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Chemical, Thermogravimetric and Elemental Characterization of Nigerian Groundnut and Cowpea Shells for Sustainable Valorization

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Abstract. In this study, the chemical, thermogravimetric, and elemental composition of Nigerian groundnut (*Arachis hypogaea L.*) and cowpea shells (*Vigna unguiculata*) were investigated to understand their potential as valuable waste resources. Analysis of the carbohydrates and lignin content was performed using the National Renewable Energy Laboratory method. Fourier transform infrared (FTIR) spectroscopy was used to determine the chemical structure of the substrates. Elemental analysis was performed using X-ray fluorescence (XRF) and an elemental analyzer to determine the carbon, hydrogen, nitrogen, and sulphur. In addition, thermogravimetric analysis was used to assess the thermal stability of the substrates. The chemical composition analysis revealed that the cowpea shells contain 21.32% cellulose, 21.46% hemicellulose, and 28.37% lignin. On the other hand, groundnut shells comprise 26.31% cellulose, 19.5% hemicellulose, and 38.33% lignin. The XRF results indicated the presence of significant elemental compositions in both substrates, including Si, Al, Mg, Na, P, Fe, K, Ca, and S. The carbon content of both substrates was found to be 43%. Thermogravimetric analysis revealed that groundnut shells exhibit a higher cellulose decomposition temperature at 350 °C, whereas cowpea shells manifest this phenomenon at 322 °C. The results show that the cowpea shells had a higher heating value as they exceeded that of the groundnut shell by 0.89 per cent. These comprehensive findings show the substantial potential of Nigerian groundnut and cowpea shells as valuable waste materials, which can be effectively used to produce valuable products such as bioethanol, biochemicals, biochar, and bio-composite materials. This research contributes to understanding the composition and properties of these agricultural by-products, thus paving the way for their sustainable use in various industrial applications.

Keywords. Agricultural waste, groundnut shells, cowpea shells, FTIR, elemental analysis, thermogravimetric analysis



1. Introduction

Understanding the composition of biomass as feedstock is the key to achieving the valorisation of waste and Sustainable Development Goal 7 of affordable and clean energy by 2030 [1]. The results obtained from the characterisation of feedstocks play a vital role in the choice of process routes, unit operations, and processes to facilitate their easy adaptation as feedstock for biorefineries. Cowpea (*Vigna unguiculata*) and groundnut (*Arachis hypogaea L.*) are significant crops grown in Nigeria. Cowpea is one of the economically important crops in Nigeria and a source of plant protein [2]. Groundnuts on the other hand are consumed worldwide as butter, groundnut oil, and groundnut bars, or as a snack when roasted or boiled. According to the Food and Agriculture Organisation of the United Nations, cowpea production in Nigeria as of 2020 was 3.7 million tonnes, while groundnut was 4.5 million tonnes [3]. The two crops belong to the legume family, with their seeds covered in shells. Figure 1 shows a picture of the groundnut and cowpea shells. Both shells are post-harvest waste generated during pod deshelling, and the word 'shells' is synonymous with husk.



Figure 1. Groundnut shells (A) and Cowpea Shells (B)

From cowpea production statistics for 2017, Jekayinfa et al. [4] estimated that 5285×10^3 tons of cowpea shells and 1899×10^3 tons of groundnut shells were generated after harvesting in Nigeria. When studying the practice of residue management in some farms in Nigeria, Adeoye et al. [5] observed that residues are left in the soil to degrade or be subjected to burning, resulting in environmental pollution, loss of soil microorganisms, and health hazards.

Agricultural residues are also known as biomass, a term for all organic matter. These residues are rich in polysaccharides and lignin, which are also renewable [6]. A recent publication by Olanrewaju et al. [7] estimated that crop residues from Nigeria could generate up to 2,033 PJ of energy per year. According to this value, cowpea and groundnut shells have an estimated energy potential of 97.61 and 30.31 petajoules/year, respectively [4]. To harness these potentials, this study aims to determine the chemical composition, inorganic elemental composition, functional groups, and thermogravimetric properties of the groundnut and cowpea shells. A thorough analysis of these properties is of substantial significance in identifying the potential applications of these residual biomass as feedstocks in a variety of fields, including but not limited to biofuels, cellulose fiber manufacturing, biochar production, bio-composite materials synthesis, and carbon nanomaterial fabrication.

