



Behaviors of metal compounds during hydrodemetallization of atmospheric residue



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ABSTRACT

Behaviors of vanadium and nickel species during hydrodemetallization (HDM) were studied. A Kuwait atmospheric residue and its hydrodemetallized products from a pilot plant at mild and severe reaction conditions were characterized by using GPC coupled with ICP-MS and high temperature GC-AED after separation of them into saturates, aromatics, resins, and asphaltenes. It was found that the HDM reactivity of the vanadium species, especially those with lower molecular weight, was higher than that of Ni species, probably due to the higher polarity of the former than the latter. HDM of the vanadium species in the asphaltene was more difficult than that in the resin. The average molecular weight of metal species through higher temperature HDM was higher than that through the lower temperature HDM, although the metal removal at the higher temperature is higher.

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Introduction

Hydrodemetallization (HDM) reaction is a primary challenge for hydrotreating atmospheric residue (AR) to remove vanadium and nickel (Hydrodevanadium; HD-V, Hydrodenickel; HD-Ni) [1]. The metal compounds in AR are removed after the decomposition of metal-containing molecules around or within catalyst pores. Subsequent removal of metal compounds from the coordinated forms in porphyrins and analogous ligands is performed through two routes [2]:

1. Stepwise ring-opening of the cyclic ligand, leading to the liberation of the metal ion onto the HDM catalyst.
2. Direct extraction of metal ion from the complex onto the HDM catalyst.

Recently, many commercial units have been designed on the basis of the capacity of the catalysts to hold metal compounds. However, the accumulation of carbon as well as metal sulfides depositing on the catalyst also results in the deactivation of the

HDM catalyst, leading to a high operating cost [3–6]. Therefore, it is desired to design an effective HDM catalyst based on the better understanding of the structure and distribution of the metal species in AR as well as their behavior in HDM.

The HDM behaviors of vanadium and nickel species have been studied with various methods and measurement. Generally, these studies have been classified into two approaches, study by using model reactions (metal porphyrin) [7–12] and directly using real atmospheric and vacuum residues. However, the model reactions cannot represent the real and/or practical HDM behavior, as they are affected by large amounts of the coexisting hetero-atom-containing compounds, such as S, N, and O-compounds. The HDM behavior in a real oil system is also not easy to be clarified due to the limitation of the current analysis methods [13].

In 2015, Liu et al. reported their study of vanadium behavior during HDM using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with electrospray ionization (ESI) method (positive), in which they showed the molecular formula of $C_nH_mN_4V_1O_1$ and $C_nH_mN_5V_1O_2$ species under extraction solvents of methanol and dimethylformamide (DMF), respectively [14]. This effort is quite challengeable, but still remaining the limitation of the analysis to get nickel porphyrins and non-porphyrinic metal (vanadium and nickel) compounds, even though the residue feed and products were pretreated through the detail fractionation.

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Generally, nickel porphyrins are not easy to be ionized in this application, compared with vanadium porphyrins [14]. In addition, there is no reference about the extraction of metals from non-porphyrinic metal complexes, so far. The fractionation information that they reported is very desirable to consider as a reference of vanadium porphyrins. However, it should be necessary to develop a fractionation method for the nickel porphyrins and also to characterize the non-porphyrinic unit of metal species in real feed and product of AR.

Recently, our research group preliminarily characterized the metal complexes of porphyrinic and non-porphyrinic units in saturate, aromatic, resin, and asphaltene (SARA) of Kuwait ARs using gel permeation chromatography connected with inductively plasma mass spectrometer (GPC-ICP/MS) and gas chromatography-atomic emission detector with high temperature injector (HT GC-AED) [15]. Though the study could not suggest the detailed molecular formula, outlines of the metal species have been successfully clarified. However, these characterizations are much valuable for discussing the behavior of the metal complexes during HDM.

In order to clarify the behaviors of metal species in HDM, an AR from a Kuwait heavy crude was hydrodemetallized under mild and severe reaction conditions with different temperature, and the feedstock and the hydrodemetallized products were separated into SARA, and then analyzed by GPC-ICP/MS and HT GC-AED. The previous study [15] was only focused on the feed ARs using the same analytical methodology. In the present study, the distributions of the metal species in the feedstock and products were compared, and their behaviors within HDM were investigated.

Experimental

Hydrodemetallization (HDM)

The AR feed was from a heavy Kuwaiti crude (Crude-D in the previous study [15]), and the properties of which were characterized and listed in Table 1. HDM of AR was carried out in a flow fixed-bed reactor (Pilot Scale) [16]. A commercial HDM catalyst (120 ml) from Advanced Refining Technologies Co., (ART-Japan) was used. The results of the catalyst characterization cannot be disclosed because of the confidentiality agreement. The test conditions are summarized in Table 2. The product oils were signed as P-M (product under mild condition with lower temperature) and P-S (product under severe condition with higher temperature).

SARA separation and characterization

P-M and P-S samples were separated first into maltene (heptane-soluble), asphaltene (toluene-soluble and heptane-insoluble), and coke (toluene-insoluble). Saturate, aromatic, and

Table 1
Reaction conditions.

	Unit	Condition
Pressure	MPa	18.5
LHSV	h ⁻¹	0.22
H ₂ gas	L/h	33
H ₂ /oil	L/L	500
Temperature	°C	360–380

resin were obtained from the maltene (ASTMD 4124-97) using the neutral alumina column, as described in one of our previous papers [15].

GPC, GPC-ICP/MS, and HT GC-AED were used for characterization of the product samples, following the same procedure as described in the previous paper [15].

Results and discussion

Samples into SARA

The mass balances (wt%) of SARA from the AR feed and products are summarized in Table 1. During HDM, amounts of resin and asphaltene compounds decreased significantly, while the amount of saturate compounds as an anti-solvent [17] increased by about two times. The increase of the aromatic compounds appears to be favored by hydrogenolysis of asphaltene (12.1–4.9 wt%). Asphaltene compounds are mainly converted into resin, aromatic, and saturate compounds at the lower temperature, and then resin and aromatic compounds are converted further to saturate. A slight increase of asphaltene amounts at the higher temperature (4.9 → 5.2) might be attributed to coupling of some refractory asphaltene molecules with other chemical species.

GPC profiles of samples

Fig. 1 shows the profiles of relative molecular weight distribution for AR feed and product oil samples (P-M, P-S). According to the GPC profiles the molecular weight of P-M shifted to lower molecular weight range, implying hydrogenolysis of the AR feed. The profiles of P-S obtained at the higher reaction temperature showed relatively narrower molecular weight range and a little bit shift to higher molecular weight range, compared to P-M, which might be attributed to the easier reaction of the molecules with lower molecular weight (decomposition of lighter molecules), and simultaneously some coupling reaction of the refractory molecules.

GPC results of SARA fractions from the AR feed, P-M, and P-S are profiled in Fig. 2. HDM at lower temperature (P-M) results in the reduction of molecular weight of asphaltene. In addition, HDM at

Table 2
Basic properties of AR feed and mass balances of SARA fractions.

Feed information [15]							
Unit	TBP cut range °C	Yield on crude wt%	Yield on crude vol%	Density at 15 °C g/ml	Gravity API	CCR wt%	Pour point °C
AR (Kuwait Crude-D)	+360	66.6	71.1	0.981	12.8	11.8	–
SARA information							
AR	Component (wt%)						
	Saturate	Aromatic	Resin	Asphaltene			
AR (Kuwait Crude-D) [15]	16.1	35.1	36.7	12.1			
P-M	22.1	39.9	33.1	4.9			
P-S	35.0	33.4	26.3	5.2			

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