Thermal Degradation Conditions Effects on Selected Biomass Wastes and Characterization of Their Produced Biochar

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ABSTRACT

Biochar has been proved to be effective in soil amelioration applications, carbon sequestration and also reduce GHG emissions which causes global warming. Biomass stands a greater chance of prevailing as a good source for the production of biochar, which in turn can be a solution for waste management. However, pyrolysis conditions for biochar production, together with feedstock characteristics largely control the physical and chemical properties of the yield biochar product. In this study, investigation on thermal degradation conditions effects on biochar production is carried out. Bio-char was produced using 35.3 litres fixed bed reactor from pyrolysis of Corn Cob (CC), Palm Kernel Shell (PKS) and Sugarcane Bagasse (SB) at temperatures ranging from 100°C to 500°C. The feedstock was also blended in ratio to each other and pyrolyzed to 250°C and 400°C.

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The analyzed results showed that higher pyrolysis temperatures resulted in lower biochar mass recovery, higher ash contents, decreased fixed carbon and moisture content. Product characterization also showed that the produced biochar, independent of biomass waste type contained negligible amount of Sulphur (S) and Nitrogen which resulted in lower emission of SO\(_2\) and NO\(_2\) during the combustion process, this behaviour is observed to be more pronounced with the blended biochar samples investigated in this study as a result, the obtained biochar product can be used directly for heating purposes. ANOVA test results for both volatile matter and Ash content of the produced biochar revealed that the P-value is greater than 0.01 independent of the biochar samples considered whereas for the fixed carbon of the same biochar samples, P-value less than 0.01 is attained. These results show how control of biomass pyrolysis conditions can improve biochar chemical properties consequently biochar produced from biomass wastes could be a suitable candidate for alternative energy fuels in terms of quality and environment concern.

Keywords: Biomass wastes; biochar; pyrolysis; temperature; characterization.

1. INTRODUCTION

In recent years, conversion of biomass into value-added products such as biofuel and biochar has attracted tremendous research interest. This can be attributed to the rising energy demands and concerns over greenhouse gas emissions, as well as worldwide soil degradation Laird et al. [1] and Lehmann [2]. As one of the most popular bioenergy conversion technologies, thermal pyrolysis of carbon-rich biomass is unique because it produces biochar in addition to biofuel. Omol et al. [3] in their recent research work involving conversion of municipal plastic wastes to fuel oil also reported the pyrolysis process as an effective approach to achieving their research objective. Findings from studies of Mary et al. [4] and Block et al. [5] have highlighted the benefits of biochar technologies, particularly concerning carbon sequestration via land application of biochar. According to [6] among all the available lignocellulose biomass, agricultural wastes such as corn stover, sugarcane bagasse, wheat straw and rice straw are produced in huge amounts globally [7]. Also pointed out that, the abundance and availability of agricultural by-products make them good raw materials for biochar production and excellent sources for waste management. Thus, biomass stands a greater chance of prevailing as a good source for the production of biochar, which in turn can be a solution for waste management. Biochar has potential as a valuable tool for the agricultural industry with its unique ability to help build soil health, increase physical properties of soil, soil pH, organic carbon content, conserve water and mitigate drought, reduce GHG emission, conserve nutrients, decrease fertilizer requirements, sequester carbon, increase crop productivity and serve as a most preferred habitat for microbes reported by [4]. According to [8] whose work involved a comparative study on biochar produced from different feedstock reported that bio-char to be a carbonaceous solid consisting of an aromatic, furnace, and aliphatic backbone and numerous oxygen defects. Roberts et al. [9] in their study reported that almost all biomass can be converted into biochar through thermal pyrolysis, a life cycle assessment of pyrolysis-bio-char systems suggested that it is more environmentally and financially viable to make biochar from waste biomass. Findings from studies of (Cao and Harris, [10]; Yuan et al. [11]) also affirm that agricultural residues (e.g. sugarcane bagasse, poultry litter, and manure) and other green waste have been proposed as good feedstock materials to make bio-char. It is interesting to highlight that biochar can be made of various waste biomass sources under different processing conditions, it is therefore very important to characterize their physicochemical properties before use. As reiterated by Cao and Harris [10] the applications and functions of biochars are highly depending on their physicochemical properties (e.g. elemental composition, surface charge, and surface area). Additionally, it is a generally known fact that large quantity of biomass materials is produced annually all over the world and hence a greater percentage of biochar production will be met through biomass as a source of energy. Despite numerous biochar importance aforementioned, these applications are not maximally utilized due to little information on thermal degradation effect and blending ratio (i.e. a mixture of different biomass) involved in the biochar production process. Given these, this study focused on the investigation of thermal degradation effect on the production of biochar from pyrolysis of selected different biomass. Three different biomass feedstocks (corn cob, palm kernel shell and sugarcane bagasse) were considered. Each feedstock was pyrolyzed for temperatures ranging from 100°C to 500°C at
interval of 100°C. Besides, Blended feedstock at mass ratio 2:1:1, 1:2:1 and 1:1:2 for temperatures 250°C to 450°C were also pyrolyzed. The biochar obtained from all the thermal degradation products were then characterized to determine their respective chemical properties.

