



Egyptian Petroleum Research Institute
Egyptian Journal of Petroleum

www.elsevier.com/locate/egyjp
www.sciencedirect.com



FULL LENGTH ARTICLE

Effect of catalyst deactivation on vacuum residue hydrocracking

Hoda S. Ahmed, Seham A. Shaban *, Mohamed F. Menoufy, Fathy Y. El Kady

Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

Received 25 September 2012; accepted 11 December 2012

Available online 27 November 2013

KEYWORDS

Hydrocracking;
Catalyst;
Deactivation;
Vacuum residue

Abstract Accelerated deactivation tests of the pre-sulfided Mo–W/SiO₂–Al₂O₃ 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.

© 2013 Production and hosting by Elsevier B.V. on behalf of Egyptian Petroleum Research Institute.

Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).

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

* Corresponding author.

E-mail address: sehamshaban@yahoo.com (S.A. Shaban).

Peer review under responsibility of Egyptian Petroleum Research Institute.



Production and hosting by Elsevier

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/SiO₂–Al₂O₃ 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/SiO₂–Al₂O₃ 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 ² /g)	104
Average pore diameter (Å)	170
Pore volume (cm ³ /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/SiO₂–Al₂O₃ 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 ³ } 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))
ASTM D2007 adopted from (Mair and Rossini (1958))

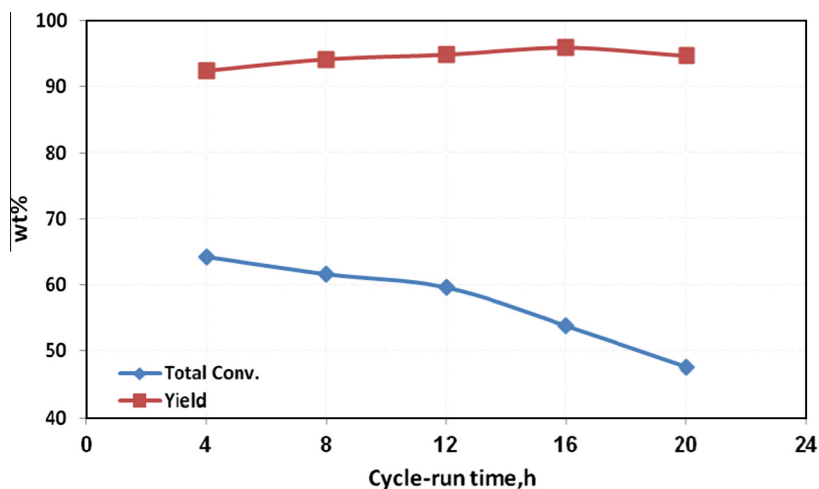


Figure 1 Effect of cycle-run times (duration time) on the total liquid yield and conversion of heavy vacuum residue (HVR).

