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A comparative study on the performance of a catalyst system for the desulfurization of two kinds of atmospheric residues, Kuwait Export and Eocene residual oils

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Abstract

Crude oil feedstock is becoming increasingly heavier with higher sulfur, conradson carbon residue (CCR) and asphaltenes contents. This trend will specifically impact residual oil processes aimed at converting the residual oil to distillate products and hydrotreating the residual oil to low sulfur fuel oils (LSFO). In this paper, the performance of a catalyst system typically used in industrial atmospheric residue desulfurization (ARDS) units was investigated using residual oils of Kuwait Export Crude (KEC) and Eocene Crude as feedstock. The catalyst system consists of a combination of five catalysts having different physico-chemical properties. The performance of the catalyst system was studied using a pilot plant equipped with two reactors in series for a complete life cycle. Sulfur content in the product for both tests was maintained at around 0.6%, by raising the temperature gradually to compensate for the catalyst deactivation. The tests were continued until the temperature of the back-end reactor (R2) reached 412 °C. The results showed that the life of the catalyst system using the atmospheric residues of KEC and Eocene was around 7500 and 3800 h, respectively. The results are discussed in terms of possible differences in the deactivation pattern caused by differences in the composition of the two types of crude oils used in the study.

Keywords: Eocene; Export Crude; Catalyst deactivation; Residue hydrotreating; Feed quality effect

1. Introduction

The main objective of atmospheric residue desulfurization processes (ARDS) is to reduce the sulfur, nitrogen, and metals (Ni, V) contents in the product. Details of the reactions taking place and the parameters affecting them are reviewed extensively in the literature [1–4]. The hydrotreatment efficiency is influenced by several variables [3,5], foremost among which are the catalyst system and the quality of the feedstock.

The hydrotreating reactions are usually carried out over catalysts containing cobalt/molybdenum (CoMo) or nickel/molybdenum (NiMo) on alumina support [6]. The catalyst system, loaded into the reactors, consists of different types of catalysts. The catalyst combination (catalyst system) is selected and designed to achieve the process objectives and maintain maximum time on stream [7–9].

The front-end of the catalyst systems are typically demetallation catalysts (HDM) that are highly porous and have moderate surface area. The large pores allow the HDM catalysts to absorb more metal deposits (high metal capacity) and to resist pore plugging. The hydrotreating activity of HDM catalysts is relatively low because of their low surface area and their composition. On the other hand, catalysts for the back-end of the catalyst system are selected to be highly active desulfurization and denitrogenation catalysts. They are normally characterized by small pore diameter and high surface area. The activity and the life of downstream catalysts can substantially decrease if the feed is not demetallized [10–13].

One of the main problems of residual oil hydrotreating is the relatively rapid deactivation of the catalysts by coke and metal deposition. The deactivation of the catalyst system passes through three different phases. The first phase is a rapid initial

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deactivation attributed to initial coke deposition on the fresh catalysts. In this loss of catalyst activity, the coke mainly blocks the micro-pores of the catalyst [14–16].

In the second stage, the deactivation rate is slow, and it is thought to be mainly influenced by metal deposition on the catalyst surface. The final stage is characterized by another rapid deactivation that is caused by pore mouth plugging of the catalyst due to both metal and coke deposition [17–19]. Coke deposition on the surface of the catalyst reduces the rate of desulfurization and seriously affects catalyst activity [17,20–22]. It is mainly attributed to asphaltenes deposited on the catalyst surface, which presumably thermally decompose and thus form coke.

Over the past decade, increased amounts of heavy oils are being introduced to the crude oil market [23,24]. Furthermore, market trend for petroleum products dictates that the refining industry should maximize the production of ultra-clean transportation fuels using hydrotreating and hydroconversion processes [25–27]. However, the data on the hydroprocessing of heavy oils reported in the literature are still scarce [28–31].

In this paper, the performance of a catalyst system for processing residual oils from a conventional crude oil and a Kuwaiti heavy crude oil was investigated for a complete life cycle of the catalyst system. The primary objective of the study was to determine the impact of crude origin on the life of the catalyst system and to attempt to correlate the results with the feed properties.

2. Experimental

2.1. Feedstock

Atmospheric residue of Kuwait Export Crude (KEC-AR) was acquired from one of the refineries of Kuwait National Petroleum Company. Dewatered and desalted Eocene crude oil was acquired from Kuwait Oil Company-Joint Operation. The crude oil was further desalted and then distilled by PARC, Pennsylvania, USA, and the atmospheric residue (Eocene-AR) was collected. Both atmospheric residues were characterized in accordance with standard procedures and the properties are listed in Table 1.

