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(RESEARCH ARTICLE)

Investigation of proximate and ultimate analysis of household generated plastic waste for feasible design of a pyrolysis pilot plant

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Abstract

Due to their various chemical structures, long chain polymeric compositions, and thermal/decomposition behavior of plastic waste (PW), it is challenging to recycle it into hydrocarbon fuels. Thus, is necessary to carry out proximate and ultimate of plastic because this will enable proper design of a feasible pilot plant for management of plastic waste (PW). In this study LDPE (low-density polyethylene), HDPE (high-density polyethylene), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC) were the evaluated PW samples. In accordance with ASTM standards E790, E897, and E830, respectively, the proximate analyses of PW's moisture content, volatiles, and ash content were carried out. A Vario Micro Element Analyzer was used to determine the PW's ultimate analysis. To determine how the composition of plastic waste (PW) changed with temperature and time, the mass loss of PW was measured using a thermogravimetric analyzer (SII 6300 EXSTAR, Seiko Instruments Inc., Tokyo, Japan. A bomb calorimeter (ASTM D 5865-85), which measures the heat produced at a constant temperature of 298 K from the burning of a dry sample, was used to experimentally calculate the heating value (HV). The results obtained revealed that all PW samples had a percentage volatile matter content ranging from 88.66 to 99.57%. Also, all the PW samples used had a low proportion of ash, ranging from 0.149% to 7.571%. Carbon and hydrogen make up the majority of all PW samples taken into consideration in the study, with trace levels of oxygen, nitrogen, and sulphur. Besides, PET PW was shown to have the greatest H/C ratio. The following is the order of the H/C ratio's performance: LDPE (0.1971) < HDPE (0.2034) < PET (0.1188) < PVC (0.1278) < PS (0.1290) < PP (0.1737). The study's findings demonstrated the potential for PW energy availability, and more significantly, the information gathered would help with the construction of a pyrolysis pilot plant.

Keywords: Proximate analysis; Ultimate analysis; Pyrolysis; Plastic waste; Heating value

1. Introduction

Even though there were less than 300 million tons of urban waste per person in 2017, by 2020, the entire amount of municipal solid waste (MSW) had increased to almost 1.8 billion tons. Furthermore, a possible increase in urban waste per capita by 2050 is indicated by the growth rate seen between 2004 and 2019 [1, 2]. Besides, by 2050, it is anticipated that the world's municipal solid waste (MSW) production will amount to 3.4 billion tons [3]. The continuous trend of urbanization is primarily responsible for this increased trajectory; by 2050, the urban population is predicted to account for almost 70% of the total population [4]. Moreover, MSW generation is mostly caused by daily activities, which poses a serious obstacle to waste reduction initiatives [5]. These results highlight how crucial it is to develop an all-encompassing and long-term strategy for MSW treatment and management systems. However, MSW is made up of both non-biodegradable solid waste, which includes plastic trash [7], and biodegradable solid waste [6]. Similar to this, the enormous demand for plastic materials in all commercial fields is driving an annual increase in the world's output of waste plastic (PW) [8–11]. But a sizable amount of PW ends up in the waste stream, which causes a number of environmental issues [12–14]. The production and buildup of PW in the environment is a serious problem, and the

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causes of this waste accumulation appear to be ongoing. Additionally, PW has emerged as one of the major environmental concerns facing the world, which is why recycling such large amounts is being tackled. Since the complexity of their waste management systems may not be improving quickly enough to meet their constantly increasing PW production, the rise in plastic use and manufacturing in both developed and emerging nations is a matter of particular worry. Additionally, the persistence of plastics in the ocean and their effects on wildlife, the oceans, and perhaps humans are causes for growing worry [15–18]. By 2025, the total amount of PW is expected to be close to 250 million tons annually. Consequently, there is a pressing need to create more efficient techniques for processing waste plastics and increasing their usage effectiveness.

