

# STRUCTURAL ANALYSIS OF ASPHALTENES IN PETROLEUM HEAVY OILS BY LASER DESORPTION MASS SPECTROMETRY

M. Fujii, Y. Sanada and T. Yoneda,  
Advanced Catalysts Research Laboratory, Petroleum Energy Center  
KSP D-1237, 3-2-1, Sakato, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan

M. Sato  
Center for Advanced Research of Energy Technology  
Hokkaido University, Kita-13, Nishi-8, Kita-ku  
Sapporo, 060-8628, Japan

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## INTRODUCTION

Asphaltenes are obtained as the precipitates when adding alkane to heavy oil such as vacuum residue, which are defined as n-heptane insoluble-toluene soluble, for example. For the reason of their heavy characteristics, they are a major component that occurs the deactivation of catalyst under the hydrotreating reaction, and make troubles such as the pipe plugging by forming sludges at the transportation. A number of analyses have been made by using many kinds of measurements, and many structure models have been proposed(1,2). In spite of these efforts, there have not been well-defined structures yet. Having the strong interaction of molecules for its chemical structure, they aggregate to form micelles as high-dimension structure in oil(3). Therefore, this would make difficult to measure the molecular weight of a unit molecule.

In this study, we have attempted to measure the molecular mass and the distribution for asphaltenes in Arabian heavy vacuum residue (AH-VR), Sumatra light vacuum residue (SL-VR) and hydrotreated oil of Arabian heavy atmospheric residue (AH-AR) by laser desorption time of flight mass spectrometry (LDMS). LDMS techniques have been applied to many kinds of heavy oils by the capability of larger mass range, but there are few observations of molecular mass above 2000 Da, especially for asphaltenes(4,5). We found that useful mass spectra were obtained from the selected measuring conditions, and compared the average molecular weight with those measured by vapor pressure osmometry (VPO) and gel permeation chromatography (GPC). Then, we made the structure analysis of asphaltenes which were fractionated by solvent or GPC separation. Furthermore, the type analysis of the homologous peaks observed at increasing the laser power was provided the difference of aromatic skeleton structures in asphaltenes.

## EXPERIMENTAL

Asphaltenes were prepared from AH-VR and SL-VR by precipitation with n-heptane according to the procedure of Japan Petroleum Institute Standard (JPI-5S-22). Maltene (n-heptane soluble) was separated to 3 fractions (saturate, aromatic and resin) by column-chromatography. LDMS were measured with Thermoquest Co., Ltd. Vision 2000 Spectrometer, using angiotensin as a calibration standard. Samples were dissolved in solution of toluene(1 or 0.1 mg/ml), and 1  $\mu$  l of the solution was dropped on the laser target, then dried in air. Laser beams were shot on the sample surface with changing the place as every shot. Spectra were

gained by averaging about 20 shots. VPO measurements were made using UIC Inc. Osmomat 070-SA with toluene as the solvent at 333K and with nitrobenzene at 373K, calibrating by benzil. GPC measurements were made using Sensyu Scientific Co., Ltd. SSC-7100 (column : Shodex K-802.5 and K-805L, 8mmI.D.300mml.) in nitrobenzene for the eluent at 373K, calibrating by polystyrene.

AH-VR asphaltene was fractionated into 4 parts (S-1~S-4) by solvent separation using mixtures of methanol / toluene. The toluene solution of asphaltene of 1/30 wt/vol% was precipitated by addition of methanol, ratio of 30/70 vol/vol. The precipitant was settled for 5 hr at 283 K, and separated by centrifugation. The soluble, then, was separated stepwise by addition of methanol / toluene mixtures of 40/60 and 45/55, respectively. GPC separation was made using Toso Co., Ltd. Model SC-8020 (column : TSKgel G 3000H, 55 mmI.D.600 mmL ) in chloroform for the eluent at room temperature, and 4 fractions (G-1~G-4) were obtained.

