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Production and Evaluation of Liquid Hydrocarbon Fuel from Thermal Pyrolysis of Virgin Polyethylene Plastics

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Abstract

Pyrolysis of virgin polyethylene plastics was studied in order to produce hydrocarbon liquid fuel. The pyrolysis process carried out for low and high-density polyethylene plastics in open system batch reactor in temperature range of 370 to 450°C.

Thermo-gravimetric analysis of the virgin plastics showed that the degradation ranges were between 326 and 495 °C. The results showed that the optimum temperature range of pyrolysis of polyethylene plastics that gives highest liquid yield (with specific gravity between 0.7844 and 0.7865) was 390 to 410 °C with reaction time of about 35 minutes. Fourier Transform Infrared spectroscopy gave a quite evidence that the produced hydrocarbon liquid fuel consisted mainly alkanes and the x-ray diffraction showed no sulfur in the produced hydrocarbon liquids.

Key Words: Polyethylene, Thermal, Pyrolysis, Kinetic study, Batch reactor, Plastic.

Introduction

Plastic is one of the most widely used materials in our day-to-day lives. Alexander Feigns it in 1862 [1].

Plastic has become a needful part in our today's world so the production of plastics has increased by an average of roughly 10% every year on a universal basis since 1950. The total global production of plastics increased from around 1.3 million tons (MT) in 1950 to 230 million tonnes in 2009, whereas the global production in 2013 reached to 299 million tonnes [2].

Generally, polyethylene (PE) is one of the largest commodity plastic material in the world Polyethylene has been widely investigated by enormous number of researchers because Polyethylene is the main component of the total plastic content of MSW. For example, polyethylene represented 55 wt.% of total plastics consumed in Australia in 2003 [3].

Polyethylene consists from two types: high density polyethylene (HDPE) and low density polyethylene (LDPE). HDPE has wide uses such as rigid containers such, Laundry Detergent bottles, Milk jugs, Fuel tanks for vehicles, Plastic Folding, chairs Lumbers, Folding tables, while LDPE uses include flexible films such as grocery and dry cleaning bags [4, 5].

Retuning plastic to its purebred carbon cycle or monomers is not easy. Also plastic is non- biodegradable material; hence, the live cycle of plastic ends at waste plastic facilities [6].

Recycling of plastics is the most attractive method. It is one of the three methods for disposal and minimization of waste plastic like Incineration and landfill. Landfilling needs large area for disposal of waste plastic and emissions of unacceptable gases also expensive method. Incineration is a distraction method and quite expensive and may raise problems with unacceptable emissions too. So landfilling and incineration are not useful methods to solve the problem of huge piles of waste plastic. The third and most effective method of plastic recycling is pyrolysis, which is a thermal cracking reaction of the large molecular weight polymer carbon chains under oxygen free environmental and produces small molecular weight molecules [7].

Pyrolysis has high capability to convert waste plastic to useful hydrocarbons. It is becoming a promising alternative in order to recover fuel oil and hydrocarbons feedstock [8, 9]. Pyrolysis process can deal with small quantities of plastic containing heteroatoms (atoms other than carbon and hydrogen like oxygen, sulfur, nitrogen, chlorine and bromine) less than 2% because the presence of hero-atoms or additives lead to many problems in the process such as corrosion and difficult to control operating condition. Heteroatoms are heavier than the (carbon and hydrogen). These elements increase the density of the plastic. This can be used as guide to choose the plastic for pyrolysis. The suitable plastics for pyrolysis can be known by taking flaked from waste plastic and adding it to jar of water. If more plastic floats than sinks, the waste plastic is acceptable.

Pyrolysis products are mainly gases, liquids, solid and coke. The liquids can either be used for further refining to produce high quality fuels or combusted for power generation. Some plants have a more complete separation system by feeding the mixture of liquid and gas into distillation columns. Diesel products can then be distilled out as in an oil refinery process. The non-condensable gases consist mainly from (H_2, C1, C2, C3, and C4). The gases can be used as fuels to heat the pyrolysis reactor, or liquefied as fuels. If the amount is insignificant, the non-condensable gases are sent to an incinerator flaring off with the air (Ash maybe contain ash) in the non-condensable gases so most commercial processes have a gas scrubber for cleaning the gases [10].

Scheirs and Kaminsky in 2006 [11] reported the advantage of the pyrolysis process that can deal, with all mixtures of waste plastic consisting of various sorts of plastics without sorting or treatment. While, Kodera et al. in the same year [12] recommended that the product oil produced from the pyrolysis process is suitable to use in industrial boilers, power generation, and burners or in refinery with feedstock.

In 1999, Williams and Williams [13] obtained 89.2% liquid from pyrolysis of LDPE in fluidized bed reactor at 500 °C while obtained 28.6% liquid in the same reactor at 700°C.

5 % of both of gas and liquid has been obtained from thermal pyrolysis of HDPE in semi batch reactor at 400°C during 4 hours [14].

