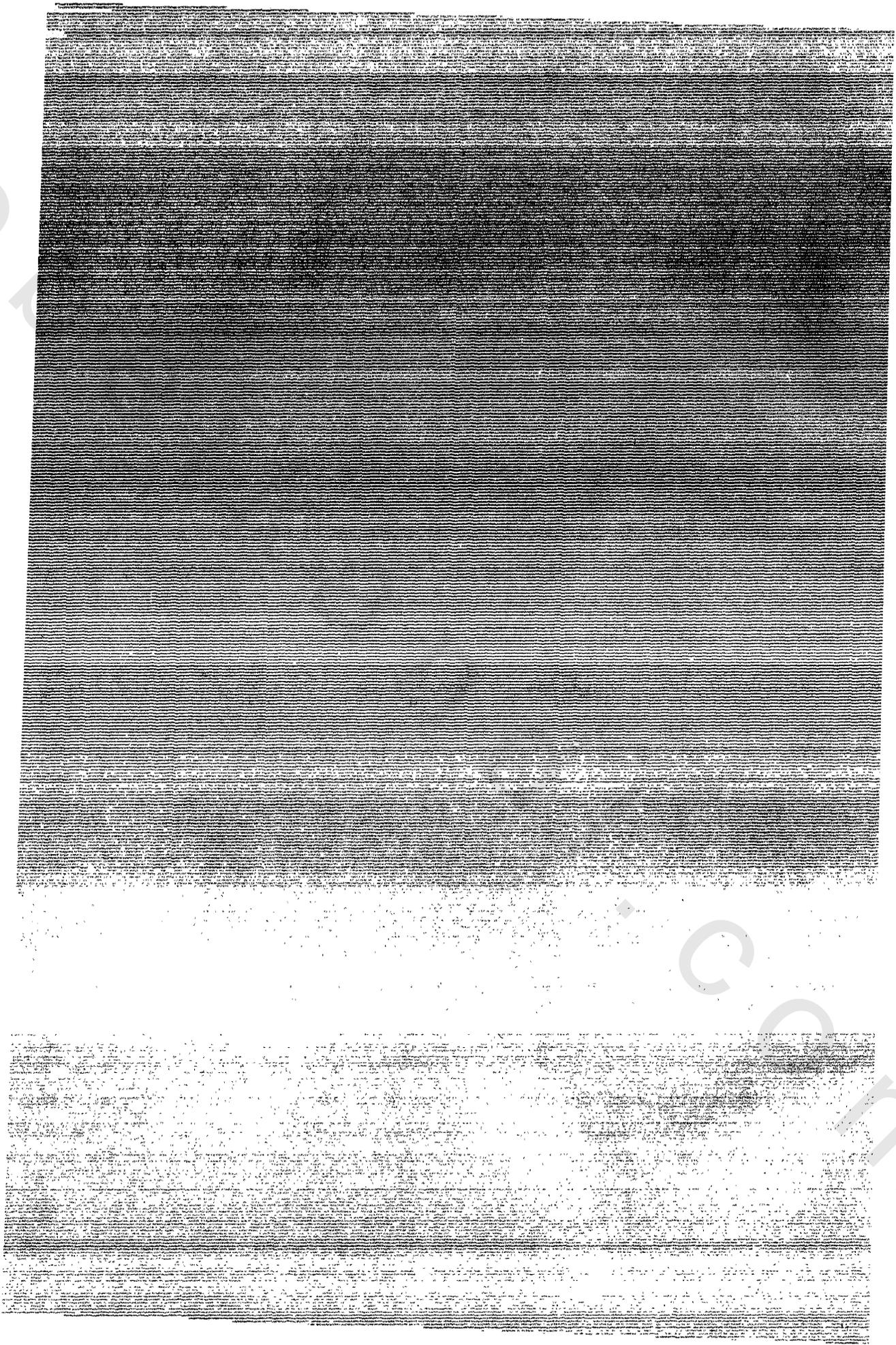


Chapter IV
Results
and
Discussion



RESULTS and DISCUSSION

Elucidation of the catalyst deactivation caused during hydrotreating petroleum fractions is one of the most important issues to improve the catalytic performance in petroleum refining processes. It is well known that hydrotreatment is used in the refining industry to remove contaminants such as sulfur (HDS), nitrogen (HDN) and metals (HDM), mainly because of technical and environmental reasons.

In hydroprocessing of petroleum products, catalyst deactivation by coke deposition is one of the major concerns in petroleum industries. The coke deposition occurs in the pores and / or on the surface of the catalyst, and always leads to loss of activity and product selectivity. During hydroprocessing, parts of the metals present in the feed will deposit on the catalyst surface and cause deactivation. Deactivation by metal is irreversible; the rate of metal deposition varies from metal to metal such as (V, Ni, Fe). In general the deactivation causes have considered to the accumulation of carbonaceous, metallic deposition and the structure changes of the catalyst components.

4.1 Effect of Operating Conditions on Product Quality of Heavy Vacuum Gas Oil:

4.1.1 Effect of Reaction Temperature:

The results of *Table (5)* and *Figures (3– 8)* represent the effect of reaction temperature on the product quality. It was shown that the yield of heavy vacuum gas oil (HVGO) was clearly affected by the reaction temperature; i.e. decreased as the activity of the sulfided $\text{CoO MoO}_3 / \text{Al}_2\text{O}_3$ catalyst increased due to the increase in reaction severity. As a result, the hydrodesulfurization (HDS) activity of the catalyst was increased continuously from 37.16 % at 300 °C to 98.31 % at 425 °C at constant pressure (50 bar), constant liquid hourly space velocity (0.5 h^{-1}) and duration time (9h) (*Figure 4*). The effects of temperature on aniline point, diesel index (DI) are given in *Table (5)* and *Figures (5& 6)*. These properties give an indication on the hydrogenation activity of the CoMo / Al catalyst. As the reaction temperature increased the aromatic content decreased from 35 % at 300 °C to 33.57 % at 350 °C, then a slow decrease from 350 – 425 °C was shown in *Figure (8)*. At the same time, the total saturates content, *Figure (7)*, increased from 64.60 to 66.80% as the reaction temperature increased from 300 to 425 °C. This is due to the hydrogenation of aromatics, which is an exothermic reaction and was favored at low reaction temperature [Gary, 2001].

Resin was decreased from 0.4 – 0.11 wt % with increasing reaction temperature. This can be attributed to the decomposition of resin present in feed to coke [Marafi and Stanislaus, 1997].

Table (5): Effect of Reaction Temperature on Hydrotreating of HVGO.

Conditions: (50 bar, 0.5 h⁻¹, 9h)

<i>Temperature, °C</i>						
<i>Characteristics</i>	<i>300</i>	<i>325</i>	<i>350</i>	<i>375</i>	<i>400</i>	<i>425</i>
Yield, wt %	86.00	85.00	84.19	83.90	83.71	83.60
Density at 15 °C	0.8580	0.8543	0.8483	0.8457	0.8405	0.8295
Sulfur content, wt %	1.150	0.790	0.400	0.200	0.057	0.031
Hydrodesulfurization, %	37.16	56.83	78.14	89.07	98.88	98.31
Aniline point, °F	174.2	177.1	179.6	180.6	181.4	182
Diesel index	59.08	60.45	63.41	64.69	66.85	71.13
Color	1.5	1.5	1.5	1.5	1.5	1.5
Pour point, °C	6	6	6	6	6	6
<i>Component analysis, wt %</i>						
Total Saturates	64.60	65.50	66.12	66.58	66.71	66.80
Total Aromatics	35.00	34.15	33.57	33.20	33.11	33.09
Resins	0.40	0.35	0.31	0.22	0.18	0.11

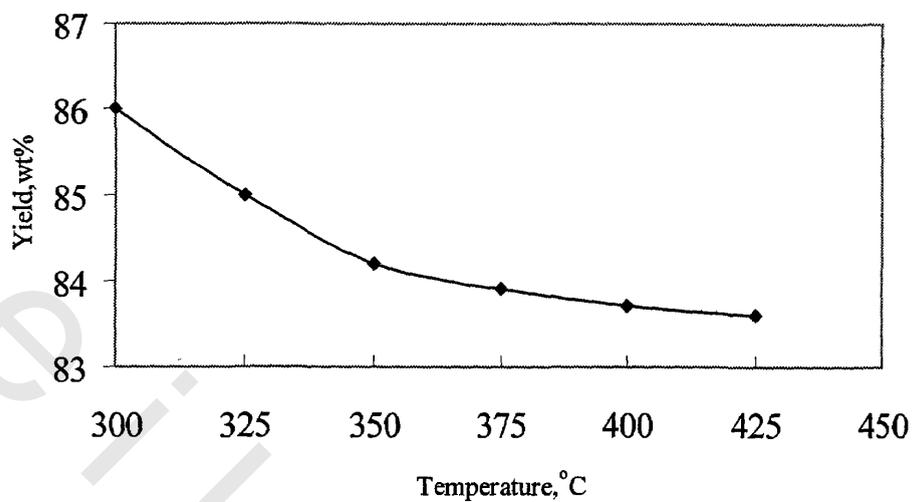


Figure (3): Effect of Reaction Temperature on Product Yield of HVGO during Hydrotreating Process.

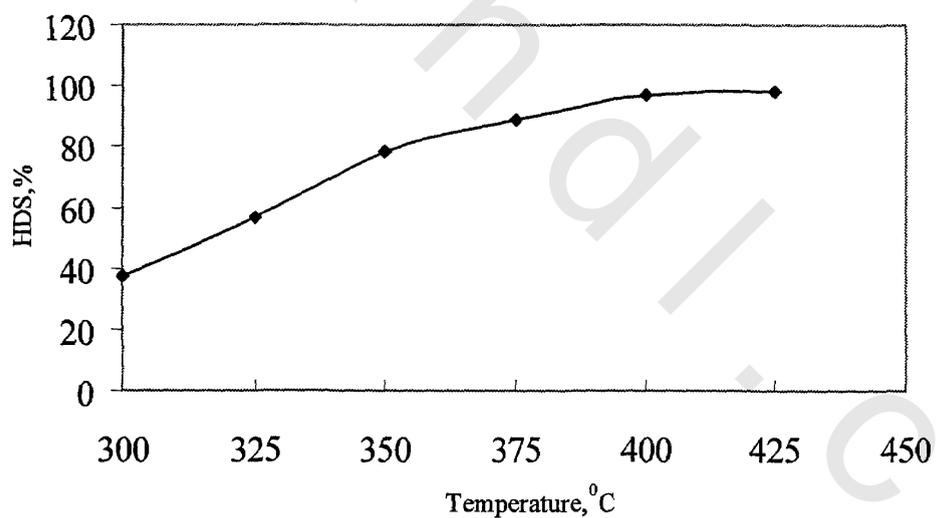


Figure (4): Effect of Reaction Temperature on Hydrodesulfurization of HVGO during Hydrotreating Process.

