Hydrocracking of Heavy Gas Oil Fraction Over NiMo/H-ZSM5 and Ni/Mordinite Catalysts

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Abstract

At present, the usage of the hydrocracking process in the refining industry has increased rapidly worldwide in recent year. The objective of hydrocracking is used to convert the heavy fractions of the feed into more valuable lighter products, such as naphtha, kerosene and middle distillates. This is an attempt to spot the appropriate catalyst support that can process heavy gas oil (HGO) feed. Heavy gas oil was chosen as a feedstock to investigate in this research by hydrocracking process on two different of zeolite catalysts ZSM-5 and Mordinite based Molybdenum and Nickel dual functional catalysts. At different temperatures (400, 425, 450 °C) using autoclave batch reactor. The results showed that the hydrocracking of HGO over NiMo/H-ZSM-5 and Ni/MORDINITE catalysts was successfully catalytically hydrocracking into gases, gasoline and distillate products. SIMDIST, GC and TGA techniques were used to analysis the feedstock and reaction products. The maximum yield of gasoline (C_5-C_{12}) obtained from the hydrocracking of HGO in the presence of NiMo/H-ZSM-5 catalyst at 450 °C hydrocracking temperature was 75.277 wt% .in case of Ni/ Mordinite, the maximum yield of gasoline (C_5 - C_{12}) obtained from the hydrocracking of HGO at 450 °C hydrocracking temperature was 68.819 wt%. Thermal Gravimetric Analysts (TGA) was used in this research to quantify the coke deposited on the surface of catalysts tested. The percentage weight loss of coked catalysts resulting from hydrocracking of HGO over NiMo/H-ZSM-5 and Ni/MORDINITE catalysts are 10.819% and 14.58% respectively.

Keywords: Hydrocracking; heavy gas oil; zeolite catalysts; ZSM-5; Mordinite; Molybdenum and Nickel.

1. Introduction

The petroleum refining industry encounters many stringent environmental and market demands for cleaner and more purified high quality fractions of fuels. Hydrocracking and hydroisomerization of hydrocarbons are among the most important basic processes in the petroleum process industry used to convert heavy fractions of crude oil into a broad range of highly valuable fractions of fuel[1]. The process of hydrocracking encountered rapid growth between 1960 and 1970 with an increase from 1000 bbl/day in 1960 to 770,000 bbl/day in 1970[2]. This rapid growth is attributed to the versatility of the hydrocracking process step and its capability of desul-furizing vacuum residua, making lubricating oils, demetalizing catalytic cracker feed, cracking(VGO) gas oils to jet fuel and gasoline, and cracking naphtha to LPG. This interest in the use of hydrocracking has been caused by several factors, including (1) the demand for petroleum products has shifted to high ratios of gasoline and jet fuel compared with the usages of diesel fuel and home heating oils, (2) by-product hydrogen at low cost and in large amounts has become available from catalytic reforming operations, and (3) environmental concerns limiting sulfur and aromatic compound concentrations in motor fuels have increased[3, 4].

2. Experimental Work

2.1. Sample Definition

Heavy gas oil distilled supplied by Zawia Oil Refinery Company was used for hydrocracking reactions. Two different types of catalysts were used material in the present work namely H-ZSM-5 and MORDINITE. Tested in the batch reactor and XRD for their activity.

2.2. Catalyst Preparation

Two kinds of zeolites were used in this work, ZSM-5 and MORDINITE. The catalyst ZSM-5 will pretreated before use to convert them from the Sodium form to H-form using ion-exchange technique. The loading of NiMo (Ni=3%, Mo=7%) on used zeolite and Loading of (Ni=7%) on MORDINITE were prepared mechanical mixing

2.3. Experimental Conditions

1. Feed heavy gas oil 25 g.

2. Catalyst 0.625 g.

3. Initial hydrogen pressure 50 bar.

4. Reaction temperature at 400, 425 and 450 °C.

5. Reaction time 1 hr.

6. Reaction pressure 120 bar.

2.4. Experimental Procedures

The reactor with 25 g feed was gradually heated via a 60 minute temperature ramp at the rate of 10 °C/min and temperature was kept at 400 °C for 1 h. All runs were made at reaction time of 1 h at temperatures of 400, 425, and 450 °C. The hydrocracking of gas oil with different ratios of catalysts NiMo/H-ZSM-5 and Ni/MORDINITE.