Shuber in 2007 [15] studied the thermal pyrolysis of LDPE in batch reactor closed system at 480°C during 10 minutes and obtained 73.3, 18.35, 0.34, 7.9 wt. % for liquid, gas, coke and unreacted LDPE ,respectively. While, The maximum yield of liquid, gas and coke was 23.96, 72.24 and 3.8%, respectively, during 290 to 760 minutes of reaction time of the thermal pyrolysis of waste HDPE in batch reactor closed system at temperature range 400- 450 °C. Increasing of reaction temperature from 400 to 550°C caused, decrease in the reaction time from 760 to 54 minutes [16].

During 2013, Thorat et al. [17] reported some types of plastics are suitable for pyrolysis process such as polyethylene, polypropylene and polystyrene 950 ml of oil can be recovered from 1 kg of them.

The present work aimed to compare the pyrolysis behavior of HDPE and LDPE. Prior to this, Thermo-gravimetric analysis aimed to understand the pyrolysis demeanor of LDPE and HDPE. Then, studying the pyrolysis behavior and reactions of two types of polyethylene (HDPE and LDPE). The best reaction conditions may be attained to produce high hydrocarbons liquid yield and good quality by changing reaction temperature and reaction time.

Experimental Work

Materials

Virgin HDPE and LDPE pellets with average particle size of 3 mm were purchased from local markets (the source of plastic` is SABIC Company). The main properties of the two polymers are shown in Table 1.

Table 1, Physical and chemical properties of virgin LDPE and HDPE

Property	LDPE	HDPE
Density (by ASTM D 1505), (g/cm^3)	0.918 - 0.934	0.956-0.963
Melt flow index (by ASTM D 1238), g/10min	0.65-4.70	0.05–0.43
Deflection temperature at 0.46 Mpa, °C	48	75-85
Melting point, °C	105-115	130-135

Thermal analysis

Thermo-gravimetric analysis (TGA) was attained to study the behavior of thermal degradation for the two types of polyethylene. The TGA monitors the weight loss of plastic versus the temperature; a function of temperature in a controlled nitrogen atmosphere.

For each test, about 20 mg of the polyethylene pyrolysis under nitrogen flow rate approximately 35 ml/min. The heating rate was 20 °C/min from surrounding temperature to 800°C. The weight loss of polyethylene verses temperature curve was recorded to know the range of effective temperature for pyrolysis.

Tests were carried out using thermo-gravimetric analyzer TGA (PC SERIIES TGA7) located in IBN SINA STATE COMPANY, Ministry of Industry and Minerals.

Pyrolysis apparatus

The apparatus used in the pyrolysis of wastes plastic consisted of batch reactor made of carbon steel of 170 mm length, 90 mm inside diameter and 110 mm outside diameter. Thermo couple (type K) with digital temperature recorder (model number), connected to the top of reactor 120 mm deep was used to measure the temperature inside the reactor.

The heat was supplied to the reactor by 3600 Watt external electrical heaters (1600 Watt heater in the bottom of the reactor and 2000 Watt heater surrounding the reactor) to get the required reaction temperature.

At the top end of the reactor, a tubing system was connected with two gate-valves. All tubes had 6 mm in diameter made from copper. Measured amount of nitrogen enters the reactor through one of the tubes located 100 mm inside the reactor with elbow shape which has three holes to distribute the nitrogen from the bottom of reactor.

The condensate liquid products are collected from the bottom of the condenser (450 mm length) and the gases product leaves the system at the top of the condenser.

The schematic diagram of the apparatus is shown in figure 1.

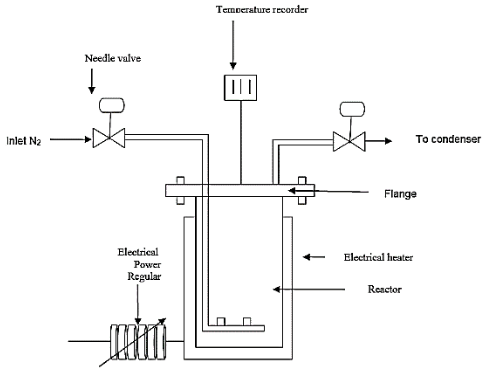

Fig. 1, Schematic diagram of the experimental apparatus

Experiment procedure

The batch reactor was first cleaned with naphtha. 50 g of a certain plastic particles (HDPE or LDPE) were weighted by using a four decimal balance.

The reactor was closed and bolted tightly by ten nets (size 10 mm). Nitrogen was supplied several times to purge the air out of the reactor (flashing the system triple for one minute each) before the experiment started. The pressure was 1 atmospheric.

The two electrical heaters were turned on to attain the required reaction temperature; the accuracy of temperature readings was about 7°C and the time zero was recorded when the gases started to get out of reactor to the condenser.

The cooling water was supplied by the chiller at a temperature of 3 to 5°C. The condenser was effective enough to drop the temperature of the pyrolysis product to less than 30 °C.

The product separated in the condenser to non-condensable gases leaves from the top of the condenser to get out of laboratory by fan.