Table 1
Properties of KEC-AR and Eocene-AR

Parameter	KEC-AR	Eocene-AR
TBP cut range (°C)	+360	+360
Density at 15 °C (g/ml)	0.9791	1.002
Gravity (API)	13.5	7.40
Total sulfur (wt%)	4.60	5.42
Nitrogen (wt%)	0.27	0.31
Kinematic viscosity at 100 °C (cSt)	65	148
Conradson carbon residue (wt%)	12.3	16.2
Asphaltenes (wt%)	4.9	9.7
V (ppm)	69	72
Ni (ppm)	21	29

AR: atmospheric residue; KEC: Kuwait Export Crude; TBP: true boiling point.

2.2. Catalyst properties

The catalyst system used in this study is a combination of five commercial catalysts acquired from a catalyst manufacturer. The system is labeled as Cat-B. The front-end catalysts, Cat-BA and Cat-BB, are HDM catalysts. The downstream catalysts, Cat-BC, Cat-BD, and Cat-BE, are highly active nickel-molybdenum HDS catalysts.

2.3. Pilot plant

The performance of the catalysts was tested using two multi-reactor pilot plants each equipped with two reactors (500 ml). The reactors in both pilot plants have identical dimensions to ensure reproducibility. The pilot plants are equipped with sampling devices between reactors to permit sampling of the product of the first reactor (R1). The reactor bed and skin temperatures are monitored by thermocouples inserted into the reactor and through the heating jacket, respectively. The tests were continued until the bed temperature of the second reactor (R2) reached 412 °C. Product samples were also analyzed for metals content. The process flow diagram of both units is shown in Fig. 1.

2.4. Pilot plant test procedure

The test procedures for evaluating the performance of the catalyst system using both feedstocks were the same. Details of the procedure are as follows.

2.4.1. Catalyst loading

The HDM catalysts, Cat-BA and Cat-BC, were loaded in the front-end reactor (R1), while the HDS catalysts, Cat-BC, Cat-BD and Cat-BE, were loaded in the second reactor (R2). The ratios of different catalysts were as recommended by the manufacturer. The total volume of catalysts was 328 cm^3. Layers of α-alumina balls were placed before the catalyst bed and between the catalyst layers. These layers reduce channeling effects, enhance oil distribution and simplify the separation of the catalysts during unloading. The catalyst beds were diluted with carborandum [32].

2.4.2. Test procedure and operating conditions

After loaded in the reactors, the catalysts were presulfided according to the procedure shown in Fig. 2. The presulfiding feed is a mixture of gas oil (99 vol%) with carbon disulfide (CS_2, 1 vol%). After presulfiding, KEC-AR was introduced at the operating conditions (300 °C, LHSV = 1.0 and H_2/oil = 680, $P = 120$ bar) for 2 h.

The reaction temperature was then increased to 370 °C, maintaining all other operating conditions constant, and the sulfur level was determined. The result was checked against sulfur level results from previous tests conducted in our laboratories to verify the reproducibility of the test at start-up. For the Eocene test, the Eocene-AR feedstock was introduced immediately after completing the verification test. Based on the sulfur level, the temperature required to achieve 0.6 wt% sulfur

