

Research Article

Thermolysis of High-Density Polyethylene to Petroleum Products

Sachin Kumar and R. K. Singh

Department of Chemical Engineering, National Institute of Technology Rourkela, Orissa 769008, India

Correspondence should be addressed to Sachin Kumar; sachin044@gmail.com

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Thermal degradation of plastic polymers is becoming an increasingly important method for the conversion of plastic materials into valuable chemicals and oil products. In this work, virgin high-density polyethylene (HDPE) was chosen as a material for pyrolysis. A simple pyrolysis reactor system has been used to pyrolyse virgin HDPE with an objective to optimize the liquid product yield at a temperature range of 400°C to 550°C. The chemical analysis of the HDPE pyrolytic oil showed the presence of functional groups such as alkanes, alkenes, alcohols, ethers, carboxylic acids, esters, and phenyl ring substitution bands. The composition of the pyrolytic oil was analyzed using GC-MS, and it was found that the main constituents were n-Octadecane, n-Heptadecane, 1-Pentadecene, Octadecane, Pentadecane, and 1-Nonadecene. The physical properties of the obtained pyrolytic oil were close to those of mixture of petroleum products.

1. Introduction

Plastic materials comprise a steadily increasing proportion of the municipal and industrial waste going into landfill. Owing to the huge amount of plastic wastes and environmental pressures, recycling of plastics has become a predominant subject in today's plastics industry. Development of technologies for reducing plastic waste, which are acceptable from the environmental standpoint and are cost-effective, has proven to be a difficult challenge because of the complexities inherent in the reuse of polymers. Establishing optimal processes for the reuse/recycling of plastic materials, thus, remains a worldwide challenge in the new century. Plastic materials find applications in agriculture as well as in plastic packaging, which is a high-volume market owing to the many advantages of plastics over other traditional materials. However, such materials are also the most visible in the waste stream and have received a great deal of public criticism as solid materials have comparatively short life-cycles and usually are nondegradable.

Thermal cracking, or pyrolysis, involves the degradation of the polymeric materials by heating in the absence of

oxygen. The process is usually conducted at temperatures between 500 and 800°C and results in the formation of a carbonized char and a volatile fraction that may be separated into condensable hydrocarbon oil and a noncondensable high calorific value gas. The proportion of each fraction and its precise composition depend primarily on the nature of the plastic waste and on process conditions as well.

In pyrolytic processes, a proportion of species generated directly from the initial degradation reaction are transformed into secondary products due to the occurrence of inter- and intramolecular reactions. The extent and the nature of these reactions depend both on the reaction temperature and also on the residence of the products in the reaction zone, an aspect that is primarily affected by the reactor design.

In addition, reactor design also plays a fundamental role, as it has to overcome problems related to the low thermal conductivity and high viscosity of the molten polymers. Several types of reactors have been reported in the literature, the most frequent being fluidized bed reactors, batch reactors, and screw kiln reactors [2].

Characteristics of thermal degradation of heavy hydrocarbons can be described with the following items.

- (1) High production of C₁s and C₂s in the gas product.
- (2) Olefins are less branched.
- (3) Some diolefins made at high temperature.
- (4) Gasoline selectivity is poor; that is, oil products have a wide distribution of molecular weight.
- (5) Gas and coke products are high.
- (6) Reactions are slow compared with catalytic reactions.

High-density polyethylene (HDPE) is the third-largest commodity plastic material in the world, after polyvinyl chloride and polypropylene in terms of volume. It is a thermoplastic material composed of carbon and hydrogen atoms joined together forming high-molecular-weight products. The effect of temperature and the type of reactor on the pyrolysis of HDPE has been studied, and some of the results are reviewed.

Wallis and Bhatia have done the thermal degradation of high-density polyethylene in a reactive extruder at various screw speeds with reaction temperatures of 400°C and 425°C. A continuous kinetic model was used to describe the degradation of the high-density polyethylene in the reactive extruder. It was found that purely random breakage and a scission rate which had a power-law dependence on molecular size of 0.474 best described the experimental data. The greatest discrepancy between the model prediction and the experimental data was the large molecular size region at short residence times; however, this only accounted for a very small percentage of the total distribution and was attributed to the presence of fast initiation reaction mechanism that was only significant at low conversions [3].