Liquid (containing wax) which was collected from the bottom of condenser in sealed cylinder. The liquid cooled to temperature 16 °C and separated by vacuum pump into liquid and wax. The liquid and the wax were weighted by the four dismal balances.

The solid remaining in the reactor was defined as a coke. Finally, weight of the gas was calculated by difference between initial weight of plastic and summation of other products' weight (liquid, wax and coke).

Results and Discussion

Thermo-gravimetric analysis and differential thermos-gravimetric analysis of the feedstock

Thermo-gravimetric analysis (TGA) defined as thermal analysis technique that measures the weight loss of material as function of temperature in controlled nitrogen environmental. TGA can be used to know in which range of temperature the material start and end degradation. TGA curves were found to estimate the temperature range that should be used to pyrolysis LDPE and HDPE [18].

The TGA curves for pyrolysis of LPDE and HDPE shown in figures 2 and 3, respectively.

The LDPE decomposition started at 349°C and was complete at 489°C while the HDPE decomposition started at 326°C and was complete at 495°C. The degradation temperature at which the original sample loses 50 % of its weight took place at about 457.49 and 466.71 °C for LDPE and HDPE, respectively. These results mean that the polyethylene and plastic stability is in order of HDPE and then LDPE due to their difference in molecular weight.

The second dotted curve in each of figures 2 and 3, represents the differential thermal gravimetric analysis (DTGA). The DTGA contains only one peak, this indicates that there is only one degradation step. The peaks appear where the temperature is in the range of 457.49 to 466.71°C for LDPE and HDPE. Theoretically, the peak of the DTGA represents the highest pyrolysis rate for the sample, whatever the product yields.