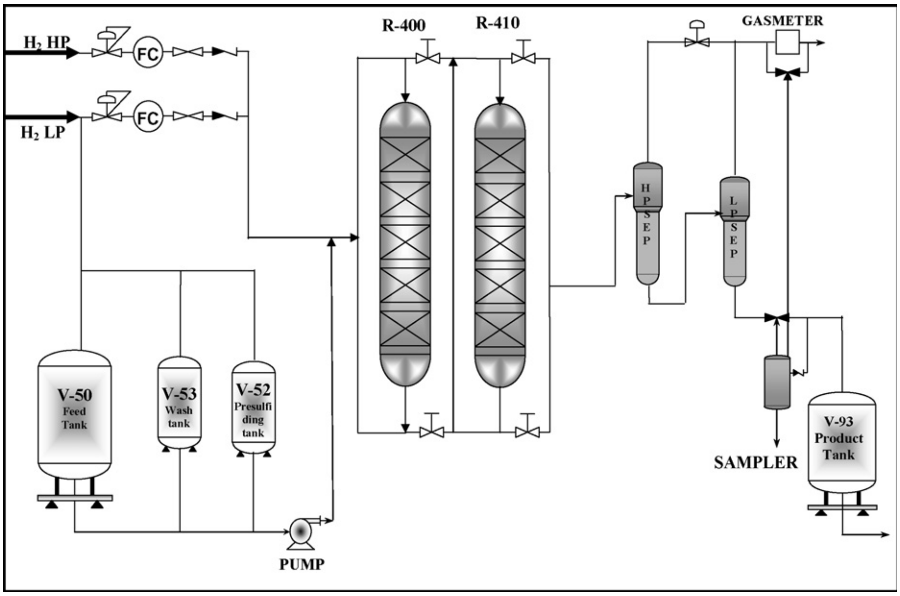


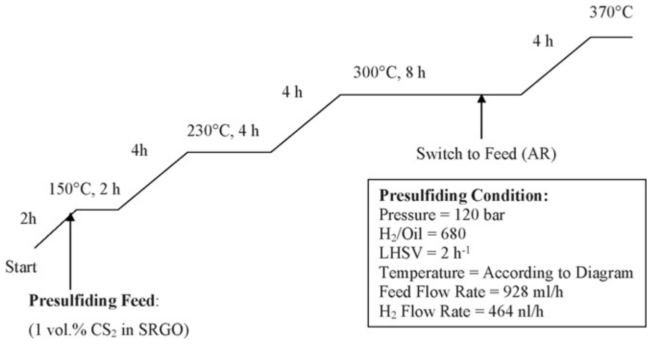
Fig. 1. Process flow diagram of the pilot plants.

in the product was estimated using Arrhenius equation and activation energy values for each catalyst previously determined in our laboratory. The temperature of the reactors was then adjusted by setting the temperature of reactor R1 at 10 °C lower than reactor R2, such that the weighted average bed temperature (WABT) for the total system was equal to the estimated temperature. The operating conditions were monitored continuously and the temperature was adjusted to maintain the sulfur level at around 0.6 wt%. Sulfur content was determined using Oxford 1000 sulfur analyzer. Vanadium content was determined without ashing using a Varian Inductively Coupled Plasma (ICP), Model Liberty series II.

3. Results

The stability of the operating conditions for the pilot plant tests is shown by the data related to the test run with KEC-AR (Fig. 3). It is seen that the pressure, feed flow rate and hydrogen flow rate remain constant (without appreciable variation) during the run. The WABT profiles for both pilot plant test runs (Fig. 4) show that the two test runs significantly differ from each other. For KEC-AR, the initial WABT required to achieve 0.6 wt% sulfur in the final product was found to be 371 °C. The temperature had to be raised rapidly for the first 500 h to maintain the sulfur level in the final product at around 0.6–0.7 wt%, and then the rate of temperature increase was slower till almost the end of the test run at around 7300 h. In comparison, for Eocene-AR, the initial temperature required to achieve 0.6 wt% sulfur was 376 °C. Furthermore, to maintain the target sulfur level, the temperature had to be increased rapidly throughout most of the test till the end of the test run at around 3800 h. Tables 2 and 3 show typical analysis results of the products collected after reactor R1 and the total catalyst system for KEC-AR and Eocene-AR, respectively. For both feedstocks, the metal content in the final product (system) decreased substantially. At start of run the total metal content (V + Ni) in the product was in the range 22–31 ppm, while at the end of run the total metal content was observed to be around 8–10 ppm.

The kinetics of residual oil hydrotreatment is complicated due to the wide variety of sulfur- and metal-containing compounds present in the feedstock [33–36]. The rate constants



Presulfiding Condition:
Pressure = 120 bar
H_2/Oil = 680
LHSV = 2 h^{-1}
Temperature = According to Diagram
Feed Flow Rate = 928 ml/h
H_2 Flow Rate = 464 nl/h

Fig. 2. Presulfiding procedure.

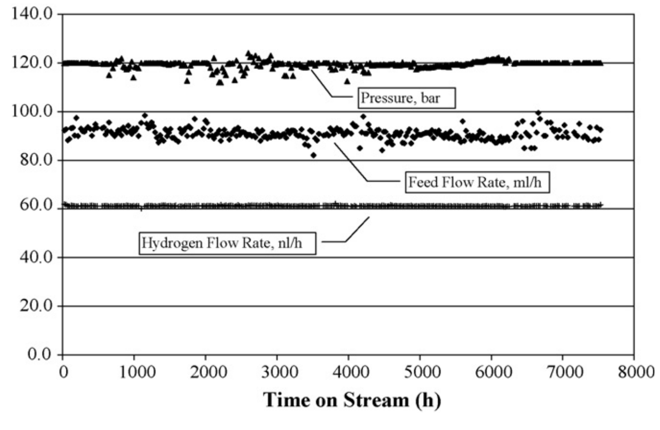


Fig. 3. Plots of process operating conditions vs. time on stream for the pilot plant test with KEC-AR.

