Indian Journal of Chemical Technology
Vol. 25, July 2018, pp. 336-344

Production and characterization of pyrolysis oil using waste polyethylene in a semi batch reactor

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Received 6 October 2016; accepted 4 August 2017

Plastic waste, polyethylene has been used as a feed stock for the production of valuable hydrocarbons via thermal pyrolysis. The thermal pyrolysis of waste polyethylene has been investigated in a specially designed semi batch reactor with L/D ratio of 1.2. Polyethylene sample of 50 g is used as feed using different reaction temperatures from 500-800°C. The reaction time of 30 min is maintained irrespective of variation in other experimental conditions. The pyrolysis oil are characterized using API gravity, flash and fire point, calorific value, carbon residue, proximate analysis, ASTM distillation and GC-FID, The maximum liquid yield of 72.6% is obtained at a temperature of 800°C, whereas the liquid yield was 61.5% at the temperature of 500°C. Though the liquid yield is maximum at 800°C, the pyrolysis oil solidifies at 32°C, which indicates higher paraffins are more. The solid char produced was minimum (9.4 wt %) at 800°C and it was maximum (20.44 wt. %) at 500°C. There is minor change in gaseous hydrocarbon yield irrespective of pyrolysis temperature. The liquid yield obtained at 700°C exhibit the properties similar to commercial diesel with boiling point range 270-320°C i.e., similar to beyond 50% distillate recovery as tested in ASTM D86. GC-FID tests of pyrolysis oil (700°C) gives comparable GC characteristics of commercial diesel.

Keywords: ASTM distillation, GC-FID, Hydrocarbon, Waste Polyethylene.

Plastics are durable, adaptable and low cost material used in industrial and domestic needs due to their light weight, mechanical strength and chemical resistance. Low density polyethylene (LDPE) polymer is the third largest product, plastic material in the world, after polyvinyl chloride and polypropylene in terms of volume. However, plastics are non-biodegradable and execute an ever growing environmental problem[1]. It is also evident that many countries have imposed banned on plastic uses due to the environmental problem. However, this can’t solve the plastic waste disposal problem entirely.

Nowadays, pyrolysis of plastic waste has become an environment-friendly method for altering and upgrading plastic solid waste into valuable fuel or chemicals[2]. This is to attain efficient recovery of raw materials and energy in order to reduce usage of waste plastic in landfill and incineration. Pyrolysis of polyethylene (PE) is frequently employed to determine the potential application of pyrolysis in plastic recycling by discovering the operative conditions and the liquid products generated in experiments[2-5]. Most of the previous works were carried out under very different conditions and the results were condition-related closely, which is disadvantageous in investigations of reaction paths for PE thermolysis[2]. Particularly, experimental approaches could hardly capture the changes at the atomic level directly. The research engineers and scientists have spent decades trying to advance the pyrolysis process and bring back the waste plastic into the manufacturing line by generating high quality chemicals and alternative fuel-like products[6]. Presently, the main focus has been on the development of an appropriate catalyst and reactor configuration that can achieve desired products.

The thermal degradation of polyethylene has been the subject of numerous studies by researchers who investigated distribution of the products generated and their composition[7,8]. The batch or semi-batch reactors were used in most of the researches for thermal and catalytic pyrolysis of virgin plastic, as well as post-consumer plastic waste, as the process parameters could be easily controlled. Some of the important parameters that were known include reaction temperature, weight ratio of plastic to catalyst, and reaction time. The reaction temperature was in the range of 300-900°C and the reaction time 30-90 min[9,10] for pyrolysis process. William *et al.*[11] studied the effect of reaction temperature ranging from 500 to 700°C on the composition of the products obtained from LDPE pyrolysis. On increasing reaction temperature led to a significant increase in single and polycyclic aromatics in the derived oil that necessitated further treatment. The carbon number distribution of the wax sample was from C11 to C57, while the oil sample was from C8 to C44. Analysis of the oils showed that at the higher pyrolysis temperatures, the concentration of aliphatic species above about C30 was greatly reduced. It was also found that for the oils, the diene/alkane ratio increased for each carbon number as the pyrolysis temperature was increased from 500°C to 700°C. Shah *et al.*[12] performed thermal pyrolysis of LDPE bags at 275°C and produced 48.6 wt. % liquid, 40.7 wt. % gaseous and rest 10.1 wt. % was residue. This result was comparable to some thermal pyrolysis process in batch reactor[13] and fixed-bed reactor[14] in laboratories. Tan *et al.*[15] revealed that extension of reaction time resulted in improved liquid product quality, but coke formation also increased. It was proposed that coke was formed from condensed asphaltenes, which existed in heavy oil itself. The liquid product formed from plastic pyrolysis was found suitable for the use as fuel in most tropical climate region. However, high pour point may be a problem in colder regions. Achilias *et al.*[14] suggested that after appropriate advancement, pyrolysis liquid can be combined with commercial gasoline or diesel and used in combustion engines. Jung *et al.*[16] studied the pyrolysis of PE and obtained liquid products (60 wt. %) confined 32% benzene, toluene and xylene (BTX) compounds and showed that the production of BTX increased with reaction temperature.