However, recycling rates based on current processing and treatment techniques are not keeping up with the exponential increase in environmental damage [2, 19]. For nations and regions to advance over the long run and for ecosystems to remain stable, it is imperative that the current state of development be addressed and resource availability improved. PW can be disposed of using a number of common techniques, including recycling, incineration, ocean dumping, landfilling, and open dumping [20, 21]. These approaches, however, raise a number of financial and environmental issues [22–24]. In recent years, researchers have shifted their attention to the recovery of energy from PW, which not only addresses the problem of managing PW but also produces energy as a product with additional value. Therefore, a low-cost, low-complexity method of addressing PW and turning it into valuable energy products is needed. The thermochemical conversion of mixed plastic waste (MPW) to fuel is a promising approach to solid waste management (SWM) and the energy demands of the transportation, industrial, and agricultural sectors. As a result, methods like pyrolysis offer a practical way to recover energy from PW. Pyrolysis of plastics can yield a wide range of products, such as chars, chemicals, oil, gas, and other compounds [25, 26]. Additionally, PW can be converted into more valuable gases like hydrogen through pyrolysis followed by a catalytic steam reforming process [27]. The pyrolysis of different types of unmixed PW has been the subject of numerous studies [28–32]. Nonetheless, low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and poly (vinyl chloride) (PVC) make up the majority of municipal/domestic PW [33–37]. Therefore, material heterogeneity and mixed-waste separation pose serious challenges to the technique's wider application. Because of its thermal breakdown characteristics, which makes it difficult to convert usable fuel into a single reactor, there haven't been any commercial units available up to this point to convert home or municipal PW into fuel. The technological components of PW conversion are poorly understood and require further research before PW may be used as fuel. One of the key thermochemical conversion processes for turning PW into useful products such carbon black, gas fuel, and liquid fuel is pyrolysis [38, 39]. The process is endothermic, generating solid pyro-char (fixed carbon and inorganic compounds like glass, metals, ash, etc.) as well as condensable vapors and non-condensable gases from the volatile matter of the input plastic waste. Pyrolysis produces inorganic compounds that are unmodified and can be used in road construction, chemical modification or recovery, or as additives for other polymers [40–42].

The majority of research has documented the use of single-type PW. As an example, Hazrat (2014) pyrolyzed high-density polyolefin between 473 and 853 K and found that the liquid product contained light oils and hydrocarbons of gums, coke, and waxes [43]. In a Parr mini autoclave set at 773 K, the batch process of converting virgin plastic (PE, PP, PS, and PET) to crude liquid fuel was also investigated. The results showed yields of 90–95 weight percent, 5–10 weight percent, and 1 weight percent of liquids, gases, and solid residue, respectively [44]. Meanwhile, using the non-catalytic pyrolysis technique, low-temperature pyrolysis of used plastic in a batch reactor with a mixture of LDPE and PP of 3 mm in length produced a standard yield of 48.6 weight percent at 548 K of liquid products [45]. Using LDPE, HDPE, PP, and PET plastics, researchers examined the catalytic and non-catalytic pyrolysis of PS in a batch microreactor at 725 K and 5–6.0 MPa of N_2 gas pressure over a one-hour residence period. After undergoing three reactions with each plastic combination containing PS, it was discovered that the 1:1 mix ratio generated the most liquid hydrocarbon fuel [46, 47]. The results of previous studies were contrasted with those of other investigations that used HDPE plastic as feedstock and conducted experiments in a batch autoclave reactor, recording a maximum output of 70 weight percent at 753 K in 20 minutes of residence time [48]. Some researchers have investigated the ability of a mixture of PP and PE plastics to thermally fracture at different temperatures in horizontal tubular reactors to create hydrocarbon fuels, and found that yields depend on the composition of the PW and residence time [49]. According to these studies, the most effective method for turning PW into fuel is pyrolysis. The impact of operating temperatures on the conversion of household PW into useful alternative fuels, however, has been the subject of very few investigations [50]. Furthermore, proximate and ultimate studies offer extremely significant information to understand the reasons for the production of specific products, as the products of pyrolysis are highly reliant on the feedstocks employed. A material's chemical makeup, including its moisture content, fixed carbon content, volatile matter content, and ash content, is the main focus of proximate analysis. The elemental composition of a substance in terms of carbon, hydrogen, nitrogen, sulphur, and oxygen is quantitatively analyzed by ultimate analysis. Proximate and ultimate analyses must adhere to international standards like ASTM, ISO, etc., in order to yield correct results. Therefore, the aim of this study is to determine the proximate, ultimate, and thermogravimetric analysis of various PW (HDPE, LDPE, PP, PVC, PET, and PS). The results obtained will serve as requirements for designing an effective pyrolysis pilot plant.

2. Materials and Methods

A variety of PW samples (PET, HDPE, PVC, LDPE, PP, and PS), a bomb calorimeter, a muffle furnace, a gas desiccator, a digital weighing balance, a pulverizer with shaker, a laboratory oven, a Vario Micro Element Analyzer, and a SII 6300 EXSTAR, manufactured by Seiko Instruments Inc. in Tokyo, Japan, are among the equipment used in this investigation. The following methods were used.