Hydrotreating was performed in a bench-scale fixed-bed continuous flow reactor system, using the demetallization catalyst. Five reactors having 18 mmI.D.560 mmL each were connected in series. The reaction conditions were: temperature at 653 K; pressure of 12 MPa; LHSV of 0.5 hr<sup>-1</sup>, and H<sub>2</sub>/oil ratio of 800 vol/vol. The feedstock was Arabian heavy atmospheric residue (AH-AR) (b.p. of 616°K). The product oil samples were obtained from the bypass line of each reactor outlet by 2% of the flow rate. These oils were distilled, and asphaltenes were prepared from the distillation residue.

## RESULTS AND DISCUSSION

### LDMS spectra of asphaltenes

The LDMS spectra of AH-VR and SL-VR asphaltenes are shown in Figure 1, where broad distribution profiles were observed up to  $m/z$  6000. Some peaks below 200 might be assigned to metals, such as Na, K and Fe. Peak intensities grew up with the laser power increasing, and many fragments appeared in lower mass range. The addition of matrix, for example, 2,5-dihydroxybenzoic acid showed no effects to suppress the fragmentation. We extracted the spectrum with stronger intensity and less fragment to calculate the weight average molecular weight ( $M_w$ ) and number average molecular weight ( $M_n$ ). It showed a broad peak in the range from  $m/z$  200 to 6000 with a maximum near 1500 and a shoulder peak near 400. The spectral shape was almost the similar for AH and SL.  $M_w$  and  $M_n$  for AH and SL with those by GPC and VPO are summarized in Table 1. It was noted that  $M_w$  or  $M_n$  obtained by LDMS was the smallest in value. It was reported that the polar solvent such as nitrobenzene was preferable to minimize the aggregation of asphaltene in measuring molecular weight, except for the calibration standard problem(6). However, the LDMS results indicated that asphaltene was measured at the stage of less aggregation. It means the values of almost an unit molecule, assuming that the whole molecules could be desorped or ionized without cracking. Again, it was noted that the average molecular weight of AH-VR asphaltene was almost the same as that of SL-VR, though the difference between AH-VR and SL-VR were appeared by means of GPC and VPO. This implies that the substantial molecules consisting of asphaltenes are not dependent upon kinds of crude oil.

Figure 2 shows the LDMS spectra of AH-VR saturate, aromatic and resin compared with the asphaltene. The saturate showed many sharp peaks below  $m/z$  200 and a broad one from 200 to 1000, the aromatic had a broad peak from 200 to 2000, and the resin had a bimodal peak from 200 to 6000. The shoulder peak near 400 appeared in the asphaltene seems to coincide with that of aromatic or resin. It would be caused by the drawing of the partial components of aromatic or resin due to the structure similarity at the precipitation. Asphaltenes were further separated into 4 fractions by solvent and GPC. The LDMS spectra of solvent separated fractions (S-1~S-4) are shown in Figure 3. The fraction, S-1, behaves bimodal peaks having 2 tops near  $m/z$  400 and 1500. The peak near 400 decreased and the peak near 1500 increased for the heavy fractions, S-2 and S-3. As for S-4, a peak near 1500 was observed only. The fraction is thought to be heavier or more polar in order from S-1 to S-4 standing upon the solvent separation mechanism(7). Therefore, the major part of S-1 is found to be aromatic or resin which might be drawn at the precipitation. There was no change in these profiles in the vicinity of 1500. This suggests that the asphaltene becomes separated as a function of solubility of micelles except for the drawn fraction, S-1 as contaminants. Figure 4 shows the LDMS spectra of GPC fractions. Their molecular weight distributions were shifted to larger in order from G-1 to G-4. While G-1 showed a bimodal spectrum in the range from  $m/z$  200 to 6000, the others were almost the same of the broad one from 200 to 6000. The profile of G-1 seems to coincide with aromatic or resin. So, it can say again that the drawn component of asphaltene would be aromatic or resin. As asphaltenes are thought to be aggregated in solvent as described earlier, they would be separated by the solubility difference of micelles, not that of molecular structure due to no differences in the LDMS spectra. This suggests that they might have the other properties related to forming micelles.