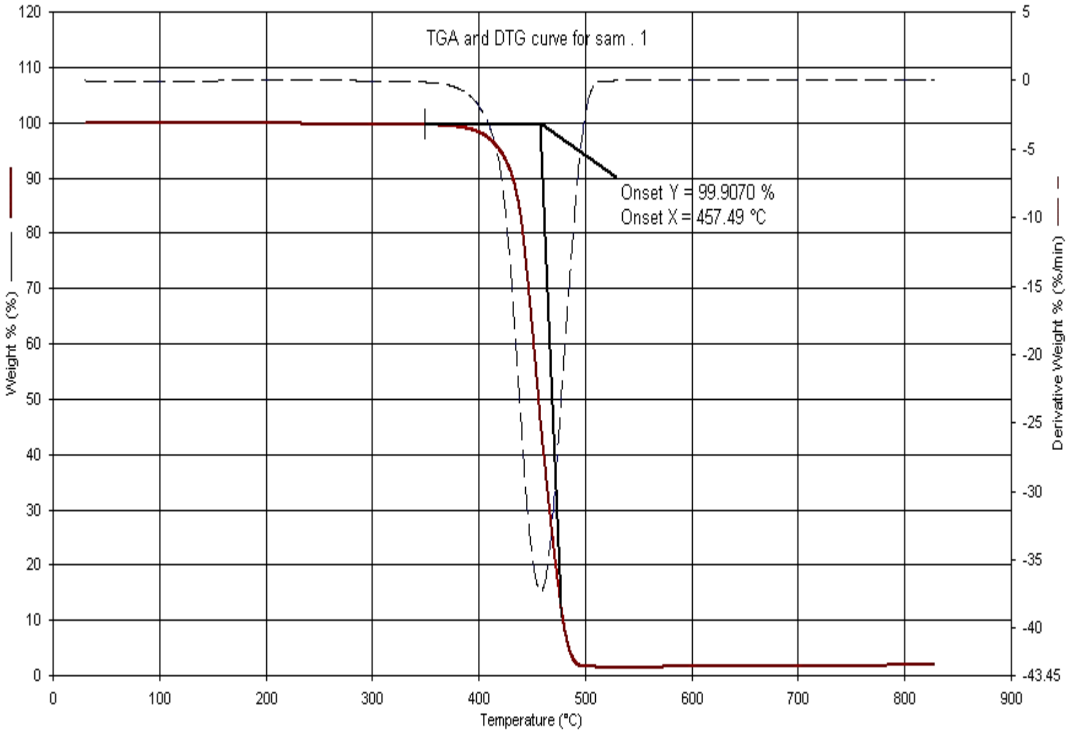

Fig. 2, TGA for virgin LDPE

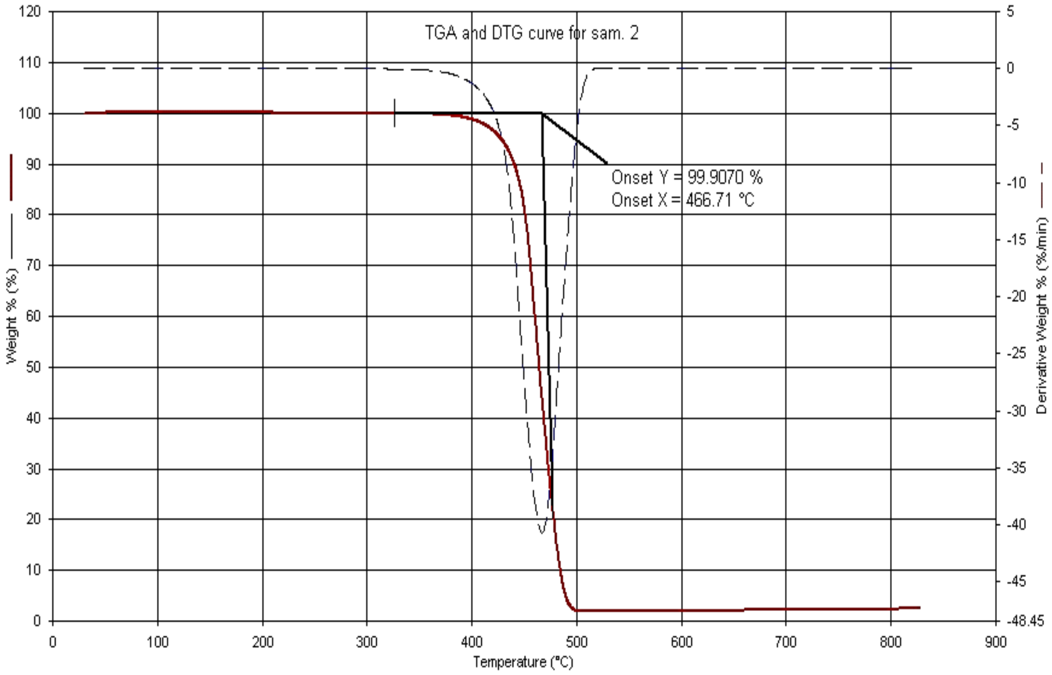

Fig. 3, TGA for virgin HDPE

The small difference in pyrolysis temperature ranges between the HPDE and LDPE may be caused by the difference in the molecular weight, the chain length and the branching of the two types of plastics. Thus, the order of decomposition temperature was LDPE less than HDPE.

Shubar [15] used TGA testing to estimate the LDPE and HDPE degradation temperature. The results show the degradation temperature ranges for degradation of LDPE about 380 to 507 °C and about 386.5 to 514 °C, for HDPE, respectively.

Effect of temperature on the plastic pyrolysis yield

The hydrocarbons (liquid and wax) are produced from thermal pyrolysis of LDPE versus time at different pyrolysis temperature as shown in figure 4. The amount of hydrocarbons increased up to 56 ml during about 11 minutes at the temperature range of 430 to 450 °C. While, at lower temperature (370°C), only 27 ml of hydrocarbons was produced through about 40 minutes of the reaction.

The hydrocarbons (liquid and wax) are produce from thermal pyrolysis of HDPE versus time at different pyrolysis temperature are shown in figure 5. The amount of hydrocarbon increases with time and temperature up to 56 ml at 450°C during 7 minutes while at lower temperature, only 21 ml of hydrocarbon was produced at 370°C during 50 minutes.

According to the collision theory [19, 20], which described the chemical reaction, increasing in reaction temperature, causes an increase in molecules activities, which means that more molecules have more energy to react. Thus, higher temperature (430 and 450°C) gives shorter time of pyrolysis.

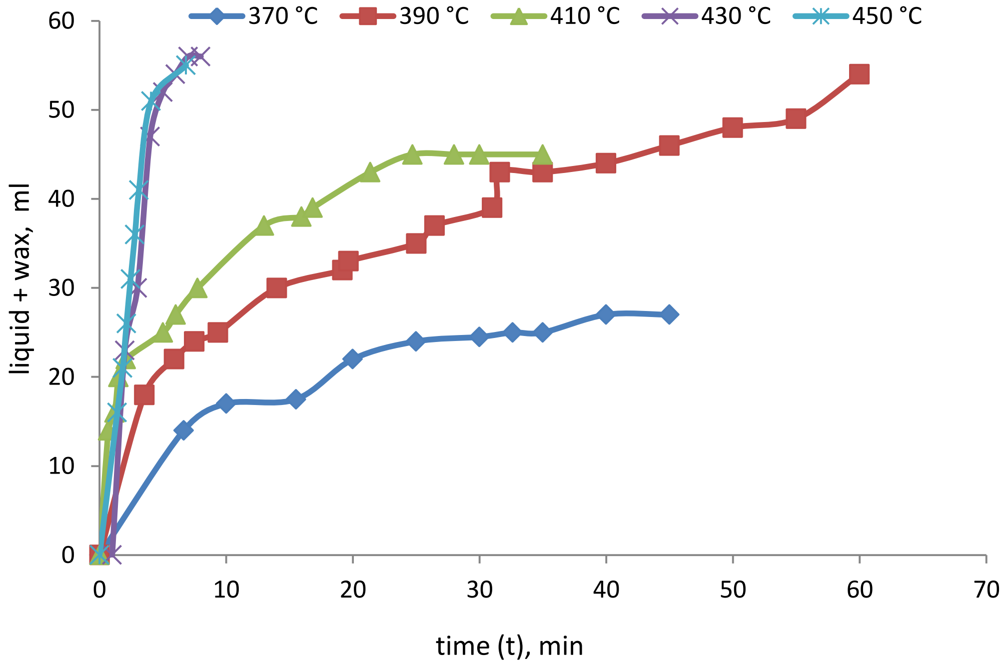

Fig. 4, The yield of hydrocarbons (liquid and wax) versus time from thermal pyrolysis of LDPE at different pyrolysis temperature