Conesa et al. studied the production of gases from polyethylene (HDPE) at five nominal temperatures (ranging from 500°C to 900°C) using a fluidized sand bed reactor. HDPE primary decomposition and wax cracking reactions take place inside the reactor. Yields of 13 pyrolysis products (methane, ethane, ethylene, propane, propylene, acetylene, butane, butylenes, pentane, benzene, toluene, xylenes, and styrene) were analyzed as a function of the operating conditions. From the study of HDPE pyrolysis in a fluidized sand bed reactor, they have found that the yield of total gas obtained increases in the range 500°C–800°C from 5.7 to 94.5%; at higher temperatures, the yield of total gas decreases slightly; the formation of methane, benzene, and toluene is favored by high residence times, but ethane, ethylene, propane, propylene, butane, butylenes, and pentane undergo cracking to different extents at increasing residence times and/or temperature; and the maximum yield of total gas obtained at 800°C from HDPE pyrolysis is 94.5% with the following composition: 20% methane, 3.8% ethane, 37% ethylene, 0.2% propane, 4.7% propylene, 0.3% butane, 0.4% butylenes, 2.2% pentane, 24% benzene, 2.1% toluene, 0.01% acetylene, and 0.02% xylenes and styrene [4].

Walendziewski and Steininger reported the thermal degradation of polyethylene in the temperature range 370–450°C. In the case of thermal degradation of polyethylene, an increase in degradation temperature led to an increase of gas and liquid products, but a decrease of residue (boiling point

TABLE 1: Composition of gas products obtained from pyrolysis of polyethylene at 400°C [1].

Component	Thermal	Catalytic	Hydrocracking
Methane	22.7	12.4	21.1
Ethane	27.4	20.4	21.2
Ethylene	1.4	2.3	0.1
C ₃	26.6	30.4	23.7
C ₄	11.0	20.3	20.7
C ₅	6.9	5.6	7.3
C ₆	2.1	3.3	3.8

> 360°C). However, the increase of gas was not too large as compared to the sharp decrease of residue with increase of temperature. The result of analysis of gas products obtained by the pyrolysis of polyethylene at 400°C is summarized in Table 1 [1].

Walendziewski carried out two series of experiments of waste polymers cracking. The first series of polymer cracking experiments was carried out in glass reactor of 0.5 dm³ volume at atmospheric pressure and in a temperature range 350–420°C, the second one in autoclaves under hydrogen pressure (\approx 3–5 MPa) in the temperature range 380–440°C. The influence of cracking parameters, that is, reaction temperature, presence and amount of cracking catalysts, composition of the polymer feed on product yields, and composition of gas and liquid fractions is discussed. It was stated that the proper selection of the process parameters makes it possible to control, in the limited range, the product composition distribution as well as yields and composition of gas, gasoline, and diesel oil fractions [5].

Walendziewski carried out the experiments of waste polymers cracking in a continuous-flow tube reactor. The main components of the reactor unit were a screw extruder as a waste plastics feeder and a tube cracking reactor equipped with an internal screw mixer. Cracking process was realized at the temperature range 420–480°C and raw material feeding rate from 0.3 up to 2.4 kg/h. The principal process products, gaseous and liquid hydrocarbon fractions, are similar to the refinery cracking products. They are unstable due to their high olefins content (especially from polystyrene cracking), and their chemical composition and properties strongly depend on the applied feed composition, that is, shares of polyethylene, polypropylene, and polystyrene. The material balance experiments showed that the main products, liquid or solid materials in ambient temperature, contain typically 20–40% of gasoline fractions (range of boiling point 35–180°C) and 60–80% of light gas oil fractions (initial boiling point > 180°C). The solid carbon residues are similar to coal cokes and even contain 50% mineral components. Their calorific values attain 20 MJ/kg and they are solid products of quality similar to brown coals [6].

