Pyrolysis of waste LDPE and waste PP plastics into fuel oil in a low-cost, lab-scale pyrolyzing unit

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Abstract Plastics cause severe environmental and societal issues when post-consumer plastics are discarded in the environment without proper management. Pyrolysis of plastic waste is a promising method for plastic waste management due to its valuable by-products such as fuel oil. The objective of the present study was to pyrolysis waste polypropylene (PP) and waste low-density polyethylene (LDPE) plastics into fuel oil in a low-cost, lab-scale apparatus at the maximum temperatures of 330 °C and 355 °C, respectively, and in turn to assess the physical properties, gross calorific value, density, kinematic viscosity, flash point, ash content, and sulfur content, of resultant fuel oil. Commercially available, recycled grades of LDPE and PP pellets, 70.0 g of each, were obtained, and pyrolysis was done in a lab-scale, low-cost batch reactor. The experiment was triplicated, and the resultant fuel oil was analyzed for physical properties by ASTM standard methods. The properties of resultant fuel oil were also compared with diesel grade criteria. Results revealed that the highest yield of fuel oil was obtained from waste PP at 79.57 wt.% while the waste LDPE resulted at 74.06 wt.% of fuel oil. No wax formation was observed in the waste PP pyrolysis process, unlike in the waste LDPE pyrolysis. The gross calorific values of waste PP and waste LDPE were 12 016 kcal/kg and 11 961 kcal/kg, respectively. It was higher than the standard value of commercial diesel. The distillation results indicated that short-chain hydrocarbon content is higher in the waste PP fuel oil sample than in the waste LDPE fuel oil sample. The results indicated that the resultant fuel oil samples were nearly closer to the diesel grade criteria. Therefore, the fuel oil produced from waste plastics is a viable alternative to traditional fossil fuels, with potential applications in power generation and transportation.

Keywords: Distillation, Fuel oil, Physical properties, Pyrolysis

Introduction

Demand for plastics is increasing day by day due to their versatile properties, including lightweight, high durability, non-corrosive, chemically inert, and economic feasibility (Syamsiro et al., 2014; Wong et al., 2015; Sharuddin et al., 2016). Plastic waste persists in the natural environment for more than hundred years due to its non-biodegradable property (Jambeck et al., 2015; Wong et al., 2015). Therefore, several environmental and health issues grow around plastic waste mismanagement. However, a future without plastics is unlikely.

Plastic waste is ubiquitous at present due to

improper disposal practices. The common plastic waste disposal methods include recycle, landfilling, pyrolyzing, and incineration. However, around 79% of plastic waste is disposed into the natural environment (Geyer et al., 2017). Recycling plastic waste is a high-cost and labour-intensive method (Panda et al., 2010). Land-filling is not a suitable method to handle plastic waste due to many unfavourable consequences such as poor biodegradability, its potential health risks to aquatic, and terrestrial animals and its impact on environmental pollution (Patni et al., 2013; Rafey &



Siddiqui, 2021). On the other hand, the incineration cost of plastic waste is significantly high at its installation and it is not practical for small communities. Moreover, uncontrolled incineration is destructive due to the emission of greenhouse gases and some highly toxic pollutants including furans and dioxins (Panda et al., 2010; Vergara & Tchobanoglous, 2012; Fan et al., 2017; Miandad et al., 2017).

Pyrolysis of plastic waste is a promising waste handling method due to the formation of the valuable by-products. It is the thermal degradation of long chain molecules into small chain molecules at different temperatures (300 - 900 °C), in the absence of an oxygen environment to produce valuable by-products including fuel oil, syn gas, and char (Wong et al., 2015; Vijayakumar & Sebastian, 2018; Eze et al., 2021; Papari et al., 2021). The mechanisms of plastic pyrolysis are identified as end-chain scission or depolymerization, randomchain scission, chain stripping, and cross-linking (Syamsiro et al., 2014).

