SOLUBILITY PARAMETER RELATIONSHIPS BETWEEN LIGNITE DERIVED ASPHALTENES AND PREASPHALTENES

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INTRODUCTION

In addition to the distillable products a sizeable portion of the low rank coal liquefaction products fall into asphaltene and preasphaltene categories. Asphaltenes are generally defined as those components in petroleum or coal liquids which under specific extraction conditions are soluble in benzene or toluene but insoluble in pentane or hexane (1,2). Preasphaltenes are those components that are soluble in pyridine or tetrahydrofuran but are insoluble in benzene or toluene. Farcasiu et al. (3) proposed the name, asphaltols, for this latter class of compounds because of the polyfunctional nature of these materials. In their work it was concluded asphaltenes are primarily monofunctional compounds while preasphaltenes are polyfunctional as determined by comparison of selective elution sequential chromatographic fractions and model compounds using thin layer chromatography (3,4). Preasphaltenes are formed in the initial stages of coal liquefaction where their formation may be responsible for the high viscosity of the products and for other processing difficulties (5). The preasphaltenes, on a weight basis, produce a viscosity about twice that for the asphaltene fraction (5).

Comparison of the structural features of asphaltenes and preasphaltenes show major differences between the two solubility categories occur with (1) their molecular weight distributions, (2) the fraction of total carbon present as aromatic carbons, (3) the fraction of total aromatic carbon present as edge aromatic carbons, (4) the fraction of oxygen present as phenolic and etheral oxygen atoms, and (5) the relative amount of hydrogen to phenolic content based on a per gram of total sample. Of all of these parameters a simple relationship of hydrogen and phenolic oxygen content has been found to establish the solubility of asphaltene and preasphaltene samples. The interrelationship between structural parameters will be discussed in this paper and in a subsequent paper (6) the relationship of these parameters to process conditions will be discussed.

EXPERIMENTAL

Liquefaction samples were obtained from the University of North Dakota Energy Research Center (formerly the Grand Forks Energy Technology Center). The reactor conditions are described in Table 1. The samples were isolated into asphaltene and preasphaltene fractions using exhaustive extraction techniques with toluene and tetrahydrofuran, respectively.

The asphaltene and preasphaltene samples were further separated using a preparative scale GPC column composed of 50 mm id x 120 cm glass column packed with Bio-Beads S-X3 (200-400 mesh) styrene-divinyl benzene copolymer. Prior to GPC separation all samples were acetylated with C-14 labeled acetic anhydride in order to convert all hydroxyl groups to acetate for minimization of hydrogen bonding during GPC fractionation. Elemental analyses were performed to determine elemental composition. Oxygen was determined by difference after

correction for labeled acetate present. The phenolic hydroxyl content was measured by combustion and C-14 counting content of resulting CO_2. Number average molecular weights of the samples were measured using a Model 117 Vapor Pressure Osmometer using pyridine as the solvent at 75°C. In normal runs, 2-3 concentrations over a range of 1 to 50 g/Kg·of pyridine were employed for extrapolation to infinite dilution.

RESULTS AND DISCUSSION

The chemical composition and structural features of a number of over 100 different lignite and bituminous coal liquefaction asphaltene and preasphaltene samples were measured. The overall percentage by weight of the starting coal falling into either the asphaltene or preasphaltene class and conditions of preparation are given in Table 1. In the case of the 15 and 26 series samples insufficient data are available to correct the percentages to a maf basis. The basic analytical data for the asphaltenes and preasphaltenes studied by Baltisberger et. al. (7) are summarized in Table 2. The three most significant structural factors are the molecular weight, oxygen functionality and nature of the aromatic carbons.

A. Solubility Parameter Relationships

The lignite and coal derived products were obtained over a range of temperatures from 400° to 480°C, under hydrogen or hydrogen-carbon monoxide pressures from 1500 to 4000 psi and various donor solvent conditions. The samples were fractionated into asphaltenes and preasphaltenes by solvent extraction using toluene and tetrahydrofuran (THF). The extracts were further fractionated by preparative GPC techniques. The isolated fractions were then analyzed for elemental composition, number average molecular weight by VPO using pyridine as the solvent, hydroxyl oxygen content by acetylation procedures and carbon structure by NMR techniques.

Plots of mole fraction of hydrogen; mole ratio of H/C; mole ratio of H/(C+N+O+S); mole ratio edge aromatic carbons/aromatic carbons, H_{aru}/C_{ar}; or moles hydrogen per 100 g sample were constructed versus the phenolic oxygen content in OH moles/100 g sample or mole fraction of OH. All the plots show a similar differentiation between asphaltenes and preasphaltenes as illustrated in Figure 1 for the moles of hydrogen per 100 g sample. The separation of the asphaltene (87%) and preasphaltene (84%) samples fall into two distinct regions of the graph. The portion of samples that did not fit were primarily low molecular weight preasphaltene and high molecular weight asphaltene samples. This is probably due to imperfections in the solubility separation. For example, part of the asphaltene fractions may have become trapped by adsorption processes in the preasphaltene portions during the extraction process. Steffgen et al. (1) have shown that great care must be taken during the fractionation of oil from asphaltene samples. It would be expected that great care should be exercised during the separation of asphaltene and preasphaltene samples. Equation 1 gives the fit for the dividing line added to Figure 1.

$$Z = H\% - (0.486 \pm 0.008)\ \text{OH mmole/g} - (4.47 \pm .02) \qquad (1)$$

Asphaltenes samples lie above the line giving positive Z values while preasphaltene samples give negative values. Samples which fit the wrong category are indicated by an X under the VTRA column of Table 2. The best differentiation occurred for the plot of molar density of moles H/100 g (wt % hydrogen) versus moles OH/100 g. Parameters which include parts of the total

data or terms calculated from parts of the data gave more mixing of the asphaltene and preasphaltene points. The most mixing occurred for H/C (Figure 2) or H_{aru}/C_{ar} (Figure 3) versus moles OH/100 g plots. Less mixing occurred for H/(C+N+O+S) while the best differentiation resulted when moles H/total sample wt were used. Correlation coefficient values (r values) computed using an IBM statistical analysis package are presented in Table 3. Overlap of the distinct regions shown in Figures 1 through 3 increased with the decreasing correlation of the parameter with mole fraction of hydrogen. Phenolic oxygen content have essentially with no linear correlation with hydrogen content for asphaltene samples while preasphaltene samples show some correlation (see Figure 4).