2. Materials and Methods

2.1 Raw Materials and Preparation

Cowpea shells (*Vigna unguiculata*) were sourced from farms located in Tunga (coordinates: $9^\circ 17' 12.048''$ N, $6^\circ 34' 59.988''$ E) in Chanchaga local government, while groundnut shells (*Arachis hypogaea L.*) were sourced from Kataeregi (coordinates: $9^\circ 21' 41.076''$ N, $6^\circ 17' 44.808''$ E) in the Katcha Local government both, in Minna, Niger State, Nigeria. The substrates were collected in March 2020 and stored in airtight bags to prevent mould growth. The substrate was washed with deionised

water and sundried for two days before grinding with a Retsch PM 100 Planetary Ball Mill (Haan, Germany). The sample was then sieved with a 425 μm laboratory test sieve, after which it was air-dried and stored in sealed containers for subsequent use.

2.2 Determination of Moisture Content, Ash, Extractive, structural carbohydrate, and lignin Composition

The extractives were removed using a Soxhlet extractor and ethanol as a solvent for 6 h; Substrate weight loss after extraction was recorded as the extractive content expressed as a percentage. The composition of glucan, xylan, acid-insoluble lignin, and acid-soluble lignin of cowpea and groundnut shells was determined using the National Renewable Energy Laboratory method (NREL) [8]. In summary, extractive-free substrates were analyzed for the composition of glucan and xylan composition by adding 3 ml of 72% sulphur to 0.3 g of the substrates and allowed to incubate for 1 h in a water bath set at 30 ° C. After which, it was diluted to a 4 % acid concentration by adding 84 ml of deionized water and autoclaved (Hirayama autoclave, HV-110: Japan) at 121 ° C, 1.3 bar for 1 h. The filtrate obtained after dilute acid hydrolysis was diluted, and the pH was adjusted with Calcium trioxocarbonate (IV). The neutralized filtrates were filled into the HPLC autosampler vial by filtering it with 0.45 μm nylon syringe filters. The glucose and xylose composition were analyzed with Agilent 1260 Infinity HPLC equipment (USA) equipped with a refractive index detector operated at 55 ° C and an Aminex HPX-87C column 300 x 7.8 mm (Bio-Rad Laboratories, Hercules, California, USA). The column temperature was set at 60 ° C and the mobile phase of 0.005 M H_2SO_4 was set at 0.6 ml/min. The acid-insoluble residue of acid hydrolysis was placed in a crucible and dried at 105 ° C for 4 h before placing it in a muffle furnace at 575 ° C for 4 h. Acid-insoluble lignin was measured gravimetrically as weight loss. The ash value was calculated from the weight of the ash in the crucibles after burning in a muffle furnace at 575 ° C. Based on the absorbance value obtained at a wavelength of 288 nm using the Agilent Technologies Cary 60 UV-vis spectrophotometer (USA), the acid-soluble lignin percentage in the filtrate was calculated. The moisture content percentage was determined using the NREL method [9] All calculations involving the conversion of glucose, xylose, absorbance readings, and insoluble residue after acid hydrolysis to glucan, xylan, soluble lignin, and insoluble lignin were executed using equations developed by the National Renewable Energy Laboratory according to each procedure.

2.3 Fourier transform infrared spectroscopy (FTIR)

The functional groups present in the chemical structure of the cowpea and groundnut shells were detected with PerkinElmer Spectrum 100 Fourier transform infrared spectroscopy (FTIR). FTIR spectra were obtained in a spectral range of 550–4000 cm^{-1} .

2.4 X-ray fluorescence (XRF) analysis

XRF analysis was performed using the Thermo Fisher ARL Perform X Sequential XRF instrument equipped with Uniquant software for elemental composition analyses for both substrates.

2.5 CHNS (Carbon, Hydrogen, Nitrogen and Sulphur) analysis and higher heating values (HHV)

The carbon, hydrogen, nitrogen, and sulphur contents of extractive-free cowpea and groundnut shells were determined using an organic elemental analyzer (Flash 2000, Thermo Fisher Scientific, USA). The percentage of oxygen was calculated as the difference between 100% and the sum of carbon, hydrogen, sulphur, and nitrogen. To estimate the higher heating value (HHV) of the substrates, Equation (1) developed by Demirbas et al. [10] was used. In their study, Equation (1) demonstrated a strong correlation between experimentally obtained HHV values and those calculated from the CHNS data.