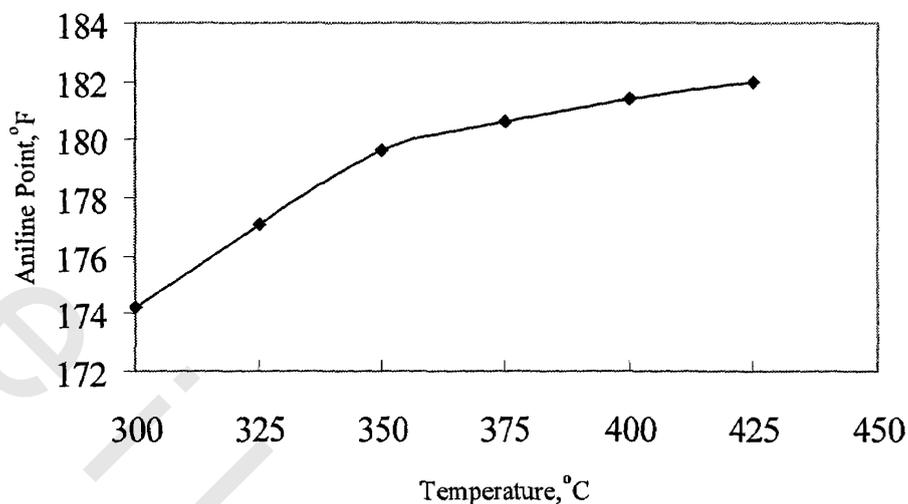


Figure (5): Effect of Reaction Temperature on Aniline Point of HVGO during Hydrotreating Process.

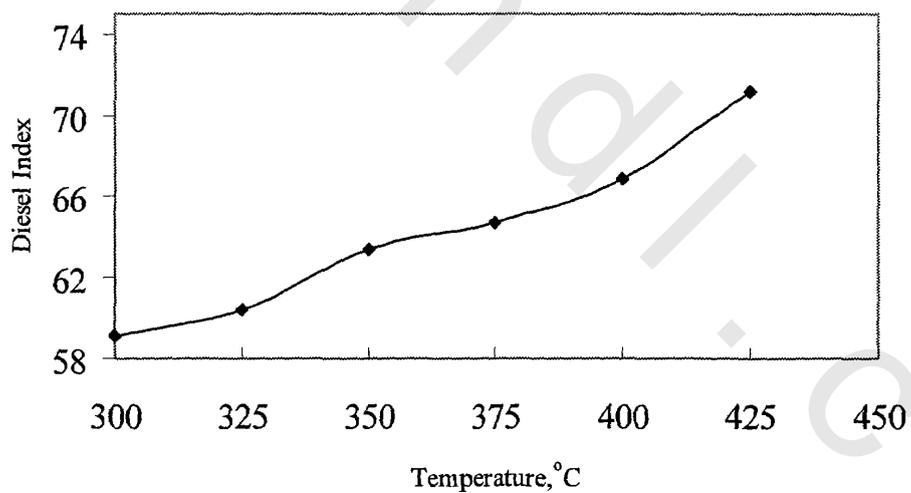


Figure (6): Effect of Reaction Temperature on Diesel Index of HVGO during Hydrotreating Process.

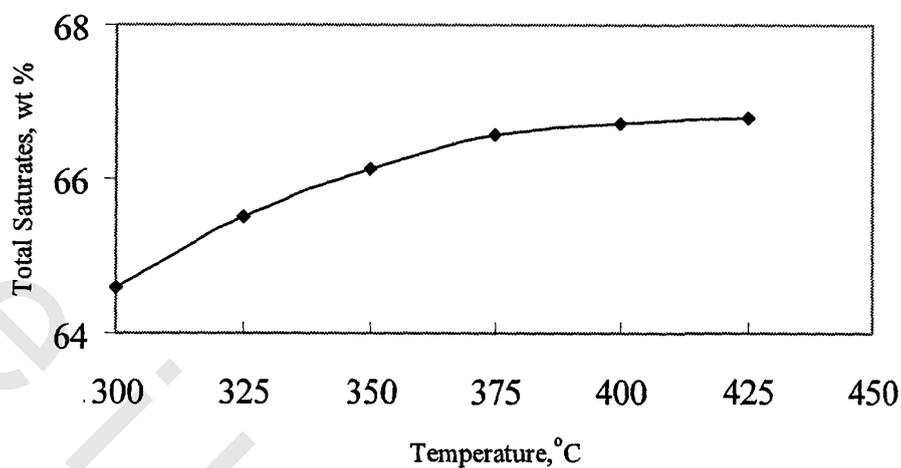


Figure (7): Effect of Reaction Temperature on Total Saturates of HVGO during Hydrotreating Process.

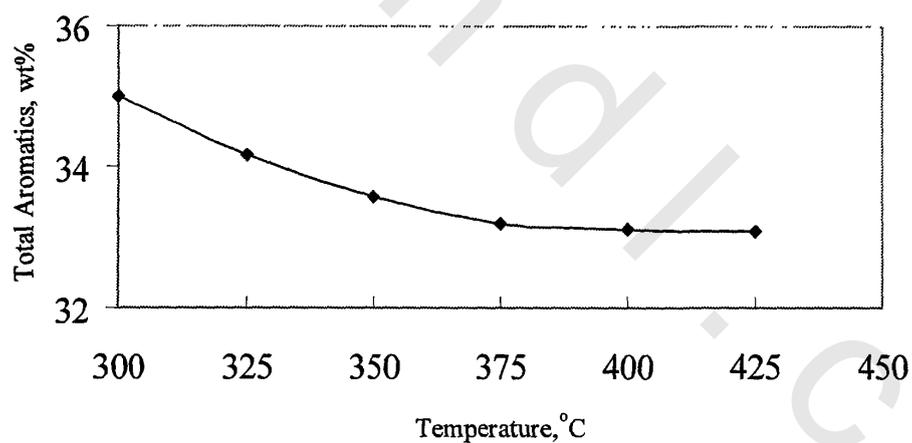


Figure (8): Effect of Reaction Temperature on Total Aromatics of HVGO during Hydrotreating Process.

4.1.2 Effect of Hydrogen Pressure:

The results tabulated in *Table (6)* and represented in *Figures (9 – 14)* show that as the total hydrogen pressure increased from 15 up to 65 bar, several effects on yield and quality characteristics of heavy vacuum gas oil were observed; i.e. HDS increased from 70.70 % to 85.19 %, DI and aniline point increased from 58.89 % to 65.01 % and 168.8 % to 182.9 %, respectively. While total aromatics content was decreased from 37.94 % at 15 bar to 30.38 % at 65 bar; this can be attributed to the increase of hydrogenation activity of the catalyst with increasing total hydrogen pressure besides the increase of saturation activity and reduction of coke formation. [Gary, 2001] [Bartholomew, 1993]

Table (6): Effect of Hydrogen Pressure on Hydrotreating of HVGO.

Conditions: (350°C, 0.5 h⁻¹, 9h)

<i>Pressure, bar</i>				
<i>Characteristics</i>	<i>15</i>	<i>35</i>	<i>50</i>	<i>65</i>
Yield, wt %	92.98	92.20	89.83	88.50
Density at 15 °C	0.8504	0.8519	0.8500	0.8471
Sulfur content, wt %	0.536	0.410	0.365	0.271
Hydrodesulfurization, %	70.70	77.59	79.92	85.19
Aniline point, °F	168.8	170.6	181.2	182.9
Diesel index	58.89	59.03	63.36	65.01
Color	1.5	2.5	2.0	2.0
Pour point, °C	9	9	9	9
<i>Component analysis, wt %</i>				
Total Saturates	61.40	61.71	67.62	69.37
Total Aromatics	37.94	37.76	32.07	30.38
Resins	0.66	0.53	0.31	0.25

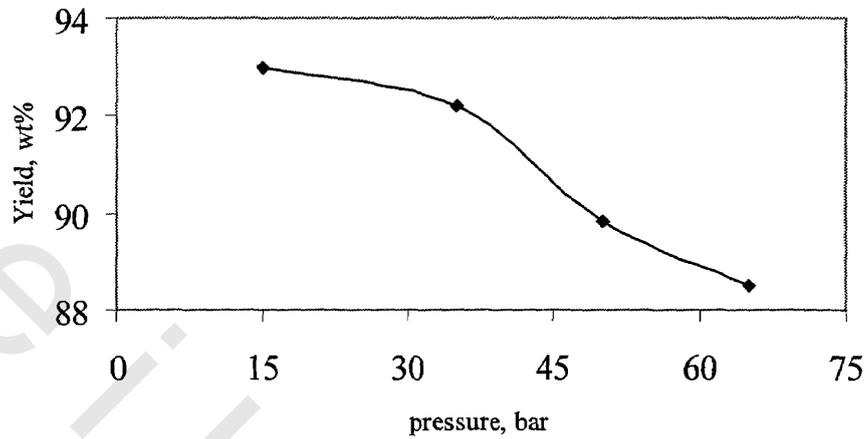


Figure (9): Effect of Hydrogen Pressure on Product Yield of HVGO during Hydrotreating Process.

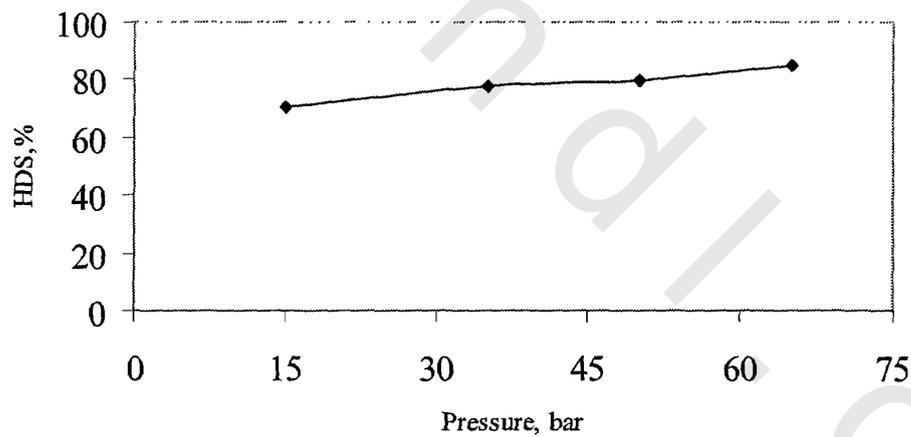


Figure (10): Effect of Hydrogen Pressure on Hydrodesulfurization of HVGO during Hydrotreating Process.