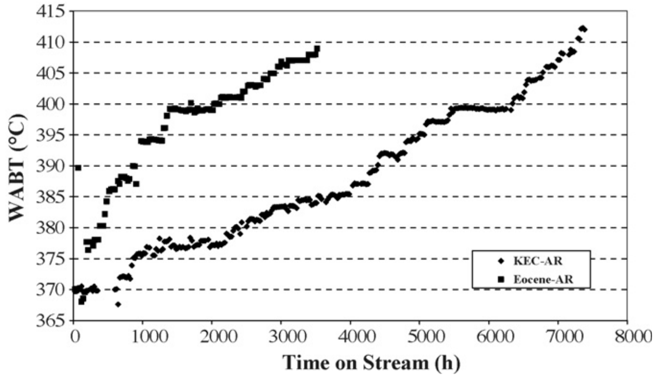


Fig. 4. Plots of weighted average bed temperature (WABT) vs. time on stream for the pilot plant tests.

for fixed bed hydrotreating reactions are normally calculated using the generalized kinetic equation [37]:

$$k = \frac{\text{LHSV}}{n-1}\left(\frac{1}{C_\text{p}^{n-1}} - \frac{1}{C_\text{f}^{n-1}}\right) \tag{1}$$

where k is the rate constant, LHSV the liquid hourly space velocity, n the rate order of reaction, and C_f and C_p are the concentrations of S, V or Ni in the feed and the product, respectively. The rate orders of different reactions as reported in the literature show significant variation, ranging between 1 and 2. The order apparently depends on the origin of the feedstock. For Kuwaiti feedstocks, an order of 2 was reported in the literature for hydrodesulfurization and vanadium removal [35,36,38,39]. Therefore, this value was adopted in calculating the rate constants in this study. Hence, Eq. (2) was used to calculate the rate constants at different time-on-stream and different temperatures for reactor R1, reactor R2, and the total system.

$$k = \text{LHSV}\left(\frac{1}{C_\text{p}} - \frac{1}{C_\text{f}}\right) \tag{2}$$

To assess the deactivation pattern of the catalysts, the rate constants were normalized to 370 °C, which is a standard temperature selected by our laboratory. The normalization of the rate constant is calculated using the Arrehenius equation [37]:

$$k_i = A\,\mathrm{e}^{-(E_\text{a}/RT_i)} \tag{3}$$

The activation energies for hydrodesulfurization (HDS) and vanadium removal (HDV) reactions for each of the five catalysts of catalyst system Cat-B are summarized in Table 4. The values are based on the results of kinetics studies on individual catalysts conducted in our laboratory. Since each reactor used in our investigation contains at least two catalysts, the activation energies for HDS and HDV for each reactor is estimated by calculating the weighted average of the activation energies of the catalysts loaded in the reactor, based on their volume distribution. For example for reactor R1, the activation energy for HDS is calculated using the following equation:

$$E_\text{HDS-r1} = \frac{\text{Vol}_\text{BA}E_\text{HDS-BA} + \text{Vol}_\text{BB}E_\text{HDS-BB}}{\text{Vol}_\text{BA} + \text{Vol}_\text{BB}} \tag{4}$$

where $E_\text{HDS-r1}$ is the weighted average activation energy for HDS for reactor R1; Vol_BA, Vol_BB, $E_\text{HDS-BA}$ and $E_\text{HDS-BB}$ are the volumes and the activation energies of Cat-BA and Cat-BB, respectively. The activation energies for HDS and HDV for the total catalyst system is estimated by calculating the weighted average of the activation energies of individual catalysts based

Table 2
Properties of the products of the total system and of reactor R1 of the pilot plant test with KEC-AR

Sample no.	Time-on-stream (h)	System		Reactor R1		Temperature (°C)		
		S (wt%)	V (ppm)	S (wt%)	V (ppm)	R1	R2	System
37	967	0.62	14.2	2.90	26.3	370.3	379.5	375.8
60	1559	0.62	12.7	3.00	25.3	370.9	380.6	376.8
94	2433	0.70	13.7	3.38	26.0	374.7	385.0	380.9
115	2937	0.70	13.5	2.96	24.4	376.9	387.6	383.3
122	3105	0.72	13.4	2.80	29.9	376.2	386.9	382.7
129	3273	0.72	13.3	2.75	30.3	377.8	388.6	384.3
135	3417	0.72	13.2	2.93	23.9	378.4	388.5	384.5
142	3585	0.70	13.2	2.92	26.2	379.3	388.2	384.6
150	3818	0.70	13.1	3.42	25.0	379.1	388.5	384.8
157	3984	0.71	12.9	3.18	25.0	379.4	389.4	385.4
164	4207	0.68	12.7	3.19	25.0	381.0	391.2	387.1
171	4375	0.66	12.3	3.32	23.0	383.2	393.3	389.3
178	4543	0.58	11.5	2.82	23.0	385.9	395.9	391.9
192	4879	0.64	10.4	2.34	18.3	388.1	397.9	394.0
206	5215	0.62	9.8	2.27	15.4	391.0	401.3	397.2
234	5887	0.65	10.6	2.10	15.6	392.9	403.5	399.3
253	6416	0.64	9.6	2.97	18.0	395.2	405.3	401.3
259	6560	0.59	8.9	2.13	18.5	397.5	408.1	403.9
275	7023	0.68	9.9	2.04	18.2	401.1	411.1	407.1
284	7335	0.65	5.0	2.00	17.0	412.2	412.1	412.1