$$HHV \left(\frac{MJ}{kg} \right) = 33.5 (\% C) + 142.3 (\% H) - 15.4 (\% O) - 14.5 (\% N) \quad (1)$$

2.6 Statistical analysis

Experiments were performed in duplicate, and standard deviations were calculated for the data obtained. To assess the significance of the experimental findings and investigate potential differences in the composition of groundnut shells and cowpea shells, a statistical test (t-test) was carried out using SPSS software. The t-test allows for the comparison of means between two groups, enabling the determination of whether there is a significant distinction between the variables. Probability values (p-value) less than or equal to 0.05 indicate that the variables vary significantly. Therefore, the null hypothesis was rejected for P-value < or = 0.05 for the compositional analysis carried out on both substrates.

2.7. Thermogravimetric analysis (TGA)

Thermogravimetric (TGA) samples were performed with the SDT Q600 V20.9 Build 20 thermal gravimetric analyzer. Approximately 17 mg to 19 mg of substrates were heated at 10 ° C / min from room temperature to 650 ° C with nitrogen gas. The temperature range was adopted to accommodate the decomposition behavior of lignocellulosic biomass at various temperatures which range from less than 200 °C to 500 °C [11].

3. Results and Discussion

3.1. Determination of Moisture content, Ash, Extractive, structural carbohydrate, and lignin Composition

Table 1 shows the lignocellulosic compositions of some biomass and the cowpea and groundnut shells studied in this paper. The variation between the glucan, xylan, acid-soluble lignin, insoluble lignin and extractives composition of both shells is statistically significant. This suggests that, despite both crops belonging to the same legume family, their respective shells feature distinct compositions that can be individually harnessed. The research by Thota et al. [12] reported 24.7 % glucan, 13.47 % xylan, 41.7 % lignin and 5.91 % extractive composition for groundnut shells from India; these results align closely with the data obtained from this study. However, research with Burkina Faso groundnut shells gave a higher cellulose content of 48 wt%, 3 wt.% hemicellulose and 28 wt% lignin [13]. The composition of the cowpea shells reported in this work closely collaborates with 24% hemicellulose, cellulose (31.82%), and 22.55% acid detergent lignin obtained by Abiola-Olagunju et al. [14] in their study using cowpea shells harvested from Ijebu-Ode in Ogun State Nigeria. These variabilities in values can be attributed to the environmental factors [15].

Both substrates have a cellulose content comparable to softwood chips, rice husk, and coffee silver skin, which has been studied as feedstock for the lignin extraction process [16], the production [17] and fermentable sugars [18]. Their hemicellulose component is also similar and close to other biomass, such as rapeseed straw, which has been studied for the production of ethanol [19]. However, cowpea and groundnut shells are rich in lignin, similar to the lignin composition of rice husk and coffee silver skin. The high lignin content of the substrates gives them an edge as feedstock for the extraction of lignin from biomass. Lignin extracted from rice husk biomass has been studied for its application in the cosmetics industry to produce sunscreen creams [20], as well as in the medical industry for its antioxidant, antimicrobial and nanoparticle base properties. Furthermore, phenolic aromatic compounds derived from pyrolytic lignin extracted from Eucalyptus wood have shown antioxidant and antimicrobial potential [21], while lignin extracted from wheat straw has shown promise as a filler in the rubber

industry[22]. Furthermore, the study by Prakash et al. [23] successfully converted the lignin obtained from sugarcane bagasse into hydrocarbon (lignin oil) through hydrothermal liquefaction (HTL) and subsequent hydrodeoxygenation (HDO).

The variations in the ash and moisture composition percentages of both shells are not statistically significant and it is noteworthy that their values depend on post-harvest handling and storage conditions [24, 25]. However, the low ash and moisture content of the substrates is an added advantage, especially during thermochemical conversion. High moisture content requires initial heating to reduce moisture content before conversion hence more cost while higher ash content leads to clinker formation on the walls of the reactors thereby reducing efficiency[26].

