

THE ROLE OF ASPHALTENES IN SHALE OIL

T.F. Yen, C.S. Wen, J.T. Kwan and E. Chow

University of Southern California
University Park, Los Angeles, California 90007

Asphaltene is ubiquitously present in bitumens regardless of whether or not the sample is naturally occurring or thermally altered. It might be noted that most naturally occurring bitumens have undergone a thermal maturation process during diagenesis.¹ Therefore, thermal process is important in the generation of asphaltene and resin molecules from any fossil fuel sources. Oil shale from lacustrine formation, such as that of the Green River Formation contains 2% to 4% of bitumens. There is asphaltene in bitumen from Green River Oil Shale but the content is only 9% to 12%. This causes the overall content of asphaltene in raw oil shale to be as low as two to five parts per thousand.

During retorting the kerogen undergoes thermal decomposition to oil, gas and insoluble coke. The intermediate is a fairly large amount of pyrobitumen which does contain asphaltene. Since asphaltene is prone to form coke, the reduction of pyrobitumen may account for the increase of coke formation. In this manner the asphaltene is formed in conventional oil shale.

Although the content of asphaltene or resin in shale oil may be low, they are responsible for the dark color as well as the viscosity. Asphaltene in shale oil may be unique since it is high in nitrogen content and, consequently, there will be a high ash content. Furthermore, nitrogen polycyclics may be carcinogenic since they are unique in shale oil asphaltene. The polarity of the nitrogen polycyclics may also exhibit the specific properties of emulsification of water and complexing of metals. It is within this context that the present study is undertaken.

EXPERIMENTAL

A total of three shale oil samples was used for this study. The oil shales used for the study are all from the Green River Formation. The first one was obtained from Paraho Project, Paraho Syncrude (PS). The chemical composition of the oil is as follows: %C, 85.8; %H, 11.3; %S, 0.5; %N, 1.4; %O, 0.99; %ash and carbon residue, 2. The API gravity at 70°F is 27.8; SSU viscosity at 210°F is 48.0. The flash point is 290°F. Water content is 2.8%. Semi-quantitative spectrographic analysis indicates that silicon, sodium, iron, calcium, nickel, vanadium and aluminum are major constituents. The second sample was a residue left from the processing of the PS through a delayed coker, henceforth referred to as residue oil (RO). The third sample was the oil obtained from Don's Welding, a small one-ton vertical retort in San Bernardino. This sample is referred to as DW. The difference between the DW and the PS is that the former also contains arsenic, copper and zinc.

Isolation of asphaltene was in accordance with the traditional procedure of precipitation with 20-fold volume of n-pentane, and followed by centrifugation and Soxhlet-extraction of the solid with n-pentane. The crude asphaltene was dissolved in benzene, hot-filtered and the benzene filtrate was lyophilized to remove the benzene.

CHARACTERIZATION

Various methods are employed for the characterization of shale oil asphaltene. Table I lists the results of isolated asphaltenes and their ultimate analyses. The percentages of carbon, hydrogen, nitrogen, and sulfur, as well as the ash content in the asphaltenes, were determined through elemental analysis in which high contents of nitrogen are found in samples. An empirical formula for each asphaltene sample was determined from vapor pressure osmometry (VPO) measurement. Since the complex molecule of asphaltene tends to associate strongly even in the dilute solution, the usual analytical procedures fail to differentiate between the molecular weight and particle weight. A technique of gel permeation chromatography (GPC) with μ Styragel column in a dilute solution under high pressure has been carried out to obtain asphaltene molecular weight of a single unit sheet. Figure 1 shows molecular weight distributions of three samples in which DW shale oil asphaltenes contain a larger percentage of high molecular weight fraction. Semiquantitative analyses of metals present in asphaltenes are listed in Table II. Apparently metal is an integral part of asphaltenes.