Table 3
The properties of the products of the total system and of reactor R1 of the pilot plant test with Eocene-AR

Sample no.	Time-on-stream (h)	System		Reactor R1		Temperature (°C)		
		S (wt%)	V (ppm)	S (wt%)	V (ppm)	R1	R2	System
7	168	0.93	20.7	2.91	32.9	370.2	369.2	369.6
14	360	0.75	16.8	2.99	28.5	372.1	382.0	378.1
21	550	0.56	14.7	2.81	26.1	380.5	389.9	386.2
28	742	0.70	13.2	0.00	24.3	382.5	392.0	388.2
35	982	0.56	11.8	3.19	22.7	387.8	398.1	394.0
42	1150	0.58	11.0	2.78	21.8	388.0	398.4	394.3
49	1330	0.61	10.3	2.79	21.0	390.1	400.1	396.1
56	1518	0.59	9.6	2.73	20.2	393.2	403.0	399.1
63	1702	0.56	9.1	2.65	19.6	395.9	403.0	400.2
70	1870	0.55	8.6	2.62	19.0	393.0	402.9	399.0
77	2062	0.66	8.1	2.81	18.5	394.0	404.1	400.1
84	2235	0.59	7.7	2.78	18.0	395.0	405.1	401.1
91	2403	0.64	7.3	2.73	17.6	395.1	405.1	401.1
98	2595	0.66	6.9	2.79	17.1	397.0	407.0	403.0
105	2801	0.69	6.6	2.58	16.7	397.9	408.0	404.0
112	3065	0.71	6.1	2.63	16.2	400.1	410.5	406.4
119	3233	0.68	5.8	2.53	15.9	401.1	411.0	407.1
126	3473	0.64	5.5	2.40	15.5	401.8	412.0	407.9
133	3661	0.61	5.2	2.25	15.1	404.1	414.0	410.1
140	3829	0.68	5.0	2.23	14.9	404.0	413.9	410.0

on the volumes of all the catalysts in the system. This method of estimating activation energies for combinations of different catalysts was verified during the conduction of the test runs. The target temperatures for maintaining the sulfur level at 0.6 wt%, which were calculated using the weighted average activation energy, were consistently found to be correct.

Based on the above, the specific equations used in calculating the normalized rate constants in this study are as follows:

1. The total catalyst system:

$$k_{ns} = k_s\,e^{(E_{as}1000/R)((1/T_s)-(1/T_n))} \tag{5}$$

2. Reactor R1:

$$k_{nr1} = k_{r1}\,e^{(E_{ar1}1000/R)((1/T_{r1})-(1/T_n))} \tag{6}$$

3. Reactor R2:

$$k_{nr2} = k_{r2}\,e^{(E_{ar2}1000/R)((1/T_{r2})-(1/T_n))} \tag{7}$$

where k_{ns}, k_{nr1}, and k_{nr2} are the normalized rate constants of hydrotreating reactions for the total system, reactor R1, and reactor R2, respectively; k_s, k_{r1}, and k_{r2} the actual rate constants of different reactions for the total system, reactor R1, and reactor R2, respectively; E_{as}, E_{ar1}, and E_{ar2} the activation energies for HDS and HDV reactions for the total system, reactor R1, and reactor R2, respectively; T_{r1}, T_{r2}, and T_s the temperatures (degrees Kelvin) of reactor R1, reactor R2, and the average for the total system corresponding to k_{r1}, k_{r2}, and k_s, respectively; T_n the standard temperature (degrees Kelvin), i.e., 370 + 273 = 643 K; and R is the gas constant.

Table 4
The activation energies of individual catalysts and weighted average activation energies of reactor R1, reactor R2, and the system

Reaction	Activation energy (kcal/mol)							
	E_{BA}	E_{BB}	E_{ar1}	E_{BC}	E_{BD}	E_{BE}	E_{ar2}	E_{as}
HDS	31.9	29.6	30.6	31.0	25.5	24.3	28.0	29.0
HDV	31.9	30.5	31.1	23.9	14.5	16.2	16.0	22.0

E_{ar1}, E_{ar2}, and E_{as} are the weighted average activation energies of reactor R1, reactor R2, and the system, respectively.

3.1. The HDS deactivation pattern

Figs. 5–7 show the normalized rate constants for the HDS reaction versus time-on-stream. A comparison of Fig. 5 with Fig. 6 shows that the HDS activity of reactor R1, loaded with HDM catalysts, is significantly lower than that of reactor R2.