In this work, the pyrolysis of low density polyethylene (LDPE) waste material was considered for investigation in a specially designed semi batch reactor using thermal pyrolysis techniques to obtain optimum temperature to achieve high liquid yield very similar to diesel and kerosene fuel. The pyrolysis oil was thoroughly characterized to check the suitability of use in diesel engine.

Experimental Section

The analysis of municipal plastic wastes shows that major amount of it contains polyethylene which is about 41.5 wt. % reported in Table 1 and has been reported in the published literature[17]. Thus, the raw material waste polyethylene (PE) was collected from the municipal dumping zone, as the municipal waste is a source of used polyethylene. The PE waste, mostly “carry bag” was first subjected to water washing and dried in open sunlight. The dried polyethylene was cut into small pieces using scissors manually. This was done to increase the heat transfer surface area of the material during melting process.

Experimental set up and method

Figure 1a shows the schematic of experimental set up of pyrolysis process consist of a semi batch reactor (Fig.1b). The polyethylene sample of 50 g was filled in reactor made of mild steel with 123 mm outer diameter, 112 mm inner diameter and 135 mm height. The dimension of the reactor was fixed based on standard design criterion of appropriate L/D ratio of 1.2. This increases the path length for vapour recirculation inside the reactor.

The nitrogen gas was introduced into reactor at the rate of 10 mL/min to ensure there is no oxygen in reactor as shown in Fig. 1c. The pyrolysis experiments of PE were performed at different temperatures of 500, 600, 700 and 800°C. The time for each set of experiments were maintained for 30 minutes. The vapour produces inside the reactor was collected using a pipeline which was connected at the top of the reactor. The pipeline was attached to a copper tube condenser followed by an ice bath to decrease the vapour temperature gradually and reduce the vapour loss at the collecting end. The pipeline was covered with wet jute to enhance rate of vapour cooling. Two conical flasks in series were kept in the ice bath and pyrolysis oil was collected as condensate. The produced gas was trapped using gas holder.

Analysis of the reaction products

ASTM distillation

ASTM distillation of pyrolysis oil was obtained using ASTM D86 method. In this test 100 mL of

Table 1 — The composition of municipal plastic waste

Name of plastic materials	Composition (wt. %)
Polyethylene (PE)	41.5
Polypropylene (PP)	24.3
Poly ethylene terephthalate (PET)	12.8
Poly vinyl chloride (PVC)	2.9
Poly lactic acid (PLA)	0.2
Poly styrene (PS)	6.6
Others	11.7