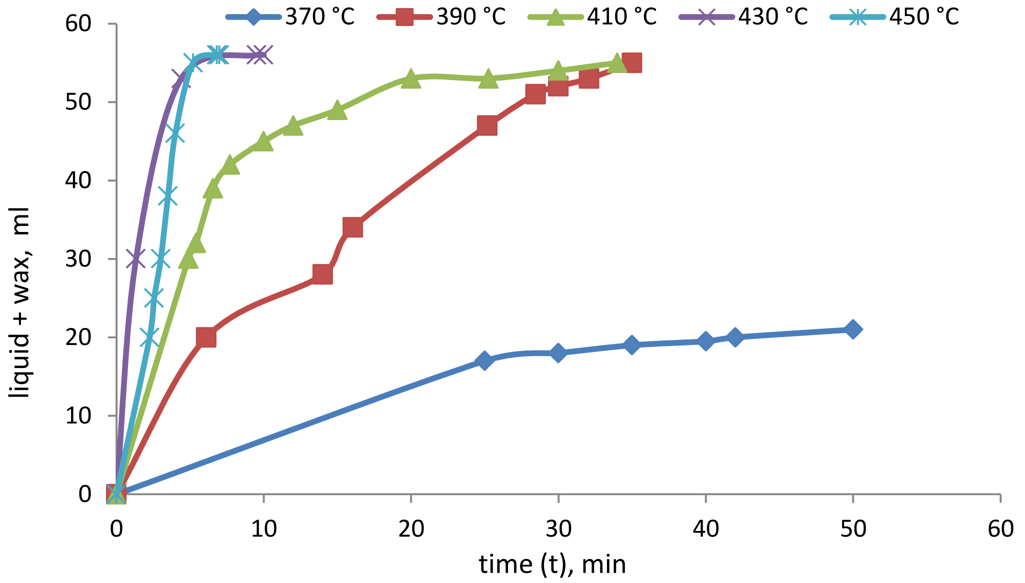

Fig. 5, The yield of hydrocarbons (liquid and wax) versus time from thermal pyrolysis of HDPE at different pyrolysis temperature

Complete time of pyrolysis the two types of polyethylene

The time for completion of thermal pyrolysis reaction of LDPE and HPDE was obtained experimentally to obtain the final amount of pyrolysis products. The time was started to calculate when the first produce hydrocarbon vapor reach to the condenser. The time was stopped when all the plastics were react i.e. no more than hydrocarbon vapor appear. The complete reaction time versus reaction temperatures for the LDPE and HDPE is shown in Table 2.

Table 2, Complete reaction time versus reaction temperatures for the pyrolysis of LDPE and HDPE

Reaction Temp., °C	Completed LDPE pyrolysis time, min	Completed HDPE pyrolysis time, min
370	40	50
390	38	35
410	35	34
430	12	10
450	11	7

The pyrolysis yields of the LDPE and HDPE at completed time were summarized in figures 6 and 7 for LDPE and HDPE, respectively.

As the liquid is the desired product, the maximum yield of liquid, which is about ±50 %, are produced from the pyrolysis of LDPE and HDPE in the temperatures between 390 and 410 °C (shaded area in table 2), which mean that the reaction needs about 35 minutes to complete for both types of the polyethylene. At these temperature range and reaction time, the lowest amount of wax (9 to 25 wt. %) and gases (22 to 44 wt. %) were produced. While, there was no significant amount of coke observed in pyrolysis process of LDPE while the highest coke produced from the pyrolysis of HDPE was 1.84 wt. %.

At low temperatures (370, 390 and 410 °C), the liquids yield was high and reaction time was longer due to secondary cracking of the pyrolysis product occurred inside the reactor but the low liquid yield at high temperature (430 and 450 °C) during shorter time was due to the formation of less cracked high molecular weight wax.

