

HYDROCRACKING OF A LOCAL HEAVY VACUUM PETROLEUM FRACTION

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ABSTRACT

The hydrocracking of a heavy vacuum petroleum fraction was studied in a trickle bed reactor using a catalyst containing 15% Ni-Mo oxides (20% Ni and 80% Mo) supported on 15% HY zeolite in a silica alumina matrix.

The effect of reaction temperature (375°-450°C) and liquid hourly space velocity (3.0-0.5h⁻¹) at a constant hydrogen pressure of 10MPa and a H₂/feed ratio of 500 l/l on the yield and the quality of the product were investigated. Fractional distillation, densities, aromatics, diesel indices, sulfur and nitrogen contents, smoke, freezing and pour points of the liquid hydrocrackates and their fractions were measured and correlated with various parameters. The activity of the catalyst for Hydrodesulfurization (HDS), Hydrodenitrogenation (HDN) and aromatic hydrogenation (Ar H) was also investigated.

INTRODUCTION

Since the advent of the hydrocracking process, there has been a steady increase in the hydrocracking capacity all over the world.

Hydrocracking is being developed and practiced in the petroleum industry for converting different types of charge stocks to middle distillates, gasoline or liquified petroleum gases. The incentives of getting a variety of valuable products from inferior grade feedstocks, led to the development of a number of large scale processes. The performance of several catalysts for hydrocracking gas oil, heavy gas oil, furnace oil, light cycle oil, ... etc, have been reported in literatures [Botchway, et al, (2003); Bhashar, et al, (2003); Valavrasu, et al., (2003); Aoyagi, et al., (2003); Landau, et al, (2003); Avraam,

et al., (2003); Bhaskar, et al., (2002); Yan-Hong, et al, (2002); Ali, (2002); Ali, et al, (2001); Hassan, et al, (2001); Isoda, et al, (1998)].

Hydrocracking catalysts are dual functional ones in which the ratio of the two functions (hydrogenation -dehydrogenation and acidic functions) falls within a narrow range.

Zeolite catalysts are widely used in petroleum refining, [Speight, (1999); Meyers, (1997); Flanigen, (2001)], petrochemistry [Meyers, (1997); Flanigen, (2001)], fine chemicals production [Tanabe, and Holderich, (1999); Nogami, (2002)] and environmental catalysts [Iwamoto, (1994)]. Despite its long history, zeolite catalysts is still an active research field, with the contributions of the various properties of the zeolite microporous crystals to catalysis performance still to be definitively elucidated. One of the most important of these properties is the crystal size which influences the external surface area and mesoporosity [Sato, et al., (2001); Arribas, et al., (2001); Sato et al., (1999); Cambor, et al., (1998)].

Zeolite is a crystalline aluminosilicate whose carbonium ion activity has been attributed to strongly acidic protons in the crystalline lattice. Therefore, zeolite based catalysts have been found to be more active catalysts [Landau, et al., (2003); Ali, et al., (2002); Hassan, et al., (2001); Sato, et al., (2001); Arribas, and Martinez, (2001); Sato et al., (1999); Cambor, et al., (1998); Al-Maymen and Al-Zaharani, (2003)].

The main objective of this study was to hydrocrack a heavy vacuum petroleum fraction, using a catalyst containing 15% of a nickel-molybdenum ion exchanged H-Y-zeolite within a matrix of clay and amorphous silica- alumina, in a trickle bed reactor under different operating conditions. The effects of temperature, and liquid hourly space velocities on the yields and qualities of the products were also investigated.

EXPERIMENTAL

Feed stock:

A heavy vacuum petroleum fraction, boiling range 330° to 472°C, was used in this investigation and kindly provided from El-Ameria Petroleum Refining Co. This feed stock was evaluated according to standard techniques and the data obtained are given in Table (1).

Table (1): Characterization of HVGO Feed Stock

Characteristic	Results	Standard methods
Specific gravity 60/60°F	0.8798	ASTM D289-65
API gravity	29.3	ASTM D287-92
Refractive index, 20°C	1.4910	ASTM D1218-92
Molecular weight	380	ASTM D 2503-82
Pour point, °C	+ 10	ASTM D97-88
Aniline point, °C	72.8	ASTM D611-82
Diesel index	47.77	Calculated
Color	7	ASTM D 1500
Sulfur content, wt. %	1.74	ASTM D 4294-90
Nitrogen content, wt. %	0.256	X-ray fluorescence
Aromatic content, wt%	39.0	Frigle - deumes method
C/H ratio	0.57	Silica gel column
ASTM distillation, vol. %		ASTM D1160
IBP, °C	330	
10%	395	
50%	441	
90%	468	
E.P, °C	472	

Catalyst:

The catalyst has been prepared via two successive impregnation of 15% H-Y zeolite in a matrix of clay and amorphous silica-alumina with a solution containing ammonium molybdate $((\text{NH}_4)_6 \text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$ and nickel nitrate $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ such that the catalyst contains 12.0 wt% MoO_3 and 3.0 wt% NiO . The clay silica-alumina matrix contains 20.0 wt% Al_2O_3 and 80.0 wt% SiO_2 . This catalyst is available normally in a finely powdered material with particle size range from 50 to 100 μm was made up into pellets of dimensions 4.22 x 5.00 mm. The pellet length dimension for such a cylindrical pellets is 1.18 mm. The pore size

distribution of a sample of pellets was measured using a Carlo-Erba series 200 mercury porosimeter. This instrument provided a measure of pore volume and the distribution of pore volume in the pore radius range from 75000°A down to 37.5°A . The catalyst has a bulk density of 0.702 g/cc, a porosity of 0.317 and an overall pore volume of 0.452 cc/g.

The zeolite pores are 13°A in size, so that the support catalyst pore volume in the range 37.5°A down to 13°A was taken to be linearly distributed to complete the cumulative pore volume/pore radius function as shown in Fig.(1). So, the pore volume contained in zeolite pores was calculated to be 0.064 cc/g.

The surface area in the zeolite pores was therefore, calculated $98.5\text{m}^2/\text{g}$ with the pellets having an overall surface area of $133\text{m}^2/\text{g}$, as shown in Table (2).

Table (2): The main characteristic of the investigated catalyst.

Catalyst characterization	Result
Shape	Pellet
Diameter, mm	14.72
Bulk density, g/ml	0.702
Grain density, g/ml	1.161
True (structural) density, g/ml	2.44
Porosity	0.317
Total pore volume, cc/g	0.452
Surface area, m^2/g	133
Zeolite pore volume, cc/g	0.064
Zeolite surface area, m^2/g	98.5

From Fig. (1), The distribution of porosity is as follows:-

- i) microporosity (up to 2nm = 0.08 cc/g which represents 17.7% of total pore volume.
- ii) mesoporosity (2-50 nm) = 0.10 cc/g which represents 22.1% of total pore volume.
- iii) macroporosity (> 50 nm) = 0.272 cc/g which represents 60.17% of the total pore volume.