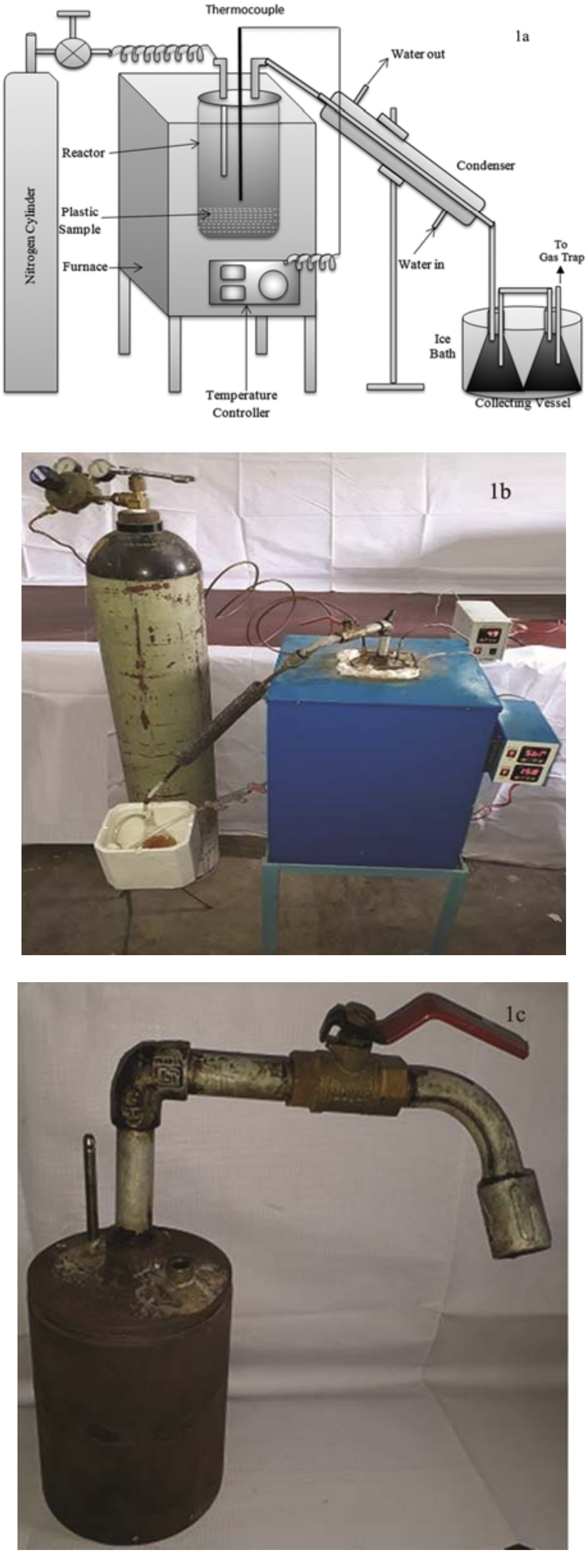

Fig. 1 — (a) Schematic of experimental set-up, (b). Semi batch reactor. (c) Nitrogen introduced in reactor.

sample is distilled in a standard flask. The distillate was condensed in a brass tube condenser, surrounded by crushed ice-water mixture to maintain temperature at 0°C. First drop from the condenser must be available in 5 to 10 min after heating started, at which the recorded temperature was mentioned as initial boiling point (IBP) of the sample. The vapour temperature was recorded at each successive 5 mL distillate collected in a measuring cylinder. The test continues in the same way till the bottom of the flask shows dryness, the temperature recorded corresponds to final boiling point (FBP). The percentage distillate collected after condensation of vapour and its corresponding temperature was recorded to get the experimental ASTM distillation characteristics. The experimental characteristics were compared with the standard plot as reported in standard literature[18].

Flash and fire point

Flash and fire point of pyrolysis oil were obtained using Cleveland open cup apparatus (ASTM D 92). Flash point is defined as the minimum temperature at which the vapours from oil sample will give a momentary flash on application of standard flame under specific test conditions. The pyrolysis oil was filled up to the mark and the temperature of the oil was slowly and uniformly raised at a rate of 3°C per min. Test flame was lighted and spring handle was rotated at every 1°C raise in thermometer. When oil sample burns momentary or flash occurred, flash point temperature was noted. Fire point temperature was noted when the oil vapours can burn continuously for at least 5 s and it occurs after the flash point, by 3-4°C.

Carbon Residue

Carbon residue of pyrolysis oil was obtained using Ramsbottom Carbon Residue Apparatus (IP 14/65). The sample of 1 g was carefully fed into a glass coking bulb which has a capillary end. The coking bulb was kept in a heating lead bath at a temperature of 550°C. The oil sample was allowed to decompose for 20 min. After heating is over, the bulb is cooled and weighted to find the carbon residue formed. This was done to check the propensity of cracking of pyrolysis oil at high temperature.

American Petroleum Institute (API) gravity

The API gravity of pyrolysis oil is calculated using the oil sample specific gravity, which is the ratio of density of oil to that of water$\left(\frac{15.6^\circ C}{15.6^\circ C}\right)$. The API gravity of the pyrolysis oil sample was calculated by the following equation (1):

$$\text{Deg. API} = \left(\frac{141.5}{\rho_{\text{pyrolysis oil}}}\right) - 131.5 \qquad \ldots(1)$$

where, $\rho_{\text{pyrolysis oil}}$ = specific gravity of fraction at $\left(\frac{15.6°C}{15.6°C}\right)$

The API gravity is used to classify oil as light, medium, heavy, or extra heavy. As the "quality" of oil is the largest determinant of its market value, the API gravity is exceptionally important for each fraction of oil sample. The oil quality and types are reported as follows[19]:

Light oil :Deg. API > 31.1
Medium oil :Deg. API between 22.3 and 31.1
Heavy oil :Deg. API < 22.3
Extra Heavy oil :Deg. API < 10.0

