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The usage of high metal feedstock for the determination of metal capacity of ARDS catalyst system by accelerated aging tests

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Abstract

For residue hydrotreating catalysts that are deactivated mainly by pore blockage due to deposition of metals, the capacity for accommodation of the deposited metals is an important parameter in determining its stability and life. The primary objective of the present work is to determine the maximum metal capacity of different catalysts that are used in different reactors of atmospheric residue desulfurization (ARDS) units by accelerated aging tests in a short duration. A feedstock with high metals content, namely, Boscan crude, was used for the tests in a multireactor pilot plant to cause complete deactivation of the catalysts by metal accumulation in a shorter period. The influence of operating temperature and LHSV on the rate of catalyst deactivation was also examined for the high metal feed. Catalyst deactivation rate was found to be more than five times faster for the high metal Boscan feed compared to the conventional atmospheric residue from Kuwait export crude. It was possible to determine MMOC of an ARDS catalyst system within 45–50 days by accelerated deactivation test using a high metal feed (e.g., Boscan crude).

Keywords: ARDS process; Heavy oil upgrading; Aging test; Coke formation; Deactivation by metal and coke

1. Introduction

Catalysts play an important role in the atmospheric residue desulfurization (ARDS) process which is widely used in petroleum refining industry for upgrading low value petroleum residues to high quality and valuable products. Graded catalyst systems in multiple reactors are used in the process to achieve hydrodesulfurization (HDS), hydrodemetallization (HDM), hydrodenitrogenation (HDN) and conversion of residues to distillates to desired levels [1–3]. The ARDS catalysts deactivate by coke and metal deposition during the course of operation [4–7]. Three stages of catalyst deactivation have been observed in fixed-bed ARDS units. The initial stage is characterized by rapid deactivation due to the coke formation, while in the second stage; the deactivation rate appears to be slow influenced by gradual deposition of metals. The final stage is characterized by rapid deactivation again caused by the final constriction of the catalyst pore mouth by metal deposition [8–10]. As the catalysts play an important role in the process, selection of the best catalyst system to suit the unit for achieving the process objectives is very important in order to maximize the benefits that catalyst brings. Precise and realistic catalyst performance evaluation and testing methods, which simulate the commercial operation close enough, are needed for this purpose.

The methodology of evaluating the performance of ARDS catalysts is considerably more complex than the evaluation of the performance of catalysts used in distillate hydrotreating units. The complexity originates from the following factors: (i) the ARDS process is utilized to hydrotreat complex feedstocks, namely, residual oil. These oils contain a very wide spectrum of hydrocarbon compounds. ARDS feedstocks are rich in polyaromatic molecules, asphaltenic species and vanadium- and nickel-containing compounds. (ii) Several objectives are normally targeted for ARDS units. Whereas the main objective is normally desulfurization, other objectives, such as nitrogen and metal removal, asphaltenes reduction and conversion to distillates, are equally important. (iii) ARDS units typically consist of three to four reactors operating in series, permitting independent control of operating conditions for each reactor. (iv) Current ARDS catalyst systems consist of at least three types of hydrotreating catalysts. Whereas each type is normally dedicated for a specific function, such as demetallization (HDM) or desulfurization (HDS), the catalysts actually

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participate in catalyzing all reactions to different degrees of activity. The overall performance of the catalyst system is, therefore, the summation of the performance of the individual catalysts. (v) In comparison with distillate hydrotreating catalysts, ARDS catalysts deactivate at much faster rates and through more than one mechanism.

These factors demonstrate the difficulty of the problem of evaluating ARDS catalysts. Considerable efforts were made by various process licensors and catalyst manufacturers to establish reliable procedures for catalyst performance evaluation, however, these procedures, remained proprietary due to the high cost associated with their development and the competitive advantage they provide to the owners. As a result, information regarding ARDS catalyst testing methodology is very limited open literature [11,12].

In a recent study, Bej [13] addressed the various approaches that have been used by different researchers in hydrotreating catalyst testing for generation of reliable and meaningful data using small-scale units. The author divided the approaches into two categories for easy understanding. These categories are: reactors for screening of exploratory catalyst formulations and kinetic studies; and reactors for process development and optimization studies.

Loffler [14] suggested that the parameters that actually should be determined are the rates of the desired reactions and the rate of catalyst deactivation. The selection of appropriate testing equipment was thoroughly reviewed by Sie [15] and Perez-Ramirez [16]. It was concluded that microflow reactors, having a catalyst inventory on the order of 20 ml, are capable of generating most of the catalytic performance data for fixed-bed processes of the petroleum refining industry. However, it appears that the utilization of the generated data has to be coupled with a model capable of predicting the performance on an industrial scale.

While the determination of basic kinetic data is apparently straightforward, the determination of the deactivation behavior is more problematic. A long life test on a bench-scale unit is one such procedure; however, it is lengthy and costly. An alternative is testing the catalysts under accelerated conditions, which is a method used to reach a set of conditions that can provide a clear indication of the deactivation pattern of the catalyst system within a reasonable time scale [17,18]. This can be carried out either by high operating severity or by high metal residue.

The literature on the methods for testing ARDS catalyst systems by acceleration is scarce. Aldag [19] reported a study on two accelerated tests that were performed using two high metal feedstocks, namely Honda and Maya residues, at high temperature (399 °C) and high LHSV (1 h^{-1}) for several days with a commercial large pore hydrotreating catalyst. The results from these tests were compared with those obtained under a normal full life test. The results indicated that Honda could be used to reproduce the vanadium deactivation profile of the normal aging run up to a metal accumulation of over 25 wt%. Maya residues, on the other hand, resulted in more rapid deactivation of the catalyst. When the deactivation parameters of the heavier residues were combined with the kinetic parameters of the refinery residues, it was possible to develop a relationship that predicted the vanadium removed for each run as a function of metal accumulation.