Low-density polyethylene (LDPE) and polypropylene (PP) are the most common types of plastic waste found in municipal solid waste (Japan International Cooperation Agency, 2016; Fan et al., 2017; Vijayakumar & Sebastian, 2018). The most common applications of LDPE plastics are shopping bags, mulch films, irrigation tubings, cling wraps, garbage bags, and squeeze bottles (Alabi et al., 2019). Furthermore, PP plastics are used for lunch boxes, microwave dishes, packaging tapes, garden furniture, ice cream tubs, hinged caps, and straws (Alabi et al., 2019: Uthpalani et al., 2022). The chemical structures of LDPE and PP polymers (Figure 1) have a higher potential to transform them into liquid fuel oil and gaseous fuel (syn-gas) products as the volatile matter is very high upon pyrolysis (Sharuddin et al., 2016).



Figure 1: Chemical structures of (a) LDPE and (b) PP polymers

Although extensive studies have been conducted on various aspects of the process of plastic pyrolysis, very few studies have been conducted on waste LDPE and PP as feed-stock for pyrolysis. Yan et al. (2015) stated that the liquid fuel yields obtained from waste LDPE and PP at the temperatures of 420 °C and 460 °C in a semi-batch reactor were around 77.07 wt.% and 65.44 wt.%, respectively. In another study on virgin LDPE pyrolysis, Aguado et al., (2007) obtained around 74.7wt.% of liquid yield by using a batch reactor at 450 °C. Furthermore, Marcilla et al., (2009a) observed that pyrolysis of

LDPE in a batch reactor at 500 °C produced 93.1 wt.% of both liquid and wax compounds.

The majority of laboratory scale plastic pyrolysis experiments have been carried out in batch reactors (Aguado et al., 2007; Marcilla et al., 2009a; Al-Salem, 2019; Budsaereechai et al., 2019). Parameters in the thermal pyrolysis process can easily be controlled in batch reactors and offer a high liquid oil yield. Furthermore, designing and manufacturing costs are low in lab-scale batch reactors (Sharuddin et al., 2016; Uthpalani et al., 2022).

Therefore, the present study was planned to assess the physical properties of resultant fuel oil from pyrolysis of LDPE and PP waste plastics in a low-cost, lab-scale batch reactor using a manual heat control system. Marcilla et al. (2009b) employed "Ice - NaCl cooling traps" to condense the vapor in their study. However, the major drawback of this rapid condensation of the vapor was the deposition of high molecular weight hydrocarbons as waxy materials in the condenser. In this study, that matter has been resolved by adapting a typical condensation process followed by bubbling the vapour into a water bath and collected the resultant fuel oil at room temperature. Moreover, the non-condensed vapor was trapped by bubbling into an organic solvent preventing emissions to the atmosphere.

Methodology

Materials

Plastic samples selected in this study represented majority of waste plastics in the natural environment. Recycled grades of low-density polyethylene (LDPE) and polypropylene (PP) were obtained from Deluxe Plastics, Colombo 11. Both polymers were employed in pellet form with a maximum particle size range of 5 - 10 mm. Plastic waste in Figure 2 referred to the recycled LDPE and PP pellets. To minimize the effect of compositional changes of the waste samples, 10 kg of each were purchased once.

Reactor

A low-cost, lab-scale batch reactor and a system (Figure 2) was used to perform the waste LDPE and PP pyrolysis process. About 70.00 g of each waste plastic sample was placed in a round bottom flask (reactor). Therein, the flask was dipped in a sand bath to maintain a constant heat flow. The temperature of the reactor was detected using a 64 Max Fluke IR thermometer. A nitrogen flow was introduced to the reaction medium throughout the experiment. The pyrolysis was carried out until all the polymer was converted to gaseous, liquid, or waxy products. All reactions were conducted in a fume hood. The experiment was triplicated.

The resultant products were passed through a condenser and bubbled into a water bath. Then again, the remaining condensable products were trapped by immersing in a toluene bath. The top layer of liquid product in the water bath was separated using a separation funnel and stored in a storage bottle for further analysis.



Figure 2: Block diagram of the experimental setup

Analysis of the products generated

percentages of the resultant products were calculated according to the equation 1.

