Hydrocraking of Low-Density Polyethylene Blended with HVGO into Fuels

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The catalytic and noncatalytic hydrocraking of LDPE/Heavy Vacum Gas Oil mixtures into fuels were carried out by batch operation. The effect of catalyst and temperature on the product distribution (gas, liquid and coke) and the properties of liquid products were investigated. The temperature had a great effect on the properties of liquid product and the product distribution. The liquid product obtained at 400 °C with or without catalyst consisted mainly of wax-like compound. As the temperature increased from 400 °C to 425 °C, this compound converted into liquid hydrocarbon. The gas yield increased at elevated temperatures. The use of catalysts was shown to have an influence on the gas and liquid yield. The maximum gas yields at 425 °C 36.6 % in presence catalyst and 47.6 % in absence of catalyst were obtained. The 70 % of the liquid product obtained under the optimum conditions were the hydrocarbons with boiling points ranging over 60 - 200 °C.

Introduction

Hydrocraking is practised in modern petroleum refineries for converting various hydrocarbons of higher boiling points into more valuable products such as gasoline, diesel and jet fuel [1]. It is a highly flexible petroleum refining process which can take feedstocks ranging from light naphthas to vacum residue [2]. Very heavy hydrocarbon deposits such as tar sands and shale oil could also be upgrated by hydrocraking [3]. Hydrocraking has been proposed as a possible feed stock recycling method for plastics.[4], [5]. Various investigators have dealt with catalytic and noncatalytic degradation of PE [6], [7] and plastics mixtures containing PE [8], [9], [10], [11].

The aim of this study is to investigate the processable of LDPE in refinery streams. For this purpose the hydrocraking of LDPE in Heavy Vacum Gas Oil (base feed for hydrocraking unit in refinery in Izmir) was carried out by using DHC - 8 catalyst.

Materials and Methods

Materials

The used Heavy Vacum Gas Oil was a broad vacuum distillate in refinery, with a boling point range of 242 - 578 °C. LDPE (T_m= 110 °C, d= 0.918 - 0.922 g/cm^3) was supplied by ALPET - Izmir as 3.2 mm extruded pellets. The used catalyst was a commercial DHC - 8 in the sulfided form. This catalyst is being used for the hydrocraking of HVGO in Izmir refinery.

Methods

Hydrocraking reactions with or without catalyst were carried out in 100 mL shaking type batch autoclave. Reactions were carried out at 65 MPa initial hydrogen pressure and 25 g. of LDPE (20 % by weight) / HVGO mixtures with or without catalyst. Catalytic hydrocraking experiments, 2.5 g. of catalyst was loaded in the reactor and hold in suspension form. Hydrocraking runs were made at reaction times of 60 and 120 min. and temperatures of 400°C, 425 °C and 450 °C. After the reaction, autoclave was cooled. The gases were analysed by GC. The reactor content was proceed as shown in Fig. 1.

