Original Research Article

EVALUATION AND VALORIZATION OF PYROLYTIC CHAR FROM COMMINGLED WASTE PLASTICS

ABSTRACT

Graphitic materials can be synthesized using a plethora of transformation processes. This work utilized waste plastic slow pyrolysis as a pathway to synthesize graphitic materials. The raw materials for the pyrolysis process were collected from a dump site in Auchi environment, Edo State, Nigeria which included grocery bags, disposable cups, plates, drinking water bottles, etc. These plastics included PP, PET, and HDPE plastics after which they were cleaned and sorted and their sizes, reduced. 40% HDPE, 40% PP, and 20% PET were the percentages for two commingled runs while three other runs were conducted with HDPE, PP, and PET waste plastics singly. A locally fabricated laboratory-scale pyrolyzer was used to convert the plastic waste into char. The reaction was carried out at 300 ^{o}C, and varied reaction times of 60, 80, 90, and 120 mins. The five Samples retrieved at the end of the slow pyrolysis were evaluated based on their elemental composition (XRF) and Physico-chemical properties like porosity, percentage moisture, and ash content. The XRF analyzer showed that the char included SiO_2 (> 16%), Al_2O_3 (6%), CaO (>19%), and some amount lost during ignition (LOI > 31%). PP was found to have the highest porosity (45.93%), HDPE at 60 minutes of slow pyrolysis had the highest (0.84%) amount of moisture and ash content (36.78%). PP alone produced the highest (67.51%) quantity of solid dry-textured char followed by HDPE (54.67) while PET was majorly waxy with the least trace of char (12.54%). These results showed that the product formed could be considered a graphitic material, for use as a solid fuel, good adsorbent, and possible catalyst.

Keywords: *Valorization, Pyrolytic char, Graphite, Waste commingled plastic, Slow pyrolysis, HDPE, Polypropylene.*

LIST OF ABBREVIATION

HDPE	High-density polyethylene
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
LOI	Lost on Ignition
SIM	Secondary ion mass spectrometry
TEM	Transmission electron microscopy
XRF	X-ray Fluorescence spectroscopy
XRD	X-ray diffraction
LIBS	Laser-induced breakdown spectroscopy
NIR	Near-infrared spectroscopy

INTRODUCTION

Solid waste is generated in all sorts of ways and can be classified based on source, such as; municipal solid waste, industrial solid waste, and agricultural solid waste [1]. In most Nigerian cities, managing solid waste is a major environmental challenge because of how much waste is produced, which is largely influenced by industrial economic structures and consumption patterns. Waste from homes, businesses, institutions (such as schools, hospitals, and universities), street sweepings, and non-hazardous solid waste from industries are all crucial sources of MSW in Nigeria [2]. The generation rate in Nigeria is estimated at 0.65-0.95 kg/capita/day, giving an average of 42 million tons of waste generated annually. This is more than half of 62 million tons of waste generated in sub-Saharan Africa annually [3]. Due to her estimated 187,896,647-person population, the amount of waste produced is rising. Therefore, a major issue for the country is where and how to channel these wastes [4].

Plastics constitute over 15% of this solid waste with organic matter holding about half the overall average composition (50%) [2]. Over the past ten years, the country's plastics consumption has grown by 7.8% annually, from 578 kilotonnes (kt) in 2007 to 1,229 kilotonnes (kt) in 2017 and is estimated to be 1,533 kilotonnes (kt) in 2020 [5]. In 2015, global plastic production reached 322 million tonnes, a dramatic increase compared to the 279 million tonnes produced in 2011 [6] and currently, global production which has reached over 300 million tonnes per year, has been attributed to the mass of the entire human population [7], [8]. The ongoing increase in plastic demand, which has been described as an unofficial barometer of income [9], [10], has the potential to increase waste accumulation. Nigeria is one of the largest consumers of plastics in Africa, with its plastic and packaging sector's rapid growth in recent decades, from around 50 companies at its inception in the 1960s to more than 3,000 manufacturers currently, according to the National Agency for Food and Drug Administration and Control (NAFDAC).

In Nigeria, incineration, sanitary landfills, open dumps, composting, etc. are the solid waste disposal methods currently in use with the most pronounced being Open dumps [1], [11]. These options, however, have proven inefficient in converting waste plastics because they have been found to aid the distortion of the ecosystem either via aerial means (generating greenhouse gases) or planetary nuisance (aesthetic disturbance) [7], [12]. As an alternative, conventional recycling which has been used has proven insufficient [12] and costly because of the restrictions on contamination of water and labor-intensive segregation of plastics before recycling, which is also laborious [11]. Unfortunately, the segregation of different plastic materials is essential since they are made of varying resin compounds for the difference in transparency and color and hence can not be skipped [13].

