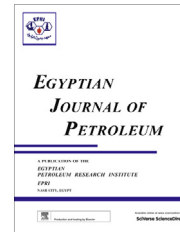




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FULL LENGTH ARTICLE

# Effect of catalyst deactivation on vacuum residue hydrocracking

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## KEYWORDS

Hydrocracking;  
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**Abstract** Accelerated deactivation tests of the pre-sulfided Mo–W/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> commercial catalyst were performed using heavy vacuum petroleum feedstock. High reaction temperature employed in the accelerated catalyst aging resulted in large amounts of carbonaceous deposition with high aromaticity, which was found to be the principal deactivation cause. The effect of catalyst deactivation on hydrocracking of vacuum residue was studied. Experiments were carried out in a batch reactor at 60 bar, feed to catalyst ratio 10:1 and temperature 425 °C. The duration time for a cycle-run was 4 h. On increasing the interval duration times from 4 to 20 h (i.e. five cycles), the quality of the hydrocracked products was decreased. In each cycle-run, a fresh feedstock was used with the same sulfide catalyst. The quality of distillate products, such as hydrodesulfurization (HDS) was decreased from 61.50% to 39.52%, while asphaltene contents of the total liquid product were increased from 2.7% to 5.2% and their boiling ranges were increased during these duration times due to the successive catalyst deactivation during the 5 cycle-runs, caused by successive adsorption of coke formation.

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## 1. Introduction

The demand for heavy fuel oil is decreasing significantly while the need for light and middle distillates is increasing. In addition, the need to upgrade heavy oil is increasing, reflecting the recent hike in crude oil prices. At the same time, environmental

concerns are being more restricted, resulting in more rigorous specifications for petroleum products including fuel oils. These trends have emphasized the importance of processes that convert the heavy oil fractions into lighter distillates and more valuable clean products [1–10].

However, hydrocracking of heavy oils differs markedly from that of light feeds, since heavy oils contain a high percentage of asphaltene and heavy metal compounds such as nickel and vanadium. The catalysts used for this process is deactivated fast due to the presence of asphaltene and metal containing molecules [11]. Many authors have focused on the initial deactivation by coke deposition followed by a steady state coke build-up on the catalyst surface [12]. Asphaltene is the primary precursor of coke, and due to its big size it cannot enter into the catalyst's mouth and blocks the entrance of the

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reactants [13]. The presence of vanadium and nickel is of particular concern because of its poisoning effect during the hydrotreating and hydrocracking of the petroleum feed stocks.

This work describes a batch-test, which was carried out to examine the effect of start-up operating conditions, described as cycle-runs of 4–20 h on the catalytic performance of the sulfided Mo–W/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst, on the hydrocracking heavy vacuum residue (HVR) and its product qualities.

## 2. Experimental

### 2.1. Feedstock

Heavy vacuum residue (its origin from Gulf of Suez mix crude oil) was kindly supplied by the Suez Oil Processing Company, used as a hydrocracking feedstock and its characteristics are given in Table 1.

### 2.2. Catalyst

A commercially available hydrocracking Mo–W/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst was used in the present study, and its chemical composition and characteristics are presented in Table 2.

### 2.3. Apparatus and procedure

The hydrocracking study was conducted under a set of operating conditions in static-phase system. The catalyst was presulfided [14] first before carrying out the hydrocracking experiments in a batch reactor magnetically stirred autoclave [1800 ml, Parr Model 4572], and heated by digital controller. Hydrocracking tests (i.e. cycle-runs) of heavy vacuum residues (HVR) were carried out under the following conditions:

Feed/catalyst ratio, 10:1 [wt/wt], initial hydrogen pressure 60 bar, reaction temperature 425 °C and duration time of a cycle-run is 4 h. At the end of each cycle-run, the autoclave was cooled down to room temperature, and gas samples were taken out for analysis. Liquid products were collected out of the autoclave for quantification and analysis, while the catalyst was filtered and washed by solvent [naphtha]. The filtered catalyst was heated in an electric oven at 110 °C for 2 h, and then cooled. The dried catalyst is loaded again into the reactor vessel and mixed with a fresh sample of the feed stock to start a

**Table 2** Catalyst characteristics and chemical composition.

<i>Characteristics</i>	
Surface area (m <sup>2</sup> /g)	104
Average pore diameter (Å)	170
Pore volume (cm <sup>3</sup> /g)	0.827
<i>Chemical composition (wt%)</i>	
W	3.75
Mo	3.98
Al	74.52
Si	17.75

second cycle-run under the same operating conditions. The previous step was repeated in successive cycle-runs, each of 4 h to reach five cycle-runs.

### 2.4. Analysis

The collected gaseous and liquid products were subjected to analysis according to ASTM standard methods. Hydrocarbon component analysis, total saturates and aromatics are determined according to the adopted methods of Mair and Rossini [15] and with the ASTM D2007.

## 3. Result and discussion

### 3.1. Effect of duration time on the conversion of the feedstock

The effects of cycle-run duration time on the conversion of the heavy vacuum residue through hydrocracking are indicated in Fig. 1. It indicates that the yield of hydrocracked liquid was increased by increasing duration time from 4 to 20 h (during the successive cycles). The increase amounted to 92.4 wt% after the 1st cycle-run, to reach 94.7% at the end of the finish cycle-run. The data indicated that the conversion reaction was conducted, using the bifunctional sulfided Mo–W/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst, on HVR feedstock, which was replaced by fresh feed after the 1st duration time (4 h). The increase in the liquid product appears to be effected by the thermal effect rather than catalytically. Therefore, the HVR conversion was decreased as a function of the rate of the catalyst deactivation, which is depending on the run time. As a result of these reasons, the distillate products were decreased from 64.2% at

**Table 1** Characteristics of vacuum residue feed stock.

Characteristics	HVR
The boiling range (°C)	350–500
Specific gravity {g/cm <sup>3</sup> } at 70 °C	0.993
Flash point (°C)	Over 320
Conradson carbon residue (wt%)	18.75
Sulfur content (wt%)	4.63
Asphaltene content (wt%)	6.4
Aromatic content (wt%)	88.91
Saturate content (wt%)	10.56
<i>Metals (ppm)</i>	
Ni	138
V	164.3

(ASTM D-1298)  
(ASTM D3828 and D3278)  
(ASTM D-189)  
(IP 63)  
(IP 143)  
ASTM D2007 adopted from (Mair and Rossini (1958))  
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