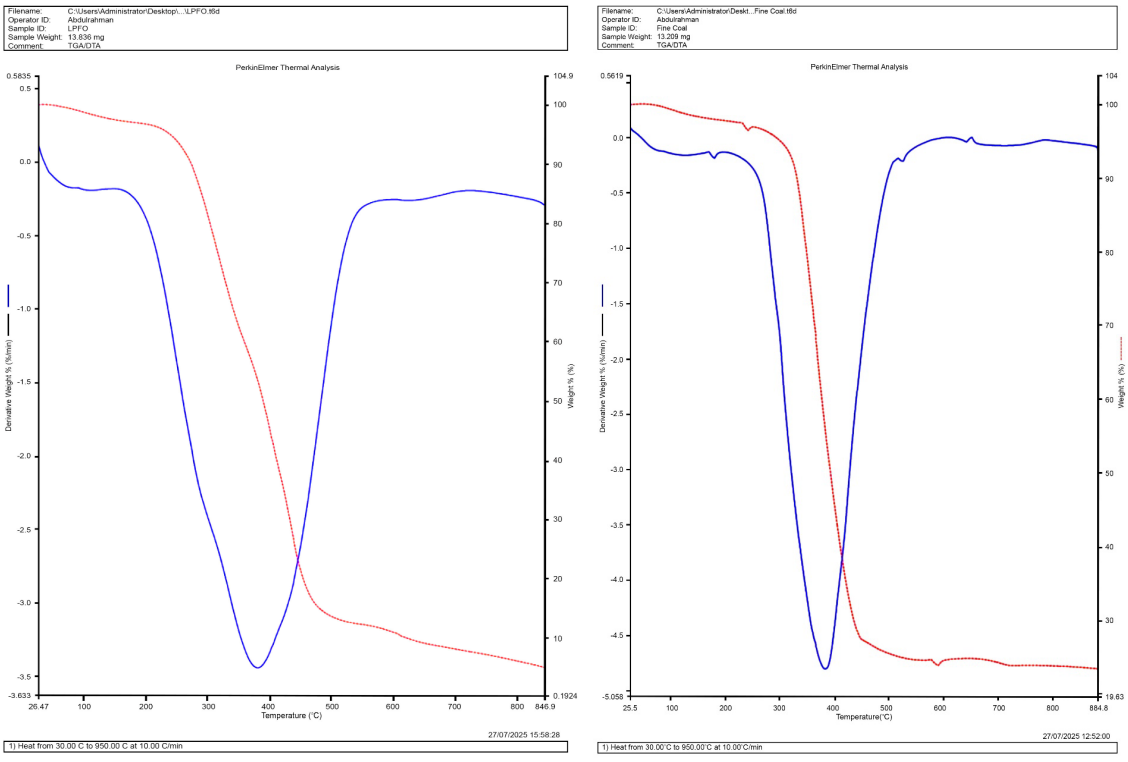
FUEL	Gross Calorific Value	Ash	Volatile Matter	Moisture
LPFO	10992.34 ± 6.43h	0 ± 0a	0 ± 0a	0 ± 0a
COAL	4496 ± 13.46f	28.85 ± 0.1g	34.1 ± 0.63b	12.07 ± 0.42f
COMPOSITE	4029.67 ± 10.41d	3.01 ± 0.06d	75.64 ± 0.06e	4.1 ± 0.16c
SUGARCANE	3956 ± 11.14c	3.68 ± 0.08e	79.3 ± 0.35f	5.14 ± 0.31d