2.1. Sample Preparation

Various PW types were gathered from homes in Benin City, Nigeria, to serve as samples for this study. PET, HDPE, PVC, LDPE, PP, and PS are the PW samples. After being cleaned and sliced into tiny pieces, the samples were put in different beakers. Lastly, the samples go through gradation analysis utilizing sieves to produce uniform particles. The gradation procedure, also known as sieve analysis, is a simple yet crucial step in determining and defining what is appropriate for the experiment. After the sample was broken up into tiny bits for this experiment, sieves were utilized to achieve a uniform particle size. The resulting homogenous particle is labeled PET, HDPE, PVC, LDPE, PP, and PS and kept in a container based on the sample. The identical procedure was done for every PW sample in order to achieve a uniform size between 0.5 and 0.8 mm [51].

2.2. Proximate and Ultimate Analysis

The moisture content, volatile matter, fixed carbon, and ash were evaluated using proximate and ultimate analysis. In accordance with ASTM standards E790, E897, and E830, respectively, the proximate analyses of PW's moisture content, volatiles, and ash content were carried out. In short, 1.5g of each PW sample was evenly placed in a sample boat and baked at 105°C for one hour in order to assess the moisture content. 1.5g of PW was placed in a sample boat in air at 550°C for one hour to determine the ash content, whereas 1.5g of plastic was placed in a sealed crucible in an electric furnace at 950°C for seven minutes to measure the volatile content. A Vario Micro Element Analyzer was used to determine the PW's ultimate analysis, and the results are displayed in Table 1. One analytical method used to ascertain the elemental composition of the PW samples is elemental analysis (EA). The test is based on measuring the amount of the relevant oxides after samples are dynamically and carefully burned in a reactor. The PW samples burn in a column that has an electronically regulated temperature and an oxidizing-reducing catalytic bed. The analyzer, a condensed form of the gas chromatograph, receives the evolved gases. Chromatographic columns separate all of the gases (H_2O, CO, CO_2, and N_2O), which are subsequently picked up by a thermally conductive detector (TCD). After the extra oxygen is removed by the reduction column, N_2, CO_2, H_2O, and SO_2 are obtained; the N, C, H, and S are then computed, respectively.

2.3. Thermogravimetric Analysis (TGA)

To determine how the composition of PW changed with temperature and time, the mass loss of PW was measured using a thermogravimetric analyzer (SII 6300 EXSTAR, Seiko Instruments Inc., Tokyo, Japan). Nitrogen was used as an inert gas at a flow rate of 150 ml per minute over a temperature range of 302 to 1174 K. In subsequent parts, differential thermogravimetric analysis was derived and examined. For all TGA analyses, a consistent sample weight of up to 10 mg was employed.

2.4. Determination of Heating Value

A bomb calorimeter (ASTM D 5865-85), which measures the heat produced at a constant temperature of 298 K from the burning of a dry sample, was used to experimentally calculate the heating value (HV) [52–54]. However, the HV of the PW is predicted using empirical models in situations where direct calorific value measurements are not practical [54]. Nevertheless, a number of models have been created to characterize and forecast the energy content of mixed solid waste (SW). The elemental composition, physical composition, or proximate composition (i.e., the amount of moisture, fixed carbon, and volatile matter) of PW are the common independent variables in these empirical models. The higher heating value (HHV) of PW, which represents its energy content, was estimated empirically using the PW samples' Chlorine (Cl), carbon (C), hydrogen (H_2), nitrogen (N_2), oxygen (O_2), and sulphur (S) concentrations as determined by the findings of the ultimate and proximate analyses.

$$y = \frac{1-x_1}{100}(0.327x_2 + 1.241x_3 - 0.089x_4 - 0.26x_5 + 0.074x_6 \qquad \ldots\ldots \qquad (1)$$

where y (MJ/kg) is the higher heating value predicted and $x1$, $x2$, $x3$, $x4$, $x5$, and $x6$ are the Cl, C, H_2, O_2, N_2, and S contents in the analysis. The empirical model considers the experimentally measured higher heating values (MJ/kg) as an output (target variable).

$$y = \frac{(1-x_1)(ax_2+bx_2+cx_4+dx_5+ex_6)}{100} \quad \ldots\ldots\ldots\ldots\ldots \ (2)$$

where x_1, x_2, x_3, x_4, x_5 and x_6 represent water Cl, C, H, N, O, and S respectively.

$$H_v(MJkg^{-1}) = 33801(C) + 144158(H) - 0.125(O) + 9413(S) \quad \ldots\ldots\ldots \ (3)$$

3. Results and Discussion

Tables 1 and 2 display the findings of the proximate and ultimate analyses of the various PW employed in this investigation.