Proximate analysis

Proximate analysis of solid residue (coke) was done following ASTM test methods (IS 1350-1959). This is an assay of the moisture, volatile matter, ash content and fixed carbon of a solid sample. The moisture content was determined by the weight loss that a sample undergoes after it has been heated at a temperature of 108°C for 30 min. The determination of volatile matter is an empirical test in which the loss in weight experiences by 1 g of sample is estimated in crucible with lid to ensure absence of air when carbonised at 925°C temperature for 7 min. is estimated. The loss is partly made up of moisture in the sample and thus true volatile matter is obtained by subtracting the moisture content of the sample. Ash content is the residue that remains after the sample undergoes complete combustion as per test method ASTM (IS 1350-1959). In ash content test first stage of heating of sample was done at a temperature of 425°C temperature using crucible with lid for 30 min and second stage at a temperature of 775°C using crucible without lid for 60 min in a muffle furnace to ensure complete combustion.

Gross calorific value (GCV) analysis

The bomb calorimeter (IP 12/63T) was used to determine the GCV of solid residue (coke) and pyrolysis oil. The GCV test was performed by weighing 1 g of sample. The sample was kept inside the bomb and the bomb was charged with oxygen from a cylinder to a pressure of 25 atm. The sample was ignited and the change in temperature at equal interval of time was recorded until it reaches at steady state. Finally GCV was calculated using standard calculation method as specified in IP 12/63T.

Gas chromatography (GC) analysis

The compositional analysis of bio-gas was evaluated by gas chromatograph (NUCON 5765) using flame ionization detector (FID) with a SE-30 10% chromosorb W packed stainless steel column (2 m × 2 mm). Nitrogen was used as a carrier gas at the rate of 40 mL min^{-1}. The oven column temperature ranged from 70 to 230°C; programmed at 7°C min^{-1} with initial and final hold time of 10 min. Injector and detector temperatures were 220 and 230°C, respectively. The injection method was used for analysis of 1µl sample. The percentages of the individual constituents were calculated by electronic integration of the FID peak areas without response factor correction[20].

Results and Discussion

Product yield of thermal cracking

Figure 2 and Fig. 3 show that the yield (wt %) of pyrolysis oil increases with the increase in

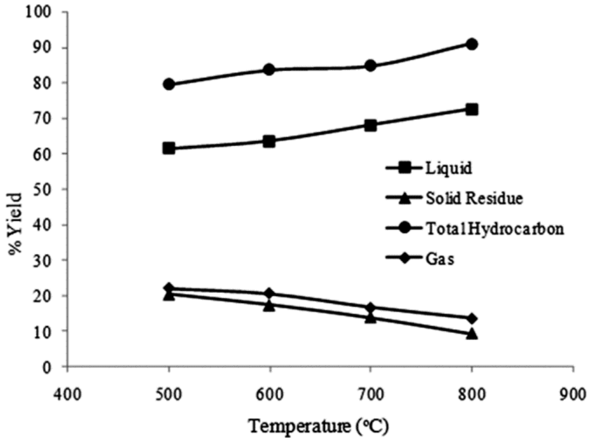

Fig. 2 — Product yield (wt. %) vs. temperature characteristics for thermal pyrolysis of polyethylene.

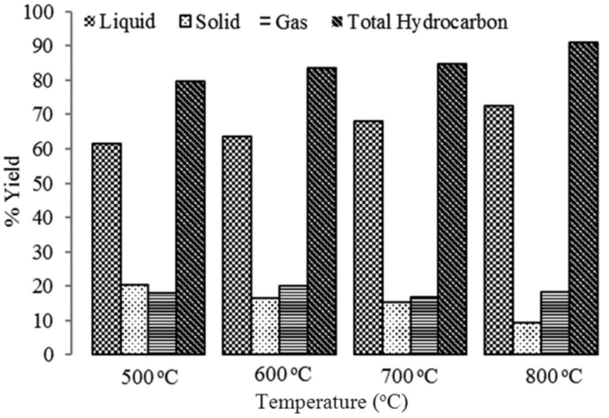

Fig. 3 — Comparison of % yield between liquid, gas, solid residue and total hydrocarbon obtained at different temperatures.

temperature. The pyrolysis oil yield of 61.54, 63.58, 68.02 and 72.66 were obtained at the temperature of 500, 600, 700 and 800°C, respectively. There was about 11 % increase in the pyrolysis oil when temperature was increased from 500 to 800°C. The high temperature does not allow the lower molecular weight hydrocarbon (mainly liquid range) to remain in the reactor for longer time. Thus, they enter in the condenser and collected as pyrolysis oil. Moreover, rate of repolymerization decreases at high temperature. In addition, with the higher amount of energy available at the higher temperature there is a tendency for an increased number of secondary reactions[21]. Thus, obtained coke is less at high temperature. On the other side, the large molecular weight hydrocarbon cracks down and form smaller fractions at low temperature process. Simultaneously, repolymerization of aromatic molecules also takes place at low temperature, which gives higher amount of coke compared to high temperature pyrolysis. The composition and properties of the pyrolysis oil were also determined using ASTM distillation and GC analyses to compare with the standard fuels.