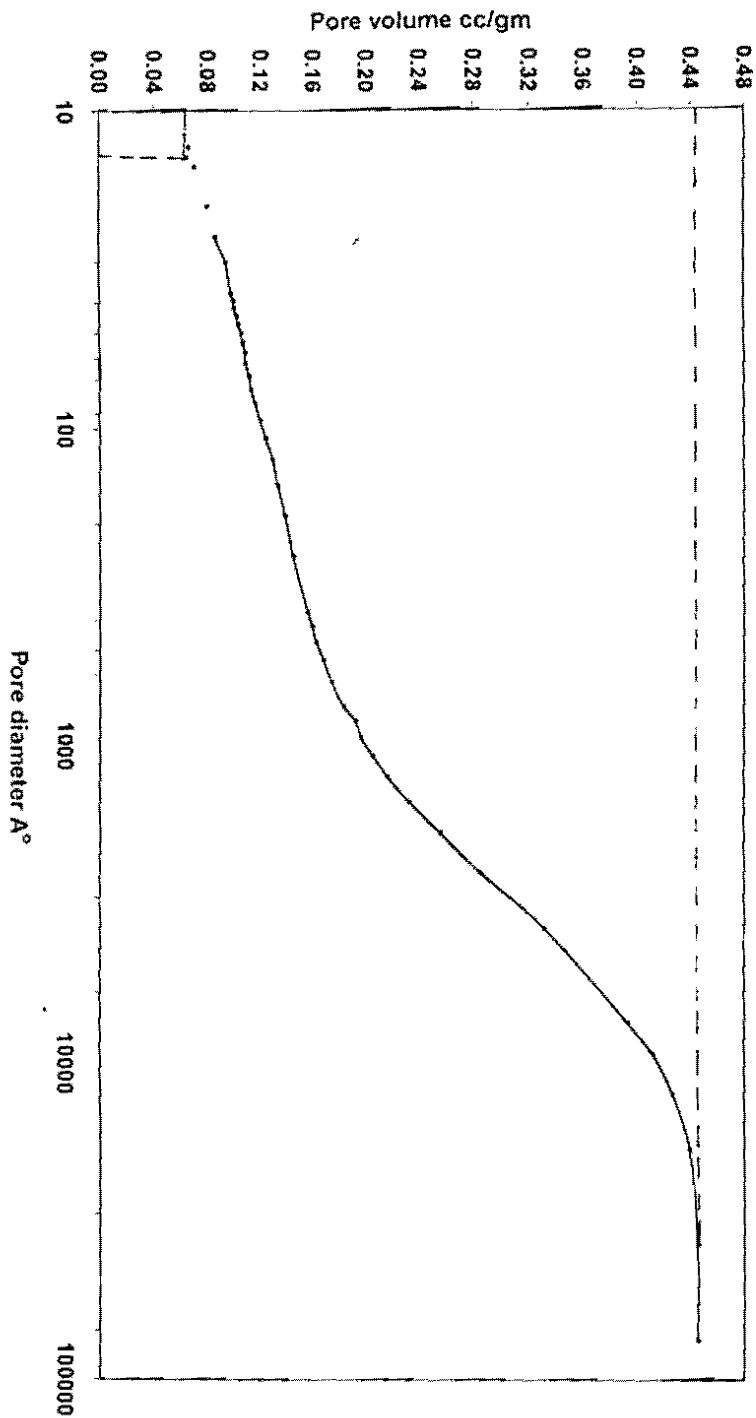


Fig. (1) Pore volume distribution for HY zeolite

Equipment, procedure and product analysis:

Detail description of the equipment, the experimental procedure, and conditions of presulfiding of the investigated catalyst and the methods of analysis, all are given elsewhere [Mohamed, (2000); Shaban, (1999)].

The yield of the total product was assumed to be 100%. The conversion was taken as the total product minus the product boiling above the initial boiling point of feed stock.

The product was distilled into gasoline up to 150°C, kerosine 150°-250°, gas oil 250°-350°C and fuel oil > 350°C

Operating condition:

The operating conditions are:-

- reaction temperature 375°-450°C.
- reaction pressure constant at 10MPa.
- liquid hourly space velocity 3.0-0.5h⁻¹ (equivalent to space time of 0.33-2h respectively).
- H₂/ feed ratio 500 l/l.

Product analysis:

The liquid products were analyzed using ASTM and other standard methods and the gaseous products by gas chromatographic analysis by using Pye Unicom 4550 with a flame ionization detector (FID). The injector and detectors temperatures were 250°C and 300°C respectively.

RESULTS AND DISCUSSION

Table (3) summarizes the products yields of the hydrocracking of the used petroleum fraction, while Table (4) gives the typical results of the main characteristics of liquid hydrocrackate fractions. Effect of reaction temperature and LHSV on hydrocarbon gas distribution and yield of hydrocrackate products are represented in Figures (2-3). Yield of gasoline, middle distillate and fuel oil versus the total conversion are shown in Figure (4). Sulfur, nitrogen and aromatic contents and percent of their removal (HDS, HDN and Ar H) are represented in Figures (5-7).

It is obvious from Table (2), that the investigated Ni-Mo/HY catalyst contains 26.5% mesopores and 55.75% macropores. The function of mesopores was to hydrocrack large molecules and to remove

heteroatoms. In contrast, the function of the micropores leads to the gas production. When small molecules were produced by thermal or catalytic cracking over the external surface, they entered the micropores and were further hydrocracked to gaseous molecules.

Sato, et al., (2001) indicated that Ni-Mo sulfide were dispersed on the mesopores surface of Ni-Mo/HY; which lead to two functions, namely, hydrogenation and hydrocracking of large molecules. In case of Ni-Mo/HY catalyst without mesopores, however the active sites for large molecules were limited to the external surface of zeolite particles

Sato, et al., (2001); Sato et al., (1999) also indicated that the cracking rate for area over the mesopores surface was faster than that over external surface of zeolite particles. The advantages of NiMo/HY zeolite with mesopores over that without mesopores in the cracking of heavy fractions are as follows:-

(i) zeolite mesopores provide favorable active catalytic sites for large molecules and (ii) well dispersed Ni Mo sulfides on the mesopores surface supply dissociative hydrogen species that enhance not only hydrocracking but also heteroatom removal from large molecules

Product distribution :

As indicated in previous studies in the literatures [Ali, et al., (2002); Hassan, et al., (2001); Sato, et al., (2001); Arribas, and Martinez, (2001); Sato et al., (1999); Cambor, et al. (1998); Al-Mayman and Al-Zaharani, (2003); Plank, (1984)], the H-Y zeolite exhibited high efficiency for catalyzing the hydrocracking of heavy gas oil. The incorporation of low amounts of zeolite in matrices of silica-alumina proved superiority over either the pure zeolite or the silica-alumina matrix alone [Sato, et al., (2001); Arribas, and Martinez (2001); Sato et al., (1999); Cambor, et al., (1998)].