For the dissolution of a compound, A, into a solvent; the molar solubility

$$A(solid) \rightleftarrows A(liq) \qquad (2)$$

of A is a function of the activity coefficient, γ_A, where K° would be the

$$\text{Solubility} = S = \frac{K^\circ}{\gamma_A}$$

thermodynamic solubility constant for equation 1. From solubility parameter theory for regular solutions the activity coefficient, γ_i, for a solute i dissolving into solvent j is given by Equation 3 (8), where δ is the value of the Hildebrand solubility parameter of the solvent or solute and V_i is the

$$RT\ln\gamma_i = V_i(\delta_i-\delta_j)^2 \qquad (3)$$

molar volume of the solute. For maximum solubility the activity coefficient should approach unity and thus it is desirable to have $\delta_i = \delta_j$. The rule of thumb used in organic chemistry is that 'like dissolve like'. The solubility regions defined by Figure 1 suggest that the ordinate, hydrogen to other elements, is a function of the π and dispersive interactions of the coal matter while the abscissa, mmoles OH/g, is a function of the hydrogen bonding. Clearly the total hydrogen and hydroxyl contents are decisive parameters for establishing the benzene or THF solubility of the coal materials.

Equation 3 predicts an increase of the solubility activity coefficient with increasing molar volume of the solute. Several attempts were made to include V_i in the correlations by plotting log (H/C + MW) or log (H/C + MW/10) versus the acidity of the samples. This approach always mixed the asphaltene and preasphaltene regions. Asphaltenes and preasphaltenes have considerable overlapping of the molecular weights although on the average the total preasphaltene sample is several hundred grams/mole higher for the same process. We observed for all series of preasphaltene samples obtained from the same process conditions that the molecular weight increased as the H/C mole ratio decreased (see Figure 4). The molecular weights of each fraction of the preasphaltenes and asphaltenes from runs 46 and 32 are shown on Figure 4 so the overlap of the molecular weight ranges can be observed. Asphaltene samples show that molecular weights are virtually independent of the H/C ratio and that the acidity changes occur in no reproducible way. The major difference shown in Figure 4 is the removal of phenolic oxygen when going to recycle conditions (run 46) as opposed to those without bottoms recycle (run 32). Other oxygen is also lowered by the recycle conditions although this factor is not apparent in

the figure. The molecular weight data for Figure 4 is given in Table 4. This behavior is representative of all the samples when individual runs are compared. Because of the different molecular weight relationships for asphaltene and preasphaltene samples, it is not surprising that molecular weight terms can not correlate directly in the solubility plots such as Figure 1.

Plots of the mole fraction of hydrogen or H_{aru}/C_{ar} versus acidity are not as effective in defining the solubility regions as is the graph of mole fraction hydrogen. A major contributing factor in these correlations is due to the relationship between aromaticity and condensation and the carbon to hydrogen mole ratio. The fraction of aromatic carbons is defined by equation 4

$$f_a = \frac{C/H - (H^*_{al}/2)}{C/H} \tag{4}$$

where C/H is the carbon to hydrogen mole ratio and H^*_{al} is the mole fraction of aliphatic hydrogens in the sample as determined by NMR measurements (9). The condensation is represented by the number of hypothetical edge aromatic carbons (H_{aru}) per total aromatic carbons (C_{ar}) as defined by equation 5,

$$H_{aru}/C_{ar} = \frac{H^*_{ar} + H^*_{al}/2 + (OH + 2\ O)/H}{F_a(C/H)} \tag{5}$$

In equation 5, H^*_{ar} corresponds to the mole fraction of aromatic protons as determined by NMR and the oxygen terms are mole ratios to total hydrogen (9). The magnitude of both f_a and H_{aru}/C_{ar} are determined to a large extent by the C/H ratio. However, the solubility of a molecule must be determined by additional factors as well as the percentage and condensation of the aromatic carbons.

Oxygen comprises 4 to 8% of the sample by weight and is 40 to 70% phenolic depending on the solubility category. Table 5 shows the percentage of oxygen as phenolics and ethers. For most of the recycle samples preasphaltenes contain 40-50% of the oxygen as phenolics while asphaltenes are 60-75% phenolic. On the other hand, non-recycle conditions lead to nearly equal amounts of etheral and phenolic oxygen for both asphaltene and preasphaltene samples. Only the phenolic content of the samples is taken into account in the abscissa. The ether content undoubtedly has an influence on the size, shape and π-π interactions of the aromatic systems. Thus, the inclusion of oxygen content with the ordinate better correlates the dispersive, size, shape and π-π interactions of the molecules. Another factor influencing solubility would be the nature of the aliphatic carbons. Liquefaction under hydrogen alone tends to produce asphaltenes and preasphaltenes with (shorter average aliphatic chain length) than do hydrogen-carbon monoxide systems (10). Lacking inclusion of a specific term for the length of the aliphatic chains, the influence of aliphatic carbons is best taken into account using the total moles of hydrogen in the abscissa. Nitrogen contents are generally small and evenly distributed, except for a sizeable fraction of low MW preasphaltenes that had appreciably higher values. Sulfur contents are also small and both asphaltene and preasphaltene contents appear to respond similarly to processing condition.

CONCLUSIONS

Comparison of the total fractions of the preasphaltenes and asphaltenes of the same process show the following.