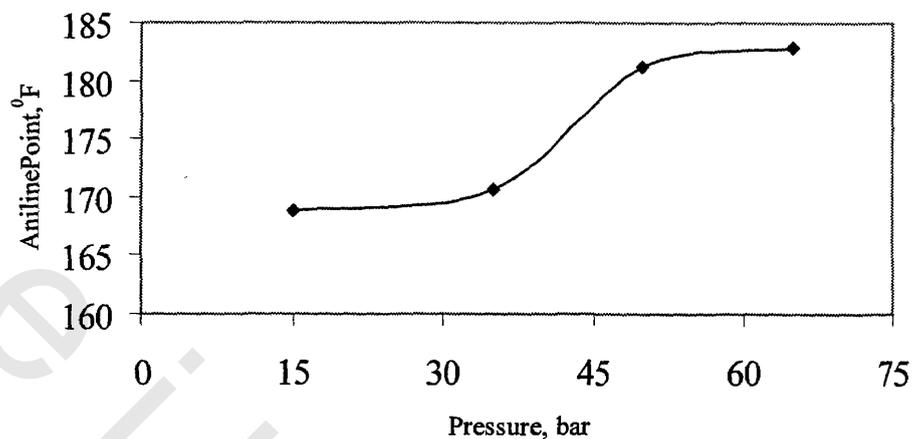


Figure (11): Effect of Hydrogen Pressure on Aniline Point of HVGO during Hydrotreating Process.

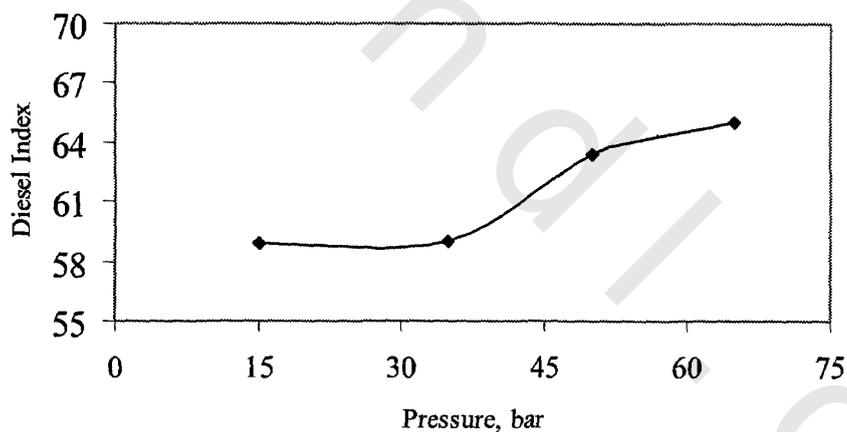


Figure (12): Effect of Hydrogen Pressure on Diesel Index of HVGO during Hydrotreating Process.

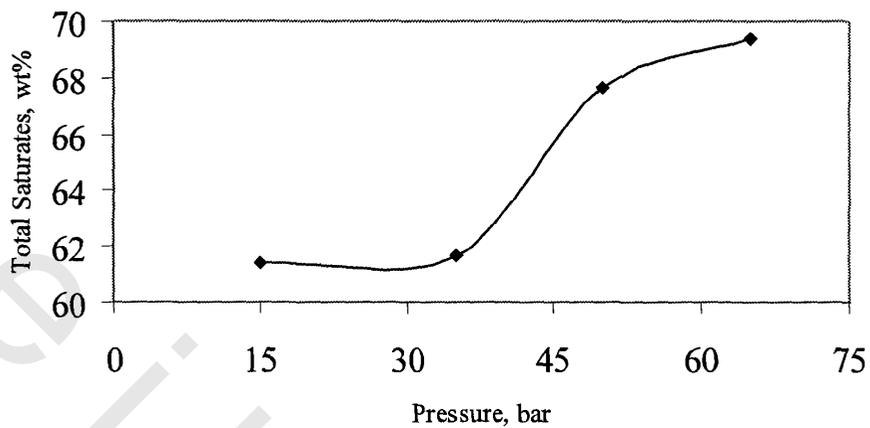


Figure (13): Effect of Hydrogen Pressure on Total Saturates of HVGO during Hydrotreating Process.

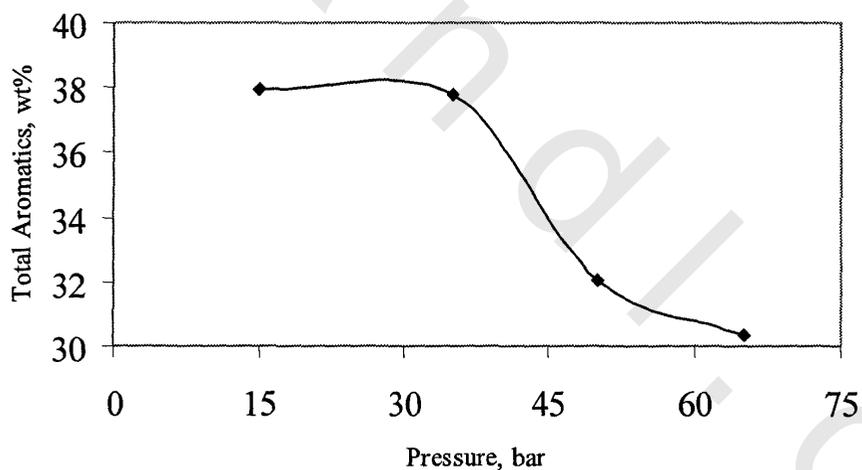


Figure (14): Effect of Hydrogen Pressure on Total Aromatics of HVGO during Hydrotreating Process.

4.1.3 Effect of Liquid Hourly Space Velocity:

The results of *Table (7)* and *Figures (15 – 20)* represent the effect of liquid hourly space velocity (LHSV) on the product quality of HVGO. Evidently, by increasing the liquid hourly space velocity from 0.5 to 1.5 h⁻¹, the hydrogenation function of the catalyst decreased due to the decrease in the contact time between the reacting HVGO molecules and the acid hydrogenation sites of the catalyst.

In spite of the decrease in HDS activity of the catalyst, it was found that the yield, density, color and total aromatics content increased while the aniline points and diesel indices were decreased. This means that no improvement in the quality of heavy vacuum gas oil by increasing L.H.S.V. from 0.5 to 1.5 h⁻¹.

Table (7): Effect of Liquid Hourly Space Velocity (LHSV) on Hydrotreating of HVGO.

Conditions: (350 °C, 50 bar, 9h)

<i>LHSV, h⁻¹</i>					
<i>Characteristics</i>	<i>0.50</i>	<i>0.75</i>	<i>1.00</i>	<i>1.25</i>	<i>1.50</i>
Yield, wt %	85.19	85.40	85.53	88.20	90.17
Density at 15 °C	0.8475	0.8491	0.8503	0.8515	0.8522
Sulfur content, wt %	0.306	0.371	0.571	0.582	0.628
Hydrodesulfurization, %	83.26	79.71	68.79	68.22	65.67
Aniline point, °F	174.2	173.5	172.4	171.6	170.6
Diesel index	61.77	60.98	60.19	59.51	58.93
Color	1.5	1.5	2.0	2.0	2.0
Pour point, °C	9	9	9	9	9
<i>Component analysis, wt %</i>					
Total Saturates	63.86	63.07	62.15	60.79	58.96
Total Aromatics	35.83	36.48	37.33	38.45	40.08
Resins	0.31	0.45	0.52	0.76	0.96

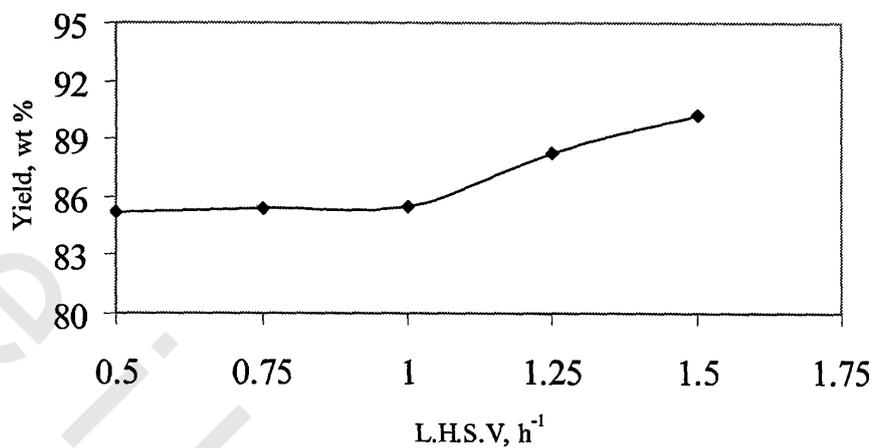


Figure (15): Effect of Liquid Hourly Space Velocity on Product Yield of HVGO during Hydrotreating Process.

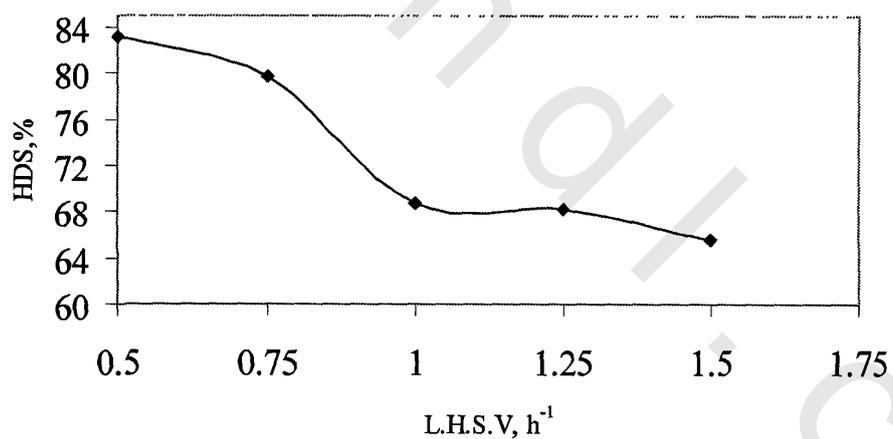


Figure (16): Effect of Liquid Hourly Space Velocity on Hydrodesulfurization of HVGO during Hydrotreating Process.

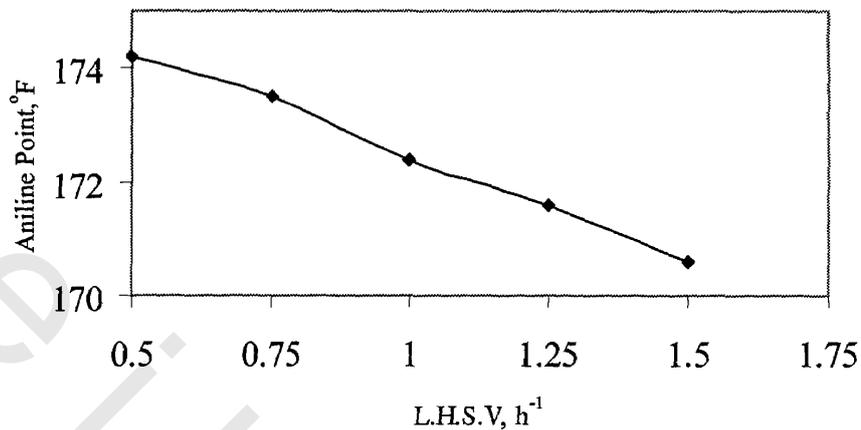


Figure (17): Effect of Liquid Hourly Space Velocity on Aniline Point of HVGO during Hydrotreating Process.