Production of hydrocarbon gases and liquid distillates through the hydrocracking of petroleum fraction on the investigated catalyst is depicted in Figure (3). Data in this figure indicate that the overall yield of the catalytic hydrocracking is high. The yield of cracked gases, and gasoline are continuously increased through increasing temperature and space time (decreasing LHSV) and the gases are always lower than the gasoline yields. The hydrocarbon gas analysis data given in Figure (2) show that dry gases (C_1 and C_2) are produced in small quantities and the yield increases with the increase in temperature and decrease in the LHSV, while the LPG constituents (C_3 and C_4) form the major gas

constituents and their total yields represent more than 80% of the total gas.

Table (3) Product yields of the hydrocracking of HVGO at different operating conditions

1:HSV R ⁻¹	Temp. °C	Gases wt%	Gasoline wt% up to 150°C	Kerosene wt% 150-250°C	Gas oil wt% 250-350°C	Fuel oil wt% > 350 °C	Total liquid yield wt% up to 350 °C	Total conversion wt% up to 350 °C
0.5	375	0.9	3.8	15.2	25.1	25.0	90.1	45.0
	400	6.6	12.8	17.4	20.0	43.2	93.4	56.8
	425	11.1	25.0	18.5	16.4	29.0	88.9	71.0
1.0	450	15.8	40.3	21.5	14.0	8.35	84.2	91.7
	375	1.8	1.6	8.5	13.1	75.0	98.2	25.0
	400	4.4	7.5	13.3	16.9	57.9	95.6	42.1
1.5	425	6.9	15.3	19.5	21.6	36.7	93.09	63.4
	450	8.4	23.1	22.1	21.0	25.4	91.6	74.6
	375	0.5	1.0	7.2	10.3	81.0	98.5	19.0
2	400	3.4	4.6	10.1	11.6	70.3	96.6	29.7
	425	4.9	9.2	14.7	15.2	56.0	95.1	44.0
	450	5.8	16.6	23.0	14.1	40.5	94.1	59.6
2.5	375	0.2	0.5	5.6	6.7	87.0	99.8	13.0
	400	2.2	3.6	8.2	8.9	76.9	97.6	23.1
	425	3.7	7.3	12.8	12.4	63.8	96.3	36.2
3	450	4.8	12.8	19.4	10.5	52.4	95.2	47.6
	375	0.2	0.5	4.1	4.2	91.0	92.8	9.0
	400	2.2	3.1	7.0	6.6	81.1	97.8	18.9
3	425	3.4	6.3	11.8	10.5	68.0	96.6	32.0
	450	5.1	10.8	19.2	5.6	39.3	94.9	40.7
	375	0.1	0.1	2.5	4.1	93.0	99.7	7.0
3	400	2.2	2.7	5.4	6.0	83.7	97.8	16.3
	425	2.7	5.6	11.0	8.9	71.8	97.1	28.2
	450	4.1	9.2	17.3	4.2	65.2	96.0	34.8

Table (4): Main Characteristics of liquid hydrocrackate fractions produced at different operating conditions.

LHSV h ⁻¹	Temp. °C	Gasoline				Kerosine				Gas oil				Fuel oil		
		Sp.Gr. g/ml	S wt. %	Ar wt. %	Sp.Gr. g/ml	S wt. %	Ar wt. %	Smoke point, °C	Freezing point, °C	Sp.Gr. g/ml	S wt. %	Pour point, °C	D.I	S wt. %	Pour point, °C	Wax content wt. %
0.5	375	0.7758	0.015	6.8	0.8265	0.010	10.2	29.3	-63	0.8559	0.022	-29.0	58.0	0.080	22.2	10.6
	400	0.7579	0.009	8.0	0.8209	0.006	14.1	27.0	-64	0.8466	0.017	-27.0	61.0	0.050	25.0	11.6
	425	0.7381	0.003	9.3	0.8126	0.003	22.5	23.0	-66	0.8400	0.017	-24.0	64.0	0.021	29.0	12.8
1.0	450	0.7213	0.002	10.3	0.8026	0.002	26.8	21.8	-69	0.8288	0.013	-20.0	67.0	0.019	31.0	13.9
	375	0.7782	0.036	10.6	0.8352	0.022	11.8	27.5	-60	0.8815	0.043	-23.0	47.0	0.152	18.8	9.3
	400	0.7703	0.024	12.1	0.8325	0.019	15.5	25.0	-61	0.8743	0.036	-21.0	48.0	0.128	21.0	10.0
1.5	425	0.7592	0.013	14.3	0.8261	0.015	27.2	21.3	-62.3	0.8674	0.032	-18.0	49.0	0.112	24.0	10.5
	450	0.7416	0.010	15.8	0.8191	0.010	31.5	19.0	-64	0.8577	0.027	-16.0	54.0	0.051	25.5	11.3
	375	0.7858	0.045	12.9	0.8403	0.041	13.3	26.8	-56	0.8901	0.077	-17.0	41.0	0.251	16.4	8.0
2.0	400	0.7782	0.032	14.3	0.8396	0.033	17.3	21.7	-58	0.8854	0.066	-15.6	43.0	0.202	17.5	8.9
	425	0.7663	0.017	16.3	0.8345	0.025	29.2	20.4	-60.5	0.8742	0.052	-14.7	45.0	0.162	19.5	9.4
	450	0.7510	0.015	18.3	0.8262	0.002	32.8	7.5	-61	0.8662	0.043	-11.8	48.5	0.101	20.6	9.8
2.5	375	0.7882	0.050	13.4	0.8483	0.052	14.4	26.3	-55.3	0.8989	0.089	-16.5	35.0	0.293	16.0	7.4
	400	0.7804	0.035	15.2	0.8443	0.040	17.9	23	-56.9	0.8923	0.077	-14.9	39.0	0.252	17.0	8.4
	425	0.7686	0.019	17.3	0.8358	0.029	29.8	19.8	-58.5	0.8804	0.061	-12.5	44.0	0.194	18.0	8.9
3.0	450	0.7511	0.016	18.9	0.8291	0.021	33.8	17	-60	0.8707	0.047	-11.0	46.0	0.135	19.0	9.4
	375	0.7959	0.053	12.5	0.8612	0.055	15.2	24.5	-55	0.9026	0.094	-16.0	31.0	0.365	15.0	7.2
	400	0.7883	0.038	15.8	0.8521	0.045	18.4	21.4	-56	0.8992	0.082	-14.3	36.0	0.308	16.2	7.8
3.0	425	0.7729	0.022	18.9	0.8392	0.031	30.8	19.0	-57.5	0.8893	0.066	-11.2	42.0	0.216	17.0	8.4
	450	0.7572	0.018	19.6	0.8343	0.023	34.6	15.9	-59	0.8753	0.050	-10.4	44.0	0.159	18.0	8.7
	375	0.7974	0.054	11.2	0.8654	0.056	16.3	22.7	-54	0.9041	0.099	-15.8	29.0	0.395	14.2	6.3
3.0	400	0.7896	0.040	16.1	0.8550	0.039	18.7	21.7	-55.6	0.9010	0.085	-14.0	34.0	0.332	15.4	7.3
	425	0.7802	0.027	20.5	0.8431	0.039	32.4	17.8	-57.0	0.8991	0.069	-10.3	39.5	0.237	16.5	8.1
	450	0.7641	0.021	21.2	0.8425	0.025	36.1	14.8	-58	0.8845	0.052	-9.4	42.5	0.182	17.6	8.0

