Full Length Article

Valorization of packaging plastic waste by slow pyrolysis

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ABSTRACT

Low and high-density polyethylene (LDPE and HDPE) and polypropylene (PP) are three most common poly-olefins profusely used as packaging materials and abundantly found in the plastic waste stream. These plastic waste samples were collected from household waste and converted into plastic derived oil (PDO) by low temperature (300 °C to 400 °C) slow pyrolysis (long isothermal holding time) in a semi-batch reactor. The PDO samples obtained had shown variation in their compositions and fuel properties based on the pyrolysis temperature. PDO from the pyrolysis of PP has high octane number (~92) and low viscosity. Noticeably, the PDO samples obtained at low temperature pyrolysis are lighter with low viscosity, high octane number and having high calorific values. ^{1}H NMR analysis revealed that the oil samples mostly consist of paraffinic and olefinic hydrocarbons. Simulated distillation (SimDist) of PDO indicated that the liquid products resemble the characteristic closer to middle distillate of petroleum fraction having very low pour point and flash point. The temperature with long pyrolysis time also influenced the evolved gas composition and yield. Trace amount of hydrogen, carbon monoxide and carbon dioxide were present in the gaseous product along with various hydrocarbon gases ranging from C_1–C_5. The degradation mechanism follows end chain scission which produces monomer units whereas random scission results most of the hydrocarbon products. Subsequent reactions like radical recombination and inter or intra molecular hydrogen transfer results in the formation of most of the olefinic components.

1. Introduction

Plastics are a standard group of synthetic or natural materials, produced from high molecular chains consist of carbon as sole or major element. Plastics are highly durable, strong, elastic and less expensive to produce, which make them ideal choice for packaging and storage applications. The global production of plastics keeps on increasing, and so does the waste generation. The lifetime span of plastics products varies from weeks for packaging to several years for building appliances (Buekens, 2006; Lazarevic et al., 2010). Packaging plastics are major contributor to the vastly generated plastic waste. India produces more than 15000 tons of plastics waste per day, majority of which are packaging waste (Kamyotra and Sinha, 2016). The high calorific value of most of the plastics (manufactured from fossil fuel) urges one to reuse them productively. Packaging plastics, used containers, used toothbrush and broken plastic utensils are very common in the dry solid waste generated in any household. These plastics are also abundantly present in municipal solid waste (MSW). Low and high density polyethylene (LDPE & HDPE) and polypropylene (PP) are three major components of any plastic waste stream. Due to the lack of management from the governing organizations, the plastic waste goes to dumping

sites along with other waste materials. In India, 60% of total plastic waste is recycled and rest goes for landfilling and incineration with other solid waste (Kamyotra and Sinha, 2016).

Pyrolysis is one of the ubiquitous process converting organic materials into various useful forms via thermochemical decomposition at elevated temperature under oxygen starving environment. The major advantage of the pyrolysis process is the conversion of low energy density material into high energy density products. Over the years, pyrolysis has been adopted as an alternative approach to upgrade plastic waste into useful products. Although, large scale application of pyrolysis in plastic waste disposal is still lacking compared to landfilling and incineration due to the process economy (high energy consumption) and the complexity involved. Pyrolysis of plastics is generally carried out at fast heating rate to a final temperature up to 700 °C or at moderate temperature (~500 °C) in presence of catalyst (Chattopadhyay et al., 2016; Kaminsky et al., 1995; Kumar et al., 2011; Siddiqui and Redhwi, 2009; Williams and Williams, 1997a, 1999b). Fast pyrolysis increases the gaseous yield and the quality of liquid fuel produced requires post pyrolysis up-gradation for using in petroleum blends (Joo and Guin, 1998). Pyrolysis of individual and mix (Williams and Slaney, 2007) plastic have been studied and carried out in batch

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Table 1
Comparison of %yield and liquid product quality obtained from the pyrolysis of various polyolefins (LDPE, HDPE and PP) and various mix plastic studied in various literature.

Material	Process	Yield (% wt)			Liquid product quality	Reference
		Liquid	Gas	Residue		
LDPE	Fluidized bed reactor (T = 500 °C, 3 g/batch, t = 15 s)	89.2	10.8	0	Wax 49%; Oil 51%	Williams and Williams (1999a)
LDPE	Fixed bed reactor (T = 700 °C, β = 25 °C/min)	84.3	15.1	0	Wax	Williams and Williams (1999b)
LDPE	Spouted bed reactor (T = 450 °C)	80	20	0	Wax	Aguado et al. (2002b)
HDPE	Microwave induced pyrolysis (T = 500 °C)	81	19.0	0	Oil/wax	Ludlow-Palafox and Chase (2001a)
HDPE	Steam Fluidized bed reactor (T = 600 °C, 3.4 kg, t = 3 h)	41	31	28	87% aliphatic	Kaminsky et al. (1995)
HDPE	Batch autoclave reactor (T = 500 °C, P = 19.2 MPa, t = 1 h)	93	7	0	Unknown	Williams and Slaney (2007)
HDPE (Waste)	Batch reactor (T = 440 °C, t = 2 h)	74	9	17	Crude	Sharma et al. (2014)
HDPE	Two stage free fall reactor (T = 500 °C, 0.14 g/min, t = 20 min)	97.4	1.8	0.8	Oil/wax; 97.36% C5–C60 < 0.05% Aromatic	Mastral et al. (2006)
HDPE	Fixed bed reactor (T = 700 °C, β = 25 °C/min)	79.7	18.0	0	Wax	Williams and Williams (1999b)
HDPE	Spouted bed reactor (T = 450 °C)	80	20	0	Wax	Aguado et al. (2002c)
PP	Batch autoclave reactor (T = 500 °C, P = 19.2 MPa, t = 1 h)	95	5	0	Unknown	Williams and Slaney (2007)
PP	Fixed bed reactor (T = 700 °C, β = 25 °C/min)	84.4	15.3	0.2	Wax	Williams and Williams (1999b)
PP	Spouted bed reactor (T = 450 °C)	92	8	0	Wax	Aguado et al. (2002c)
PP	Batch reactor (T = 740 °C β = 10 °C/min)	48.8	49.6	1.6	> 40% olefins	Demirbas (2004)
Real waste (PE, PP, PS, PET, PVC)	Batch reactor (T = 500 °C, β = 20 °C/min, t = 30 min)	40.9	25.6	33.5	93.4% Aromatics	Adrados et al. (2012)
Simulated waste (PE, PP, PS, PET, PVC)	Batch reactor (T = 500 °C, β = 20 °C/min, t = 30 min)	65.2	34.0	0.8	73.9% Aromatics	Adrados et al. (2012)
Mixture (American plastic council)	Tubing bomb micro reactor (T = 445 °C, P = 800 psig, t = 60 min)	~85	~10	~5	Crude	Shah et al. (1999)

T = pyrolysis temperature; P = reactor pressure; t = residence time or reaction time and β = heating rate, PS = polystyrene, PET = polyethylene terephthalate, PVC = polyvinyl chloride and FBP = final boiling point.