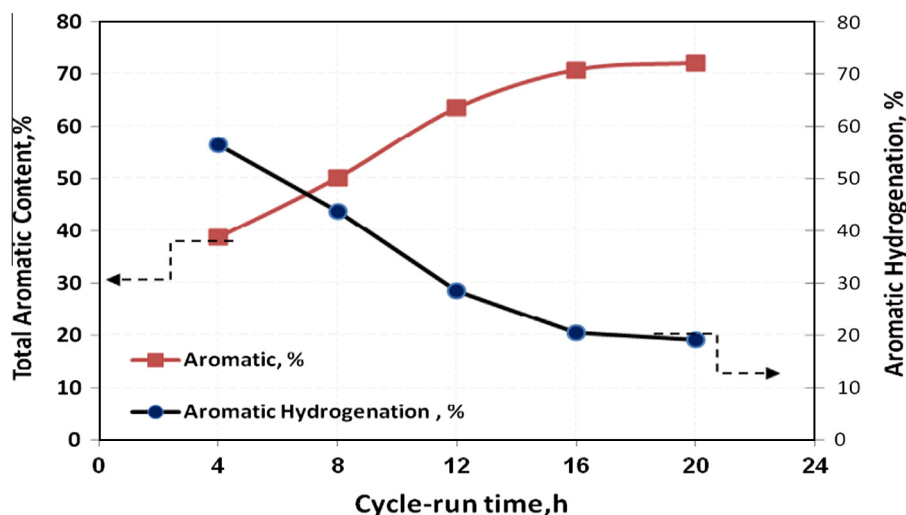


Figure 2 Effect of cycle-run times (duration time) on total sulfur content and hydrodesulfurization rate (HDS) of heavy vacuum residue (HVR).

the 1st cycle-run to 47.6% at the end of the 5th cycle-run due to the increase in the duration time.

Fig. 2 shows that sulfur content decreased the original feedstock from 4.63% to reach 1.78% at the end of the first 4 h, and then sulfur was increased successively to 2.8% at the end of the duration time. It means that hydrodesulfurization activity was decreased from 61.61% to 39.51%, i.e. the rate of HDS declined due to a decrease in catalyst cracking activity over time as a result of the increased coke formation and metal deposition on the surface catalyst by adding fresh feed in each duration time at the same catalyst [16–19].

The asphaltene content in the overall liquid product was decreased from 6.4 in feed to 2.7 at the end of first 4 h and then increased when duration time increased to reach the 5th cycle-run (i.e. after 20 h) and amounted to 5.2% (Fig. 3). In general, heavy vacuum residue contains oils, resins and asphaltene, the amounts of these asphaltene are the main concern since these compounds are the primary cause of catalyst deactivation and considered to be the principal precursor of coke. Asphaltene is a very large complex material.

During hydro processing of heavy vacuum residue, oil and resin fractions are converted to lighter fragments very fast compared to asphaltene fraction. Asphaltene is believed to be soluble mainly in resin, solubility of asphaltenes decreases during conversion of the resin. It is essential that during hydrocracking, resins are converted at a similar rate as asphaltenes. Otherwise, as much greater rate of the conversion of resins than that of asphaltenes would result in the compatibility of the components of the feedstock. This would lead to asphaltene coagulation on the catalyst surface [12,20]. Therefore, asphaltenes are precipitated on the catalyst surface and block the catalyst pore mouth. Therefore, the coke deposition was increased drastically from 0.76% to 3.7% by increasing duration time, which is the main cause of the initial loss of micro pores and surface area of the catalyst (Table 3) [19,21,22]. This result suggests that there is an optimal combination of surface area and pore diameter giving the highest catalyst activity. Conradson carbon residue (CCR) is found to follow the same trend of asphaltenes. The resulted data of properties of the hydrocracked products such as sulfur,

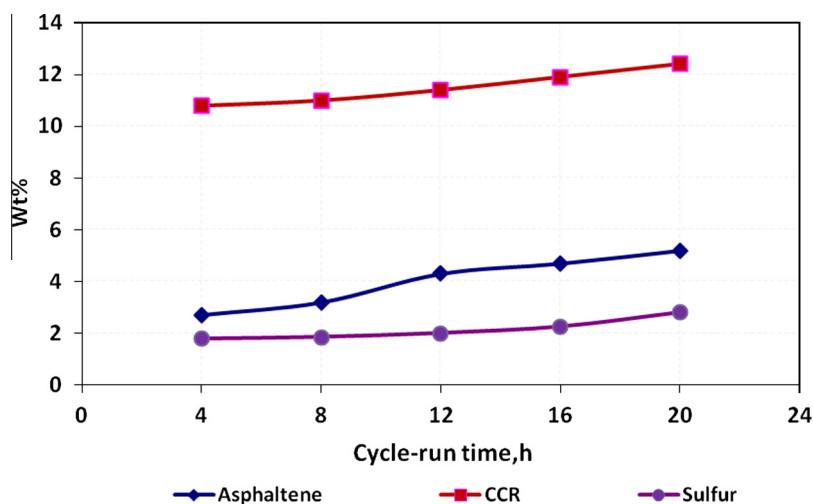


Figure 3 Effect of cycle-run times (duration time) on the characteristics of hydrocracked liquid products.