3. Results and Discussions

This section deals mainly with the results of hydrocracking of heavy gas oil obtained from this study. GC, GC-MS and SIMDIST were used in this research to identify the hydrocarbon and boiling point distribution of feedstock (gas oil) and reaction product. Also TGA technique was used to quantify the coke deposited on the surface of catalysts.

3.1. Yields and Conversion

The yields of reaction product gases, liquids and coke obtained from the hydro cracking of HGO at 400, 425 and 450°C are given in Table 3.1. It is clear from this table that both reaction temperature and catalyst type have strong influence on the yield of reaction products. Table 3.2 shows the results of conversion and yield of gases (C_1-C_4), gasoline (IBP-207°C), condensate 207 °C and coke using MORDINITE and H-ZSM5 catalysts. It is obvious from this table that as hydrocracking temperature increases the gas and conversion increases, as well as gasoline yields increase.

3.2. GC Results

As stated earlier that GC has been used to identify the hydrocarbon present in feedstock (HGO) and reaction products. Carbon distribution of feedstock (HGO) and reaction products at different hydrocracking temperature using both H-ZSM5 and MORDINITE are shown in Figures 3.1 and 3.2.
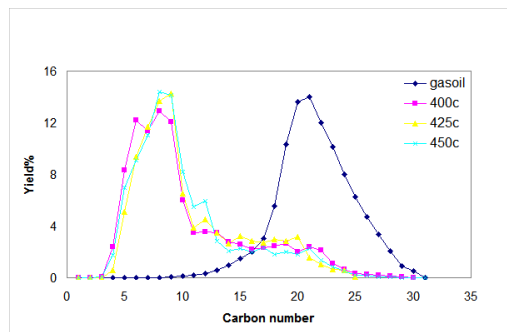

Figure 3.1: Carbon distribution of feedstock (HGO) and reaction product using H-ZSM5 catalyst
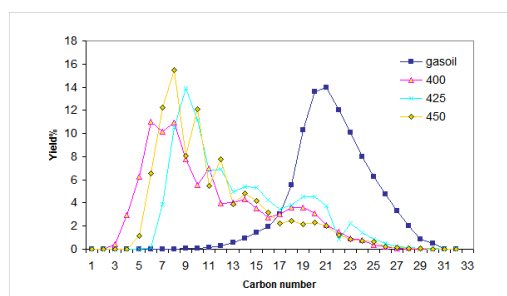

Figure 3.2: Carbon distribution of feedstock (HGO) and reaction product using MORDINITE catalyst

Table 3.1: Yields of gases, liquid and coke from hydrocracking of HGO

Products	Temperature °C	H-ZSM5 HGO	MORDINITE HGO
Gas	400	11.06	10.07
Liquid	400	80.80	80.00
Coke	400	8.14	9.93
Gas	425	12.10	11.17
Liquid	425	78.0	74.80
Coke	425	9.90	14.02
Gas	450	19.57	18.20
Liquid	450	69.60	67.20
Coke	450	10.82	14.6

Table 3.2: Products distribution of hydrocracking experiments of HGO

Feedstock	Temperature °C	Gas	Gasoline	207^+	Coke	Conversion
HGO/NiMo/H-ZSM5,Wt %	400	11.06	22.77	58.03	8.14	33.83
HGO/NiMo/H-ZSM5,Wt %	425	12.10	31.56	46.44	9.90	43.66
HGO/NiMo/H-ZSM5,Wt %	450	19.57	37.07	32.53	10.82	56.64
HGO/ MORDINITE, Wt %	400	10.07	23.40	56.59	9.93	33.47
HGO/ MORDINITE, Wt %	425	11.17	27.81	46.99	14.02	38.98
HGO/ MORDINITE, Wt %	450	18.20	34.58	32.62	14.60	52.78

The Figure 3.1 shows the carbon distribution of feedstock and reaction product of hydrocracking of gas oil using NiMo/H-ZSM5 catalyst. It is clear from figure, the HGO has shifted to light components at 400, 425, and 450°C, so the dominated component for reaction product at 400°C was C8 12.9% and at 425°C was C_9 14.2% .as well as at 450 °C was C_8 14.4%. Figure 3.2 shown the carbon distribution of feedstock and reaction products over Ni/MORDINITE catalyst, it is obvious at 400°C ,425°C dominated component was C_9 and it is yield was 10.9%, 13.8% and at 450 was C_8 with yield 15.4%. The maximum yield of gasoline (C_5-C_{12}) obtained from the hydrocracking of HGO in the presence of H-ZSM5 catalyst at 450°C hydrocracking temperature was 75.2% (by weight). In case of MORDINITE, the maximum yield of gasoline (C_5-C_{12}) obtained from the hydrocracking of HGO at 450°C hydrocracking temperature was 68.8% (by weight).

