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Pyrolysis of High-density Polyethylene for the Production of Fuel-like Liquid Hydrocarbon

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Abstract

Pyrolysis of high density polyethylene (HDPE) was carried out in a 750 cm^3 *stainless steel autoclave reactor, with temperature ranging from 470 to 495° C and reaction times up to 90 minute. The influence of the operating conditions on the component yields was studied.*

It was found that the optimum cracking condition for HDPE that maximized the oil yield to 70 wt. % was 480°C and 20 minutes.

The results show that for higher cracking temperature, and longer reaction times there was higher production of gas and coke. Furthermore, higher temperature increases the aromatics and produce lighter oil with lower viscosity.

Keywords**:** pyrolysis, high density polyethylene, kinetics, activation energy**.**

Introduction

Polyethylene is the major component of the total plastic content of the municipal solid waste (MSW). For example it represents 55 wt. % of total plastics consumed in Australia in 2003 [1].

Recycling is one of three ways for utilization and minimization of the huge amount of waste. The others are landfilling and incineration with or without energy recovery. Neither landfilling nor incineration can solve the growing problem of huge amount of waste [2].

Recycling can be classified into the following categories: primary recycling or re-extrusion, secondary mechanical recycling and tertiary (chemical or thermal recycling) [3].

Pyrolysis involves the degradation of the polymers by heating in an inert atmosphere. The process is usually conducted at moderate temperatures between 400-800 °C and results in the formation of volatile fractions that may be separated into condensable hydrocarbon oil and a non-condensable high calorific value gas [4-6].

Plastic pyrolysis may serve as a stand alone operation or preferably as a pretreatment to yield a stream to be blended into a refinery or petrochemical feed stream [7], Where the liquid obtained had a low octane number although the oil has a high cetane number due to its low aromatics content [8].

Polyolefin resins (contain only carbon and hydrogen i.e. PE, PP) of various origins are a desirable pyrolysis feedstock [9]. So, pyrolysis appears to be a technique that is able to reduce a bulky, high polluting industrial waste while producing energy and/or valuable chemical compounds [10].

As an advantage, pyrolysis can treat all the mixtures consisting of various types of plastics without separation or treatment [11].

The produced oil is distributed to end users, typically as a cheaper substitute for heavy oil and it can be used in industrial boilers, burners, and power generators [12].

Ng et al. [8] held a thermal decomposition for PE in a batch reactor at a temperature range of 450 to 500° C, and the reaction was carried out for 10 minute. The final pressure at the reaction temperature ranged from 1.38 to 16.13 MPa. The gases were analyzed by gas chromatography, and the other products were separated into naphtha, gas oil and residue by distillation. The amount of residue decreased with temperature, and the amount of gas increased with temperature. The yield of gas oil was maximized at 470° C, and it consisted primarily of normal saturates and lesser amounts of α-olefins. Only small amounts of branched hydrocarbons were detected in pyrolysis products.

Pinto et al. [13] carried out thermal decomposition for PE and PP in 1 liter autoclave .They tried to optimize the polymer pyrolysis on experimental conditions used. It was suggested that the run temperature of 450° C, reaction time of 30 min and an initial pressure of 0.14 Mpa is the optimum. The alkanes formed in greater amounts were those with carbon atoms between 5 and 11. Branches and cycled alkanes appeared in very low concentrations with the exception of methylcyclohexane.

Miskolczi et al. [2] applied thermal cracking for polyolefin's (PE, PP) at 525° C with a horizontal tubular reactor. It was found that the cracking parameters (the type of waste polymers and residence time) affected not only the yields but also the composition of products.

Miller et al., [14] used a thermal atmospheric pressure pyrolysis that converts high molecular weight molecules to lower molecular weight in the lube oil range. The major by product is diesel with little production of C4-gas. The pyrolysis yield products were in the range of 37 to 57 wt. %, whereas the potential lube yields were 60-70 wt. %.

The aim of this work is to investigate the pyrolysis behavior of HDPE in a batch process. The effects of the cracking parameters (reaction temperature and residence time) on the yield, group composition, distribution of distillate fractions and final properties of fuel like liquid products were also investigated.