Tanaka et al. [20] reported on the accelerated deactivation of a hydrotreating catalyst and a comparison with the long-term deactivation of the catalyst in a commercial plant. A high reaction temperature employed in the accelerated aging resulted in large amounts of carbonaceous material with high aromaticity, which was found to be the major cause of deactivation. However, this work indicated that the accelerated aging tests did not fully represent practical deactivation.

A recent study in this laboratory was carried out by Al-Jasem [21] on an ARDS catalyst system consisting of three types of catalysts, namely, HDM, HDS and HDS/HDN using accelerated tests by high severity operating conditions, such as high temperature and/or high LHSV. The results revealed that acceleration under these conditions leads to deactivation at a faster rate than normal unaccelerated conditions (base case). In the present work, an accelerated aging test method was developed for evaluating the performance of ARDS commercial catalyst system consisting of three catalysts, namely, HDM (A), HDS (B) and HDS/HDN (C) using a multireactor pilot plant unit. A feedstock with high metals content, namely Boscan crude, was used for the tests to cause complete deactivation of the catalyst due to metal accumulation in a shorter period. The influence of operating temperature and LHSV on the rate of catalyst deactivation was also examined for the high metal feed. More attention was paid for the determination of the maximum metal on catalyst (MMOC) for the individual catalysts and the overall catalyst system by accelerated aging tests in a short period. MMOC is an important parameter that could be used in a simulation model together with kinetic parameters for predicting the life of ARDS catalyst systems.

2. Experimental

2.1. Materials and methods

2.1.1. Feedstock

Kuwaiti straight run atmospheric residue from Kuwait Export Crude (KEC-AR), and Boscan crude were used as feedstocks in the experiments. The KEC-AR is essentially the same feed used at Kuwaiti refineries in their ARDS units, while the Boscan feed with high metal loading was obtained from Venezuela. The main characteristics of KEC-AR, and Boscan crude feedstocks are presented in Table 1. It is seen that Boscan feed is heavier with higher content of metals (V and Ni) S, N, CCR and Asphaltenes. The total metal content of Boscan feed is almost 13 times higher than that of the KEC-AR.

2.1.2. Catalyst

A catalyst system consisting of three catalysts, namely, A, B, and C was used in this study. The same system was used previously in KNPC ARDS units. The first catalyst is (HDM) MoO_3/Al_2O_3, the second is (HDS) $NiMo/Al_2O_3$ and the third is (HDS/HDN) $NiMoP/Al_2O_3$. They were all in the form of

Table 1
Feedstock characteristics

Property[a]	Unit	KEC-AR	Boscan crude
Density @ 15 °C	g/ml	0.9774	0.9998
API gravity	–	12.84	10.22
Density @ 100 °C	g/ml	0.9265	0.9485
Kinematic viscosity @ 50 °C	cSt	765.1	3480
Kinematic viscosity @ 100 °C	cSt	57.6	172
Conradson carbon residue (CCR)	wt%	12.20	16.3
Carbon content	wt%	83.4	85.5
Hydrogen content	wt%	11	12.0
Molar H/C	–	1.58	1.68
Total sulfur	wt%	4.40	5.4
Total nitrogen	wt. ppm	2840	6120
Metals content			
V	wt. ppm	63	1180
Ni	wt. ppm	21	128
Asphaltenes	wt%	4.5	10.2
Disdistillation Simdist ASTM D-2887			
IBP		237	200
5%		335	302
10%		372	341
20%		419	391
30%		454	427
40%		488	459
50%		522	493
FBP		738	736
Volume recovery	%	54.8	63.7

[a] The accuracy in the results are ±2% for sulfur, metal, nitrogen, asphaltenes, elemental analysis and distillation, ±0.1 for API and density, and ±0.5% for viscosity measurement.

Table 2
Characteristics of the HDM, HDS and HDS/HDN catalysts

Property	Unit	HDM, A	HDS, B	HDS/HDN, C
Bulk density	g/ml	0.4–0.6	0.6–0.8	0.7–0.8
Surface area	m^2/gm	150–250	200–300	150–200
Pore diameter	–	Large	Medium	Small
Metal capacity	–	High	Medium	Low
Demetallization	–	High	Medium	Low
Desulfurization	–	Low	High/Medium	High
Denitrogenation		Low	Medium	High

extrudates. The major characteristics of the three catalysts are shown in Table 2.

2.2. Hydrotreating experimental setup for accelerated testing study

A two reactor residue hydroprocessing pilot plant unit (manufactured by ZETON technology) was used for the hydrotreating experiments. The reactors are identical, and each reactor has a total volume of 658 ml with an internal diameter of 2.8 cm. The pilot plant can be operated in different modes (e.g., parallel, series, feed upflow or downflow), according to the desired experiment. In this study, the reactors were operated in series with feed in downflow mode. The schematic diagram of the pilot plant unit is shown in Fig. 1.

Reactor 1 and reactor 2 (R1 and R2) were loaded with HDM, HDS, and HDS/HDN catalysts according to Table 3. The catalysts were diluted with an equal volume of medium size carborundum (1 mm in diameter) and charged into the reactors. The catalyst bed was placed in the reactor in such a way that it was in the mid-section of the reactor. Coarse carborundum and inert α-alumina balls were placed above and below the catalyst beds. Thermocouples inserted into a thermowell at the center of