3.3. Effects of hydro cracking Temperature and Catalyst Type on the Product Distribution

The influence of hydrocracking temperature on the yield of gases, gasoline, 207^+ distillate and coke are investigated using MORDINITE and H-ZSM5 catalysts. In Table 3.2 the yield of gas, gasoline, 207°C and coke obtained from hydro cracking of HGO at different hydro cracking temperature are presented. For MORDINITE catalyst and H-ZSM5 catalysts, it is clear from this table, as the hydro cracking temperature increases from 400°C to 425°C, the yield of gases increases, whilst the yield of 207 °C decreases. But as the hydro cracking temperature raised to 450°C, the yield of gasoline decreases. This can be explained that part of the gasoline formed was cracked to gases.

3.4. Hydrocracking of Gas Oil over Ni/ MORDINITE

Figure 3.3 shows the reaction product at different temperature throughout the period of temperature from 400 to 450°C. In case of hydrocracking of heavy gas oil over Ni/ MORDINITE, it has seen that at 400°C and 425°C.
The gas at 400°C (10.07%) less than gas at 425°C (11.17%). the distillate 207+, at 400 °C and 425 °Cis (56.5%), (46.9%), the cook at 400°C (9.93) and at 425°C it was (14.02%). The gasoline is increases from (23.4%) to (27.8%) at 400°C and 425°C.In contrast, when we used the hydrocracking of gas oil at 450°C over Ni/Mo, it is clear from that figure
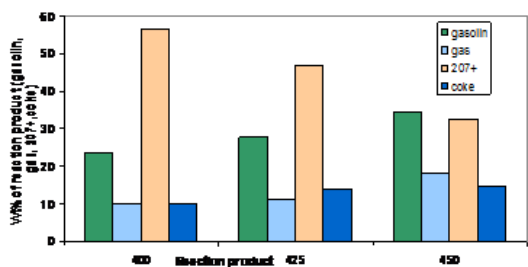
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Figure 3.3: Reaction product from hydrocracking of heavy gas oil over Ni/ MORDINITE

, the gas and cook at 450°C more than the gas and cook 400 °C and 425 °C. The gasoline (34.5%) at 450°C sharply increases.

3.5. HydrocrackingGas Oil over NiMo/H-ZSM5

Figure 3.4 illustrates the reaction product from hydrocracking using NiMo/H-ZSM5 at different temperature it is noted from that figure, the gas, gasoline and coke rise at all temperature but the distillate is gradually decreased.
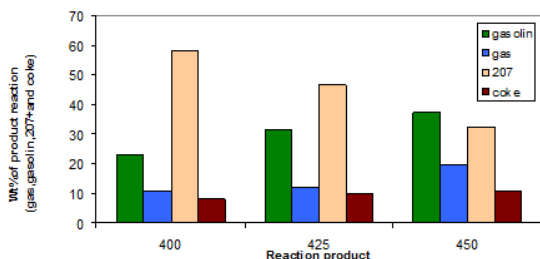

Figure 3.4: Reaction product from hydrocracking of heavy gas oil over NiMo/H-ZSM5

3.6. Effect of Reaction Temperature on Conversion

The associations of nickel with molybdenum are the most active for hydrogenation reactions, so hydro cracking catalyst are from NiMo phases. Figure 3.5 shows the changes in gas oil conversion with reaction temperature over NiMo/H-ZSM5 catalyst. Where the conversion reaches to 56.6 % at 450°C. While Figure3.6 shows the changes in gas oil conversion with reaction temperature over Ni/ MORDINITE catalyst. The conversion over NiMo/H-ZSM5 was higher than that over Ni/ MORDINITE

at all reaction temperature studied in this research. Where the conversion reaches to only 52.7% at 450°C compared to 56.6% at 450 °C over NiMo/H-ZSM5 catalyst.
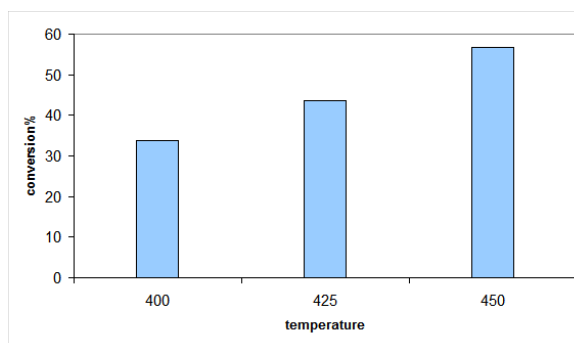

