

# STRUCTURAL ANALYSES OF PETROLEUM ASPHALTENES AND RESINS AFTER HDM AND SUBSEQUENT HDS TREATMENTS

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## Introduction

In our laboratory, we are developing a new two-stage process for upgrading petroleum residues, which consists of a slurry phase in the first stage and a fixed bed in the second stage. In this new process, the catalyst life in the second stage is one of the keys and its elongation is an important subject. Thus far we have been investigating the effects of operation conditions in the first stage on the fouling at the middle of run for the catalysts in the second stage, using a quasi two-stage process, *i.e.*, hydrodemetallization (HDM) and hydrodesulfurization (HDS) [1]. Consequently, we found followings: (i) a minimum fouling rate of the HDS catalysts existed around 400 °C of HDM temperature, (ii) the HDS catalysts were deactivated predominantly by coke rather than metals under the present conditions and (iii) effect of substances soluble in light gas oil (soft coke) on HDS catalyst deactivation could not be negligible under certain HDM reaction conditions.

In order to further understand the coke deactivation and to obtain a certain index which reflects coke deactivation, characterization of asphaltenes was performed since asphaltenes are likely to form coke and cause catalyst deactivation in resid hydrotreatings [2-4].

In this study, structural changes of asphaltenes after HDM and HDS treatments were examined, especially paying an attention to the change of polycondensed aromatic skeletons. In addition, resins were also characterized because some parts of resins might act as the soft-coke. We report the results of above characterization.

## Experimental

Both HDM ( $\text{Mo}/\text{Al}_2\text{O}_3$ ) and HDS ( $\text{NiCoMo}/\text{Al}_2\text{O}_3$ ) catalysts were commercially available and supplied from a Japanese catalyst company. HDM treatments were carried out with a fixed-bed reactor using Kuwait atmospheric residue (KW-AR; S = 4.45 wt%, Ni/V = 20/61 ppm) as a feed under the following conditions; temperature 370 - 430 °C, pressure 14 MPa, LHSV 0.5 h<sup>-1</sup>, H<sub>2</sub>/Oil 2000 scfb. HDS treatments were subsequently conducted using the HDM product oils as feeds; temperature 390 °C, pressure 8 MPa, LHSV 0.5 h<sup>-1</sup>, H<sub>2</sub>/Oil 5000 scfb.

Asphaltenes were isolated from the HDM and HDS product oils as *n*-heptane-insoluble and toluene-soluble substances. Resins were separated from maltene by column chromatography.

LD-MS measurements were performed with Thermoquest Co., Ltd. Vision 2000 Spectrometer using angiotensin as a calibration standard. The details on the measurement were described elsewhere [5]. From the LD-MS measurement, we can obtain a molecular weight distribution as well as an average molecular weight (*M<sub>n</sub>*). <sup>1</sup>H and <sup>13</sup>C-NMR spectra (TMS base) were recorded on a JEOL JNM-

LA400 in a gated proton decoupled mode. Chromium acetylacetonate was added to obtain quantitative  $^{13}\text{C}$ -NMR spectra. The assignments of chemical shift range for  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were made according to the literature [6-9].

The structural parameters listed in Table 1 for asphaltenes and resins were obtained with the data from  $^1\text{H}$  and  $^{13}\text{C}$ -NMR, LD-MS and elemental analyses, referring to the method by other workers [7-9]; In brief,  $C_s$ ,  $CCH_3$ ,  $Cn-ar$  and  $Coher$  were directly obtained from  $^{13}\text{C}$ -NMR, and  $Cus$  from  $^1\text{H}$ -NMR with the combination of elemental analyses data. Then,  $Cint$ ,  $Cout$ ,  $Csub$ ,  $Ra$  and  $n$  were calculated using above parameters.

## Results and Discussion

### 1. Structural change of asphaltenes and resins after HDM treatment

Figure 1 shows the LD-MS spectra of asphaltenes after the HDM treatment with different temperature. A significant difference was observed in the molecular weight distribution; the shape of the broad band tailing to 5800  $m/z$  was almost the same below 400  $^\circ\text{C}$ , while it became polydispersed above 400  $^\circ\text{C}$ . Especially, two peaks at 600 and 1100  $m/z$  are clearly seen when HDM temperature is 430  $^\circ\text{C}$ . On the other hand, the molecular weight distribution of resins became narrow as the HDM temperature increased. The  $Mn$  for asphaltenes and resins monotonously decreased with HDM temperature.