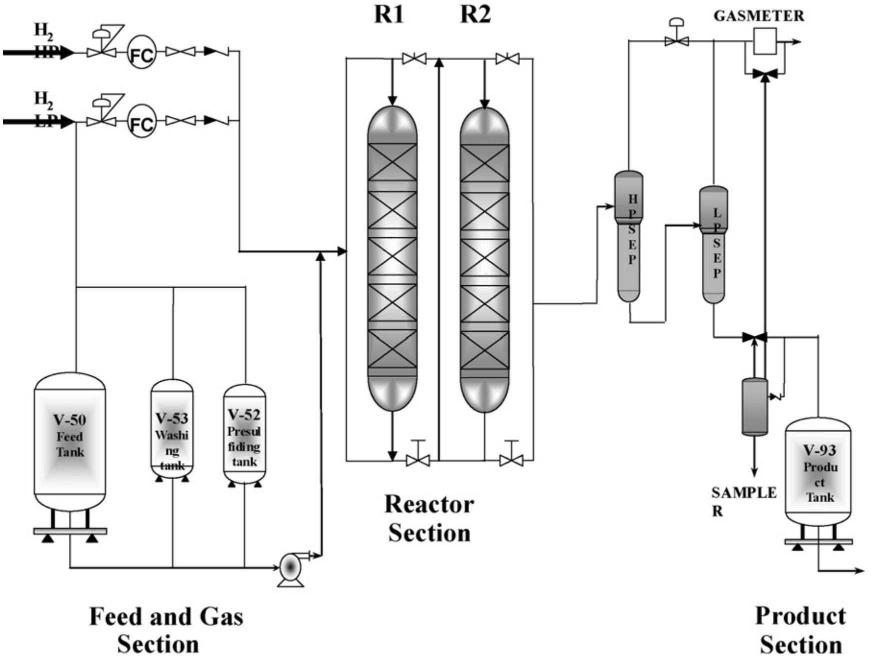

Fig. 1. Pilot plant unit schematic diagram.

Table 3
Catalysts and reactor loading

Reactor	Catalyst	Volume (ml)	Volume (%)	Weight (g)	Weight (%)
1st	HDM, A	128	38.9	61.5	30.6
2nd–first layer	HDS, B	157.7	48	107.3	53.4
2nd–second layer	HDS/HDN, C	42.7	13	32	15.9
Total		328.4	99.9	200.8	99.9

the catalyst bed were used to monitor the reactor temperature at different points.

After loading the catalyst, the reactors were fixed in place in the unit. The system was tested for leaks with nitrogen and hydrogen at high pressure (i.e., 130 bar) and then purged with nitrogen at a flow rate of 100 l/h and at 5 bar pressure. During nitrogen purging, the reactors were warmed up to 150 °C. After nitrogen purging, hydrogen was introduced into the reactor and the catalyst was then presulfided using straight-run gas oil containing 3 wt% dimethyl disulfide (DMDS) under the following conditions:

$$\mathrm{LHSV} = 2\,\mathrm{h}^{-1};\quad \mathrm{H_2/oil} = 570\,\mathrm{ml/ml};\quad \text{pressure} = 120\,\mathrm{bar};\quad \text{temperature} = 150{-}350\,^{\circ}\mathrm{C}$$

During presulfiding, the reactor temperature was increased from 150 °C to 350 °C by ramping at a rate of 15 °C/h. After reaching 350 °C, presulfiding was continued for 7 h under the stated conditions. The presulfiding feed was then stopped and the feedstock was introduced. The conditions were then adjusted to the desired operating temperature, pressure, hydrogen flow and LHSV. Table 4 shows the operating conditions used for the aging studies using AR and Boscan crude as feedstocks. After presulfiding with gas oil using standard procedures, the operating conditions were adjusted and the test run was initiated with Kuwait atmospheric residue (KEC-AR). Following 14 days of testing, Boscan crude oil was introduced for 20–45 days, depending on the operating severity (i.e. reaction temperature and LHSV) to obtain the MMOC. Atmospheric residue feed was introduced after this period for one week before the termination of the run.

During each run and after 8 h stabilization under the set conditions, liquid product from R1 and R2 were collected over a 24 h period for both reactors 1 and 2. Sulfur content of feed and product samples was determined using an Oxford 1000 sulfur analyzer. An automatic Cosmo analyzer based on IP-143 method was used to determine asphaltenes. Metals (V and Ni) were analyzed without ashing on a model Liberty series II, Inductively Coupled Plasma (ICP) equipment manufactured by Varian. Total nitrogen content of the feed and product samples was determined using an Antek 7000 elemental analyzer. Density, viscosity and CCR were determined by standard IP190 and, D-445, and micro-reactor procedures I-71, respectively. A standard D-86 method was used to determine distillation recovery.

2.3. Calculation procedures

The HDS reaction rate constant was calculated using the following nth order rate equation:

$$k = \mathrm{LHSV}(n-1)^{-1}\{S_{\mathrm{p}}^{1-n} - S_{\mathrm{f}}^{1-n}\} \quad \text{for}\, n > 1$$

where LHSV is the liquid hourly space velocity (ml/(ml h)); n is the reaction order; S_{f} is concentration of S (wt%) in the feed; and S_{p} is the concentration S (wt%) in product. In our previous studies, the reaction order was found to be 2 for HDS reaction in hydroprocessing of KEC-AR feed [23,24]. The value of 2 was used in the above equation for calculating the HDS rate constant.

2.3.1. Normalized rate constant

Actual rate constants derived from catalyst test runs are usually normalized by established catalyst testing facilities to a randomly selected temperature, which is adopted as a standard by the testing facility. This procedure enables the researchers of the facility to compare the results of various pilot plant test runs, irrespective of the temperature of the test run. In our laboratory, the selected standard temperature is 370 °C. The normalization of the rate constant is based on the Arrehenius equation. The value of the activation energy for HDS was determined through kinetics studies on individual catalysts conducted by Marafi et al. [23,24].

The maximum metals capacity of individual catalysts and total catalyst system as well as the relation between metal on catalyst and rate of HDS reaction were obtained through the accelerated deactivation test within 60 days. The information obtained in this study together with kinetic parameters and a simulation model could be used for predicting the life of ARDS catalyst systems [22].