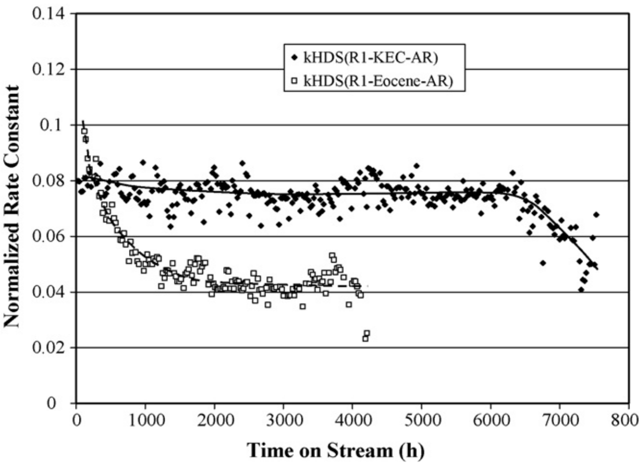


Fig. 5. Comparison of the normalized hydrodesulfurization rate constants for the catalysts of reactor R1 of KEC-AR and Eocene-AR test runs.

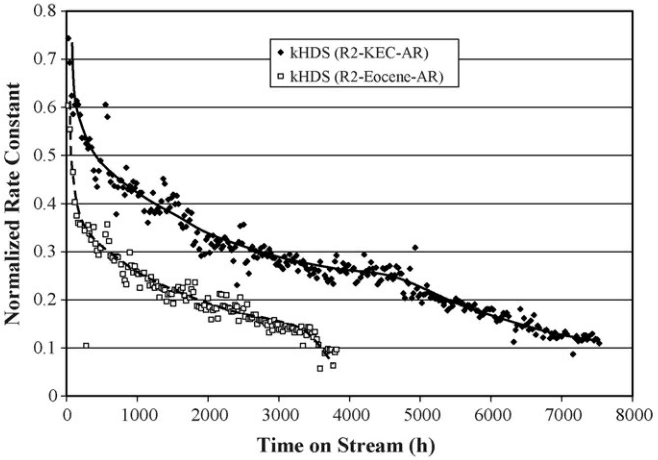


Fig. 6. Comparison of the normalized dehydrodesulfurization rate constants for the catalysts of reactor R2 of KEC-AR and Eocene-AR test runs.

Furthermore, the rate constants for KEC-AR are consistently higher than those for Eocene-AR throughout the duration of the test runs.

Fig. 5 shows that when Eocene-AR is used as feedstock, the activity of HDM catalysts loaded in reactor R1 decreases rapidly during the first 1000 h on stream and then remains practically constant till the end of the test. In contrast for KEC-AR, the activity of the HDM catalysts remains practically constant for the first 6000 h on stream and then decreases rapidly till the end of the test.

For the HDS catalysts loaded in reactor R2, very sharp deactivation was observed during the first 200 h on stream for the Eocene-AR feedstock, and the subsequent deactivation behavior was nearly similar to that of the KEC-AR feedstock till the end of the test run (Fig. 6). For KEC-AR, the deactivation of the catalysts was relatively rapid during the early stages of the test and then slow till around 5000 h on stream, and finally the rate of deactivation increased till the end of the test. The deactivation of the total catalyst system followed a trend similar to that observed for reactor R2 (Fig. 7).

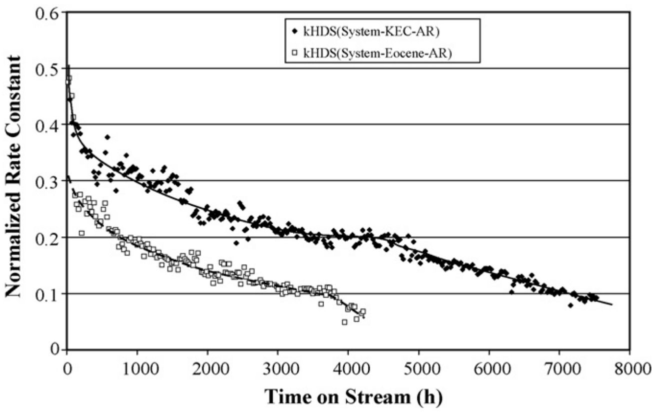


Fig. 7. Comparison of the normalized dehydrodesulfurization rate constants for the total catalyst system of KEC-AR and Eocene-AR test runs.