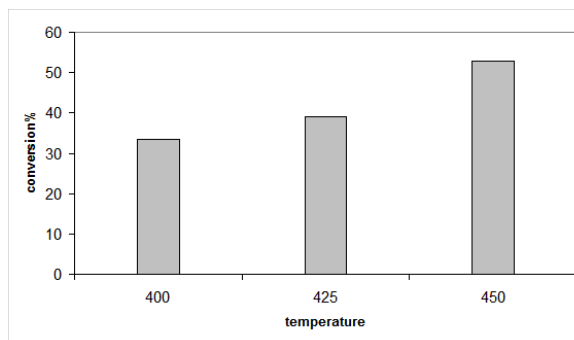**Figure 3.5:** Gas oil conversion over NiMo/ H-ZSM5 catalyst at various reaction temperatures

Figure 3.6: Gas oil conversion over Ni/ MORDINITE catalyst at various reaction temperatures

3.7. Thermal Gravimetric Analysis (TGA) Technique

This technique was used in this research to quantify the coke deposited on the surface of catalyst. The results of these tests are presented in Figures 3.7,3.8. As previously mentioned, the deposition of coke over the acid solid catalysts is an important factor in the deactivation processes of these materials. The degradation of organic compounds over zeolites materials generates a carbonaceous residue, which remains retained inside the pores, in the surface of the material or in both ones. The deactivation of zeolites due to coke deposition is very important. When the amount of coke on the surface and in the pores increases, the number of available

acid sites and the local diffusion possibilities decreases, thus decreasing the activity of the catalyst. In this work, the percent of coke formed during hydrocracking reactions of HGO using two catalysts has been determined using TGA technique. The interpretation of the results corresponding to the temperature of the coke oxidation is complex, because there are different influencing factors. Firstly, it depends on the composition of the coke, which changes for each catalyst and for each pyrolyzed mixture. In addition, the location of the coke in the zeolite framework and the possible diffusion effects, which can difficult the access of the oxygen to the molecules of coke, also affects the oxidation temperature. On the other hand, the amount of coke formed also depends on the same factors, and the zeolite and the type of pyrolyzed mixture determine the nature, the amount and the location of the carbonaceous residues formed in each case. According to the literature[5].
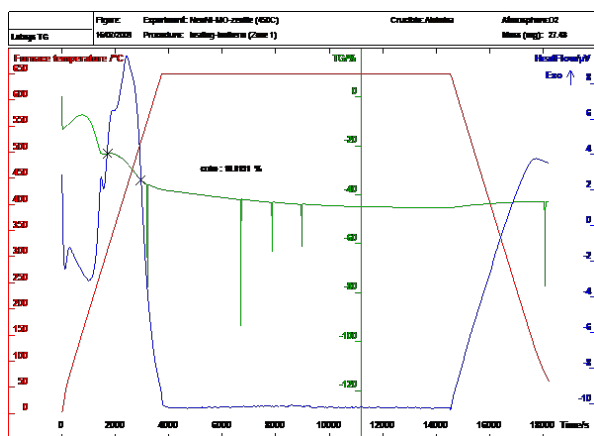

Figure 3.7: TGA curves of used H-ZSM5 catalyst, hydrocracking temperature (450 °C)

In general, the carbonaceous deposits can be classified into two types; hard coke, which derives from aromatic hydrocarbon and usually, forms at high temperatures, and soft coke, which tends to form at low temperatures. When the pore size of the zeolites is small, the reactions between voluminous aromatic compounds with important steric hindrances are restricted, and the coke formation tends to be very low. When the pore size is intermediate, the reactions of cyclation and dehydrogenation to give aromatic simple compounds and cycloparafines are possible, and could favour the formation of soft coke. In the zeolites of great pore size, the aromatic compounds can react to give more complex
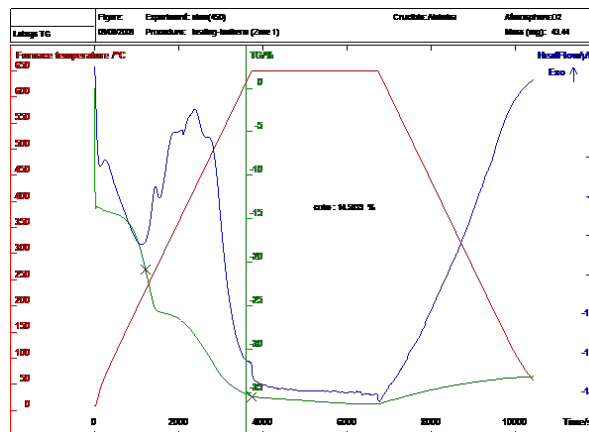