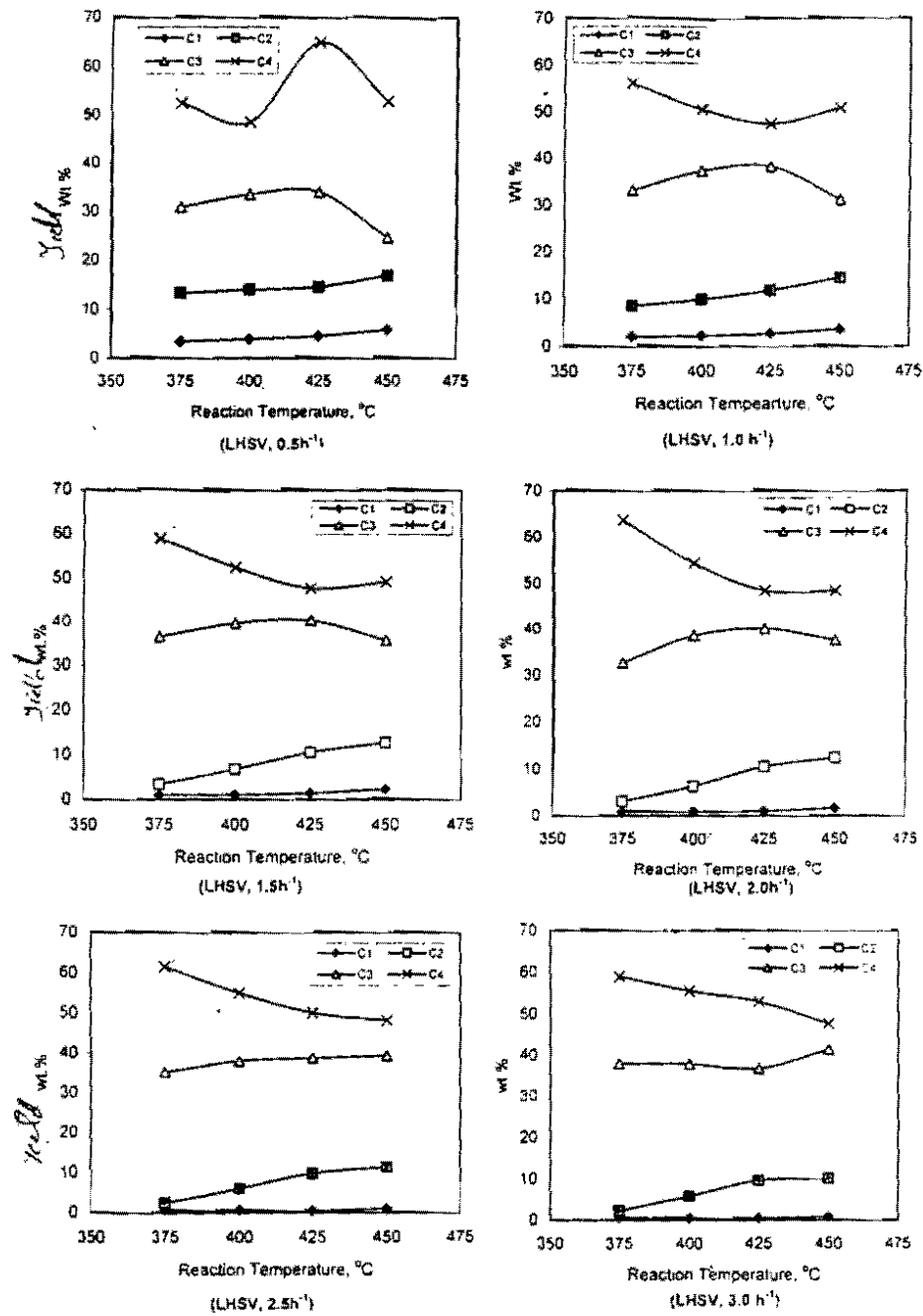


Fig. (2) Effect of reaction temperature and LHSV on hydrocarbon gas distribution

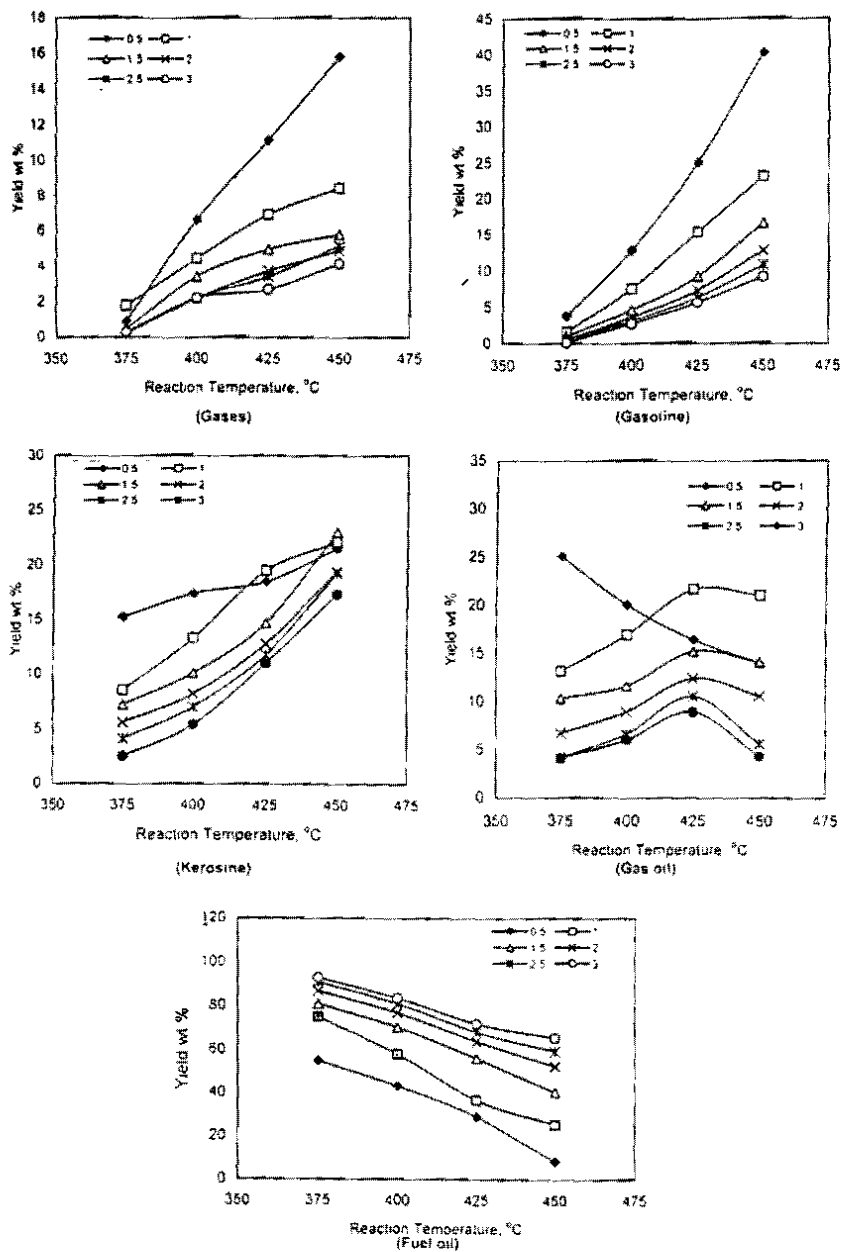


Fig. (3) Effect of Reaction temperature and LHSV on yield of hydrocrackate products

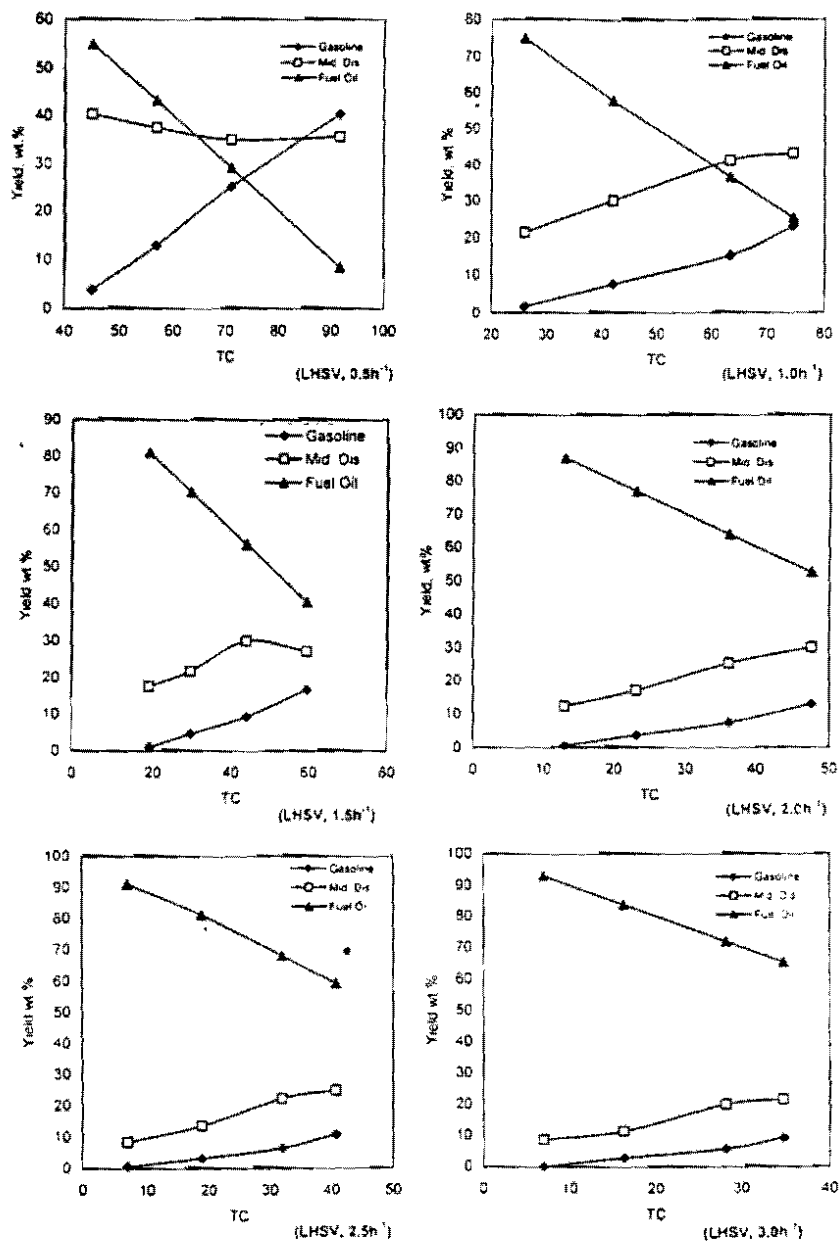