First, preasphaltene samples increase in the fraction of aromatic carbons and degree of condensation with increasing molecular weight. Asphaltenes samples, on the other hand, increase in the fraction of aromatic carbons with decreasing molecular weight. The degree of condensation maximizes at high and low molecules weight values.

Second, asphaltene samples have lower f_a and higher H_{aru}/C_{ar} values than the preasphaltenes. Asphaltenes contain fewer condensed aromatic molecules than do the preasphaltenes.

Third, the phenolic acid content is lower for the asphaltene samples in general. This acidic property works in combination with the total hydrogen content to ultimately determine into which solubility category a sample may fall.

Fourth, Table 3 shows that the recycle preasphaltene samples contain a higher percentage of oxygen and much of that is due to increased other (non phenolic) oxygen, possibly in ethers. Recycle asphaltene samples contain about 60-70% phenolic oxygen, while preasphaltenes contain 40-50% phenolic oxygen. Non-recycle conditions lead to higher total oxygen contents of both categories and to nearly the same distribution between asphaltene and preasphaltene samples. Recycling of the vacuum bottom leads to an etheral oxygen removal. This is probably one reason for the success of the plot of mole fraction of total hydrogen versus phenolic content rather than the plot of H_{aru}/C_{ar} versus phenolic content gives a better separation of asphaltene and preasphaltene samples. The mole fraction of the hydrogen term takes in account the oxygen content of the sample further separating the regions of Figure 1.

Fifth, molecular weight ranges of the two categories overlap. When a number of samples within a narrow range was examined, one observed that the majority of the preasphaltenes lie in a range from 600 to 2500 g/mol while the asphaltenes lie between 300 to 600 g/mol. Preasphaltene samples increased in phenolic content with decreasing molecular weight (see Figure 4). Asphaltene samples show random phenolic content with molecular weight. However, inclusion of the molecular weight directly in a solubility plot similar to Figure 1 was not successful.

For the lignite process samples studied, the differentiation of the asphaltene and preasphaltene samples follow equation 1 rather well for over 80% of the samples. Hydrogen and phenolic content seem to be the only parameters needed to specify into which solubility category the hexane insoluble portions (non distillable) of a lignite liquefaction process may lie. The implication is that it is desireable to lower the phenolic oxygen content while raising the H/C mole ratio during liquefaction.

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Table 1. Asphaltene and Preasphaltene Yields and Continuous Process Operating Conditions

Sample	Yield, wt % maf Coal Asphaltenes[a]	Preasphaltenes[a]	Conversion	Gas	Gas Flow scfh	Press, Psig	Temp, °C	Coal[b]
Bottoms Recycle Operation[c]								
44-12[d]	9	5.0	92	$CO-H_2$	52	1978	458	B3
46-16[e]	14	7.0	52	$CO-H_2$	52	2013	458	B3
41-14	12	6.0	92	$CO-H_2$	44	3841	459	B3
45-15	10.5	5.5	88	H_2	55	3934	461	B3
58-15	11.3	5.7	95	H_2	41	2651	459	BB2
53-18	NA	NA	92	H_2	32	2006	469	POW1
69-12	15.6	6.3	87	$CO-H_2$	38	2633	458	POW1
103-17[f]	NA	NA	96	$H_2S-CO-H_2$	38	4050	438	ZAP2
Single Pass Operations[c]								
15-2[g]	(9)	(9.5)	NA	$CO-H_2$	27	4000	404	B3
26-7[g]	(7.8)	(6.4)	85	$CO-H_2$	28	3825	463	B3
26-11[g]	(8.3)	(5.3)	81	$CO-H_2$	29	3890	483	B3
32-3[h]	9.8	6.2	82	$CO-H_2$	32	3765	450	B3
34-4[h]	24	16	87	$CO-H_2$	70	4020	459	B3

[a]Yields in parenthesis are percentages of total SRL or SRC. Insufficient data is available to convert the number to a maf basis.

[b]Beulah and Indianhead are B3 and Zap2 Great Plains lignite samples; Big Brown is BB2 Gulf Coast lignite sample; and Powhattan is POW1 bituminous coal sample.

[c]Bottoms recycle utilized the product slurry containing ash, insolubles, and SRL as solvent for the subsequent pass in an open tubular reactor. Single pass utilized an anthracene oil and coal were passed through the reactor once (see DOE/GFETC/QTR-78/T4, NTIS).

[d]A heavy hydrogen donor (HAB1) was spiked each pass.

[e] Started up initially with a good H-donor solvent (HAB1).

[f]Feed gas ratio of CO to H_2 was 6:94. H_2S was nominally fed at 5 wt % of coal.

[g]CPU operation with a CSTR reactor and AO1-10% tetralin solvent.

[h]CPU operation with an open tubular reactor and AOD1 solvent (a distillate cut of AO1).

