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# Production of Hybrid Biochar by Retort-Heating of Elephant Grass (*Pennisetum Purpureum*) and Low Density Polyethylene (LDPE) for Waste Management and Product Development

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- ✓ Biochar,
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- ✓ Energy,
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#### Abstract

In a bid to achieve energy and environmental sustainability research efforts are now being channeled to product development from waste materials especially in developing countries. The aim of this study was to convert elephant grass (Pennisetum Purpureum) and low density polyethylene (LDPE) to produce hybrid biochar in a top-lit updraft biomass conversion reactor with retort heating. The conversion was a hybrid one involving the simultaneous carbonisation of both feedstocks in a self-regulating low-cost process having no electrical power requirement. The yield of hybrid biochar and biomass biochar was 27.3 wt% (at 382°C peak temperature) and 13.8 wt% (at 371°C peak temperature) respectively. The products were characterised using Scanning Electron Microscope with energy Dispersive X-ray Spectroscopy (SEM-EDS), Fourier Transform Infra-Red Spectroscopy (FTIR) and Brunauer-Emmet-Teller (BET) analysis. The FTIR confirmed that the functional groups in the biomass were preserved. The specific surface area of the biomass biochar and hybrid biochar was 356.3 m<sup>2</sup>/g and 427.2 m<sup>2</sup>/g respectively. It was observed that the quantity and quality of was higher for the hybrid conversion process than for the biomass conversion alone. The study has been able to successfully achieve the twin goal of solid waste management and product development.

#### 1. Introduction

Solid waste management a major challenge of the 21<sup>st</sup> century due to increasing population, urbanisation and lifestyle changes due to technological development [1]. This problem is even more pronounced in developing countries such as Nigeria where solid waste management is a major concern [2]. With increasing global change pressures coupled with existing un-sustainability factors, cities in developing countries are most likely to experience difficulties in efficiently managing municipal solid wastes. Unplanned urbanisation growth will result in increasing quantities and complexity of the generated wastes [3]. Municipal solid waste management constitutes one of the most crucial health and environmental problem facing African cities [4]. Most cities spend 20-50% of their annual budget on solid waste management [5] and only 20-80% of the waste is collected [6]. The waste density ranged from 280 to 370 kg/m<sup>3</sup> and the waste generation rates ranged from 0.44 to 0.66 kg/capita/day [7]. Pyrolysis is a way to utilise the carbon in plants before it can become a meal for eaters and return it to the soil as pure carbon biochar [8]. Pyrolysis mimics the natural process that turned ancient plants into coal: When biomass is heated up with no oxygen supply it melts into carbon, syngas and bio-oil [9].

Almost the same solutions are proffered to management of LDPE which include biodegradation in a solid waste medium [10], pyrolysis, gasification and carbonisation.

The packaged water industry is characterised by both small and medium to large scale industries that pack and machine-seal sachet water and also offer bottled water to consumers [11]. Packaged water has become the preferred mode of drinking water both at home and in public. Bottled and sachet water is available in different sizes to satisfy different consumer needs. This water is referred to as "pure water" by many of the locals in Nigeria. The sachet water industry is a vibrant and highly profitable sector since there is always ready market demand for its products, especially in the dry season. The small scale sachet water companies usually produce between 15,000 sachets (500 bags) and 45,000 (1500 bags) sachets per day and have much smaller distribution coverage, more often distributing their products in and around the towns/communities where their factories are located [11, 12]. Usually each bag contains 20 sachets of 500 mL of water. The medium scale water companies have the technology, resources and adequate logistics support to produce both bottled and sachet water for more than one town and even may be able to cover a city. The large scale water companies produce both bottled and sachet water for sale nationwide, and most operate water packaging factories and depots in several towns and cities [13]. They usually produce and supply over 5000 bags of sachet water per day. There has been a proliferation of sachet water producing companies all across the country due to the relatively low start-up capital required. This has led to a very high plastic waste generation in Nigeria.