A typical infrared spectrum of potassium bromide pellet from PS asphaltene is given in Figure 2. A number of similarly well defined bands are shown in all samples. The broad absorption band centered at 3220 cm^{-1} is assigned as hydrogen-bonded O-H or N-H which interpretation has been reported in coals^{2,3} and coal asphaltenes.⁴ Two low-intensity bands at 3010 and 3050 cm^{-1} represent aromatic C-H stretching. Wiberly⁵ has shown that the aromatic C-H band shifts to values as high as 3052 cm^{-1} as ring number decreases. The strong absorption bands falling between 2840 and 2950 cm^{-1} are due to naphthenic and/or aliphatic C-H vibration. The two vibrations of the methyl group are located at 2950 and 2885 cm^{-1} , and the methylene band, which is the strongest, at 2915 cm^{-1} . Another methylene frequency occurs at 2840 cm^{-1} . An intense absorption band located at 1600 cm^{-1} has been assigned partly caused by a conjugated C=C band and partly by carbonyl, C=O group. Two very intense bands at 1455 and 1375 cm^{-1} are due to bending frequency of symmetric C-CH₃ and/or methylene, and symmetry C-CH₃, respectively. The group of bands located at 1255 , 1090 and 1030 cm^{-1} may be assigned to aromatic oxygenated compounds, such as aromatic ethers.² Differences of absorption intensities of these bands among three asphaltene samples are apparent from Fig. 3. Three fairly definite bands in the spectrum of PS asphaltene in comparison to ill-defined weak bands in the spectra of DW and RO asphaltenes are consistent with the highest value of O/C ratio in PS asphaltene (Table I). The long wavelength bands at 860 , 800 and 750 cm^{-1} are considered aromatic out-of-plane frequencies and are important with regard to the nature of the structure of aromatic clusters. The four-adjacent C-H bending band at 720 cm^{-1} and the five-adjacent band at 695 cm^{-1} are very weak in spectra (Fig. 3). The long-chain alkyl band at 735 cm^{-1} is only present in the spectrum of RO asphaltene. This long-chain methylene structure in RO asphaltene is further confirmed by the X-ray diffraction.

A number of parameters can be obtained by resolving the γ - and (002)-bands in the X-ray scattering pattern (see Table III). The (002)-spacing which appears in graphite and carbon blacks is accepted as representing the spacing between the layers of condensed aromatic system.⁵⁻⁷ The γ -band centered around $(\sin\theta)/\lambda = 0.10\text{-}0.11\text{ \AA}^{-1}$ has been assigned to be associated with spacing in the saturated portion.^{5,8} Accordingly, a comparative estimate of the aromaticity, f_a , can be made from the areas of the resolved peaks corresponding to the γ - and the (002)-

bands.⁵ The distance between aromatic sheets, d_m , is obtained from the maximum of the (002)-band and the distance between the saturated portion of the molecule, d_s , is obtained by using the value from the γ -band. X-ray diffraction also permits a determination of the average height of the stack of aromatic sheets, l_c , and the average diameter of the aromatic sheets, l_a based on the Scherrer crystallite size formula⁹ or on the Diamond's curve.¹⁰ The X-ray diffraction pattern of the RO asphaltene is strikingly different from the others; it shows the sharp doublet of (100)- and (200)-bands at 4.15 and 3.70 Å as shown in Fig. 4. Yen¹¹ in his study of native asphaltic molecule, has reported these two peaks as wax-like long-chain alkyl compounds. In comparison with the doublet bands, the results of X-ray diffraction of the three samples are very similar. It is to be noted that PS asphaltene has a smaller value of l_a , the layer diameter, among them.

The hydrogen-distribution data obtained by NMR has been applied to the analysis of carbon structure, with particular emphasis on estimating several important structural parameters as listed in Table IV. A typical NMR spectrum of PS asphaltene is provided in Fig. 5 in which subgroups are assigned for aromatic and saturated hydrogen resonances.¹² From the area under the component peaks, it is possible to estimate values for the degree of substitution of the aromatic sheets. The aromaticities obtained from NMR data depend largely on two parameters: one being the ratio of hydrogen to carbon for the α -paraffinic groupings, and the other refers to the ratio for all nonaromatic groupings other than α -position. In this investigation, these two ratios were given the value 2 for all asphaltenes. Data from NMR also permit the determining of the shape of the condensed aromatic sheets by estimating the value of the ratio of aromatic hydrogen to carbon of the hypothetical unsubstituted aromatic sheet. The results for asphaltenes are tabulated in Table IV. The other structural parameters including total numbers of aromatic ring carbon, substituted aromatic ring carbon, and aromatic ring per molecule, as well as the average number of carbon atoms per saturated substituent are shown in the same table. The H_I/CA value for RO asphaltene is lower than those of the PS and DW asphaltenes. The number of rings in the condensed aromatic ring system per molecule varies from one, as in the case of DW asphaltene, to 3-4 in the case of the RO asphaltene.