Table 1 Result of Proximate Analysis of PW

S/N	PW	Moisture (%)	Volatile Matter (%)	Ash (%)	Fixed Carbon (%)
1	HDPE	0.215	98.35	0.212	1.223
2	LDPE	0.189	98.65	0.149	1.012
3	PVC	0.299	88.66	7.571	3.47
4	PET	0.007	88.99	2.092	8.911
5	PP	0.069	99.57	0.280	0.081
6	PS	0.201	98.18	0.168	1.451

Table 2 Result of Ultimate Analysis of PW

S/N	PW	C (%)	H (%)	N (%)	S (%)	Cl (%)	O (%)	H/C Ratio
1	HDPE	82.86	16.85	0.00	0.28	0.00	0.01	0.2034
2	LDPE	83.32	16.42	0.00	0.24	0.00	0.02	0.1971
3	PVC	37.78	4.83	0.14	0.16	56.73	0.36	0.1278
4	PET	87.98	10.45	0.60	0.14	0.00	0.83	0.1188
5	PP	84.92	14.75	0.04	0.23	0.00	0.06	0.1737
6	PS	88.51	11.42	0.00	0.02	0.00	0.05	0.1290

Figures 1 through 3 display the results of the proximate analysis for each PW. All PW samples had extremely low moisture contents, and the results were as follows: As illustrated in Figure 1, PET (0.007) < PP (0.069) < LDPE (0.189) < PS (0.201) < HDPE (0.215) < PVC (0.299). As a result, PVC had the greatest moisture content and PET the lowest of the PW under investigation. Because PW are already processed materials with all moisture removed, they have no pore space for further moisture to enter their structure before, during, or after consumer use, which is why their moisture content is so low [55].

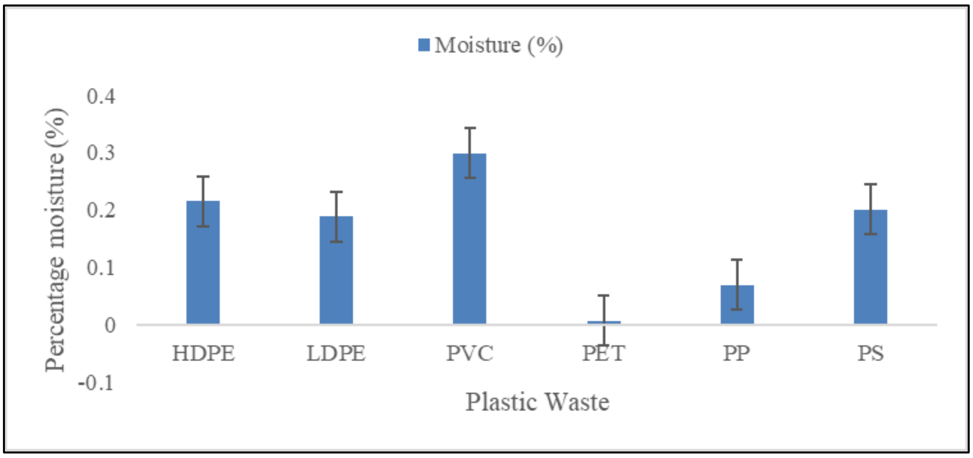

Figure 1 Evaluation of moisture content of PW

Furthermore, the results showed that, with the exception of PVC (3.47%) and PET (8.911%), all of the PW that was collected had lower percentages of fixed carbon and higher levels of volatile matter (> 88%) as shown in Figure 2. All PW samples had a percentage volatile matter content ranging from 88.66 to 99.57%. PP had the greatest percentage volatile matter (%VM), whereas PS, HDPE, and LDPE had similar volatile matter contents. PVC and PET, on the other hand, have the lowest and nearly identical %VM. The amount of time it will take for solid fuels to burn out is indicated by their percentage VM content. The low moisture content and high volatile matter in PW indicate that plastics will provide a useful fuel source [56].