The yields of the resultant liquid oil and char were obtained by taking their weights. The yield

Percentage of the resultant product yield =
$$\frac{W}{W0} \times 100\%$$
(1)

W = Weight of the resultant product

 W_0 = Weight of the initial plastic waste pellets

The physical properties of the resultant liquid oil including calorific value (gross) (kcal/kg), density at 15 °C (kg/m³), kinematic viscosity (cSt.), ash content (wt.%), water content (mg/kg), flash point (°C), sulfur content (wt.%) were measured according to ASTM standard methods (American Society for Testing Materials (ASTM), 1997).

Statistical analysis

The standard deviation of the product yields was calculated by triplicated analysis using the Microsoft Excel software.

Results and discussion

The maximum reaction temperature in the thermal pyrolysis of waste PP is 330 °C, whereas the maximum temperature in the thermal pyrolysis of

waste LDPE is 355 °C. The time taken to complete the pyrolysis process of waste PP and waste LDPE was 55 minutes and 70 minutes, respectively. This indicates that the waste PP was pyrolyzed at a lower temperature (330 °C) and a shorter time than the waste LDPE.

The resultant products from the pyrolysis of waste LDPE and waste PP feed-stock are shown in Figure 3 and the yields from the waste LDPE and the waste PP are shown in Figure 4. The highest fuel oil yields of waste PP and LDPE were 79.57 ± 1.66 wt.% and 74.06 ± 2.98 wt.% respectively. The wax formation was only observed in LDPE waste pyrolysis and the yield was 6.17 ± 0.14 wt.%. The yield of char in waste PP and waste LDPE pyrolysis were 14.64 ± 0.36 wt.% and 8.34 ± 1.87 wt.%, respectively. The resultant gas yield of waste PP was calculated as 5.79 ± 0.84 wt.%, whereas that of waste LDPE was 10.83 ± 0.83 wt.%.



Figure 3: Resultant products of waste PP (a) fuel oil, (b) char, and of waste LDPE (c) fuel oil, (d) char (e) wax from the pyrolysis process



Figure 4: The yields of pyrolysis of waste PP and waste LDPE

Table 1 summarizes the physical properties of the resultant fuel oil from the waste plastic pyrolysis process. The properties of commercial diesel fuel are also included in Table 1 for comparison (Syamsiro et al., 2014; Sharuddin et al., 2016). According to the results, the calorific values of both waste fuel oils were greater than commercially used diesel fuel. In terms of density, values were not comparable with the commercial grade of diesel fuel. The density values of the pyrolysis fuel oils were comparable with the gasoline standard value and were in the range of 720 - 780 kg/m³ (Sharuddin et al., 2016). The viscosity of the fuel is a very important parameter in the petroleum industry since it plays a major role in the fuel injection process (Ahmad et al., 2015). The kinematic viscosity of waste LDPE fuel oil was very close to the kinematic viscosity of diesel. However, the viscosity of fuel oil resulting from the waste was much lower than the viscosity of diesel. In terms of ash content and water content, both waste PP and waste LDPE fuel oils have negligible amounts.

The flashpoint of the pyrolysis oils was much lower than that of diesel fuel. However, a high value of flash point is important in terms of security of storage. Sulfur content was very low in both fuel oil samples as 11.3 wt.% and 11.7 wt.% of waste PP and waste LDPE, respectively. The calculated cetane index gives an idea about the ignition quality of diesel fuels (Ahmad et al., 2015). The calculated cetane index of waste PP fuel oil was nearly close to that of commercial diesel fuel which means it has excellent combustion properties. On the other hand, fuel oil of waste LDPE has a higher number of calculated cetane index than commercial diesel. Therefore, combustion properties of waste LDPE fuel oil were not as good as the combustion properties of waste PP fuel oil. However, the overall data showed that the fuel oil from both waste PP and waste LDPE pyrolysis was nearly closer to the properties of commercially used diesel.