Table 2. Structural Features of Asphaltene Samples

RUN	PER	FRACT	WTPCT	VTRA[b]	Wt % C	H	N	O	S	MWVPO	OH	HTOC	HARUCAR	NMR[c] HAR	HAL	HOTH	Z[b]
15	2	0	100.00	.	83.75	6.09	0.81	8.15	1.21	500	1.853	0.872	0.852	36.3	48.3	12.4	0.7
15	2	1	5.33	.	81.73	6.30	0.91	9.85	1.21	2129	1.974	0.925	0.855	27.3	45.1	24.4	0.9
15	2	2	5.37	.	81.81	5.52	0.90	10.56	1.21	1510	1.986	0.809	0.671	22.3	40.3	33.8	0.1
15	2	3	8.52	.	81.61	5.86	0.77	10.54	1.22	1011	2.104	0.862	0.748	23.4	42.6	30.5	0.4
15	2	4	12.58	.	81.70	6.01	1.01	10.04	1.23	722	2.355	0.883	0.827	25.9	48.7	21.5	0.4
15	2	5	15.02	.	82.25	6.44	0.60	9.46	1.25	592	2.747	0.940	0.922	28.1	50.8	16.7	0.6
15	2	6	20.94	.	83.21	6.20	0.67	8.70	1.23	417	2.235	0.895	0.887	33.7	50.6	12.1	0.6
15	2	7	13.83	.	89.26	6.10	0.48	2.98	1.17	288	1.121	0.820	0.780	46.5	47.4	4.2	1.1
15	2	8	4.35	.	90.48	5.55	0.46	2.37	1.14	261	0.410	0.736	0.691	56.5	38.4	4.4	0.9
15	2	9	1.05	.	91.68	5.45	0.51	1.22	1.13	261	0.170	0.714	0.638	61.7	28.1	9.9	0.9
26	7	0	100.00	.	87.76	5.26	1.08	5.07	0.82	500	1.241	0.720	0.700	54.7	38.1	4.7	0.2
26	7	1	8.50	X	84.03	4.69	1.16	9.30	0.82	1663	1.231	0.669	0.640	50.1	30.6	16.6	-0.4
26	7	2	8.50	X	86.40	4.63	0.89	7.25	0.82	1104	1.241	0.644	0.608	50.8	34.2	12.3	-0.4
26	7	3	9.70	X	86.13	4.59	1.07	7.38	0.82	888	1.282	0.640	0.619	51.5	36.6	9.0	-0.5
26	7	4	9.70	.	86.25	4.95	0.87	7.10	0.83	595	1.412	0.689	0.664	50.5	37.5	9.2	-0.2
26	7	5	13.90	.	87.19	5.37	0.91	5.69	0.84	480	1.763	0.739	0.740	51.6	44.1	1.0	0.0
26	7	6	19.00	.	88.53	5.29	0.55	4.80	0.83	344	1.492	0.717	0.710	54.5	41.6	1.0	0.1
26	7	7	19.90	.	90.96	5.25	0.73	2.26	0.80	344	0.620	0.693	0.655	62.6	32.4	3.7	0.5
26	7	8	9.80	.	89.45	4.76	0.69	4.32	0.79	344	0.180	0.639	0.631	74.5	20.9	4.3	0.2
26	7	9	2.50	.	87.20	4.76	0.47	6.79	0.78	344	0.110	0.655	0.676	78.7	16.5	4.5	0.2
26	11	0	100.00	.	87.08	5.83	0.98	4.89	1.22	500	1.221	0.804	0.756	46.8	41.3	9.9	0.8
26	11	1	2.90	X	83.22	4.61	1.28	9.67	1.22	1556	1.282	0.665	0.592	37.4	36.2	23.6	-0.5
26	11	2	3.30	.	83.51	4.96	1.26	9.05	1.22	1205	1.282	0.713	0.628	37.9	35.0	24.5	-0.1
26	11	3	6.00	.	83.54	5.08	1.15	9.01	1.23	924	1.342	0.729	0.617	24.7	47.4	25.2	-0.0
26	11	4	11.00	.	84.61	5.58	1.02	7.57	1.23	690	1.442	0.791	0.694	37.1	37.6	22.8	0.4
26	11	5	15.00	.	84.74	5.61	0.88	7.51	1.25	517	1.833	0.794	0.734	38.0	42.3	16.4	0.2
26	11	6	30.00	.	86.63	5.82	0.64	5.68	1.24	353	1.602	0.806	0.804	46.4	48.4	2.5	0.6
26	11	7	14.80	.	90.70	5.65	0.17	2.30	1.18	267	0.380	0.748	0.704	56.0	39.5	3.9	1.0
26	11	8	22.30	X	91.89	5.32	0.33	1.29	1.16	261	9.000	0.695	0.662	69.9	27.4	2.6	-3.5
26	11	9	8.60	X	92.95	4.84	0.39	0.65	1.16	262	3.000	0.625	0.591	78.5	17.9	3.5	-1.1
32	3	0	97.00	.	84.35	5.95	1.22	7.93	0.55	390	2.571	0.846	0.808	40.9	39.7	15.2	0.2
32	3	1	3.10	.	83.16	5.43	2.06	8.82	0.54	1360	1.834	0.783	0.648	33.3	30.9	32.4	0.1
32	3	2	5.60	.	83.05	5.48	1.51	9.42	0.54	1540	2.043	0.791	0.697	35.3	34.2	26.8	0.0