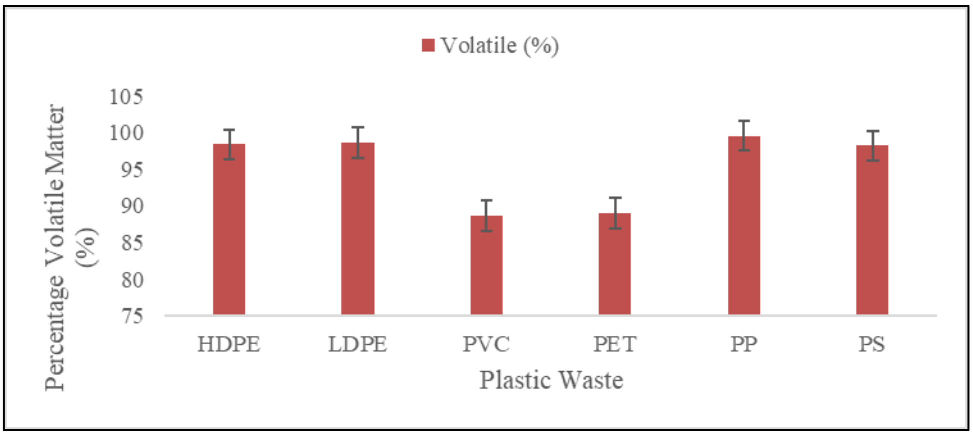

Figure 2 Evaluation of percentage volatile matter of PW

All PW had a low proportion of ash, ranging from 0.149% to 7.571%, according to the data obtained. In plastic, a high ash content is typically defined as more than 10% by weight (wt.%). This result suggests that the plastic components contain a considerable amount of inorganic impurities, such as colors, fillers, or manufacturing leftovers. Since a high proportion of ash lowers the calorific value of fuel. Thus, the samples' low ash content indicates that PW are appropriate for energy generation [55]. Furthermore, the residue left over after the extraction of the fuel's moisture, volatile matter, and ash contents is known as the fixed carbon content. The percentage of fixed carbon in all PW examined in this study is extremely low (0.081–8.911%). Although it can vary greatly depending on the type of plastic, a high fixed carbon content is typically defined as more than 50% [56].

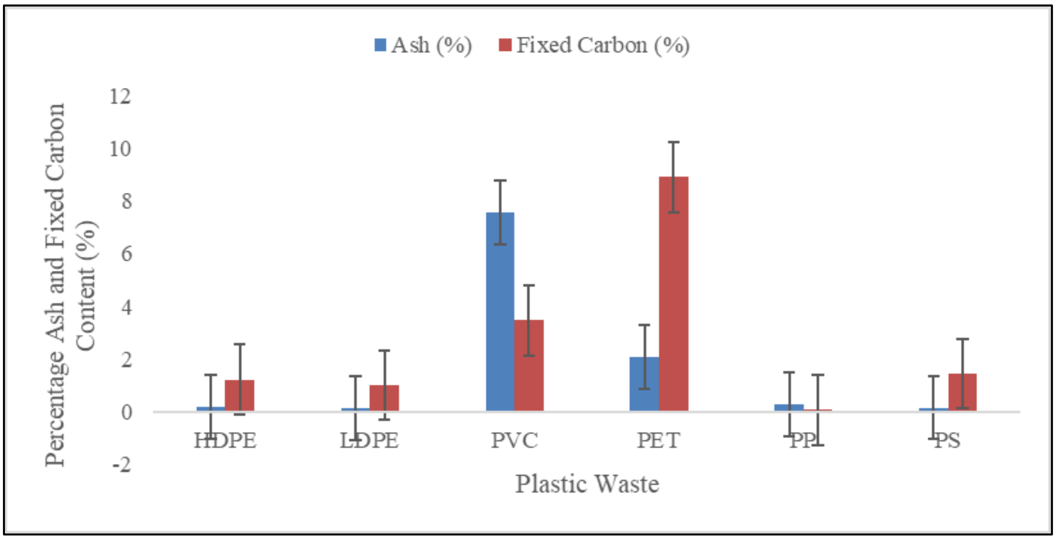

Figure 3 Evaluation of percentage ash and fixed carbon content of PW

The proportion of the sample's different elemental compositions is specified by the PW sample's ultimate analysis, which is shown in Table 2. Carbon and hydrogen make up the majority of all PW samples taken into consideration in the study, with trace levels of oxygen, nitrogen, and sulfur (Figure 4). Additionally, as Figure 4 illustrates, chlorine was largely absent except for the PVC sample (56.73%).