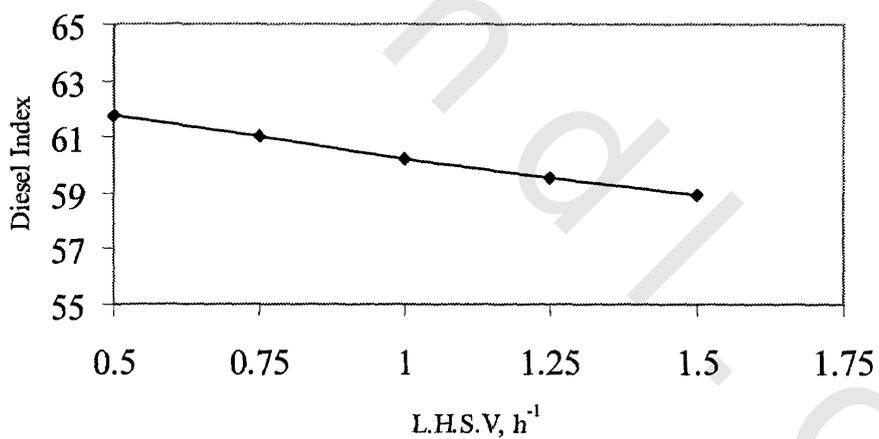


Figure (18): Effect of Liquid Hourly Space Velocity on Diesel Index of HVGO during Hydrotreating Process.

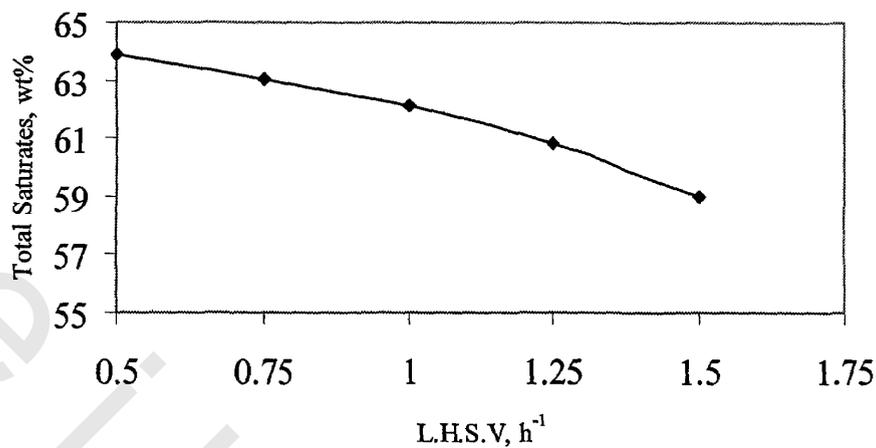


Figure (19): Effect of Liquid Hourly Space Velocity on Total Saturates of HVGO during Hydrotreating Process.

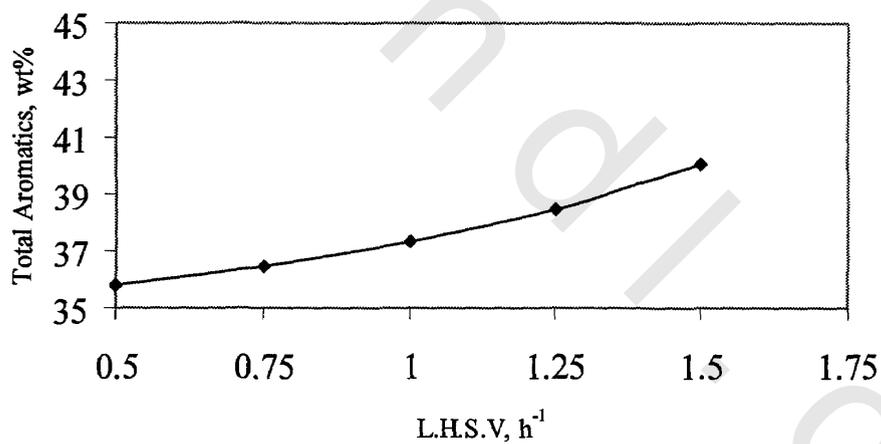


Figure (20): Effect of Liquid Hourly Space Velocity on Total Aromatics of HVGO during Hydrotreating Process.

4.1.4 Effect of Operating Conditions on the Activity of the Catalyst:

As indicated in the experimental part, the Co –Mo/ Al catalyst was charged in the reactor of the cata – test unit in three successive zones; each was separated by glass beads and glass wool. The hydrotreatment process of heavy vacuum gas oil was carried out under the following operating conditions: reaction temperature from 300 to 425 °C and a duration time of 54 h, hydrogen pressure from 15 to 65 bar and a duration time of 36 h and liquid hourly space velocity from 0.5 to 1.5 h⁻¹ and a duration time of 45 h. At the end of runs of each variable (temperature, pressure and liquid hourly space velocity), a sample from the catalyst was taken from each zone in the reactor and the coke content was calculated.

Tables (8& 9) and Figure (21) represent the coke formation and distribution of coke after 54 h at the end of the reaction temperature range. It shows that, the first zone of the reactor was accumulated by coke than second and third zone. At the first zone the percentage of coke formed after 54 h equals 4.83 wt %, while at the second and third zone it was 3.75& 3.42 wt %, respectively.

In case of pressure for the first, second and third zones, respectively; and after 36 h the coke content was equal to 4.14, 2.02& 2.04 wt %; while in case of L.H.S.V. and after 45 h it was 3.72, 3.29& 3.26 wt % for each of the three zones, respectively.

Coke deposition on the reactor zones can be arranged as follows:

First zone > second zone > third zone

This is attributed to the deposition of coke, which comprises the large part of deposits on hydrotreating catalyst, may concentrate in fixed beds at the reactor entrance and pellet edges [Bartholomew, 1993].

Important process variables in hydrotreating catalyst deactivation are temperature, hydrogen pressure and liquid hourly space velocity; coke formed in case of temperature was higher than in case of pressure and L.H.S.V.

At elevated reaction temperatures coke deposits concentrate near the front of the active reaction zone in the catalyst bed and near pellet edges causing more rapid plugging of catalyst pores [Takahashi et al., 2005].

Table (8): *Coke Deposited after each Operating Variable Produced from Different Zones of Reactor.*

<i>Zone</i> <i>Operating variable</i>	<i>Coke, wt %</i>			
	<i>First</i>	<i>Second</i>	<i>Third</i>	<i>Total coke</i>
Reaction temperature, °C	4.83	3.75	3.42	12
Hydrogen pressure, bar	4.14	2.02	2.04	8.19
Liquid hourly space velocity, h ⁻¹	3.72	3.29	3.26	10.28

Table (9): *Coke Distribution after each Operating Variable Produced from Different Zones of Reactor.*

<i>Zone</i> <i>Operating variable</i>	<i>Coke, wt %</i>		
	<i>First</i>	<i>Second</i>	<i>Third</i>
Reaction temperature, °C	40.25	31.25	28.5
Hydrogen pressure, bar	50.55	24.66	24.91
Liquid hourly space velocity, h ⁻¹	36.19	32	31.71

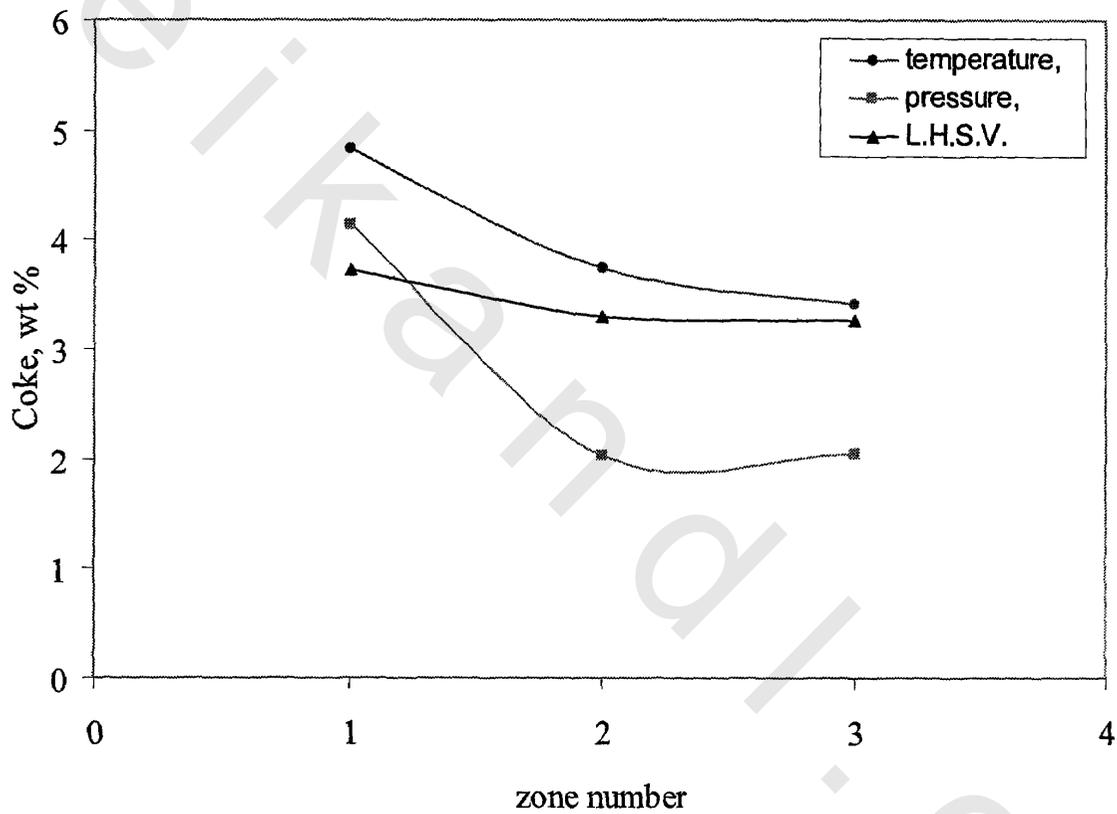


Figure (21): Effect of Different Operating Conditions on Coke Deposition at Different Reactor Zones.

4.2 Catalyst Deactivation Using Different Feed Stocks:

4.2.1 Catalyst Deactivation on Using HVGO:

The influence of initial coking on hydrodesulfurization (HDS) reaction was investigated by the analysis of the hydrotreated products as for sulfur content. The rate constant for (HDS) reaction at various coke levels was calculated using the kinetic equation [Marafi and Stanislaus, (1997)].

$$K_{HDS} = LHSV \frac{1}{n-1} \left(\frac{1}{S_p^{n-1}} - \frac{1}{S_f^{n-1}} \right)$$

Where:

LHSV is the liquid hourly space velocity

n is the reaction order =1.5

S_F is the sulfur content in the feed (wt %)

S_p is the sulfur content in product (wt %).