Table 4
Run conditions for accelerated aging tests with high metal content feedstock

Feed	Temperature (°C)	P (bar)	LHSV (h^{-1})	$\mathrm{H_2}$/oil (L/L)	$\mathrm{H_2}$ flow (l/h)	Feed flow (ml/h)	Time (days)
Kuwait AR	390	120	0.28	680	62.5	92	14
Boscan crude	370 and 390	120	0.28 and 0.56	680	62.5–125	92–184	20–50
Kuwait AR	390	120	0.28	680	62.5	92	7

The procedure for determining MMOC involves first the determination of the accumulated amounts of metals (MOC) per 100 g of the catalyst for each reactor and for the total catalyst system at various periods throughout the duration of a test run. The calculations are based on the following equations:

$$\mathrm{MOC}_{\mathrm{R1}i} = \sum_{i=1}^{i=j}\{ f_{\mathrm{f}i} d_{\mathrm{f}} (t_i - t_{i-1})[(V_{\mathrm{f}} - V_{\mathrm{R1}i}) + (\mathrm{Ni}_{\mathrm{f}} - \mathrm{Ni}_{\mathrm{R1}i})]10^{-6}(100/W_{\mathrm{CA}})\}$$

$$\mathrm{MOC}_{\mathrm{R2}i} = \sum_{i=1}^{i=j}\{ f_{\mathrm{f}i} d_{\mathrm{f}} (t_i - t_{i-1})[(V_{\mathrm{R1}i} - V_{\mathrm{p}i}) + (\mathrm{Ni}_{\mathrm{R1}i} - \mathrm{Ni}_{\mathrm{p}i})]10^{-6}(100/W_{\mathrm{CB/CC}})\}$$

$$\mathrm{MOC}_{\mathrm{s}i} = \sum_{i=1}^{i=j}\{ f_{\mathrm{f}i} d_{\mathrm{f}} (t_i - t_{i-1})[(V_{\mathrm{f}} - V_{\mathrm{p}i}) + (\mathrm{Ni}_{\mathrm{f}} - \mathrm{Ni}_{\mathrm{p}i})]10^{-6}(100/W_{\mathrm{CT}})\}$$

where $\mathrm{MOC}_{\mathrm{R1}i}$, $\mathrm{MOC}_{\mathrm{R2}i}$, and $\mathrm{MOC}_{\mathrm{s}i}$ are the total metal accumulated in grams per 100 g of catalyst for reactor 1, reactor 2, and total system at time t_i; $f_{\mathrm{f}i}$ is the feed flow rate at time t_i in ml/h; d_{f} is the density of feed in g/ml; $(t_i - t_{i-1})$ is the time duration between two consecutive samples in h; V_{f}, $V_{\mathrm{R1}i}$, and $V_{\mathrm{p}i}$ are the concentrations of vanadium in ppm in the residual feed, product of reactor 1, and the final product at time t_i; Ni_{f}, $\mathrm{Ni}_{\mathrm{R1}i}$, and $\mathrm{Ni}_{\mathrm{p}i}$ are the concentrations of nickel in ppm in the residual feed, product of reactor 1, and the final product at time t_i; W_{CA}, $W_{\mathrm{CB/CC}}$, and W_{CT} are the weights of CAT-A, CAT-B and CAT-C, and the total catalyst system; 10^{-6} is the conversion factor for ppm to g; the 100 multiplier is for adjusting weight of catalyst to 100 g.

3. Results

In the initial studies, the effects of the two feeds (i.e., Boscan crude and KEC-AR) on catalyst deactivation with time-on-stream were examined. The results obtained with the conventional KEC-AR feed are presented in Fig. 2, which shows the HDS activity as a function of time-on-stream for the catalysts in each reactor, R1 and R2, as well as for the overall catalyst system (R1 + R2). The HDS activity results obtained for different catalysts with the high metal Boscan crude are presented in Fig. 3.

A comparison between the results presented in the two figures clearly indicates that catalyst activity decline is more rapid for Boscan crude than for KEC-AR. In the case of KEC-AR, the HDS activities of the catalysts in the second reactor (R2) and the over all catalyst system (R1 + R2) decrease at a relatively rapid rate during the first 500 h and then reach a steady state with stable activity for nearly 5000 h. Following this steady state, the catalyst deactivates slowly and loses about 80% of the original activity after around 8000 h on stream. The HDS activity of the HDM catalyst in the first reactor shows a different behavior with an increase during the initial period, followed by a steady state activity and a rapid decline after 6000 h on stream. For the Boscan feed, both the overall catalyst system and the catalyst in the second reactor deactivate continuously at a rapid rate losing more than 90% of their original activity within 1800 h. The HDM catalyst in the first reactor (R1) also loses >90% of its original activity during this period even though its activity increases by about 50% during the initial period. These results clearly indicate that the high metals containing Boscan crude can be used to accelerate deactivation of hydrotreating catalysts.

The amount of metals accumulated on catalysts in reactors (R1) and (R2) and on the total catalyst system (R1 + R2) during the Boscan crude hydrotreating is plotted as a function of time-

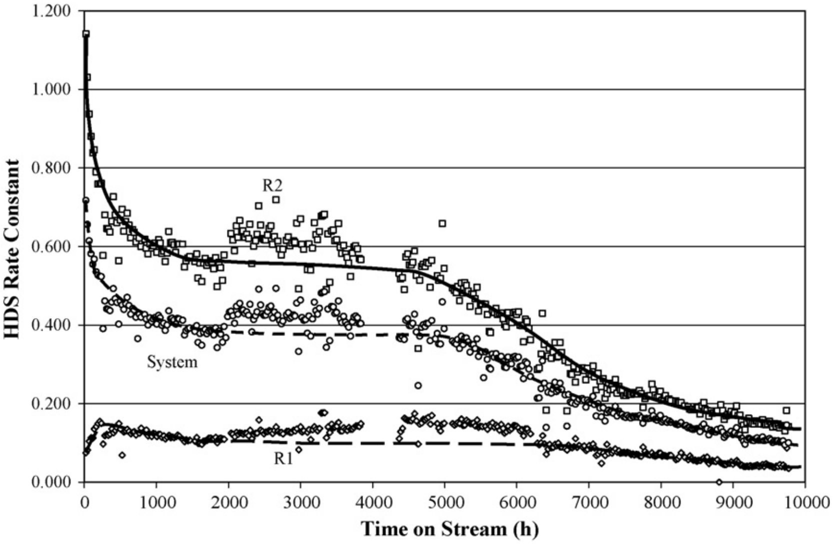

Fig. 2. Plots of normalized rate constants for desulfurization at 370 °C for reactor 1 (R1), reactor 2 (R2), and the total catalyst system for hydrotreating KEC-AR feedstock at LHSV = 0.28 h^{-1} and 370 °C.

