CATALYST DEACTIVATION DURING HYDROTREATING PROCESS

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ABSTRACT

The deactivation of a Co-Mo/ γ – alumina hydrotreating catalyst is investigated in a cata – test micro reactor unit by using heavy vacuum gas oil (HVGO) and a blend of 40: 60 % HVGO and heavy vacuum residue (HVR) as feed stocks at the following constant operating conditions: temperature of $350^{\circ}C$, pressure of 50 bar, H_2 / oil ratio of 250 L/L and LHSV of 0.5 h^{-1} with different durations ranging from 3 – 24 h. The results showed that a rapid coke build up on the catalyst surface is very fast during the first hours of run reaches as high as 3.9 wt. % and 10.2 wt. % in case of HVGO and feed blend respectively, within 3 h. and then tends to level off or reach as an equilibrium value within 24 h. The drops in catalyst surface area were particularly high (28.57 % and 41.71 %) for HVGO and feed blend respectively during the first 3 h. of operation. Pore size distribution analysis indicated that the coke which formed during the first hours was deposited predominantly in the narrow pores < 50 A° of the catalyst. The improvement of surface area after regeneration is very important to reuse the catalyst again incase of HVGO than the feed blend.

INTRODUCTION

The study of catalyst deactivation during hydroprocessing of heavy oil fractions is one of the most important aspects to improve the catalytic performance in petroleum refining processes [Ancheyta, et al.

(2003); **Furimsky and Massoth (1999); Maity, et al. (2007) and Vogelar, et al. (2006)].** Catalysts deactivation is caused by: metal deposition on active catalytic surface which is irreversible and whose rate depends on the metal level in the feed; the carbonaceous material deposition and precipitation on the external as well as internal structure of catalyst, pore constriction and blockage, characterized by a very strong loss in activity **[Tailleur and Capriodi (2005)].**

Cokes formed very rapidly during the first hours of time - on stream, and deactivation of catalyst by this material appears to rapidly reach a pseudo steady state level **[Hauser, et al. (2005) and Matsushita, et al. (2004)]**, while metals in the feed (mainly V and Ni) are converted to their sulfides, which deposit within the pores and irreversibly deactivate the catalyst.

Metals, mainly vanadium build up until pore mouth plugging. With a low-metals feed-stock, there is an initial activity loss as coke is deposited on the catalyst. This is followed by a more gradual loss in activity as the metals deposited. However, with a high metals feed stock, there is a more rapid and severe deactivation after the initial coke deposition **[Furimsky, (1998); Beaton and Bertolacini (1991); Rana, et al. (2007) and Ancheta, et al. (2005)].**

Regeneration is carried out by burning off the deposits in an oxygen – rich stream. Logically, regenerate composition is related to the necessity of avoiding excessive temperature rises that may damage the catalyst. The temperature needed for regeneration must be carefully controlled to avoid catalyst sintering **[Delmon, et al. (1980); Pierre (2007) and Christoph and Andreas (2005)].**

The present work considers, a series of vacuum gas oil hydrotreating runs with different durations ranging from 3 to 24 hours, conducted together with a blend mixture, 40 % vacuum gas oil and 60 % heavy vacuum residue.

EXPERIMENTAL

Feed stock:

Heavy vacuum gas oil (HVGO) kindly supplied from Suez Petroleum Company and feed blend (40 - 60) 40 % heavy vacuum gas oil and 60 % heavy vacuum residue (HVR) were used in this investigation. The main characteristics of feeds are collected in Table 1.

Table (1): Main characteristics of feed stocks

Characteristics	HVGO	Feed Blend
Specific gravity,60/60 ^{O}F	0.8744	0.9829
Sulfur content, wt %	1.83	3.95
Nitrogen content, wt %	0.063	-
Conradson carbon residue, wt %	-	13.01
Asphaltene content, wt %	-	7.74
Pour point, ^{O}C	12	-
Aniline point, ^{O}F	168.8	-
Olefins content, wt %	12.9	-
Color	5.5	-
Component analysis, wt %		
Total Saturates	57.06	10.61
Total aromatics	42.63	79.92
Resins	1.41	9.47
Metal analysis, PPM		
Vanadium (V)	-	98.4
Nickel (Ni)	-	82.8

Catalyst:

A commercial Co-Mo/γ-alumina hydrotreating catalyst (surface area = 175.5 m^2/g, pore volume = 0.4254 cc/g, average pore diameter = 194 A$^\circ$; CoO = 4.1 % and MoO$_3$ = 12.8 % was used in this investigation.