The results clearly demonstrate that the HDS activity of the catalyst decreases from 86.84 % at the first 3 h to reach 83.01 % after 12 h and then decreases to 77.05 % after 24 h as shown in *Table (10)*. The loss of HDS activity caused by coke deposition on hydrotreated catalyst may be due to the coke blocking in edges and corners of the active MoS₂ crystallites.

The catalytic active sites in the sulfided Co-Mo/ γ Al₂O₃ catalyst used in this study are responsible for promoting hydrotreating reactions as

hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (the sulfur vacancies in MoS₂ crystallites) [Abd El – Wahed et al., 2007]. These crystallites remain dispersed on the alumina surface as hexagonal slabs; coke deposition may cover these active sites leading to a decrease in their activity towards the hydrotreating reactions as HDS and hydrogenation.

The other characteristics of the products which are shown in *Table (10)* as yields, density, aromatic contents, and diesel indices were also affected by coke deposition.

Table (10): *Effect of Time on Stream on the Product Quality of HVGO during Hydrotreating Process.*

Conditions: (350 °C, 50 bar, 0.5 h⁻¹)

<i>Time, h</i>					
<i>Properties</i>	3	6	9	12	24
Yield, wt %	76.90	78.50	80.29	83.93	92.89
Density at 15 °C	0.8453	0.8472	0.8475	0.8478	0.8479
Sulfur content, wt %	0.241	0.301	0.306	0.311	0.420
Hydrosulfurization, %	86.84	83.55	83.26	83.01	77.05
Rate constant (K _{HDS})	1.589	1.529	1.524	1.519	1.410
Aniline point, °F	174.2	174.2	174.2	174.2	174.2
Diesel index	62.53	61.88	61.77	61.67	61.64
Color	1.5	1.5	1.5	1.5	1.5
<i>Component analysis, wt %</i>					
Total Saturates	62.89	63.02	62.85	62.79	62.71
Total Aromatics	36.22	36.34	36.70	36.90	37.10
Resins	0.89	0.64	0.45	0.31	0.19

4.2.2 Catalyst Deactivation on Using Feed Blend:

On the other hand, the products quality of the yields produced from hydrotreating the blend mixture is given in *Table (11)*. The data show that at the first 3h, the hydrodesulfurization activity was first decreased to 74.94 %, then it was decreased sharply to 46.08 % after 6 h and finally the rate of decrease slows down to reach about 36.46 % after 24 h.

It was also found that asphaltene content, Conradson carbon residue (C.C.R) and aromatic content were increased sharply from 3 – 6 h, and a small increase was noticed from 6 – 24 h. After 6 h, asphaltene and coke deposition changed from 4.01 to 6.79 % and from 13.2 to 14.0 %, respectively, when TOS was increased from 6 to 24 h. This may be attributed to the physico – chemical characteristics of the feed blend as given in *Table (1)*. The feed blend contains 7.74% asphaltene content and 181.2 PPM metals content (Ni and V) and Conradson carbon residue 13.01%; this causes greater amounts of carbon and metals deposition on the catalyst at the first hours [Murti et al. 2005] [Sahoo et al. 2004].

Tables (10) and (11) represent the comparison between the quality characteristics of the products after the hydrotreatment of HVGO and that of feed blend. From the obtained results, it is clear that the yield and aromatic content are higher in case of feed blend than those in case of HVGO, which is due to the more catalyst deactivation as a result of higher coke deposition.

Table (11): *Effect of Time on Stream on the Product Quality of Feed Blend during Hydrotreating Process.*

Conditions: (350 °C, 50 bar, 0.5 h⁻¹)

<i>Time, h</i> <i>Properties</i>	<i>3</i>	<i>6</i>	<i>9</i>	<i>12</i>	<i>24</i>
Yield, wt%	87.44	93.88	95.33	97.22	99.50
Density at 15 °C	0.9260	0.9350	0.9380	0.9450	0.9480
Sulfur content, wt %	0.990	2.130	2.350	2.450	2.510
Hydrodesulfurization %	74.94	46.08	40.51	37.97	36.46
Rate constant (K_{HDS})	2.960	1.820	1.600	1.500	1.440
Asphaltene content, wt%	0.88	4.01	5.31	6.18	6.79
Conradson carbon residue, wt%	1.604	9.980	10.250	10.310	10.650
<i>Component analysis, wt%</i>					
Total Saturates	52.36	47.52	44.18	41.68	39.11
Total Aromatics	46.01	49.84	53.06	55.44	58.00
Resins	1.63	2.64	2.76	2.88	2.89

4.3 Effect of Time on Stream (TOS) on Coke Formation:

A series of heavy vacuum gas oil and feed blend hydrotreating experiments with duration time ranging from 3 h to 24 h were conducted to investigate the influence of processing time on coke build up on the catalyst surface. *Figure 22* represents the relation between time on stream and coke formation from HVGO and feed blend hydrotreatment. The results show that the coke formation is very rapid during the early hours of the run. More than 3.9 wt % and 10.2 wt % carbon is deposited on the catalyst within the first 3 h of operation in case of HVGO and feed blend, respectively. After the rapid coke build up during the initial period, coking slows down and tends to level off or reach an equilibrium value within 24 h [Ancheyta et al., 2002]. Coke deposited in case of blend was higher than that of HVGO; this may be attributed to the amount of the carbonaceous deposits formed from the heavy components in the feed stocks [Tanaka et al., 1998]. It is not surprising since asphaltenes, which are very large polyaromatic compounds, are the major coke precursors.

This confirms that deposition of coke is the main source of catalyst deactivation during the first hours of the run [Manuel et al., 2000].

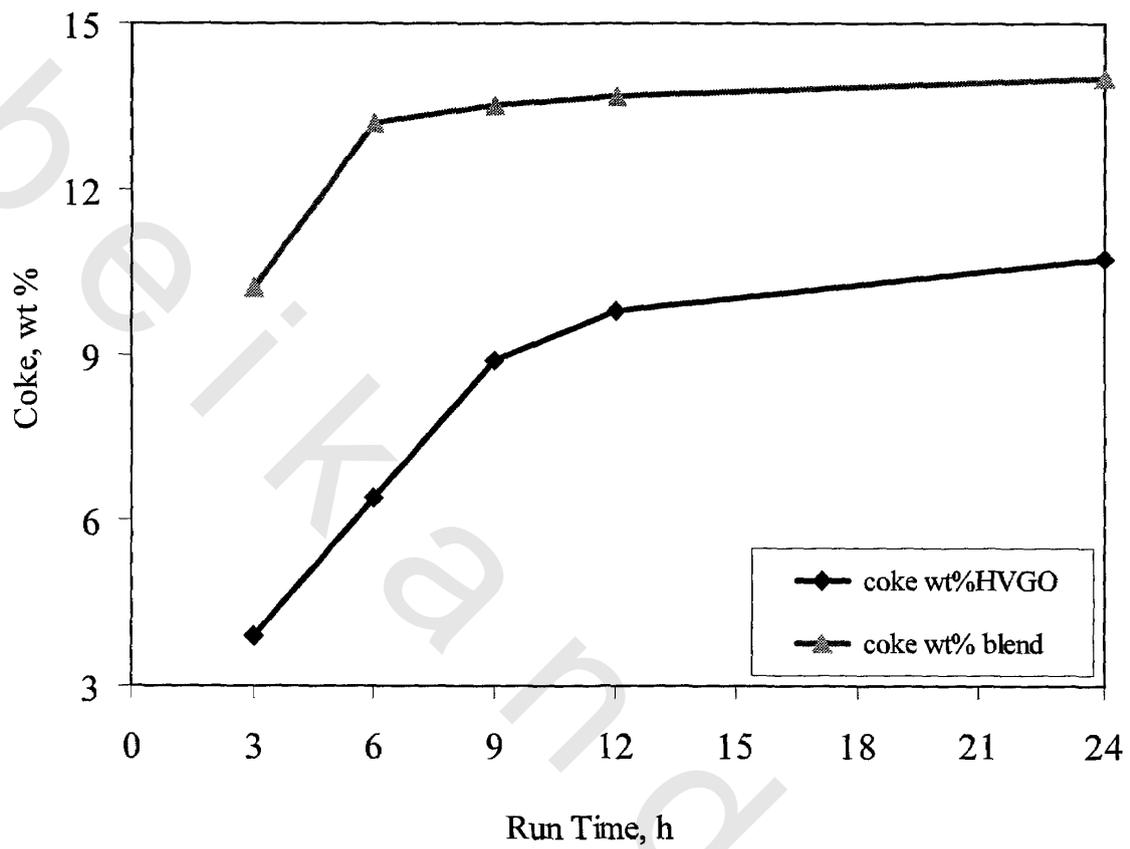


Figure (22): Effect of Time on Stream on Coke Yield Using Different Feed Stocks during Hydrotreating Process.

4.4 Effect of Time on Stream (TOS) on Metal Deposition:

Nickel and vanadium removals showed different behavior during time on stream (TOS). This can be attributed to the difference in Ni - and V - porphyrin type structure. In case of V, the linked oxygen atom forms strong bond with the catalyst surface while Ni does not have this oxygen link. It should also be mentioned that the initial V content is about 3 times higher than Ni content (*Figure 23*) and this difference affects metal deposition on the catalyst where the rate of Ni deposit formation is strongly influenced by formation of V deposits.

During blend hydroprocessing, asphaltenes are converted to smaller molecules and metals (porphyrine and non - porphyrine types) transformed and deposited into the catalyst causing catalyst deactivation. The molecules do not penetrate deeply into the catalyst and accumulated as metal sulfides into the pore mouth and block the way to enter the reactants. Metal deposition is affected deeply by the pore size distribution of the catalyst [Furimsky, 1998].