(Onwudili et al., 2009), semi-batch (Lopez-Urionabarrenechea et al., 2012) and fluidized bed reactors (Costa et al., 2010; Kaminsky et al., 2004; Liu et al., 2006; Williams and Williams, 1997b, 1999b). Various other reactor configurations like conical spouted bed reactor (Aguado et al., 2002c; Elordi et al., 2009), rotary kiln reactor (Aguado et al., 2002a; Serrano et al., 2003), microwave pyrolysis (Ludlow-Palafox and Chase, 2001b; Undri et al., 2013) etc. have also been utilized. The recent review articles (Chaukura et al., 2016; Lopez et al., 2017; Miandad et al., 2016) summarize the overall waste plastics treatment schemes in detail. Table 1 summarizes the key results obtained from the pyrolysis of plastics (LDPE, HDPE, PP and their mixture) using various reactor configurations. However, the detail analysis of fuel properties of the pyrolysis products and the effect of pyrolysis conditions on fuel properties have not been reported.

Onwudili et al. (2009) investigated the effect of temperature (350–500 °C) and time duration (1 h and 2 h) on the compositions of the products obtained when pure LDPE and polystyrene (PS) and their mixture were pyrolysed in a pressurized batch reactor under inert N_2 atmosphere. They suggested that LDPE thermally degrades into oil at 425 °C, and the extent of oil production decreases beyond this temperature. Wong and Broadbelt (2001) studied the effect of long-duration by maintaining two moderate temperatures, 350 and 420 °C for 180 min and 18 h while performed the pyrolysis of polypropylene and polystyrene. They observed that the conversion of polypropylene increased with reaction time at 350 °C while no significant change happened at 420 °C beyond 90 min. Long reaction time can improve the product quality as heavier components decompose into lighter and low molecular weight products, which would be useful as fuels and chemicals. A detailed study considering the effect of reaction time at varying temperature on the quality of plastic pyrolysis products and their physical properties can be a useful insight to the applicability of such process in a more economical way. Properties of liquid products and gas composition were investigated in detail and it has been highly anticipated that the results obtained will ascend the understanding of the applicability and limitation of these waste materials as a feedstock for the production of alternative liquid fuel.

2. Materials and methods

2.1. Materials

The pyrolysis experiments were performed with both virgin and waste plastics. For the pyrolysis of individual plastics, virgin samples were used while the mixed sample was prepared using waste plastics. Virgin LDPE, HDPE, and PP were procured from Haldia Petrochemicals Limited, India. Physical properties of these plastics are reported in Table 2. The materials received were in pellet form of size around 3–5 mm. The collected materials were manually cut to make 1–2 mm average particle size before subjecting to thermal gravimetric analysis (TGA). Granulated samples were directly used for the lab scale pyrolysis experiments.

For a comprehensive understanding, waste samples of above three plastics were collected from household waste like packaging plastics, empty plastic containers, and bottles. Materials collected were cleaned and segregated according to their resin identification code. Dry samples were cut manually into small pieces of size 1–2 cm for the pyrolysis

Table 2
Physical properties of the materials.

Plastics	Density (kg/m³)	Glass transition temperature (°C)	Melting point (°C)
LDPE	934	− 125	111 ± 2
HDPE	950	− 80	132 ± 1
PP	900	− 10	168 ± 1

experiments. Segregated samples were mixed (RMIX) together in the proportion of 30 wt% LDPE, 30 wt% HDPE and 40 wt% PP. All hydrocarbon standards (ASTM D5307 internal standards) and gas sampling bags (Tedlar bags) were procured from Sigma Aldrich. Dichloromethane (HPLC grade) and deuterated chloroform (CdCl$_3$ of 99.8% purity), procured from Merck, were used to dilute the liquid products for analyses.

2.2. Experimental

Thermal degradation study was carried out for individual plastics using TGA (NETZSCH 209 F1 TG) equipment in inert environment (N$_2$ gas) with a flow rate of 60 ml/min (40 ml/min as purge and 20 ml/min as protective gas) at a heating rate of 10 °C/min. TGA analysis was carried out to determine the temperature range at which degradation occurs. Differential scanning calorimetry (DSC) instrument (Manufacturer: Metler-Toledo, DSC 1 STAR System) with a temperature range of −30 °C–200 °C at heating and cooling rates of 5 °C/min was used to determine the melting points while densities and glass transition temperatures were provided by the manufacturer.

Thermochemical conversion of plastics to plastic derived oil (PDO) were conducted in a semi-batch tubular reactor (SS 316) having a capacity of 1000 ml, heated externally by a tubular electrical furnace, controlled by a PID controller (reactor temperature) supplied by Dass & Co. (India). Based on the TGA data, three pyrolysis temperatures (350, 375 and 400 °C) were selected for all the experiments except for the pyrolysis of PP (325, 350 and 375 °C) as the degradation range of PP is lower than LDPE and HDPE. The following processing sequence was adopted: samples were heated at a rate of 20 °C/min and subsequently held at the final temperature for 8 h. The schematic representation of the experimental setup is shown in Fig. 1. 50 g sample was taken for each run. N$_2$ gas was purged continuously at a flow rate of 200 ml/min to maintain the inert environment inside the reactor and to sweep out the pyrolysis vapour products. Reactor outlet passed through a long glass condenser which takes the circulating cooling water below 5 °C from a water circulating chiller. The condenser outlet was then passed through a conical (side arm) flask submerged in an ice bath to confirm complete condensation of vapour effluent. The amount (by weight) of the collected liquid products were measured and stored in the refrigerator for further analysis. The uncondensed gaseous product coming out of the side arm flask were collected in the tedlar bags at regular intervals and rest of the time the gas was vented out. At the end of each experiment, the residue deposited at the bottom of the reactor was collected and weighed. The yield of non-condensable gaseous product was estimated by the difference.