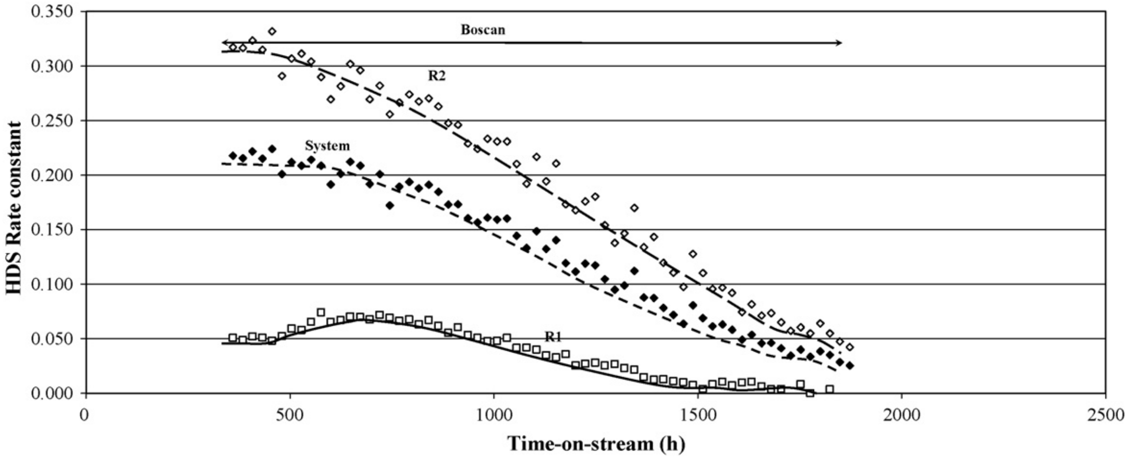

Fig. 3. Plots of normalized rate constants for desulfurization at 370 °C for reactor 1 (R1), reactor 2 (R2), and the total catalyst system for hydrotreating Boscan at LHSV = 0.28 h^{-1} and 370 °C.

on-stream in Fig. 4. It is seen that the HDM catalyst in reactor 1 has accumulated more metals than the HDS and HDS/HDN catalysts in reactor 2. The metal deposition rate on the catalyst in R1 increases linearly with a rate of 0.1 g/h till around 1200 h on-stream, and afterwards the rate decreases to 0.06 g/h. For reactor 2 (R2), the plot shows that the metals deposition rate is 0.02 g/h at start of run up to around 1200 h on-stream, and then increases to 0.03 g/h. This shows that the metals starts to spill over from reactor 1 (R1) at higher concentration at around 1200 h on-stream and indicates that the HDM catalyst is approaching its metal capacity limit. For the total system, metal deposition rate is observed to increase linearly with a rate of 0.04 g/h up to 1800 h on-stream. These results also demonstrate the HDM catalyst A has a higher metal capacity than the other catalysts (B and C) comprising the system.

In the case of hydrotreating of the regular KAR over the same catalyst system, the metal deposition rates on R1, R2 and (R1 + R2) catalyst are 0.006 g/h, 0.001 g/h and 0.003 g/h, respectively (Fig. 5). The total amounts of metals deposited on the catalysts during 1200 h of operation are, 7.2 g/h, 1.02 g/h and 3.1 g/100 g catalyst for R2 and (R1 + R2), respectively, whereas with the high metal Boscan feed, substantially larger amounts of metals are deposited on the catalysts during the same duration of operation.

In the next set of experiments, accelerated aging tests were conducted using Boscan feed at different LHSVs and temperatures keeping other parameters constant to determine the conditions that would give the maximum metal on catalyst in a shorter time. Plots of HDS rate constants (K_s) for R1, R2 and the total system (R1 + R2) vs. metal on catalyst (MOC) as shown in Figs. 6–8 were made for each run for the purpose of estimating MMOC under various operating conditions used in the present study.

The MMOC can be determined at the intersection of extrapolation of the rapid deactivation of the region at the end of run (EOR) with the *x*-axis when the catalyst activity is close to zero. Plots of HDS rate constant vs. MMOC for the catalysts in R1, R2 and the total system (R1 + R2) were trended and

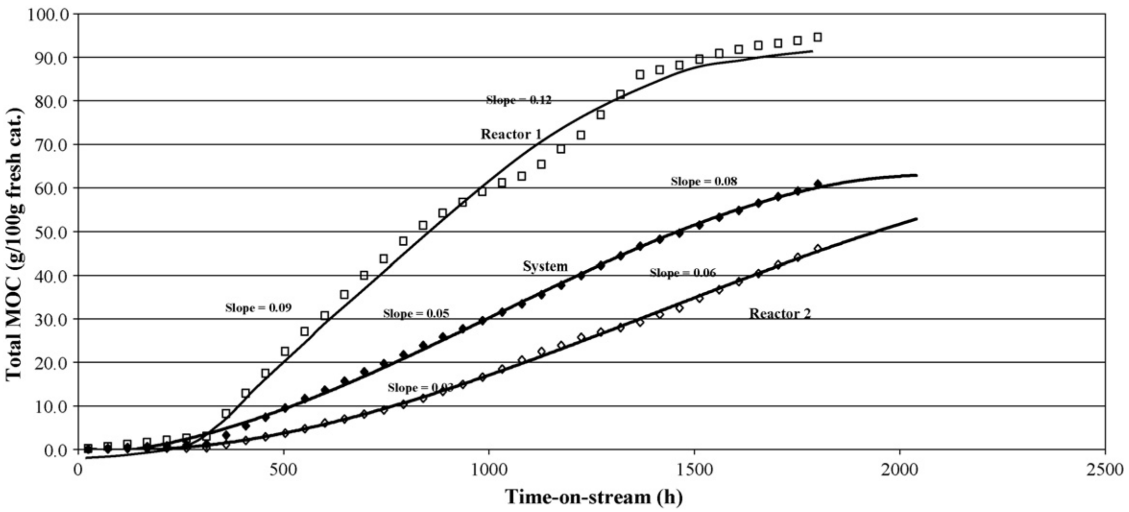

Fig. 4. Plot of metals on catalysts in reactors 1 and 2, and on the total catalyst system versus time-on-stream for hydrotreating Boscan crude at LHSV = 0.28 h^{-1} and 370 °C.