Catalytic Activity Test:

The hydrotreating experiments with varying operating times were conducted in a fixed-bed cata-test unit. Fifty milliliters of catalyst together with an equal amount of glass beads was charged in the reactor and used in each run. Two feeds were used: HVGO and a blend of 40 % HVGO and 60 % HVR as shown in Table (1). More details about the cata-test unit, catalyst loading, experimental procedure and catalyst pre-sulfiding were reported elsewhere [**Menoufy, et al. (2002)**]. Deactivation study was carried out at the following constant conditions: 350°C of reaction temperature, 50 bar of total H$_2$ pressure, and 250 L/L hydrogen - to - oil ratio, 0.5 h^{-1} of liquid hourly space velocity (LHSV) and time on stream (TOS) 3, 6, 9, 12 and 24 h.

The most important properties of the products were measured using the following standard (ASTM) methods:

Specific gravity 60/60 $^\circ$F	ASTM D-1298
Aniline point. $^\circ$F	ASTM D 611-82
Pour point, $^\circ$C	ASTM D 97-88
Color	ASTM D-1500
Conradson- carbon residue, wt%	ASTM D-189
Asphaltene content, wt%	IP - 143
Sulfur content, wt%	IP - 336

Metals analysis was conducted by using atomic absorption spectrometer. Perkin- Elmer 800, Surface area and average pore diameter of the catalysts were carried out using quanta chrome NOVA automated gas sorption system, model 2002 and mercury porosimeter.

At the end of each run, the coked catalyst was removed. soxhlet extracted with cyclohexane then toluene and then dried in an electric oven at 110°C for 2h then cooled. The washed and dried spent catalyst sample was taken off to be analyzed for carbon, metals, BET surface areas. pore volume and pore size distribution.

Regeneration:

The washed catalyst was then heated at different temperature in an electric oven to eliminate the carbon and sulfur residues in air as CO_2 and SO_2 respectively.

The temperature is increased from 100 to $350°C$ at rate of $50°C$ /h then the product is maintained at $350°C$ for 1h, heated to $450°C$ at $25°C$ /h, and maintained at this temperature for 24h.

After cooling to room temperature the percentage of coke was determined by loss of weight before and after consumption.

RESULT AND DISCUSSION

1- Effect of time on stream on the products quality

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)]**.

$$K_{HDS} = LHSV \frac{1}{n-1} (\frac{1}{S_P^{n-1}} - \frac{1}{S_F^{n-1}})$$

Where LHSV is the liquid hourly space velocity, n is the reaction order =1.5, SF is the sulfur content in the feed (wt %) and Sp 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 then decreased to 77.05 % after 24 h as shown in Table (2). 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 MoS_2 crystallites.

The catalytic active sites in the sulfided Co-Mo/ γ Al_2O_3 catalyst used in this study are responsible for promoting hydrotreating reactions as hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (the sulfur vacancies in MoS_2 crystallites).

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 (2) as yields, density, aromatic contents, and diesel indeces were also affected by coke deposition.

Table (2): Effect of time on stream on the product quality of HVGO during hydrotreating process

Conditions: (350°C. 50 bar. 0.5 h^{-1})

Time, h Properties	3	6	9	12	24
Yield, wt %	76.90	78.50	80.29	83.93	92.89
Density, 60/60 $^\circ$F	0.8453	0.8472	0.8475	0.8478	0.8479
Sulfur content, wt %	0.2409	0.3011	0.3063	0.3110	0.4200
Hydrodesulfurization, %	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, $^\circ$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
Component analysis, wt %					
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

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

Table (3): Effect of time on stream on the product quality of feed blend during hydrotreating process.

