

Pyrolysis of Polyethylene Waste in Free Falling Reactor

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In this study, the pyrolysis of polyethylene wastes in free falling reactor at 500-750 °C was investigated. In the quantitative evaluation of pyrolysis products it was observed that the yield of gas products increases whereas the yield of solid and liquid products decreases with increasing temperature. Pyrolysis products were analysed by using of gas chromatography. 1- Olefins, branched paraffins and n-paraffins were determined in gas and liquid hydrocarbon fractions. Because of the importance for chemical and petrochemical industry, 1- olefins selectivity and ASTM –Distillation curve of the pyrolysis products were also determined. The selectivity of the 1-olefins in total hydrocarbons decreases but the selectivity of branched hydrocarbons in total product increases with increasing temperature. ASTM-Distillation curves of the pyrolysis products were compared with ASTM-Distillation curves of Kerkuk –Crude oil and showed that the pyrolysis products contain more volatile hydrocarbons than Kerkuk-Crude oil. As results of these evaluations, it can be concluded that the polyethylene wastes could be efficiently converted into the valuable chemicals and liquid fuels.

Introduction

Environmental pollution increases day by day all over the world. Solid wastes (especially plastic wastes) are very important in environmental pollution. About 20 % of used plastic can be reused. The remainder must either be recycled into petrochemical feedstock or can be used reducing agent in thermal process or as a fuel [1]. Of the plastic discharged as a waste, packing materials make up 50-70 % of the total. Of this amount, 89 % are polyolefins (polyethylene, polypropylene, polystyrene and poly (vinyl chloride), with polyethylene being about 63 % of all packing waste [2]. With the rapid growth of plastic consumption in industrial societies during the last decade, interest and concern in the problems of plastic waste have increased dramatically, and the complexity of relevant issues has been recognised. As most plastics are produced from oil, the recycling of plastics and rubber wastes is of increasing importance [3,4].

Pyrolysis is one of the possible technologies for the conversion of waste to useful products. It offers the facility for preserving the available polymer hydrocarbons and producing valuable petrochemicals. The yields of the products obtained from a pyrolysis process are due to the raw material decomposition (primary reactions) and to the reactions suffered by the primary volatiles (secondary reactions). The extension of the secondary reactions depends on the experimental equipment as well as the operating conditions. To obtain products of good economic value, it is necessary to control and regulate the reactions. For an efficient cracking, the reaction has to be rapid -like a “ flash pyrolysis”- it is also necessary to limit the residence time in the

reactor or in the pyrolysis zone, so as to avoid recombinations and undesired reactions [5].

In this paper we report on the flash pyrolysis of polyethylene waste, product yields, 1-olefin and branched hydrocarbons selectivity as a function of the pyrolysis temperature and simulated ASTM-Distillation curves of the derived oils.

Materials and Materials

In the flash pyrolysis experiments, 5 g of plastic waste including polyethylene was used. The waste plastic samples were cutted into a 2 mm in size. The flash pyrolysis reactor is a stainless steel pipe with 120 cm length and 5 cm internal diameter. The reactor was heated in five independent zones so as to obtain a temperature gradient from the top to bottom of the reactor. The experiments were carried out with the temperatures varies in the range of 500 –750 °C. Nitrogen gas was used as a sweeping gas and introduced from the top of the reactor with a constant flow of 40 mL/min. The polyethylene samples were dropped from the top of the reactor so as to reach the pyrolysis temperature at the bottom side of the reactor in a short period. The products were condensed by using two sample collecting bottle inserted into the ice-salt cooling bath. Condensable products (solid wax and liquids) were collected in the first bottle. The remaining products were led to the second sampling bottle, which contains toluene as a solvent. The sampling from gas products was carried out by using two way gas sampling tube and, remaining gas was discharged into the atmosphere. The liquid and gas products, which occurred after the pyrolysis, were analysed by using capillary gas chromatography given the set of conditions in Table 1 and 2.

Table 1: Operating conditions of capillary gas chromatography used for analysis of liquid products

Chromatography		Chrompack, CP 9000
Integrator		IBM PC
Column	Stationary Phase	CB Cil 5B-Methyl Silicon (cross bonded)
	Diameter	0.22 mm
	Length	10 m
Carrier Gas		Nitrogen (Column flow rate: 0.4 mL/min, Make up flow: 30 mL/min)
Detector		Flame Ionization Detector (FID)
Temperature	Oven	Temperature program 40 °C to 200 °C
	Heating Rate	10 °C/min
	Detector	240 °C
	Injector	230 °C

Table 2: Operating conditions of capillary gas chromatography used for gas product analysis

Chromatography		Hewlett Packard 5890 Series II
Column	Filling Material	Propack Q
	Diameter	1/8
	Length	6 m
Carrier Gas		Hydrogen (Column flow rate: 20 mL/min)
Detector		Thermal Conductivity Detector (TCD)
Temperature	Column	125 °C
	Detector	200 °C
	Injector	200 °C

Because it can be distilled more than 50 vol.% of Kerkuk crude oil below 350 °C, it is accepted as one of the high quality oil all over the world. For that reasons, our results were compared with Kerkuk crude oil using ASTM D-2887. In this method, a standard mixture which consists of n-paraffins having different boiling point temperatures were analysed in order to plot the simulated distillation curves by using gas chromatography which were given the operating conditions in Table 3. Next, the product mixture in toluene was also analysed by using gas chromatography at the same operating conditions. After the evaluation of the chromatographs, the ASTM – Distillation curves were plotted and the volumetric fractions of the products, which is boiled below 350 °C, were determined and compared with Kerkuk crude oil.