Continued

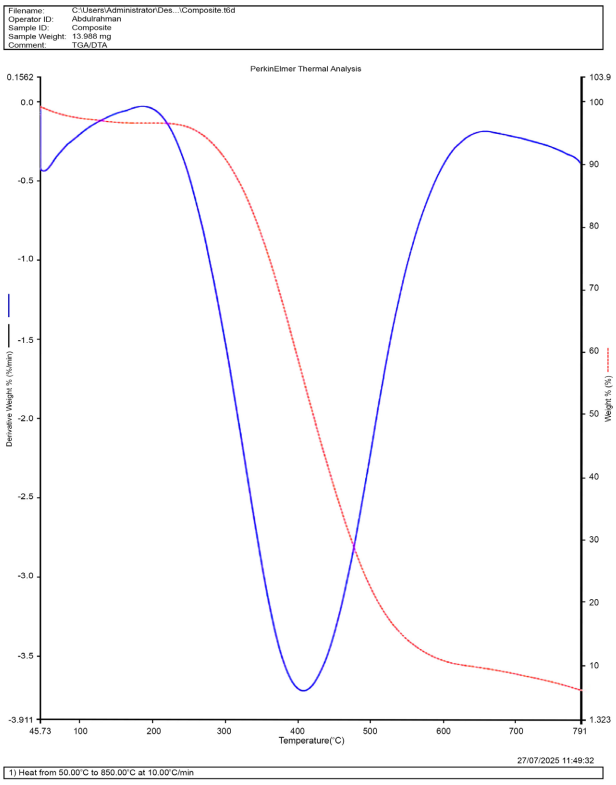
COCONUT	4585 ± 9.17g	2.78 ± 0.09c	62.52 ± 0.1c	2.9 ± 0.27a
GROUNDNUT	3822.34 ± 8.63b	2.07 ± 0.06b	79.34 ± 0.12f	4.94 ± 0.36d
SAWDUST	3732.67 ± 8.51a	3.59 ± 0.05e	82.01 ± 0.08g	7.97 ± 0.36e
PALM KERNEL	4188.34 ± 9.72e	6.24 ± 0.12f	72.63 ± 0.07d	3.7 ± 0.27bc
CORNCOB	3805.67 ± 10.27b	1.77 ± 0.04a	82.58 ± 0.09h	3.24 ± 0.31ab
P-Value	0.00	0.00	0.00	0.00
LSD	17.01	0.1220	0.4251	0.502

Table 2. TGA Mass Loss of biomass, composite and fossil fuels across major thermal decomposition stages.

Samples	Temperature Range			
	27˚C - 110˚C	110˚C - 400˚C	400˚C - 900˚C	Char
Fine coal	0.867 ± 0.02d	53.1 ± 0.02f	22.7 ± 0.00b	23.5 ± 0.03g
Coconut husk	4.11 ± 0.03h	80.9 ± 0.02i	6.8 ± 0.00a	8.14 ± 0.04e
Composite	2.04 ± 0.02g	38.2 ± 0.03c	53.2 ± 0.02h	5.98 ± 0.03c
Corncobs	1.36 ± 0.04d	71.2 ± 0.00h	23.5 ± 0.01c	3.73 ± 0.00a
Groundnut shell	0.378 ± 0.03b	32.9 ± 0.00a	51.0 ± 0.02g	15.5 ± 0.02f
LPFO	1.54 ± 0.00f	52.9 ± 0.00e	40.7 ± 0.02f	4.95 ± 0.00b
PKS	1.34 ± 0.02e	69.3 ± 0.03g	25.4 ± 0.01d	3.73 ± 0.02a
Sawdust	0.231 ± 0.01c	37.9 ± 0.02b	55.8 ± 0.00i	6.13 ± 0.03d
Sugarcane Bagasse	0.592 ± 0.01c	52.6 ± 0.00d	31.4 ± 0.00e	15.6 ± 0.03d