Figure 3.8: TGA curves of used MORDINITE catalyst, hydrocracking temperature (450 °C)

compounds that favour the formation of hard coke. Figure 3.7 shows the TGA curves for used H-ZSM5 at 450°C hydrocracking temperature. The sharp drop of the mass loss chart (E) starts at 45mg up to 15mg indicates that the carbon was oxidised to CO_2, according to the following stock metric equation. Figure 3.8 shows the TGA curves for used MORDINITE at 450°C hydrocracking temperature. The sharp of the mass loss chart starts at (35) mg up to (14) mg indicates that the carbon was oxidised to CO_2.

3.8. Simulated Distillation (SIMDIST) Results

As mentioned earlier that SIMDIST technique was used in the current research to identify the boiling point distribution of the feedstock (HGO) and cracking products at different hydrocracking temperature using MORDINITE and H-ZSM5 catalysts. The I.B.P of feedstock (HGO) was 275°C whilst, the F.B.P was 375°C. In case of MORDINITE catalyst, during the hydrocracking reaction the I.B.P was reduced to 78.4, 84.6 and 61.9°C at hydrocracking temperature varies from 400-450°C. The gasoline fraction obtained from the hydrocracking reaction was ranged from (61.62% to 68.81%) at the same hydrocracking temperature. When we used H-ZSM5 catalyst, the I.B.P was reduced to 108.1, 53.4and 53.7°C at hydrocracking temperature varies from 400-450°C.The gasoline fraction obtained from the hydrocracking reaction was ranged from (69.8% to 75.27%) at the same hydrocracking temperature. However, at 450°C, which is the highest hydro cracking temperature used in this

study, the gasoline yields were 68.81% for HGO/ MORDINITE and 75.27% for HGO/H-ZSM5 (See Figuers3.9 and 3.10).It has been observed that the catalysts used have slightly effect on the boiling point distribution of the reaction product whereas the cracking has strong influence on the boiling point distribution. At 400 oC and 425°C, hydrocracking of HGO/H-ZSM5 gave the highest liquid containing 69.8% and 64.5% gasoline respectively, whereas in hydrocracking of HGO/ MORDINITE, gasoline yields were 61.6% and 53.39%, respectively. HGO/H-ZSM5 produced a much greater amount of material boiling below 450°C. HGO/ MORDINITE had less recovery of material boiling below 450°C than HGO/H-ZSM5. In general, as the temperature increased from 400 to 425°C, light fractions obtained from hydrocracking increased. Figure 3.10 shows the boiling point distribution of feedstock (HGO) and reaction products at different hydrocracking temperature using MORDINITE catalyst. The boiling point distribution of the reaction product at 425°C and 450°C were similar.
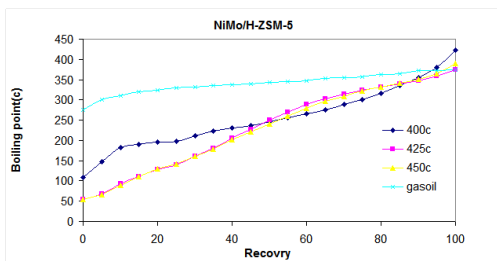

Figure 3.9: The effect of temperature and catalyst on the boiling point distribution range of liquid products from HGO hydrocracking using H-ZSM5 catalyst
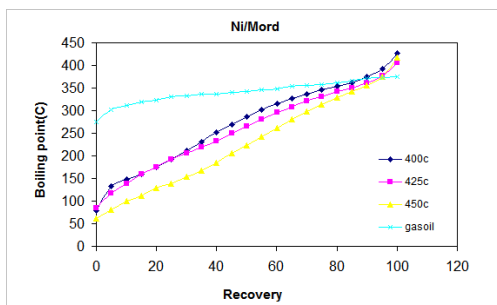