Thermal waste management techniques are currently common in developed countries, and they will represent a fantastic technological advance in a developing country like Nigeria. These conversion processes are combustion, pyrolysis, gasification, and torrefaction [14]. However, pyrolysis has been the most beneficial, being environmentally friendly, flexible in scale, and a helpful process in the recovery of fuels [15], [16]. Pyrolysis also has economic advantages as it does not require as many feedstock pre-treatment steps as other treatment methods [17]. Pyrolysis is often referred to as a flexible process [13] because involves a change of chemical composition creating volatile products (gas & oil up to 80wt.%) and leaving a solid residue enriched in carbon, known as char at temperatures between 300 – 800°C [15]. The process parameters can be altered to generate products based on personal preferences. The interest in thermochemical conversion of plastic waste, particularly pyrolysis, has increased considerably over the last few years, primarily since China stopped accepting post-consumer plastic waste in

2018, after having taken up to 45% of the world's plastic waste for recycling, landfilling and incineration [18]. Pyrolysis depends on a series of factors, including temperature, residence time, heating rates, feedstock composition, presence of moisture or toxic elements, and the use and types of catalysts [19].

Waste plastic pyrolysis has been widely explored both directly and with the use of various catalysts to obtain the liquid hydrocarbon fraction (oil). Rahman et al. [20] carried out the catalytic pyrolysis of polyethylene into liquid hydrocarbon using mesoporous kaolin clay with an 83wt.% oil yield and was found to be free from aromatic compounds which are potentially mutagenic and carcinogenic. Attique et al. [21] also compared thermal cracking of polyethylene with catalytic cracking using Keggin tungstoborate/kaolin clay composite as catalysts. They obtained a 99% polymer conversion with 84 wt.% as fuel oil and a negligible amount of solid char while a 22 wt.% solid residue was obtained using thermal pyrolysis. They concluded that the prepared composites were cost-effective and excellent cracking catalysts that could be recommended for the highly efficient conversion of waste plastic materials to petrochemicals at an industrial scale. Furthermore, Aisien et al. [15] compared thermal cracking to spent FCC catalyst for the breakdown of waste polypropylene into liquid oil. He concluded that thermal pyrolysis gave a higher yield of liquid oil (83.3 wt.%) while the use of the catalyst decreased the liquid oil yield to 77.6 wt.%. However, the analysis of the result showed that the liquid oil's fuel properties were like that of gasoline and diesel.

Plastics have also been listed as being highly potent in the production of graphene, carbon spheres, carbon nanotubes, and graphene nanosheets [22]–[32]. The solid fraction of pyrolytic products has found application as a carbon precursor in the synthesis of synthetic graphite due to its availability, sustainability, and cost-effectiveness [33]. Globally, most natural graphite is used in electrodes, refractories, lubricants, foundries, batteries, graphite shapes, decarburizing, steelmaking, and friction products such as brake linings. Refractory and high-technology applications make graphite a critical material in industrialized countries [34]. However, despite all of the excellent properties and wide application of graphite, the primary concern that arises is supply risk issues. Graphite has been labeled as a 'supply risk' material [35] due to its vast demand and a limited reserve of natural sources. Thus synthetic graphite will be a great alternative in filling the gap between supply and demand. Production of synthetic graphite has attracted tremendous interest in recent years, considering the increasing demand each year [33]. Sharma et al. [31] synthesized graphene crystals from solid waste plastics (PE & PS) pyrolysis by the chemical vapor deposition method. They concluded that the injection rate of the waste plastics was the major determining factor for the production of graphene materials. Ruan et al. [30] also synthesized graphene from cookies, chocolate, grass, plastics, roaches, and dog feces at 1050 ℃ on the back of a copper foil. Garg et al. carried out catalytic pyrolysis of waste plastics for the production of graphene nanosheets (GNs). Characterization of the GNs showed low resistivity at low temperatures and an inverse relationship between resistivity and temperature. They concluded that the resulting GNs would be good for thermoelectric applications.