3.2 FTIR analysis

Figure 2 illustrates the spectral peaks observed in both groundnut and cowpea shells. The infrared (IR) range analysis of the shells reveals three distinct regions: the single-bond region ($2500 - 4000 \text{ cm}^{-1}$), the double-bond region ($1500 - 2000 \text{ cm}^{-1}$), and the fingerprint region ($600 - 1500 \text{ cm}^{-1}$). Analyzing the chemical structure of both shells using FTIR, the spectrum shows peak formations at wavenumbers of 3320 cm^{-1} , 1621 cm^{-1} , 1513 cm^{-1} , 1426 cm^{-1} , 1327 cm^{-1} , 1244 cm^{-1} , 1026 cm^{-1} and 587 cm^{-1} for groundnut shells. The cowpea shell spectrum shows peaks at 3281 cm^{-1} , 1612 cm^{-1} , 1418 cm^{-1} , 1368 cm^{-1} , 1322 cm^{-1} , 1240 cm^{-1} , 1024 cm^{-1} and 896 cm^{-1} . Peaks at 3320 and 3281 cm^{-1} confirm the existence of hydrogen bonds (CH and N-H stretch) for alkynes and functional groups of primary amine [27] on both substrates. The peaks at 1621 cm^{-1} for groundnut shells and 1612 cm^{-1} for cowpea shells are associated with the functional group of aromatic rings [28] found in hemicellulose [29]. The 1513 cm^{-1} wavenumber in the groundnut shell spectrum exists within the band range of $1515 - 1511 \text{ cm}^{-1}$, representing the C=C stretching of the aromatic ring in lignin [29, 30]. Peaks at a wavenumber of 1426 and 1418 cm^{-1} have band assignments of asymmetric deformation [30, 31], part of the functional groups found in lignin [31, 32]. C=O stretch of the syringyl bond at the 1327 and 1322 cm^{-1} wavenumbers belongs to functional groups commonly found in lignin [30]. The peak at 1368 cm^{-1} in the fingerprint region in the cowpea shell spectrum indicates the deformation of the H-C bond in cellulose and hemicellulose [33].

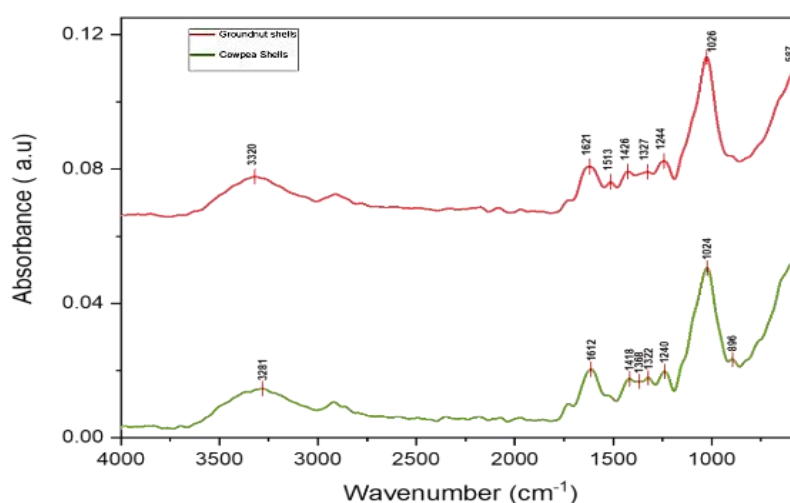


Figure 2. FTIR spectra of groundnut and cowpea shells

Peaks (1244, 1240, 1024 and 1026) cm^{-1} in the fingerprint regions of both substrates indicate that functional groups of alcohols, carboxylic acids, esters, and ethers functional groups are present [28, 30]. These functional groups are typical of hemicellulose and cellulose glycosidic links or lignin [33, 34]. The 587 cm^{-1} peak indicates the presence of a stretch bond (alkyl halides) in the biomass of groundnut shells [28]. A C-H bond indicating the presence of aromatic hydrogen was also formed in the cowpea shell spectrum at 896 cm^{-1} : this functional group is attributed to the lignin in the substrate [35]. These peaks therefore identify and confirm the presence of cellulose, hemicellulose, and lignin in the substrates.