Figure 3.10: The effect of temperature and catalyst on the boiling point distribution range of liquid products from HGO hydrocracking using MORDI-NITE catalyst

3.9. Gas Chromatograph- Mass Spectra (GC/MS) Results

The liquid products from hydrocracking of the blend at 400,425 and 450°C were analyzed by GC/MS, in order to identify and quantify the hydrocarbons present in feedstock and reaction products. The GC spectra of HGO and reaction product at 450°C using Ni/MORDINITE and NiMo/H-ZSM5 are given in figures 3.11 and 3.12 show the named the hydrocarbon compound present in feedstock and reaction product. It is observed from these figures that the lighter compounds formed during the reaction. In order of increasing retention time, the two major compounds of peaks were alkene and alkane. All these organic compounds were present in all the reaction product. The hydrocracking temperature; catalyst type strongly influenced the amount of each product.
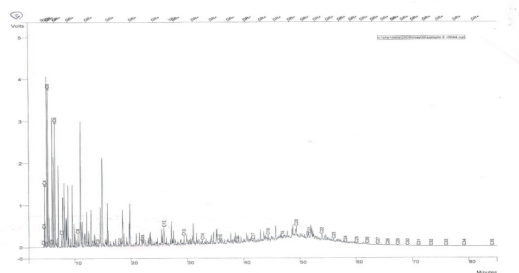

Figure 3.11: GC-MS spectra of reaction product from hydrocracking of HGO at 450oC, using Ni/MORDINITE catalyst
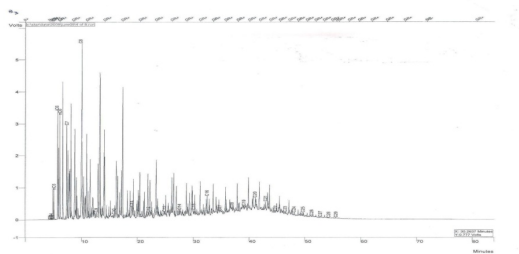

Figure 3.12: GC-MS spectra of reaction product from hydrocracking of HGO at 450oC, using NiMo/H-ZSM5 catalyst

4. Conclusions

Summary of the results on the hydrocracking of HGO using Ni/Mordinite and NiMo/H-ZSM5 cat-

alysts are as follows:

1. Hydrocracking of HGO over H-ZSM5, and MOR-DINITE catalysts was successfully catalytically cracked into gases, gasoline and distillate products. SIMDIST, GC and TGA techniques were used to analysis the feedstock and reaction products.

2. The results showed that hydrocracking of HGO was a complicated parallel and serial reaction including hydrogenation, isomerization, and cracking (ring opening and dealkylation).

3. All prepared catalysts with Nickel (3 wt%)and Molybdenum(7 wt%) on supported ZSM-5, and Nickel(7 wt%) on supported MORDINITE achieved the highest hydrocracking and hydrogenation activity. The results showed that nearly 52.6%conversion could be achie-ved at 450 °C with tested catalysts NiMo/H-ZSM-5 and 56.5% conversion could be achieved with tested catalysts Ni/ MORDINITE.

4. Hydrocracking of HGO in the present of NiMo/H-ZSM-5 catalyst at 450°C hydrocracking temperature shows the most interesting results with high selectivity toward gasoline range (49.06 wt%). And the reaction products formed during the hydrocracking of HGO are formed to be within the carbon distribution ranging from (C_5-C_{12}).

5. Hydrocracking of HGO was studied increase, the yield of gases; gasoline and coke are increases, whilst the yields of distillate (207 °C) are decreases.

6. It has been found that the hydrocracking temperature has strong influence on the conversion and product distribution. When Ni/ MORDI-NITE was used as a catalyst, it was noted that as the hydrocracking temperature increase from 400-450°C, the liquid yield was decreased from 80 to 67.2% by weight. But when NiMo/H-ZSM-5 was used as a catalyst, it was noted that as the hydrocracking temperature increase from (400-450°C), the liquid yield was decreased from 80.8 to 69.6% by weight.

7. TGA technique was used to quantify the coke deposited on the surface of H-ZSM5, and MORDI-NITE catalysts. The combustion of coke deposits on the surface of catalyst showed that the Ni/ MORDINITE catalyst produces more coke than NiMo/H-ZSM-5 catalysts. This fact has been attributed to the different pore structure.

5. Acknowledgment

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