Experimental Work

Materials

Feedstock

HDPE pellets were obtained from the State Enterprise of Petrochemicals Industry/Basrah. The main properties of HDPE polymer are shown in Table 1.

Nitrogen gas

Nitrogen gas was supplied from Dijlah factory with a purity of 99.9%.

Table 1 Physical and chemical properties of feedstock

Property	HDPE Sepilex HHM5502	Test method
Density (g/cm3)	0.9550	ASTMD 1505
Melt flow index (g/10 min)	0.35	ASTMD 1238
Deflection temperature (°C)	75-80	-
Melting point (°C)	130-135	-
Average particle diameter (mm)	3	-

Pyrolysis apparatus and procedure

The pyrolysis was performed in a 750 cm^3 stainless steel autoclave of 5 mm thick wall, equipped with a motor driven stirrer with two blades used for agitation. Thermocouple (type K) with digital temperature recorder was used. A pressure gauge 1- 250 bar (0.1-25MPa) was connected to the top of the reactor to read the pressure inside the reactor.

Heat was supplied to the reactor by 1200 Watt electrical heater connected to a voltage regulator in order to adjust the heating temperature. A schematic diagram of the experiments is shown in Fig. (1).

A tubing system was connected to the top of the reactor. All tubing had (302 mm OD and 204 mm ID) thick stainless steel wall. A big metal container positioned in a cooler was ready to quench the reactor inside it after each run. The quenching process was done by using cooled water at 4° C.

The autoclave was first cleaned with sand paper, and solvents, and then it was loaded with a measured amount (175 g) of the pellets and closed. The autoclave was then bolted tightly and evacuated by applying vacuum 0.068MPa then tested with N_2 gas by flushing the system twice to remove any air present. The reactor was closed at atmospheric pressure and it generated maximum pressure of approximately 5MPa at 495° C. After the charged feed reached 200° C, the stirrer was put in motion.

Reactor temperature was increased to the pre-set temperature by turning on the electrical heater. The accuracy of temperature readings was less than 5° C and the time zero was taken as the time after which the reaction melt reached the specified reaction temperature.

After reaching the specified time in any temperature the heating was stopped and the reactor quenched in the water bath of 4° C. Then, after reaching about 25° C, the gaseous products were vented and the products were weighted. The mass balance of reactants and products was estimated and analyzed.

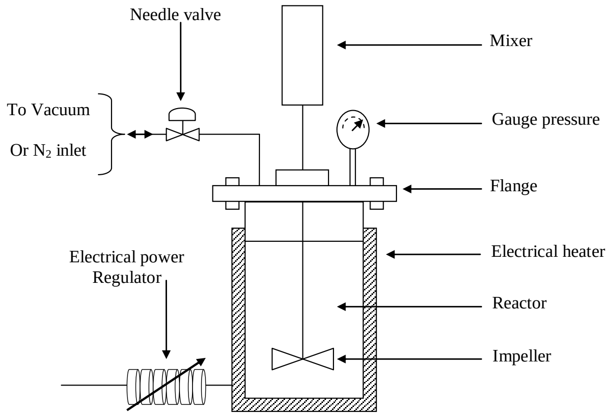

Fig. 1 Schematic diagram of the experimental apparatus

Analysis Methods

Yields calculations

The mass of gas formed was determined by the weight loss after discharging. The product slurry was then removed from the reactor. About 10 g of the slurry product was solvent-extracted with hexane to remove the oil formed. The hexane-insoluble were extracted with THF to remove asphaltenes and preasphaltenes. In all these runs, the amounts of asphaltenes and preasphaltenes were negligible. The THF-insolubles were then extracted with decalin at 140 °C [15].

Preliminary distillation (IP 24/55)

50 cm^3 Liquid product was distillated in atmospheric pressure and constant heating rate (about 5 cm^3 /min) in the following fractions: (IBP-140° C), (140-200° C), (200-270° C) and (>270° C).