DISCUSSION

In fossil fuel conversion, it is generally recognized that asphaltene is the transition stage from fossil fuel source to oil products. Therefore, the asphaltene generation and elimination is one of the main and important control factors of the conversion process. Present knowledge of the skeletal structural of the shale oil asphaltene is presented in this paper.

In contrast with the carbon skeletons of kerogen which has very low f_a value,¹³ the aromaticity of asphaltene ranges from 0.4 to 0.5. The high temperature retorting of oil shale tends to yield more aromatic hydrocarbons than those which are present in the original raw oil shale, the latter has undergone maturation. The thermally induced aromatization for the difference in properties of asphaltene series is well recognized.¹⁴ For example, asphaltene fraction can be converted into carbene fraction and resin fraction can also be converted into asphaltene fraction.¹⁵ All these conversions can be accomplished by thermal processes.

The proton NMR spectra of the shale oil asphaltene are similar to those of the petroleum asphaltene and of the coal-derived asphaltenes as well. The degree of substitution, σ or C_{SU}/H_I of the shale oil asphaltene is larger than 0.5. It falls closer to petroleum asphaltene than coal asphaltene, since the majority of the latter is less than 0.5. In contrast, the cluster compaction parameter, H_I/C_A or HCC, of shale oil asphaltene is higher and closer to coal asphaltene than to petroleum asphaltene. The value of H_I/C_A for petroleum asphaltene ranges from 0.3 to 0.5 and those for coal asphaltenes 0.6 to 0.8. It is recognized that coal asphaltene contains more or less smaller kata-condensed cluster.¹⁸ The petroleum asphaltene has large, peri-condensed systems.^{12,17} The value of 1.0 or 0.95 is not possible; one of the reasons of such high values is possibly the higher contents of nitrogen atoms in the system which may effect the computation; other reasons being the assumption of X, Y coefficients of 2. Another parameter, the substituents chain length, N_{SC} or C_6/C_{SU} for the shale asphaltene is medium-sized, i.e. between 2 to 3 carbons. For comparison, the coal asphaltene is about 1 to 2 carbon atoms (methyl or ethyl); and the petroleum asphaltene is 4 to 6 carbon atoms. In general, for NMR data alone, one can state that the shale oil asphaltene contains heavily substituted linked or kata-condensed system.¹⁶ The system is small and the substituents average between 2 to 3 carbons.

What is more striking is the fact that in one of the shale oil asphaltenes studied (RO), there is actually either the long-chain paraffin or substituent present as indicated by the sharp bands at 3.70 and 4.15 Å by X-ray diffraction. This is further supported by the observation of polymethylene peak in the infrared spectra of RO asphaltene. In previous work, such crystalline sharp peaks have been found in a few petroleum asphaltenes,¹¹ especially when asphaltene has undergone thermal processing by visbroken process. At present the delayed coker processing of shale oil may also form considerable amount of paraffins which are coprecipitated down with other asphaltene molecules.

The layer diameter for the shale oil asphaltene is 7-12 Å by Diamond's curve fitting of the X-ray diffraction data. This value is compatible to NMR data in which the aromatic number varies from 1 to 3. The inconsistent data between number of aromatic carbons per molecule and ring number per molecule probably are due to the high content of nitrogen atoms in the system.

The high nitrogen content of shale oil asphaltene could affect the mineral content or ash content in asphaltenes. This property also will contribute to the surface and colloidal nature of shale oil to form emulsions with water. Finally, the hydrogen bonding is found both in shale oil asphaltene and in coal asphaltene. Purified petroleum asphaltene does not possess hydrogen bonding. Hydrogen bonding in shale oil asphaltene also originates from its high content of nitrogen.

