

## CHARACTERIZATION OF ASPHALTENES FROM PROCESSED RESIDS

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Keywords: asphaltene, ring size, molecular weight

### Introduction

The current and future trend for petroleum processing is towards conversion of heavier and heavier fractions into useful products such as gasoline and diesel. Asphaltenes, the heptane insoluble fraction of heavy oils, are a solubility class and not a specific boiling range. They tend to be the hardest fraction to process in the refinery because of their high molecular mass, aromaticity and heteroatom and metal (S, N, Ni, V) content. Molecular characterization of asphaltenes is important since a more thorough understanding of the chemical nature of the constituents should lead to more efficient processing schemes.

A major hurdle in the accurate representation of the molecular structure of asphaltenes has been the determination of the molecular weight. The main problem is the formation of molecular aggregates depending upon factors such as polarity of the solvent, temperature, concentration and others. Over the past 15 years or so, the apparent molecular weight of asphaltenes has dropped significantly lower as the cause and effect of aggregation on molecular weight was determined. Molecular weights as high as 500,000 have been reported for some asphaltenes in the past with weights as low as 600 appearing in the literature recently depending on the analytical method used.[1-2]

The problem of molecular aggregation has been studied by a number of techniques [5-11] including SAXS and SANS. Using SANS, Thiyagarajan, *et al.* [12] found that at room temperature that asphaltenes are highly ordered rod like species with lengths up to 500Å. As asphaltene samples are heated up, these large aggregates are broken up into smaller rod like species with average lengths of less than 100Å at temperatures of above 50°C. Further shrinkage of the aggregates occurs when the asphaltene is heated to 340-400°C resulting in spherical particles with radii of about 12Å. Returning the sample to 20°C resulted in a low intensity signal implying irreversible thermochemistry. Espinat, *et al.* [14] also using SANS, found that the size of the colloidal asphaltene particles decreased with increasing temperature or with increasing dilution with resin material and increased with the addition of *n*-hexane. Finally, Storm, *et al.* [13] found by SAXS that for asphaltenes from several sources at 93°C that the colloidal particles had an average radii of 30-60 Å. They also found that the average particle size was independent of the heteroatom content of the asphaltene. The exact mechanism by which aggregation occurs has not been established.

Recently mass spectrometry has been used to determine a limiting lower value for the molecular weight for asphaltenes. This technique found that the upper limit for the molecular weight of Ratawi asphaltene was 814 versus 2360 from VPO. The upper limit for an asphaltene from the Alaskan North Slope was determined to be less than 1270 versus 3248 from VPO. High resolution mass spectrometry (HRMS) is a well-established technique for determination of composition of petroleum distillates by compound types. HRMS provides exact mass measurement of molecular and fragment ions, allowing distinction of molecular of equal nominal mass but of different double bond equivalents. The exact mass measurements also allow classification of hydrocarbon (saturated and unsaturated) and sub-classification into heteroatom-containing (e.g., nitrogen, oxygen and sulfur) molecules. In this paper we use high resolution sector field mass spectrometry to determine the comparative speciation of the composition of the asphaltenes from resid subjected to processing conditions.

### Experimental

The resid was obtained by vacuum distillation of an asphaltene rich Maya crude oil. Asphaltenes were isolated by addition of a 40:1 excess of *n*-heptane to the Maya resid in toluene at 50 °C. The suspension was stirred overnight and filtered. The *n*-heptane was distilled from the filtrate to obtain the deasphalted oil (DAO). The yield of DAO was 83% of the resid. The precipitate was dissolved in a minimum of toluene and re-precipitated with a 40:1 excess of *n*-heptane. This precipitate was filtered, washed with *n*-pentane, and vacuum dried at 100 °C. The yield of asphaltene was 27% of the resid. The resid was processed under hydrotreating conditions at 425°C with 2000 psi H<sub>2</sub> with 0.05 weight per cent organic Mo catalyst. The extent of the reaction was monitored by GC methods.