Table 3: Operating conditions of capillary gas chromatography used for ASTM D-2887

Chromatography	PACKARD 433 Model
I. Column	
Filling material	5 % Sebaconitril Chromsorb Paw 80-100 mesh
Diameter	1/8 "
Length	12.2 m
II. Column	
Filling material	Phenyl Iso Cynate Porasil C80-100 mesh
Diameter	1/8 "
Length	1.2 m
Carrier Gas	Hydrogen (Column flow rate: 30 mL/min)
Detector	Thermal Conductivity Detector (TCD)
Column	35 °C
Detector	100 °C
Injector	80 °C

Result and Discussion

The samples were pyrolysed at the temperatures varied from 500-750 °C. The distribution of gas, liquid and solid fraction of pyrolysis product was given in Figure 1. As shown on this figure, the yield of gas products increases with increasing temperature and the value is about 80 wt.% at 600-700 °C whereas this value is 90 wt.% at 750 °C. The gas product contains mainly methane, ethylene, propylene, butylene and some other light hydrocarbons. The yield of liquid product is 35.3 wt.% at 500 °C. This value decreases with increasing temperature and, is about 15.0 wt.% at 600-700 °C whereas the value decreases to 8.6 wt.% at 750 °C. The solid fraction decreases with increasing temperature, continuously, and the yield of this fraction is 1.1 wt.% at 750 °C. Bridgewater (1992) has reported that: flash pyrolysis maximises liquid yields at relatively low temperatures of typically 500 °C but less than 650 °C. Similar flash pyrolysis but at relatively higher temperatures of 700 °C maximises gas yields. Scott (1990) studied the pyrolysis of polyethylene and obtained yields of gases and liquids similar to those obtained in the present work.

The using of nitrogen as a sweeping gas diminished the 1-olefins selectivity because of reducing of secondary reactions. The selectivity of the 1-olefins and branched hydrocarbons in total hydrocarbons as a function of temperature was given in Figures 2-3. With increasing temperature, the selectivity of the 1-olefins in total hydrocarbons decreases but the selectivity of branched hydrocarbons in total hydrocarbons increases.

ASTM-Distillation bar graphics of the liquid hydrocarbons mixture obtained by the flash pyrolysis of polyethylene wastes at 350 °C showed that the distilled fraction of the pyrolysis products are more volatile than the Kerkuk-Crude oil. From Figure 4, it can be seen that the fraction distilled at 350 °C is 64 wt.% for Kerkuk-Crude oil whereas this fraction is above 68 wt.% for flash pyrolysis products.

Conclusion

As a result of the flash pyrolysis experiment, it was decided that the yield of gas products increases with increasing temperature. C₁-C₄ gas hydrocarbon fractions and, C₅-C₂₈ liquid hydrocarbon were observed by Gas chromatographic analysis. There was a decreasing in the yield of liquid product as well as a tendency to the selectivity of low molecular weight hydrocarbons especially 1-olefins was observed with increasing temperature. Because the products were swept out of the system continuously by inert gas during the operation, the low selectivity of isomers was observed. The Nitrogen carrier gas reduced the extent of secondary reactions such thermal cracking, repolymerization and recondensation. The liquid products obtained from the flash pyrolysis were compared with the Kerkuk-Crude oil and all of the ASTM-Distillation bar graphics showed that the liquid products are more volatile than the Kerkuk-Crude oil. As a result of all evaluations, it was determined that the products of flash pyrolysis operation of polyethylene wastes can be used as a feedstock for petrochemical industry. Because of the high selectivity of 1-olefins in pyrolysis products, these liquid hydrocarbons can be also used for chemical industry. In this way, an effective evaluation possibilities of polyethylene waste being an environmental pollutant was proposed in result of this study.