ACKNOWLEDGMENTS

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TABLE I Elementary Analyses of Shale Oil Asphaltenes

Asphaltene	PS	RO	DW
Yield (%) ^a	1.19	2.01	1.69
Elemental Analysis ^b			
Carbon	75.58	81.25	79.73
Hydrogen	7.51	8.26	8.17
Nitrogen	3.41	4.31	3.49
Sulfur	0.72	0.81	1.15
Oxygen ^c	6.73	3.04	4.64
Ash	5.99	2.35	2.82
Atomic Ratio			
H/C	1.19	1.22	1.23
N/C	0.039	0.046	0.037
S/C	0.004	0.004	0.005
O/C	0.067	0.028	0.044
Molecular Weight ^d			
	709	630	605
Empirical Formula			
	C _{50.1} H _{59.4} N _{2.0} O _{3.4} S _{0.2}		
	C _{43.7} H _{52.7} N _{2.0} O _{1.2} S _{0.2}		
	C _{41.3} H _{50.5} N _{1.6} O _{1.3} S _{0.2}		

^aAverage of at least 2 runs. ^bExpressed in weight percentage.

^cBy difference. ^dBy VFC in benzene.

TABLE II Semiquantitative Analysis of Metals from Shale Oil Asphaltenes (ppm)

Asphaltene	DW	PS	RO
Si	12,000	25,000	10,000
Fe	130	1,500	120
Mg	15	230	21
Ca	4	620	8
Na	ND 50	TR 50	ND 50
Al	8	91	91
As	47	59	74
Ni	62	52	68
V	8	5	4
Cu	34	9	36
Zn	100	ND 10	140
Co	4.1	15	6.8
Loss on Ignition (%)			
	97.2	94.1	97.7

TABLE III Aromaticity and Crystallite Parameters for Shale Oil by X-Ray Diffraction

Asphaltene	DW	PS	RO
f _a	0.39	0.43	0.42
d _m ^a	3.57	3.57	3.57
d _y ^a	4.17	4.41	4.41
L _c ^a	15	15	16
M	5	5	5
L _a ^{a,b}	19	13	20
L _a ^{a,c}	12	7	12

^aAll expressed in Å.

^bFrom Scherrer's Eqn.

^cFrom Diamond's Curve.

TABLE IV Values for Structural Parameters of Shale Oil Asphaltenes from NMR Data

Asphaltene	DW	PS	RO
f _a ^a	0.49	0.50	0.47
σ ^b	0.58	0.62	0.56
HCC ^c	1.00 ^h	0.95 ^h	0.86
CAR ^d	20.4	20.4	20.7
CSR ^e	11.8	11.9	8.6
NAR ^f	1.03	1.52	3.64
NSC ^g	2.10	2.23	3.13

^aAromaticity; ^bDegree of Substitution as C₅₀/H₁

^cAromatic hydrogen to carbon ratio of the hypothetical unsubstituted aromatic portion, H₁/C_A

^dTotal number of aromatic ring carbon per molecule; ^eTotal number of substituted aromatic

ring carbon per molecule; ^fTotal number of aromatic ring carbon per molecule; ^gAverage number of

carbon atoms per saturated substituent, C₅/C_{SU}

^hBased on coefficients X, Y of 2. If more than

2, this value will be considerably less.

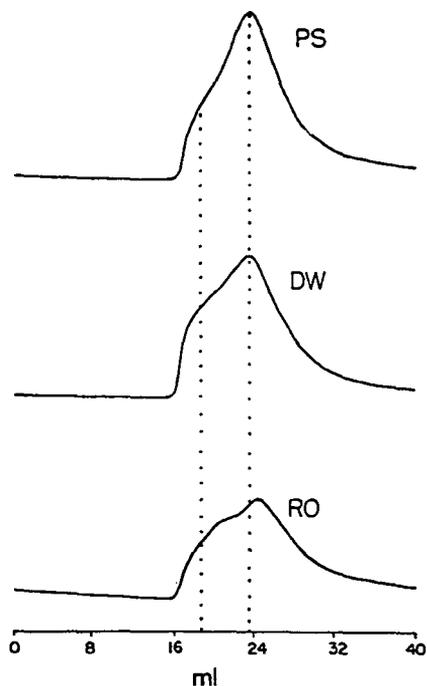


Fig. 1. Molecular Weight Distribution Patterns of three Shale Oil Asphaltenes Determined from HPLC. (the lower numbers of elution volume represents higher molecular weight).