Other tests

- Method of measuring aromatic plus olefin fractions (ASTM D 1019-68).
- Olefin content (IP 128/63).
- Liquid density measurements (ASTM D 1505). The density was taken to both the fuel like product and the light distillate (<270°C).
- Liquid viscosity (ASTM D 2515).

Results and Discussion

Effect of reaction time and temperature on product yield

The effect of reaction time on the formation of gas, oil, coke and un-reacted polymer at different reaction temperature was studied in time range up to 90 minute. Results of this investigation were presented in Fig. 2 to Fig. 4.

For HDPE pyrolysis at 480° C the gas increased to about 56 wt. % , while at 495° C it increased up to 69.5 wt. %.

It can be deduced that the primary pyrolysis of PE takes place through a free-radical transfer that leads to low yield of gases. Nevertheless, the more gases obtained from secondary pyrolysis of waxes at gas phase can be interpreted as a consequence of the propagation reaction [16].

The produce oil at 470° C increased up to a maximum yield about 71 wt. % at about 30 minute and then decreased to reach about 50 wt. % at 90 minute as in Fig.2.

The oil produce from HDPE at 480° C reaches maximum (about 70) at 20 minute and then decreases with the reaction time increases, as seen in Fig. 3.

Hence, there exists an optimum reaction time at which the liquid products are maximized. This optimum time occurs around at 20 minutes for HDPE.

Ramdoss and Tarrer, [17] found that optimum time was 5-10 minutes for producing oil from post consumer PE and PP waste at 500°C.

The other observation in Fig.s 2 to 4 was the coke formation where the coke raised up to 0.5 wt % at 480° C and 90 minute for HDPE pyrolysis as in Fig. 3. Coke formation was likely the result of the secondary reactions of products (coke precursors) formed during the primary pyrolysis process. These results agree with those of Horvat and Ng, [18].

The experimental results in Fig.s 2 to 4 show that practically all the mass of PE is exhausted when the maximum point for oil production was reached. The oil yield decreased since the secondary gas and coke were formed. It is also seen that the mass fraction of the plastic being decomposed decreases with pyrolysis time.

Park et al. [19] and Walendziewski [20] had concluded that shorter times favor larger yields of liquid and longer reaction times favors larger gas yields at the same temperature.

The main effect of increasing temperature within this range of temperature 470 to 495° C was increases the rate of formation of gases and decreases the rate of formation of solid residue (un-reacted plastic). Fig. 5 demonstrates the effect of temperature on the yield of gas, oil, coke and plastic itself (HDPE) at the optimum time.

It was found that the gas yield resulting from decomposition HDPE increased from about 14 wt. % to about 25 wt. % when the pyrolysis temperature was raised from 470° C to 495° C. This increasing in gas yield was probably due to the increase in the rate of main chain sigma bond cleavage reactions in the more thermally energetic high temperature environments. Also the growing yield of gas could be caused by the differences in stability of polymer chains. Therefore at 495° C, the C-C bonds cracked more rapidly than at lower temperature (i.e. 470° C) and these results in higher gas yield [18].

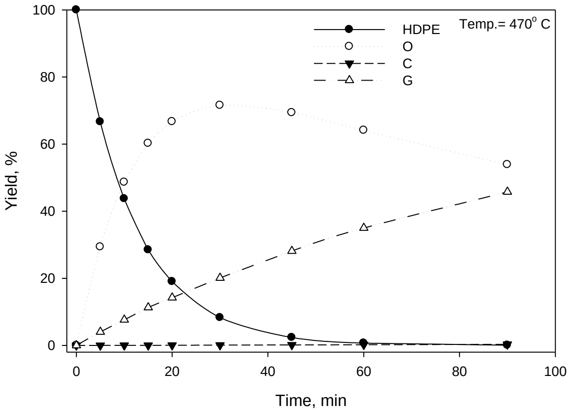

Fig. 2 Yields of different products from pyrolysis of HDPE at 470° C reaction temperature