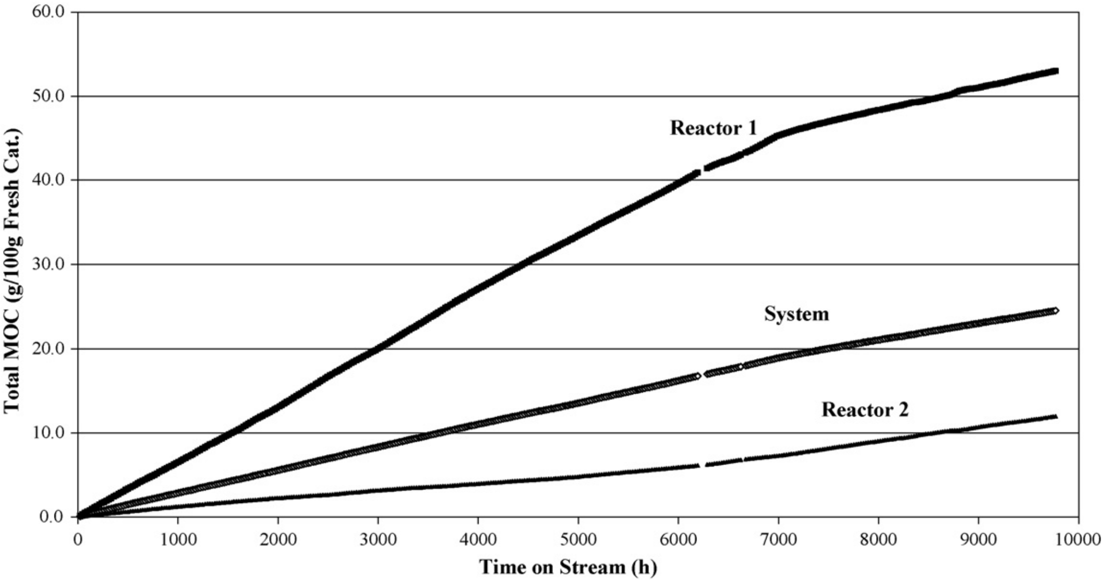

Fig. 5. Plot of metals on catalysts in reactors 1 and 2, and on the total catalyst system versus time-on-stream for hydrotreating KEC-AR at LHSV = 0.28 h^{-1} and 370 °C.

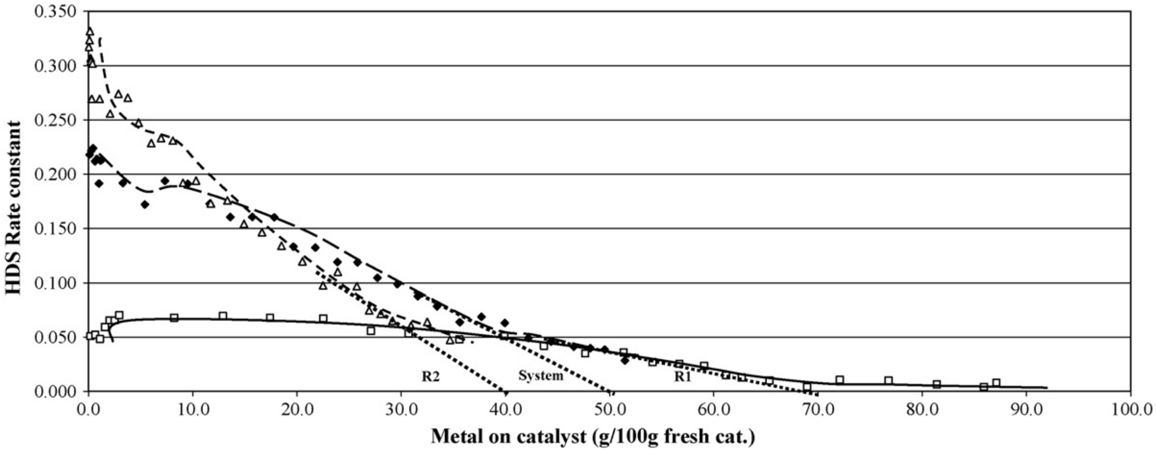

Fig. 6. Plot of hydrodesulfurization (HDS) normalized rate constant for reactors 1 and 2 (R1 and R2) and the total catalyst system versus metal-on-catalyst (MOC) of each catalyst bed for hydrotreating Boscan at LHSV = 0.28 h^{-1} and 370 °C.