32	3	3	6.90	.	84.04	5.77	1.48	8.16	0.55	1010	2.164	0.824	0.696	32.2	34.6	29.4	0.3
32	3	4	9.80	.	83.34	6.00	1.23	8.88	0.55	640	2.335	0.864	0.793	32.5	41.8	21.7	0.4
32	3	5	14.80	.	83.57	6.08	1.06	8.73	0.56	552	2.792	0.873	0.808	31.7	43.2	20.5	0.3
32	3	6	20.90	.	82.83	6.21	1.05	9.33	0.57	390	3.424	0.900	0.916	34.5	49.7	10.3	0.1
32	3	7	22.20	.	83.98	6.07	1.04	8.35	0.56	297	2.861	0.867	0.924	40.3	55.0	-0.0	0.2
32	3	8	12.10	.	88.94	5.72	0.91	3.91	0.52	242	0.970	0.771	0.767	56.8	41.6	-0.0	0.8
34	4	0	94.00	.	83.55	5.99	1.28	8.62	0.57	388	3.107	0.861	0.858	40.1	43.7	11.0	0.0
34	4	1	2.80	.	84.43	5.73	1.99	7.30	0.55	2330	2.221	0.815	0.614	27.8	29.6	38.7	0.2
34	4	2	5.30	.	84.58	5.68	2.06	7.13	0.55	1280	2.471	0.805	0.638	29.9	32.4	33.4	0.0
34	4	3	7.30	.	84.33	5.84	1.63	7.64	0.56	1050	2.663	0.831	0.691	31.1	34.2	30.2	0.1
34	4	4	10.80	.	84.31	6.00	1.56	7.56	0.56	765	2.969	0.854	0.736	30.5	38.5	26.1	0.1
34	4	5	16.40	.	83.93	6.18	1.38	7.93	0.57	550	3.502	0.884	0.815	31.5	42.9	20.0	0.0
34	4	6	21.70	X	83.02	6.16	1.36	8.87	0.59	374	4.377	0.890	0.909	33.7	50.9	8.3	-0.4
34	4	7	20.60	.	85.64	6.11	0.98	6.72	0.56	324	2.736	0.856	0.863	42.2	48.6	4.8	0.3
34	4	8	12.00	.	90.12	5.90	0.72	2.75	0.51	256	0.682	0.786	0.751	56.2	38.4	4.2	1.1
41	14	0	100.00	.	87.58	6.65	1.36	4.14	0.27	372	1.570	0.911	0.762	37.4	34.1	26.1	1.4
41	14	1	10.80	.	84.37	5.97	2.03	7.39	0.24	1250	1.493	0.849	0.661	29.1	31.7	36.7	0.8
41	14	2	5.40	.	85.51	7.03	1.52	5.69	0.24	740	1.532	0.986	0.691	23.2	27.8	46.9	1.8
41	14	3	7.30	.	86.09	6.98	1.43	5.28	0.21	645	1.593	0.973	0.713	23.8	32.2	41.7	1.7
41	14	4	11.40	.	85.84	6.95	1.22	5.78	0.22	470	1.842	0.971	0.784	27.5	36.0	33.9	1.6
41	14	5A	23.30	.	86.08	7.01	1.22	5.47	0.22	350	2.094	0.977	0.815	30.4	35.9	30.7	1.5
41	14	5B	28.50	.	88.37	6.30	1.25	3.87	0.21	280	0.985	0.856	0.740	42.7	35.6	20.2	1.4
41	14	5C	13.40	X	92.09	5.10	1.17	1.43	0.20	250	6.200	0.665	0.613	69.2	23.5	7.3	-2.4
44	12	0	100.00	.	88.52	5.57	0.87	4.71	0.32	378	0.962	0.755	0.694	54.2	31.0	13.1	0.6
45	15	0	100.00	.	88.68	6.39	1.17	3.48	0.27	384	1.599	0.865	0.759	43.8	35.4	18.3	1.1
46	16	0	100.00	.	90.10	5.93	1.09	2.55	0.32	333	1.136	0.790	0.704	54.5	29.2	14.4	0.9
46	16	1	9.20	.	86.34	5.51	1.53	6.39	0.23	876	1.247	0.765	0.607	40.5	24.0	33.3	0.4
46	16	2	22.90	.	87.16	6.22	1.09	5.33	0.19	431	1.464	0.857	0.727	38.9	33.6	25.1	1.0
46	16	3	25.90	.	88.69	6.27	1.17	3.66	0.21	290	1.124	0.848	0.771	47.1	37.3	13.8	1.3
46	16	4	25.80	.	91.65	5.74	0.68	1.73	0.20	250	0.399	0.751	0.697	62.5	29.8	7.0	1.1
46	16	5	16.20	X	93.37	5.06	0.64	0.73	0.20	260	5.300	0.650	0.621	81.1	15.1	3.7	-2.0
53	18	0	100.00	.	89.02	5.68	1.80	2.65	0.85	336	0.960	0.765	0.682	54.5	30.1	13.7	0.7
58	15	0	100.00	.	88.47	6.09	1.70	3.48	0.26	322	1.339	0.826	0.750	52.0	31.9	13.9	1.0
69	12	0	100.00	.	88.54	5.97	1.93	2.63	0.93	347	1.012	0.809	0.709	48.9	31.7	17.8	1.0