Among plastics PE and PP, they have been extensively researched in terms of pyrolysis because they account for the majority of PSW due to their versatility in a wide range of applications [17], [36]. PE has been reported to have a carbon content ranging between 83.9 to 86.1 %, whilst PP has a range of carbon between 85.5 to 86.1 % [37]. Due to the significant amount of carbon present in the major polymers that make up PSW, pyrolysis is a preferred treatment and method for the valorization of plastics. Ko et al. [27] upcycled waste PET at 900 ℃ followed by boronassisted catalytic graphitization at 2400 °C. Their result showed that it was possible to graphitize the non-graphitizable property of PET yielding a higher crystallinity and degree of graphitization (80.6%). High char content in the pyrolysis of PE results from the presence of HDPE while high gas content results from LDPE fractions [17]. Jamradloedluk & Lertsatitthanakorn [38] pyrolyzed HDPE at 400 – 450 °C to produce char containing 51.40% volatile matter, 46.03% fixed carbon, 2.41% moisture content, and 0.16% ash. The high calorific value and density of these char briquettes made them useful as a fuel for combustion processes. They also evaluated Miandad et al. [39] evaluated waste plastic pyrolysis products from both single waste plastics and combined plastics and concluded that a PP/PE combination produced the highest amount of char (24.8%). Therefore, this research has investigated waste plastics pyrolysis under low temperatures (slow pyrolysis) and without a catalyst for char production. The research focused on pyrolyzing PET, HDPE, and PP because of their potential high char content [8], [24], [35], [39]–[42] and it hopes to address the environmental concerns of the indiscriminate disposal of these highly used and abundant waste materials while possibly also serving an alternative material for graphite, char briquettes for energy production, and/or activated carbon. It also compares the physicochemical and oxide properties of the produced char with that of local and commercial graphite to determine its substitute for graphite production.

MATERIALS AND METHODS

Materials and Methods

Collection of feedstock

The plastic waste used as the raw material in the pyrolysis process was collected from the Edo State University Uzairue students' hostels. They included grocery bags, disposable juice cups, plates, and drinking water bottles. These plastic materials were selected because they are the primary source of plastic waste produced and litter the University environment. The waste plastic was pretreated as shown in figure 1. These plastics and methods were chosen based on their char-producing properties as discussed in the literature [43]. The pyrolysis experiment was carried out using single component materials or a mixture (co-mingled) of these plastic wastes in different ratios.

Figure 1: Preparation of Raw Material

Experimental Set-up

A locally fabricated laboratory scale pyrolysis unit was set up for the slow thermal pyrolysis operation along with their ancillary equipment including the heating cylinder (LPG) and the inert gas cylinder (N_2), the vacuum pump, and the coolant (water). The feed material was fed into the pyrolyzer and heated to a constant 300 ^{o}C temperature with varying residence times of 60, 80, 90, and 120 mins respectively. Batch pyrolysis was carried out using 465.64g each of waste plastic samples, which was the maximum allowable mass the reactor could hold for co-mingled and single component plastic waste samples as shown below;

Sample I: 40% PP, 40% HDPE, 20% PET pyrolyzed at 300 □ with a residence time of 60mins.
Sample II: 40% PP, 40% HDPE, 20% PET pyrolyzed at 300 □ with a residence time of 120mins

Sample III: 100% HDPE pyrolyzed at 300 ℃ with a residence time of 90mins.

Sample IV: 100% PP pyrolyzed at 300 ℃ with a residence time of 80mins.

The product which contained a combination of char and wax was collected from the heating chamber at the end of each experiment after allowing the system to cool down at room temperature.

Characterization

The physicochemical characteristics of the recovered char were carried out along with an elemental composition using X-ray Fluorescence Spectroscopy (XRF Thermo 9900) analysis. The physicochemical properties of the char obtained, such as the pore volume, porosity, moisture content, and ash content, were determined using the ASTM standard method such as ASTM D4404-18 for pore volume, ASTM C380 for porosity, ASTM C562-15 for moisture content, and ASTM C561-16 for ash content.

RESULTS AND DISCUSSION

Thermal pyrolysis

Thermal degradation of the plastic produced char with dark brown wax. Table 1 shows the percentage yield of the products at different residence times. The results also showed the variation in the mass composition of feedstock shown in table 1 on the product.