Regardless of the accruing benefits like access to portable drinking water and employment generation through sachet water trade, due to sachet water production and consumption, the indiscriminate disposal of the waste in various undesired sites such as along the streets, gutters, motor parks, schools, markets, homes, and venues of social functions etc. poses many environmental threats. The sachets are made of non-biodegradable synthetic polyethylene (polythene) which does not decompose in the soil even after many years [14]. The polythene even when subjected to burning produces major known and harmful greenhouse gases (GHGs) like carbon monoxide, nitrous oxide and carbon dioxide. The management plan proposed in Ghana was producer responsibility and management of product at end of life [15]. In Japan, it has been used as a metallurgical raw material to save up to 1.5% energy requirement in Japan's Iron and Steel industry, there it was discovered that adding 1% waste plastics in raw coal did not deteriorate the coke strength and waste plastics recycling process using coke ovens started at Nippon Steel Nagaya and Kimitsu in 2000 [16].

In this study, elephant grass (*Pennisetum Purpureum*) was co-carbonised with low density polyethylene (LDPE) to produce hybrid biochar in a top-lit updraft biomass conversion reactor using the method described by Adeniyi, et al. [17]. In the method, an updraft gasifier with retort heating was used. The goal of the process is two-pronged. Firstly, the management of plastic wastes and is of paramount interest. Secondly is the energy conservation from the plastic and the readily available biomass to produce valuable products.

#### 2. Methodology

#### 2.1 Sourcing and preparation of biomass and plastics

Dried sample of elephant grass (*Pennisetum purpureum*) was gotten from open fields of the university of Ilorin community, Nigeria. Low Density Polyethylene was obtained from used sachet water disposed in a municipal solid waste dumpsite in Ilorin, Nigeria. The sachets were cleaned with distilled water and air dried at room temperature. Dry bamboo (*Bambusa vulgaris*) stalk and stem of African balsam (*Daniellia olivieri*) were used as combustion fuel in the reactor. These were also locally sourced.

#### 2.2 Experiments

Details of experiments are exactly as those described in previous reports [17, 18]. The biomass conversion was conducted in the 48.5 cm high reactor with full dimensions and schematics provided elsewhere [17]. The hybrid co-conversion of biomass and plastic was conducted in the 53 cm high reactor with full dimensions and schematics provided elsewhere [18]. A CASON CA380 Infra-red thermometer (Accuracy;  $\pm 0.1^{\circ}$ C, Max; 380°C) was used for monitoring the temperature of the process. Weighed amounts of the biomass were loaded into the reactor. For the co-conversion batch, the feed was in the ratio 35:1 biomass to LDPE as reported in the recent related works [5, 19]. The disparity is not greatly pronounced in terms of volume due to the very low effective density of the plastic.

The reactors consist of a centrally oriented conversion chamber within its' set-up and possessing several small air holes at the base. The chamber houses the feed to be converted while the combustion fuel for heat generation occupies the 'heating gap' between the chamber and the reactor itself. A vertically oriented exhaust pipe ensures the elutriation of combustion gases. Round and triangular holes at the bottom of the reactor allow the updraft of oxygen/air to the combustion front at the top of the heating gap. Both experiments were performed simultaneously and at similar process time of 80 minutes. Since the process is self-regulating, the experiment is terminated only after ambient temperature is achieved again. The system can also be described as a retort-heating system which carefully recycles thermal energy from the controlled combustion of biomass for the carbonisation of waste materials to useful product. The fuel was reduced to ashes and the products (biomass biochar and hybrid biochar) were removed and stored in air-tight containers.