Table 2. Structural Features of Preasphaltene Samples

RUN	PER	FRACT	WTPCT	VTRA[b]	Wt % C	H	N	O	S	MWVPO	OH	HTOC	HARUCAR	NMR[c] HAR	HAL	HOTH	Z[b]
15	2	1	15.40	.	80.47	4.95	1.59	12.42	0.56	2716	1.801	0.739	0.690	35.1	35.7	25.6	-0.4
15	2	10	1.92	X	88.58	6.21	0.53	3.77	0.90	272	0.569	0.842	0.729	42.5	37.6	19.0	1.5
15	2	11	1.25	.	75.01	4.88	0.24	18.98	0.88	272	4.400	0.781	0.913	51.7	37.7	10.5	-1.7
15	2	12	0.60	.	84.88	5.21	0.35	8.68	0.88	272	5.000	0.737	0.742	55.9	36.1	8.0	-1.7
15	2	2	26.44	.	80.50	4.78	1.40	12.70	0.61	2497	1.878	0.713	0.668	35.4	35.2	25.5	-0.6
15	2	3	17.32	.	80.36	4.79	1.31	13.54	0.00	2055	1.973	0.716	0.702	34.4	40.6	20.9	-0.6
15	2	4	7.36	.	80.04	5.14	0.98	13.31	0.53	1228	2.377	0.771	0.778	31.6	47.3	16.5	-0.5
15	2	5	7.11	.	78.48	5.52	0.95	14.53	0.52	823	2.736	0.844	0.895	31.0	50.0	14.0	-0.3
15	2	6	7.70	.	78.15	5.79	0.97	14.55	0.53	619	2.949	0.890	0.966	30.4	52.4	12.1	-0.1
15	2	7	4.27	.	78.03	6.01	1.00	14.38	0.58	459	2.944	0.924	1.023	30.9	54.4	9.9	0.1
15	2	8	6.78	X	79.57	6.26	1.12	12.06	0.99	382	2.896	0.944	0.992	31.9	49.9	13.5	0.4
15	2	9	3.85	X	82.17	6.42	0.84	9.62	0.95	314	1.919	0.938	0.905	34.9	42.3	19.9	1.0
26	7	1	8.49	.	83.86	4.74	2.01	8.85	0.54	1874	1.381	0.678	0.658	53.4	29.3	14.3	-0.4
26	7	10	2.40	.	91.68	5.69	0.31	1.69	0.63	404	2.800	0.745	0.708	65.6	30.8	3.6	-0.1
26	7	2	23.36	.	85.31	4.66	1.73	7.50	0.80	1496	1.479	0.656	0.616	50.7	31.6	14.5	-0.5
26	7	3	19.60	.	83.91	4.74	1.47	9.31	0.58	1314	1.694	0.678	0.677	55.5	29.5	11.5	-0.6
26	7	4	13.52	.	82.80	5.02	1.36	10.08	0.73	640	2.261	0.728	0.761	46.4	44.8	4.3	-0.5
26	7	5	8.40	.	82.69	5.46	1.29	10.01	0.55	488	3.037	0.792	0.831	38.9	51.9	3.6	-0.5
26	7	6	7.84	.	81.63	5.74	1.20	10.76	0.67	404	3.338	0.844	0.909	41.2	49.9	3.1	-0.4
26	7	7	6.08	.	83.98	6.03	1.09	8.18	0.72	404	3.227	0.862	0.886	41.1	48.4	5.2	-0.0
26	7	8	4.96	X	88.06	6.16	0.49	4.62	0.66	404	1.255	0.839	0.810	46.4	44.4	7.2	1.1
26	7	9	4.96	X	90.61	6.05	0.32	2.38	0.64	404	0.205	0.801	0.746	55.3	37.4	7.0	1.5
26	11	1	21.68	.	85.79	4.61	1.49	7.63	0.48	1039	1.021	0.645	0.623	56.8	28.9	12.1	-0.4
26	11	2	31.24	.	86.03	4.73	1.34	7.41	0.50	829	1.426	0.659	0.645	54.2	33.9	8.9	-0.4
26	11	3	22.22	.	85.67	4.79	1.35	7.70	0.49	621	1.501	0.671	0.671	54.7	35.8	6.3	-0.4
26	11	4	9.17	.	84.88	4.82	1.32	8.29	0.69	480	1.882	0.682	0.695	53.0	38.6	4.5	-0.6
26	11	5	3.03	X	84.81	5.54	0.93	8.06	0.67	480	0.985	0.784	0.799	55.5	37.0	5.7	0.6
26	11	6	1.86	X	90.56	5.56	0.36	2.87	0.65	480	0.212	0.736	0.696	62.2	31.5	5.9	1.0
26	11	7	0.78	.	91.23	5.28	0.23	2.61	0.64	480	3.900	0.695	0.666	71.1	24.0	4.8	-1.1
26	11	8	0.15	.	91.32	5.27	0.61	2.15	0.64	480	3.200	0.693	0.645	74.0	16.2	9.7	-0.8
32	3	0	97.00	.	83.22	5.06	2.16	8.99	0.57	588	3.115	0.730	0.721	40.8	43.2	9.9	-0.9
32	3	1	16.20	.	83.78	4.53	2.30	8.85	0.54	1320	1.912	0.649	0.564	39.8	29.7	26.3	-0.9
32	3	2	19.90	.	83.38	4.70	2.40	8.97	0.55	1800	2.376	0.677	0.647	42.2	38.8	14.0	-0.9
32	3	3	13.30	.	82.37	4.95	2.15	9.97	0.56	837	2.935	0.721	0.696	41.8	35.8	16.5	-0.9
32	3	4	12.40	.	83.01	5.07	2.39	8.93	0.59	648	4.374	0.732	0.747	42.7	43.0	5.7	-1.5
32	3	5	13.00	.	81.25	5.36	1.94	10.86	0.58	570	3.714	0.792	0.839	45.3	42.0	5.7	-0.9
32	3	6	11.30	.	80.25	5.56	1.88	11.72	0.59	397	4.179	0.831	0.888	40.2	45.2	7.1	-0.9
32	3	7	8.80	.	76.52	6.04	1.95	14.91	0.59	290	4.053	0.946	1.046	33.6	47.1	12.6	-0.4
32	3	8	2.70	X	83.95	6.25	2.53	6.72	0.55	241	2.291	0.893	0.804	34.6	40.4	21.4	0.7
34	4	0	97.00	.	83.49	5.07	2.15	8.73	0.56	612	2.824	0.729	0.715	41.2	43.0	10.2	-0.8
34	4	1	13.60	.	83.58	4.55	2.73	8.61	0.53	2020	1.616	0.653	0.550	37.4	30.5	28.5	-0.7
34	4	2	24.30	.	83.58	4.72	2.44	8.72	0.54	1780	1.925	0.677	0.600	39.5	33.1	23.3	-0.7
34	4	3	13.90	.	82.98	5.03	2.57	8.88	0.55	940	2.525	0.727	0.694	39.8	40.9	14.2	-0.7
34	4	4	12.20	.	82.50	5.18	2.26	9.50	0.56	690	2.957	0.753	0.738	38.7	43.4	12.2	-0.7
34	4	5	12.60	.	81.24	5.30	1.96	10.92	0.57	470	3.187	0.783	0.804	39.6	44.7	9.7	-0.7
34	4	6	9.80	.	80.53	5.40	2.00	11.49	0.57	390	3.545	0.805	0.848	37.8	48.2	7.5	-0.8
41	14	0	100.00	.	85.27	5.17	1.98	7.35	0.24	671	1.790	0.727	0.631	43.5	28.3	24.7	-0.2
41	14	1	21.40	.	86.72	4.47	1.56	7.03	0.21	2850	1.321	0.619	0.530	47.8	24.0	25.2	-0.6
41	14	2	16.60	.	85.00	4.73	2.01	8.05	0.21	1420	1.603	0.667	0.590	45.2	28.0	23.5	-0.5
41	14	3	26.10	.	84.48	5.02	1.91	8.44	0.15	740	2.010	0.713	0.661	44.5	33.4	18.1	-0.4
41	14	4	24.10	.	83.96	5.51	1.81	8.50	0.22	430	2.492	0.788	0.744	41.5	37.3	16.6	-0.2
41	14	5	11.80	X	86.90	6.02	1.65	5.23	0.21	290	1.102	0.831	0.679	42.2	26.6	29.3	1.0
44	12	0	100.00	.	87.76	4.90	1.44	5.69	0.21	600	1.540	0.670	0.621	58.8	23.5	14.6	-0.3
45	15	0	100.00	.	85.58	5.28	1.57	7.42	0.15	676	1.783	0.740	0.649	43.3	29.9	23.4	-0.1
46	16	0	100.00	.	88.48	4.85	1.44	4.80	0.44	608	1.604	0.657	0.609	59.0	25.5	12.2	-0.4
46	16	1	15.50	.	87.64	4.12	2.03	6.07	0.14	2650	0.808	0.564	0.531	69.5	12.0	16.6	-0.7
46	16	2	14.40	.	87.16	4.28	1.90	6.48	0.18	1420	1.232	0.589	0.551	61.7	19.6	15.9	-0.8
46	16	3	23.10	.	86.52	4.46	1.81	6.99	0.21	806	1.426	0.619	0.584	57.7	24.6	14.6	-0.7
46	16	4	25.60	.	86.64	4.93	1.58	6.69	0.16	390	1.777	0.683	0.650	54.7	29.7	12.0	-0.4
46	16	5	21.30	X	87.29	5.60	1.41	5.49	0.21	290	0.861	0.770	0.695	54.2	25.9	18.4	0.7
53	18	0	100.00	.	85.80	4.55	2.28	6.51	0.87	701	1.433	0.636	0.568	53.9	23.3	19.6	-0.6
58	15	0	100.00	.	86.68	5.05	2.50	5.62	0.15	620	1.804	0.699	0.631	53.8	25.0	17.6	-0.3
69	12	0	100.00	.	86.56	4.88	2.47	5.16	0.93	702	1.177	0.676	0.584	52.1	23.9	21.6	-0.2