2.3. Characterization of PDO

The characterization of PDO was carried out in both qualitative and quantitative manner. The compositional analysis of the PDO was performed with the help of analytical techniques like nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR) and gas chromatography with flame ionization detector (GC-FID). Attenuated total reflection (ATR) method in the wavenumber region of 4000–600 cm^{-1} was used for FTIR analysis. The physical properties like density (ρ), dynamic viscosity (μ) and calorific value were measured using pycnometer, rheometer (Anton Parr MCR 301) and bomb calorimeter (Parr 1341) respectively. Fuel properties like flash point (FP), pour point (PP) and cloud points (CP) were calculated using standard ASTM methods.

2.3.1. ^{1}H NMR analysis of PDO

NMR analysis was performed in an Ascend™ 600 (make: Bruker) spectrometer operating at 600 MHz. Samples were dissolved in deuterated chloroform and all the spectra were acquired at 25 °C. Chemical shifts were reported as ppm from tetramethylsilane (TMS) based on the lock solvent. Free induction decay file (from ^{1}H NMR) was analyzed in ACD 1D NMR software for post processing. ^{1}H NMR analysis was performed to identify the presence of various functional groups (paraffin, olefin and aromatic). The quantification of the compositions and determination of research octane number (RON) were accomplished based on the correlations given by Meyers et al. (1975a, 1975b), Joo and Guin (1998) and Sinag et al. (2006) utilizes these correlations successfully in the characterization of reformed plastic pyrolysis oil and oil obtained from the co-pyrolysis of lignite and LDPE respectively. These correlations entail several equations (Eqs. (1)–(6)), consisting of parameters *A*, *B*, *C*, *D*, *E* and *F* which represent the integrated area of the spectral regions, parts per million (ppm) from TMS reference peak as listed in Table 3 (Fig. S1). These correlations have been established based on the known standard mixture (with an error margin of ± 2%).

Aromatics, vol. %

$$= \frac{(A + C/3)0.97 \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B} \quad (1)$$

Paraffins, vol. % $= \dfrac{(D - 2B + E/2 + F/3)1.02 \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B}$
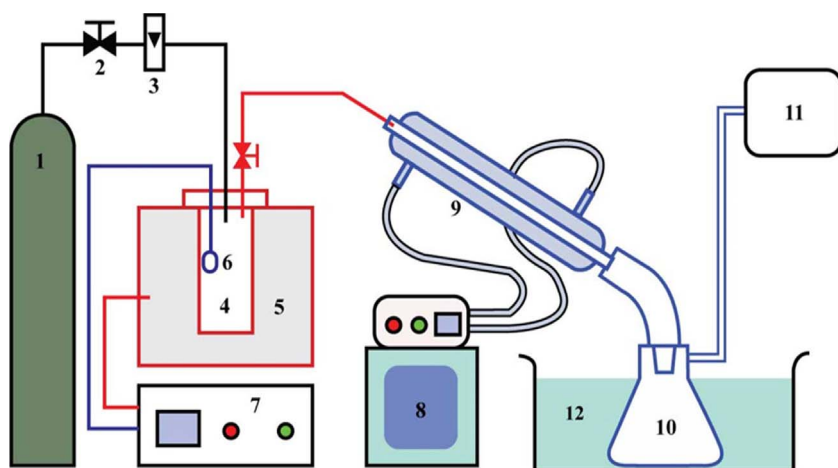
$$(2)$$

Fig. 1. Schematic representation of the semibatch pyrolysis setup.

1. Nitrogen cylinder, 2. Regulator valve, 3. Rotameter, 4. Pyrolysis reactor,
5. Tubular furnace, 6. Thermocouple, 7. PID controller, 8. Water circulator,
9. Condenser 10. Conical flash to collect liquid, 11. Tedlar bag, 12. Ice bath

Table 3
NMR spectral region (Meyers et al., 1975a, 1975b).

	Proton type	Chemical shift region
A	ring aromatic	6.6–8.0
B	olefin	4.5–6.0
C	α-methyl	2.0–3.0
D	methane (paraffins)	1.5–2.0
E	methylene(paraffins)	1.0–1.5
F	methyl(paraffins)	0.6–1.0

$$Olefins, vol. \% = \frac{3.33B \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B} \tag{3}$$

$$H/C = \frac{A + B + C + D + E + F}{(A + C/3)1.28 + (D - 2B + E/2 + F/3)1.02 + 3.42B} \tag{4}$$

It was established in petroleum studies that there is a close correlation exists between the amount of branching in the structure of a paraffinic hydrocarbon and its octane number (Albahri, 2003). A measure of the amount of branching is known as 'isoparaffin index' (Meyers et al., 1975a), which is the measured ratio of $CH_3:CH_2$ in the paraffin. The $CH_3:CH_2$ ratio for an unknown paraffin or a mixture of paraffins can be determined experimentally by nuclear magnetic resonance (NMR) spectrometry.

$$\text{Isoparaffin index} = CH_3/CH_2 = (F/3)/(E/2) \tag{5}$$

$$\text{RON} = 80.2 + 8.9 \text{ iso-paraffin index} + 0.107 \text{ aromatics (vol.\%)} \tag{6}$$

2.3.2. Simulated distillation (SimDist) analysis of PDO

Gas chromatograph (Make of Thermo Fisher, GC Trace 1110) installed with TR-Simdist (10 m × 0.53 mm × 2.65 m) column (Make: Thermo scientific) was used to execute the simulated distillation of the PDO samples by following the ASTM D5307 method. SimDist is a chromatographic procedure which translates retention times into boiling points. The GC oven temperature was programmed as, initially maintain at 40 °C for 2 min, then ramp at a heating rate of 5 °C/min to achieve 350 °C and then hold the final temperature for 5 min. The high purity N_2 gas was used as a carrier gas with a flow rate of 8 ml/min and 2 μl of diluted sample was infused to the injector (360 °C). The detector temperature was maintained at 350 °C. Two internal hydrocarbon standards (ASTM D5307 from Supelco), 48182 (C_3-C_9) and 48179 (C_{10} to C_{44}) were used to determine the retention time of n-paraffins which help establishing the carbon number distribution of PDOs.