#### 2.3 Product characterisation

The products (biomass biochar and hybrid biochar) recovered from the process were characterised to ascertain some of their properties using Scanning Electron Microscope with energy Dispersive X-ray Spectroscopy (SEM-EDS), Fourier Transform Infra-Red Spectroscopy (FTIR) and Brunauer-Emmet-Teller (BET) analysis. Scanning Electron Microscopy (SEM, Phenom proX, Phenom-World BV, Netherlands) was used to study the surface morphology of the particles of the biochar. A double adhesive was placed on a sample stub. The sample was sprinkled on the sample stub and subsequently taken to a sputter coater (quorum-Q150R Plus E) and coated with 5 nm of gold. The sample was placed on a charge reduction sample holder and introduced into the column of the SEM machine. It was firstly viewed with a NavCam before being sent to SEM mode. The acceleration voltage of the microscope was set to 15 kV and magnification at 1000 – 1500×. FTIR (Shimadzu, FTIR-8400S, Japan) was used to determine the functional groups and complexes present in both biochar samples. The spectra were recorded using transmittance method in the 4000 - 650 cm<sup>-1</sup> region with 30 sample scans. BET analysis (Quantachrome NovaWin ©1994-2013, Quantachrome Instruments v11.03) was used to study the particle and pore dimensional characteristics of the products. The surface area, pore volume and size of the chars were measured. The surface properties of the char samples were studied using a Multipoint BET surface area and the DR (Dubinin-Radushkevic) method for the pore volume and width (diameter). The chars were characterized by N<sub>2</sub> adsorption test at 77 K. 100 ml/min of dry nitrogen was introduced into the sample tube to prevent contamination of the clean surface, then the sample tube was removed and the sample weighed. The sample tube was fixed to the volumetric apparatus, and then the sample was evacuated to 2 Pa pressure. Adsorbate was introduced to give the lowest desired relative pressure, and then the volume adsorbed was measured.

#### 3. Results and Discussion

## 3.1 Temperature profile

Temperature readings were taken at the various points  $T_b$ ,  $T_m$ ,  $T_t$ , and  $T_i$  for each of the reactor at a time interval of 10 minutes to generate a temperature profile along the time of carbonisation.  $T_b$ ,  $T_m$ ,  $T_t$ , and  $T_i$  represents temperatures at the bottom (side), middle (side), top (side) and within the reactors respectively. The initial set of temperature measurements was done before ignition and the final set was done when the system had come into equilibrium with atmospheric conditions. The temperature profiles for the biomass conversion and hybrid co-conversion are shown in **Figure 1a** and **Figure 1b** respectively. The self-regulating nature of the process is observed from both profiles. As the combustion of the biomass fuels commences in the heating gap, the thermal energy is recycled for the carbonisation process (retort heating). Due to the cylindrical orientation of the heating gap, a synergistic effect can be observed as temperature ( $T_i$ ) within the reactor rises higher than those within the heating gap ( $T_b$ ,  $T_m$ ,  $T_t$ ) For both conversion cases. Furthermore, the peak temperature for biomass conversion and hybrid coconversion were  $371^{\circ}$ C and  $382^{\circ}$ C respectively.

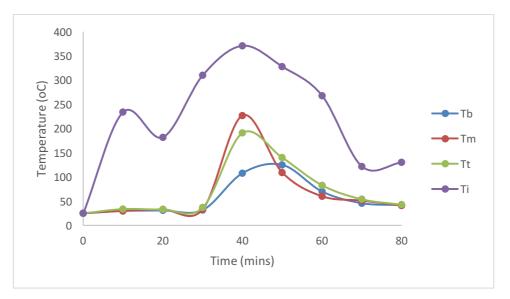
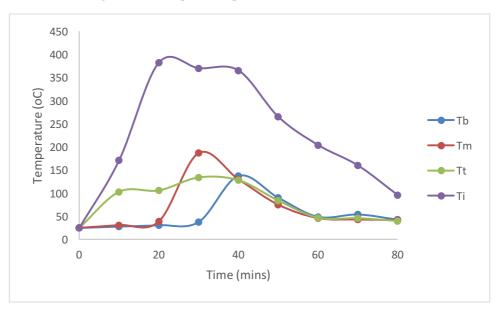


Figure 1a. Temperature profile for biomass conversion





#### 3.2 Product yield

The bio-char yield for both processes was computed using the system of equations in Eqn. 1-3 [17,18].