Table 1: Percentages of Sample yield Obtained

S/N	SAMPLE	% Solid yield	% Liquid yield	% Gas yield	Residence time (mins)
1	HDPE,PP,PET	**38.23**	-	-	60
2	HDPE,PP,PET	**33.89**	-	-	120
3	HDPE	**54.67**	-	-	90
4	PP	**67.51**	-	-	90
5	PET	**12.64**	-	-	90

Table 1 presents the product yield obtained for each sample at different residence times. In the work presented by Miandad *et al* in 2017 [39], the GC-MS results showed that different kinds of compounds were produced from pyrolysis of each plastic type individually and in a mixture. Also, Jamradloedluk & Lertsatitthanakorn, 2014 [38] concluded that with HDPE alone, it was possible to achieve a high amount of char (>50 wt.%). Results from table 4.1 show that the highest yield (67.51%), was recorded at a residence time of 90mins, consisting of PP plastic alone followed by HDPE (54.67%). This result coincides with the findings from Jamradloedluk

& Lertsatitthanakorn in 2014 and Miandad *et al* in 2017. PET on the other hand gave very little product which was waxy in nature. Ko *et al.* [27] already posited that PET required a two–step pyrolysis method in order to convert it to char and possible graphite. This might be the reason for the small product with its waxy nature.

In commingled forms, Table 1 showed a yield between 34% to 38% char. However, the presence of PET might be the reason for the low char-producing properties at 300□ and a residence time of 60 to 120mins. Also, it is seen that as the residence time increased from 60 minutes to 120 minutes, the amount of char reduced by 20.21g. This is supported by the principle of slow pyrolysis which is characterized by a lower temperature (≤ 500 ℃) [40]. Sun *et al.* [44] who also investigated the effect of residence time and temperature increase on the biochar products from pyrolysis concluded that at low temperatures (300 ℃) and an increase in plastic residence time, the amount of biochar produced reduces gradually [45], [46].

X-ray Fluorescence Spectroscopy (XRF)
For this characterization, four samples were prepared and tested using XRF spectroscopy, and the results, showing the percentage of elemental components are presented in Table 2 as follows;

Table 2: XRF results of char samples (material analysis)

component	sample I	Sample II	Sample III	Sample IV	Sample V
SiO_2	19.83	17.55	16.68	28.90	-
Al_2O_3	6.26	6.02	6.05	0.29	-
Fe_2O_3	2.47	2.22	0	5.28	-
CaO	21.22	19.08	25.20	20.98	-
MgO	0.16	0.44	0.20	0.97	-
K_2O	0.20	0.19	0.08	0.03	-
Na_2O	0	0	0	0	-
SO_3	0.00	0.00	0.00	0.00	-
Cl	0.00	0.00	0.00	0.00	-
LOI	33.47	31.33	47.94	42.60	> 99.99
SIM	2.97	6.88	3.84	1.23	-
ALM	13.41	16.15	-	0.25	-
H_20	-	-	-	-	-

Sample V could not be characterized using XRF because the XRF equipment required a solid sample at a temperature at which the sample always melted. The proximate analysis and XRF results of natural and synthetic graphite are compared with the results obtained from the product analysis.

Physicochemical characterization
The physical properties of the sample materials were noted and compared to the actual appearance of graphite. These tests include color, conductivity, melting point solubility, and physical and morphological properties such as surface area, moisture content, pore volume, porosity, etc.

From the physical examination of samples, the following color appearances were observed.

Sample I (PP, HDPE, and PET) had a dark grey coloration with spots of colored particles, which could result from coloration used in plastics feedstock utilized. The texture was dry and powdery.

Sample II (PP, HDPE, PET) had a dark black coloration. It had a dry and powdery texture with traces of wax particles embedded in it. Also, it had a characteristic strong harsh smell.

Sample III (HDPE) had a dark grey coloration with a strong harsh smell and a powdery consistency.

Sample IV (PP) had a pitch black coloration with a strong harsh smell. However, its consistency was neither powdery nor waxy.

Sample V (PET): had a yellowish-brown coloration with a strong harsh smell. However, its consistency was majorly wax with traces of solid particles.

Table 3: Physicochemical parameters of Samples

S/N	Sample	**Ash content**	**Pore vol. (ml)**	**Porosity (%)**	$\%M_C$
1	HDPE, PP, PET	**0.3678**	**0.532**	**27.96**	**0.84**
2	HDPE, PP, PET	**0.2839**	**0.498**	**25.34**	**0.72**
3	HDPE	**0.1253**	**0.911**	**43.28**	**0.18**
4	PP	**0.0342**	**1.015**	**45.93**	**0.05**
5	PET	**0.0677**	**0.013**	**0.897**	**0.19**

Pore Volume and Porosity

The pore volume for the samples was determined at 70□ for 5 minutes. The results obtained are presented in Table 3 above show that the product char obtained had good pore volumes. Also, the pyrolytic char samples with the commingled plastics had lesser smaller pore volume (0.532ml & 0.498ml) and porosity (27.96% & 25.34%) than those of the single plastic char. PET on the other hand was waxy and would naturally have the least porosity (0.897).