2. MATERIALS AND METHODS

2.1 Material Sourcing and Preparation of Feedstock

The biomass feedstock used in this study are; sugarcane bagasse (SB), corncob (CC), Palm Kernel Shell (PKS). The SB was obtained from a sugarcane plantation in Idanre, Ondo State, Nigeria. It was received at a moisture content of about 50% wt and crushed in a mortar to extract the juice. It was then sundried at the surrounding temperature until the moisture content was reduced to about 4% wt. It was milled into a smaller particle size (Fig. 1a) to increase the rate of pyrolysis reaction. The PKS was obtained from a palm tree plantation situated at Okitipupa in Ondo State, Nigeria. It was sundried to reduce the moisture content. After sun-drying, it was then milled in a local grinding machine to smaller particle size presented in (Fig. 1b). For the CC, it was locally sourced from Akure, Ondo State, Nigeria. The CC was sundried at surrounding temperature and milled using local grinding machine. It was then sieved to a smaller particle as shown in Fig. (1c). The blending of feedstock was achieved by mixing the selected three feedstocks (Fig. 1d) in the ratio 1:2:1, 1:1:2 and 2:1:1 respectively. The first sample was mixed in mass-ratio 1:2:1 (0.75 kg of SB, 1.5 kg of PKS and 0.75 kg of CC), the second sample was mixed in mass-ratio 1:1:2 (0.75 kg of SB, 0.75 kg of PKS and 1.5 kg of CC) while the third sample was mixed in mass-ratio 2:1:1 (1.5 kg of SB, 0.75 kg of PKS and 0.75 kg of CC). The pictures of the processed feedstock used in this study are shown in Fig. 1.

2.2 Experimental Setup and Method

The reactor used for the pyrolysis is a fixed bed reactor developed by [9] and is located at Mechanical Engineering Department Workshop of the Federal University of Technology, Akure. The reactor has a capacity of 35.1 liters and was designed to pyrolyse 3 kg of biomass per batch. Fig. 2 shows a schematic representation of the experimental set up, comprising of the thermal reactor (fixed bed type), an exhaust hood attached to the reactor, a cyclone (for efficient separation of dust particle from gas), supply ducts, air-cooled heat exchanger, a fan, and temperature measuring devices. Presented in Fig. 3 is the experimental setup used in this study.