$$m_{Bio-c \ ar} = (M_3 - M_2)$$
Eqn. 1  

$$m_{raw} = (M_1 - M_2)$$
Eqn. 2  

$$Yield_{Bio-c \ ar} = \frac{m_{Bio-c \ ar}}{m_{raw}} \times 100\%$$
Eqn. 3

Where  $M_1$  = mass of conversion chamber + Feed (in grams),  $M_2$  = mass of conversion chamber (in grams),  $M_3$  = Weight of conversion chamber + Product (in grams). For the biomass conversion of elephant grass (*Pennisetum purpureum*), the values used and obtained were  $M_1$  = 625 g,  $M_2$  = 480 g,  $M_3$  = 500 g. For the hybrid co-conversion of elephant grass (*Pennisetum purpureum*) with LDPE waste, the values used and obtained were  $M_1$  = 900 g (plastic = 25 g),  $M_2$  = 625 g and  $M_3$  = 700 g. Computing these values, we obtain biochar yields summarised in Table 1.

Table 1. Summary of reactor performance

Index	<b>Biomass conversion</b>	Hybrid co-conversion
Process Time	80 mins	80 mins
Peak Temperature	371°C	382°C
Bio-char Yield	13.8 wt%	27.3 wt%

The biomass biochar yield of 13.8 wt% (at  $371^{\circ}\text{C}$  peak temperature) in this study is similar to the 14.29 wt% (at 300°C peak temperature) obtained for the same feedstock in a previous investigation [17]. The slightly lower yield can be attributed to the higher carbonisation temperature for the process leading to more intense thermal breakdown of the biomass [20]. The biomass biochar yield of 13.8 wt% is also higher than 6.98 wt% (at 220°C peak temperature) for plantain fibers done using the same apparatus and methodology. This shows the inherent suitability of elephant grass (*Pennisetum purpureum*) for biochar production from carbonisation by retort-heating. In addition, the biochar yield from the hybrid co-conversion is about two times higher than for biomass conversion (**Table 1**). This is due to the effect of the polymers in the reactor. Plastics have hydrocarbon building blocks which make them have higher carbon content than biomass. The richer the carbon source, the higher the biochar yield (under the same set of conditions). Furthermore, the higher oxygen content of the biomass is another reason for the lower char yield as the oxygen take up carbon atoms from the base material in the synthesis of gaseous oxygenates (CO, CO<sub>2</sub>) there by reducing the overall yield of biochar. This effect is reduced in the hybrid co-conversion process. Besides the improvement of biochar yield, this effect of will also lead to a higher carbon content in the hybrid char. This was confirmed by the EDS results.

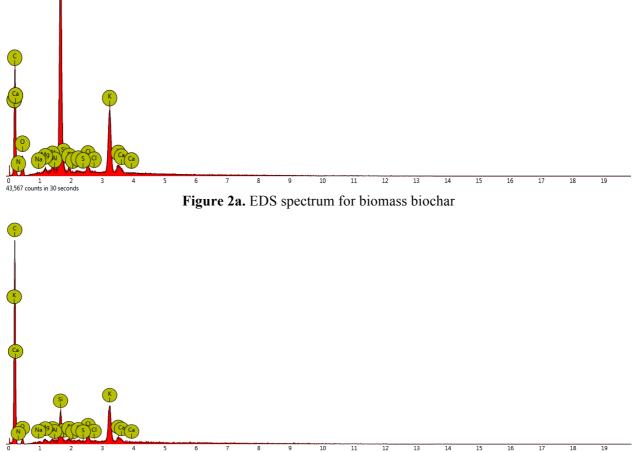
## 3.3 Product composition

The composition of the products was determined using Energy Dispersive X-ray spectroscopy (EDS). The spectrums are shown in Figures 2a-b and the results summarised in Table 2. The only major component missing is Hydrogen as EDS is usually not able to detect this. From the results in Table 2, it can be observed that the hybrid biochar is richer in carbon content than the biomass biochar. There are usually a variety of inorganic matters alongside the major biomass components which are magnified in the product composition due to their non-volatility. These tend to concentrate in the char. However,

plastics have a very rich in carbon with far less inorganic elements. This is by consequence manifested in the final product obtained from the hybrid co-conversion process.