Conditions: ($350^{\circ}C$, 50 bar, 0.5 h^{-1})

Time, h Properties	3	6	9	12	24
Yield, wt%	87.44	93.88	95.33	97.22	99.50
Density, 60/60 $^{\circ}F$	0.926	0.935	0.938	0.945	0.948
Sulfur content, wt %	0.99	2.13	2.35	2.45	2.51
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
Component analysis, wt%					
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

It is also observed that after 6 h of run asphaltene conversion and consequently coke formation are drastically reduced (asphaltene and coke deposition changed from 4.01 to 6.79 % and from 13.2 to 14 % when TOS was increased from 6 to 24 h respectively). Asphaltene content, conradson carbon residue (C.C.R), aromatic content were increased sharply from 3 - 6 h and small increase from 6 – 24 h.

This behavior is attributed to that the feed blend contains (7.74%) asphaltene content and (181.2 PPM) metals content (Ni and V) and conradson carbon residue 13.01%. These properties of feed, Table (1), differ than the feed 100% of vacuum gas oil and cause great amount of

carbon and metals deposited on the catalyst at first hours [**Murti, et al. (2005) and Sahoo, et al. (2004)**].

Tables (2) and (3) represented the comparison between the quality of characteristics of hydrotreatment 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 in case of HVGO, which is due to the more catalyst deactivation as a result of higher coke deposition.

2- Effect of time on stream on coke formation

A series of heavy vacuum gas oil and blend hydrotreating experiments of duration 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 1. represented the relation between time on stream and coke formation of HVGO and feed blend hydrotreatment and these 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; which 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 poly aromatic compounds, are the major coke precursors. This confirms that deposition of coke is the main source of catalyst deactivation during first hours of run [**Manuel, et al. (2000)**].
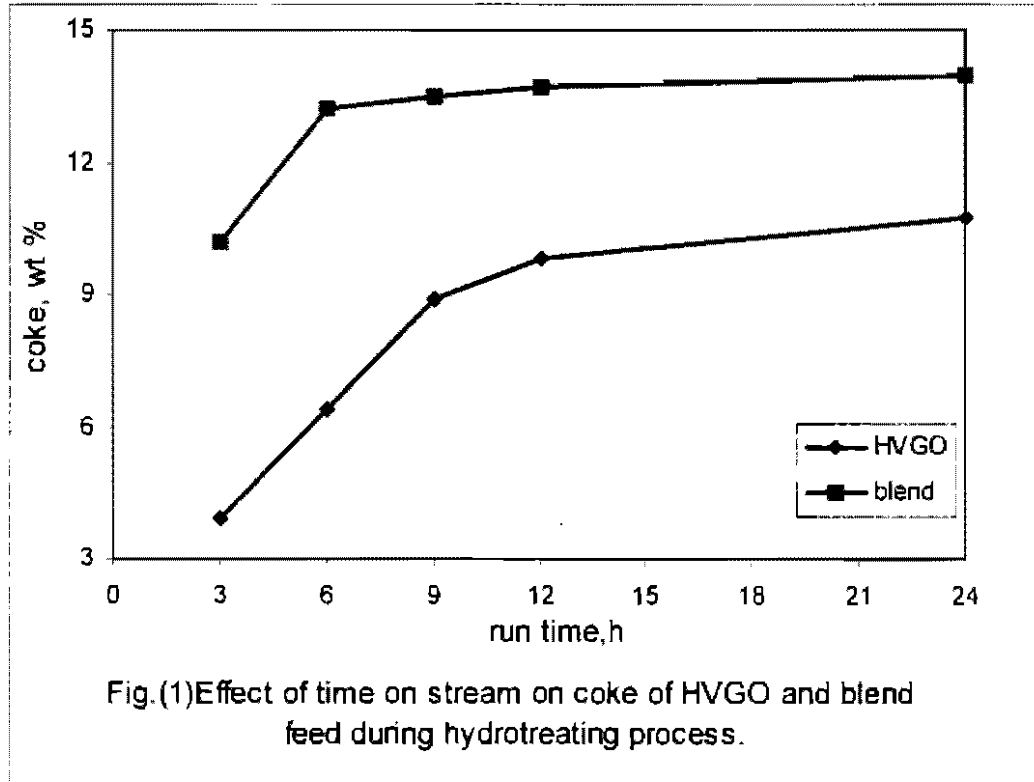
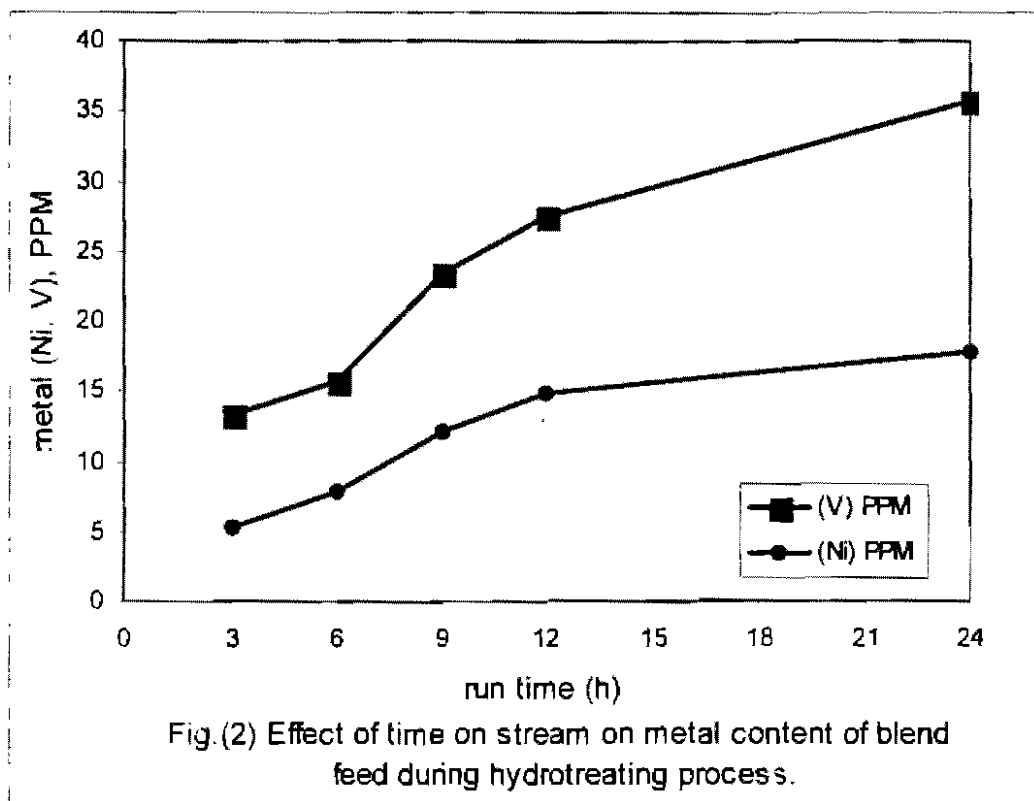## 3- Effect of time on stream on metal deposition

