Hydrotreatment of two atmospheric residues from Kuwait Export and Lower Fars crude oils

Taegon Kim [a], Adel Al-Mutairi [b], Abdulazeem M.J. Marafi [b], Joo-Il Park [a,*], Hiroki Koyama [c], Seong-Ho Yoon [a], Jin Miyawaki [a], Isao Mochida [a]

[a] *Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka 816-8580, Japan*
[b] *Petroleum Refining Department, Petroleum Research & Studies Center, Kuwait Institute for Scientific Research, PO Box 24885, Safat 13109, Kuwait*
[c] *Advanced Refining Technology KK, 3-17-35 Niizo-Minami, Toda, Saitama 335-8502, Japan*

HIGHLIGHTS

- The performance on hydrotreatment of LFC- and KEC-AR was investigated over.
- Two ARs showed different reactivities on S-species (rate constant, activation energy).
- Demetallization processes progress very similarly, regardless of the AR and metallic species.

GRAPHICAL ABSTRACT
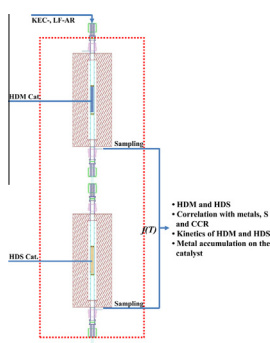
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ABSTRACT

Hydrodesulfurization (HDS) and the hydrodemetallization (HDM) of vanadium and nickel (HDV and HDNi) of two Kuwaiti atmospheric residues (ARs) from contrasting crudes (Kuwait Export, KEC; Lower Fars, LFC) were compared using the same commercial HDM and HDS catalysts in two stage flow reactors (HDM, first stage; HDS, second stage) under 18.5 MPa of H_2 at 370–395 °C. The catalysts were stabilized by passing KEC-AR for 600 h.

The kinetic parameters of HDS, HDV, and HDNi were analyzed with the removal of sulfur and metals assumed to be 1.0 and 1.2 orders of reactions, respectively, in both reactors. The calculated rate constants were fitted to Arrhenius plots with reasonable linearity. The rate constants of HDS were similar in the first stage, whereas the rate constants of KEC-AR were certainly higher than that of LFC-AR in the second stage. HDS proceeded more rapidly over the HDS catalyst of the second reactor, but the activation energy was higher. The reactive sulfur species of both ARs were removed at similar rates in the first stage, and the differing refractory sulfur species of the two ARs were removed in the second reactor. HDV and HDNi of both ARs appear to progress similarly in both reactors, but the activation energy is higher in the second reactor. Demetallization appears saturated in the second reactor at higher reaction temperatures. Similar HDV and HDNi reactivities between the ARs suggest they share a similar mechanism in which the petro-porphyrins must first be liberated from the asphaltene moieties of ARs and be exposed to the catalyst surface. This mechanism indicates that the most refractory metal species require higher activation energies before they are extracted as metal sulfides.

The metal accumulation on HDM catalyst suggests that HDV and HDNi share similar reactivity, which contradicts previous notions. The discrepancy may be due to this study's focus on the initial stage of the run.

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* Corresponding author. Tel.: +81 92 583 7633; fax: +81 92 583 7640.
  E-mail address: parkjoo9@asem.kyushu-u.ac.jp (J.-I. Park).

1. Introduction

The demand for petroleum products is still growing in response to the increasing automotive and industrial needs of rapidly developing countries. Consequently, petroleum exploration and production companies are expanding their efforts, which results in the increased production of heavier and more contaminated crude oil [1–4]. As a potential first step toward refining these crudes for use in power generation and generating sulfur-free fuels for domestic transportation, their atmospheric residues (ARs) can undergo hydrotreatment. These ARs often carry larger amounts of sulfur, vanadium, and nickel in their crudes, and some crudes are rich in nitrogen. Therefore, it is very important to clarify these contaminants' reactivities, catalyst dependence, and deactivation and metal deposition profiles with respect to the hydrotreatment reactions [5–12]. Li et al. reported that HD-Ni over NiMo/γ-Al$_2$O$_3$ catalyst synthesized by one-pot method with controlled precipitation of precursors using urea and ammonium carbonate as additives, and show the influence of urea/Al parameter on catalysts to HDM reactivity [5]. CoMo catalysts supported on the various support materials (Al, Al–Ti, Al–Si, C) as heavy crude oil hydroprocessing catalysts have been studied for the early stage of deactivation by Maity et al. [6]. In addition, Marafi and Stanislaus reviewed the spent catalyst waste management and reported the real example through preparation of heavy oil hydrotreating catalyst from spent residue hydroprocessing catalysts [7,8]. They also reported the comparative study of HDM and HDS catalyst with the different heavy feeds [9,10]. Interestingly, the comparative investigation on heavy oil hydroprocessing catalysts according to reactor type was studied by Rana et al. [11]. Long et al. showed the mechanistic behaviors on initial decay of HDM catalyst, which was very important to understand the phenomena of metal adsorption on the catalyst [12].