Fig. (4) Yields of gasoline, middle distillate and fuel oil versus total conversion at different reaction conditions.

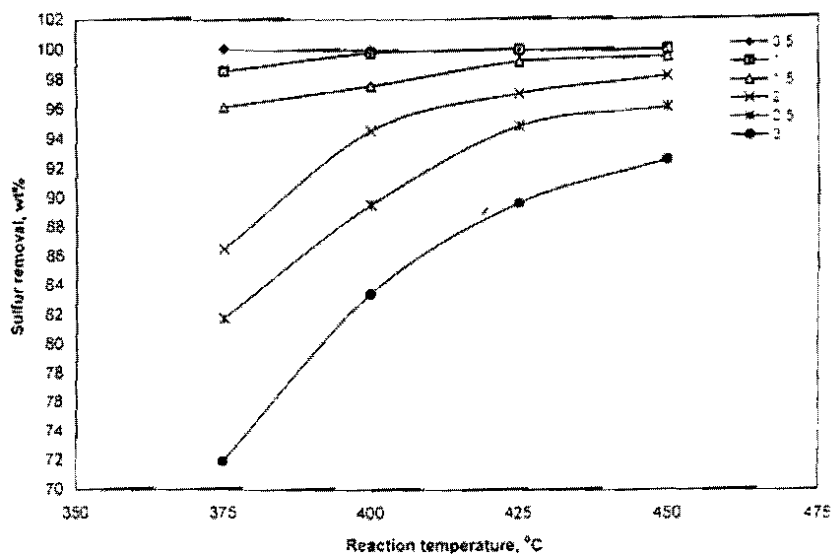


Fig. (5b) Effect of reaction temperature on the sulfur removal (HDS) of the total liquid product at different LHSV