Fig. 1. Samples of all the processed feedstock

Fig. 2. Schematic diagram of the pyrolysis unit
2.2.1 Experimental procedure

The experimental tests were conducted by initially measured 3.0 kg of each feedstock sample using chemical balance. Each of the samples was fed manually into the reactor chamber for thermal degradation at varying temperature of 100°C to 500°C at an interval of 100°C. High-temperature adjustable gaskets were used to seal the joints and fittings of the hot parts of the connecting pipe, reactor and cyclone. The reactor lid was screwed with bolts to ensure that there is no ingress of air and leakages of the vapour. K-type thermocouple was inserted using the probe to monitor the inner temperature of the reactor being controlled by the temperature controller installed on the reactor chamber. At an initial run, the temperature controller was preset at 100°C and the reactor’s heater was plugged into an electric power source, heating the feedstock internally. At 100°C, the controller triggered off the electric power source automatically. The reactor was allowed to cool down to aid the easy collection of the left-over char (biochar) from the reactor chamber. This procedure was observed for other pyrolysis temperature conditions while the obtained biochar products were labelled with respect to each sample pyrolyzed temperature condition as presented in Figs. 4-9. At the end of each run, all the parts of the system were cleaned before reassembling for the next run. Considering the blended samples, 3.0 kg of mixed sample was also obtained and given sample label as A, B and C. Each of the samples contains a mass of CC, PKS and SB respectively which are sums up to give the 3.0 kg. Sample A contains a mass ratio of 1:2:1 for CC:PKS:SB respectively, sample B contains a mass ratio of 1:1:2 for CC:PKS:SB respectively, while sample C contains a mass ratio of 2:1:1 for CC:PKS:SB respectively. Each sample was pyrolyzed in the reactor at a temperature of 250°C and 400°C respectively. The yields of the bio-char obtained at each temperature were compared and the effect of temperature on the yield of biochar was equally evaluated.

2.3 Bio-char Characterization

The bio-chars obtained at the end of the experimental tests were characterized using proximate and ultimate analysis for fuel properties. Figs. 4-9 show the pictures of biochar produced after different pyrolysis temperatures in this study.

2.3.1 Proximate analysis of the Bio-char

From the proximate analysis, the following were obtained; moisture content (MC), volatile matter (VM) consisting of gases and vapours given off during pyrolysis, fixed carbon (FC), ash content (AC) which is the inorganic residue remaining after combustion of the sample, and heating value (HV) based on complete combustion of the sample to carbon dioxide and liquid water.
Fig. 4. Sugar cane bagasse bio-char

Fig. 5. Corn cob bio-char

Fig. 6. Palm kernel shell bio-char

Fig. 7. Blended feedstock (1:1:2)

Fig. 8. Blended feedstock (2:1:1)
2.3.1.1 Moisture content determination

To determine the moisture content, the following equipment was employed; Petri dish, spatula, bean balance, muffle furnace, desiccator and stopwatch. The mass of the Petri dish was determined using a digital beam balance and recorded as \( w_1 \). 1.00 g of the sample was added to the Petri dish and reweighed, with the new mass and recorded as \( w_2 \). The Petri dish containing the sample was heated in a muffle furnace at a temperature of about 105°C for three hours before being removed and allowed to cool to room temperature and weighed again to a third mass and recorded as \( w_3 \). The percentage moisture content (MC) was calculated using the adopted relation from Gupta, [12] given as follow:

\[
MC = \frac{w_2 - w_3}{w_2 - w_1} \times 100\% 
\]  

(1)

where \( w_1 \) is the mass of the Petri dish in (g), \( w_2 \) is the mass of the Petri dish with the sample (g), \( w_3 \) is the mass of the Petri dish with the sample after being heated and allowed to cool to room temperature (g).

2.3.1.2 Volatile Matter Determination

The instrument used to carry out the analysis of volatile matter includes crucible, spatula, beam balance, muffle furnace, desiccator and stopwatch. The sample was identified and given a sample label. The mass of the crucible was determined with the aid of digital beam balance and recorded as \( w_4 \). 1.00 g of the sample whose volatile matter was to be determined was added to the crucible and weighed, the mass was recorded as \( w_5 \). The crucible containing the sample was then heated in a muffle furnace at 750°C for three hours before being removed and allowed to cool down to room temperature, and further weighed to obtain a new mass recorded as \( w_6 \). The percentage volatile matter (VM) was calculated using Eq. (2) as follow:

\[
VM = \frac{w_6 - w_4}{w_5 - w_4} \times 100\% 
\]  

(2)

Where,

\( w_4 \) is the mass of the crucible (g), \( w_5 \) is the mass of the crucible with the sample (g), \( w_6 \) is the mass of the crucible with the sample after being heated and allowed to cool to room temperature in (g).