	Method	Commercial Grade	Experimental Results	
Physical properties		Diesel	Waste PP	Waste LDPE
Calorific value (gross) (kcal/kg)	ASTM D 240 - 17	10 151	12 016	11 961
Density at 15 °C (kg/m ³)	ASTM D 1298 - 12b (2017)	820.0 - 860.0	780.9	791.6
Kinematic viscosity (cSt.)	ASTM D 445 - 18	2.140 ^a	1.756 ^b	2.178 ^b
Ash content (wt.%)	ASTM D 482 - 13	0.0100	≤0.0001	≤0.0001
Water content (mg/kg)	ASTM D 95 – 13 (2018)	Max 50.00	0.00	0.00
Flash point (°C)	ASTM D 93 - 18	52	Ambient	Ambient
Sulfur content (wt.%)	ASTM D 4294 - 16E1	Max 3000.0	11.3	11.7
Calculated cetane index	ISO 4264	48.00-55.00	55.69	64.47
Win amostia missosita (aCt) @	40 °C b V: a set a set	and the (a St.) @ 50	°C	

Table 1: Physical properties of the resultant liquid oil product in both PP and LDPE waste plastics

^a Kinematic viscosity (cSt.) @ 40 °C; ^b Kinematic viscosity (cSt.) @ 50 °C

Several studies have reported higher calorific values in the range of 9960 - 10557 kcal/kg from the oil produced from different plastic feedstocks including PP, LDPE, high-density polyethylene (HDPE), and mixtures of these plastics (Onwudili et al., 2009; Sharuddin et al., 2016; Miandad et al., 2019). The energy values reported were very closer to the commercial grade diesel and gasoline (Sharuddin et al., 2016). In addition, Lee et al. (2015) and Rehan et al. (2016) studied the potential of using fuel oil produced in pyrolysis for electricity generation in diesel engines. Moreover, many researchers employed the produced liquid oil as transportation fuel after blending with conventional diesel at different ratios (Kumar et al., 2013; Budsaereechai et al., 2019; Gupta et al., 2019; Praveenkumar et al., 2022)

Table 2 shows the distillation data of waste PP and waste LDPE fuel oils. These results show the variation of short-chain hydrocarbons and longchain hydrocarbons in the resultant fuel oil.

Volume (%)	Boiling point (°C)	
	Waste PP	Waste LDPE
Initial boiling point	63.0	93.0
10	129.0	163.0
20	151.0	190.0
30	163.0	222.0
40	197.0	246.0
50	238.0	268.0
60	265.0	294.0
70	300.0	304.0
80	335.0	330.0
85	348.0	338.0
90	350.0	354.0
95	-	374.0
	Residue (mL)
	6.6 (Brown colour)	4.5 (Waxi-type residue)

Table 2: Distillation results/ Boiling point distribution of waste PP and waste LDPE

The fuel oil produced from the PP waste sample has much lower boiling points than that of oil generated from waste LDPE (Table 2). Therefore, to produce fuel oil from the PP waste pyrolysis requires lower heat energy than that of the heat energy of waste LDPE. In that case, it can be concluded as the longchain hydrocarbon fraction is higher in the waste LDPE fuel oil sample than that in the waste PP sample. Further, long chain hydrocarbons require more heat energy to enter the vapor phase. Therefore, lower chain hydrocarbon fraction may be employed more in the waste PP oil sample.

Conclusions

Waste PP and waste LDPE pyrolysis were carried out using a low-cost, lab-scale pyrolysis system. The results indicated that the type of feedstock used in pyrolysis affects the resultant product yields and the properties of fuel oil. The fuel oil fraction formed from the pyrolysis of waste PP was higher than the amount formed from PE pyrolysis. The properties of the resultant fuel were nearly closer to the commercially used diesel fuel. With aid of suitable catalysts, the quality of the fuel oil formed can be further enhanced for commercial products.

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Conflicts of interests

The authors declare no conflicts of interest.

Author contributions

PGIU; conducted all the experiments, data analysis and prepared the original draft. DSMDS; supervision, funding acquisition, writing, review, critical feedback, and editing. VPAW; supervision, writing-review, critical feedback, and editing. JKP; supervision, writing-review, critical feedback, and editing. TVS; supervision, review, critical feedback, and editing.

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