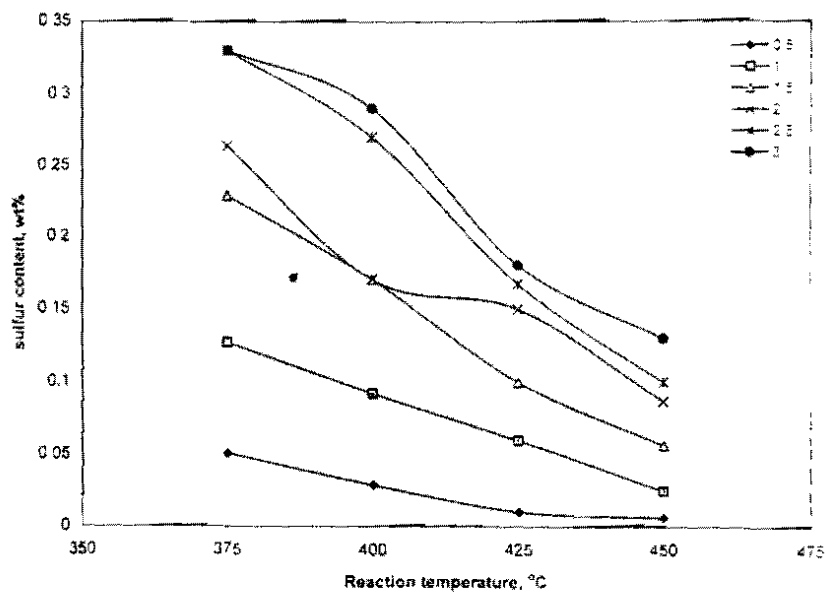


Fig. (5a) Effect of reaction temperature on the sulfur content of the total liquid product at different LHSV

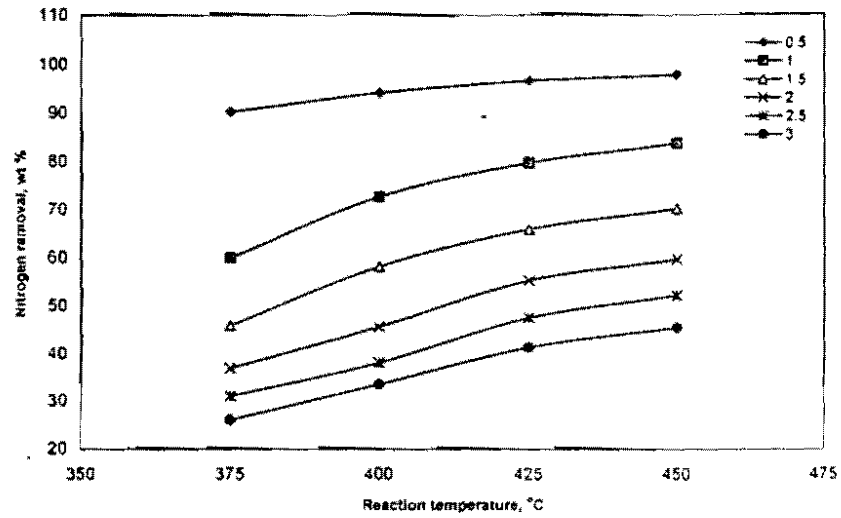


Fig. (6b) Effect of reaction temperature on the nitrogen removal of the total liquid product at different LHSV

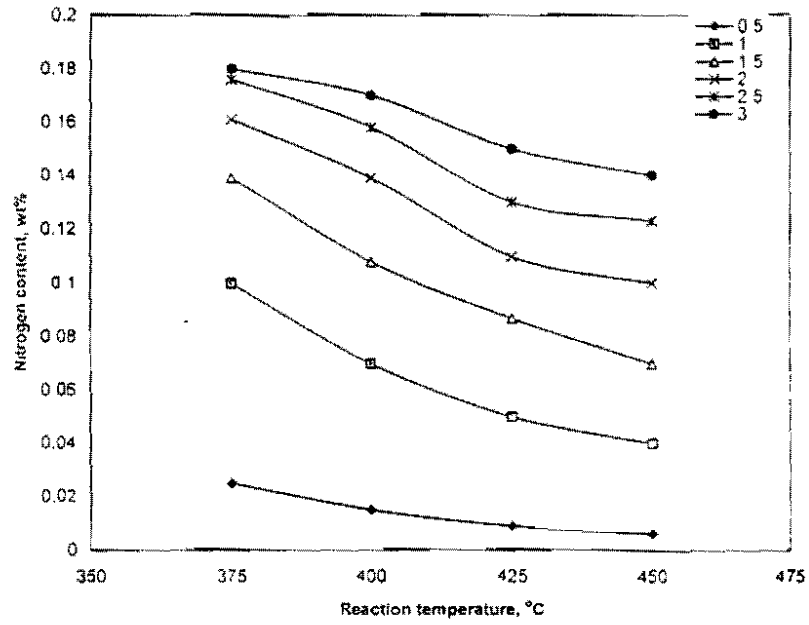


Fig. (6a) Effect of reaction temperature on the nitrogen content of the total liquid product at different LHSV.

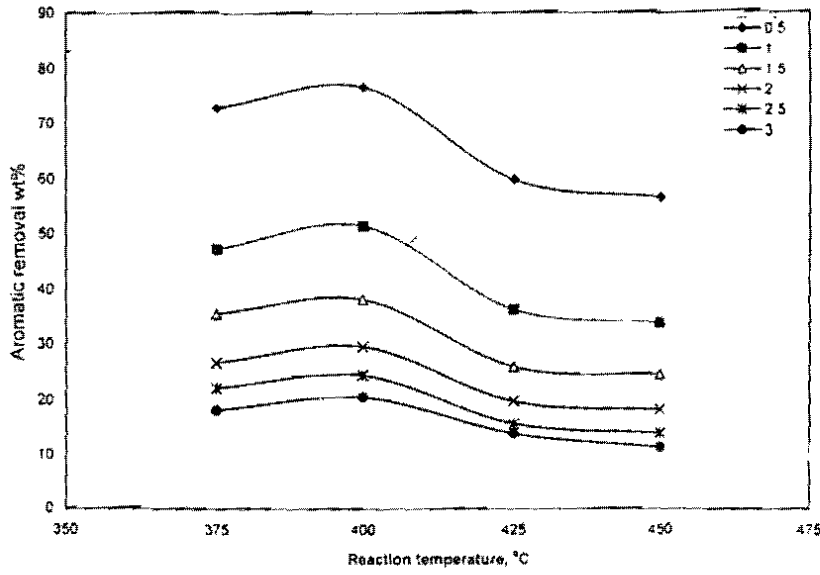


Fig. (7b) Effect of reaction temperature on Aromatic removal of the total liquid product at different LHSV