2.4. Gas chromatography (TCD and FID) for gases

The analysis of non-condensable gases was carried out with the help of gas chromatograph (Thermo Fisher, GC Trace 1110). The concentrations of hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2) were identified by using thermal conductivity detector (TCD). Flame ionization detector (FID) was used to determine the hydrocarbons (saturated and unsaturated) components. GC configuration for TCD and FID analysis has been summarized in Table 4. Gas standards (Chemtron science laboratories, India) with known concentrations were used to identify and quantify the components. The gross and net calorific values of dry gaseous products were calculated using the mixing rules (Lackner et al., 2013).

3. Results and discussion

3.1. Thermogravimetric analysis and semi-batch pyrolysis yield

TGA is a standard technique which measures the weight loss with time/temperature. The details of the procedure can be found in our

Table 4
GC configuration for both TCD and FID detection for the analysis of hydrocarbon gases.

Parameters	Analytical Condition	
	TCD	FID
Column (make)	60/80 Carboxen-1000 (Supelco)	TG-BOND Alumina (Thermo scientific)
Length	4.57 m	30 m
Int. Diameter	2.1 mm	0.53 mm
Carrier gas	Helium	Helium
Flow rate (Carrier gas)	30 ml/min	4 ml/min
Oven temperature program	40 °C (5 min) 200 °C at 5 °C/min	130 °C Isothermal
Injector temperature	150 °C	200 °C
Detector temperature	150 °C	200 °C
Sample injection	1.0 ml	1.0 ml

previous work (Das and Tiwari, 2017). Fig. 2 shows the TGA and DTG curves for LDPE, HDPE, PP and RMIX under non-isothermal (10 °C/min) condition in the temperature range of 200 °C to 600 °C. The degradation pattern of all three plastics was similar as it was perceived from the shape of the weight loss curves. The values of temperature at maximum degradation rate or peak temperature (T_{max}), temperature at which degradation started (onset temperature, T_o) and finished (end temperature, T_e) vary with source material. Lone peak of DTG suggested the overall single step degradation of all three materials. Degradation characteristics were found similar for LDPE and HDPE, since both have similar polymer backbone. Degradation of PP started at lower onset temperature (T_o) 300 °C due to the fact that every other carbon atom of PP polymer chain is a tertiary carbon which is responsible for branching. Branching makes the polymer chain weak and more susceptible to degradation then linear polymers like polyethylene. In case of RMIX (Fig. 2(d)), three peaks (DTG curves) were observed which indicate the maximum degradation points of individual plastics in mixture. Although RMIX having 40% PP, the first peak was observed at 460 °C (Fig. 2(d)) which is 20 °C higher than the maximum degradation temperature of PP. This is due to the synergistic effect when all three materials degrade together (Wong and Broadbelt, 2001). Detailed TGA analysis and kinetic study of the same materials has been carried out to establish the thermal degradation characteristic of individual plastics (Chan and Balke, 1997; Consea et al., 1996; Diaz Silvarrey and Phan, 2016; Kayacan and Doğan, 2008; Wu et al., 1993). Diversity in the maximum degradation temperature suggests the effect of molecular structure of the plastics in the degradation process (Das and Tiwari, 2017).

The yields of three main products obtained from the lab scale pyrolysis experiments; plastic derived oil (PDO), gas and residue are summarized in Table 5. In all the cases the yields of both PDO and gaseous products were significant. Oil yield was found maximum at higher reaction temperature and reverse trend was observed for gaseous products. The pyrolysis of PP produced the highest amount of PDO compared to other individual plastics. Higher yields of wax residue from LDPE and HDPE at lowest pyrolysis temperatures were achieved due to inorganic/char content and incomplete conversion as the feed need high activation energy (170–230 kJ/mol for LDPE and 140–230 kJ/mol for HDPE) compared to PP (130–170 kJ/mol) (Aboulkas et al., 2010; Das and Tiwari, 2017). Thus, increasing pyrolysis temperature or time to a certain extent may crack the unconverted plastic sample (feed) to increase the yields of gas and liquid. The PDO obtained at different temperatures may vary from light hydrocarbon oil (at low temperature) to moderately heavy hydrocarbon oil (at high temperature). Comparing the waxy residue to higher boiling vacuum gas oil fraction from petroleum distillation (Sharma et al., 2014) shows its potential to be used as lubricant base-stock and further refining (dewaxing/wax isomerization) may result API group II/III lubricant base oils.
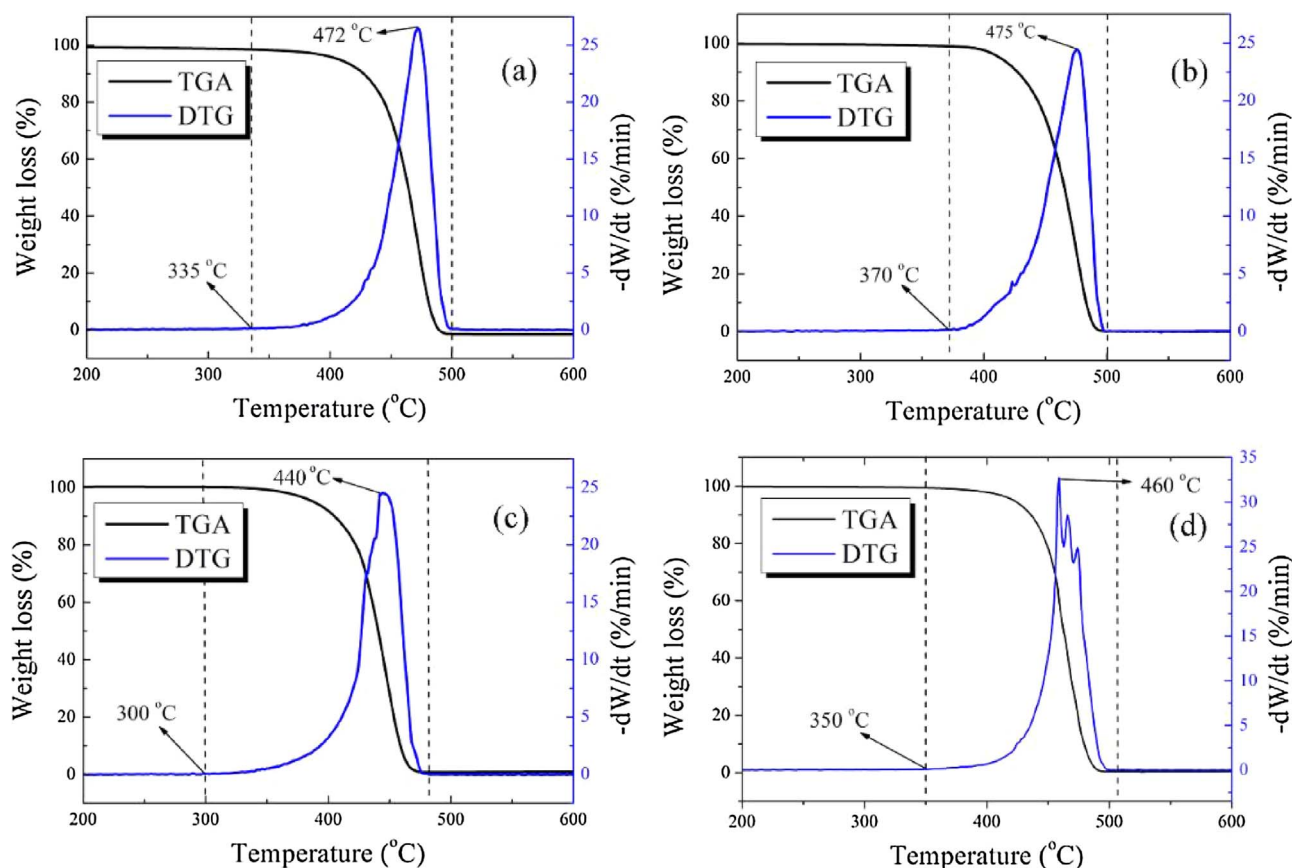
Fig. 2. Non-isothermal TGA and DTG analysis of (a) LDPE, (b) HDPE, (c) PP and (d) RMIX at 10 °C/min.