Table 3 Effect of duration time on the characteristics of Mo–W–Si–Al catalyst.

Duration time (h)	Fresh	4	8	12	16	20
Surface area (m^2/g)	104	70.30	68.6	66.03	64.20	62.26
Surface area reduction (%)	–	32.4	34.0	36.5	38.3	39.8
Average pore diameter (\AA)	170	136	132	127	122	118
Pore volume (cm^3/g)	0.827	0.570	0.568	0.566	0.564	0.562

conradson carbon residue and asphaltene as function of duration time, were not improved due to the decay of the catalyst activity. The deactivation after the first 4 h may be attributed to the deposition of the heavy metals (Ni, V) during successive cycles [23]. Thus, the rate of deactivation depends on the run time.

The effect of duration time (cycle-runs) on hydrocarbon groups' composition (saturates and aromatics) of the liquid products is indicated in Fig. 4. It shows that the rate of aromatic hydrogenation is decreased from 56.3% to 19.0% as there is an increase in aromatic content from 38.7 to 72.0 wt% with increasing the operation time. This is attributed

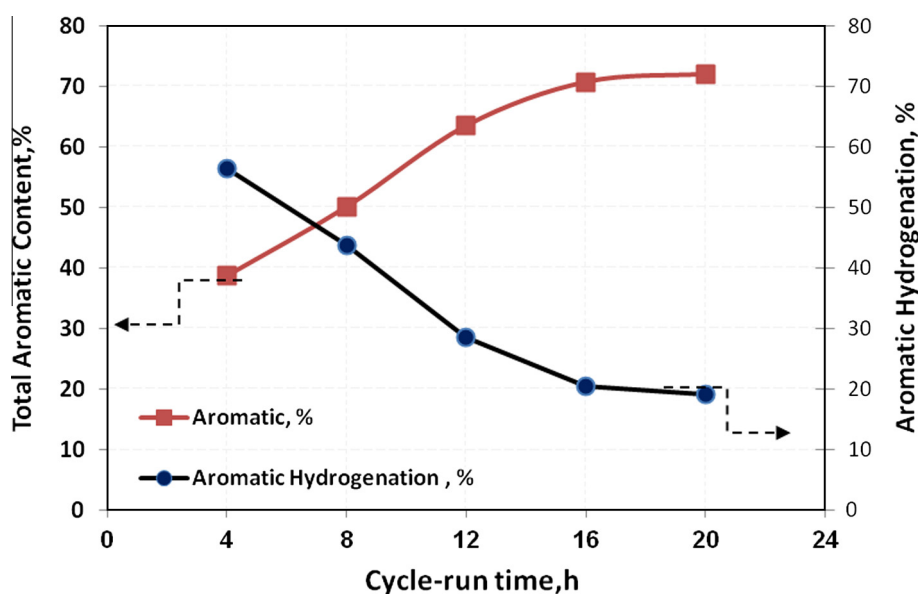


Figure 4 Effect of cycle-run times (duration time) on the total aromatic and aromatic hydrogenation of content of hydrocracked heavy vacuum residue (HVR).

Table 4 Characteristics of distillate products during hydrocracking of HVR (ASTM D5949).

Duration time (h)	4	8	12	16	20
Characteristics					
<i>Distillate up to 350 °C</i>					
Sulfur content (wt%)	0.52	0.56	0.68	0.78	0.91
Color	3.5	6.0	7.5	8.0	8.0
Pour point (°C)	-15	-18	-18	-21	-21
<i>Distillate above 350 °C</i>					
Sulfur content (wt%)	1.26	1.29	1.32	1.47	1.89
Conradson carbon residue (wt%)	18.52	20.30	21.52	23.52	25.2

Table 5 ASTM distillation of HVR (ASTM D-1160).