A number of studies have been reported in which a range of catalysts and reaction conditions have been employed to convert waste plastics into the hydrocarbon liquid using pyrolysis during the past four decades. The most commonly used catalysts in the catalytic degradation of high-density

Polyethylene are solid acids (zeolite, silica-alumina) [7–13] and spent FCC [14, 15].

This work focuses on characterization of liquid product obtained from thermal pyrolysis of virgin high-density polyethylene at different temperature ranges. Thermal pyrolysis of high-density polyethylene pellets was done in a semibatch reactor at a temperature range of 400°C to 550°C and at a heating rate of 20°C/min. The effect of pyrolytic temperature on reaction time, liquid yield, and volatiles was also studied. The obtained liquid product was characterized by different physical and chemical properties using GC-MS and FTIR.

2. Materials and Methods

HDPE pellets (2.5 mm in size) obtained from Reliance Industries Ltd., India, with density 0.945 g/cc³, Melt Flow Index (MFI) value 0.2–15 g/10 min⁻¹ (at 190°C and 2.16 kg load), and melting point 133°C were used for experiments. These plastic pellets were used directly in the thermal pyrolysis reaction. The proximate analysis of HDPE pellets was done by ASTM D3173-75 and ultimate analysis was done using CHNS analyzer (Elementar Vario El Cube CHNSO). Calorific value of the raw material was found by ASTM D5868-10a.

Thermogravimetric analysis of the HDPE sample was carried out with a Shimadzu DTG-60/60H instrument. A known weight of the sample was heated in a silica crucible at a constant heating rate of 293 K/min operating in a stream of nitrogen with a flow rate of 40 mL/min from 32°C to 700°C.

The pyrolysis setup consists of a semibatch reactor made of stainless-steel tube (length: 145 mm, internal diameter: 37 mm, and outer diameter: 41 mm) sealed at one end and an outlet tube at other end as shown in the previous study [16]. The reactor is heated externally by an electric furnace, with the temperature being measured by a Cr-Al : K-type thermocouple fixed inside the reactor, and temperature is controlled by external PID controller. 20 g of HDPE sample was loaded in each pyrolysis reaction. The condensable liquid products/wax were collected through the condenser and weighed. After pyrolysis, the solid residue (wax) left out inside the reactor was weighed. Then, the weight of gaseous/volatile product was calculated from the material balance. Reactions were carried out at different temperatures ranging from 400 to 550°C.

Fourier transform infrared spectroscopy (FTIR) of the pyrolysis oil obtained at optimum condition was taken in a Perkin-Elmer Fourier transformed infrared spectrophotometer with resolution of 4 cm⁻¹, in the range of 400–4000 cm⁻¹ using Nujol mull as reference to know the functional group composition. The components of liquid product were analyzed using GC-MS-QP 2010 (Shimadzu) using flame ionization detector. The GC conditions, column oven temperature progress, column used, and MS conditions are given in the Table 2.

3. Result and Discussion

3.1. Proximate and Ultimate Analyses of Virgin HDPE. The proximate and ultimate analyses of virgin HDPE sample

TABLE 2: GC-MS conditions.

GC-MS-OP 2010 Shimadzu		
GC conditions		
Column oven temperature	70°C	
Injection mode	Split	
Injection temperature	200°C	
Split ratio	10	
Flow control mode	Linear velocity	
Column flow	1.51 mL/min	
Carrier gas	Helium 99.9995% purity	
Column oven temperature progress		
Rate	Temperature (°C)	Hold time (min)
—	70	2
10	300	7.0 (32 min total)
Column: DB-5		
Length	30.0 m	
Diameter	0.25 mm	
Film thickness	0.25 μm	
MS conditions		
Ion source temperature	200°C	
Interface temperature	240°C	
Start <i>m/z</i>	40	
End <i>m/z</i>	1000	

TABLE 3: Proximate and ultimate analyses of virgin HDPE.