Next, we tried to analyze the asphaltenes in the hydrotreated oils to make sure the structural changes by the reaction. Figure 5 shows the LDMS spectra of those asphaltenes (Rx-1, Rx-3 and Rx-5), prepared from the product oils of the first, the third and fifth reactor, respectively. It was observed that the profiles became flat and the peak of  $m/z$  1500 in the profiles shifted to smaller mass near 600 with increasing the reaction pass. As there occurred the transfer from asphaltenes to maltenes, and the decrease of asphaltene contents under hydrotreating, it is hard to estimate the structural changes from analyzing the residual oil. But, we could insist that the molecular weight lowering of asphaltenes molecules would occur under hydrotreating.

#### **Type analysis of homologous LDMS peaks**

When increasing the laser power for the sample prepared by the solution of 0.1 mg/ml, many sharp homologous peaks appeared in the range from 200 to 5000, together with a lot of fragment peaks. The spectra of AH-VR asphaltene are shown in Figure 6. This phenomenon implies that the cracking of side chains attached to aromatic cluster and skeleton in asphaltenes was caused by the laser abrasion resulting the homologous compounds series with cracked fragments. The prominent series with a  $\Delta m$  of 24 interval is assigned to cata-type aromatic compounds. The ring number increases with one by two carbons. The proposed structural change of condensed aromatic rings is shown in Figure 7. The appearance of homologous peaks was also

observed in SL-VR as well as hydrotreated oils. We make sure the type analysis for these series of an interval of  $m/z$  24 for AH-VR and SL-VR. The analysis is that (1) general formula of hydrocarbons is expressed as  $C_nH_{2n+z}$ , and (2) separation of hydrocarbons belonging to a given group with the definite  $z$ -value from the spectrum having lots of sharp peaks in LDMS. Calculation was computed by a personal computer system. The plots of the various types in the sample shown in Figure 8 provide "finger printing" of asphaltene. The notations mean that each series are classified by the component of the initial mass. It is clear that the type distribution in the asphaltene is dependent upon the kind of crude oils, while the average molecular weight and its distribution are the almost same. That is, the type analysis provides one of characterization of mixture of hydrocarbon and asphaltenes. LDMS is a useful tool for the structure analysis of asphaltenes with complexity and will be applied to obtaining deep insight of structure such as shape and size of aromatic skeleton.

## CONCLUSIONS

The structures of the asphaltene in petroleum heavy oils were investigated from molecular weight distribution by LDMS. It was observed that the mass spectrum of asphaltene in AH-VR was in the range from  $m/z$  200 to 6000 having two peaks, and that the former was small near 400 and the latter was large and broad near 1500. This distribution was almost the same for that in SL-VR, but not for that in the hydrotreated oil, which showed the shifting of the peak to the lower mass. From the results of fractions by solvent fractionation and GPC for AH-VR asphaltenes, it is found that the peak near 400 is assigned to aromatic or resin fraction drawn at the separation and that asphaltenes in micelles are comprised from the same molecular weight distribution.

Type analysis was made for the homologous peaks of a  $\Delta m$  of 24 in the range from 200 to 5000, which appeared by increasing the laser power. The appearance of these peaks might be suggested the number of aromatic cata-condensed ring system, that is, asphaltene would be association of compounds with the similar aromatic ring structures.

## ACKNOWLEDGMENTS

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## LITERATURE CITED

- (1) Speight, J. G., *The Chemistry and Technology of Petroleum*, Marcel Dekker Inc.
- (2) Yen, T. F. and Chilingarian, G. V., *asphaltenes and asphalts, I*, Elsevier Science
- (3) Moschopedis, S. E., Fryer, J. F. and Speight, J. G., *Fuel*, **55**, 227(1976)
- (4) Parker, J. E., et al., *Fuel*, **72**, 1381(1993)
- (5) Hunt, J. E., Lykke, K. R. and Winans, R. E., *Pre. Pap. ACS. Div. Fuel Chem.*, **36**, 1325(1991)
- (6) Nali, M. and Manclossi, A., *Fuel Scie. and Tech. Int'l*, **13**, 1251(1995)
- (7) Andersen, S. I., Keul, A. and Stenby, E., *Petr. Scie. and Tech.*, **15**, 611(1997)

