

STRUCTURE AND REACTIVITY OF THE ASPHALTENE FRACTION OF AN ARABIAN LIGHT/MEDIUM CRUDE MIXTURE

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Keywords: Asphaltene, Structure, Cracking reaction

INTRODUCTION

In the petroleum industry, further utilization of distillation end points (i.e. residua) is of high interest because petroleum refineries will have to deal with much heavier crude in the future decades. Petroleum asphaltenes, which are operationally defined as pentane- or heptane-insoluble and toluene-soluble organic materials of crude oil or the bottoms from a vacuum still, are the heaviest fraction of the crude oil, and their amounts and structures are known to be source dependent. In upgrading processes of residua, asphaltenes are responsible in sludge formation due to their flocculation, which reduces the flow and plugs down stream separators, exchangers, and towers. They show bad behavior in poisoning and reducing the activity of hydrocracking catalysts with its high heteroatom content, trace metals, and high tendency in coke formation. In order to overcome their problematic issues, the role of asphaltenic materials in the upgrading processes should also be interpreted at the level of molecule. Under these circumstances, the better comprehension of asphaltene structure is essential. Although enormous amount of effort has been paid to the structural elucidation of asphaltenes for several decades, their precise molecular description does not exist yet. On the basis of detailed NMR work along with complementary information from various analytical techniques employed, many researchers have concluded that asphaltenes are the mixture of polydispersed-condensed polyaromatic units, with heteroatoms contents, bearing alicyclic sites, and substituted and connected with each other via aliphatic chains. In their researches, asphaltenes were precipitated either from the crude sample or residue. The latter type asphaltene structurally may be different from the former type because at distillation temperatures, in general 300-500°C, some extent of cracking and condensation reactions may take place simultaneously. There are a number of studies which have postulated chemical models for asphaltenes, the most recent ones being based on the ¹H/¹³C NMR data and elemental composition. The models, in general, consist of one or two units of polyaromatic units in varying condensation degree combined with alicyclic sites and connected by aliphatic chains, most of the aliphatic chains being attached to the aromatic carbons[1-7]. Some researchers have used degradative methods such as pyrolysis and oxidation methods to gain more precise insight into the molecular characteristics of asphaltenes. The former method involves formation of smaller fragments and accompanies their identification, the identified components being considered as covalently bonded moieties of asphaltene molecules[8]. Strausz *et al.* were the first group applied the ruthenium-ions catalyzed oxidation (RICO) reaction to asphaltenes to recognize aliphatic types[9]. They processed the invaluable information from the RICO reaction along with those from NMR and pyrolysis studies to comprehend the structure of Alberta oil sand asphaltenes and consequently proposed a very different model structure: instead of a single condensed aromatic system with a large number of rings, a set of smaller aromatic units, heteroaromatics and naphthenic units with aliphatic substituents linked by aliphatic bridges comprised the structure. Particularly, the presence of relatively polymeric naphthenic and aliphatic sites in this molecule is a striking feature. The structure of heavy fraction of crude oil and their conversion to value products have also been of our interest.

In this paper, we have processed the information from the NMR work of the asphaltene sample together with data from the RICO reaction of the asphaltene to elucidate the distribution of the aliphatic carbons more precisely. The detailed analytical information over this sample is summarized within a model structure. As to the reactivity of the asphaltene, its hydrocracking reaction using metal loaded Y-type zeolite catalyst was elucidated, the results being compared with the case of the other lighter fractions.

EXPERIMENTAL SECTION

Samples.

The propane insoluble fraction of the vacuum residue of Arabian crude mixture (80% light and 20% medium) was provided from Nippon Oil Ltd. Co. The asphaltene sample used in this study was the insoluble fraction (21wt% yield, based on propane insoluble) from the pentane Soxhlet extraction of the provided sample. The elemental composition of the asphaltene sample is 83.7% C, 7.5% H, 0.84% N, 6.8% S, 0.012% Ni, 0.038% V, on dry basis and has an H/C atomic ratio of about 1.08.

Analysis of the asphaltene sample.