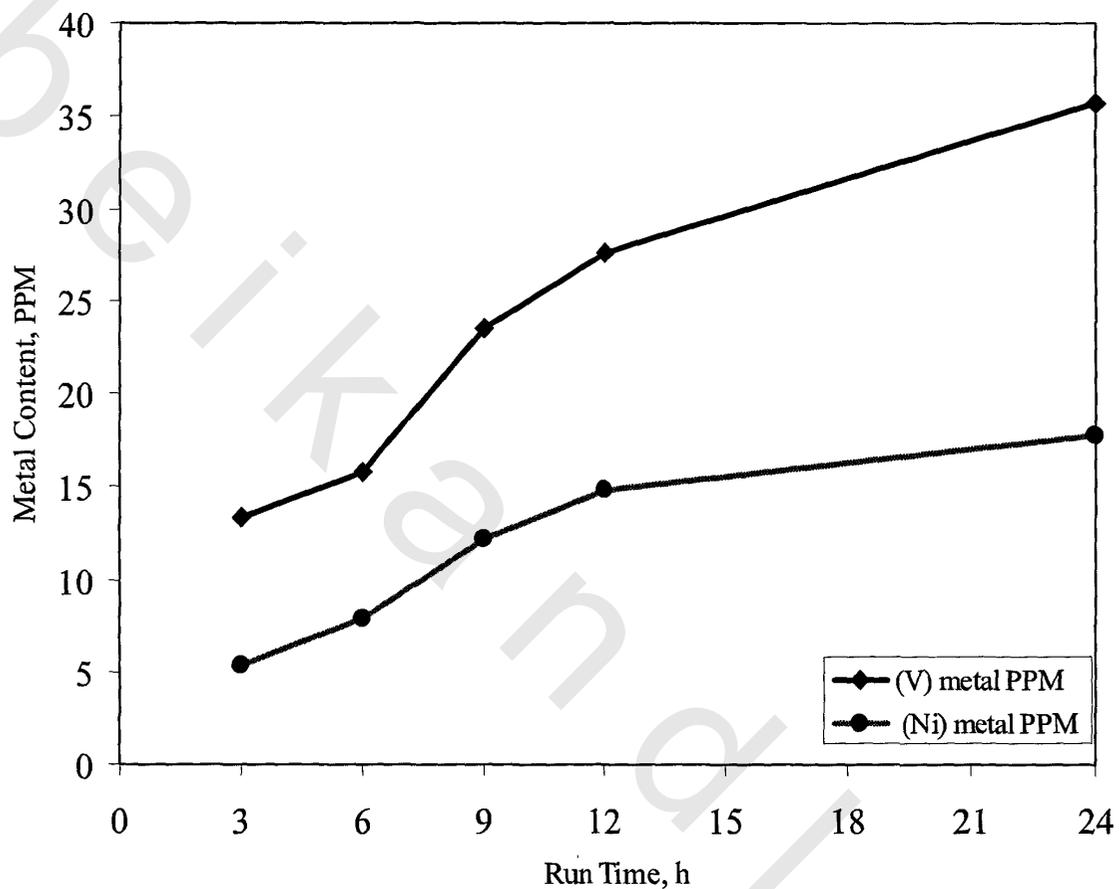


Figure (23): Effect of Time on Stream on Metal Content Using Feed Blend during Hydrotreating Process.

4.5 Effect of Time On Stream on Catalyst Textural Analysis:

The surface area and pore volume of the used catalyst samples from the different runs conducted at varying duration times were measured with a view to gain additional information on the influence of initial coke on catalyst deactivation by loss of surface area and porosity. The surface area and pore volume of the catalyst are plotted as a function of processing time in *Figures (24& 25)*. The decrease in surface area is particularly rapid during the first 3 to 6 h and then slows down.

A similar decrease is also noticed in the catalyst pore volume, *Figure 25*. With increasing processing time, the decrease of surface area and pore volume of spent catalyst in case of hydrotreated feed blend was higher than in case of hydrotreated HVGO. The observed loss in surface area and pore volume of the catalyst during processing could be attributed to coke deposition.

The micropores present in the fresh catalyst contribute significantly to the catalyst total surface area. Blockage of these micropores with coke deposition [Marafi and Stanislaus, 1997] can be expected to lead to decrease of both pore volume and surface area.

Surface area decreases about 41.71 % in case of feed blend and 28.57 % in case of HVGO due to coke and metal deposition.

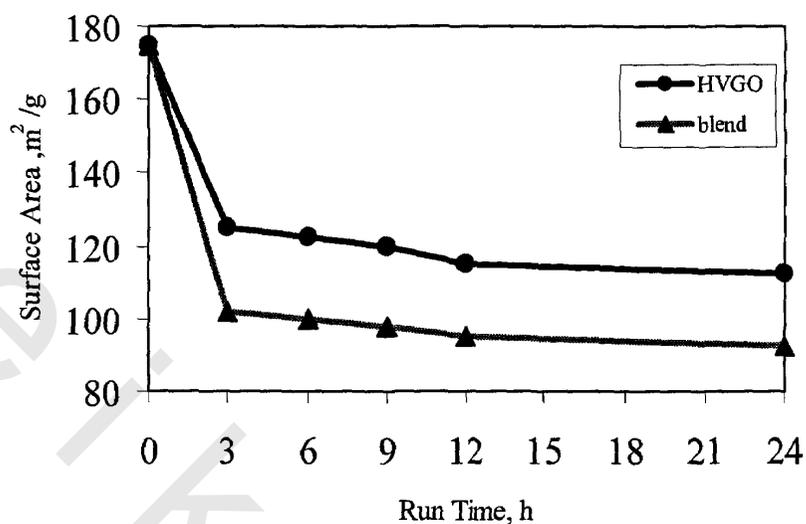


Figure (24): Effect of Time on Stream on Catalyst Surface Area during Hydrotreating processes of HVGO and Feed Blend.

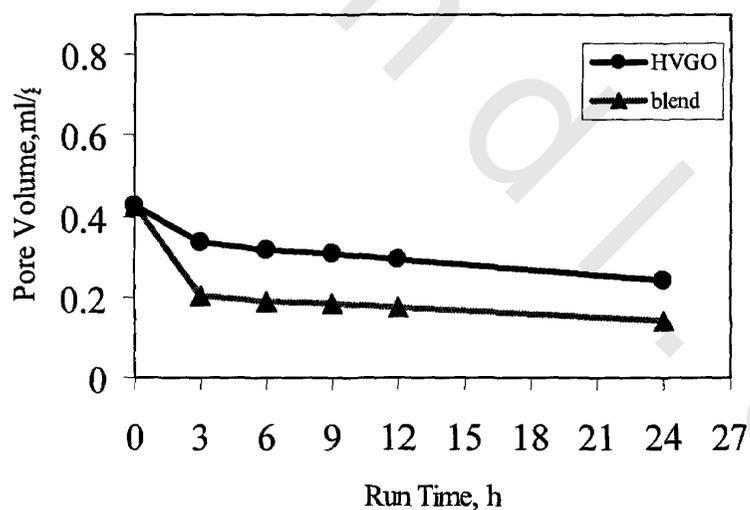


Figure (25): Effect of Time on Stream on Catalyst Pore Volume during Hydrotreating Processes of HVGO and Feed Blend.

The initial coke deposited during the early hours of the run had a significant effect on the pore size distribution of the catalyst. Pores smaller than 50 and 100 Å diameters appear to be affected more by the initial coke deposition than the large pores. Thus the total volume of the micropores having diameter less than 50 Å is found to be reduced by 73.05 % and 83.98 % for HVGO and feed blend, respectively. The narrow meso - pores (50 – 100 Å diameters) are not appreciably affected during the first hours, but they become progressively blocked by coke with increasing TOS. Thus within 3 h of operation, the volume located in meso - pores decreases by 21.21 % and 52.73 % for HVGO and feed blend, respectively. Large meso - pores and macropores are not affected to any significant level by the initial coke deposits. Catalyst pore size distribution, thus, plays an important role in catalyst deactivation by coke deposition, particularly during the early stages of the run, as indicated in *Table (12)*.

Table (12): Pore Size Distribution of Coked Catalyst Samples at Different Duration Times.**Conditions:** (350 °C, 50 bar, 0.5 h⁻¹)

Diameter, <i>A</i>	BET, m ² /g		Total pore volume, ml/g		Pore size, <i>A</i>											
					>50		50-100		100-250		250-400		Total meso pores		>400	
	Time	HVGO	FB*	HVGO	FB*	HVGO	FB*	HVGO	FB*	HVGO	FB*	HVGO	FB*	HVGO	FB*	HVGO
Fresh	175.5	175.5	0.425	0.425	0.026	0.026	0.273	0.273	0.054	0.054	0.024	0.024	0.351	0.351	0.049	0.049
3h	125.0	102.0	0.338	0.203	0.007	0.004	0.215	0.129	0.065	0.039	0.013	0.008	0.293	0.176	0.038	0.023
6h	122.5	100.0	0.316	0.190	0.006	0.004	0.200	0.120	0.056	0.034	0.018	0.011	0.274	0.164	0.036	0.022
9h	120.0	98.0	0.310	0.183	0.006	0.004	0.003	0.002	0.067	0.040	0.200	0.120	0.270	0.162	0.034	0.021
12h	115.0	95.0	0.294	0.177	0.006	0.003	0.137	0.082	0.088	0.053	0.033	0.020	0.258	0.155	0.031	0.019
24h	112.5	92.5	0.240	0.144	0.005	0.003	0.076	0.046	0.105	0.063	0.031	0.019	0.212	0.128	0.023	0.014

FB*=Feed blend

4.6 Regeneration of the Catalyst:

4.6.1 Regeneration of the Catalyst at the End of Each Parameter:

The specific surface area of the catalyst used at the end of each parameter was found to be:

In case of temperature: $110\text{m}^2/\text{g}$

In case of liquid hourly space velocity: $114\text{ m}^2/\text{g}$

In case of pressure: $120\text{ m}^2/\text{g}$

After regeneration the specific surface area of the regenerated used catalyst was found as follows:

- $140\text{ m}^2/\text{g}$ after reaction temperature runs which represent 79.8 % of the specific surface area of fresh catalyst
- $144\text{ m}^2/\text{g}$ after liquid hourly space velocity runs which represent 82.0 % of the surface area of fresh catalyst
- $150\text{ m}^2/\text{g}$ after reaction hydrogen pressure runs which represent 85.5 % of the surface area of fresh catalyst

Therefore, regeneration is successful in case of pressure rather than liquid hourly space velocity and temperature.

The coke concentration near the pore entrances increases faster than at the inner parts of the pore system. At the end of the reaction temperature runs, the specific surface area of the catalyst was lower than in case of hydrogen pressure and liquid hourly space velocity; this is attributed to the deactivation caused by the occurrence of structural modification as well as the hydrotreating operations

which are usually conducted at temperature of 300-425 °C [Aarão Reis, 2005], and also the temperature represents the most important variable affecting reaction and deactivation [Gary, 2001].

4.6.2 Regeneration of the Catalyst by Different Methods:

Table (13) shows a comparison between the coke removal on the catalyst samples after their regeneration on using both burn off and extraction by THF methods.

From the results of *Table (13)*, it is clear that the coke removal on using the burn off method was increased with TOS from 3 to 24 h; i.e. the removal values range from 3.9% to 10.72% and from 10.2% to 14.0% for both HVGO and feed blend, respectively. While in case of THF extraction method the coke removal was decreased; i.e. it ranges from 7.39% to 0.49% and from 9.65% to 1.28% on using HVGO and feed blend, respectively. This may be due to the mainly dissolution of coke precursors with an average molecular weight less than 600 and a fairly large aromatic skeleton. [Hauser et al., 2005] [Mochida et al., 1989]. THF extraction indicates that the solubilization of coke is reduced with increasing TOS [Ali et al., 2006]. This is attributed to the fact that THF removes mainly the smaller aromatic compounds with fairly alkyl side chains and hetero-compounds from the coke. The structure of coke remaining on the catalysts possesses large polynuclear aromatic cores with a considerably high number of short alkyl substituents [Hauser et al., 2005].