Analysis of the product

ASTM distillation

The distillation or volatility characteristics of hydrocarbons have an important effect on their safety and performance, mainly in the case of fuels and solvents. The boiling point range gives information on the composition, properties, and behaviour of the fuel. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapours. The distillation characteristics are critically important for both automotive and aviation gasolines, affecting starting, warm-up, and tendency to vapour lock at high operating temperature or at high altitude, or both.

Figure 4 shows comparison between standard fuel[18] and pyrolysis oil obtained at different temperature. The boiling point range of pyrolysis oil obtained at temperature of 500, 600 and 700°C lies in between gasoline and kerosene for the recovery of distillate 0-30%. Similarly, the boiling point range of pyrolysis oil obtained at the temperature of 500°C lies in between JP-4 and kerosene for the recovery of distillate 30-95%. In addition, the pyrolysis oil obtained at 500°C tends to behaves as kerosene above 60% recovery. Whereas, interestingly pyrolysis oil obtained at the temperature of 600 and 700°C behave similar to diesel oil above 50% of distillate recovery (Fig. 4).

As we know, ease of starting is governed by initial boiling point (IBP) to 10% range boiling point. Lower IBP is preferred for cold climates. Vapour locking problem will be less and ease of starting will be excellent as the IBP of the pyrolysis oil obtained at the temperatures of 500, 600 and 700°C are 43, 43.5 and 44°C respectively, which are low. It is observed in Table 2 that 10% distillate temperatures are low for the pyrolysis oil obtained by thermal process irrespective of pyrolysis temperature. This indicates that flash point of the pyrolysis oils shall be lower than the kerosene and diesel. Which will results in better ignition and start up of automobile if the pyrolysis oils are used in the diesel engine after further processing. Rate of acceleration follows after the starting operation which is best judged by the mid region boiling point (30-60%). The pyrolysis oil obtained at 600°C and 700°C also meet the above criteria.

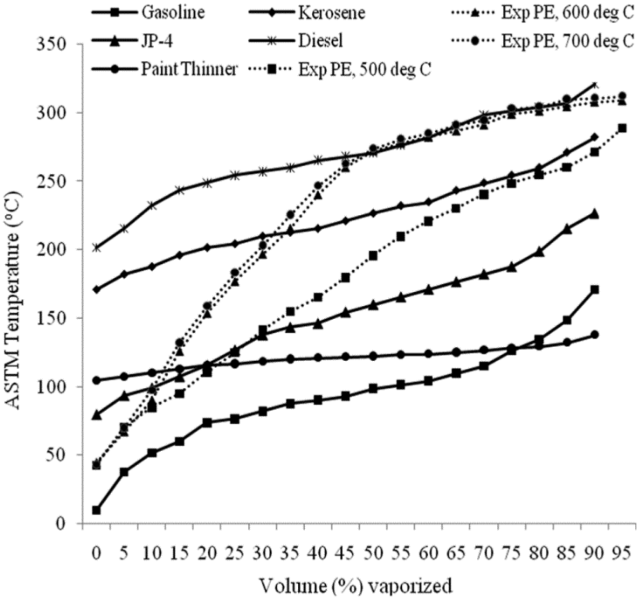

Fig. 4 — Volume percent vaporized vs. ASTM temperature characteristics of pyrolysis oil and standard fuel.

Table 2 — Important physical properties of pyrolysis oil obtained at 500, 600 and 700°C

Pyrolysis oil obtained at different temperature (°C)	IBP (°C)	10% Distillate temperature (°C)	50% Distillate temperature (°C)	90% Distillate temperature (°C)	FBP (°C)
500	43	90	196.1	271.4	276.5
600	43.5	90	270.2	304.2	311.4
700	44	97.7	273.8	310	318

Flash and fire point of pyrolysis oil

Flash and fire point of the pyrolysis oil obtained at the temperatures of 500, 600, 700 and 800°C are shown in Table 3.