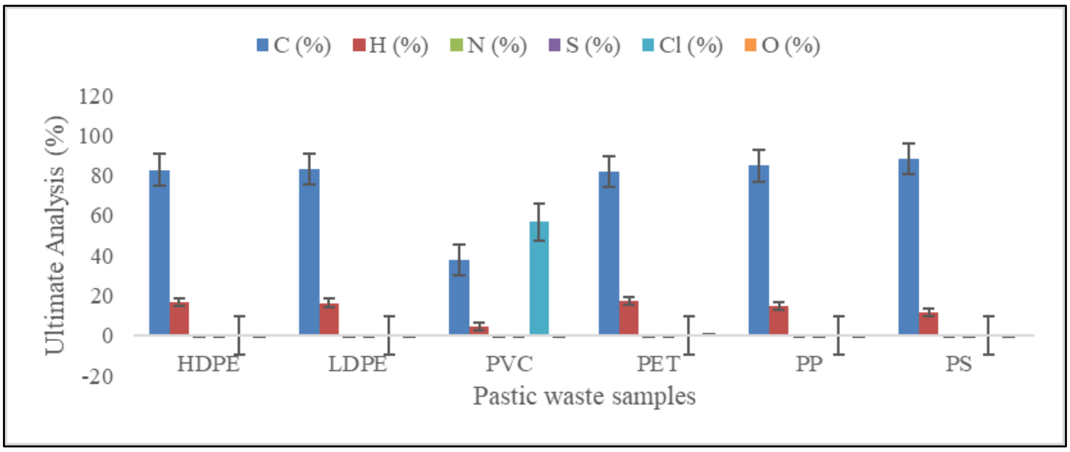

Figure 4 Proximate analysis of PW

Given that PW have a relatively high structural fraction of carbon and hydrogen, this indicates that they are feasible fuel sources [56]. Since these oxides are released during the combustion of solid fuel, the percentage of nitrogen and sulphur in their structure determines the rates of release of these oxides. Furthermore, the ultimate analysis of the complete PW sample and the results obtained are consistent with the findings of [57], which indicated a comparable range of carbon percentages in HDPE and PP. Consequently, the findings obtained fall within the permissible tolerance range, and the manufacturer's usage of a mixture of different compositions during the plastic's production is typically the source of the discrepancy. The combustible and incombustible carbon carbonate concentrations are essentially included in the high carbon (C) content. The amount of unwanted emissions, such as NOx and SOx, two crucial pollutants from the combustion process of a fuel feedstock, is determined by the nitrogen (N) and sulphur (S) levels. All of the PW samples in this investigation include trace amounts of S and N, as shown in Table 2 and Figure 4, demonstrating that PW is a clean and sustainable fuel source. Furthermore, compared to other PW samples, PET PW was shown to have the greatest H/C ratio (Figure 5). The following is the order of the H/C ratio's performance: LDPE (0.1971) < HDPE (0.2034) < PET (0.1188) < PVC (0.1278) < PS (0.1290) < PP (0.1737). The PW's heating value will decrease when the H/C ratio decreases.