Table 2. Structural Features of 103[a]

					Wt %									NMR[c]				
RUN	PER	FRACT	WTPCT	VTRA[b]	C	H	N	O	S	MWVPO	OH	HTOC	HARUCAR	HAR	HAL	HOTH	Z[b]
103	17	0	100.00	.	87.77	5.62	1.70	4.67	0.24	560	2.120	0.768	d	-	-	-	0.1
103	17	1	16.60	.	87.51	4.57	1.90	5.67	0.34	1600	0.690	0.627	-	-	-	-	-0.2
103	17	2	11.40	.	84.67	5.36	2.46	6.77	0.73	930	1.470	0.760	-	-	-	-	0.2
103	17	3	14.30	.	86.10	5.76	2.12	5.65	0.37	510	1.920	0.803	-	-	-	-	0.4
103	17	4	19.80	.	85.51	6.06	1.82	6.04	0.57	330	2.460	0.851	-	-	-	-	0.4
103	17	5	21.70	.	85.59	6.39	1.47	6.26	0.29	140	2.050	0.896	-	-	-	-	0.9
103	17	6	14.10	.	87.07	6.11	1.21	5.17	0.45	140	0.940	0.842	-	-	-	-	1.2

a. 103 is a total SRL containing both asphaltenes and preasphaltenes.
b. X in VTRA indicates Z = H% - 0.486(OH) - 4.67 mismatch. If Z = negative sample is a preasphaltene. If Z = positive sample is an asphaltene.
c. $H_{ar} + H_{al} + H_{OH} = 100$, sum of mole fractionof aromatic, aliphatic and phenolic protons equals 100. To obtain H_{OH} subtract $H_{ar} + H_{al}$ from 100. H_o equals mole percent of protons on aliphatic carbons more than one carbon unit from an aromatic ring, alpha + other protons equals total aliphatic protons.
d. Data not measured.

Table 3. Correlation Coefficients (r) Between Various Asphaltene and Preasphaltene Parameters

Asphaltenes	r value			
Parameter	H[a]	H/M[b]	H/C[c]	H_{aru}/C_{ar}[d]
H	1.0	0.996	0.943	0.56
H/M	---	1.0	0.970	0.60
H/C	---	---	1.0	0.64
H_{aru}/C_{ar}	---	---	---	1.00
OH	-0.14	-0.13	-0.100	0.03

Preasphaltenes				
Parameter	H	H/M	H/C	H_{aru}/C_{ar}
H	1.0	0.998	0.97	0.91
H/M	---	1.0	0.98	0.93
H/C	---	---	1.0	0.96
H_{aru}/C_{ar}	---	---	---	1.0
OH	0.78	0.793	0.82	0.83

a. Mole fraction of hydrogen (wt %).
b. Mole ratio of H/(C+N+O+S).
c. Molar H/C ratio.
d. Mole ratio of edge aromatic to aromatic carbon.