S/N Element		Biomass Biochar		Hybrid Biochar		
		Atomic Conc.	Weight Conc.	Atomic Conc.	Weight Conc.	
1	Carbon	74.13	57.79	86.89	75.46	
2	Silicon	9.63	17.55	1.95	3.95	
3	Potassium	4.17	10.57	3.46	9.79	
4	Oxygen	9.57	9.94	4.59	5.31	
5	Nitrogen	0.85	0.78	1.26	1.27	
6	Chlorine	0.38	0.89	0.50	1.29	
7	Calcium	0.26	0.67	0.25	0.72	
8	Aluminum	0.33	0.57	0.26	0.50	
9	Phosphorus	0.26	0.52	0.26	0.58	
10	Magnesium	0.26	0.40	0.28	0.50	
11	Sulfur	0.12	0.24	0.19	0.44	
12	Sodium	0.06	0.08	0.11	0.18	

Table 2. Major elemental composition of the biomass and hybrid	d biochar
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21,445 counts in 30 seconds

Figure 2b. EDS spectrum for hybrid biochar

## 3.4 Biochar surface morphology

The surface morphology of the products was determined using SEM. Figures 3a-b and 4a-b shows the SEM micrographs of the biomass biochar and hybrid biochar respectively. The surface

characteristics of the biomass biochar showed its amorphous nature while the hybrid biochar showed a regular of a hexagonal ring. Both biochar had heterogeneous structures with the hybrid char being noticeably more porous. This is indicative of large surface area of the products with the hybrid char potentially having a higher surface area [21]. This inference was confirmed by the BET results. The white dots on the surface of the hybrid biochar in **Figures 4a-b** are possibly oxides of potassium and silicon as these are the other major elements besides carbon (see **Table 2**).

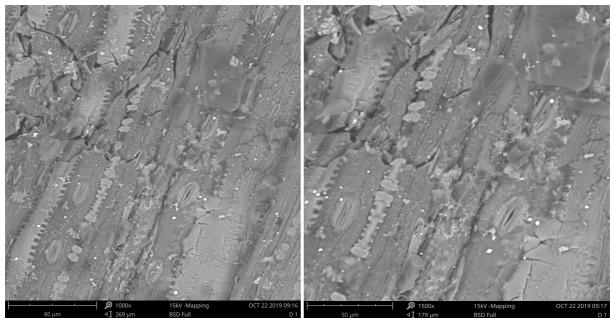


Figure 3. SEM micrograph of biochar, at (a) 1000× and (c) 1500×

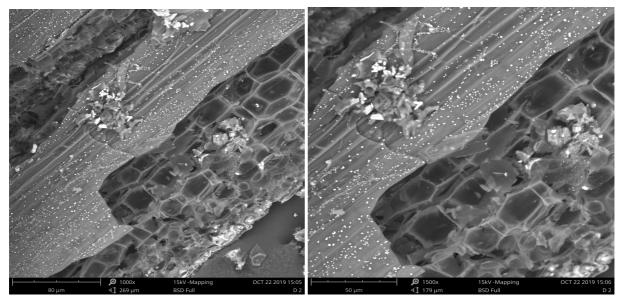


Figure 4. SEM micrograph of hybrid biochar, at (a)  $1000 \times$  and (c)  $1500 \times$ 

## 3.5 Biochar functional groups

**Table 3** shows the functional groups of raw biomass, biomass biochar and hybrid biochar as seen in the spectra obtained by FTIR analysis in **Figures 5a-c** respectively. Small peaks at 779 cm<sup>-1</sup> for raw biomass and 771 cm<sup>-1</sup> for both biochar samples shows the presence of out of plane C-H bending deformations in the lignin and cellulose content [17]. The peaks 1404 cm<sup>-1</sup> and 1396 cm<sup>-1</sup> characterised by aromatic C-C ring observed in the spectra for both biochar respectively may be caused by increase in

the carbon content due to the gasification reactions on the biomass [22]. The C-O-C (aliphatic ether or alcohol) stretching vibrations is characterised by the band at 1018 cm<sup>-1</sup> for the raw biomass which then shifted to 1041 cm<sup>-1</sup> after conversion [23, 24]. These bands also correspond to the alkoxyl (C-OH) group [25].