The RICO reaction was performed by stirring the mixture of the asphaltene sample (1 g), H₂O (30 ml), CCl₄ (20 ml), CH₃CN (20 ml), NaO₂ (15 g), and RuCl₃·nH₂O (40 mg) at 40°C for 24 h. During the reaction, N₂ gas was flowed and the resulting CO₂ was purged through CaCl₂ and ascarite containing tubes. The amount of CO₂ formed was determined from the weight increase of ascarite. The details of the workup procedure have been given elsewhere[10]. NMR analyses were conducted by a JEOL JNM-GSX-400 spectrometer operating at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR measurements. The NMR samples were prepared by mixing approximately 100 mg of the sample with 1 ml of CDCl₃; tetramethylsilane (TMS) was used as an internal standard. The quantitative ¹³C NMR measurements were acquired by adding a relaxation agent, chromium

trisacetylacetonate (Cr(acac)₃, 0.2 M) in inverse gated decoupling system with a pulse delay of 5 s, acquisition time of 1.088 s and pulse width of 3.3 μ s. The distortionless enhancement by polarization transfer (DEPT) spectra were collected for flip-angles of 45°, 90°, and 135°. The acquisition time was the same as those for the quantitative carbon runs. A pulse delay of 2 s and a carbon-proton coupling constant of 125 Hz were used. The carbon 90° pulse was 10 μ s, while proton 90° pulse was 26.3 μ s. The GPC tests of the THF or CHCl₃ solutions of the asphaltene (0.5 mg/ml and 1.4 mg/ml, respectively) were performed by a Shimadzu system with 1 ml/min flow rate of THF or CHCl₃ carrier solvents, respectively, at a UV wavelength of 270 nm. The columns used in these tests were Shodex KF-802 and Shodex AC-802 for THF and CHCl₃ carrier solvents, respectively. Standard polystyrene samples were used for the calibration of relationships between molecular weight and retention time. MALDI-TOF/MS (Matrix assisted laser desorption ionization-time of flight/mass spectrometry) spectra were obtained by a Voyager RP mass spectrometer of Perspective Biosystems Co. The linear TOF mode was used with an accelerating voltage of 30 kV in positive ion. One μ l of THF solution of the sample with 2.5 μ g/ml concentration was applied to target and let it evaporate at atmospheric condition.

Hydrocracking reaction of the asphaltene sample.

A mixture of heavy oil (1.0 g) and metal-loaded zeolite (0.5 g) was placed in a 70 ml SUS316 autoclave, which was pressurized up to 6.9 MPa with cold hydrogen, and heated up to a desired temperature range (400°C) at a heating rate of 8K/min. Before collection of the gaseous products, these were passed through aqueous iodine solution (1 mol/l, 20 ml) to recover hydrogen sulfide produced. Gaseous hydrocarbon products were analyzed quantitatively by a gas chromatograph. The iodine solution was diluted to 200 ml by deionized water, 20 ml of which was submitted to titration with sodium thiosulfate solution (0.1 mol/l), using aqueous starch solution as an indicator. After the collection of gaseous products, the autoclave was opened, the inside of which was then washed with tetrahydrofuran (THF) to recover liquid and solid products. After the filtration of the resulting mixture to remove coke and catalyst, the products were separated into three fractions, gasoline + THF (the fraction distilled off by a rotary evaporator at 65°C, atm. 5 mmHg), gas oil (the fraction distilled off by a glass tube oven at 150°C, atm. 5 mmHg, corresponds to the fraction with bp < 310°C), and residue (THF soluble and undistilled fraction). Due to the severe difficulty in weighing of THF plus gasoline fraction in an accurate way the yield of gasoline fraction was calculated based on subtraction of the yield of the other fractions (gas, light oil, residue, hydrogen sulfide, and coke) from total of 100%. Amounts of coke were estimated based on the weight and elemental analysis of THF insoluble portion.

RESULTS AND DISCUSSION

Structural analysis of the asphaltene

RICO reaction afforded the acid products from the aliphatic portion of the sample. The amount of lower carboxylic acids (C₂-C₅) was 3.9 mol/100molC in asphaltene, corresponding to ~5.5 aliphatic carbon/100C. Figure 1 shows the distribution of aliphatic monoacids up to C₂₈ including C₂-C₅ acids. The amount of longer *n*-alkanoic acids showed a smooth decrease as the carbon number increased. Therefore, the most of the alkyl groups attached to the aryl carbon or the monomethylene bridge carbon are in the range of C₁-C₇. We recovered the diacids ranging from C₄ to C₂₀ from aqueous and dichloromethane (DCM) soluble phases of the product. Their distribution was shown in Figure 2. These acids represent alkyl bridge structures connecting two aryl units and α,ω -triaryl substituted bridges, however, short chain acids (C₄-C₆) may also arise from oxidation of various hydroaromatic structures. Several amounts of ethanedioic acids were detected, this acid representing biaryl linkages in the sample. Although this acid implies the significance of biaryl linkages, its amount can not represent the amount of such type of bond due to its relative instability. Propanedioic acid could not be observed, because it can not survive the RICO reaction. Therefore, no direct evidence could be obtained from the reaction products. We also recovered the aliphatic polycarboxylic acids which were formed from three or more aryl-substituted alkyl bridges or alicyclic parts of partially saturated condensed structures. Other polymeric aliphatic fraction could not be analyzed by GC, but was analyzed by NMR in detail. The weight of this fraction was >90% of the DCM extract. The weight and elemental composition of DCM soluble fraction indicates that the amount of carbon atom in this fraction corresponds to 24.6 C per 100 C atoms in asphaltene. GPC analysis of this fraction after methylation (methyl esterification of acids) shows a number-averaged MW of 821 Da. Figure 3 shows the ¹³C NMR spectrum of DCM soluble fraction before methylation. This fraction had <4% aromatic, 87.9% aliphatic, 6% carboxylic and 3.1% carbonyl carbon. The results indicated that the dominant part of this fraction is comprised of polymeric aliphatic structures. The fact that this fraction had an aliphatic hydrogen to aliphatic carbon ratio of 1.72, calculated on the basis of ¹H/¹³C NMR and elemental analysis data, confirms the presence of alicyclic sites. The aliphatic region of the ¹³C NMR spectrum (Figure 3) consists of sharp bands on a broad hump between 10 and 50 ppm, much of this broad hump being ascribed to naphthenic carbon. DEPT analysis of this fraction was also very helpful to assume the structure of this fraction. Aromatic acids were recovered from the aqueous phase of the products workup. Such acids correspond to the presence of condensed aromatic moieties.