Flash point and fire point of diesel fuel are 55 and 62°C, respectively. whereas, for kerosene these are 38 and 46°C, respectively[22]. Flash and fire point of pyrolysis oil are in the range of 35-36°C and 39-42°C, respectively irrespective of pyrolysis temperatures (Table 3). This indicates that the flash point of pyrolysis oil is comparable to the light petroleum distillate fuel e.g., kerosene and diesel. Thus, during handling and storage of pyrolysis oil, additional precautions are required.

Carbon residue of pyrolysis oil

High levels of carbon residue can however impair the combustion quality of the fuel oil, promoting increased wear and fouling of engine components. Carbon residue is the amount of carbon that is made by a chemical process, when oil is heated in absence of oxygen.

The diesel fuel and lube oil mainly, suffer from the deposition of carbon residue. As the diesel fuel contain aromatic compound, which favourably reacts via evaporation and repolymerization results in complex molecule structures that appears as carbon residue. Table 4 shows that the carbon residues of pyrolysis oil obtained at different temperature are in the range of 2.2-2.8 % (wt. %) which is very less. This implies that the aromatic content in the pyrolysis oil is less and have a less tendency for carbon deposition in diesel engine.

Table 3 — Flash and fire point of pyrolysis oil obtained at 500, 600, 700 and 800°C

Pyrolysis oil obtained at different temperature (°C)	Flash Point (°C)	Fire Point (°C)
500	35	39
600	36	41
700	36	42
800	35	41

Table 4 — Carbon residue of pyrolysis oil obtained at 500, 600, 700 and 800°C

Pyrolysis oil obtained at different temperature (°C)	Carbon residue (wt. %)
500	2.4
600	2.2
700	2.5
800	2.8

API gravity of pyrolysis oil

The API gravity of pyrolysis oil obtained at different temperatures are presented in Table 5. It is seen from Table 5 that the API gravity of pyrolysis oil obtained at the temperature of 500, 600, 700 and 800°C are greater than 31.1 Deg.

According to Tiab *et al.*[19] if the API gravity of oil > 31.1 the oil is designated as light oil. The light oil is composed of a high number of paraffins, which are straight and branched chain hydrocarbons that have high hydrogen to carbon ratio.

Proximate analysis of the solid residue

The proximate analysis of solid residue (coke) was performed to determine the parameters wt. % e.g. moisture, volatile matter, ash content and fixed carbon. The results of proximate analysis are shown in the Table 6. It is seen from the Table 6 that with the increase in pyrolysis temperature, the ash content, moisture and volatile matter decreases. The reason may be, at low temperature pyrolysis % yield of coke obtained is high than the high temperature pyrolysis which contain large molecule hydrocarbons and thus could be further decomposed to lower hydrocarbon. The volatile matter of 15.86 wt. % was obtained for the coke obtained at the temperature of 500°C. Whereas, the volatile matter of 7.91 wt. % was obtained for the coke obtained at the temperature of 800°C. The coke obtained was almost dry irrespective of pyrolysis temperature. Thus, moisture (wt. %) of all the residue (coke) were in the range of 0.39-0.21 wt. %. The ash content was 14.20 wt. % for the low temperature pyrolysis (500°C), whereas, it was 8.92 wt. % for high temperature pyrolysis (800°C). May be

Table 5 — API Gravity of pyrolysis oil obtained at the temperature of 500, 600, 700 and 800°C

Pyrolysis oil obtained at different temperature (°C)	Specific gravity	API Gravity (Deg.)
500	0.7381	60.2032
600	0.7599	54.7038
700	0.7684	52.6536
800	0.7818	49.4856

Table 6 — Proximate analysis of solid residue obtained at the temperature of 500, 600, 700 and 800°C.

Pyrolysis Temperature (°C)	Ash content (wt. %)	Moisture (wt. %)	Volatile matter (wt. %)
500	14.20	0.39	15.86
600	9.47	0.28	10.59
700	9.19	0.25	8.32
800	8.92	0.21	7.91

the low temperature process produces the coke containing more complex molecule resinous structure compared to the high temperature process. This results in high wt. % of ash at low temperature (500°C).

Calorific value of pyrolysis oil and solid residue

The gross calorific value (GCV) of pyrolysis oil obtained at the temperature of 500, 600, 700 and 800°C are summarized in Table 7.