Moisture Content

The results above showed a decreasing weight sample with the increase in heating time. However, a relationship cannot be established between the composition of the char samples and the moisture.

Ash Content Determination

From the results shown in Table 3, the products had high ash content with the highest being in sample I. Low ash content is indicative of a high fixed carbon value as displayed by Jamradloedluk & Lertsatitthanakorn, 2014 [35], [38], [47]. Hence, the low ash content in this work is indicative of either a higher volatile matter or a fixed carbon content [35], [38], [47] as might be seen from Table 4 below.

Table 4: Comparison of Graphite from various sources with this study.

Parameter	Graphite source		
	Coal ash	Natural Graphite (%)	This Study

	[48]	[49]	[26]					
				I	**II**	**III**	**IV**	**V**
Moisture %	0.5	***	***	0.84	0.72	0.18	0.05	0.19
Ash	22.4	***	2 – 9	0.368	0.284	0.123	0.034	0.068
Pore vol.	***	***	***	0.532	0.498	0.911	1.015	0.013
F. Carbon %	75.1	24.2	***	-	-	-	-	-
Porosity %	***	***	***	0.280	0.253	0.433	0.460	0.90
SiO_2	4.0 – 24	83 – 93	21 – 33	19.83	17.55	16.68	28.90	-
Fe_2O_3	0 – 2.0	0 – 2.5	6 – 27	2.47	2.22	0	2.28	-
Al_2O_3	1 – 12	3 – 12	10 – 22	6.26	6.02	6.05	0.29	-
MgO	0 – 0.4	0 – 0.6	1 – 6	0.16	0.44	0.20	0.97	-
CaO	0 – 3	0 – 0.2	0 – 5	21.22	19.08	25.20	20.98	-
SO_3	0 – 1	***	*4.72	0.00	0.00	0.00	0.00	-
Na_2O	0 – 0.5	0 – 0.5	**47.36	0.00	0.00	0.00	0.00	-
LOI	60 – 90	1 – 2	***	33.47	31.33	47.94	45.60	>99.99

* upper bandwidth of oxygen composition **lower bandwidth of oxygen composition *** Not reported

An overview of the results presented in Table 4 above shows the percentage of elemental components such as SiO_2, Fe_2O_3, Al_2O_3, and other oxides common to naturally occurring graphite and synthetic graphite (coal-ash sourced and pyrolytic char from this work). Natural graphite essentially contains silicon oxide ($SiO_2 > 83\%$) with traces of Aluminum oxide ($Al_2O_3 > 3\%$) and highly volatile matter (LOI) as reported by Jara et al., 2020 [50]. Coal-ash graphite on the other hand contains a high portion of volatile matter (LOI > 60%) with considerable amounts of silicon oxide and Aluminum oxide ($Al_2O_3 > 1\%$) [35]. This work shows a high combination of both silicon oxide ($SiO_2 > 16\%$), calcium oxide (CaO > 19%), and volatile matter (LOI > 31%). The presence of a high combination of these metallic oxides makes the pyrolytic char a good consideration for graphite as shown in Table 4 [26], [35], [50], catalyst precursors as used in biodiesel production [51]–[55], [55]–[57], or adsorbent materials [38]. The presence of very high LOI indicates high volatile matter and possible use as solid fuels [38].

CONCLUSION

The production and evaluation of pyrolytic char from waste plastics including PP, PET, and HDPE using a locally made laboratory scale pyrolyzer led to the following conclusions;

1. PP and HDPE had the highest percentage of char produced followed by the commingled plastics.
2. The amount of char decreased with an increase in time while using the slow pyrolysis method.
3. PET had the least amount of char produced and the highest amount of wax formed owing to the use of slow pyrolysis and possible acid formation.

4. The char under these conditions had good pore volumes and indicative good porosity (> 25%), low moisture content with the highest being 0.84% and the least being 0.05%, and low ash content (< 37%) indicative of high fixed carbon and/or volatile matter.
5. The results of the XRF characterization obtained showed the presence of major elemental oxides such as SiO_2 (> 16%), Al_2O_3 (6%), and CaO (>19%), in considerably high quantities among other properties like the amount lost in the ignition of the sample (LOI).
6. Therefore, the products obtained from this process had good graphitic properties and could be modified appropriately to suit varied applications.

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