3.2. Liquid product analysis

3.2.1. FTIR and NMR analysis

Compositional analysis of PDO samples was accomplished using FTIR and ^{1}H NMR spectroscopy. Acquired data revealed that the hydrocarbon compositions are mainly dominated by paraffinic and olefinic groups. Since there was no aromatic ring in the main chain of the polymers, the presence of aromatics was found nearly negligible as it can be observed in Fig. 3. The signatures of FTIR (Fig. 4) spectra were found consistent with the ^{1}H NMR findings. The area of the spectrum between 3000 cm^{-1} and 2850 cm^{-1} demonstrated the presence of −CH$_3$, −CH$_2$ and C−H groups of highly aliphatic components in PDO. In addition, sp^3 C−H bending appeared in the range of 1470–1350 cm^{-1} as a set of two or more peaks. The peak near 3000 cm^{-1} (3075 cm^{-1}) was observed in the PDOs from PP indicated a sp^2 C−H stretch, which implies that PDOs from PP is highly unsaturated. Peaks in the vicinity of 1575 and 1675 cm^{-1} as well as those between 875 and 950 cm^{-1} indicated C=C stretches. A *mono* substituted double bond (RCH=CH$_2$) has shown two peaks in all the spectra: one at approximately 990 cm^{-1} and the other 910 cm^{-1}. Peak near 720 cm^{-1} pointed to the *cis* di-substituted double bond.

At different pyrolysis temperatures, the functionality of the PDOs

Table 5
Pyrolysis yield from individual and mix plastic and the PDO fractions obtained from SimDist analysis.