Table 1. Composition of Groundnut shells, Cowpea shells and some selected wastes

| *Composition (%) | Glucan | Xylan | Acid-Insoluble Lignin | Acid soluble Lignin | Moisture | Extractives | Ash | References |
|------------------------------|---------------------------|---------------------------|---------------------------|--------------------------|--------------------------|--------------------------|--------------------------|------------|
| Biomass | | | | | | | | |
| Cowpea shells | 21.32 ^a ± 0.11 | 21.46 ^a ± 0.30 | 28.37 ^a ± 0.03 | 8.36 ^a ± 1.09 | 5.96 ^b ± 0.65 | 2.10 ^a ± 0.14 | 1.05 ^b ± 0.21 | This study |
| Groundnut shells | 26.45 ^a ± 0.78 | 19.50 ^a ± 0.84 | 38.33 ^a ± 0.49 | 2.5 ^a ± 0.71 | 5.7 ^b ± 0.71 | 5.05 ^a ± 0.21 | 1.75 ^b ± 0.35 | This study |
| Softwood chips powder | 27.01 ± 2.06 | 5.18 ± 0.31 | 25.5 ± 2.05 | 3.0 ± 0.55 | - | 4.7 ± 0.93 | 0.6 ± 0.20 | [16] |
| Brewer's spent grains | 16.47 ± 1.39 | 11.45 ± 0.49 | 12.9 ± 0.50 | 6.5 ± 0.20 | - | 10.5 ± 2.22 | 4.1 ± 0.06 | [16] |
| Rice Husk | 22.7 | 17.5 | 33.9 | - | 9 | - | 12.6 | [17] |
| Corn cob | 41.6 ± 0.6 | 33 ± 0.4 | 16.1 ± 0.2 | - | - | - | 2.8 ± 0.5 | [36] |
| Groundnut shell | 24.70 ± 0.48 | 13.47 ± 0.36 | 41.74 ± 0.49 | - | - | 5.91 ± 0.63 | - | [12] |
| Oil palm empty bunch (OPEFB) | 30.9 ± 1.40 | 18.2 ± 0.40 | 22.07 ± 0.69 | 5.65 ± 0.04 | 9.51 ± 1.46 | 12.9 ± 2.25 | 0.10 ± 0.01 | [37] |
| Rapeseed straw | 35.5 | 18.5 | 16.8 | - | - | 13.1 | 5.3 | [19] |
| Coffee silverskin | 22.8 ± 0.01 | 5.02 ± 0.01 | 34.02 ± 0.02 | 1.7 ± 0.22 | - | - | - | [18] |
| Barley straw | 22.7 ± 0.9 | 14.4 ± 0.3 | 19.4 ± 0.6 | 1.6 ± 0.1 | - | - | - | [38] |

These results are expressed on the oven-dried weight of the substrates. ^a indicates significant differences between the means of groundnut shells and cowpea shells, while ^b does not suggest significant differences.

3.3. XRF analysis

Most biomass contains inorganic elements as part of its composition. XRF analysis of groundnut and cowpea shells shows that Si, Al, Mg, Na, P, Fe, K, Ca and S are the main inorganic elements in the

substrates. In Table 2, corn cob, OEFB (oil palm-empty fruit bunch), banana peel, corn cob and elephant grass have higher silicon, magnesium, phosphorus, potassium, and calcium than groundnut shells and cowpea shells studied in this work. However, their elemental composition is comparable to that of pine bark. Inorganic elements in biomass are beneficial. Compounds such as potassium can be recovered from biomass ash and used as raw material for fertilizer production [39]. The extraction of silicon from rice husk ash has also been studied to produce solar-grade silicon [40]. The composition (such as potassium, chlorine, sulfur and calcium) of biomass waste can also negatively impact its successful use in the production of valuable products [41]. The presence of these elements in biomass is a source of contaminants in the production of pyrolysis oil (bio-crude oil) [42, 43]. They also have an adverse effect (fouling, slagging, agglomeration, and corrosion) on power generation plants that use biomass for direct combustion [41]. However, research studies have shown that pretreatment of biomass cassava peels, corn cobs, rice husks, sugarcane bagasse, yam peels [44]; pine bark and switchgrass [41]; rice and wheat straw [45] reduces these elements to minimal concentration. Therefore, the low concentration of elemental compounds in Nigeria groundnut shells and cowpea shells is an added advantage, since reducing its elemental composition will require minimal pretreatment.