(a) (b)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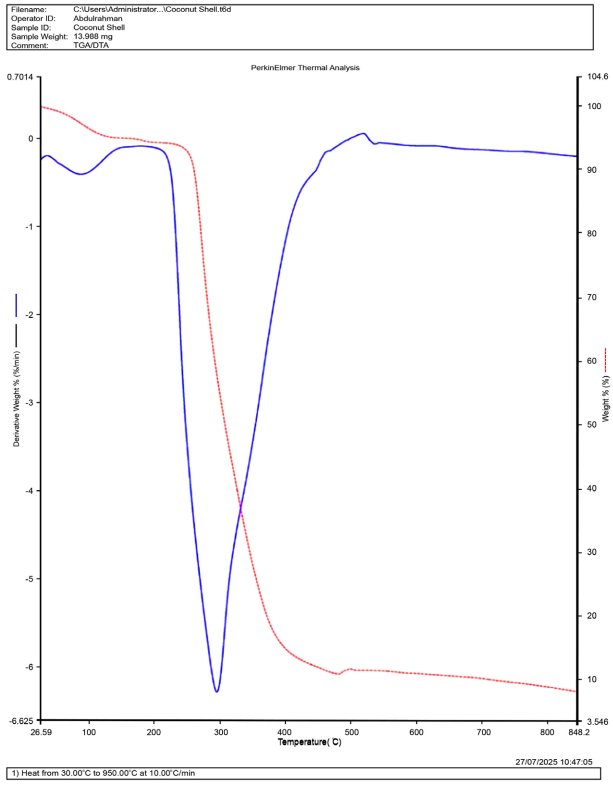
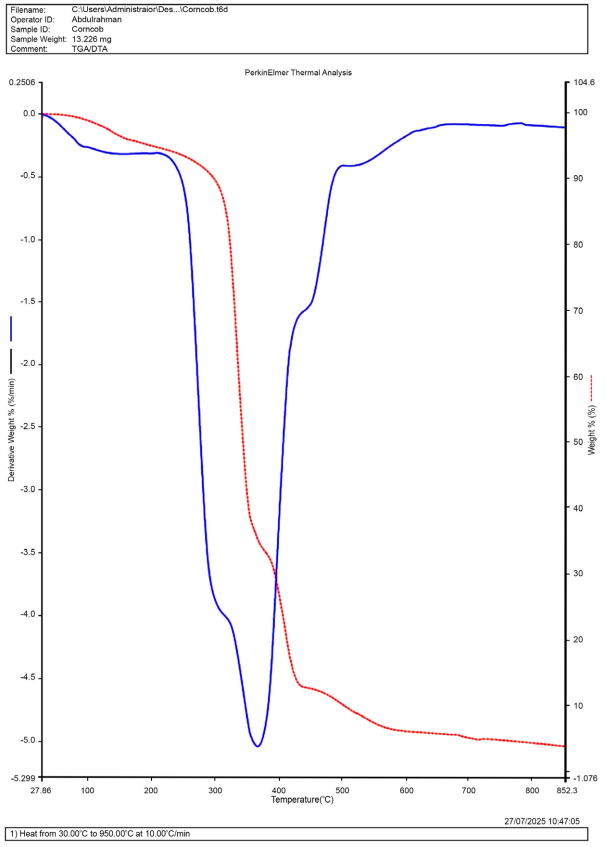
Operator ID: Abdulrahman
Sample ID: Composite
Sample Weight: 13.988 mg
Comment: TGA/DTA
PerkinElmer Thermal Analysis
Derivative Weight % (%/min)
Weight % (%)
Temperature(°C)
27/07/2025 11:49:32
1) Heat from 50.00°C to 850.00°C at 10.00°C/min

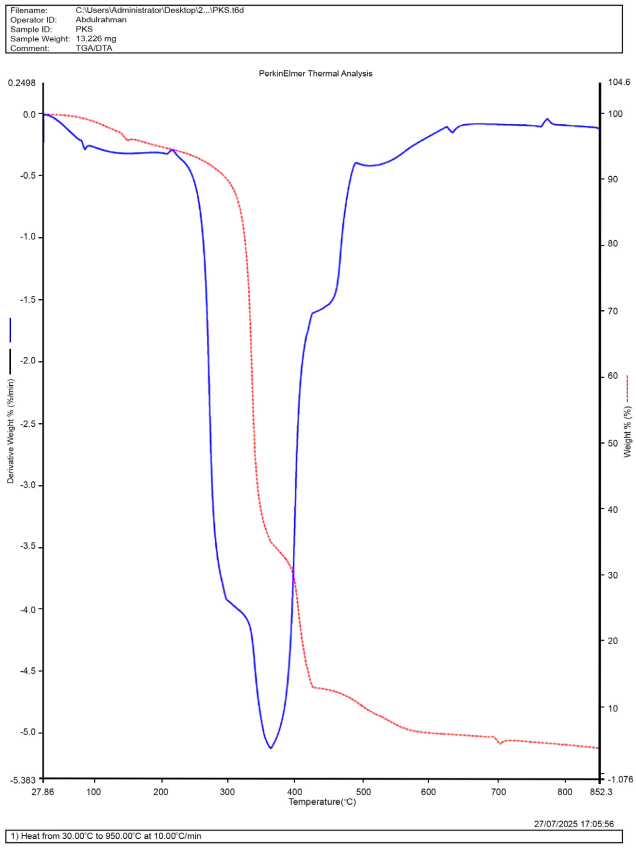
(c)


Filename: C:\Users\Administrator...\Coconut Shell.t6d
Operator ID: Abdulrahman
Sample ID: Coconut Shell
Sample Weight: 13.988 mg
Comment: TGA/DTA
PerkinElmer Thermal Analysis
Derivative Weight % (%/min)
Weight % (%)
Temperature(C)
27/07/2025 10:47:05
1) Heat from 30.00°C to 950.00°C at 10.00°C/min