Properties	Virgin HDPE
Proximate analysis	
Moisture content	0.00
Volatile matter	99.92
Fixed carbon	0.00
Ash content	0.08
Ultimate analysis	
Carbon (C)	83.29
Hydrogen (H)	13.93
Nitrogen (N)	0.20
Sulphur (S)	0.07
Oxygen (O)/others	2.51
GCV (MJ/kg)	47.64

are shown in Table 3. The volatile matter is 99.9% in the proximate analysis, due to the negligible percentage of ash in virgin HDPE sample; its degradation occurs with minimal formation of residue. The oxygen is 2.51% in the ultimate analysis of virgin HDPE. The nitrogen and oxygen in the virgin HDPE sample may not be due to the fillers but due to the other ingredients which are added to resin during the manufacturing of HDPE.

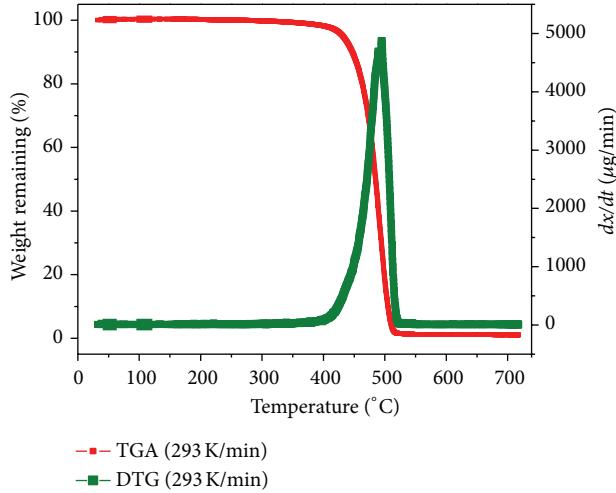


FIGURE 1: TGA and DTG curves of virgin HDPE.

3.2. TGA and DTG Analyses of Virgin HDPE Sample. Thermogravimetric analysis (TGA) is a thermal analysis technique which measures the weight change in a material as a function of temperature and time in a controlled environment. This can be very useful to investigate the thermal stability of a material or to investigate its behavior in different atmospheres (e.g., inert or oxidizing). TGA is applied in determination of the study of thermal stability/degradation of virgin HDPE in various ranges of temperature.

From the TGA curve as shown in Figure 1, the virgin HDPE degradation started at 380°C and was completed at 510°C for a heating rate of 293 K/min in nitrogen atmosphere. The degradation temperature at which weight loss of 50% (T_{50}) takes place was about 460°C for virgin HDPE. The temperature range for waste HDPE was 390°C to 490°C, and maximum weight loss occurred at temperature 440°C as demonstrated [16]. A similar trend of nature during the analysis of HDPE decomposition by TGA/DTG has been reported by Aboulkas et al. [19]. Differential thermogravimetry (DTG) is exactly the same as TGA, except the mass loss versus time output is differentiated automatically to give the mass loss rate versus time. Generally, both the mass loss and mass loss rate versus time are produced automatically. This is quite convenient as the rate of thermal decomposition is proportional to the volatilization or mass loss rate. Differential thermogravimetry (DTG) curve for virgin HDPE contains only one peak; this indicates that there is only one degradation step in Figure 1, showing that the dominant peak is from 390°C to 510°C where the conversion takes place. Similarly, maximum weight loss occurs at 498°C from DTG profile of HDPE pellets [20].

3.3. Effect of Temperature on Product Distribution. The pyrolysis of virgin HDPE yielded four different products, that is, oil, gas, wax, and residue or coke. The distributions of these fractions are different at different temperatures and are shown in Table 4.

The condensable oil/wax (a mixture of alkanes that falls within the $20 \leq n \leq 40$ range; they are found in the solid state at room temperature and begin to enter the liquid phase past approximately 37°C) and the noncondensable gas/volatiles fractions of the reaction constituted major product as compared to the solid residue (coke) fractions. The condensable product obtained at low temperature (400°C) was low viscous liquids. With increase in temperature, the liquid became viscous/wax at and above 450°C. The hydrocarbon is continuously cracking; the wax may be representative of the intermediate-molecular-weight products. The recovery of condensable fraction was very low at low temperature, that is, at 400°C and increased with gradual increase of temperature. From Table 4, it is observed that at low temperature the reaction time was more, due to which secondary cracking of the pyrolysis product occurred inside the reactor and resulted in highly volatile product. The low-temperature molecular weight changes without volatilization are principally due to the scission of weak links, such as oxygen, incorporated into the main chain as impurities. Similarly, the low liquid yield at high temperature was due to volatilizing higher-molecular-weight products before undergoing further cracking and more noncondensable gaseous/volatile fractions due to rigorous cracking.