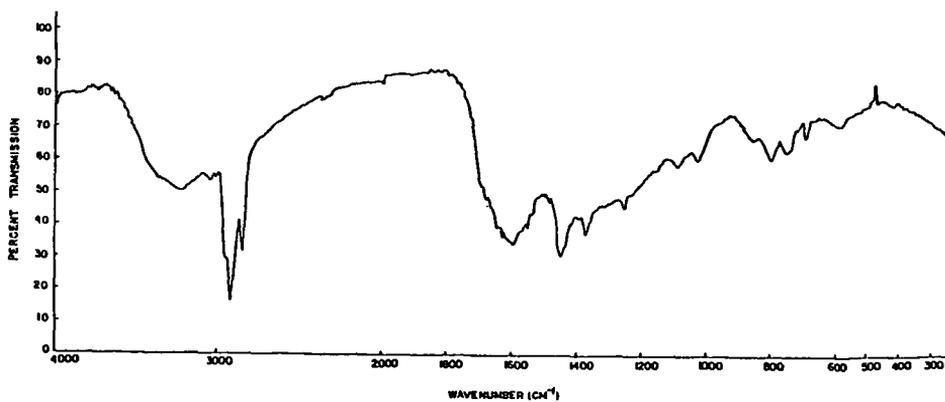


Fig.2. Infrared Spectrum of a Paraho Syncrude Asphaltene, (KBr Solid Phase).

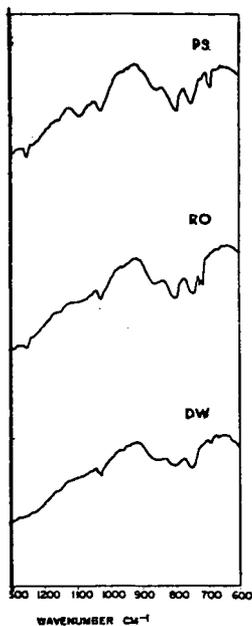


Fig. 3. Aromatic C-H Bending Vibrations of Three Shale Oil Asphaltenes.

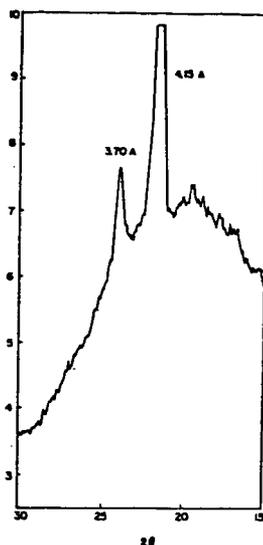


Fig. 4. X-ray Diffraction Scan of the Medium Angle Region of a Residue Oil Asphaltene from a Delayed Coker. (Sharp Bands indicate Crystalline Peaks).

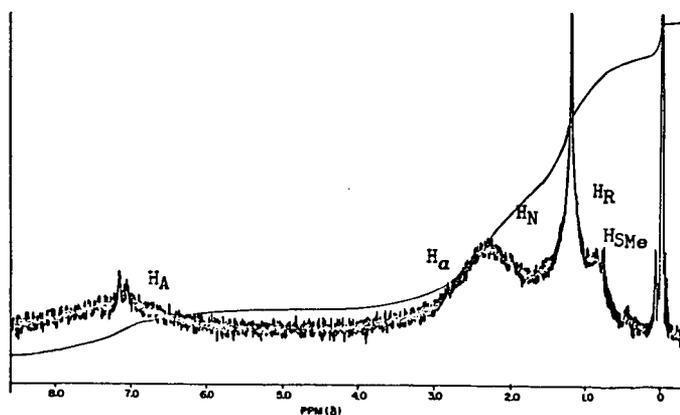


Fig. 5. Proton NMR Spectrum of a Paraho Synerude Asphaltene.