489

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**CHEMISTRY AND STRUCTURE OF
COAL-DERIVED ASPHALTENES, PHASE II**

Quarterly Progress Report, July–September 1976

T. F. Yen

1976

Work Performed Under Contract No. E(49-18)-2031

University of Southern California
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ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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CHEMISTRY AND STRUCTURE OF
COAL-DERIVED ASPHALTENES
Phase II

Quarterly Progress Report for the Period
July-September 1976

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219

ABSTRACT

Additional elemental analyses, and molecular weight determinations have been carried out on the various components of the solvent fractionated coal liquids from the three direct general processes for coal liquefaction. The atomic C/H ratios are found to increase in the direction carboid > asphaltene > coal. Completed chromatography of asphaltenes on silica gel and Amberlyst-15 indicates that basic and non-basic asphaltene components may be separated into two major fractions by this method. This offers an alternative to the use of dry HCl (1) which may introduce chlorine chemically into at least one of the separated components.

A preliminary correlation has been observed between the color index, I, and the number of aromatic carbons per average molecule of asphaltene and carboid.

Carbon aromaticity values, f_a , determined directly by the ^{13}C -NMR method have been found to be 0.07 ± 0.01 higher than those previously determined by the x-ray method for asphaltenes.

Mass spectroscopy at 16 eV and 70 eV has been used to obtain spectra believed to represent the envelope of asphaltene parent peaks, and the envelope of asphaltene fragment peaks formed by either α or β elimination with the latter predominant.

OBJECTIVE AND SCOPE OF WORK

It is the objective of this project to isolate the asphaltene fractions from coal liquids from a number of liquefaction processes. These asphaltene fractions may be further separated by both gradient elution through column chromatography, and molecular size distribution through gel permeation chromatography.

Those coal-derived asphaltene fractions will be investigated by various chemical and physical methods for characterization of their structures. After the parameters are obtained, these parameters will be correlated with the refining and conversion variables which control a given type of liquefaction process. The effects of asphaltene in catalysis, ash or metal removal, desulfurization and denitri-fication will also be correlated. It is anticipated that understanding the role of asphaltenes in liquefaction processes will enable engineers to both improve existing processes, and to make recommendations for operational changes in planned liquefaction units in the U. S.

The objective of Phase I was to complete the isolation and separation of coal liquid fractions and to initiate their characterization.

The objective of Phase 2 is to continue the characterization of coal asphaltenes and other coal liquid fractions by use of physical and instrumental methods. The structural parameters obtained will be used to postulate hypothetical average structures for coal liquid fractions.

SUMMARY OF PROGRESS TO DATE

During this quarter the following tasks have been undertaken and/or completed:

- (1) Sample acquisition has continued throughout the quarter.
- (2) Training of new technical personnel is underway.
- (3) Establishment of sample data bank.
- (4) Chromatography of asphaltenes on acidic ion exchange resins is being carried out.
- (5-11) Characterization of coal liquid fractions by various physical and instrumental methods is continuing.

These tasks are listed in the milestone chart in Fig. 1. Detailed discussion of technical progress is found in the next section.

Fig. 1 - Milestone Chart

(1) Establishment of Sample Data Bank

Previously unreported analytical data on starting coals and various solvent fractions are reported in Tables I-III.

The C/H ratios of the carboids could be indicative of their mechanism of formation. If their formation pathway is:

(2) Coal $\longrightarrow$ Asphaltenes $\longrightarrow$ Resin + Oil.

then the carboid could have a C/H ratio higher than that of the original coal. This would be the case if these materials are formed by polymerization of reactive coal depolymerization moieties which are not stabilized by addition of hydrogen.

^areferred to as 'asphaltols' in the cited work

Table I. - Coal Samples Ultimate Analysis, %

<u>Coal Sample</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>O</u>	<u>Ash</u>
Synthoil(West Kentucky, hvA5 Homestead Seams 9,11,12,13)	60.7	4.8	1.2	5.5	11.3	16.5
FMC-COED(West Kentucky, hvBb Colonial Seams 9 & 14)	70.0	4.7	1.6	3.3	8.9	11.5
PAMCO(West Kentucky, hvBb Colonial Seams 9 & 14)	70.79	5.06	1.56	3.92	7.17	10.78
Cat. Inc.(Wyoming, sub-bituminous Bellicup Seam Roland-Smith)	67.82	4.83	1.08	0.64	17.86	7.25

Table II. - PAMCO Solvent Fractions Ultimate Analysis, %*

<u>Fraction</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>O**</u>	<u>Ash</u>	<u>MW***</u>
Coal Liquid ^a	87.37	7.37	0.84	0.17	4.25	0.10	
Oil ^a	90.12	8.14	0.54	0.34	0.86	0.52	
Resin ^a	86.39	7.08	1.40	0.13	5.00	0.01	
Asphaltene	85.03	6.06	1.45	1.11	6.35	1.50	471(426)****
Carbene	87.60	5.70	1.49	0.67	4.54	0.47	
Carboid	85.39	4.92	1.00	1.19	7.50	1.65	600****

*Moisture and ash free

**By difference

***VPO in benzene, average of two different samples MW 510 and 432 = 471

****VPO in DMF

^aSample contaminated with Dowtherm aromatic heat-transfer fluid as received. Oil and resin fractions therefore unrepresentative of SRC process.