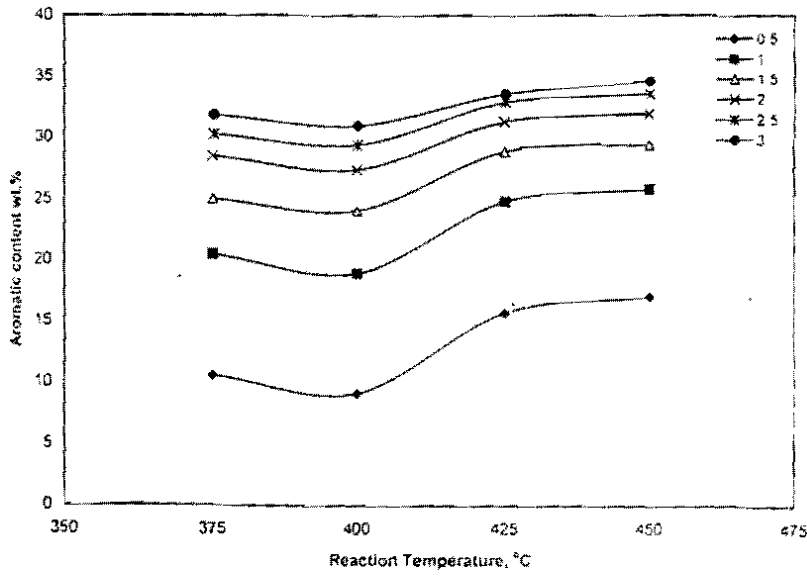


Fig. (7a): Effect of reaction temperature on Aromatic content of the total product at different LHSV.

Although gasoline is produced in small amounts at 375°C, a sharp increase is indicated at higher temperature. The yield continues to increase considerably as the reaction temperature is raised from 375° up to 450°C. Under a fixed set of operating conditions, variation in the reaction temperature has a more marked effect on the catalyst activity and consequently the gasoline yield than variation in LHSV.

With respect to the interrelation between the two middle distillate components (kerosine and gas oil) and their production among other hydrocracked products, the view is different. Middle distillates are the major hydrocracking products and the yield of gas oil almost always surpasses that of kerosine at the least severe conditions (lower temperature and space time). However, at higher temperature (450°C) the yield of gas oil declines till becomes lower than the yield of gasoline and kerosine Table (3). Such decline is attributed to secondary hydrocracking reactions which starts to be significant at higher temperature (450°C).

Optimum production of gas oil can be achieved at 375°C and LHSV of 0.5h⁻¹ (2h space time). On the other hand, optimum production of kerosine can be achieved at 450°C and 1.5h⁻¹ LHSV (0.67h space time) depending on the need for gasoline and gases. Gasoline becomes the major hydrocracking product at 450°C and a space time of 2h. The investigated catalyst possesses a support that supplies the catalyst with the cracking function. However the metallic component employed in the form of sulfide (Ni-Mo sulfide) should have not only supplied hydrogenation-dehydrogenation function of the catalyst but significantly contributed to the cracking activity due to higher Ni-Mo sulfide contents that has drastically increased the production of lighter fraction.

The ratio of gasoline to middle distillate increased with temperature at higher LHSV but at lower LHSV there was a sudden rise in the curve at the temperature range (400°-450°C) Fig. (8). Petroleum fraction molecules appear to be cracked primarily to from middle distillate, gasoline and gas. When the severity of hydrocracking increases at higher temperatures and lower space velocities, the formed M.d. starts cracking simultaneously to gasoline and gases. As the cracking severity further increases the gasoline may also starts cracking simultaneously to light naphtha and gases.

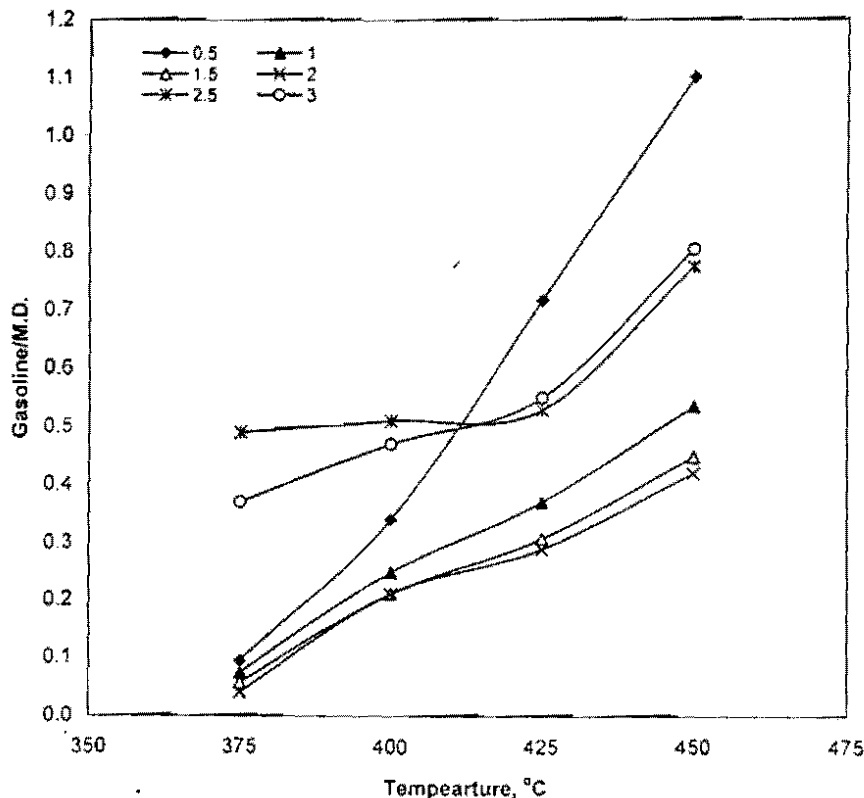


Fig. (8) Effect of reaction temperatures and LHSV on gasoline/ M.D ratio

Product characteristics:

Dual functional catalyst possesses some common properties represent the sum of their catalytic functions, namely, hydrogenation and acidic functions which are affected to different extends by the process variables. This leads to a disequilibrium in the balance controlling their activities. This is reflected in the product distillation as well as the quality characteristics of the fractions

The cracking activity increases continuously with increase in temperature and/or decrease in LHSV, where as the hydrogenation activity within the applied reaction temperature is favoured by reduction in the reaction temperature and /or LHSV. This is evident from examination of the main characteristics of the fractions obtained under different experimental conditions. Specific gravities, sulfur and nitrogen contents decreased continuously with the rise in temperature and / or decrease in LHSV. As the hydrogenation activity increases, more

aromatics are converted to the respective naphthenes. As a result, the aromatic contents of the kerosine and gas oil fractions falls and their smoke points and diesel index go up respectively.