The GCV of pyrolysis oil obtained at a temperature of 700°C was maximum i.e. 11360 Cal g^{-1}, whereas, it was minimum 8657.37 Cal g^{-1} for the pyrolysis oil obtained at the temperature of 500°C. The GCV of standard diesel, gasoline and kerosene are 10717 Cal g^{-1}, 11315 Cal g^{-1} and 11052 Cal g^{-1} respectively. Table 7 shows that GCV of pyrolysis oil obtained at the temperature of 600°C and 700°C are comparable to standard diesel and kerosene. The ASTM characteristics also give similar information for the pyrolysis oil (600°C and 700°C) to be very close to standard diesel and kerosene (Fig. 4). However, pyrolysis temperature 500°C produced the oil close to gasoline. The GCV of solid residue (coke) obtained at the temperature of 500, 600, 700 and 800°C were 2405.67 Cal g^{-1}, 2240.47 Cal g^{-1}, 2171.19 Cal g^{-1} and 1940.81 Cal g^{-1} respectively. This data shows that GCV of coke decreases with the increase in pyrolysis temperature. The, reason may be, the volatile matter content in solid residue is more at low temperature pyrolysis (500°C) compared to high temperature (800°C) as reported in Table 6.

Gas Chromatography

The reproducibility of experimental data were checked performing the experiment in three different batches keeping the pyrolysis conditions similar in all the experiments. Figure 5 shows the gas chromatography analysis of pyrolysis oils of batch-1, batch-2 and batch-3 using SE-32 column coupled with flame ionization detectors (FID). It is seen from Fig. 5 that the retention time and corresponding peaks of the GC analysis are in the same position for all three pyrolysis oils obtained in batch-1, batch-2 and batch-3. This ensures that the pyrolysis oil contains similar composition for all three batches.

Figure 6 shows the GC-FID of the pyrolysis oil derived by the pyrolysis of the polyethylene at 700°C, commercial kerosene oil and diesel oil. The chromatograms for pyrolysis oil (700°C) are very close to kerosene and diesel oil in the range between 7 and 18 minutes of retention time. This range may be specifically interesting for the pyrolysis oil (700°C) which contains major compounds, are similar as that of kerosene oil and diesel oil in terms of chemical structure[22]. However, within the retention time range 1 to 7 min and 18 to 20 min GC peaks are found for pyrolysis oil and diesel oil only and it may be because of compounds lining similar boiling point range. The

Table 7 — Gross calorific value of pyrolysis oil obtained at 500, 600, 700 and 800°C.

Pyrolysis oil obtained at different temperature (°C)	GCV (Cal g^{-1})
500	8657
600	10442
700	11360
800	10756

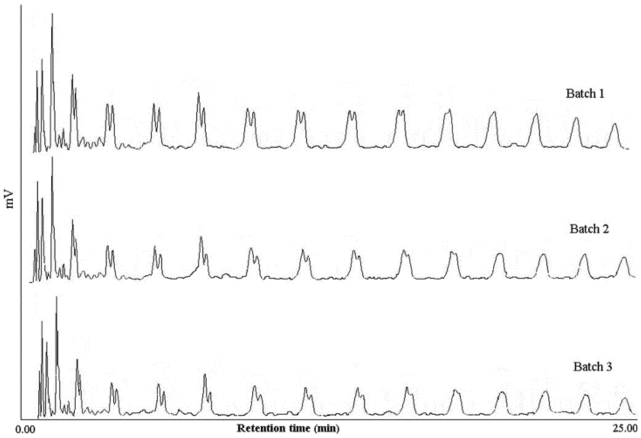

Fig. 5 — Gas chromatography characteristics of pyrolysis oil obtained at 500°C in three different batches batch-1, batch-2 and batch-3.

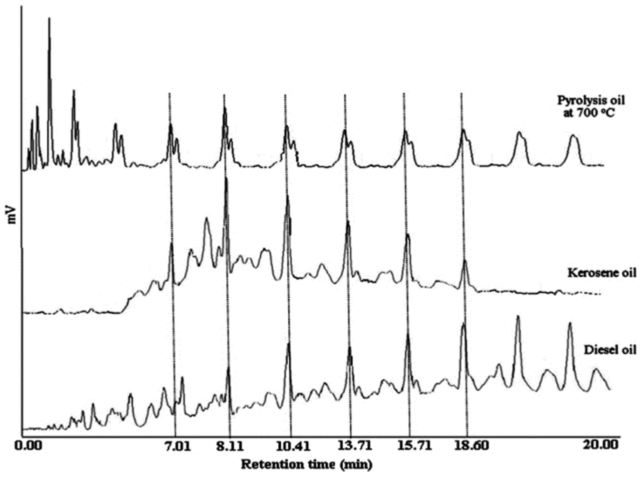

Fig. 6 — Gas chromatography characteristic of pyrolysis oil obtained from the polyethylene at a temperature of 700°C, Kerosene oil (commercial) and Diesel oil (commercial).