2.3.1.3 Ash Content Determination

In the determination of the ash content, the similar equipment and procedure adopted for the volatile matter was used. In this case, the crucible containing the sample was heated at temperature of 1000°C. The determined masses of crucible, ash content and crucible, and the heated sample, then the cooled ash content in the crucible was determined and recorded as \( w_7 \), \( w_8 \) and \( w_9 \) respectively. The percentage ash content (AC) was calculated using Eq. (3) given as:

\[
AC = \frac{w_9 - w_4}{w_7 - w_4} \times 100\% 
\]  

(3)
Where,

\( w_1 \) is the mass of the crucible with the sample (g), \( w_2 \) is the mass of the crucible with the sample after being heated and allowed to cool to room temperature in (g).

**2.3.1.4 Fixed Carbon Content**

The fixed carbon (FC) of the considered sampled was estimated by determining the difference between 100 %wt. and the sum of the obtained moisture content, volatile matter content and ash content as follow:

\[
FC = 100 - (MC + VM + AC)
\]  

**2.3.2 Ultimate analysis of the bio-char**

The purpose of this test was to determine the elemental composition content of the bio-char produced in this study. This was determined using an Elemental Analyzer (Thermo FlashEA 1112), according to the ASTM-D 5291 method. 5 ml of the bio-char sample was put in a tin capsule and placed in a vertical quartz tube. It was then combusted at 900°C in a furnace heated using helium stream with pure oxygen. The resulting mixture of combustion gases was passed over a catalyst layer (copper) to remove any excess oxygen and to reduce the nitrogen oxides to elemental nitrogen. It was then sent to the chromatographic column where the individual components were separated and identified with an automatic Elemental analyzer - EAGER300. Oxygen content was estimated by the difference between 100% and the sum of the other contents.

**3. RESULTS AND DISCUSSION**

**3.1 Characterization of Raw Biomass Wastes**

The raw biomass samples were characterized using proximate and elemental analyses, as presented in Tables 1 and 2 respectively. The proximate analysis of the raw biomass samples presented in Table 1 shows that moisture percentage ranges between 7 and 10%, ash content ranges from 2.54 to 3.09% and the volatile matter (VM) and fixed carbon (FC) ranged between 62.7 to 73.5% and 5.12 to 6.52% respectively. Raw SB biomass sample recorded higher moisture content (10.13%) followed by PKS (9.65%) and CC (7.59%). The volatile matter was high in PKS (73.50%) followed by SB (67.12%). According to Table 2, the elemental analysis of the raw biomass samples showed that the three samples CC, PKS and SB have high carbon contents of 97.46%, 98.07% and 96.91% respectively. The obtained proximate and elemental analysis result in this study is very close to those observed in the studies of [13,14].

**3.2 Characterization of Bio-char Samples**

Proximate and elemental analyses results obtained for the bio-char produced from individual biomass samples; CC, PKS and SB are presented in Tables 3, 4 and 5 respectively.

**Table 1. Proximate analysis of samples**

| Parameter          | Biomass wastes (wt %) on dry basis |
|--------------------|-----------------------------------|
|                    | Corn Cob (CC) | Palm Kernel Shell (PKS) | Sugarcane Bagasse (SB) |
| Ash content        | 2.54          | 1.93                  | 3.09                  |
| Moisture content   | 7.59          | 9.65                  | 10.13                 |
| Fixed carbon (FC)  | 6.53          | 5.12                  | 6.51                  |
| Volatile matter (VM)| 62.70        | 73.50                 | 67.12                 |