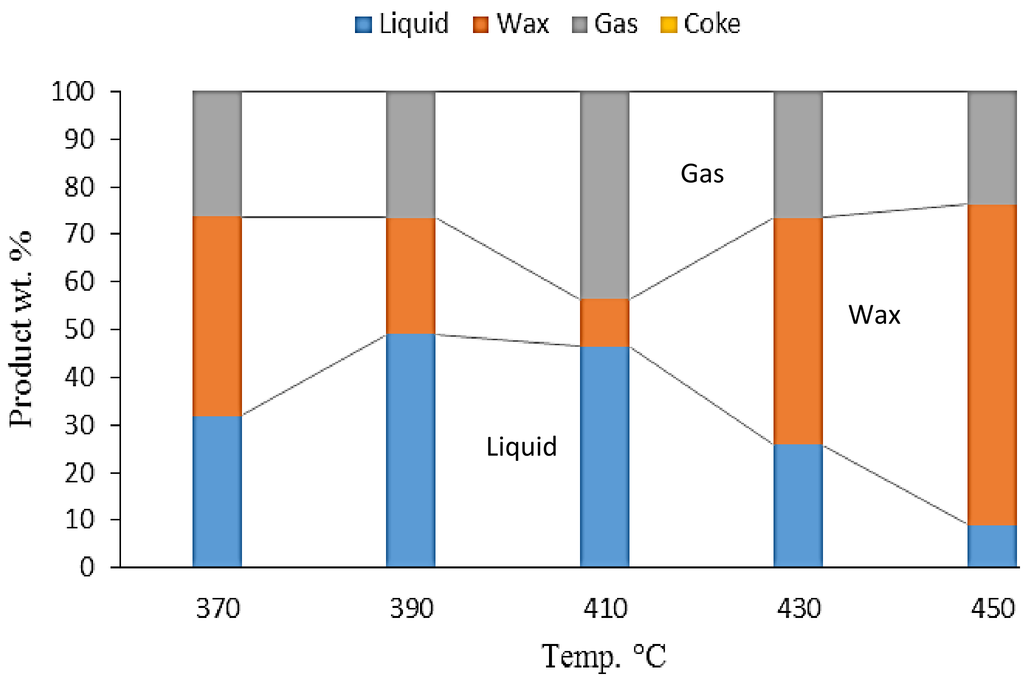

Fig. 6, Final products weight present of the LDPE pyrolysis

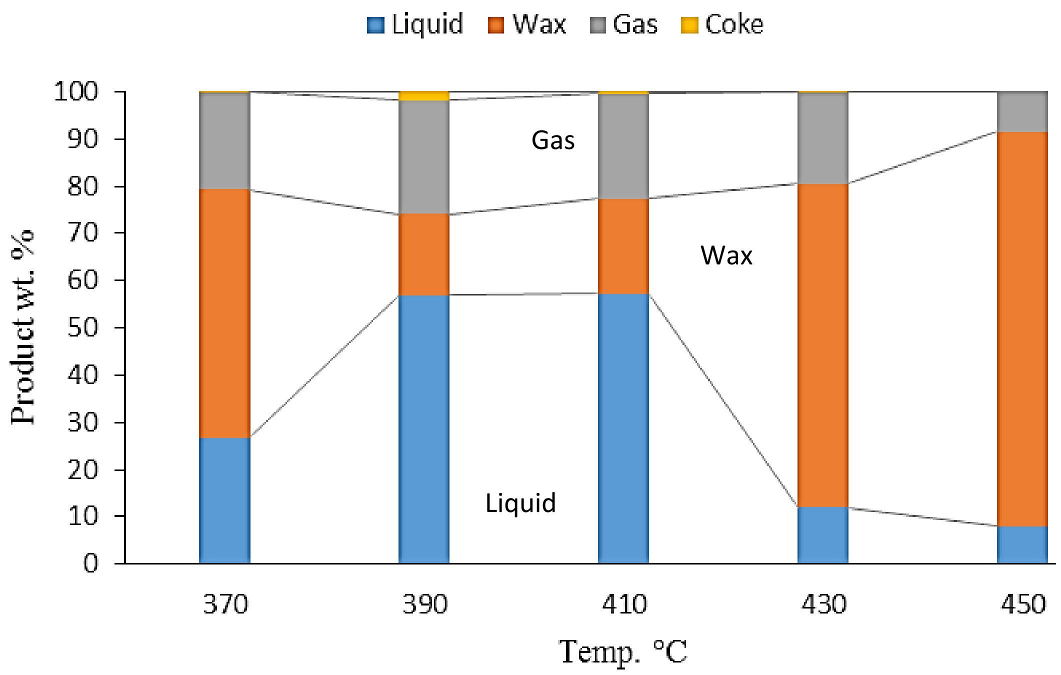

Fig. 7, Final products weight present of the HDPE pyrolysis

Characterization of hydrocarbon liquid yield

Hydrocarbon liquid fuel were collected from pyrolysis of LDPE and HDPE in open system batch reactor in the temperature range of 390 to 410 °C and reaction time of about 35 minutes.

Fourier Transform Infrared Analysis

Fourier Transform Infrared spectroscopy (FTIR) is a significant test technique that detects different characteristic functional groups present in oil. Onto interaction of infrared light with oil, chemical bonds can absorb infrared radiation in specific wavelength ranges that neglected the rest of the structure of molecules.

Figures 8 and 9 show the HDPE and LDPE had no different FTIR spectra. FTIR indicated that the structures of oils obtained from thermal pyrolysis of the two types of polyethylene are very similar.