Table 4. Molecular Weight Values for Runs 46 and 32

Sample	Molecular Weight[a] Asphaltene	Preasphaltene
46-1	875	2650
46-2	430	1420
46-3	290	810
46-4	250	390
46-5	260	290
32-1	1360	1320
32-2	1540	1800
32-3	1010	840
32-4	640	650
32-5	550	570
32-6	390	400
32-7	300	---

[a]determined by VPO, solvent pyridine

Table 5. Comparison of Oxygen Functionality for Various Asphaltene (A) and Preasphaltene (PA) Samples

Sample	Recycle[a]	Oxygen Content mmoles/g Total O_2	Phenol	% O_2 as phenol
41 PA	yes	4.39	1.79	41
41 A	yes	2.48	1.57	63
45 PA	yes	4.42	1.78	40
45 A	yes	2.09	1.60	77
53 PA	yes	3.92	1.43	37
53 A	yes	1.61	0.96	60
69 PA	yes	3.13	1.12	36
69 A	yes	1.60	1.01	63
103 Total[b]	yes	2.91	2.12	73
32 PA	no	5.61	3.12	55
32 A	no	5.51	2.57	52
15 PA	no	7.89	2.11	17
15 A	no	5.09	1.85	36
26 PA	no	5.16	1.89	37
26 A	no	3.16	1.24	40

[a]No indicates petroleum derived solvent passed once through. Yes indicates bottom recycle solvent used.

[b]In this case asphaltene and preasphaltene sample not separated. H_2S run.

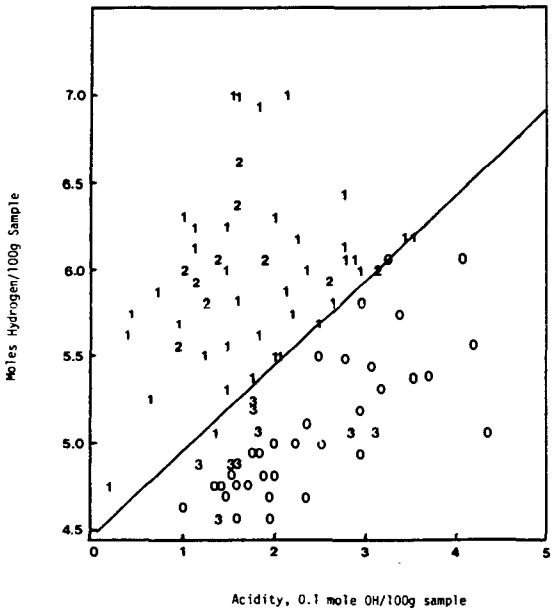

Figure 1 The hydrogen and acid content of asphaltene (1) and preasphaltene (0) fractions. Total preasphaltene (3) and asphaltene (2). Samples (unfractionated) are also plotted.

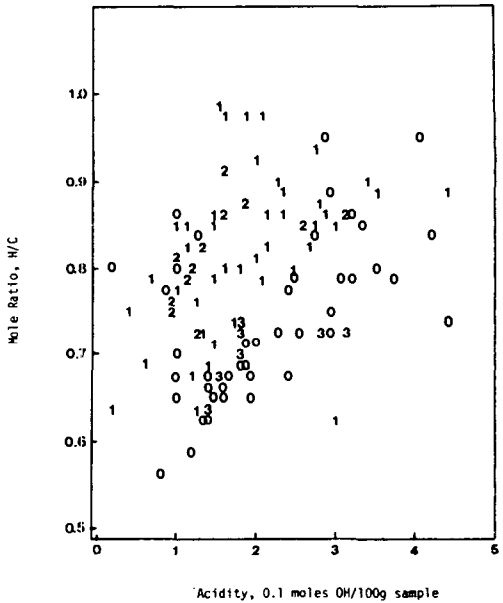

Figure 2 The relationship of H/C mole ratio to acidity of asphaltene (1), and preasphaltene (0) fractions. Total preasphaltenes (3) and total asphaltenes (2) are also plotted (unfractionated).

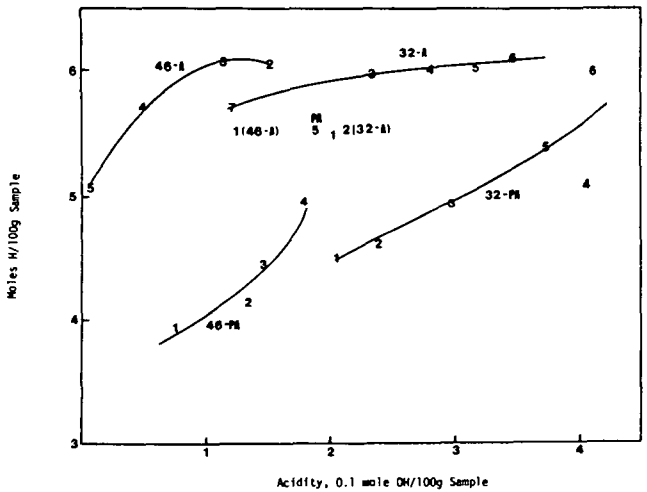

Figure 4 Hydrogen and phenolic hydroxyl dependence of Runs 32 and 46. A=Asphaltene, PA=Preasphaltene; Molecular wt decreases with fraction number 1-7.

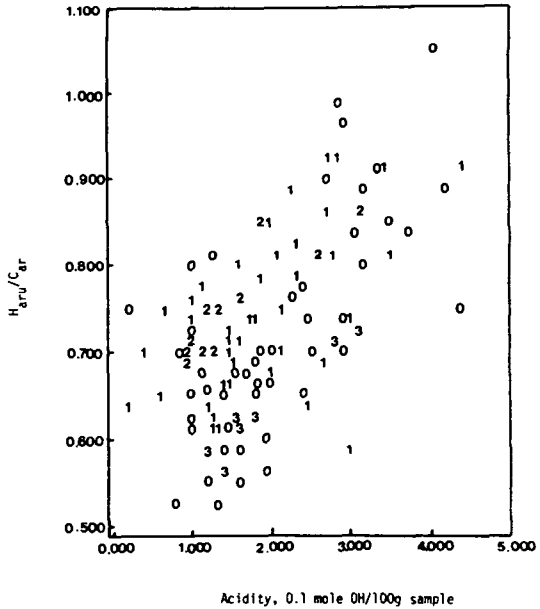

Figure 3 The degree of condensation and acidity of asphaltene (1) and preasphaltene (0) fractions. Total preasphaltene (3) and asphaltene (2) samples (unfractionated) are also plotted.