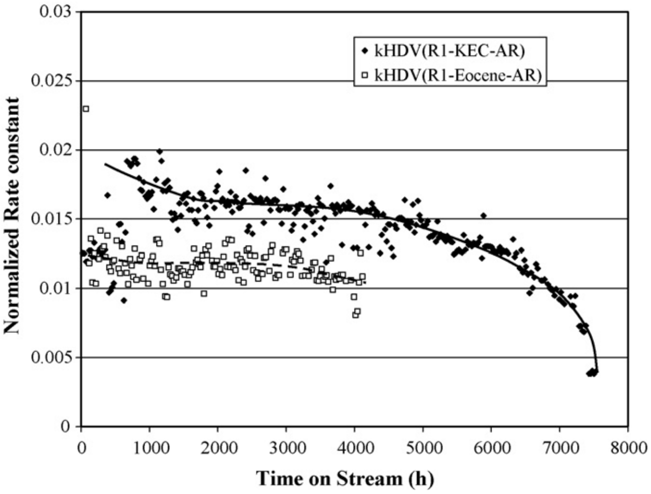


Fig. 8. Comparison of vanadium removal normalized rate constants for the catalysts of reactor R1 of KEC-AR and Eocene-AR test runs.

3.2. Vanadium removal deactivation pattern

Figs. 8 and 9 show plots of the normalized HDV rate constants versus time on stream. As shown in Fig. 8 the normalized HDV rate constants for KEC-AR are higher than those for Eocene-AR throughout the test run duration. For KEC-AR, the deactivation is slow till the middle of the run, and subsequently starts to accelerate till the end of the run. In contrast, for Eocene-AR very slight deactivation is noticed during the whole test run.

The deactivation patterns of HDV for reactor R2 were found to be significantly different for the two test runs (Fig. 9). For KEC-AR, the catalyst deactivated rapidly at start of run, and then the normalized rate constant remained practically constant for most of the test till the last 1000 h, when it started to decrease. On the other hand, for Eocene-AR, the normalized rate constant was observed to increase till the middle of the run, and then it remained nearly constant till the end of the run. For the total catalyst system, the deactivation pattern is similar to that of reactor R2.

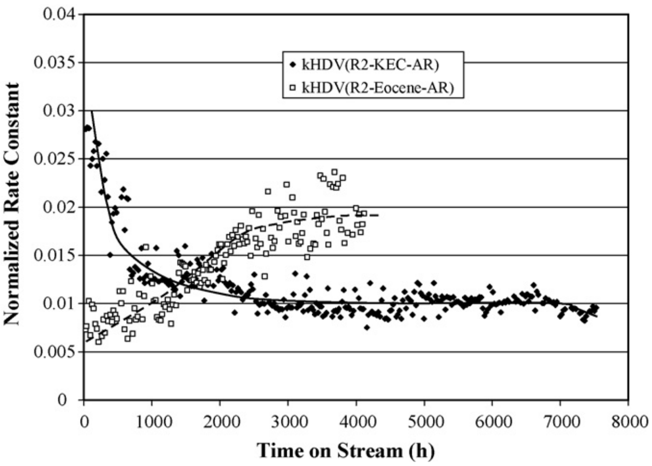


Fig. 9. Comparison of vanadium removal normalized rate constants for the catalysts of reactor R2 of KEC-AR and Eocene-AR test runs.

4. Discussion

Differences in the processability of crude oils from different origins have been noted in the literature [40]. However, detailed studies related to the effect of the origin of crude oil on the hydroprocessing of petroleum residual oil are scarce. Takeuchi et al. [41] reported one of the earliest studies addressing the performance of two types of hydroprocessing catalysts using different heavy oils. They found that the feedstock reactivities correlate with the total metal content of the residual oil. On the other hand, Dolbear et al. [42] provided limited data on the demetallation reactivities of several resids from different origins, and concluded that no correlation exist between the bulk properties of the residual oil and its reactivity. Rather, they found that the HDM reactivities correlate with the metal content in the resin fractions of the residual oil.

In this study, the life performance of a typical industrial catalyst system used in atmospheric residue desulfurization was investigated using two residual oil feedstocks originating from KEC and Eocene crude oils. The main differences in the bulk characteristics of the two residual oils are the sulfur, asphaltenes, and CCR contents, with Eocene-AR having significantly higher values than those for KEC-AR. The metals (vanadium and nickel) in both feedstocks are nearly equal. The tests were performed such that the sulfur content of the product is maintained at around 0.6–0.7 wt% by adjusting the temperature to compensate for the loss of activity of the catalyst system as the test progressed. This mode of operation is adopted since it resembles typical refinery practices.

As indicated previously, the initial temperature to achieve a sulfur content of 0.6 wt% in the product for Eocene-AR was found to be approximately 5 °C higher than that for KEC-AR. This is most probably due to the higher sulfur content in Eocene-AR (5.4 wt%), as compared with KEC-AR (4.6 wt%). It is also possible that this increase in initial temperature is due to the differences in the type of sulfur compounds and their distribution among various components of the residual oils. Such differences are known to affect the processability of residual oils. In the absence of detailed analysis of the feedstocks, it is not possible to draw a definite conclusion. However, the relatively slight increase in temperature required to achieve the same level of sulfur in product indicates that the sulfur-containing species in both feedstocks have similar reactivities.