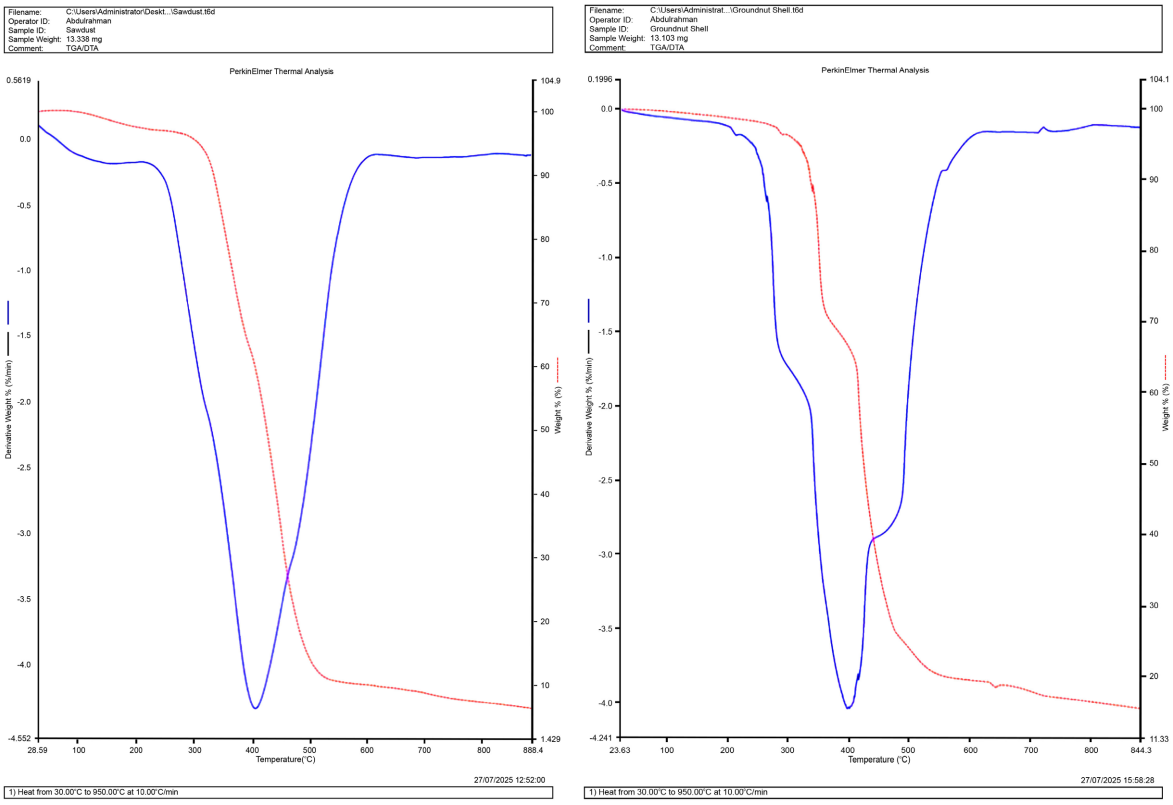
(d)


Filename: C:\Users\Administraior\Des...\Corncob.t6d
Operator ID: Abdulrahman
Sample ID: Corncob
Sample Weight: 13.226 mg
Comment: TGA/DTA
PerkinElmer Thermal Analysis
Derivative Weight % (%/min)
Weight % (%)
Temperature(°C)
27/07/2025 10:47:05
1) Heat from 30.00°C to 950.00°C at 10.00°C/min