	Obs			
Functional group	Raw Biomass	Biomass Biochar	Hybrid Biochar	References
C-H bending	779	771	771	[17]
C-O-C (epoxy) or C-OH (alkoxyl)	1018.45	1041.6	1041	[23, 25]
Aromatic C=C ring	-	1404.22	1396	[22]
C=C ring	1635.69	1620.26	1573.97	[22, 23]
C=O stretch	-	1790	1797	[26]
Aliphatic CH <sub>2</sub> and CH <sub>3</sub> groups	2924.18	2885.6	2808	[27]
CHO (aldehyde)	-	2739	2715	[28]
O-H stretch (alcohol, carboxylic group)	3904-3109	3973-3093	3911-3086	[17]

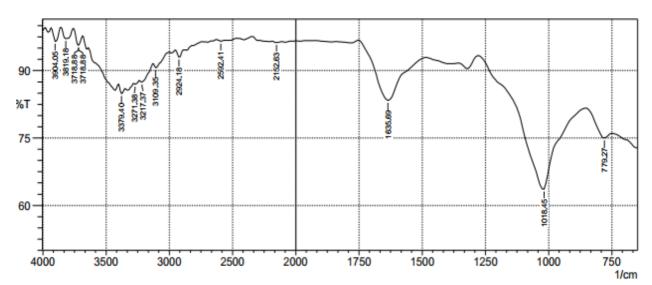


Figure 5a. FTIR spectrum of raw biomass

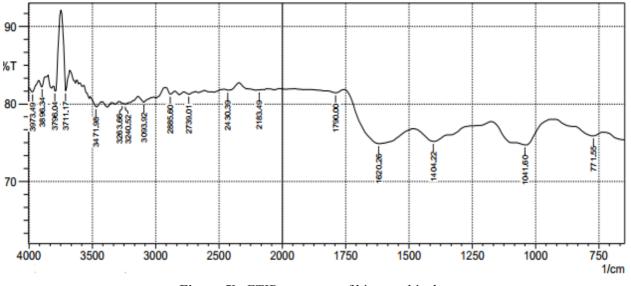


Figure 5b. FTIR spectrum of biomass biochar

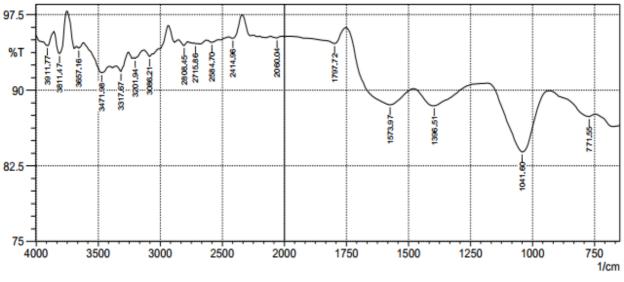


Figure 5c. FTIR of hybrid biochar

The peak 1635 cm<sup>-1</sup> observed in the biomass spectra which shifted to 1620 cm<sup>-1</sup> and 1573 cm<sup>-1</sup> in biomass biochar and hybrid biochar respectively may be attributed to the stretching vibrations of aliphatic and aromatic C=C ring of the secondary hydroxyl [22, 23]. It may also be attributed to C=O stretch of carbonates and lactonic groups of the biochar [24]. The carbonyl (C=O) vibrations of ester are characterised by small peaks observed at 1790 cm<sup>-1</sup> and 1797 cm<sup>-1</sup> for biomass biochar and hybrid biochar respectively [26, 29, 30]. The small peak at 2924 cm<sup>-1</sup> (**Figure 5a**) is attributed to the C-H stretching vibrations of methoxy, methylene and methyl groups [27, 31]. These groups are characterised by band 2888 cm<sup>-1</sup> in both biochar. The peak at 2739 cm<sup>-1</sup> and 2715 cm<sup>-1</sup> as observed in the spectra for biomass biochar and hybrid biochar correspond to the CH stretch of the CH=O (aldehyde) group [28]. The peaks in the region 3973-3109 cm<sup>-1</sup> correspond to the OH group of alcohols, phenols, ketones and carboxylic acids [17, 32, 33]. The presence of functional groups such as hydroxyl (OH) and carboxyl (C=O) groups suggest that the biochar could be used in soil amendment for the improvement of the cation exchange capacity and as a potential adsorbent [31]. The FTIR has shown that the functional groups in the biomass were preserved and as such the hybrid biochar can be used in soil amendment for the improvement for the improvement of the cation exchange capacity and as a potential adsorbent [34].