The peaks between 2960 cm^{-1} and 2850 cm^{-1} indicated the presence of CH_3 $(CH_2)_nCH_3$ functional groups which are indicative of alkanes species as. The presences of peaks in the region of 1350 to 1500 cm^{-1} due to the deformation vibrations of C–H bonds confirm the presence.

The structures of polyethylene and polypropylene are very similar and their thermal decompositions are probable to produce similar compositions in the derived liquid hydrocarbon [13].

The liquid obtained from thermal pyrolysis of waste HDPE [16] in batch reactor in temperature range 400 to 550 °C consist mostly of alkane and alkenes with carbon number ranges (C9 to C24). While, the (FTIR) spectrometry show the oil produced from thermal pyrolysis of polyethylene in fixed bed reactors that consist from aromatic and aliphatic species such as alkanes and alkenes [21].

the reported FTIR spectrometry [15] improved the liquid obtained from thermal pyrolysis of the two types of polyethylene in batch reactor at 480 °C contain similar structure of alkenes and aromatic. Also contained alkanes with small difference.

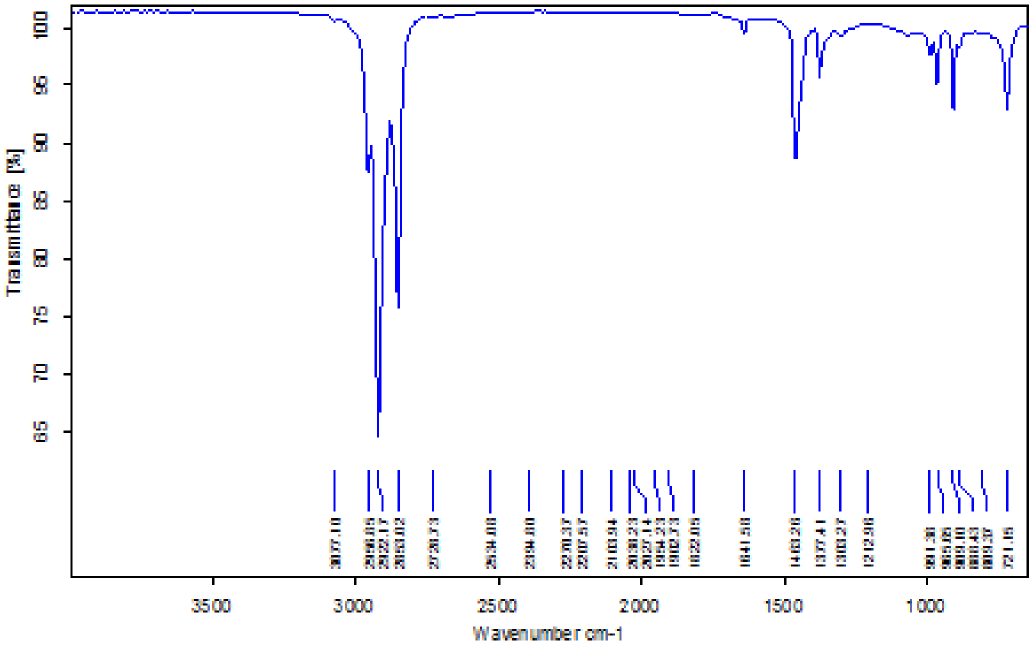

Fig. 8, FTIR for liquid produced from pyrolysis of LDPE

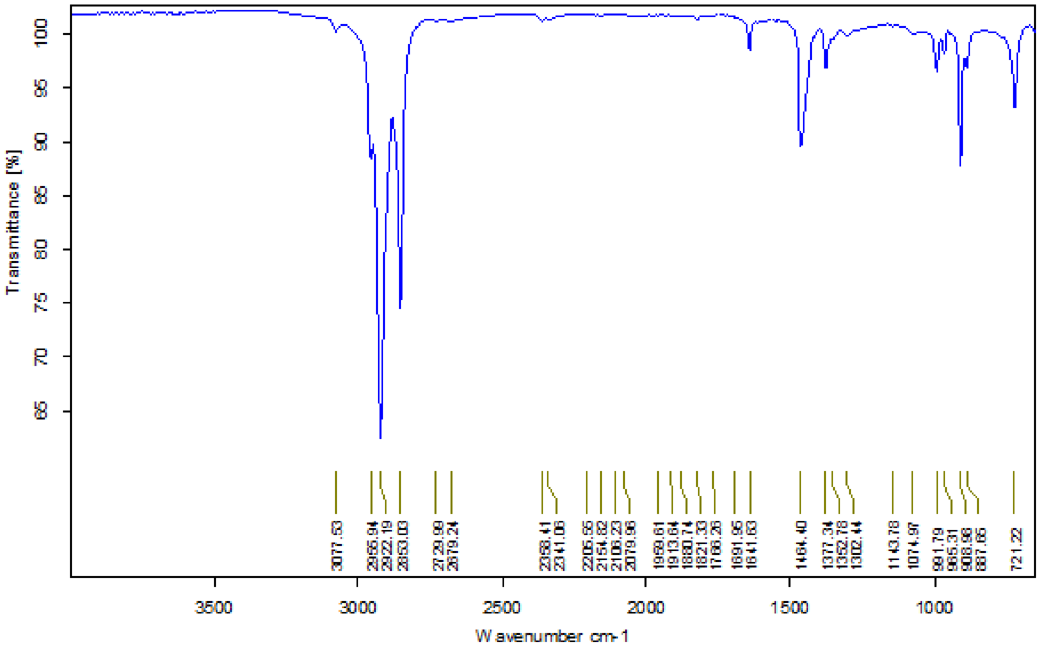

Fig. 9, FTIR for liquid produced from pyrolysis of HDPE

Simple distillation

Simple distillation for hydrocarbon liquid produced from pyrolysis of LDPE and HDPE was done at atmospheric pressure.