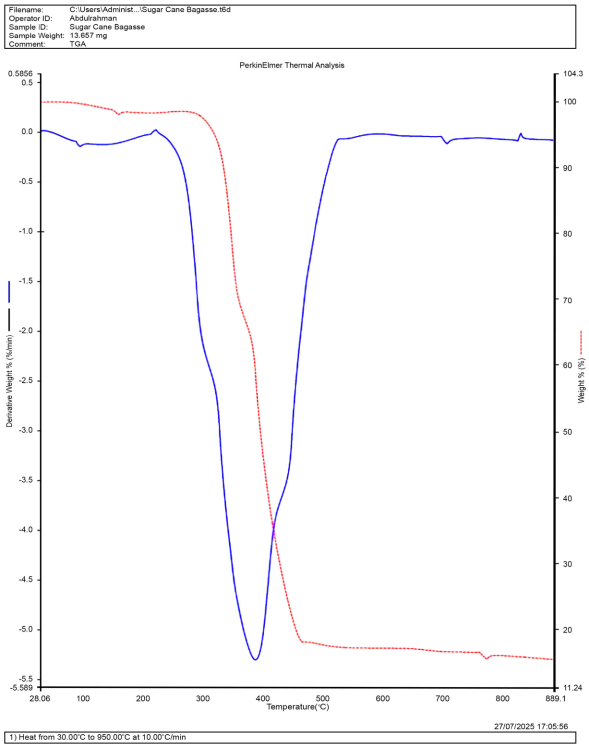
(e)


Filename: C:\Users\Administrator\Desktop\2...\PKS.t6d
Operator ID: Abdulrahman
Sample ID: PKS
Sample Weight: 13.226 mg
Comment: TGA/DTA
PerkinElmer Thermal Analysis
Derivative Weight % (%/min)
Weight % (%)
Temperature(°C)
27/07/2025 17:05:56
1) Heat from 30.00°C to 950.00°C at 10.00°C/min

(f)



(g) (h)



(g)

Figure 2. DTA and TDG profiles of LPFO, Fine coal, coconut husk, composite biomass, corncobs, groundnut shell, palm kernel shell, sugarcane bagasse and sawdust fuels illustrating their pyrolysis and combustion behavior.

4. Discussion

As shown in Table 1, the fuels exhibited substantial variation in gross calorific values, ash content, volatile matter and moisture content. According to Table 1, the coal sample had the highest moisture content of 12.07%, the least being LPFO with 0.00% followed by coconut husk, corncobs, palm kernel shell, composite biomass, groundnut shell, sugarcane bagasse, and saw dust respectively as revealed in table. Statistical analysis using analysis of variance (ANOVA) reveals a significant difference in moisture content of all fuels while, least significant difference (LSD) test indicates palm kernel and corn cobs are statically similar. The residual moisture values are low or moderately low due to varying harvest dates, weather conditions (in this case, dry season), genetics and soil composition [20]. The moisture content has the ability to influence the energy value and combustion performance [20]. Lower moisture improves combustion efficiency, as buttressed by [21]. Moisture content can also influence how the fuel is handled and its storage. All the samples except coal were sun dried to remove some moisture according to [22] while coal was air dried according to ASTM D 5373-02. as, the main controlling parameter of the combustion process after drying is the ratio between the amount of air added and the amount of air (oxygen) necessary for a complete combustion of the combustible parts of the fuel [23].

The gross calorific value (GCV) is a key fuel property of any fuel, as it represents the energy released during combustion [24]. From Table 1, the LPFO sample recorded the highest GCV of (10992 Kcal/Kg) and it is used here as benchmark because LPFO is a conventional high grade liquid fuel, widely used in cement plants. Its high energy density reflects its effectiveness in sustaining the high temperature requirement of clinker formation, making it a suitable upper limit comparator for evaluating alternative fuels. Relative to LPFO, all biomass exhibited lower GCVs, with coconut husk (4585 Kcal/Kg) and palm kernel shell (4188 Kcal/Kg) showed the highest values among the agricultural biomass options. Coal, traditionally used in cement production has a GCV of 4496 Kcal/kg, placing it between the higher quality biomass fuels and the lower calorific options, these results align with reported ranges of 3500 - 4500 Kcal/kg for low rank-coal coals [25]. Groundnut shell and sawdust showed considerably lower GCVs (3800 and 3733 Kcal/kg. Statistical analysis using ANOVA shows a significant difference in GCV across most fuels while LSD test indicates no significant difference in gross calorific values between corncob and groundnut husk. The comparative high GCV of coconut husk and palm kernel shell suggests as that these fuels could serve as feasible partial substitute for fossil fuels in cement kilns. However, their operational performance must still consider biomass moisture content, which can influence thermal efficiency in the kiln.