Table 2. Elemental Composition of cowpea shells, groundnut shells and some selected biomass

| Element (%) | Silicon (Si) | Aluminium (Al) | Magnesium (Mg) | Sodium (Na) | Phosphorus (P) | Iron (Fe) | Potassium (K) | Calcium (Ca) | Sulphur (S) | References |
|------------------|--------------|----------------|----------------|-------------|----------------|-----------|---------------|--------------|-------------|------------|
| Biomass | | | | | | | | | | |
| Cowpea shells | 0.24 | 0.02 | 0.58 | 0.04 | 0.04 | 0.02 | 1.06 | 0.67 | 0.05 | This work |
| Groundnut shells | 0.13 | .04 | 0.19 | 0.04 | 0.01 | 0.02 | 0.43 | 0.35 | 0.02 | This work |
| Banana peel | 2.05 | NR | 2.82 | 0.66 | 2.85 | trace | 58.47 | 2.95 | NR | [39] |
| Corn cob | 6.54 | NR | 6.81 | 0.51 | 12.26 | 0.38 | 31.46 | 0.97 | NR | [39] |
| OPEFB | 11.11 | NR | 5.92 | 0.36 | trace | trace | 50.74 | 3.44 | NR | [39] |
| Elephant grass. | 6.08 | trace | NR | NR | NR | 4.331 | 41.86 | 5.62 | NR | [46] |
| Pine barks | NR | 0.04 | 0.089 | 0.005 | NR | 0.01 | 0.06 | 0.75 | 0.008 | [41] |

(OEFB: oil palm empty fruit bunch; NR: Not reported)

3.4 CHNS (Carbon, Hydrogen, Nitrogen and Sulphur) analysis and higher heating value (HHV)

CHNS analysis determines the carbon, hydrogen, nitrogen, and sulphur mass fraction composition of an organic sample. The higher heating value defines the fuel value of biomass and serves as a basis for comparing fuels [47]. It also represents the highest energy it can produce per unit of mass [48]. The carbon, hydrogen, nitrogen, sulphur, and oxygen content of the substrates aligns with other values reported by different authors for agro-waste. The energy value of the cowpea and groundnut shells is within the range of most agricultural residues, as seen in Table 3. This absence of sulphur is advantageous because it suggests that the utilisation of these shells as fuel sources would minimise sulphur-related environmental concerns. Furthermore, the analysis revealed a negligible nitrogen content in both substrates. This characteristic is advantageous because it indicates that the combustion of these shells would result in minimal nitrogen emissions. Nitrogen emissions during combustion are associated with environmental and health concerns, including the formation of nitrogen oxides (NO_x),

which contribute to air pollution and smog formation [49]. Therefore, the low nitrogen content of groundnut and cowpea shells enhances their appeal as a fuel source due to the potential reduction in nitrogen emissions.

Table 3. CHNS (O) analysis data and higher heating values for cowpea shells, groundnut shells and some selected agro-wastes

| | Carbon % | Hydrogen % | Nitrogen % | Sulphur % | *Oxygen % | HHV (MJ/kg) | References |
|-------------------------------------|--------------|-------------|-------------|-----------|--------------|--------------|------------|
| Cowpea shells | 43.20 ± 0.34 | 5.99 ± 0.05 | 0.07 ± 0.00 | ND | 50.74 ± 0.39 | 15.18 ± 0.24 | This study |
| Groundnut shells | 43.05 ± 0.34 | 5.48 ± 0.05 | 0.39 ± 0.00 | ND | 51.09 ± 0.39 | 14.29 ± 0.23 | This study |
| Corn cob (yellow maize) | 44.5 ± 0.9 | 5.58 ± 1.2 | 0.17 ± 0.6 | ND | 49.75 ± 1.1 | 15.18 | [50] |
| Corn cob from the Zama star (White) | 44.70 ± 1.2 | 5.69 ± 1.5 | > 0.1 | ND | 49.62 ± 1.1 | 15.24 | [50] |
| Corn husks of <i>Z. mays</i> | 41.94 ± 0.9 | 5.72 ± 0.6 | 0.5 ± 1.2 | > 0.01 | 52.29 ± 0.7 | 14.04 | [50] |
| Wheat straw | 44.1 | 6.0 | 0.4 | 0.01 | 45.0 | 16.4 | [48] |
| Groundnut shell | 52.96 | 6.24 | 0.59 | 0.22 | 40.20 | 16.19 | [51] |
| Coconut Flesh waste | 58.33 | 14.33 | 1.32 | 1.37 | 24.65 | 28.85 | [52] |