Variation of structural parameters for asphaltenes and resins with HDM temperature was described in Figure 2. The aromaticity ( $fa$ ) of asphaltenes and resins changed with HDM temperature in a similar manner; the  $fa$  was almost unchanged up to 400  $^\circ\text{C}$  and steeply increased above 400  $^\circ\text{C}$ . For asphaltenes, the  $Csub$  began to decrease around 400  $^\circ\text{C}$  while the  $Ra$  and  $n$  remained. For resins, on the other hand, the  $n$  decreased with HDM temperature without remarkable changes in  $Ra$  and  $Csub$ . These observations lead to the conclusion that the steep increase of  $fa$  for asphaltenes and resins is due to the decrease of the number of alkyl side chains and to the shortening of them, respectively. Variations of internal quarternary aromatic carbon ( $Cint$ ) and outernal one ( $Cout$ ) give us useful information on the aromatic skeleton. For asphaltenes, an increase of  $Cint$  from 10 to 17 and a decrease of  $Cout$  from 21 to 17 were observed with an increase of HDM temperature up to 410  $^\circ\text{C}$ , indicating the structural change of the aromatic skeleton from cata- to peri-type. It might be because of the difference in the reactivities of cata- and peri-type polycondensed aromatics that this structural change appeared.

### 2. Structural change of asphaltenes and resins after HDS treatment

In our previous study, an increase in the fouling rate of HDS catalysts was observed when HDM temperature was raised from 390 to 400  $^\circ\text{C}$ . It is, therefore, of interest to examine the structural changes of asphaltenes and resins by the HDS treatment. Variations of  $fa$  and  $Ra$  before (B) and after (A) the HDS treatment were shown in Figure 3. In this figure, the symbols,  $As$  and  $Re$ , indicate asphaltenes and resins, respectively, and the number is an HDM temperature. By the HDS treatment, the aromatic ring number ( $Ra$ ) for asphaltenes increased while that for resins slightly decreased. This indicates that condensation reactions are more likely to occur for asphaltenes than resins during HDS treatments. Although significant difference by the HDM temperature was unfortunately not detected in the structural parameters, the LD-MS measurements for asphaltenes showed the clear difference: when the HDM temperature was 390  $^\circ\text{C}$ , the  $Mn$  and molecular weight distribution were almost unchanged while 410  $^\circ\text{C}$ , the  $Mn$  increased by HDS treatment and heavy fractions which were not detected before

the HDS treatment were observed, indicating that condensation reactions took place. Such condensation reactions of asphaltenes could cause the coke deactivation of HDS catalysts.

### Conclusions

Heavy fractions (asphaltenes and resins) after HDM and HDS treatments were characterized to understand the deactivation of HDS catalysts. It was found that the increase of aromaticity ( $f_a$ ) for both asphaltenes and resins by HDM treatment was attributed to the loss of alkyl chains and that polycondensed aromatic skeleton of asphaltenes changed toward peri-type. We confirmed that the asphaltenes tended to polycondense during the HDS treatments if the HDM temperature was over 400 °C.

### Acknowledgements

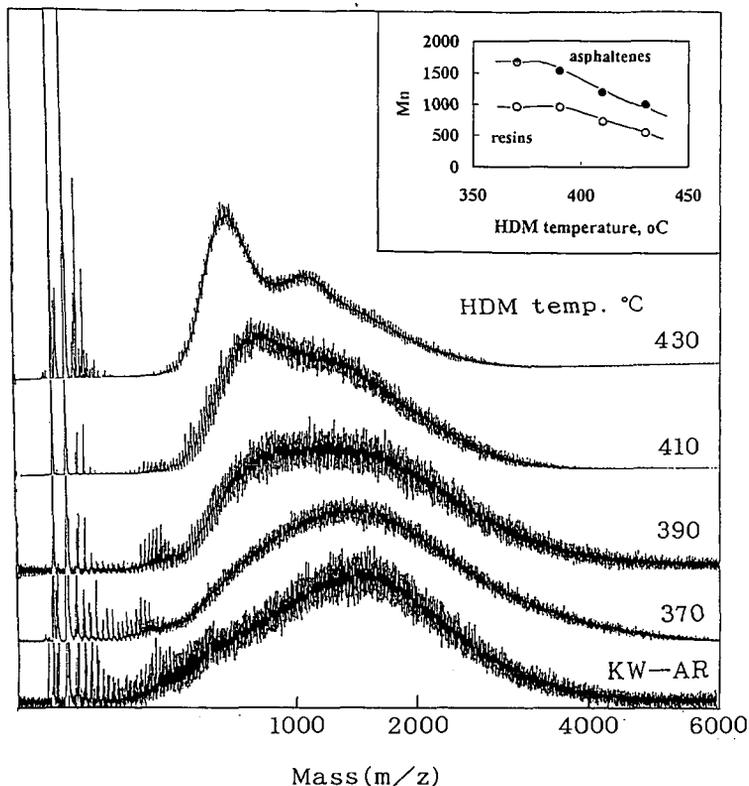
This work has been carried out as a research project of Petroleum Energy Center with subsidy of the Ministry of International Trade and Industry. The authors are grateful to Drs. H. Iki and K. Hayasaka of Nippon Mitsubishi Oil Co. Ltd. for their kind help in NMR measurements.