Nickel and vanadium removals showed different behaviour 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 (Fig. 2) 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 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)**].

Fig.(1)Effect of time on stream on coke of HVGO and blend feed during hydrotreating process.

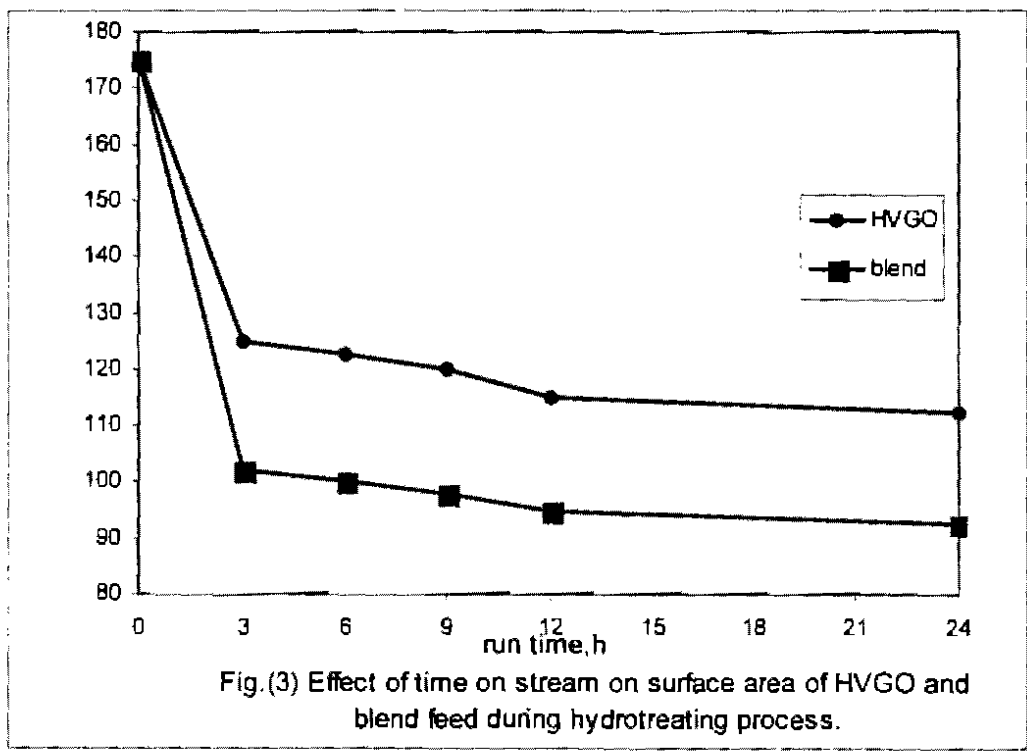Fig.(2) Effect of time on stream on metal content of blend feed during hydrotreating process.

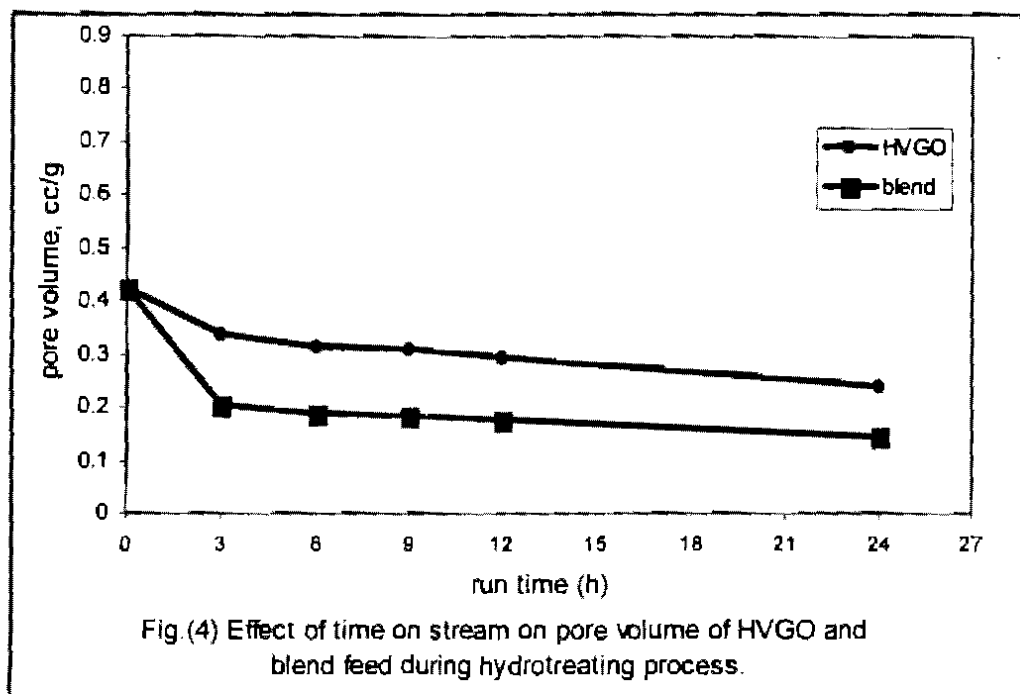## 4- Effect of time on stream on catalyst textural analysis

The surface area and pore volume of the used catalyst samples from the different runs conducted at varying duration time 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 Figs. (3,4). The decrease in surface area is particularly rapid during the first 3 to 6 hr and then slows down.

A similar decrease is also noticed in the catalyst pore volume, Fig. 4. 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 micro pores present in the fresh catalyst contribute significantly to the catalyst total surface area. Blockage of these micro pores with coke deposition [**Marafi and**

Stanislaus (1997)] can be expected to lead to loss 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.