A Kratos three-sector MS-50 mass spectrometer was used to obtain high resolution mass spectra of asphaltenes. The full-scan high-resolution (dynamic resolution of 10,000-40,000) electron

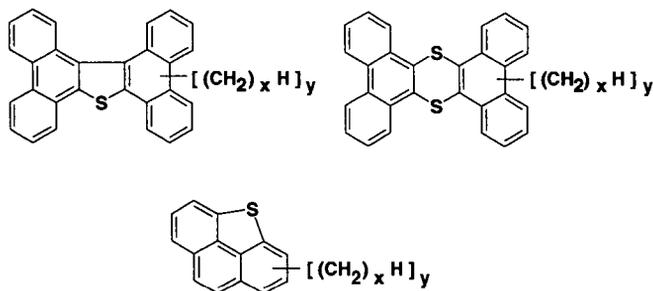
ionization (EI) mass spectra were acquired with a Kratos MS50TA triple sector tandem mass spectrometer of EBE design. High boiling perfluorokerosene was introduced via a heated inlet. Calibration to mass 900 was routinely achieved at a scan rate of 10 s/decade. The source temperature was 250 °C. Ionization method was the electron impact (70 eV). The samples were inserted into the source on a high-temperature probe. The accelerating voltage was a nominal 8 kV. The spectra were collected and recorded on the MACH 3X data system. Group analysis for all scans with ions above background was averaged and only those which occur a minimum of at least four times was saved. Formulae which fit within  $\pm 3.5$  millimass units are assigned for each averaged ion peak. The formulae are sorted by hydrogen deficiency and heteroatom content. Absolute response factors for each type of compound are not available, equal molar ionization sensitivities are assumed for all homologs in the analysis.

## Results

The mass spectra from the asphaltene fraction generally show ion intensity from 100 to almost 850 amu. The average mass of the observed spectra is about 400 amu. While this does not represent the average molecular mass when one takes into consideration that fragmentation occurs under electron impact conditions, for very aromatic species electron impact is a good indicator for molecular distributions. When the fact that asphaltenes are highly aromatic ( $C_{ar}$ -60%) is taken in account, the distributions may be only 50 to 100 amu higher. The elemental analysis calculated from the high resolution mass spectral data are in good agreement with those from traditional techniques, with aromaticity values slightly lower for the mass spectral data. This means that the mass spectral data is representative of the actual sample. Furthermore, at least 90% of the asphaltene is volatilized in to the mass spectrometer.

In the high resolution mass spectrum thousands of peaks can be measured. This number of peaks makes reducing the data into a more manageable form necessary. The double bond equivalent (dbe) and the heteroatom content can be calculated from the exact mass data without any assumptions. Sulfur combinations may be misrepresented, but oxygen and nitrogen should not have a high probability of misrepresentation. However, the elemental analysis data extracted from the mass data show that these errors are minimal. Detailed distributions of asphaltene sulfur and nitrogen organic molecules as a function of double bond equivalent for three processing levels (35%, 70% and 85%) are shown in Figure 1.

Several features are readily apparent. First, the mass limit of the ions (~800 amu) suggests that the ring size may be as high as 10 rings. Second, the sulfur containing species are processed fairly efficiently. Heteroatomic sulfur in benzothiophenes (dbe=6) is particularly well removed by processing as almost no dbe=6 is observable in the most processed sample (compare Fig. 1A and Fig. 1C). Likewise those sulfur species of dbe=9, of which dibenzothiophenes are a possibility, are processed efficiently. However, the larger S-containing species in the range of 12-35 dbe are unchanged or even concentrated under these processing conditions. Based on the mass spectral exact mass formulae, the following structures are suggested:



The  $y$  in the structures means that multiple substitution is observed in the mass spectrum and the  $x$  means that the chain length can vary.

The number of isomers of each species is quite high and mass spectrometry alone cannot discern them. A two-sulfur structure consistent with mass spectral data is also shown.

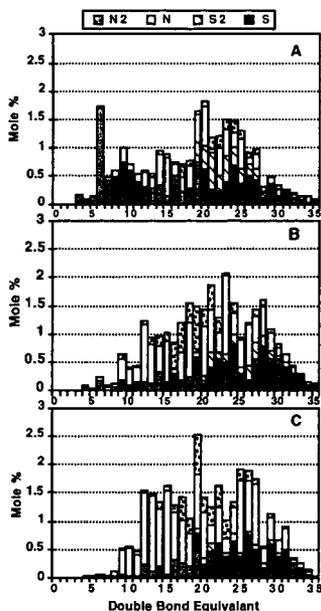


Figure 1. Sulfur and Nitrogen containing species for asphaltenes from processed resids. A, asphaltenes from 30% conversion; B, 70% conversion; C, 85% conversion.