3.4. Effect of Temperature on Reaction Time. The effect of temperature on the reaction time of the reaction for the pyrolysis of virgin HDPE plastic is shown in Figure 2. The pyrolysis reaction rate increased and reaction time decreased with increase in temperature. High temperature supports the easy cleavage of bond and thus speeds up the reaction and lowers the reaction time. HDPE with long linear polymer chain with low branching and high degree of crystallinity led to high strength properties and thus required more time for decomposition. This shows that temperature has significant effect on reaction time and yield of liquid, wax, gaseous products, and solid residue (coke). A similar effect

TABLE 4: Distribution of different fractions at different temperatures in thermal pyrolysis of virgin HDPE.

Temperature (°C)	Oil (wt%)	Residue (wt%)	Wax (wt%)	Gas/volatile (wt%)	Reaction time (min)
400	31.3	5.65	7.7	45.35	680
450	52.46	3.95	8.9	34.69	175
500	44.32	1.29	28.99	25.4	80
550	8.83	0.68	52.02	38.47	50

TABLE 5: GC-MS analysis of virgin HDPE pyrolytic oil.

R. time (min)	Area %	Name of compound	Molecular formula
6.301	1.24	1-Decene	C ₁₀ H ₂₀
6.450	1.12	Decane	C ₁₀ H ₂₂
8.105	2.04	1-Undecene	C ₁₁ H ₂₂
8.238	1.78	n-Undecane	C ₁₁ H ₂₂
9.735	3.50	1-Dodecanol	C ₁₂ H ₂₆ O
9.855	3.19	n-Dodecane	C ₁₂ H ₂₆
11.541	4.62	1-Tridecene	C ₁₃ H ₂₆
12.615	5.30	1-Tetradecene	C ₁₄ H ₂₈
12.711	4.82	Tetradecane	C ₁₄ H ₃₀
12.772	0.65	7-Tetradecene	C ₁₄ H ₂₈
13.909	5.40	1-Pentadecene	C ₁₅ H ₃₀
13.997	5.13	Pentadecane	C ₁₅ H ₃₂
15.039	0.48	1,19-Eicosadiene	C ₂₀ H ₃₈
15.130	5.36	1-Hexadecene	C ₁₆ H ₃₂
15.210	5.60	n-Octadecane	C ₁₈ H ₃₆
15.261	0.51	Cyclohexadecane	C ₁₆ H ₃₂
16.203	0.49	1,19-Eicosadiene	C ₂₀ H ₃₈
16.283	5.09	1-Nonadecene	C ₁₉ H ₃₈
16.357	5.52	n-Heptadecane	C ₁₇ H ₃₆
16.406	0.51	1-Heptadecene	C ₁₇ H ₃₄
17.378	4.43	1-Octadecene	C ₁₈ H ₃₆
17.447	5.47	Octadecane	C ₁₈ H ₃₈
17.493	0.69	1-Octadecene	C ₁₈ H ₃₆
18.419	3.26	1-Nonadecene	C ₁₉ H ₃₈
18.482	4.67	Nonadecane	C ₁₉ H ₄₀

of temperature on reaction time for waste HDPE has been demonstrated [16].

4. Characterization of the Liquid Product

4.1. FT-IR of the Oil Sample Obtained at 450°C. Fourier transform infrared spectroscopy (FTIR) is an important analysis technique which detects various characteristic functional groups present in oil. On interaction of an infrared light with oil, chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range regardless of the structure of the rest of the molecules. Figure 3 shows the FTIR spectra of virgin HDPE oil. The C–H stretching vibrations at frequency 3078.11 cm⁻¹ indicate the presence of alkenes. The presence of alkanes is detected at 2918.68 cm⁻¹ with C–H stretching vibrations. The C=C stretching vibrations at frequency 1647.39 cm⁻¹ indicate the presence of alkenes. The presence of alkanes was detected

TABLE 6: Physical properties analysis of virgin HDPE pyrolytic oil.