Table (13): Comparison between Coke Removal by Using Burn off and THF Methods with HVGO and Feed Blend at Different Times.

Time, h	Decoked by burn off		Decoked by THF	
	HVGO	Feed Blend	HVGO	feed Blend
3	3.9	10.2	7.39	9.65
6	6.4	13.2	6.00	9.10
9	8.9	13.5	2.31	3.5
12	9.8	13.68	1.42	2.93
24	10.72	14	0.49	1.28

4.6.2.1 Effect of Regeneration on the Activity of the Catalyst:

Referring to *Figure (22)*, it is clear that the layout of coke on the catalyst was increased with the increase of TOS. This increase was sharp with the first hours until 12 h, then slows down and tends to level off or reach an equilibrium value within 24 h. To compare the catalyst activity for the hydrotreatment process before and after regeneration a hydrotreatment process was carried out using HVGO and feed blend at 350°C reaction temperature, 50 bar hydrogen pressure and liquid hourly space velocity of 0.5 h⁻¹ for 12 h.

The catalyst was then regenerated using the burn off method and the regenerated catalyst was tested for the HDS of both HVGO and feed blend under the same operating conditions. The results indicated that the regenerated catalyst attains 87.39 % and 66.66 % from the fresh catalyst activity for both HVGO and feed blend, respectively.

4.6.2.2 Effect of Regeneration on the Characterization of the Catalyst:

4.6.2.2.1 Specific Surface Area:

The regeneration of spent catalyst set up by burn off in air has a marked effect on the specific surface area of the catalyst in case of HVGO and feed blend. The specific surface area of the fresh catalyst was 175.5 m²/g, decreased to 115 m²/g and 95.00 m²/g after 12h for HVGO and feed blend, respectively. After regeneration the area increased to (154 m²/g and 117m²/g) for both HVGO and feed blend. Alternatively, the loss of surface area of spent catalyst equals to 34.47 % and 45.87 %, but after regeneration of the catalyst the loss becomes 12.25 % and 33.34 % for HVGO and feed blend, respectively, as given in *Table (14)*.

The improvement of surface area after regeneration is very important to reuse the catalyst again in case of HVGO than the feed blend; this is due to the presence of metals which can not be removed by burn off regeneration method.

Table (14): *Effect of Regeneration on the Loss of Surface Area of HVGO and Feed Blend during Hydrotreating Process.*

<i>Loss of surface area (m²/g) %</i>	<i>Spent</i>	<i>Regeneration</i>
<i>Feed</i>		
HVGO	34.47	12.25
Feed blend	45.87	33.34

4.6.2.2.2 Infrared Spectroscopic Analysis (FT-IR):

Coke deposits of different ages were characterized using FT-IR analysis; the infrared spectra (bands) obtained by this technique for CoMo/Al₂O₃ catalyst as fresh, spent and regenerated catalyst samples are discussed as follows.

4.6.2.2.2.1 Infrared Spectroscopic Analysis of HVGO Hydrotreatment Catalyst:

Acidity is the main character to indicate the activity of the catalyst. It contains the Lewis and Brønsted acid sites. From FT-IR spectrum strong bands are observed in the regions 3600 - 3400 cm⁻¹ for all of the investigated catalyst samples (fresh **a**, spent **b** and regenerated **c**) *Figure (26)*.

In the region from 3500 - 2750 cm⁻¹ Figure (26): Strong IR bands were observed, which are assigned to the OH valance vibration of adsorbed moisture and OH groups of the Al₂O₃ catalyst carrier [van Doorn and Moulijn, 1990].

The infrared band at 3065.84 cm⁻¹ shown in *Figure (26 b)*, which is attributed to aromatic -CH, was appeared in sample (b) but is not appeared in samples a and c; this is due to the coke deposit on the spent catalyst (b) [Martin et al., 2004].

The region 2000 - 1000 cm⁻¹: the carbonyl C=O (1750-1650 cm⁻¹) [Ibarra et al., 1995] and aromatic C=C stretching zone (1630-1500 cm⁻¹) were observed and can be attributed to oxygen and highly conjugated poly aromatic structure, respectively [Matsushita et al., 2004],

In the samples b and c the intensity of aromatic bonds C=C is increased from the fresh catalyst sample (a) to the spent sample (b) and regenerated sample (c) due to coke deposits. These results are confirmed by the presence of both aromatic rings and alkyl group in coked samples [Martin et al., 2004].

The IR - bands in the region 3600 - 1000 cm⁻¹: are corresponding to the organic compounds in the infrared spectrum. The bands characterizing the inorganic compounds in the infrared spectrum are shown in the region 1000 - 400 cm⁻¹.

The initial or original bands for the CoO and MoO without alumina was appeared at *the regions* $664.6 - 572.88$ and $855 - 542 \text{ cm}^{-1}$, respectively, in this study, the fresh catalyst sample Co Mo / Al has very strong spectrum bands observed at $667.11 - 530$ and $900 - 800 \text{ cm}^{-1}$. The shift of these bands may be due to the presence of alumina support with Co and Mo [Shaban, 1999].

In *Figure (26 b)*, (the spent catalyst sample), the broad bands located at 827.08 and 574.98 cm^{-1} may be due to the vibration of both Mo-S and Co-S, respectively.

The appearance of bands located at 741.83 and 730.90 cm^{-1} in the spent catalyst sample (b) may be related to the formation of Co-Mo-S phase formed from the introduction of Co with Mo atom at the surface of alumina or localization of the Co atoms on the MoS₂ edges [Shaban, 1999] [Topsøe et al., 1981].

Figure (26 c) represents the IR bands for CoMo / Al catalyst sample (b) after its regeneration at $450 \text{ }^{\circ}\text{C}$. The same bands in the sample (a) are present in this figure and the bands refer to C=O and C=C in sample b is smaller which can be attributed to the burn off of some deposited coke.

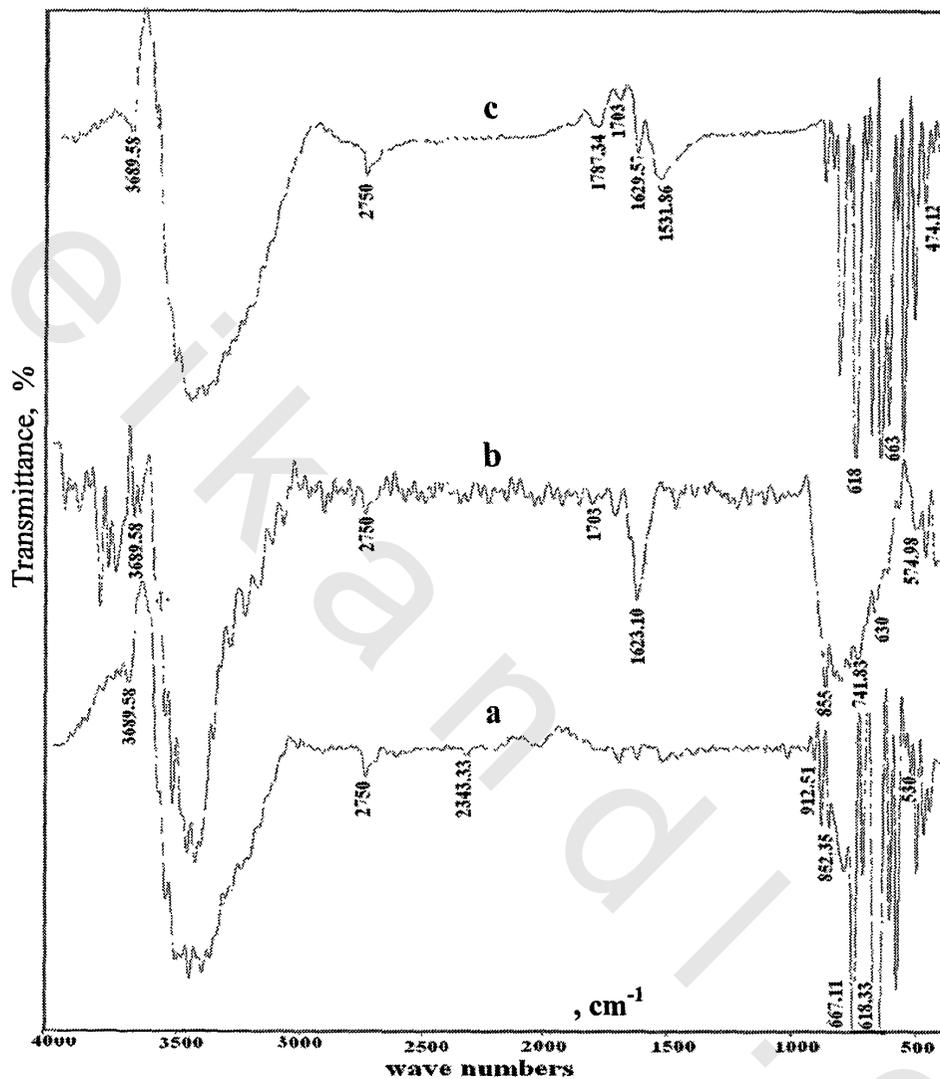


Figure (26): Infrared Spectroscopic Analysis of HVGO Hydrotreatment Catalyst.

4.6.2.2.2 Infrared Spectroscopic Analysis of Feed Blend Hydrotreatment

Catalyst:

In *Figure (27)* the same bands in the region $3500 - 3400 \text{ cm}^{-1}$ are shown as in HVGO hydrotreatment catalyst sample, which refer to OH band. Aliphatic carbons corresponding to C-H stretching vibration in the region $3000 - 2848.84 \text{ cm}^{-1}$ and the region $1500 - 1299 \text{ cm}^{-1}$ are also presents [Martin et al., 2004] [van Doorn and Moulijn, 1990].

In the region $2000 - 1000 \text{ Cm}^{-1}$, *Figure (27 d&e)*, the same bands are observed for C=C and C=O, as in sample (b). The sample (e) is not active for reusing again in the hydrotreatment process due to the coke deposited and the heavy metals present, which are not completely removed during the regeneration step.

From the previous discussion, it was found that the catalyst sample used in HVGO hydrotreatment step after regeneration is better than that used for the feed blend.