| Feed material	Pyrolysis temperature (°C)	Product distribution (%wt)			PDO fractions (%wt)		
		PDO	Gas	Residue wax	Light (C$_6$-C$_{11}$)	Middle (C$_{12}$-C$_{20}$)	Heavy (C$_{21}$-C$_{32}$)
LDPE (Virgin) (LDPE = 50 g)	350 °C	48.75 ± 2.55	21.27 ± 2.61	29.98 ± 0.6	11.72	80.12	8.16
	375 °C	71.56 ± 3.28	22.53 ± 2.09	5.91 ± 1.9	12.41	73.13	14.46
	400 °C	81.4 ± 2.57	16.58 ± 2.81	2.02 ± 0.33	12.63	58.64	28.73
HDPE (Virgin) (HDPE = 50 g)	350 °C	49.28 ± 3.66	27.52 ± 2.71	23.2 ± 1.35	29.52	66.8	3.68
	375 °C	76.73 ± 2.55	22.14 ± 1.85	1.13 ± 0.77	17.6	73.7	8.7
	400 °C	81.48 ± 3.05	17.8 ± 2.11	0.72 ± 0.51	12.32	76.38	11.3
PP (Virgin) (PP = 50 g)	325 °C	54.02 ± 5.36	29.79 ± 3.5	16.19 ± 1.86	34.89	61.79	3.32
	350 °C	81.31 ± 1.81	16.8 ± 0.89	1.89 ± 0.36	32.01	58.54	9.46
	375 °C	81.97 ± 2.47	17.26 ± 2.36	0.77 ± 0.11	30.33	56.64	13.03
RMIX (from waste) (LDPE = 15 g; HDPE = 15 g; PP = 20 g)	350 °C	57.3 ± 3.65	26.98 ± 2.68	15.72 ± 2.3	27.24	69.04	3.72
	375 °C	71.44 ± 1.7	28.21 ± 2.99	0.35 ± 0.2	26.54	62.84	10.62
	400 °C	76.38 ± 2.12	23.22 ± 1.49	0.4 ± 0.15	12.44	60.39	27.17
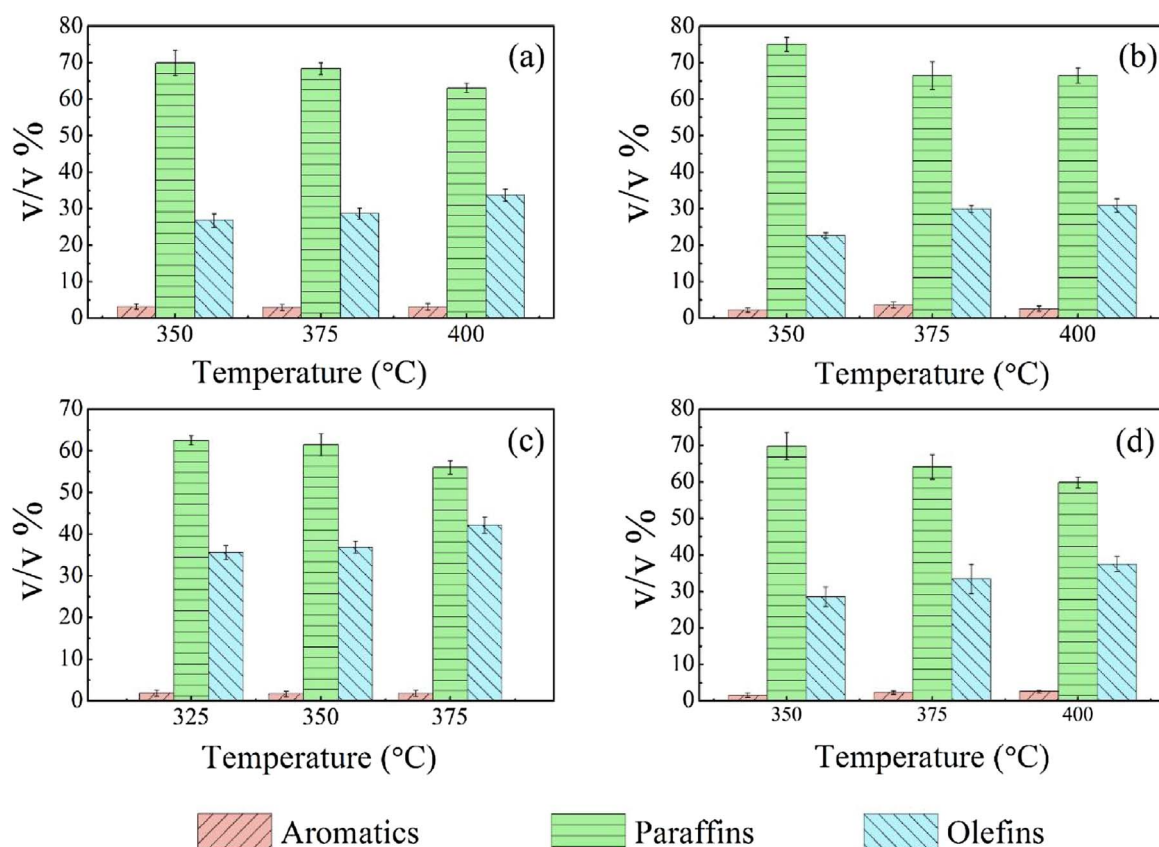
Fig. 3. Volume fraction of paraffin, olefins and aromatics of the PDO at various isothermal pyrolysis temperature for (a) LDPE, (b) HDPE, (c) PP and (d) RMIX.

constituents remained consistent. Practically identical elucidations have been reported in literature (Sharma et al., 2014; Williams and Williams, 1997a,b). Williams and Williams (1997a) described the stretches around 1650 cm^{-1} at higher temperature due to the presence of dienes and broadening of peaks (unsaturation) at 2850 and 2950 cm^{-1} with increasing temperature. Quantification of hydrocarbon compositions of PDOs was carried out by ^{1}H NMR spectroscopy using the correlations provided by Meyers et al. (1975b). Paraffin and olefin concentrations of the PDOs were found in the range of 60–70% and 30–40% respectively. The results (Fig. 3) showed that the oil derived from PP is relatively more olefinic and, the paraffins concentration reduces and olefins concentration increases with temperature. The similar trend was also observed by Marcilla et al. (2009) under dynamic temperature conditions. This is because of the presence of one extra methyl group in every other carbon atom in the PP polymer chain, which according to Pinto et al. (1999) stabilizes the intermediate radicals by forming double bond between two carbon atoms. At elevated temperature, polyethylene (PE) and polypropylene (PP) undergo random scission and create radicals. The radicals then undergo β-scission to produce monomers which are stabilized by intra-molecular or intermolecular hydrogen transfer. Successive β-scission reactions of the secondary radicals prompt the formation of olefins and dienes. On the other hand, the intermolecular hydrogen transfer leads to the formation of paraffins. At high temperature, the chances of successive β-scission with intramolecular hydrogen transfer is highly anticipated due to the abundance of hydrogen atom in the radical chain.

Isoparaffin index and research octane number (RON) of the PDO samples obtained from the feed considered are reported in Table 6. It can clearly be observed that the PDO from PP possess higher RON (> 91) value compared to the oil produced from LDPE and HDPE. This is primarily due to the higher content of the olefins in the PDO from PP (Fig. 3), Increase in olefin yields with increase in temperature also attributes to higher values of isoparaffin index and RON.

3.2.2. Simulated distillation (SimDist) analysis of PDO

A profound effect of the temperature on carbon number distribution of the oil sample was established from SimDist analysis (Figs. S2 and S3) and the oil fractions were grouped (by %wt) as light (C_6-C_{11}), middle (C_{12}-C_{20}) and heavy (C_{21}-C_{32}). Table 5 shows that the light fraction decreases while the heavy fraction increases with increase in temperature and the major quantity of PDO belongs to the middle fraction. More than 30% PDO obtained from the pyrolysis of PP belongs to the range of lighter fraction which is higher compared to the light fraction in the PDOs obtained from other source materials. This higher quantity of lighter fraction (from PP) also prompted to high RON value (> 91) determined from NMR analysis.

The boiling point distribution curve with cumulative yield for the PDO obtained from RMIX feed is shown in Fig. 5. It can be observed that around 90% yield of the liquid (distilled under 350 °C) was obtained for the first two pyrolysis temperatures (350 °C and 375 °C), which is the range of most of the middle distillates like kerosene and diesel while the yield decreases to 70% at 400 °C. The pyrolysis experiments carried out for a long duration of 8 h under low-temperature conditions selectively produce light to moderate liquid hydrocarbon (C_6-C_{20}) product from the chosen plastic waste.