**Table 2. Elemental analysis of samples**

| Parameter      | Biomass wastes (wt %) on dry basis |
|----------------|-----------------------------------|
|                | Corn Cob (CC) | Palm Kernel Shell (PKS) | Sugarcane Bagasse (SB) |
| Carbon (C)     | 97.46         | 98.07                  | 96.91                  |
| Nitrogen (N)   | 0.29          | 0.43                   | 0.18                   |
| Hydrogen (H)   | 2.22          | 1.45                   | 2.90                   |
| Sulphur (S)    | 0.04          | 0.05                   | 0.01                   |
| Energy Content MJ/kg | 16.46       | 17.86                  | 14.61                  |
Table 3. Proximate and elemental analysis of Corn Cob (CC)

| Temp°C | Proximate analysis | Elemental analysis |
|--------|-------------------|--------------------|
|        | MC    | AC   | VM   | FC   | HV   | C    | H    | N    | S    | H/C  |
| 100°   | 3.89  | 7.74 | 60.38| 29.35| 20.79| 80.31| 7.58 | 0.13 | 0.04 | 0.09 |
| 200°   | 3.44  | 9.10 | 61.36| 26.10| 23.33| 82.23| 8.97 | 0.06 | 0.03 | 0.11 |
| 300°   | 3.34  | 9.51 | 66.26| 20.23| 25.12| 90.93| 17.68| 0.06 | 0.03 | 0.19 |
| 400°   | 3.24  | 9.70 | 68.11| 18.52| 25.32| 92.26| 19.62| 0.06 | 0.01 | 0.21 |
| 500°   | 3.11  | 9.83 | 70.87| 17.63| 25.92| 97.45| 21.60| 0.05 | 0.01 | 0.22 |

Table 4. Proximate and elemental analysis of Palm Kernel Shell (PKS)

| Temp°C | Proximate analysis | Elemental analysis |
|--------|-------------------|--------------------|
|        | MC    | AC   | VM   | FC   | HV   | C    | H    | N    | S    | H/C  |
| 100°   | 3.78  | 2.07 | 57.63| 36.52| 18.46| 88.23| 1.70 | 0.14 | 0.23 | 0.02 |
| 200°   | 3.60  | 5.50 | 60.81| 30.09| 18.89| 90.15| 2.27 | 0.07 | 0.16 | 0.02 |
| 300°   | 3.50  | 10.56| 61.64| 24.29| 20.47| 94.50| 9.69 | 0.05 | 0.11 | 0.10 |
| 400°   | 3.49  | 11.76| 62.42| 22.32| 24.05| 97.93| 11.65| 0.03 | 0.08 | 0.12 |
| 500°   | 3.38  | 12.90| 63.31| 20.40| 24.26| 98.07| 13.48| 0.03 | 0.01 | 0.13 |

Table 5. Proximate and elemental analysis of sugarcane bagasse (SB)

| Temp°C | Proximate analysis | Elemental analysis |
|--------|-------------------|--------------------|
|        | MC    | AC   | VM   | FC   | HV   | C    | H    | N    | S    | H/C  |
| 100°   | 3.62  | 7.11 | 58.07| 31.20| 18.90| 72.61| 13.42| 0.14 | 0.04 | 0.18 |
| 200°   | 3.32  | 8.84 | 59.28| 28.56| 19.38| 73.86| 21.73| 0.08 | 0.03 | 0.29 |
| 300°   | 3.36  | 9.24 | 63.06| 24.25| 21.60| 78.16| 26.08| 0.05 | 0.03 | 0.33 |
| 400°   | 3.31  | 11.35| 64.12| 21.22| 21.94| 86.39| 27.34| 0.06 | 0.01 | 0.31 |
| 500°   | 3.12  | 13.01| 65.54| 18.33| 23.03| 96.91| 29.55| 0.03 | 0.01 | 0.30 |

It can be seen from Tables 3 to 5 that the increase in pyrolysis temperature resulted in the pyrolyzed sample moisture content decrease. The results from the Tables also revealed that independent of the biomass type considered in this study, sample, CC recorded higher moisture (3.89% wt), followed by Palm Kernel Shell (PKS) and Sugarcane Bagasse (SB) 3.78% wt and 3.62 %wt respectively. The volatile content of bio-char also increased from 60.38% wt to 70.87% wt for (CC), 57.63% wt to 63.31% wt for (PKC) and 58.07% wt to 65.54% wt for (SB). For the three samples shown in the Tables, fixed carbon decreases with increase in pyrolysis temperature while the samples ash content increases with increase in pyrolysis temperatures with the SB sample recorded the highest ash content of (13%) compared to sample CC observed with ash content of (9.8%). This result indicates that biochar produced from CC is of medium ash content agreeing with Xiu et al. [15] who classified biomass based on ash content as: low (< 5% wt), medium (5-10%wt) and high (>10%). Additionally, the bio-char elemental analysis shows that the carbon contents increase with an increase in pyrolysis temperature with PKS recorded the highest (98.07% wt) value followed by CC with (97.46% wt).The increase in carbon content of the obtained biochar with an increase in the pyrolysis temperature is also observed for the blended sample results shown in Table 6. These results are in consistent with those reported by Alburquerque et al. [16].