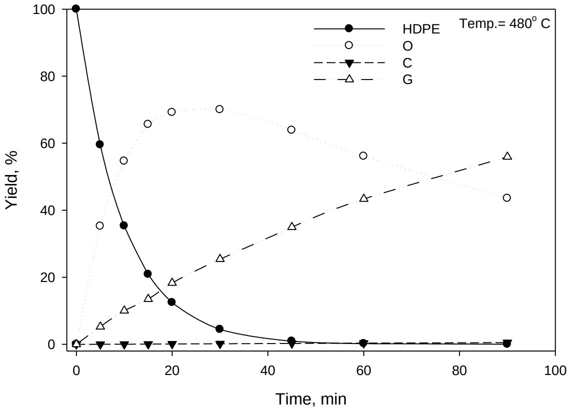

Fig. 3 Yield of different products from pyrolysis of HDPE at 480° C reaction temperature

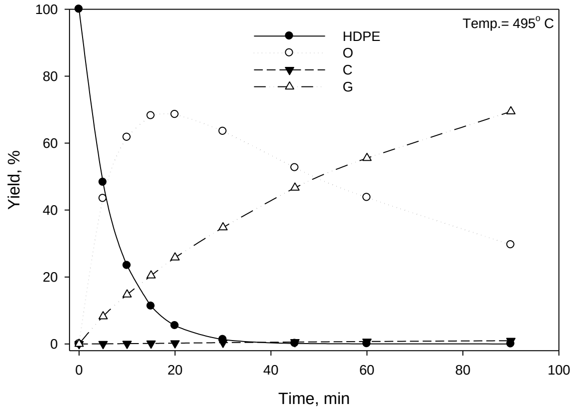

Fig. 4 Yield of different products from pyrolysis of HDPE at 495° C reaction temperature

The effect of temperature on the yield of oil was tracked. There was an increase in the yield of oil from about 67 wt. % to about 69 wt. %. Then, it could be seen that there was a slight decrease in oil yield at optimum cracking time.

It was noticed that the decomposition temperature influence the amount of volatile products. As the decomposition temperature increases the minimum length of the fragment which can evaporate under the prevailing conditions also increases [10, 21].

The effect of temperature on coke formation at fixed time was also studied. It can be seen from Fig. 5 that the coke increased from about 0.05 wt. % at 470° C to about 0.23 wt. % at 495° C, both at 20 minute for HDPE pyrolysis. The reason might be the mobility of the thermally generated free radicals.

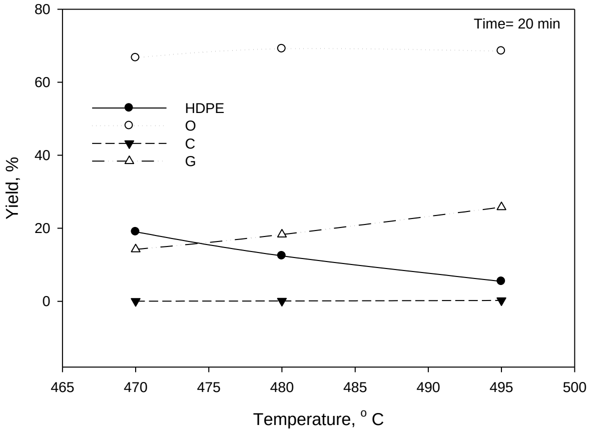

Fig. 5 Variation of components yield with pyrolysis temperature of fuel like liquid produced from HDPE pyrolysis at 20 minute reaction time

The effect of reaction temperature on the plastic itself was shown in Fig. 5. It is clear that the decomposition of HDPE increased with increasing reaction time. These observations are in good agreement with the results of Conesa et al. [16] and Wong et al. [22].

The density and viscosity of produced fuel-like liquid hydrocarbon were 0.9076 g/cm^3 and 2.056 Cst, respectively, at 480° C and 20 minute.

Effect of reaction time and temperature on group composition

From Fig. 6 it is obvious that aromatic is formed in a large extent with increasing the pyrolysis time. It can be raised up from about 11 to about 15 wt. % for HDPE at 480° C and 90 minutes reaction time.