The initial boiling points were 87 and 114 for the hydrocarbon liquid fuels produced from the pyrolysis of LDPE and HDPE, respectively.

Figure 10 shows the accumulative volume of produced hydrocarbon liquid fuels. Both hydrocarbon liquids have the same fractions distribution with total light fractions (below 250 °C) of about 54 to 54.4 Vol. %. Liquid hydrocarbons with these fractions are rich sources for producing valuable petroleum fraction such as gasoline, kerosene, and gasoil.

These results are in a good agreement with the previous work [22].

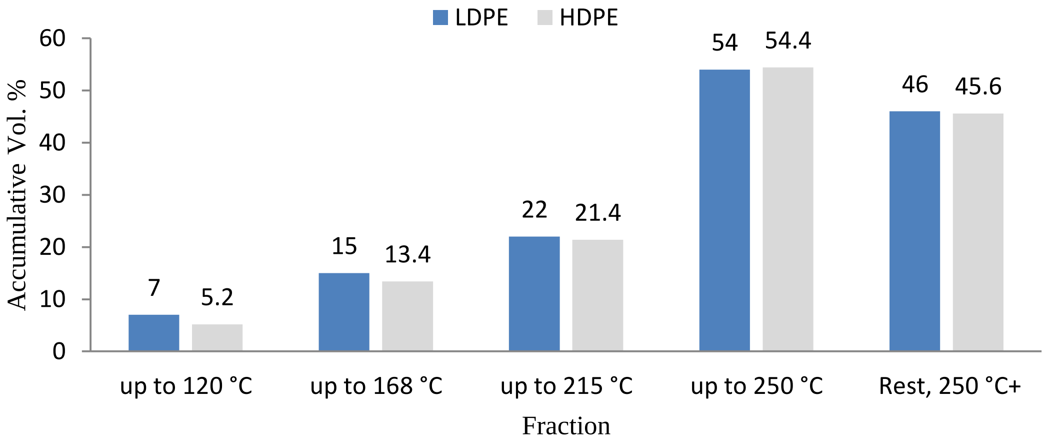

Fig. 10, Accumulative volume percent versus fraction range of hydrocarbon liquid fuel

Sulfur content

The sulfur content of all produced liquids from thermal pyrolysis of LDPE and HDPE is zero percent.

Generally polyethylene plastics does not contain sulfur and water in the monomer (ethylene) which is composed of only carbon and hydrogen. The reported sulfur content of oil obtained from catalytic pyrolysis of mixture waste plastic in cylindrical reactor at temperature range of 300 to 350ºC is 0.002 wt. % [23].

Other characterization properties

Specific gravity, kinematic viscosity, flash point, and pour point were measured for the produced hydrocarbon liquid fuel. Table 3 summarizes these properties for hydrocarbon liquid fuels produced from the pyrolysis of LDPE and HDPE.

Table 3, Characterization properties of the hydrocarbon liquid fuel

Property	LDPE	HDPE
Sp. Gr., -	0.7844	0.7865
Viscosity, cSt	2.85	3.49
Flash point, °C	36	33
Pour point, °C	15	25

The characterization properties of the produced hydrocarbon liquid are in good agreement with the reported [22, 23].

Conclusion

1. TGA analysis of LDPE and HDPE samples occurs in a single step and depends on their structure. The stability was found from TGA to be in the order of HDPE greater than that of LDPE, due to different in molecular weight.
2. Polyethylene pyrolysis products consist of a mixture of gas, oil, wax, and coke. The ratio of each product can be changed by changing the reaction condition such as temperature between 370 and 450 °C.
3. The optimum temperature range for pyrolysis of polyethylene plastics was 390 to 410 °C.
4. The reaction time for complete pyrolysis of polyethylene plastic was about 35 minutes.
5. The yield of liquid obtained was about 48.98 and 57.24 % for thermal pyrolysis of LDPE and HDPE, respectively.
6. The FTIR shows no significant differences between thermal and catalytic pyrolysis of polyethylene in composition of alkanes group.
7. The sulfur content of all liquids produced from thermal and catalytic pyrolysis of LDPE and HDPE is zero percent.
8. The liquid fraction derived from thermal and catalytic pyrolysis of the two types polyethylene could be used as source of gasoline, kerosene, and gasoil.

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