ND- not detected. *Implies measured by the difference

3.5 TGA analysis

TGA analysis was carried out to characterise the thermal stability of the groundnut and cowpea shells. Figure 3 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the groundnut shells. The decomposition of the groundnut shells occurred in three stages. The first stage occurred in a temperature range between 30 and 160 ° C with double peaks, corresponding to 9.5 % weight loss. This decomposition is attributed to moisture loss and the loss of volatile matter [53-55]. The second stage occurred from 160 ° C to 388 ° C, which coincides with a 50 % weight loss of the initial mass of the substrate. This result agrees with the 50 % weight loss at 160 to 380 ° C obtained for the TG analysis of the groundnut shells by Pawar and Panwar [55]. A less defined peak range of 200-300 ° C can be seen in the thermogravimetric curve, which is attributed to the decomposition of hemicellulose overlapping with the decomposition of cellulose [54]. A cellulose peak was formed at approximately 350 ° C, consistent with a report by Dez et al.[54]. The last stage starts at 388 ° C and forms a tail to 650 ° C. The rear is attributed to the gradual breakdown of lignin at high temperatures [56, 57]. The gradual decomposition of lignin without forming a defined peak is consistent with the TG-DTG curve obtained by Cagnon et al. [57]. Figure 4 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves. Like groundnut shells, decomposition occurs in three stages. The disintegration in the first stage occurred from room temperature to 169 ° C, with a weight loss of 12 % attributed to moisture loss [55]. This implies that groundnut shells have less moisture and volatile matter than cowpea shells. In the second stage (169- 373 ° C), a significant peak occurred at 322 ° C for cowpea shells with a weight loss of 52 %. Weight loss within this temperature range of 287 and 371 ° C is associated with cellulose decomposition [56]. Cowpea shells exhibited a slightly higher weight loss than

groundnut shells. This can be attributed to its lower lignin composition, which implies that it is less recalcitrant than groundnut shells. The deformation in the derivative thermogravimetric curve occurred within 200 -300 ° C, characteristic of hemicellulose [54]. A similar trend of tail formation was also observed in the TG-DTG curve for groundnut shells in the last stage of decomposition with a weight loss of 13 per cent. The naturally occurring cellulose fibres identified in these substrates possess considerable potential as raw materials for the bio-composite industry. In a study conducted by Norizan et al. [58], the investigation of polyester composites with sugar palm yarn showcased that augmenting the biomass content in the composites leads to an increase in thermal stability.

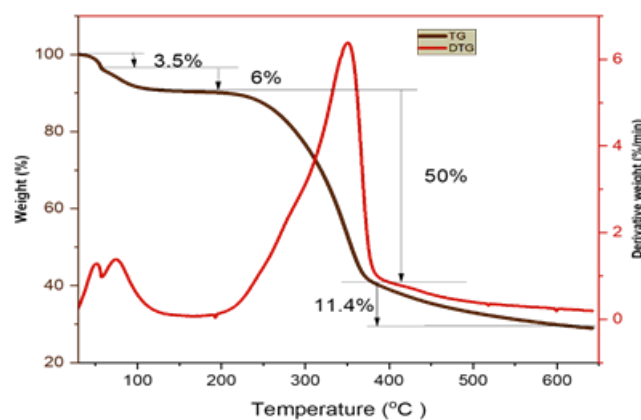


Figure 3. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for the groundnut shell

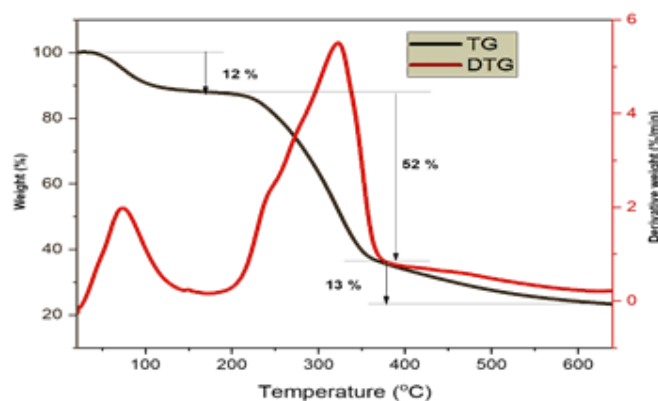


Figure 4. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for cowpea shell

Conclusion

This study provides a comprehensive analysis of the chemical composition, elemental characteristics and thermochemical properties of groundnut and cowpea shells obtained from Nigeria. The data obtained offer valuable insights that can inform the selection of suitable processing methods to effectively convert these agricultural residues into valuable products in multiple industries, thereby promoting sustainability and utilizing renewable resources. Furthermore, the study highlights the underexplored cowpea shells, despite their substantial production quantity, thus emphasizing the significance of investigating their potential applications in the production of bio-alcohols, bio-oil, and bio-composites.

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