According to Table 1, ash analyzed for each fuel is in the order; $1.76 < 2.06 < 2.77 < 3.01 < 3.59 < 3.67 < 6.2 < 28.85$. Ash is the noncombustible residual or mineral matter produced from fuel combustion [26]. The coal sample had the highest ash of 28.85% which indicates that it is a lignite formation, followed by

palm kernel shell, sugar cane bagasse, saw dust, composite biomass, coconut and groundnut shell respectively with the least being corn cobs with 1.76%. Statistical analysis using ANOVA shows a significant difference in gross calorific value across almost all fuels while LSD shows no significant difference in ash values between corncob and groundnut husk. During clinker production process, the organic part of waste fuel is totally destroyed while the inorganic compounds and heavy metals in the ash are assimilated in the clinker phases or substitute calcium or silicon in the silicate phases of the clinker. However, due to their origin these wastes introduced into the cement making process, introduce several elements that may affect the process itself as well as the composition and quality of clinker [27]. Higher ash invariably leads to increased silica and other inorganic components in resultant clinker which may affect the quality. Studies by [10] and [28] confirm that biomass with high volatile matter and low ash increases flame stability and reduces fouling risks.

Volatile matter analyzed for each fuel in **Table 1** is in the order; 34.10 < 62.52 < 72.62 < 75.63 < 79.30 < 79.33 < 82.00 < 82.57. The coal sample had the least volatile matter of 34.10% followed by coconut, palm kernel shell, composite biomass, groundnut shell and sugar cane bagasse with equal volatile matter (VM) and saw dust respectively with the highest being corncobs with volatile matter of 82.6%. These findings are consistent with biomass combustion behavior documented by [29] and [30]. The highest volatile matter observed in corncobs followed by sawdust, is an indicator of combustibility. This suggests rapid ignition and flame propagation, qualities favorable for kiln firing. Statistical analysis using ANOVA indicates a significant difference in volatile matter across almost all fuels while LSD indicates no significant difference in volatile matter of sugarcane bagasse and ground nut husk. High volatile matter (VM) observed in biomass can boost combustion efficiency. The volatile matter content of fuel affects storage behavior (oxidation, danger of spontaneous combustion, and loss of heating value), required fineness for pulverization, burner settings, combustion behavior, and efficiency [26].

From **Table 2**, mass loss between 27˚C - 110˚C corresponds to moisture loss, dominated by coconut husk (4.11%). All DTA peaks in **Figure 2** indicate their combustion reaction was exothermic. Biomass fuels displayed higher mass loss in the volatile release zone (110˚C - 400˚C) as revealed in **Table 2**, consistent with their high cellulose and hemicellulose content. The DTG peak of composite fuel and sawdust are similar, DTG peak of palm kernel shell and corncobs are also similar, suggesting similarity in their major composition (cellulose/hemicellulose). Mass loss at 27˚C - 110˚C can be attributed to moisture loss, the moisture is within the range 0.231% - 4.107%, with the least moisture from sawdust while higher moisture is from coconut husk fuel, the values for moisture content for all fuel are reasonably low, high moisture content of fuel in the kiln can cool the flame zone affecting clinker formation. Active pyrolysis occurs at temperature between 110˚C - 400˚C with high volatilization. At this stage, hemicellulose and cellulose

break down in biomass. Percentage mass loss for both fossil and agricultural biomass are within the range of 37.91% - 80.91% with the highest mass loss observed in coconut husk fuel while least mass loss observed in sawdust, indicating coconut husk contains more hemicellulose and cellulose compared to other biomass and sawdust contains least among the biomass samples. Mass loss at temperatures above 400˚C are within the range of 6.83% - 55.77%, with the highest mass loss observed in sawdust while coconut husk in contrast is observed to have the least mass loss, indicating saw dust contains more lignin compared to other biomass and coconut shell contains least. The observed chars are within the range of 3.73% - 23.46% with the highest char observed in fine coal while least observed in palm kernel shell and corncobs. Residue left after pyrolysis otherwise known as char is mostly fixed carbon and inorganic minerals in form of ash. The highest char in fine coal is consistent with proximate analysis of ash observed in the same sample.

A limitation of this study is that, it focuses primarily on proximate and thermal analyses without incorporation other fuel characteristics such as elemental composition, ash mineralogy and trace metal content.

5. Conclusion

Adoption of these biomass from agricultural waste and its composite blend fuel offer practical benefits as sustainable alternatives to fossil fuels for cement production in Nigeria, providing acceptable calorific values, thermal properties and combustion qualities. Their incorporation in cement pyro processing can support decarbonization goals within the industry while reducing dependence on non-renewable fossil fuels.

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Conflicts of Interest

The authors declare no conflicts of interest.

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