The GPC test for the whole asphaltene sample show a range starting well below 200 Da extending over 100 000 Da, while MALDI-TOF/MS indicates the ions higher than 200 Da. This discrepancy confirmed the existence of adsorption phenomenon in the case of GPC procedure. On the other hand, MALDI-TOF/MS test led ionization above 200 m/z extending over 3000 m/z, giving maximum abundance about 450 m/z. Nevertheless, inefficient ionization for polydispersed materials are known to be an impediment of this method to lead underestimation of the higher mass components[1]. Thus, caution must be exercised when interpreting average molecular weight distribution values from MALDI, especially for highly polydispersed complex molecules. We understand that no conclusive-absolute molecular weight could be estimated based on the techniques presented above, however, it seems that GPC method with THF eluent provides more

applicable information compared to others employed in our study: the number averaged molecular weight was estimated as 801 Da.

The structural information was drawn from the combination use of ^1H and ^{13}C NMR data and elemental data. Figure 4 shows the ^{13}C NMR spectrum of the asphaltene sample, having the general features in accordance with previous work. The aromatic region consists of a broad featureless absorption, whereas the aliphatic region contains discrete sharp peak overlapping a broad hump. These sharp peaks are commonly attributed to the chain carbon and methyl substituents on aromatics, alkyl chains, and naphthenic units. Also here, DEPT analysis provides helpful information to differentiation of CH_3 , CH_2 , and CH carbons.

We applied a methodology in construction of a model structure for the asphaltene tentatively in a manner similar to that of bituminous coal[12]. The types of aromatic main units were deduced from the results obtained by the pyrolysis(py)/GC and RICO reaction. The XPS study revealed the sulfur structures as sulfide, thiophenic and sulfoxide. The type and distribution of aliphatic chain structure, functionality, and naphthenic structure were postulated based on the RICO, py/GC, and NMR data. We should emphasize that the asphaltene is consisted of mixture of hundreds of organic molecules rather than a single macromolecule structure. We tried to draw several molecules in the proposed chemical structural model for asphaltene, and four molecules of different structures were contained in the proposed model (Figure 5).

Hydrocracking reactions of the asphaltene

Figure 6 compares the hydrocracking results of the propane-insoluble heavy oil and its deasphalted (pentane-soluble) fractions at the temperature range of 350-400°C with the presence of Pd-Ni loaded Y type zeolite catalyst. As it can clearly be seen deasphalted heavy oil sample showed higher reactivity toward hydrocracking reaction. The removal of asphaltene increased the total liquid and gaseous products (bp. <310°C) roughly by the factor of 2 at 350°C, from 30% to 53% at 375°C, and 42% to 65% at 400°C. Even if we consider the conversion values of the propane-insoluble sample on asphaltene free basis, i.e. it is assumed that asphaltene does not convert to low boiling yields, but contributes to the residue fraction, the resulting values, except for the highest temperature, are far less than those of the deasphalted sample. Asphaltene free calculations of total hydrocracked products were 24, 44 and 64 % with respective increase of the reaction temperature. The comparison of these values with those from deasphalted sample suggests that the effect of the removal of asphaltene on the hydrocracking of the heavy oil became less with increasing the reaction temperature. The effect of asphaltene removal was more remarkable on HC gaseous product formation at all temperatures, their increase varying by the factor of 2-3 even at higher temperature, this indicating the effect of asphaltene removal on hydrocracking activity even at 400°C. These results reveal that asphaltene greatly retards hydrocracking reactions upon probably reducing the activity of the catalyst, especially at the lower temperatures.