Figure 2 shows the mass spectra for the three conversion levels of processing for a double-bond equivalent of 9. Although this class of molecules make up a small fraction of the total of the samples (~ 0.15 mole %), we can follow the processing on a molecular class basis. The asphaltenes in the 35% processed resid sample (Fig. 2A) show species from  $m/z$  300 to 700, in addition to fragment and molecular species in the 180 to 250 range. These high mass species correspond to dibenzothiophenic structures with either multiple alkyl substitutions or chain lengths or combinations of both.

Chromatographic separation or tandem mass spectrometry could identify which combinations of chain length and substitution are present. Further processing as shown in Fig. 2 tends to shorten the chain length of the molecule leaving only few short chains on the molecule. We suggest that the most resistant molecules are probably those that are substituted at positions adjacent to the sulfur.

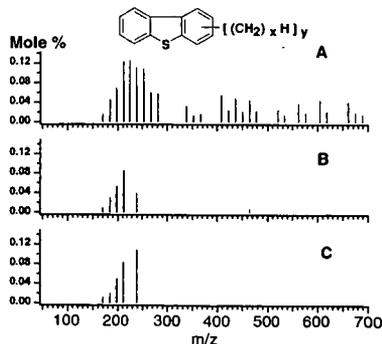
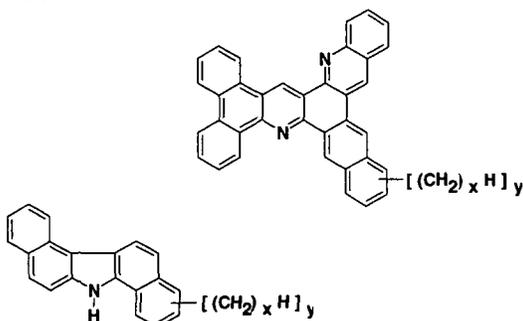


Figure 2. The mass distribution of sulfur-containing, double-bond equivalent=9 species. A, asphaltenes from 35% conversion; B, 70%; C, 85% conversion.

Nitrogen-containing species show a similar pattern to the sulfur pattern, but with one notable exception. The nitrogen species are much more resistant to processing. They are essentially untouched and perhaps concentrated. A similar pattern of multiple-alkyl substitution is found. Multiple nitrogens in rings systems are also present. Examples of suggested structures for the nitrogen-containing species follow:



Such structures differ markedly from those published elsewhere. Others have shown more condensed structures. Our data do not support more condensed ring systems, but rather more open ring systems.

Hydrocarbon molecules are also found in the processed asphaltenes. As processing severity increases the mass intensity shifts to larger aromatic rings systems. The existence of hydrocarbons, while surprising may be explained in terms of the separation and aggregation properties of the asphaltenes. Asphaltenes are separated only by precipitation. As the asphaltenes precipitate they form aggregates which may trap hydrocarbons. In addition, if the asphaltenes aggregate under processing conditions, some of the aggregate may escape aromatic treating, leaving sources of large aromatic hydrocarbons in the asphaltene fraction.

### Conclusion

Our mass spectral studies of asphaltenes from hydrotreated resid have shown them to be highly aromatic and present as extended open ring systems as high as 11 rings. Sulfur containing species with ring sizes smaller than 5 rings are effectively processed, while larger ring systems are more resistant to processing. The heteroatom containing species in the asphaltenes are multisubstituted with alkyl chains. Processing tends to remove the alkyl chains and/or reduce their, leaving the core ring system.

### Acknowledgment

This work was performed under the auspices of the U. S. Department of Energy, under contract number W-31-109-ENG-38. This work was supported by a CRADA agreement between Amoco Corporation and Argonne National Laboratory under the U. S. Department of Energy-Bartlesville, Fossil Energy Project.

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