Duration time (h)	4	8	12	16	20
Vacuum distillation					
Initial boiling point (°C)	86	98	118	138	168
10% Distilled at (°C)	120	150	160	170	180
20% Distilled at (°C)	160	172	190	220	240
30% Distilled at (°C)	200	202	224	250	260
40% Distilled at (°C)	240	254	266	282	290
50% Distilled at (°C)	285	294	294	318	320
60% Distilled at (°C)	340	340	340	340	340
Recovered	60	58	56	54	52
Residue	38	40	42	44	46
Loss	2	2	2	2	2

to the decrease of hydrogenation activity of the catalyst due to coke and metal deposition which inhibit the activity of active sites of the catalyst.

The data indicated in Table 4 shows the quality of the distillate products as their boiling ranges, up to 350 °C the sulfur contents and color of the first fraction were increased from 0.52 to 0.91 and 3.5 to 8.0, respectively, through increasing the duration time. This light fraction characterized by its pour point which was decreased due to the increase of saturate compounds.

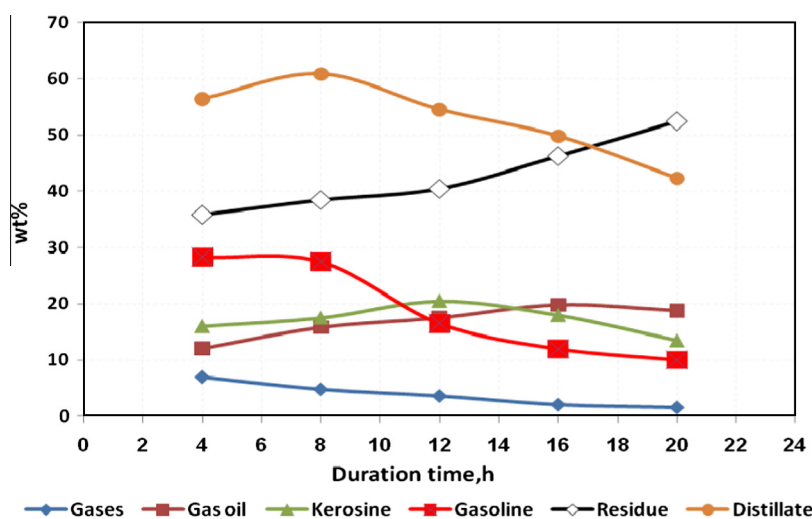
On the other hand, the quality of the heaviest residue above 350 °C follows the same trend of the quality of the light distillate, where sulfur content and conradson carbon residue were increased from 1.26 to 1.89 and 18.52 to 25.20 wt%, respectively, on increasing the duration time.

3.2. Effect of duration time on the hydrocracked product distribution

Table 5 shows the relation between the vacuum distillation and boiling ranges of distillate. Increasing the duration time the initial boiling point of distillates increases from 86 °C at the end of 1st cycle-run after 4 h then at the end of the 5th cycle-run, i.e. after 20 h. reached to 168 °C. Fig. 5 shows that the effect of duration time on hydrocracked distillate product distribution. It shows that the liquid distillates produced during the hydrocracking reactions were decreased while heavy fractions were increased which is attributed to the cracking activity of the catalyst that decreases as the duration time increases and the selectivity toward producing liquid distillates is decreased. The catalyst activity toward the conversion of the residue drops rapidly during the first cycle.

4. Conclusion

The obtained data assume that the decrease in heavy vacuum residue conversion is reflected by the concentration change of

**Figure 5** Effect of duration time on distillate distribution of hydrocracked heavy vacuum residue (HVR).

the hydrocarbon groups, such as saturates, aromatics, resin and asphaltenes of the feed stocks as hydrocracking reaction progresses, and also catalyst activity. The rate of catalyst deactivation depends on the operating run times, i.e. cycle-run time.

Therefore, the quality of hydrocracked products with respect to sulfur, Conradson carbon residue and asphaltenes content was affected by increasing accumulation of undesirable materials in the feed from first cycle due to the adsorption of these materials on catalyst surface, and increased as the run-times increased to five cycles.