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**Table 1.** Structural parameters of average molecules for asphaltenes and resins.

Symbol	Definitions	Symbol	Definition
Car	aromatic carbons	Co <sub>ther</sub>	carbons attached to oxygen
Cal	aliphatic carbons	C <sub>int</sub>	internal quaternary aromatic carbons
C <sub>us</sub>	unsubstituted aromatic carbons	C <sub>out</sub>	external quaternary aromatic carbons
C <sub>s</sub>	alkyl-substituted (methyl group excluded) aromatic carbons	C <sub>sub</sub>	alkyl-substituted aromatic carbons
CCH <sub>3</sub>	methyl-substituted aromatic carbons	fa	aromaticity
C <sub>n-ar</sub>	carbons at the junction of aromatic and naphthenic ring	R <sub>a</sub>	aromatic ring number
		n	average length of alkyl side chain



**Figure 1.** LD-MS spectra of asphaltenes after HDM treatments and average molecular weights of asphaltenes and resins.

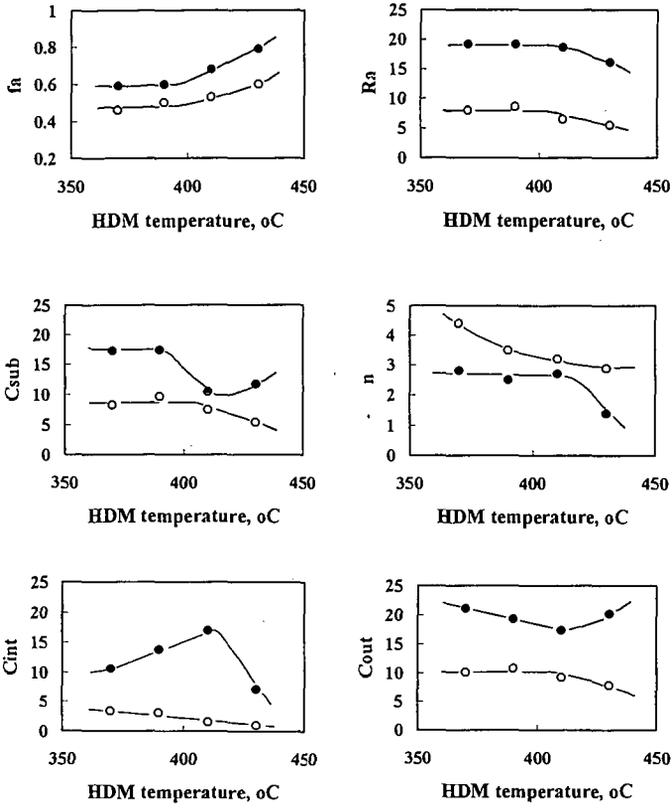


Figure 2. Structural parameters of asphaltenes and resins after HDM treatments; ● asphaltenes, ○ resins.

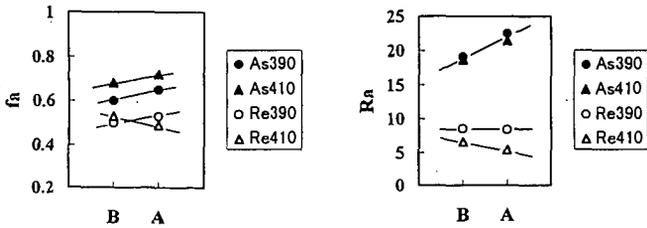


Figure 3. Structural parameters of asphaltenes and resins before(B) and after(A) HDS treatments