Whereas, of the entire sample considered in this work, it is noticed that nitrogen and sulphur contents decreased with increasing pyrolysis temperature. This shows that on combustion the produced bio-char would generate low SO\(_2\) and NO\(_2\) emissions which make the obtained bio-char suitable for long term stability in the environment as pointed out in the study of [4].
Table 6. Proximate and elemental analysis of blended samples

| Sample | Temp T °C | Proximate analysis | Elemental analysis |
|--------|-----------|--------------------|-------------------|
|        | MC | AC | FC | VM | HV | C | H | N | S | H/C |
| A      | 250 | 4.79 | 9.77 | 76.41 | 31.32 | 23.52 | 89.72 | 5.51 | 0.07 | 0.01 | 0.06 |
|        | 400 | 4.59 | 13.27 | 73.66 | 27.32 | 24.26 | 94.23 | 10.22 | 0.04 | 0.01 | 0.11 |
| B      | 250 | 4.31 | 28.35 | 57.50 | 31.42 | 23.83 | 78.61 | 17.30 | 0.07 | 0.02 | 0.22 |
|        | 400 | 4.15 | 32.53 | 51.12 | 24.33 | 24.26 | 82.62 | 23.33 | 0.05 | 0.07 | 0.28 |
| C      | 250 | 4.57 | 11.50 | 76.38 | 28.52 | 24.87 | 85.31 | 9.63 | 0.07 | 0.01 | 0.11 |
|        | 400 | 3.53 | 10.70 | 78.35 | 23.52 | 22.85 | 90.31 | 14.62 | 0.06 | 0.01 | 0.16 |

3.3 Characterization of the Blended Samples

The results from proximate and elemental analysis of the blended samples A, B and C pyrolyzed at a temperature of 250°C and 400°C are presented in Table 6. Sample A contains a mass ratio of 1:2:1 for CC:PKS:SB respectively, sample B contains a mass ratio of 1:1:2 for CC:PKS:SB respectively, while sample C contains a mass ratio of 2:1:1 for CC:PKS:SB respectively.

From Table 6, sample A has the highest moisture content (4.791%) at 250°C and as expected, the moisture content decreases with increase in pyrolysis temperature. It shows that the blended content (mixed biomass wastes) have higher moisture content than the unblended biomass waste. It is interesting to highlight that high moisture content affects the conversion efficiency and the heating value of the biomass and has the potential to deteriorate its energy during storage as a result of decomposition. However, it can be noticed from the table that compared to Sample B, in this work Sample C recorded highest Fixed Carbon (78.345% wt) followed by sample A (76.413% wt) at pyrolyzed temperature of 400°C. It is also noticed that the blended samples C in this study revealed higher FC (78.345%) at 400°C compared to the unblended sample of FC (70.867%) at 500°C. Moreover, the result from the elemental analysis shows that the blended sample has a lower nitrogen and sulphur contents compared to the unblended sample aforementioned. Thus, it can be inferred that the blended samples C can be used as a good source of energy without environmental impact (non-toxic to the environment).

3.4 Effects of Temperature on Bio-char Yield

Investigation on the influence of pyrolysis temperature on the product yield of pyrolysis is also carried out in this study and the obtained result is as shown in Figs. 10 and 11. The percentage char yield is estimated using Eq. (5);

\[ Y_C = \frac{M_C}{M_R} \times 100 \]  

Where,

- \( Y_C \) is Yield char (%);
- \( M_C \) is Mass of char (kg);
- \( M_R \) is Mass of Raw biomass (kg).