Aromatics content in the gasoline product decreases as a function of increasing space time but increase with increasing reaction temperature. This is attributed to enhancing both ring-saturation at longer space times, and enhancing the degradation of higher molecular weight aromatics present in the petroleum fraction feed stock with increasing reaction temperatures to become gasoline components. Generally, the aromatic contents in the produced hydrocracked gasolines are appreciably higher than those present in most straight run gasolines obtained out from crude oils [Nelson, (1969)].

Similar to gasoline, aromatics in kerosine decrease with increasing space time and increase with increasing reaction temperature. However, aromatics in the hydrocracked kerosines are much higher than in the produced gasolines.

The aromatics hydrogenation may have contributed to the increase of aromatics in both gasolines and kerosine with increasing reaction temperature. These hydrocracked kerosines can safely fullfill the most critical specification of aviation turbo-fuels such as specific gravity, smoke point, sulfur content, and freezing point. On the other hand, the pour points of the hydrocracked gas oils obtained are considerably lower than any straight run gas oil fraction [Nelson, (1969)]. This is an indication of the high isomerization activity of the employed catalyst since branching of paraffinic molecules largely depresses the pour points

Hydrodesulfurization (HDS), Hydrodenitrogenation (HDN) and Aromatic Hydrogenation (Ar H) of the total liquid hydrocracked product:

Ni-Mo of 3.0 wt % NiO and 12.0 wt % MoO₃ allow the optimum reduction of Mo by sulfiding under the used reaction conditions which provides the largest amount of Ni-Mo-S phase for the highest hydrogenation activity. However, such a site has no performance for the hydrogenation of species. More Ni than 5 wt % allows the excess reduction of MoS₂ to metallic species, decreasing the number of active sites, i.e. Ni of 5 wt% to 15 wt % of Mo sulfide led to the highest activity for hydrotreatment from Fig. (7a-b) [Isado, et al., (1998); Nash, (1989)].

Increasing reaction temperature up to 400°C affects a progressive aromatic removal from the heavy gas oil under study. However, further

increase of temperature to 450°C results in an opposite response, where aromatic contents in the product are significantly increased to a value larger than those even reached at 400°C. This is attributed to a shift of the thermodynamic equilibrium from hydrogenation to dehydrogenation and hydrogenolysis of poly nuclear aromatics. In addition, aromatic removal increased to a large extent by decreasing LHSV.

Aromatics and sulfur in gas, oil fuels are required to be severely limited in the near future. High aromatic contents in diesel fuel lower the fuel quality as they have low cetane number [Suchanek, (1990)]. In addition aromatics in diesel fuel have been reported [Ma, and Mochidal, (1994)], to contribute significantly to undesired emission in exhaust gases from diesel engines.

Deep aromatic saturation is a reversible reaction favoured at low temperature by using high activity catalyst. The overall catalyst activity may be limited due to the rate of diffusion of reactants into pores. Therefore, large pore catalysts will be chosen to minimize diffusion resistance.

The aromatic and nitrogen hydrocarbons present in the feedstock (especially the poly aromatic hydrocarbons) retard the HDS reactions [Lavap, and Satarfield, (1988)].

Fig (5-b) shows that under operating conditions (temp. and LHSV), the investigated catalyst exhibit higher activity for sulfur removal. The high activities of the catalyst can be interpreted in terms of its acidic support which leads to more Ni-Mo-O groups (which are the precursors of Ni-Mo-S groups). This will produce more HDS activity [Callant, et al., (1995)]. The higher acidities of the investigated catalyst enhance the cracking capability, which would result in the increase of HDS activity. Both hydrogenation and cracking capabilities of the catalyst are beneficial to the HDS activity.

The removal of organic nitrogen is essential to many different refinery processes. It is well known that nitrogen molecules have a significant influence on coke formation, as many of these molecules are known to be coke precursors. Kinitically, organic nitrogen molecule have a pronounced inhibitive effect on hydrotreating reactions such as HDS, Ar H and other hydrogenolysis reactions. Moreover, removal of nitrogen is important in order to lower the emission of nitrogen oxides when oil fractions are burned.

Fig (6-b) shows that under all operating conditions (temp. and LHSV), the investigated catalyst is active for HDN. This activity is likely

due to the neutralization of some of the basic nitrogen compounds by acid sites on the non-zeolitic catalyst component and the resulting protection of the zeolite from nitrogen poisoning [Kyong, and Baik, (1998)].

In general, HDN conversions are relatively low as compared to HDS under the operating conditions used. The reason for this is that the hydrogenolysis of C-N bond in polyaromatic molecules requires the previous hydrogenation of the aromatic ring containing the heteroatom, to which its extent is limited.

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التكسير الهيدروجيني للسولار المفرغ الثقيل

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تم دراسة التكسير الهيدروجيني للسولار المخل، الثقيل فى مفاعل ذو طبقة ثابتة وذلك باستخدام حفاز يحتوى على ١٥% من اكاسيد النيكل والموليدنيوم (٢٠% نيكل ٨٠% موليدنيوم) المحمل على ١٥% من الزيوليت الهيدروجيني Y مع سليكا الومينا. لقد تم دراسة تأثير كلا من درجات حرارة التفاعل (٣٧٥ - ٤٥٠ °م) والسرعة الفراغية (٣,٠ - ٠,٥ س - ١) مع ثبات كل من ضغط الهيدروجين عند ١٠ ميجاباسكال ونسبة الهيدروجين الى مادة التغذية عند ٥٠٠ لتر/لتر وذلك على كل من كمية المنتج وجودته. كما تم دراسة الخواص المختلفة للسائل المنتج مثل الكثافة والمواد العطرية ومعامل الديزل محتوى الكبريت والنتروجين - كلا من نقط التدخين والتجميد والانسكاب مع علاقته بظروف التشغيل المختلفة بالإضافة الى دراسة نشاطية الحفاز لإزالة الكبريت والنتروجين والمواد العطرية بواسطة الهدرجة.