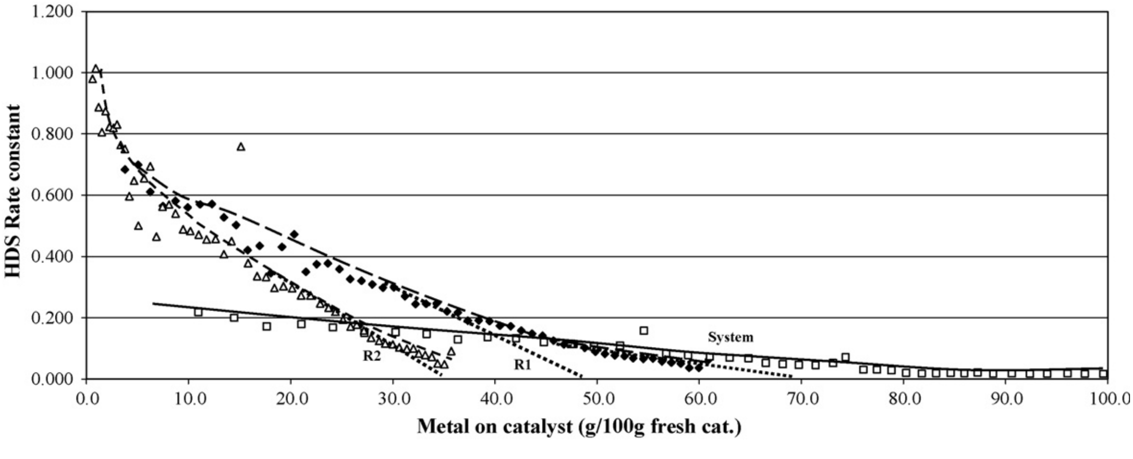

Fig. 7. Plot of hydrodesulfurization (HDS) normalized rate constant for reactors 1 and 2 (R1 and R2) and the total catalyst system versus metal-on-catalyst (MOC) of each catalyst bed for hydrotreating Boscan at LHSV = 0.28 h^{-1} and 390 °C.

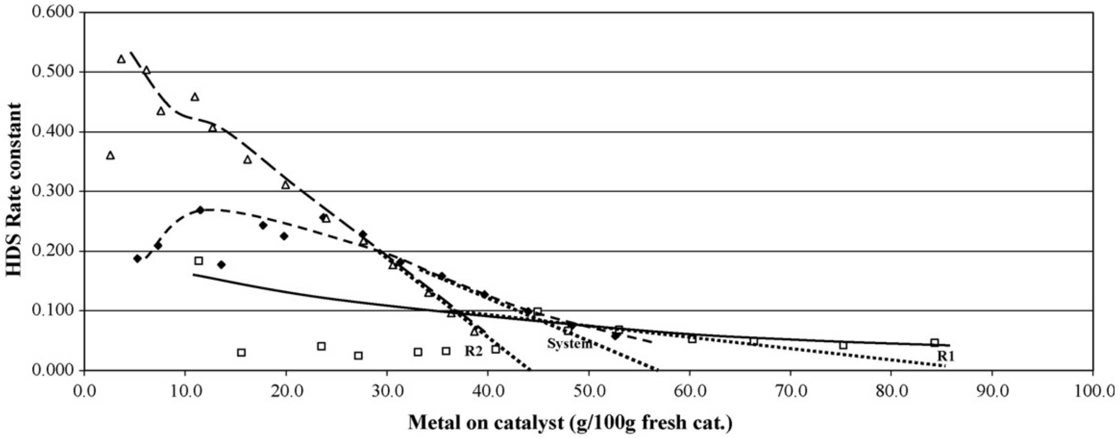

Fig. 8. Plot of hydrodesulfurization (HDS) normalized rate constant for reactors 1 and 2 (R1 and R2) and the total catalyst system versus metal-on-catalyst (MOC) of each catalyst bed for hydrotreating Boscan at LHSV = 0.56 h^{-1} and 390 °C.

extrapolated to intersect the *x*-axis as shown in Figs. 6–8 to obtain values for MMOC_{R1}, MMOC_{R2}, and $\text{MMOC}_{\text{R1+R2}}$, respectively.

MMOC values obtained for the runs conducted at different temperatures and LHSVs are summarized in Table 5. The results show slight variation in the MMOC values when different operating conditions are used. Although the MMOC depends to a large extent on the physical characteristics of the catalyst system for a given feedstock, higher severity operating conditions (i.e., high temperature or higher LHSV) lead to further acceleration of catalyst deactivation giving reasonable MMOC values in shorter operating period (within 45–50 days).

4. Discussion

Catalyst deactivation in residual oil hydrotreating process is caused primarily by continual build up of metal deposits within the catalyst pores. The capacity of a catalyst for metals accumulation is an important parameter in determining its stability and life. The deposited metals can block the pores and restrict the access of the feed molecules to the catalytic site. If the catalyst has a large capacity to accumulate the metals, they will be distributed more uniformly through the pore network and as a result, it will deactivate at a shown rate and provide a greater useful bed life. The extent of metal deposition on the catalyst has been used as an index of catalyst age in a many studies. Metal capacity of catalysts have been used together with kinetic data, initial activities and the deactivation behavior by many researchers for developing models for predicting the deactivation of residue hydrotreating catalysts [25–31].

Reviews of the model development, assumptions made, and mathematical formulations for various models were discussed recently by Kam and co-workers [22,30]. Subsequently, a model based on the pore-filling by metal deposits, was developed by these authors for deactivation of residue hydrotreating catalysts. Measurement of the maximum metal capacity of the individual catalysts and the total catalyst system by short duration tests is, therefore, an important requirement for predicting the performance of residue hydrotreating catalysts.

In the present study, the maximum metal capacity of different catalysts (e.g., HDM, HDS and HDS/HDN) used for residual oil hydrotreating was determined by normal and accelerated aging tests. The tests were conducted in a multi reactor pilot plant using a high metal feedstock (Boscan Crude) for deactivating the catalyst at a faster rate. The results revealed the following:

- Catalyst deactivation rate is more than five times faster for the high metal Boscan feed than the conventional KEC-AR feed.
- Operating at higher LHSVs and lower temperatures results in higher metals uptake by the catalysts.
- Maximum amount of metals deposited on the HDM catalyst in reactor 1 (R1) is substantially large than that on the HDS and HDS/HDN catalysts in reactor 2 (R2).
- It is possible to determine MMOC of an ARDS catalyst system within 45–50 days by accelerated deactivation test using a high metal feed (e.g., Boscan crude).