Table 8 — Comparison of peaks observed at about same retention time between pyrolysis oil (700°C), commercial kerosene and diesel.

Peak position at retention time for Pyrolysis oil (700°C) (min)	Area %	Peak position at retention time for commercial Kerosene(min)	Area %	Peak position at retention time for commercial Diesel (min)	Area %
0.72	2.02	Peak not observed	-----	0.72	0.03
0.82	0.55	Peak not observed	-----	0.80	0.03
0.97	0.25	0.96	0.01	0.95	0.01
1.14	5.74	1.12	0.01	1.12	0.07
1.61	0.50	1.58	0.01	1.56	0.15
1.98	3.26	1.95	0.01	1.92	0.55
2.87	0.66	2.82	0.01	2.82	0.05
3.19	0.02	Peak not observed	-----	3.22	0.54
3.65	2.25	Peak not observed	-----	3.60	0.27
4.06	0.59	3.99	0.47	3.98	2.98
4.67	0.01	Peak not observed	-----	4.71	2.21
5.22	0.63	5.24	2.00	5.19	4.26
5.57	2.84	5.65	0.86	5.60	1.57
6.14	0.06	Peak not observed	-----	6.19	0.04
6.40	0.18	6.49	6.07	6.41	1.16
7.01	0.52	7.02	8.18	6.95	2.42
8.11	0.02	8.14	0.98	8.06	0.62
8.35	0.03	Peak not observed	-----	8.40	1.41
9.55	2.68	Peak not observed	-----	9.55	5.71
10.10	0.02	10.01	0.11	10.01	0.43
10.41	0.17	10.43	0.30	10.40	1.79
11.63	2.37	Peak not observed	-----	11.71	5.95
12.54	0.10	Peak not observed	-----	12.56	0.50
12.85	0.03	12.91	0.74	12.89	2.46
13.71	0.49	13.76	10.14	13.74	6.07
14.44	0.05	14.37	0.02	14.45	0.19
14.95	0.01	Peak not observed	-----	15.03	1.58
15.71	0.32	15.68	2.94	15.69	5.54
16.66	0.05	16.60	0.22	16.64	1.61
18.60	0.06	18.52	0.13	18.62	4.01
19.33	5.35	19.29	0.26	19.42	6.96

important and prominent peaks obtained at same retention time for the pyrolysis oil (700°C), commercial kerosene oil and diesel oil are grouped and the results are shown in Table 8 for comparison, as it is difficult to find out the individual components and their isomers in the pyrolysis oil. Table 8 shows the retention time and peak % area of different components of pyrolysis oil (700°C), commercial kerosene and diesel from GC-FID. A comparison is shown to check the suitability of the use of pyrolysis oil in diesel engine and confirm its composition. It is clearly seen in the Table 8 that the retention time and corresponding peaks of the pyrolysis oil (700^{o}C) almost matched with majority of the components of diesel which are highlighted in the table. The ASTM distillation (Fig. 4) also substantiate the GC data of pyrolysis oil (700°C) to be in the line similar to diesel.

Conclusion

The experimental results of PE pyrolysis and analyses of products show that the process can be a very good option for production of valuable liquid hydrocarbon suitable for diesel engine. In addition, this method may possibly reduce the plastic waste load to dumping ground. Pyrolysis oil of mostly diesel range at a temperature of 700°C is produced with the proper selection of L/D ratio of the reactor of 1.2 and with the control of pyrolysis temperature. The maximum liquid yield of 72.6% at a temperature of 800°C is obtained by thermal pyrolysis with minimum amount of coke formation (9.48 wt %). However, the properties of pyrolysis oil at 800°C did not match with the diesel and kerosene. The pyrolysis temperature of 600°C and 700°C results in the liquid yield of 63.58% and 68.02% which are found to be similar to diesel after 50 % distillate. The flash point and fire point of pyrolysis oil are found to be in the range of diesel and kerosene irrespective of pyrolysis temperature. Lower amount of carbon residue of pyrolysis oil of 2.2 -2.8 wt % is an indication of low aromatic content. The maximum calorific value of pyrolysis oil is 11360 Cal g^{-1} for pyrolysis temperature of 700°C. GC-FID test of pyrolysis oil at 700°C, confirm it to be similar to commercial diesel. All these ensure that the pyrolysis oil contain low molecular weight paraffinic hydrocarbons may be suitable for the use in diesel engine and as domestic fuel.

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