3.2.3. Fuel properties of PDO

The PDO samples obtained from the pyrolysis process at various conditions have the similar attributes like the existing refinery end product like gasoline and diesel (middle distillates). The fuel properties (estimated using ASTM methods) of all the PDO samples are summarized in Table 6. The pyrolysis temperature and feed quality have substantial influence on the fuel properties of the end products. High calorific values (> 45 MJ/kg) were estimated for all the samples. The oils have low viscosity and the viscosity of the PDO increased with the increase of pyrolysis temperature due to the abundant presence of long-chain hydrocarbons in the liquid product obtained from high-
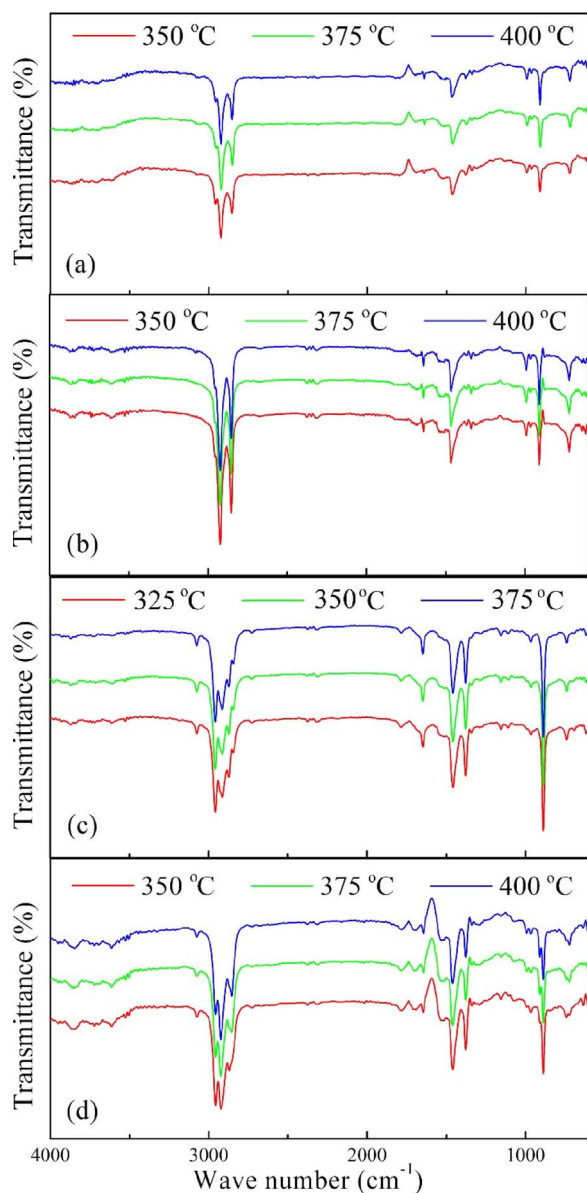
Fig. 4. FTIR-ATR spectra of PDO obtain at three pyrolysis temperature a) LDPE, b) HDPE, c) PP and d) RMIX.

temperature pyrolysis. The PDO samples from PP were found with low density, high research octane number (RON) and low cloud point (CP) and pour point (PP). The high concentration of olefins in the oil sample makes the product less susceptible to form crystals at a lower temperature (Sweeney, 1970). The liquid products from the mixed feed

(RMIX) exhibited the characteristics of a middle distillate (diesel) petroleum product, having calorific value around 47 MJ/Kg, viscosity as low as 0.09 cP (at pyrolysis temperature 350 °C) and comparable pour point (−2 °C) and flash point (35 °C).

Conventional Indian diesel standard (BSIII) (Guttikunda and Mohan, 2014) has pour point values of 3 °C (winter) and 15 °C (summer) and flash point of 35 °C (Abel) and 66 °C (Pensky Martens closed cup) (Lance et al., 1979). It is clearly noticeable that the fuel properties of the PDOs from both PE and RMIX are equivalent to diesel (Table S1) as around 70% of the PDO belongs to the carbon number range of C_{11}-C_{20}. With high RON and low pour point values, the PDO from PP has shown more gasoline like characteristic, thus it can be considered a possible blend component for gasoline with minimum chemical reforming. Hence, simply increasing the pyrolysis time at moderate temperature the plastics can be converted into alternative liquid fuels. Sharma et al. (2014) upgraded the fast pyrolysis liquid product from HDPE waste (grocery bags) by distillation. A direct comparison can be made with the slow pyrolysis end product with the fast pyrolysis distilled product as most of the properties like density, calorific value, cloud point, pour point and flash point etc. are under corresponding range.

3.3. Pyrolysis gas analysis

Plastics have carbon and hydrogen in their polymer backbone, so the thermal degradation process at an elevated temperature with a long pyrolysis time leads to the production of significant amount of hydrocarbons gases. The pyrolysis gas evolution pattern and its compositions demonstrate a comparative trend for all the feed (Williams and Williams, 1999b). The gaseous products collected at various interval during the pyrolysis of RMIX were identified and the average volume% are reported in Table 7.

Methane, ethane, ethylene, propane, propylene, *n*-butane, 1-butene and *n*-pentane were found in significant quantities. A trace amount of permanent gases like hydrogen, carbon monoxide and carbon dioxide were also present, possibly due to the presence of any impurity in the feed. The unsaturated hydrocarbons like ethene, propylene and butene and their derivatives were also observed, which actually produce due to random scission degradation mechanism of plastic followed by stabilization of the intermediate radicals. The concentrations of hydrogen, carbon dioxide and carbon monoxide decreased with the decrease of pyrolysis temperature. Nitrogen free gross calorific value (GCV) and net calorific value (NCV) of the gases were found in the proximity of 105 MJ/m^3 and 96 MJ/m^3 which favor its potential utilization as fuel gas.