Table 1. Properties of asphaltenes

Sample	LDMS		GPC		VPO	(Mn)	density	fa	H/C
	Mw	Mn	Mw	Mn	nitrobenzene 373K	toluene 333K	g/cm <sup>3</sup>	III-NMR	-
AH-VR	2040	1560	2280	1840	2870	12710	1.165	0.52	1.05
SL-VR	1980	1490	-	-	3170	12870	1.115	-	1.03

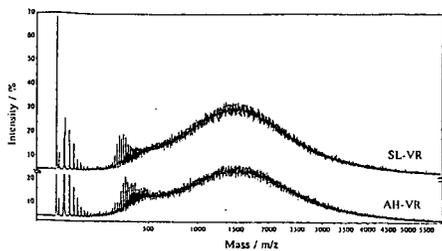


Figure 1. LDMS spectra of asphaltenes

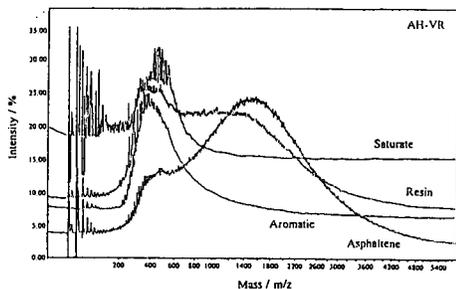


Figure 2. LDMS spectra of fractions by column chromatography

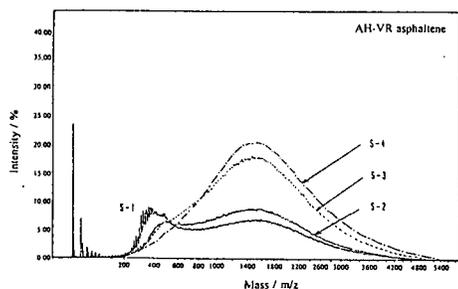


Figure 3. LDMS spectra of fractions by solvent separation

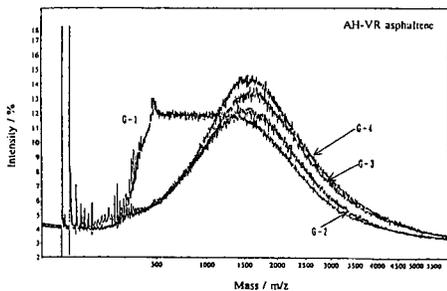


Figure 4. LDMS spectra of GPC fractions

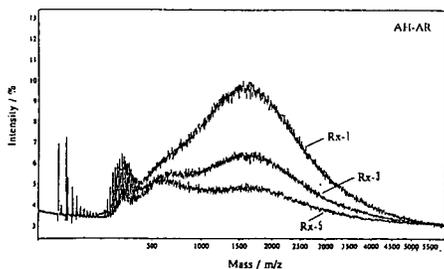


Figure 5. LDMS spectra of asphaltenes in the hydrotreated oils

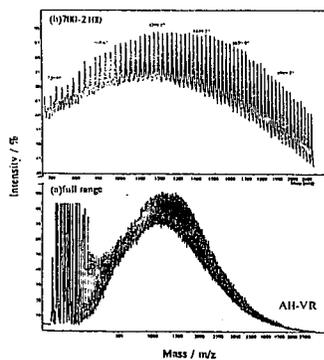


Figure 6. Homologous peaks of LDMS spectrum

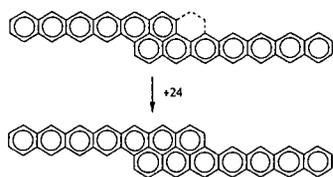


Figure 7. A model of structural changes with a  $\Delta m$  of 24

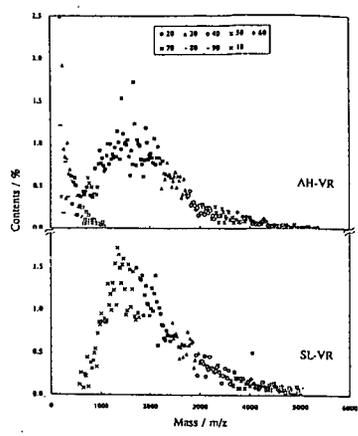


Figure 8. Type analyses of homologous peaks