Figs. 10 and 11 revealed that as the pyrolysis temperature increases, bio-char yield decreases. At lower temperature 100°C, PKS has a higher yield (87 wt. %) followed by CC (52 wt. %) and SB (34 wt. %) respectively. These results are similar to the typical behavior observed in the study of Novak et al. [18] who reported that more biochar was recovered at the lower pyrolysis temperatures due to minimal condensation of aliphatic compounds, and lower losses of CH, H₂ and CO.

The decrease in char yield at higher temperature is consistent with an increase in volatile matter. The increase in the yield of volatile components could be caused by the difference in thermal stability of the polymer chain. Both the linear and branched hydrocarbons have decreasing thermal stability with an increase in temperature, therefore at 500°C the C=C bonds cracked more likely than at lower temperature and this resulted in higher yields of volatile products. The blended feedstock also has the same trend of reduced biochar as temperature increases, this can be attributed to the same cracking and decomposition as exhibited on an individual basis. The observed reduction in bio-char yield with increment in pyrolysis temperature in this study agree with [19] who reported that the decrement of the biochar yield with increasing temperature could either be due to higher primary decomposition of the feedstock or secondary decomposition of the biochar residue. This behaviour is also due to dehydration of hydroxyl groups and thermal degradation of ligno-cellulose structures of the biochar residue as reported by [20,21].
Fig. 10. Effect of temperature on bio-char yield (Unblended Bio-char)

Fig. 11. Effect of temperature on bio-char yield (Blended Bio-char)

Fig. 12. The energy content of bio-char from blended samples
3.5 Determination of Bio-char Energy Content

Generally, the high heating values (HV) of chars make them attractive sources for clean energy production instead of fossil-based solid fuels. In this study, the energy content of the produced bio-char is determined with the use of oxygen bomb calorimeter. The results from Fig. 12 revealed that the heating values of biochar increased in this study slightly with an increase in pyrolysis temperature (100-500°C) from (20.79 kJ/g to 25.92 kJ/g, 18.46 kJ/g to 24.26 kJ/g, 18.90 kJ/g to 23.03 kJ/g) for CC, PKS and SB respectively. Similar behaviour is observed for the blended samples considered in this work. This is due to the increase in carbon content in bio-char with increased temperature as observed in the previous study of [16]. Although a general trend of increase in heating value with increase in temperature was observed, blending ratio of feedstock could affect this behaviour as it can be seen from Fig. 13 that the higher heating value of sample C decreased with increase in temperature. In addition, sample C contains a higher percentage of CC compared to Samples A and B.

3.6 Statistical Analyses

With the view to establish degradation effect of pyrolysis temperature conditions on the fuel properties of the selected biomass waste investigated in this work, analysis of Variance (ANOVA) test was carried out considering the obtained data of the samples (CC, PKS and SB) for their volatile matter, fixed carbon and ash content. Since the same experimental set up was used to carry out the observed experimental tests results for both elemental and proximate analysis presented in (Tables 3-5), equality of their obtained analyzed results was checked for and a significance level of 0.01 was chosen for the test. The Null Hypothesis $H_0$ and the Alternative Hypothesis, $H_a$ considered for the pyrolyzed samples (CC, PKS and SB) as obtained from the MATLAB statistical platform used is defined as follows:

Null Hypothesis,

$H_0: \mu_{CC} = \mu_{PKS} = \mu_{SB}$

Alternative Hypothesis,

$H_a$: Atleastoneisdifferent

To consider the null hypothesis, the mean of the three feed stocks obtained analyzed results is considered to be equal, while the alternative hypothesis states that at least one is different.