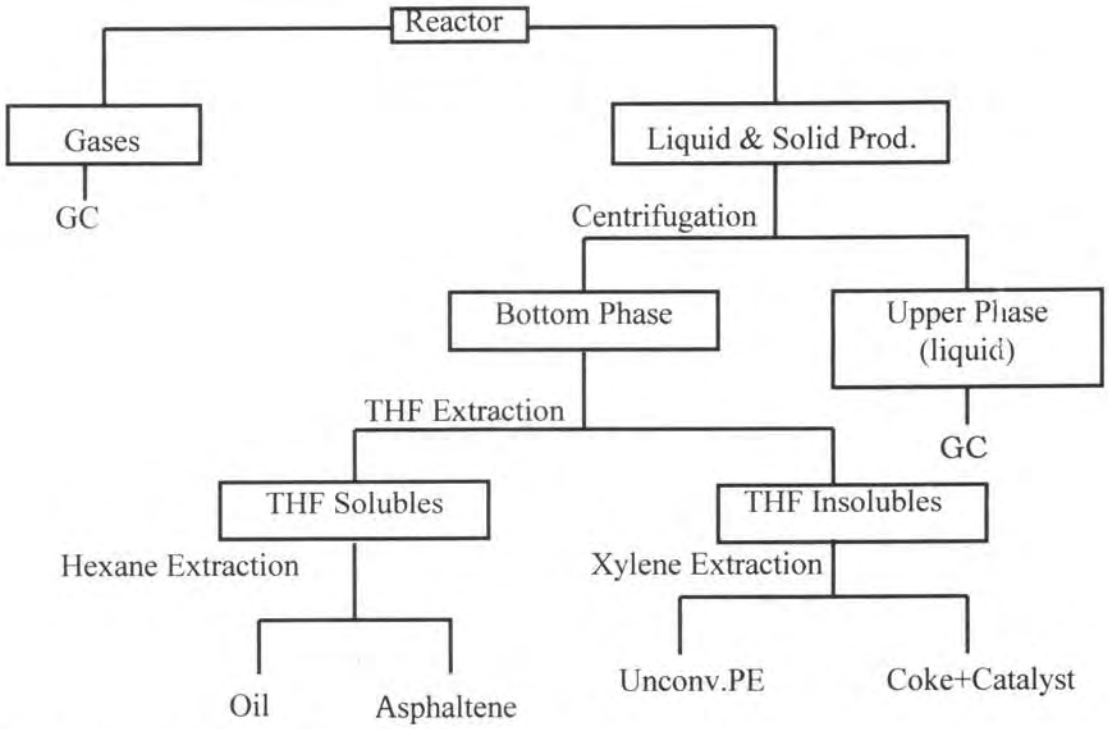

Figure 1 Product Analysis Procedure

Result and Discussion

The distribution of hydrocraking products of HVGO / LDPE mixtures depending on the temperature and the use of catalyst is given at Table - 1 in comparison with the results obtained with that of hydrocraking products of HVGO itself. As shown in Table - 1 the temperature has a significant effect on the product distribution. The liquid and gas products showed an increase as the temperature in the absence of the catalyst. In the presence of the catalyst, the yield of liquid products and the degradation of PE increased at 425 °C and 450 °C, whereas it was observed to have a negligible effect at 400 °C. Most interestingly, gas yield increased with increasing temperature up to 425 °C. However, further increase in the temperature resulted in a decrease in gas yield. The catalyst was observed to have considerable effect on the boiling point range of the liquid product at 450 °C. On the other hand, the heavy fractions in the liquid products have diminished in the presence of catalyst at 425 °C. The presence of PE affected the craking of HVGO.This effect has been observed at all temperatures. This may be explained by taking into account the reaction between the primer degradation of HVGO and PE:

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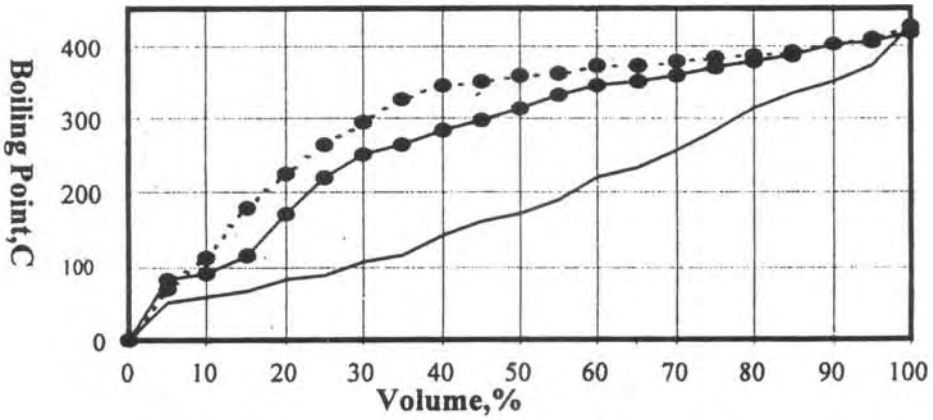
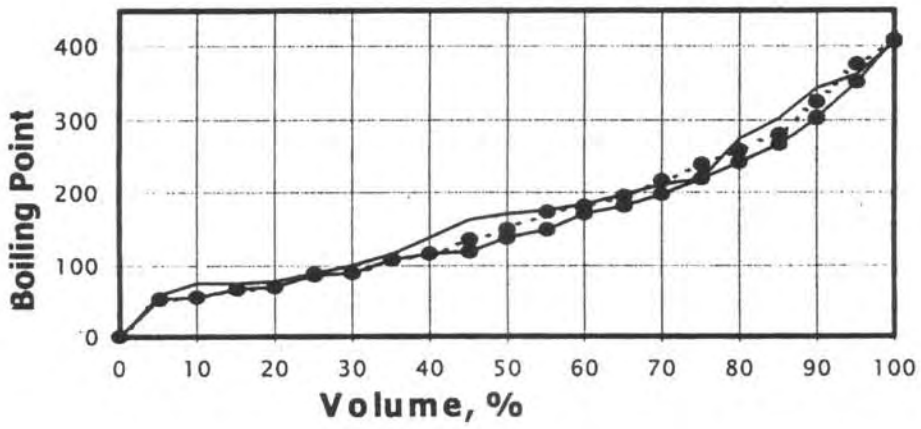


Simulated Distillation Curve of the Liquid Products from HC of HVGO/PE at 425 °C.
— HVGO; —•— HVGO/PE; ---•--- HVGO/PE + catayst



Simulated Distillation Curve of the Liquid Products from HC of HVGO/PE at 450 °C.
— HVGO; —•— HVGO/PE; ---•--- HVGO/PE + catayst

Products Distribution of Hydrocraking from HVGO / PE Mixture

Reaction Temperature, °C	400				425						450					
Feed, 25 g.	**HVGO**		**HVGO / PE**		**HVGO**			**HVGO / PE**			**HVGO**			**HVGO / PE**		
Catalyst, 2.5 g. DHC - 8	-	+	-	+	-	-	+	-	-	+	-	-	+	-	-	+
Reaction Time, min.	120	120	120	120	90	120	120	60	120	120	60	120	120	60	120	60
Reaction Products, wt %																
Gas [1]	15.68	6.16	3.92	6.40	30.40	47.20	65.19	26.84	20.28	36.60	53.20	73.36	63.52	47.60	40.52	29.32
Liquid	55.44	wax	wax	wax	49.12	40.52	30.36	25.24	31.16	38.00	46.80	24.40	29.36	52.00	56.00	60.48
THF Soluble	28.56	93.84	76.08	69.80	20.28	11.24	4.44	38.48	44.36	0.20	-	2.20	7.12	nil	3.28	8.20
Asphaltene	1.96	-	11.20	6.28	-	-	-	2.88	3.48	nil	-	-	-	-	-	-
Coke	0.01	-	-	3.80	nil	1.04	nil	0.01	-	nil	nil	nil	2.48	0.01	nil	2.00
Undegraded PE [2]	-	-	100.00	100.00	-	-	-	45.20	21.40	27.00	-	-	-	-	-	-

[1] Calculated from mass balance

(2) Based on PE charge