The quality of hydrocarbon groups (saturates and aromatics), initial boiling point and boiling range of the hydrocracked distillate, were affected by increasing duration time.

Light distillate decreased while heavy distillate was increased with increased duration time.

The data obtained in this work revealed that when heavy feeds, such as heavy vacuum residues, used for hydroconversion, deactivation of catalyst is the main cause of refinery plant shut-impact on catalyst deactivation [20]. Also, catalyst deactivation can be concerned by two terms, carbon and metal depositions.

References

- [1] A. Marafi, S. Fukase, M. Al-Marri, A. Stinslous, *Energy Fuels* 17 (2003) 661–668.
- [2] M.M. Hossain, M.A. Sales, M.A. Shalabi, T. kimurate, *Appl. Catal. A* 278 (2004) 65–71.
- [3] M.S. Rana, V. Sámano, J. Ancheyta, J.A.I. Diaz, *Fuel* 86 (2007) 1216–1231.
- [4] A.-M. Gilaua, R.V. Buskirkb, M.J. Small, *Energy Policy* 35 (2007) 5526–5534.
- [5] M.S. Rana, V. Sámano, J. Ancheyta, J.A.I. Diaz, *Fuel* 86 (2007) 1216–1231.
- [6] C. Song, X. Ma, *Appl. Catal. B* 41 (2003) 207–238.
- [7] M.S. Jamala, M. Ismail, M.Y. Miah, M.N. Haquea, S.K. Banik, *Bangladesh J. Sci. Ind. Res.* 44 (4) (2009) 473–478.
- [8] H.S. Ahmed, F.Y. El-kady, *Energy Source* 30 (2008) 247–258.
- [9] M.F. Menoufy, F.Y. El-kady, O.I. Sif EL-Dine, H.S. Ahmed, 4th Conference and Exhibition on Chemistry in Industry, Petroleum Refining and Petroleum Session, Manama, Bahrain, 14–16 October 2002.
- [10] H. Fukayama, S. Terai, *J. Pet. Sci. Technol.* 25 (2007) 227–287.
- [11] R. Henderson, M. Rod Well, A. Harji, *Hydrocarbon Process* 84 (9) (2005) 54.
- [12] J. Ancheyta, M. Rana, E. Furimsky, *Catal. Today* 109 (1–4) (2005) 1–2.
- [13] E. Furimsky, *Appl. Catal. A* 171 (1998) 177–206.
- [14] H.S. Ahmed, M.F. Menoufy, Effect of heavy residue's feed blending on hydrocracking. *Al-Azhar Bulletin of Science, Proceeding of 14th Int. Sci. Conf.* 27–29 March (2001) 77–86.
- [15] B.J. Mair, F.D. Rossini, *ASTM* 224 (1958) 9.
- [16] M. Marafi, A. Stanislaus, *Appl. Catal. A* 159 (1997) 259–267.
- [17] H.S. Ahmed, *Mansoura J. Chem.* 32 (1) (2005) 249–258.
- [18] S.T. Sie, *Appl. Catal. A* 212 (1–2) (2001) 129–151.
- [19] J.A. Moulijn, A.E. van Diepen, F. Kapteijn, *Appl. Catal. A* 212 (1–2) (2001) 3–16.
- [20] G. Centeno, J. Ancheyta, A. Alvareza, G. Marroquina, F. Alonso, A. Castillo, *Fuel* 100 (2012) 73–79.
- [21] S.K. Sahoo, S.S. Ray, I.D. Singh, *Appl. Catal. A* 278 (2004) 83–91.
- [22] S.K. Maity, J. Ancheyta, F. Alonso, J.A. Vázquez, *Catal. Today* 130 (2008) 405–410.
- [23] N.I. Manuel, K. Viatches, E.R. Daniel, *Appl. Catal. A* 199 (2000) 263–273.