The ANOVA test analysis was carried out by considering the following assumptions:

- If P-value is not less than 0.01 significance level chosen then the null hypothesis is considered accepted (or will not be rejected).
- Also, if F value is less than F-critical value, i.e. considering F distribution graph, then the null hypothesis is considered accepted (or will not be rejected).
- Acceptance of the null hypothesis signifies that the analyze sample data is not influenced by pyrolysis temperature condition visa viz for rejection of the null hypothesis.
Table 7. ANOVA test analysis result for the sample ash content

| Source of variation | SS     | df | MS    | F      | P-value | F-crit  |
|---------------------|--------|----|-------|--------|---------|---------|
| Between Groups      | 75.9447| 4  | 18.98612 | 5.090546 | 0.016871 | 5.994339 |
| Within Groups       | 37.29682 | 10 | 3.729682 |         |         |         |
| Total               | 113.2413 | 14 |        |        |         |         |

Table 8. ANOVA test analysis result for the sample volatile matter

| Source of variation | SS     | df | MS    | F      | P-value | F-crit  |
|---------------------|--------|----|-------|--------|---------|---------|
| Between groups      | 124.5749 | 4  | 31.14372 | 4.782957 | 0.020416 | 5.994339 |
| Within groups       | 65.11395 | 10 | 6.511395 |         |         |         |
| Total               | 189.6888 | 14 |        |        |         |         |

Table 9. ANOVA test analysis result for the sample fixed carbon

| Source of variation | SS     | df | MS    | F      | P-value | F-crit  |
|---------------------|--------|----|-------|--------|---------|---------|
| Between groups      | 376.1358 | 4  | 94.03394 | 16.0806 | 0.000235 | 5.994339 |
| Within groups       | 58.47664 | 10 | 5.847664 |         |         |         |
| Total               | 434.6124 | 14 |        |        |         |         |

Presented in Tables 7-9 are the obtained ANOVA test analysis results with reference to thermal degradation effect of the pyrolyzed samples.

According to Table 7, the ANOVA test results revealed that the P-value is greater than 0.01 (i.e. $P > 0.01$) independent of the biochar samples chemical property: (Ash content) for all biomass wastes pyrolyzed in this work. A similar response was observed in Table 8 for the same ANOVA test targeting the effect of temperature on the volatile matter. Considering these results responses, the null hypothesis of the analyzed biochar sample investigated is accepted more so, the calculated means of the biochar samples obtained data are also observed to be equal. This behaviour implies that temperature condition does not significantly affect the volatile matter and ash content of the produced biochar when either of the feedstock is subjected to pyrolysis condition. However, for the fixed carbon ANOVA test results presented in Table 9, it can be noticed that the P-value is less than 0.01 ($P < 0.01$), signifying that the pyrolysis temperature has a significant effect on the fixed carbon content of the produced biochar in this work.

4. CONCLUSION

Sugarcane bagasse (SB), Palm kernel shell (PKS) and Corn cob (CC) was pyrolyzed at varying temperatures of 100°C to 500°C, and selective pyrolyzed temperatures of 250°C and 400°C for both unblended and blended bio-char production. Product characterization of the produced bio-char showed that they contained high moisture content. The energy content of the obtained bio-char products in this study is characterized as (20.79 kJ/g to 25.92 kJ/g, 18.46 kJ/g to 24.26 kJ/g, 18.90 kJ/g to 23.03 kJ/g) for CC, PKS and SB respectively. It is also observed that independent of the biomass wastes considered in this work, the Bio-char yield decreases with increasing pyrolysis temperature with PKS presented best bio-char yield. It is also noticed that the blended samples C in this study revealed higher FC (78.35%) at 400°C compared to the unblended samples of FC (70.87%) at 500°C. Similarly, a significant effect of pyrolysis temperature conditions is observed only for the fixed carbon content of the produced Biochar with attained P-value lesser than 0.01 in the statistical analysis conducted by using ANOVA test method in this study. This behaviour justifies the general trend of increase in the heating value of the produced biochar with an increase in temperature consequently aids an increase in carbon content of the attained bio-charas reported in the open literatures. Additionally, elemental analysis of the obtained bio-char showed that the product contain negligible amount of Sulphur and Nitrogen which resulted in lower emission of SO$_2$ and NO$_2$, this behaviour is observed to be more pronounced with the blended bio-char sample considered in this work as a result, the obtained bio-char product can be used directly for heating purposes. Overall analysis indicates that bio-char
produce from biomass wastes would be a suitable candidate for alternative energy fuels in terms of quality and environment concern.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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