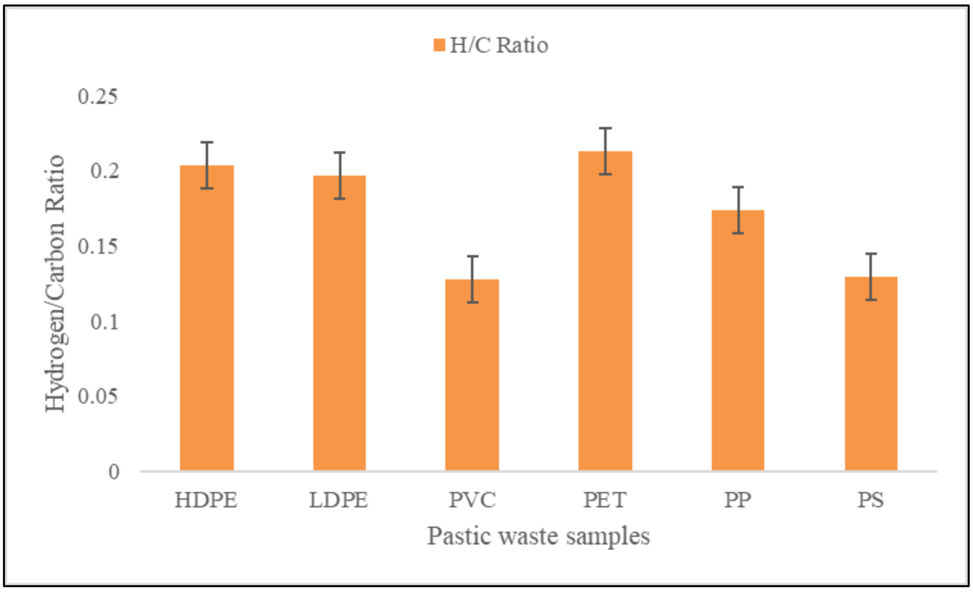

Figure 5 Comparative analysis of H/C ratio of PW

A bomb calorimeter was used to determine PW's heating value in accordance with ASTM D 5865-85 standards. The quantity of energy released when a fuel burns fully is measured by the heating value. Megajoules per kilogram (MJ/kg) is a common unit of measurement used to describe the energy content of fuels. As illustrated in Figure 6, the outcomes achieved are as follows: The results of [58], which showed that HDPE (44 ± 0.36 MJ/kg), PET (22.96 ± 0.03 MJ/kg), and PP (46.50 ± 0.11 MJ/kg) were nearly identical to those of HDPE (44.57 MJ/kg), LDPE (44.44 MJ/kg), PS (41.22 MJ/kg), PVC (41.01 MJ/kg), PP (44.53 MJ/kg), and PET (22.87 MJ/kg) obtained in this study. As a result, it displays the highest energy that can be recovered from the PW sample source in theory [59].

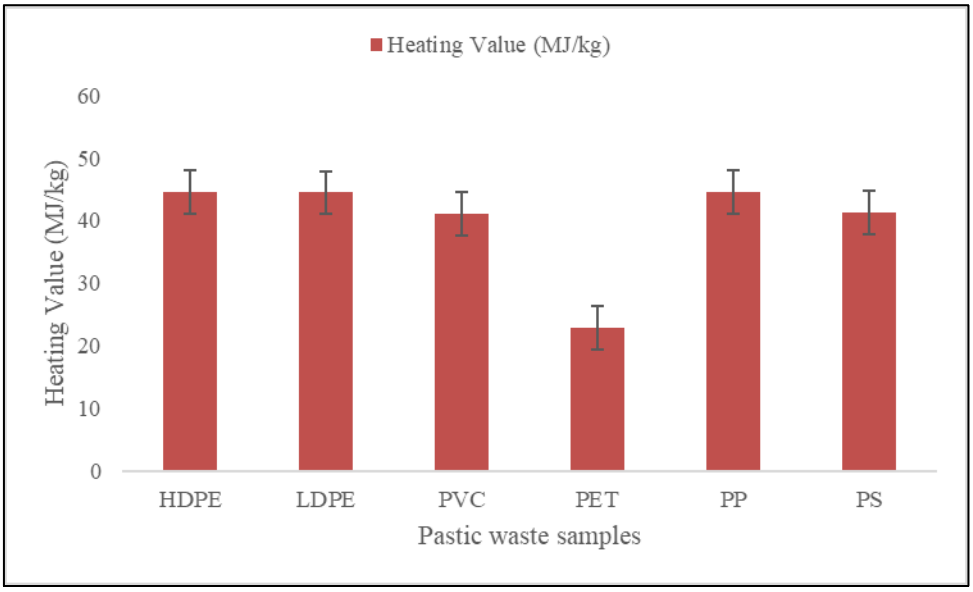

Figure 6 Comparative analysis of heating value of PW\

Table 3 and Figure 7 display the thermogravimetric (TG) values for the PW samples. Because of the very small amount of ash that was found, thermograms were generally comparable and confirmed a single degradation phase for every PW sample with full degradation.