3.4. General aspects of pyrolytic degradation mechanism of plastics

The thermal degradation mechanisms of plastics evolved from three general polymer chain reactions viz. polymeric chain scission, side group reaction and recombination reaction (Moldoveanu, 2005). Under

Table 6
Characterization of PDO sample.

| Feed Material		LDPE			HDPE			PP			RMIX		
Temperature, °C		400	375	350	400	375	350	375	350	325	400	375	350
Density, kg/m^3	Pycnometer	807	804	803	810	808	804	794	790	790	802	800	801
Calorific value, MJ/kg	ASTM D4809	46.23	46.29	46.77	46.43	46.49	46.81	45.59	45.92	45.97	46.37	46.44	46.79
Isoparaffin index	^{1}H NMR	0.16	0.18	0.22	0.16	0.19	0.21	1.41	1.31	1.21	0.37	0.43	0.63
H/C ratio	^{1}H NMR	1.78	1.81	1.81	1.81	1.82	1.85	1.62	1.64	1.62	1.73	1.74	1.75
RON	^{1}H NMR	82.13	82.27	82.55	82.14	82.24	81.99	92.94	91.21	91.17	83.73	83.86	86.01
Viscosity, cP, at 25 °C	Rheometer	0.17	0.16	0.12	0.17	0.15	0.13	0.9	0.7	0.56	0.31	0.13	0.09
Cloud point (CP)	ASTM D97	18.2	9	4	4	13.3	15	−15	−11	−5	8	3	1
Pour point (PP), °C,	ASTM D97	15	5.6	1	0	2	4	−23	−17.5	−12	4	0	−2
Flash point, °C	ASTM D92	41	39	33	37	36	32	39	35	34	37	35	35
Fire point, °C	ASTM D92	47	44	40	41	40	38	44	40	39	41	42	40
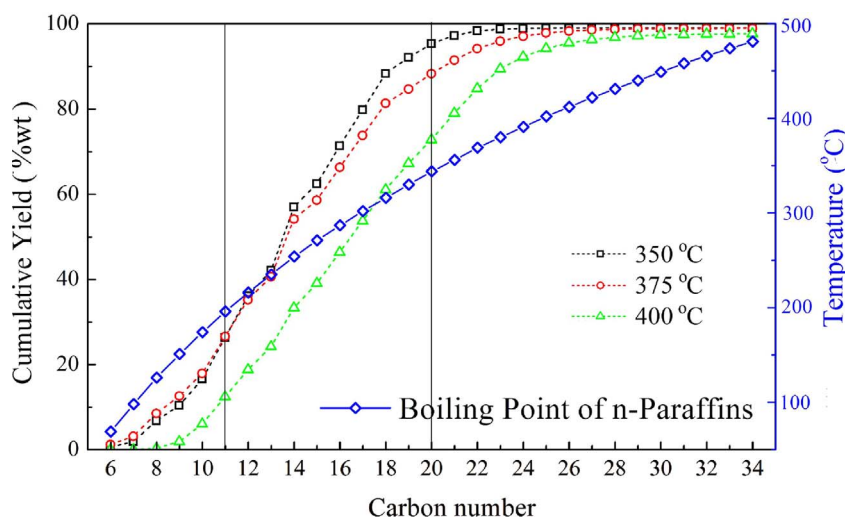
Fig. 5. Cumulative yield (% wt) of hydrocarbons with respect to carbon number and the boiling range of n-paraffins and for PDO obtained at three temperature from the pyrolysis of RMIX sample.

Table 7
Composition (% vol) and GCV and NCV of gas derived from pyrolysis of RMIX.

Gas composition	From the pyrolysis of RMIX at		
	400° C	375 °C	350 °C
Methane	5.69	5.56	4.95
Ethane	8.85	8.02	11.03
Ethylene	3.24	2.54	2.36
Propane	6.69	7.9	6.78
Propylene	28.32	28.87	32.93
Propadiene	0.55	0.5	0.32
n-Butane	2.97	2.9	2.52
Trans-2-Butene	0.6	0.69	0.43
1-Butene	3.34	3.01	2.13
Isobutylene	8.11	8.04	8.52
Cis-2-butane	0.47	1.89	0.35
Isopentane	0.12	0.16	0.04
n-Pentane	28	27.8	26.44
Methyl Acetylene	0.37	0.49	0.22
Hydrogen	1.36	0.96	0.44
Carbon monoxide	0.44	0.16	0.17
Carbon-di-oxide	0.88	0.51	0.37
GCV (MJ/m^3)	105 ± 1.51	106.89 ± 2.08	105.67 ± 1.62
NCV (MJ/m^3)	96 ± 1.77	97.71 ± 1.8	96.98 ± 2.06

the influence of heat, the polymer chain breaks (end chain or random chain scission) at weak links (sp^3 bond) and forms radicals. According to Levine and Broadbelt (2009) most of the scission reactions in polymer degradation take place at β position of the polymer chain. The end chain β-scission requires less energy than random chain β-scission, hence at low temperature slow pyrolysis the production of gaseous hydrocarbon is high. Both random and end chain β-scission reactions are responsible for the lighter fractions (C$_6$-C$_{20}$) of the liquid products while the formation of olefin is due to the radical recombination reactions followed by inter or intramolecular hydrogen shift. In addition to β-scission, the thermal degradation of plastics might undergo α-scission, methyl scission or hydrogen scission. Scission of C−H (α-scission) bond under low-temperature pyrolysis is thermodynamically less favorable. The α-scission refers to the breaking of σ bond (sp^2 carbon). The dissociation energy of α-scission (83–94 kcal mol^{-1}) is more than β-scission (61.5–63 kcal mol^{-1}) (Luo, 2002). Hence, at low-temperature pyrolysis the β-scission reactions are more likely to occur. The pyrolysis at high temperature (∼ 400 °C) may facilitate the α-scission reactions that may eventually lead to the formation of heavy fraction in oil.

4. Conclusion

The low temperature pyrolysis of household plastic waste consists of LDPE, HDPE and PP resulted in a major yield (∼ 82%) of liquid product (PDO) which mostly comprises of paraffins and olefins. Increasing the temperature increases the yield of PDO but produces heavier oil with long hydrocarbon chains (> C$_{20}$). On the other hand, the PDO obtained at lower temperature (350 °C) have superior fuel properties like high calorific value and low viscosity, pour point and flash point. The degradation process at low temperature and long duration supports the polymer scission reaction (end chain and random) and leads to the production of lighter hydrocarbons. The data obtained in this study are useful in the context of utilization of pyrolysis process to produce targeted value added products like gasoline or diesel from plastic waste. More investigations with respect to streamlining the process conditions, process design and prudent assessment are required to scale up the process. Nevertheless, the isothermal process expends lesser energy compared to non-isothermal process, makes the present investigation more engaging in terms of waste to energy transformation framework. Plastic derived oil (PDO) produced under low-temperature pyrolysis from waste LDPE, HDPE and PP can address the demand of alternate fuels as well as utilization of plastic waste.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.resconrec.2017.09.025.

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