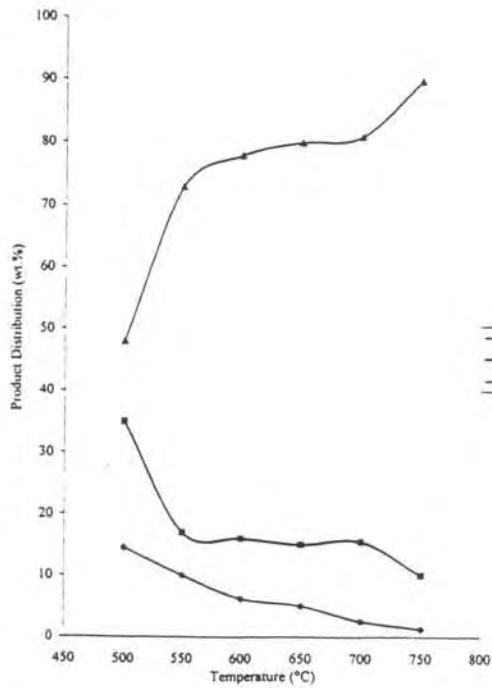


Figure 1: Distribution of Flash Pyrolysis Products

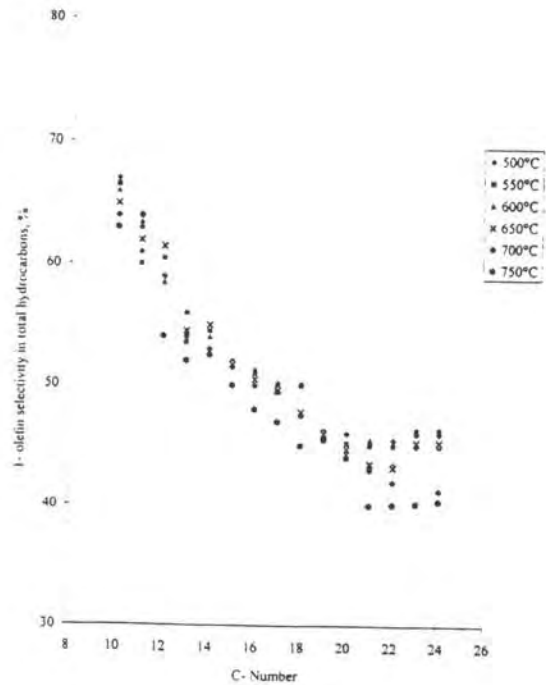


Figure 2: The selectivity of 1-olefin in total hydrocarbons as a function of temperature for the flash pyrolysis operation

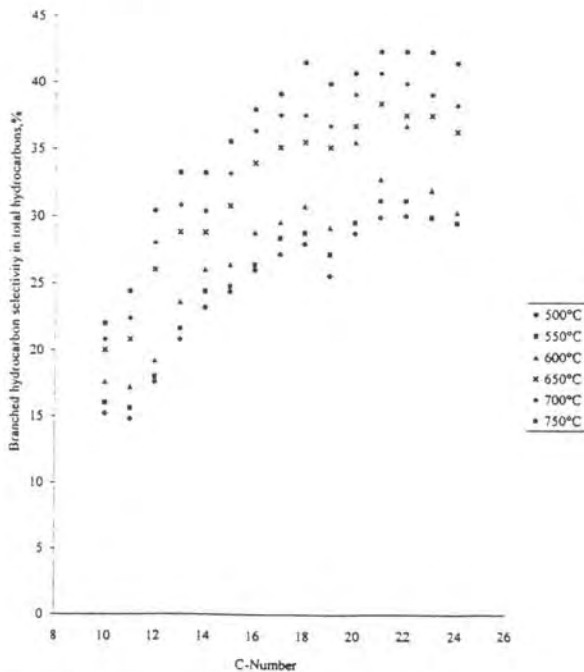


Figure 3: The selectivity of branched hydrocarbons in total hydrocarbons as a function of temperature for the flash pyrolysis operation

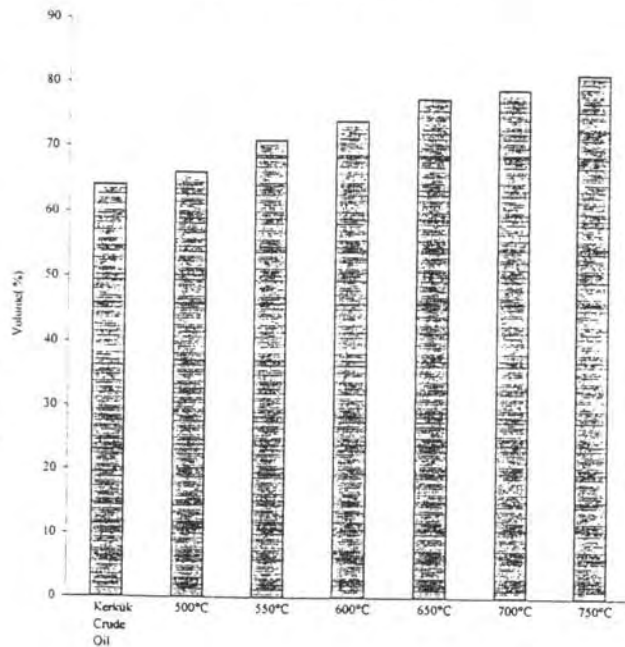


Figure 4: ASTM-Distillation bar graphics of the liquid products obtained from flash pyrolysis at 350°C

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