The deactivation patterns for the HDS reaction shown in Figs. 6 and 7, particularly those for KEC-AR, are the typical S-shaped patterns known to be exhibited by residual oil hydroprocessing catalysts. The deactivation of hydroprocessing catalysts was thoroughly reviewed in the literature [20,43]. The deactivation is mostly attributed to coke and metals deposition. It appears that as soon as a hydroprocessing catalyst is exposed to a hydrocarbon feedstock, massive deposition of coke takes place. Recent studies in our laboratories showed the presence of two types of coke on the catalyst, an easily removable soft coke and a more refractory surface coke. After 240 h of operation, a large fraction of the soft coke is converted into refractory coke [16]. This coke deposition accounts for the sharp deactivation of the catalysts in reactor R2 and the total system during the start of the run. The subsequent relatively low deactivation rate at the middle of the run is probably due to the deposition of vanadium and nickel sulfides. This is followed by rapid deactivation at the end of the run, which is presumably due to further coke deposition caused by thermal cracking at high temperatures.

The higher deactivation rate of the catalyst system towards hydrodesulfurization for Eocene-AR is probably due to the higher asphaltene content. In a recent review on the role of asphaltenes in hydroprocessing catalyst deactivation [29], it was concluded that precipitation of asphaltenes from heavy oils and residue is a potential cause of catalyst bed plugging. It was also noted that the asphaltene quality plays a more important role than the asphaltene quantity in catalyst deactivation. The increase in asphaltene aromaticity and ring condensation brings about a higher coke yield. Further work will be carried out to assess the characteristics of asphaltenes in both KEC-AR and Eocene-AR to determine the causes of the deactivation pattern observed.

The deactivation pattern of the HDM catalysts (Fig. 5) for KEC-AR is significantly different from that of the HDS catalysts. The catalyst activity remained practically stable throughout most of the test run, despite the deposition of foulant metals. It is possible that the deactivating effect of the foulant metals is being compensated for enhancing the catalysts activities through the promoting effect of the deposited metals (Ni and V) [44].

For the HDV deactivation patterns shown in Figs. 8–10, the trend for KEC-AR is as expected. The activity of the catalysts declined rapidly at start of run due to coke deposition, and then decreased slowly as the test progressed due to foulant metals deposition. However, for Eocene-AR, it was observed that the activity of the HDV catalysts (reactor R2) actually increased. We do not have currently a concrete explanation for this phenomena. However, it may be possible that the coke has a beneficial effect in promoting the HDV reaction. Such beneficial effect was reported by Glasson et al. [45] in a study conducted on an industrial CoMo catalyst. Further work is required to determine the causes of this enhancement in activity.

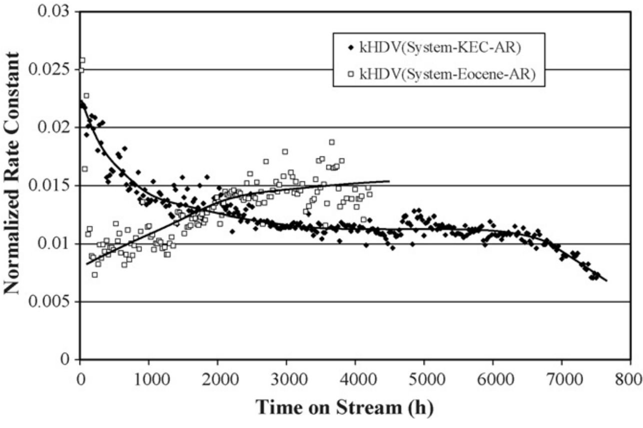


Fig. 10. Comparison of vanadium removal normalized rate constants for the total catalyst system of KEC-AR and Eocene-AR test runs.

5. Conclusions

The performance of a catalyst system used in commercial atmospheric residue desulfurization, was studied using two types of residual oils from KEC and Eocene crude oils. The catalyst system consists of five HDM and HDS catalysts having different physico-chemical properties. The study was conducted under constant sulfur conditions by gradually increasing the reaction temperature. Significant differences in deactivation behavior of the catalyst system were observed for the two types of residual oils. These differences resulted also in considerably shorter life cycle for the Eocene feedstock. Since the metal contents for both residual oils are almost the same, the main reason for the difference in performance is attributed to the contents and the composition of the asphaltenes in the feedstocks. The deactivation behavior was also found to vary between the HDM and HDS catalysts. These variations are consistent with reported studies on the impact of asphaltenes and coke deposition on residual oil hydrotreating catalysts. The results of this study highlight the need for developing new generation of residual oil hydrotreating catalysts that are resistant to coke deposition.

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