Fig.(3) Effect of time on stream on surface area of HVGO and blend feed during hydrotreating process.

Fig.(4) Effect of time on stream on pore volume of HVGO and blend feed during hydrotreating process.

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 A^o diameters appear to be affected more by the initial coke deposition than the large pores. Thus the total volume of the micro pores having diameter less than 50 A^o is found to be reduced by (73.05 % and 83.98 %) for HVGO and feed blend respectively. The narrow meso pores (50 – 100 A^o 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 (21.21 % and 52.73 %) for HVGO and feed blend the volume located in mesopores (20 - 200 A^o) meso pores is lost. Large meso pores and macro pores are not affected to any significant level by the initial coke deposits. Catalyst pore distribution. thus. plays an important role in catalyst deactivation by coke deposition. particularly during the early stages of the run, as indicated in Table (4).

Table (4): Pore size distribution of catalysts coked for different duration.

Conditions: (350°C, 50 bar, 0.5 h⁻¹)

Diameter A° \ Time	BET m²/g		Total pore volume cc/g		>50		50-100		100-250		250-400		Total meso		>400	
	HVGO	FB*	HVGO	FB*	HVGO	FB*	HVGO	FB*	HVGO	FB*	HVGO	FB*	HVGO	FB*	HVGO	FB*
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	102	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	0.316	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	98	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	95	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

5- Regeneration of the catalyst:

The regeneration of spent catalyst set up by burn off in air are very affected on the surface area of HVGO and feed blend. The surface area of the fresh catalyst was 175.5 m^2/g, decreased to 115 m^2/g and 95.00 m^2/g after 12h respectively. After regeneration the area increased to (154 m^2/g and 117 m^2/g) for both HVGO and feed blend. Alternatively the loss of surface area of spent catalyst equals to 28.57 % and 41.71 %, but the regeneration of catalyst becomes 12.61 % and 33.34 % respectively are given in Table (5). The improvement of surface area after regeneration is very important to reuse the catalyst again incase of HVGO than the feed blend.

Table (5): Effect of regeneration on the loss of surface area of HVGO and feed blend during hydrotreating process

Loss of surface area (m^2/g) % catalyst	Spent	Regeneration
HVGO	28.57	12.61
Feed blend	41.71	33.34

CONCLUSIONS

- HDS activity of the catalyst decreases from 86.8 % at the first 3 h. to reach 77.05 % after 24 h. for the HVGO and 74.94 % at 3 h. to reach 36.46 % after 24 h. for feed blend. This drop due to the coke coverage of the active sites is responsible for the hydrotreating reactions.

- 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.

- Ni and V removals showed different behaviors during TOS due to the differences in the Ni – and V – porphyrin type structure.

- Catalyst pore distribution plays an important role in catalyst deactivation by coke deposition particularly during the early stages of the run.

- Regeneration has the benefit of eliminating the first cause of deactivation to due coke deposition.

ACKNOWLEDGEMENT

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دراسة على تهميد الحفاز أثناء عمليات المعالجة الهيدروجينية

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دراسة تهميد الحفاز $CoMo/Al_2O_3$ أثناء عملية المعالجة الهيدروجينية باستخدام المفاعل ومع استخدام مادة التغذية من السولار المخلخل وخليط من السولار المخلخل والمتبقي الثقيل المخلخل بنسبة 40ـ60% تحت الظروف الآتية: درجة الحرارة 350 م° والضغط الهيدروجيني 50 بار و سرعة التغذية 0.5 س$^{-1}$ ونسبة مادة التغذية إلى الهيدروجين 250 ل/ل مع اختلاف في الوقت (3-24) ساعة. تدل النتائج على أن الفحم يتكون في الساعات الأولى من بدء التجربة على سطح الحفاز ثم بعد ذلك يصل إلى مرحلة الثبات. من دراسة انخفاض مساحة السطح و حجم المسامات للحفاز في حالة خليط من السولار المخلخل والمتبقي الثقيل المخلخل اكبر من السولار المخلخل.

ولإعادة تنشيط الحفاز وجد أنه في حالة السولار المخلخل يكون أعلى منه في حالة خليط من السولار المخلخل و المتبقي الثقيل المخلخل.