The polymerized fraction or coke formations seem to be not likely reason for the detrimental effect of the asphaltene since both the whole and deasphalted residue approximately yielded similar amount of these fractions. Our laboratory recently showed that Pd-Ni-Y catalyst is very active in hydrocracking and hydrodesulfurization reactions[13]. We have also showed that the molecule should diffuse into the cage so that sufficient reactions take place[14,15]. The asphaltene molecules with large molecular segments probably reduce the effective diffusion of molecules which are capable to enter through the pores, by plugging the entrance points. At higher temperatures, probably, the adsorption phenomenon becomes less favorable, due to the reduced adsorption strength and the more effective solubility of the asphaltene molecules within the reaction medium, thus resulting in overall increased effective diffusibility of the units with appropriate sizes.

SUMMARY

This work summarized the structural characterization of the vacuum residue asphaltene based on the mainly spectroscopic and pyrolytic methods, and discussed the results with combination use of those from the RICO reaction. Then, a structural model for the asphaltene was presented. The reactivity of the asphaltene was also discussed from the catalytic hydrocracking reaction of it in a batch reactor using metal-loaded Y-type zeolite catalyst.

ACKNOWLEDGMENT

This work was carried out as a research project of The Japan Petroleum Institute commissioned by The Petroleum Energy Center with the subsidy of The Ministry of International Trade and Industry.

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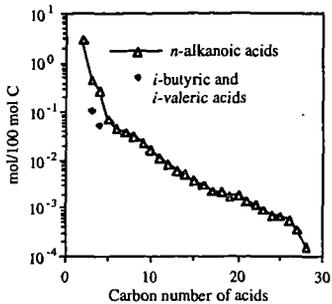


Figure 1. Distribution of aliphatic monoacids from RICO reaction.

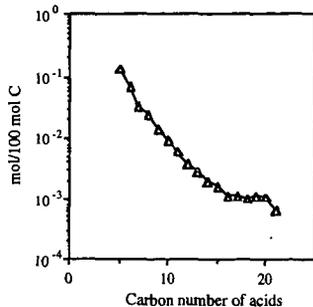


Figure 2. Distribution of aliphatic diacids from RICO reaction.

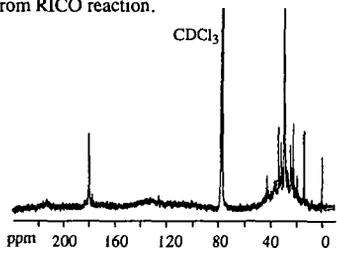


Figure 3. ¹³C NMR spectrum of the dichloromethane soluble fraction of RICO product.

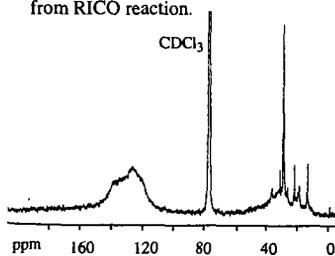


Figure 4. ¹³C NMR spectrum of the asphaltene.

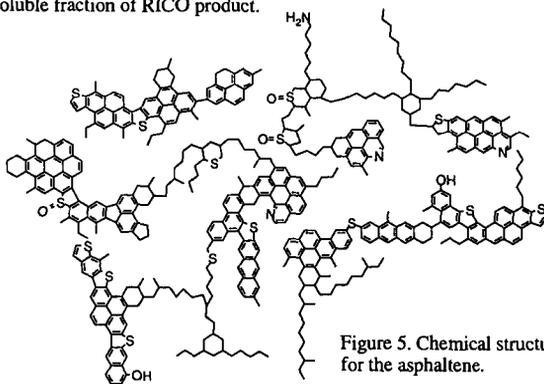


Figure 5. Chemical structural model for the asphaltene.

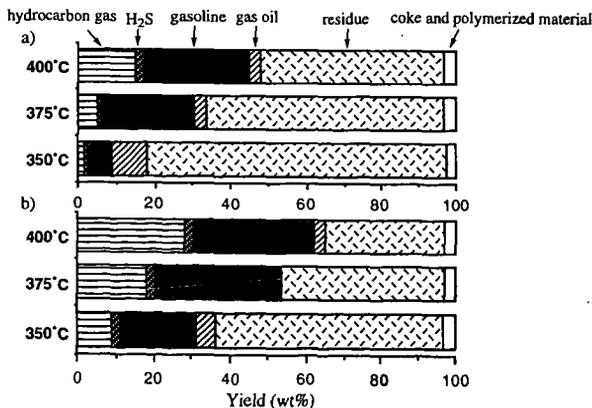


Figure 6. The comparison of hydrocracking conversion results on (a) C_3 -heavy oil sample and (b) C_3 -soluble portion of the C_3 -heavy oil sample.