#### 3.6 Biochar textural properties

BET analysis was used to study the particle and pore dimensional characteristics of the biochar. The results are summarised in **Table 4**. The specific surface area of the hybrid biochar is significantly greater than that of the biomass biochar. This indicate a good potential in its utilisation as adsorbents in removing chemical species from aqueous media [35].

Properties	<b>Biomass Biochar</b>	Hybrid Biochar
BET surface area $(m^2/g)^a$	356.3	427.2
Micropore volume $(m^3/g)^b$	0.145	0.152
Total pore volume $(m^3/g)^c$	0.214	0.217
Pore diameter (nm) <sup>c</sup>	2.138	2.105
<sup>a</sup> Multipoint Brunauer, Emmett and Teller (BET) method <sup>b</sup> Dubinin-Radushkevic (DR) Method <sup>c</sup> Barrett, Jovner & Halenda (BJH) adsorption method		

Table 4. Summary of textural Properties of the products

The micropore volume and total pore volume are only slightly greater in the hybrid biochar than the biomass biochar. The pore diameter for both products was slightly greater than 2 nm which indicates that the biochar are mesoporous though very close to the microporous range. The range for mesoporous is 2-50 nm.

## 3.7 Justification of the study approach

In this section, we discuss the key reasons behind the approach taken in this study. An attempt to co-carbonise biomass and plastic was done with an eye for the practical implementation of the process in waste management. As observed by Duru, et al. [36], the major components of a typical municipal solid waste stream in Nigeria is about 55% biomass (albeit food waste), 19% plastics, 11% paper (also biomass) with the rest being, textile, metals and glass. The choice of feed stock was made in such a way that a typology of biomass and of plastic are represented with the biomass having a far greater proportion in the feed. From the study, it was observed that the quantity of yield and quality of product (in terms of carbon content and specific surface area) is higher for the hybrid conversion process than for the biomass conversion alone. This is a very positive result.

A second key justification is the use of a retort heating technique. Here, thermal energy evolved from the controlled combustion of biomass is used for the carbonisation process. The temperature profile shows that the process is self-regulating and inherently safe [5]. Despite the fact that very high temperatures are not achieved, this is quite favourable since the product of interest is the biochar, and was produced within the limit of thermal capacity obtainable from the biomass employed. Furthermore, an important implication of retort heating is the lack of electrical power requirement for the process [34]. This significantly mitigates cost, and makes the design more enticing to potential investors especially in developing African countries (like Nigeria) where steady power supply is still not yet achieved. Retort heating also underlines the usability of the process even in remote locations or in on-site applications [37].

## Conclusion

The co-conversion of elephant grass (*Pennisetum purpureum*) and low density polyethylene (LDPE) was successfully achieved in an updraft biomass reactor with retort heating and there was significant improvement in char quality with the process. The reactor yield was 27.3 wt% for the hybrid co-conversion and an improvement from the 13.8 wt% observed in the biomass conversion. The FTIR has also shown that the functional groups in the biomass were preserved and as such the hybrid char can be used in soil amendment for the improvement of the cation exchange capacity and as a potential adsorbent. The specific surface area of the biomass biochar and hybrid biochar was 356.3 m<sup>2</sup>/g and 427.2 m<sup>2</sup>/g respectively. From the study, it was observed that the quantity of yield and quality of product (in terms of carbon content and specific surface area) is higher for the hybrid conversion process than for the biomass conversion alone giving the hybrid conversion a definite advantage. Furthermore, the retort heating techniques ensures low cost, high biochar yield and no electrical power requirement. The study has been able to successfully achieve the co-conversion of biomass and plastics (as typologies of MSW major components in Nigeria) to valuable products with a twin goal of waste management and product development.

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