This indicates that higher aromatic content was found with higher residence times. The cause may be that in closed systems volatile products remain in the reaction zone and are in equilibrium with liquid phase and can contribute to secondary reactions, such as ring formation and aromatization. Mosio-Mosiewski et al. [23], Pinto et al. [13] and Ng, et al. [8] agreed with this trend.

The effect of pyrolysis time on the alkene content during HDPE pyrolysis is obvious in Fig. 6. It can be seen that the alkene content decreased slightly from about 15 % at 10 minute to 11% at 90 minutes and 480° C for HDPE. The reason of this phenomenon was the probabilities of secondary reactions (e.g. re-polymerization of alkenes) become higher with long cracking time [2].

The effect of reaction temperature in the ranges of 470 to 495° C on the relative amounts of alkanes, alkenes and aromatics at their optimum reaction time, where shown in Fig. 7, which illustrated that the aromatic content at the optimum time for the polymers increases with increasing the temperature.

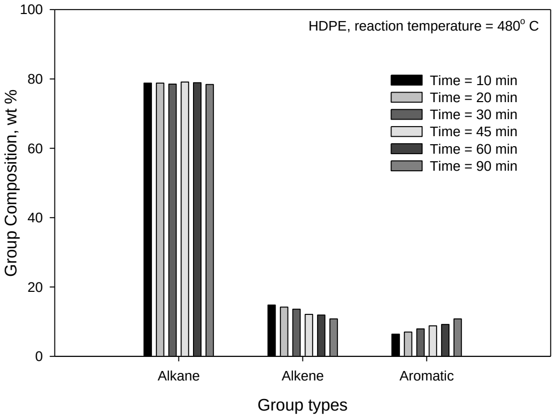

Fig. 6 Group composition analysis of fuel like liquid (<270° C) produced from pyrolysis of HDPE at 480° C reaction temperature

The aromatic content increased from about 4 to about 15 wt. %. The formation of aromatics at high temperatures occurs due to lighter hydrocarbons such as ethene and propene reacting to form aromatic compounds as benzene and toluene. It was reported that at higher temperatures ethene and propene were unstable [24].

Fig. 7 shows that the increase in this temperature range started to decrease alkenes from about 17 to about 11 wt. %. According to the mechanism of alkane and alkene formation, alkene formation is a uni-molecular reaction and alkane formation is a bimolecular reaction. So, higher temperature makes alkane formation (intermolecular propagation reaction), the more favorable reaction. Bockhourn et al, [25] pointed out that the contribution of energies of activation energy to the apparent alkane and alkene formation was 42 and 112 kJ /mol, respectively.

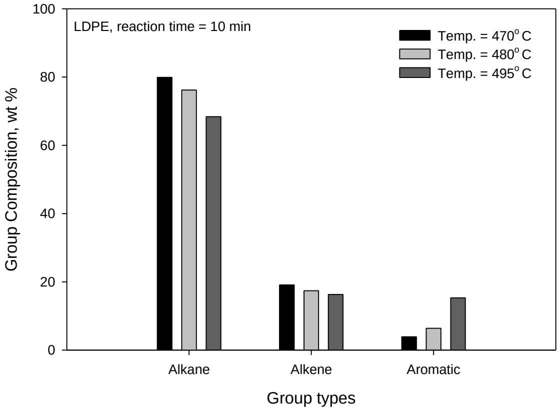

Fig. 7 Group composition analysis of fuel like liquid (<270° C) produced from pyrolysis of HDPE at 20 min reaction time

Effect of reaction time and temperature on the distillate fractions

The effect of pyrolysis time on the relative amount of fractions of oil produced from atmospheric distillation was shown in Fig. 8. It can be seen that the first two fractions IBP-140° C and 140-200° C increased with increasing pyrolysis time up to 90 minute.

The first fraction IBP-140° C raised from 6 wt % to 15 wt % and the second fraction (140-200 °C) raised from 15 wt % to 36 wt %. The third fraction (200-270° C) increased slightly during the first 45 minute, and then it began to decrease. While the residue (>270°C) decreased sharply during the first 45 minute, then it began to increase slightly.