Tests	Results obtained	Test method
Specific gravity at 15°C/15°C	0.8013	IS:1448 P:16
Density at 15°C in kg/cc	0.8006	IS:1448 P:16
Kinematic viscosity at 40°C in Cst	3.3	IS:1448 P:25
Kinematic viscosity at 100°C in Cst	1.4	IS:1448 P:25
Conradson carbon residue	<0.01%	IS:1448 P:122
Flash point by Abel method	10°C	IS:1448 P:20
Fire point	15°C	IS:1448 P:20
Cloud point	28°C	IS:1448 P:10
Pour point	18°C	IS:1448 P:10
Gross calorific value in MJ/kg	44.27	IS:1448 P:6
Sulphur content	0.03%	IS:1448 P:33
Calculated Cetane Index (CCI)	70	IS:1448 P:9
Distillation		IS:1448 P:18
Initial boiling point	72°C	
Final boiling point	364°C	

by C–H scissoring and bending vibrations at 1440.22 cm⁻¹. The presence of alcohols, ethers, carboxylic acids, and esters is detected by C–O stretching vibrations at 907.61 cm⁻¹, and the C–H bending vibrations at frequency 719.92 indicates the presence of phenyl ring substitution bands. The results were found consistent when compared with the results of GC-MS.

4.2. GC-MS of the Oil Sample. The GC-MS analysis of the oil sample obtained by the thermal pyrolysis of virgin HDPE was carried out to know the compounds present in the oil (Figure 4) and is summarized in Table 5. It has been observed that the pyrolytic oil contains around 25 compounds. Taking into account the area percentage, the highest peak areas of total ion chromatogram (TIC) of the compounds were n-Octadecane, n-Heptadecane, 1-Pentadecene, Octadecane, Pentadecane, and 1-Nonadecene. The components present in HDPE are mostly the aliphatic hydrocarbons (alkanes and alkenes) with carbon number C₁₀–C₂₀.

4.3. Physical Properties of Oil Sample. Table 6 shows the results of physical property analysis of oil obtained from pyrolysis of virgin HDPE. The appearance of the oil is dark brownish free from visible sediments.

From comparison with other transportation products as shown in Table 7, the density and viscosity of liquid product can be modified by blending it with commercial transportation products. The flash point of the liquid product is in a comparable range, and a pour point of 18°C is acceptable for

TABLE 7: Product properties comparison of HDPE pyrolytic oil with commercial transportation products.

Properties	Specific gravity 15°C/15°C	Kinematic viscosity at 40°C (cst)	Flash point (°C)	Pour point (°C)	GCV (MJ/kg)	IBP (°C)	FBP (°C)	Chemical formula
HDPE pyrolytic oil	0.8013	3.3	10	18	44.27	72	364	C ₁₀ –C ₂₀
Waste HDPE pyrolytic oil [16]	0.7835	1.63	1	-15	42.81	82	352	C ₁₉ –C ₂₄
Gasoline [17]	0.72–0.78	—	-43	-40	42–46	27	225	C ₄ –C ₁₂
Diesel [17]	0.82–0.85	2–5.5	53–80	-40 to -1	42–45	172	350	C ₈ –C ₂₅
Biodiesel [17]	0.88	4–6	100–170	-3 to 19	37–40	315	350	C ₁₂ –C ₂₂
Heavy product oil [18]	0.94–0.98	>200	90–180	—	-40	—	—	—