The results showed a higher rate of deactivation for the Boscan crude compared to KEC-AR. The values of

Table 5
MMOC g/100 g of fresh catalyst at different reaction condition using Boscan feedstock for accelerated test

MMOC/TOS	Temperature 370 °C and LHSV = 0.28 h^{-1}	Temperature 390 °C and LHSV = 0.28 h^{-1}	Temperature 390 °C and LHSV = 0.56 h^{-1}
Time-on-stream with Boscan (days/h)	61 (1464)	52 (1264)	24 (564)
MMOC, reactor 1, catalyst A	70	68	85
MMOC, reactor 2, catalysts B and C	40	34	45
MMOC, total system	50	48	55

0.00096 k_{HDS}/day for KEC-AR feed, and 0.0048 k_{HDS}/day in the case of Boscan are found with a ratio of 5:1 (Figs. 2 and 3). This is not unexpected since the Boscan crude has 13 times higher metals content than the KEC-AR. Howel et al. [32] compared the relative catalyst life of a typical HDS catalyst for processing a high metals ($V = 370$ ppm) Maya residue and a low metals ($V = 103$ ppm) Arabian heavy residue, and found that the rate of catalyst deactivation was significantly faster and the catalyst life was about 70% shorter for the Maya residue. Miyauchi and de Wind [33] studied the effect of metals in the feed on the cycle length of a catalyst system consisting of three types of catalysts. Three feedstocks with different levels of metals (140 ppm, 85 ppm and 65 ppm) were used in the study. The results showed that the amount of metals present in the feed strongly affected the catalyst cycle length. Whereas a cycle length 400 days could be achieved with 65 ppm metals containing feed, only 165 days were possible with 140 ppm metals in the feed. The results of our studies with Boscan crude are consistent with the above findings.

The rapid loss of activity can be attributed to both the obstruction of catalyst pores by deposited metals and the chemical changes that occur when the deposited metals interact with the original active sites on the catalyst. During the course of operation with Boscan crude, the HDM catalyst in the first reactor has accumulated 85 wt% and the total catalyst system in both reactors has accumulated 55 wt% metal (V + Ni) deposits. Obviously such massive loadings must have a serious effect on the pore structure of the catalyst and the ability of large molecular species in the residual oil feed to diffuse freely through the pores.

Deposition of a substantially larger amount of metals on the HDM catalyst in reactor 1 (R1) than on the catalysts in reactor 2 (R2) can be primarily due to its location in the process unit as well as to its high porosity. The metals containing feed first enters reactor 1 (R1), and passes through the catalyst bed in the reactor before entering the second reactor. In the first reactor, where the feed comes into contact with the catalyst first, hydrodemetallization reactions begin to occur and the metals (V + Ni) removed from the feed start depositing on the catalyst surface. As more and more feed is processed, more and more metals continue to deposit on the catalyst. Accumulation of the metals causes deactivation of the catalyst in the first reactor. As a result, the metals and the other impurities present in the feed come into contact with the catalyst in the next reactor in the series, and the metals start depositing on the catalyst in this reactor. With increasing processing time, the activity of the catalyst in this reactor also declines due to the accumulation of the metals.

The capacity a catalyst for metals uptake depends on its pore size and initial activity. These parameters determine the diffusion rate and the chemical reaction rate of metals containing molecules [34,35]. The HDM catalyst in the first reactor has large pores. It contains low concentrations of Mo (3–4 wt%) without any Co or Ni promoters, and as a result it has a low intrinsic activity. The ratio of diffusion rate to reaction rate will be high for such catalysts. Consequently, the metal bearing molecules will diffuse deeper into the pores and the metal deposits will be formed throughout the pore network. The HDS/HDN catalysts in the second reactor have narrow pores and have high intrinsic activity for promoting all hydrotreating reactions including HDM. In the narrow pore catalysts, the diffusion rate is low, and due to the high activity the HDM reaction rate is high, and as a result, the ratio of reaction to diffusion rate will be high. Hence the metals containing molecules will react as soon as they enter the pores depositing more metals near the pore mouths. The entire pore network will not be available for metals deposition in these catalysts. In consequence, they have low metals capacity.

The severity of the operating conditions used for the accelerated aging test was also found to influence the rate of catalyst deactivation and the MMOC. Operating at higher temperatures resulted in an overall reduction in the amount of total metals deposited on all catalysts. Increasing the feed flow (LHSV) increased the MMOC. Since increasing reaction temperature increases the HDM reaction rate, the ratio of reaction rate to diffusion rate will increase leading to the deposition of more metals on the outer edge of the catalyst. This will lead to rapid plugging of pore mouths and reduce the effectiveness factor. The internal pores of the catalysts will not be utilized for metals absorption when pore mouth plugging occurs, and consequently, the catalyst's capacity for metals uptake and the MMOC will be reduced.

At higher LHSVs, more metals enter the reactor since the feed flow is higher, but at the same time, the contact time between the feed molecules and the catalyst surface will be low. Consequently the HDM reaction rate will decrease and a uniform distribution of the metals with in the catalyst pellet will occur due to increased diffusion and slower HDM reaction rate. As a result higher MMOC can be expected at higher feed flow rates. In a previous study [36], the amount of metals deposited on the catalyst was found to increase progressively with increasing space velocity during hydroprocessing of Kuwait vacuum residue. Operating at high flow rates and high temperature could increase both diffusion and reaction rates and lead to the deposition of larger amount of metals in a shorter period.

5. Conclusions

In the present work, an accelerated aging test method was developed for evaluating metal capacity of ARDS commercial catalyst system consisting of three catalysts, namely, HDM (A), HDS (B) and HDS/HDN (C) using a multireactor pilot plant unit. A feedstock with high metals content, namely Boscan crude, was used for the tests to cause complete deactivation of the catalyst due to metal accumulation in a shorter period. The influence of operating temperature and LHSV on the rate of catalyst deactivation was also examined for the high metal feed. More attention was paid for the determination of the maximum metal on catalyst for the individual catalysts and the overall catalyst system by accelerated aging tests in a short period.

- Catalyst deactivation rate is more than five times faster for the high metal Boscan feed than the conventional KEC-AR feed.
- Operating at higher LHSVs and lower temperatures results in higher metals uptake by the catalysts.

- Maximum amount of metals deposited on the HDM catalyst in reactor 1 (R1) is substantially large than that on the HDS and HDS/HDN catalysts in reactor 2 (R2).
- It is possible to determine MMOC of an ARDS catalyst system within 45–50 days by accelerated deactivation test using a high metal feed (e.g., Boscan crude).

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