Table 3 Results of the thermogravimetric (TG) of PW

S/N	PW	Temperature (K)			
		Onset	**Peak**	**Endset**	$\Delta T = Enset - Onset$
	PW	**Onset**	**Peak**	**Endset**	
1	PET	623	789	819	196
2	HDPE	613	757	794	181
3	LDPE	607	741	776	169
4	PP	592	701	716	124
5	PS	549	658	684	135
6	PVC	523	619	627	104

The TG characteristic temperatures (Tonset, Tpeak, and Tendset) of the investigated PW samples were as follows: PVC < PS < PP < LDPE < HDPE < PET, as is evident from Figure 7 and Table 3. Because the third carbon atom reduces the stability of the polymer, it is anticipated that the pyrolysis temperatures of PVC, PS, and PP will be lower than those of LDPE, HDPE, and PET [60]. Furthermore, [61] found that, in contrast to linear polymers like LDPE and HDPE, substituted and branched polymers like PS and PP disintegrate at lower temperatures. Additionally, LDPE is less dense and has a lower thermal decomposition temperature than HDPE due to its higher degree of branching. Furthermore, the kind and degree of the contact between the two polymers throughout the degradation process can be ascribed to this finding [62].

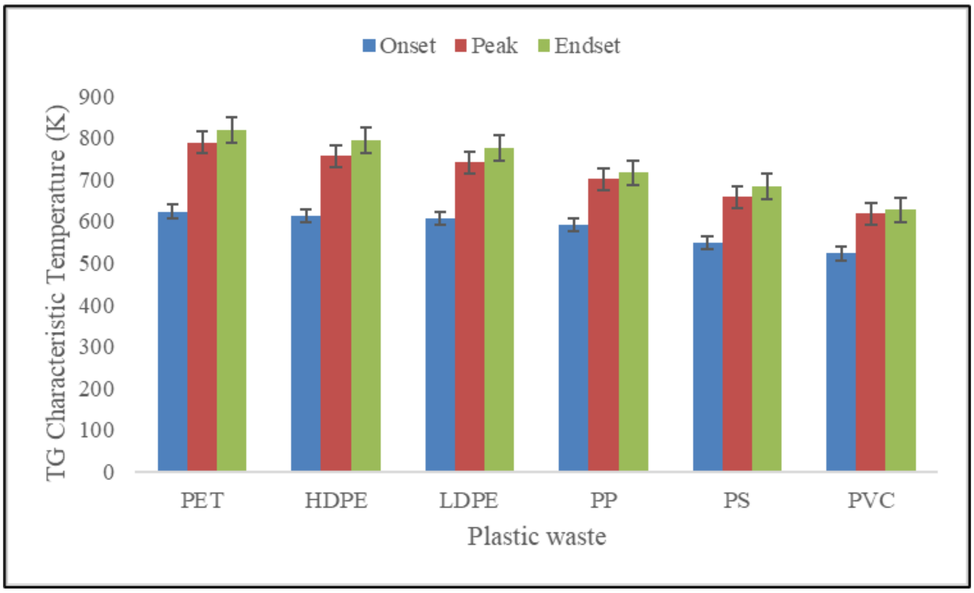

Figure 7 Analysis TG characteristic temperatures

4. Conclusion

The resulting conclusions based on this research which to study the ultimate and proximate analysis of PW for feasible design of a pilot pyrolysis plant for energy recovery form PW shows that all PW samples had extremely low moisture contents, PET (0.007) < PP (0.069) < LDPE (0.189) < PS (0.201) < HDPE (0.215) < PVC (0.299). PVC had the greatest moisture content and PET the lowest of the PW under investigation. With the exception of PVC (3.47%) and PET (8.911%), all of the PW that was collected had lower percentages of fixed carbon and higher levels of volatile matter (> 88%). PP had the greatest percentage volatile matter (%VM), whereas PS, HDPE, and LDPE had similar volatile matter contents. PVC and PET, on the other hand, have the lowest and nearly identical %VM. The percentage of fixed carbon in all PW examined in this study is extremely low (0.081–8.911%). Carbon and hydrogen make up the majority of all PW samples taken into consideration in the study, with trace levels of oxygen, nitrogen, and sulphur. Furthermore, compared to other PW samples, PET PW was shown to have the greatest H/C ratio. The following is the order of the H/C ratio's performance: LDPE (0.1971) < HDPE (0.2034) < PET (0.1188) < PVC (0.1278) < PS (0.1290) < PP (0.1737). More so, the heating value of the different PW used in this study was obtained as HDPE (44.57 MJ/kg), LDPE (44.44 MJ/kg), PS (41.22 MJ/kg), PVC (41.01 MJ/kg), PP (44.53 MJ/kg), and PET (22.87 MJ/kg). Thus, sufficient can be recovered from the PW sample. Therefore, the outcome of the study shown the potential of energy availability from PW, and most importantly, the data obtained will aid in designing a pyrolysis pilot plant

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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