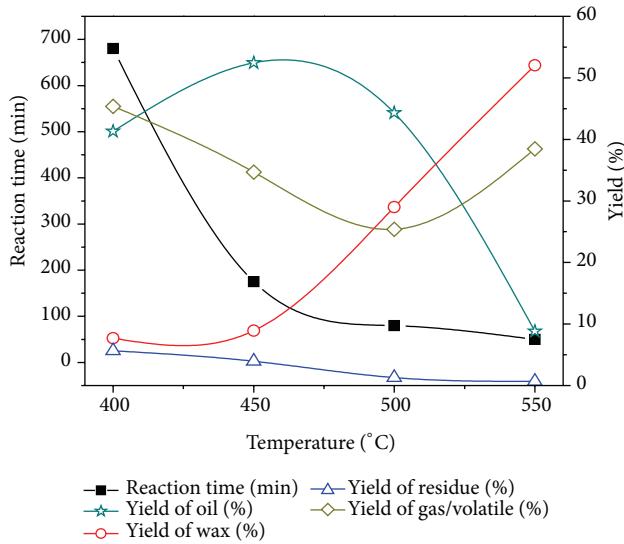


FIGURE 2: Effect of temperature on reaction time and product distribution.

most geographic regions. HDPE pyrolytic oil has GCV of 44 MJ/kg which is more as compared to that of gasoline and diesel; therefore, this liquid product would perform relatively superior in engines. From the distillation report of the oil, it is observed that the boiling range of the oil is 72–364°C, which infers the presence of mixture of different oil components such as gasoline, kerosene, and diesel in the oil. The liquid product contains substantial amount of volatiles as its initial boiling point is below 100°C. From this result, it is observed that these could be possible feedstocks for further upgrading or use of lighter compounds as a diesel product.

5. Conclusion

Thermal pyrolysis of virgin HDPE was performed in a semibatch reactor made up of stainless steel at temperature range from 400°C to 550°C and at a heating rate of 20°C/min. The liquid yield is highest at 450°C, highly volatile products are obtained at low temperature, and the products obtained at 500°C and 550°C are viscous liquid and wax. Reaction time decreases with increase in temperature. The functional group

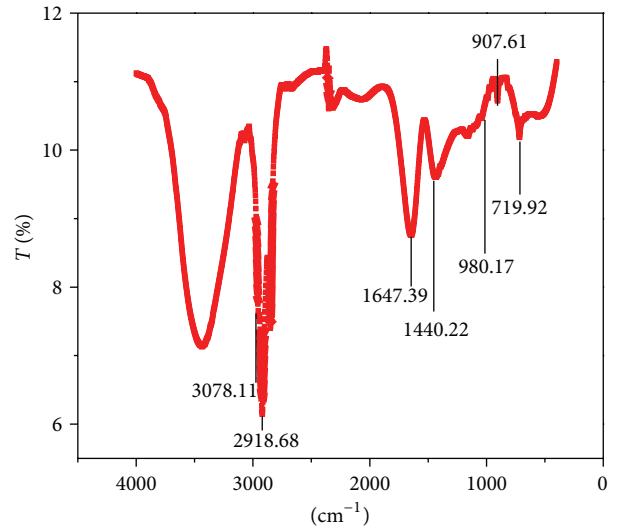


FIGURE 3: FT-IR spectrometry of virgin HDPE pyrolytic oil.

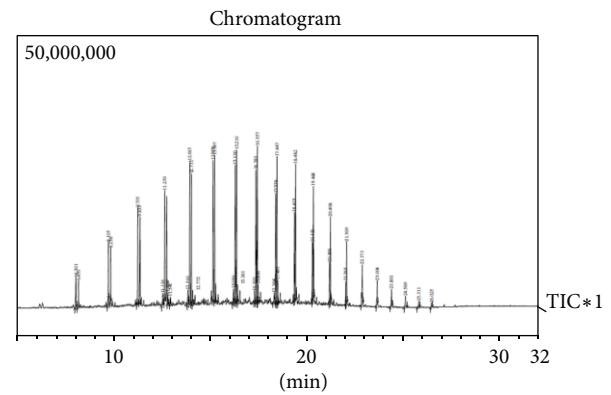


FIGURE 4: GC plot of oil obtained at 450°C.

present in the virgin HDPE pyrolytic oil is similar to the other plastic pyrolytic oils given in several literatures. It was found that the pyrolytic oil contains around 25 types of compounds having carbon chain length in the range of C₁₀–C₂₀. The physical properties of pyrolytic oil obtained were in the range of other pyrolytic oils and moderate-quality products. It has been shown that a simple batch pyrolysis method can

convert virgin HDPE to liquid hydrocarbon products with a significant yield which varies with temperature.

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