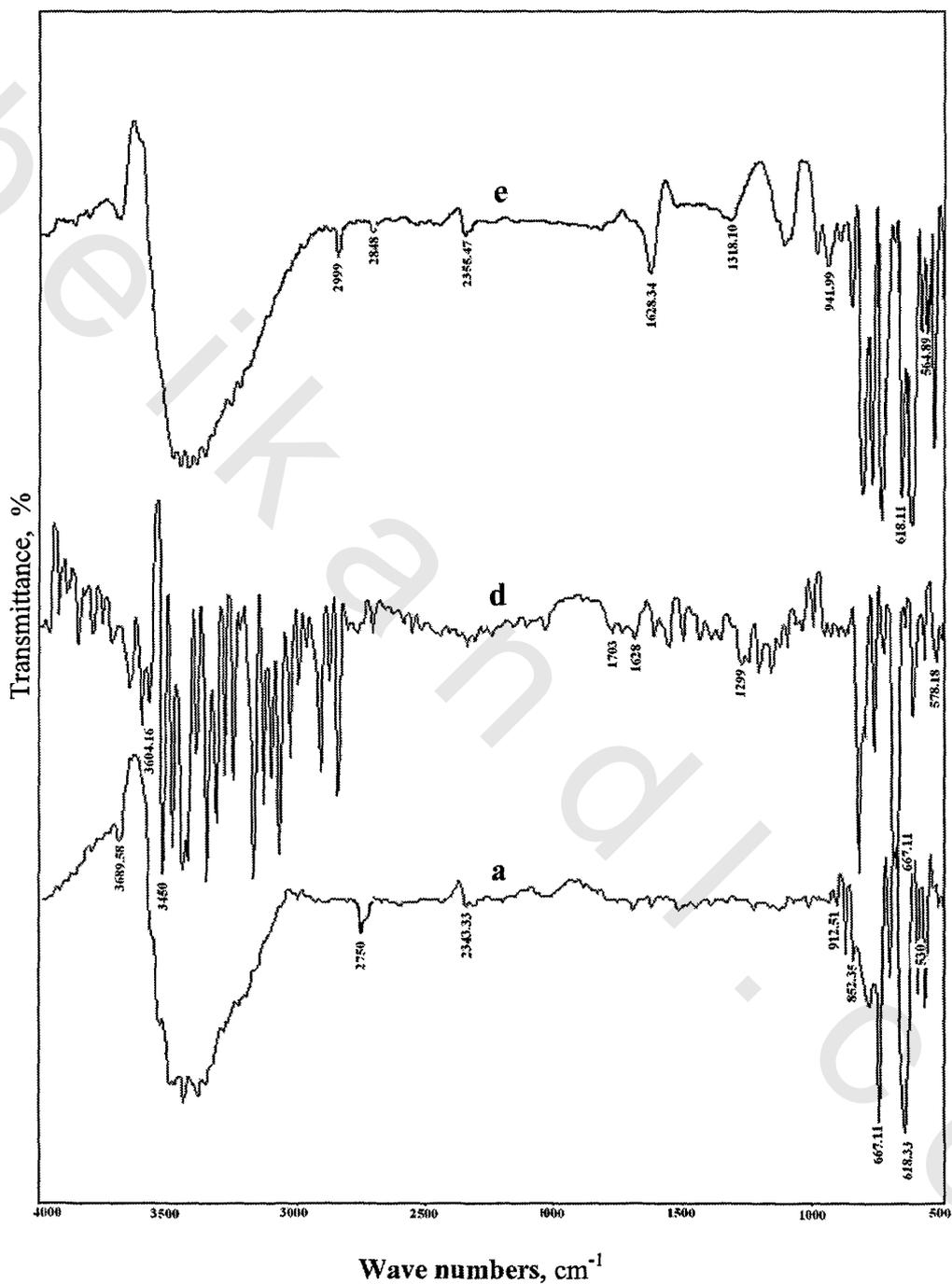


Figure (27): Infrared Spectroscopic Analysis of Feed Blend Hydrotreatment Catalyst.

4.6.2.2.3 X- Ray Diffraction (XRD):

4.6.2.2.3.1 X- Ray Diffraction of HVGO Hydrotreatment Catalyst:

X- ray diffraction analysis was carried out for the CoMo/Al catalyst, samples (fresh **a**, spent **b** and regenerated **c**) using HVGO as a feed.

Figure (28 a, b and c) illustrates the x-ray patterns of these samples. From this figure, it can be seen that for all catalyst samples, the patterns observed are poorly crystalline. The diffraction pattern of the fresh catalyst (**a**) shows the broad peaks related to γ Al_2O_3 support at the diffraction angles $2\theta = 45.74^\circ$ and 66.46° (at d spacing 1.98 \AA and 1.4 \AA , respectively, JCPDS Powder Diffraction File Card 10 - 425 and the absence of the characteristic reflections of Co_3O_4 ($2\theta = 36.84^\circ$ and 65.22°) and MoO_3 ($2\theta = 23.4^\circ$, 25.8° and 27.6°).

The diffraction pattern of the fresh catalyst indicates that molybdenum atoms are well dispersed on alumina support. It is also observed that the XRD peaks intensity decrease with the addition of metal atoms and it is more prominent in cobalt promoted catalyst and indicating that molybdenum is strongly bonded with the alumina support and hence more molybdenum dispersed phases are expected to be present [Maity et al., 2004] [Suokoh et al., 1997].

For the spent catalyst (b), the reflection pattern shows that Co_3O_4 and MoO_3 are not also observed because the deposition of coke on the catalyst. But when the regeneration step occurs, the X-ray diffraction pattern obtained for this sample was found to be nearly the same as compared with the fresh sample as shown in *Figure (28 c)*.

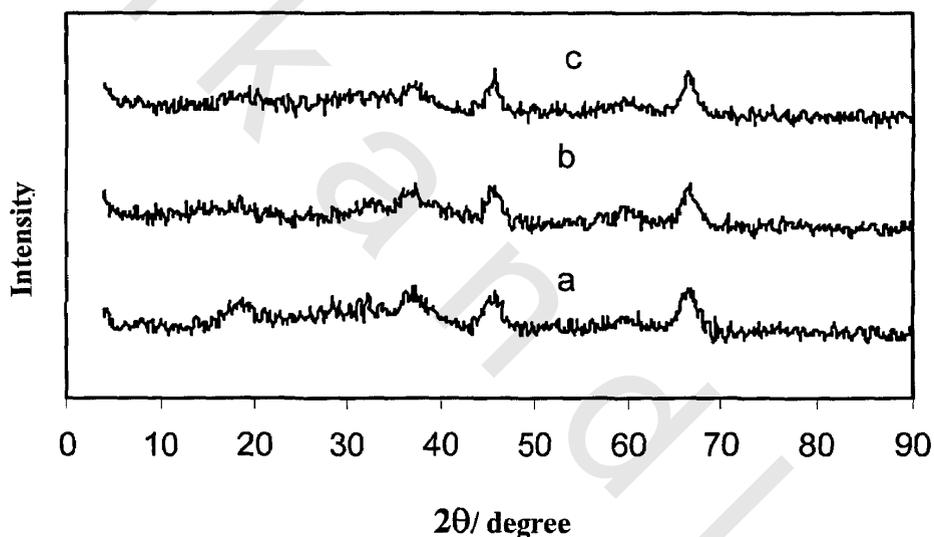


Figure (28): X- Ray Diffraction Patterns of HVGO
Hydrotreated Catalyst.

4.6.2.2.3.2 X- Ray Diffraction of Feed Blend Hydrotreatment Catalyst:

Figure (29) shows the XRD patterns obtained for the catalyst samples (a), (d) and (e) with feed blend hydrotreatment process.

The diffraction angle of γ Al_2O_3 are observed at $2\theta = 66.4^\circ$ and 45.74° in all catalyst samples (a), (d) and (e). Other diffraction peaks observed for the samples (d) and (e) which may be due to the presence of Ni and V as heavy metals in the feed blend. For the catalyst sample (d) the diffraction pattern of NiO is observed at $2\theta = 62.55^\circ$ and 37.22° (d spacings 1.48 Å and 2.41 Å) and the pattern of Ni_3O_4 is obtained at $2\theta = 51.84^\circ$, 39.94° (d spacings 1.76 Å and 2.25 Å).

The XRD peaks characteristics for vanadium metal are represented in the XRD pattern as metal oxide. (V_2O_5) at $2\theta = 49.636^\circ$, 47.427° , 42.32° , 33.3° & 20.228° with the corresponding, d spacings of 1.83, 1.91, 2.1, 2.68 & 4.38 Å, respectively.

Another phase of vanadium oxide V_6O_{13} is also indicated by its XRD peaks located at $2\theta =$ diffraction pattern of 30.088° , 25.328° , 18.86° and 15.128° and d spacings of 2.96, 3.51, 4.69 and 5.85 Å, respectively.

When the catalyst sample (e) is regenerated at 450 °C, the XRD peaks of NiO and V₂O₅ are observed at the same angles and d spacings but the other phases of Ni₃O₄ and V₆O₁₃ are disappeared due to the effect of regeneration temperature which transforms these phases to another stable phase.

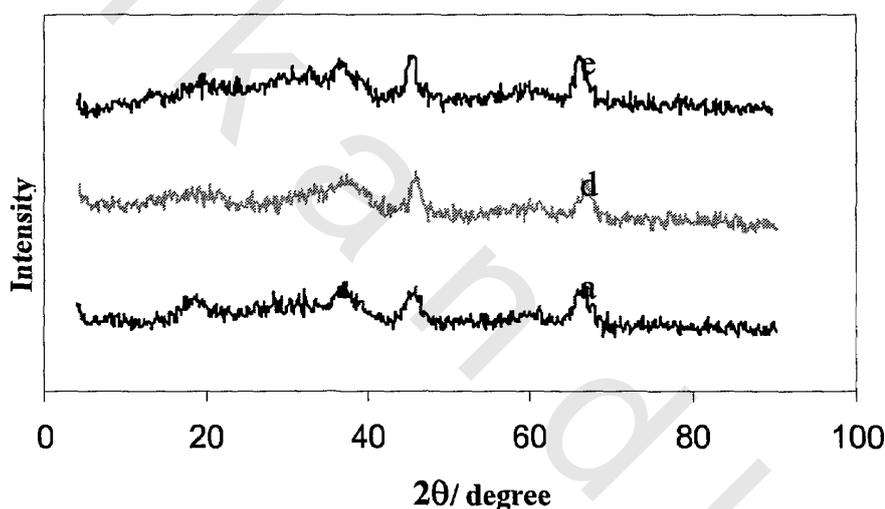


Figure (29): X- Ray Diffraction Patterns of Feed Blend Hydrotreated Catalyst.

4.6.2.2.4 Crushing Strength:

The extent of duration and chemical processes on the catalyst affect its crushing strength during TOS. The significant variation in crushing strength is observed in *Table (15)*. This table shows that the spent catalyst samples after test runs from 3h to 24h had a crushing strength of 20.86 to 22.94 kg/cm². The increase of duration time from 3h to 24h affected the crushing strength due to the introduction of coke into the pores of the catalyst.

Alternatively, the coke formed during the test runs was increased if the duration time increased. This increase causes an increase in crushing strength, leading to the production of hard solid catalyst.

Table (15): *Effect of Coke on Crushing Strength of Catalyst Samples after Different Time on Stream.*

<i>Catalyst</i>	<i>Coke</i>	<i>Crushing strength kg/cm²</i>
Fresh	---	19.43
After 3h	3.9	20.86
After 6h	6.4	21.74
After 9h	8.9	22.29
After 12h	9.8	22.63
After 24h	10.72	22.94