The results suggest that as pyrolysis time increased, the heavier products decomposes to lighter ones, because at higher pyrolysis time the carbon chain was exposed to more forceful thermal decomposition effects, due to its being under harsh environment for a long time. Rangarajan et al. [25] and Walendziewski and Steininger [9] agreed with these findings.

When distilling the fuel like products from HDPE pyrolysis, it was noticed that the first two fractions (IBP-140° C and 140-200° C) increased with increasing the pyrolysis temperature from 470 to 495° C at fixed reaction time. The heavier fractions (200-270° C) and the residue (>270° C) decreased with increasing the reaction temperature for both polymers, as shown in Fig. 9.

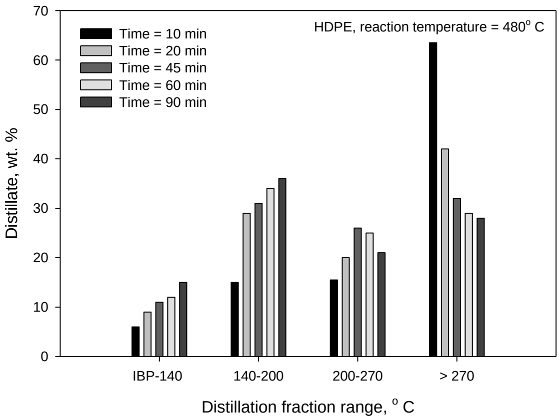

Fig. 8 Variation of distillate fractions weight percent with reaction time of fuel like liquid produced from HDPE pyrolysis at 480° C reaction temperature

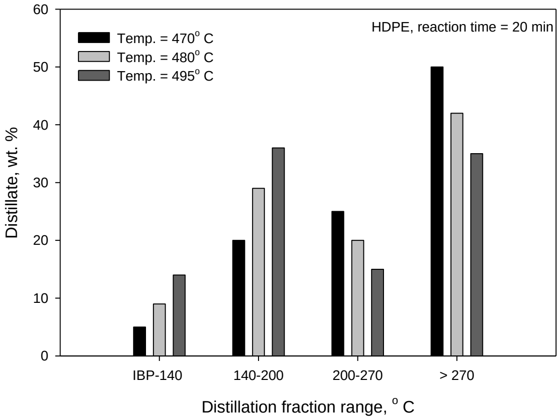

Fig. 9 Reaction temperature effects on the distribution of distillate fractions of fuel like liquids and light products out from HDPE pyrolysis at 20 minute

This may be explained that among the various product fractions in each of the polymers, higher energy would be required to produce lighter fractions because on the average it takes more derivative steps to form the lighter products. Also high temperature increased the rate of volatilization of longer chains, where they undergo β-scission at a rate much higher than that found in light fractions. This observation fit the trend observed by Ranjargan et al. [25].

Conclusions

Based on present work, the following points can be concluded:

1. PE pyrolysis yields a mixture of oil, gas. The higher the pyrolysis temperature and the longer the reaction times increase the gas yield.
2. There was an optimum temperature and pyrolysis time and which the liquid products is maximized. This optimum temperature occurs around 480 °C and the optimum reaction time was 20 minute for HDPE with oil yield 69.2 wt %.
3. It was found that for higher cracking temperature and longer reaction time, there was higher production of gases and coke. Gas yield was increase from 14.23 % at 470° C to 25.78 % at 495° C at 20 minute reaction time, while gas yield increased up to 55.92 % at 90 minute.
4. Aromatics increased with temperature and time while alkenes decreased.
5. Distillation of fuel-like liquids show more light fractions for fuel like liquid produced at higher temperature and longer time.

Nomenclature

C	Mass fraction of coke , wt. %
E	Activation energy , J/mol
G	Mass fraction of gas , wt. %
O	Mass fraction of oil, wt. %
P	Mass fraction of un-reacted plastics , wt. %

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