A more direct comparison can be made between the performances and behaviors of ARs from contaminated crudes when the same catalyst is used [13–15]. Kinetic and catalytic characterizations can further clarify their reactivity and quality. We expect the kinetic parameters of these feeds and catalysts to correlate well with their structural analyses.

In the present study, two hydrotreated ARs from the crudes of Kuwait Export (KEC) and Lower Fars (LFC) were tested in a flow reactor set up that consisted of hydrodemetallization (HDM) and hydrodesulfurization (HDS) reactors. The catalysts were stabilized under a flow of KEC-AR feed (600 h), and LFC-AR and KEC-AR were tested while varying reaction temperatures to compare their reactivities for HDS, HDM (removal of vanadium and nickel), and hydrodenitrogenation (HDN) over the HDM (1st reactor) and HDS (2nd reactor) stages with all other condition remaining the same.

The kinetic results in the first and second reactors were analyzed with respect to each of their reaction orders. HDS of ARs has often been assumed to follow a 1.5 order, which should describe the reaction progressions of reactive and refractory sulfur species in a single kinetic equation. However, our study applied two stages, thus it may be adequate to assume first order with the respective reactions in the 1st and 2nd reactors. HDM has often been considered first order, but we currently postulate a higher order due to the formation of metal sulfides from multiple porphyrin molecules that appear to participate in this reaction, which are revealed by the effects of a favorable H$_2$S presence.

The rate constants are calculated based on a series of reaction temperatures, and they are plotted according to the Arrhenius equation to determine the activation energy for the respective reactions taking place in each reactor. We evaluate the assumed

reaction orders in accordance with their linearity in the series of plots. We further discuss the reactivities of the two ARs in terms of their rate constants and activation energies in each reactor with an aim to correlate these findings with those of their molecular analyses.

Concerning the hydrotreatment of ARs from heavier crudes, the HDM reactivity and catalytic roles are two of the most critical aspects to consider; therefore, we analyzed used catalysts to clarify the metal deposition profiles (particularly at the initial stage of the hydrotreatment). It is also important to compare the reactivity of V and Ni complexes in AR when designing HDM reactors and determining effective catalysts for processing heavily contaminated crude oil. V is often considered more reactive than Ni thus it is preferentially deposited on the catalyst surface. Kinetic analysis and metal deposition in HDM are expected clarify our understanding of these processes.

2. Experimental

2.1. ARs and catalysts

Kuwait Export (KEC) and Lower Fars (LFC) crudes were distilled under atmospheric pressure to their respective distillates and residues, and their atmospheric residues (360 °C) were tested. The crude fractions, their yields as well as basic properties of ARs are summarized in Table 1. The commercial HDM and HDS catalysts were supplied from ART (Advanced Refining Technologies Co.). The results of characterization cannot be disclosed because of the confidential problems.

2.2. The reaction conditions and analyses

Two-stage flow reactors with fixed catalyst beds were applied to the HDM and HDS treatments of ARs. The HDM and HDS catalysts were packed into the containers of the 1st (120 mL) and 2nd (180 mL) reactors, respectively. The test conditions are summarized in Table 2. The reaction temperatures of the 1st reactor (HDM) were set at 371.9–392 °C, and the temperature of the 2nd reactor (HDS) was maintained at 5 °C higher than that of the 1st reactor to observe the temperature dependence of the HDM and HDS rates. Total sulfur of feedstock and hydrotreated products was determined by Ultra-Violet fluorescence method and total nitrogen was measured by chemical luminescence method (TS-100V, Mitubishi Chemical Analytech Co. Ltd.). The concentration of V and Ni in the feeds and products were determined by ICP–MS (SPS 1700 HVR).

Table 1
Physical properties of atmospheric residues from two Kuwaiti crudes.

	KEC-AR	LFC-AR
Density(g/ml)	0.9808	1.0292
Sulfur (wt%)	4.748	6.611
Nitrogen (wt ppm)	2980	3431
Nickel (wt ppm)	20.5	44.0
Vanadium (wt ppm)	68.5	162.0
Total Ni & V (wt ppm)	89.0	206.0
Conradson Carbon Residue (wt%)	12.3	16.6
TBP of Crude Oil (wt%)		
IBP-260 °C	29.8	15.1
260–340 °C	12.1	11.1
340–350 °C	1.5	1.7
350–360 °C	1.7	1.8
Residue (360 °C+)	52.3	69.2