Table III. - Molecular Weights of Carboids

<u>Sample</u>	<u>MW*</u>
Synthoil	938
FMC-COED	394
Cat. Inc. SRC	1026
PAMCO SRC	600

*Determined in N,N-DMF

Table IV. - Atomic C/H Ratios of Coal Liquid Solvent Fractions

<u>Fraction</u>	<u>Synthoil</u>	<u>FMC-COED</u>	<u>Cat.Inc.SRC</u>	<u>PAMCO SRC</u>
Original Coal	1.05	1.24	1.17	1.16
Coal Liquid	0.86	0.90	1.34	(0.99) ^a
Oil	0.76	0.73	1.09	(0.92) ^a
Resin	0.94	0.96	1.13	(1.02) ^a
Asphaltene	1.12	1.06	1.32	1.07
Carbene	1.23	1.13	1.49	1.28
Carboid	1.29	1.16	1.54	1.45

^aPAMCO coal liquid contaminated with Dowtherm aromatic heat-transfer fluid as received.

asphaltenes probably depends on the coal liquefaction process conditions. For example, the FMC-COED process, which involves pyrolysis of coal, leads to the formation of carboids, and asphaltenes with lower C/H ratios than those of the starting coal. Since the FMC-COED process involves pyrolysis of coal to produce distillable liquids and char, the pyrolysis products with higher molecular weights and C/H ratios would be less likely to distill, and more likely to end up converted to char. Therefore, the FMC-COED coal liquid that we receive, which consists of the condensed and filtered pyrolysis vapors, contains more lower molecular weight, lower C/H ratio carboids, and asphaltenes.

Work forecast:

Additional samples will be solvent fractionated by the standard method, and analyzed as above, as they are received. The data will be correlated with other information, and with the results of various physical and instrumental analyses.

(2) Separation of Asphaltenes by Solvent Elution Chromatography

Work accomplished:

In a previous quarterly report results were presented for the solvent elution chromatography of asphaltenes on silica gel (3). During the present quarter, separations of all available asphaltenes were carried out on an acidic ion exchange resin (Amberlyst-15) as described earlier (4). Two fractions were obtained by exhaustive elution with benzene, and pyridine. The Amberlyst-15 chromatography weight % recovery data are presented along with previously obtained silica gel results in Table V. The analyses of the various chromatographic fractions are presented in Tables VI-IX.

The analytical results indicate that good recoveries of asphaltenes, generally greater than 84 weight %, may be obtained by chromatography on either silica gel or Amberlyst-15. With both types of support, two major fractions could be separated by exhaustive elution with suitable solvents. The first fraction contains a substantially reduced % nitrogen, while the second fraction contains a substantially increased % nitrogen. Nitrogen balances are reported for all of the chromatography fractions. In most cases, the observed nitrogen balances are within 20% of the expected values^a. We believe these results are satisfactory considering the uncertainty

^aTwo cases are being repeated as recoveries in excess of 100% were observed. See Table X.

Table V. - Chromatography of Asphaltenes

<u>Asphaltene</u>	<u>SILICA GEL</u>			<u>AMBERLYST-15</u>		
	<u>Tot. Wt.% Recovered</u>	<u>Normalized Wt. % By Solvent</u>		<u>Tot. Wt.% Recovered</u>	<u>Normalized Wt. % By Solvent</u>	
		<u>Benzene</u>	<u>Et₂O</u>		<u>Benzene</u>	<u>Pyridine</u>
Synthoil*	84	57	43	86	42	58
FMC-COED	88	38	62	(100)**	35	(65)
Cat. Inc. SRC	89	66	34	(100)**	50	(50)
PAMCO SRC	88	51	49	91	48	52

*A more polar fraction 5% by weight could be eluted with CH₃CN.

**Being repeated; all pyridine probably not removed.

Table VI. - Analysis of Synthoil Asphaltene Chromatography Fractions

<u>Column (Solvent)</u>	<u>% Composition*</u>						<u>MW***</u>
	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>O**</u>	<u>Ash</u>	
(Starting Asphaltene)	86.78	6.53	2.14	0.46	4.09	0.37	715
Amberlyst-15(Benzene)	88.43	6.71	0.50	0.59	3.67	0.40	540
Amberlyst-15(Pyridine)	87.12	6.66	2.80	0.51	2.91	1.29	906
(Starting Asphaltene)	86.85	6.48	1.63	0.56	4.03	0.35	738
Silica Gel(Benzene)	89.15	6.57	0.58	0.99	2.71	0.97	614
Silica Gel(Et ₂ O)	85.17	6.86	1.60	0.73	5.64	1.19	560

*Moisture and Ash Free

**By Difference

***VPO in Benzene

Table VII. - Analysis of FMC-COED Asphaltene Chromatography Fractions

<u>Column</u>	<u>Solvent</u>	<u>% Composition*</u>						<u>MW***</u>
		<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>O**</u>	<u>Ash</u>	
(Starting Asphaltene)		82.14	6.47	1.70	2.58	7.11	0.79	458
Amberlyst 15	Benzene	82.84	6.79	2.95	1.50	7.92	0.76	438
Amberlyst 15	Pyridine	78.22	6.78	2.71	1.33	10.96	0.31	569
Silica Gel	Benzene	83.83	6.30	1.06	1.93	6.88	1.38	445
Silica Gel	Et ₂ O	79.67	6.48	1.54	1.33	10.98	1.23	340

*Moisture and Ash Free

**By Difference

***VPO in Benzene

Table VIII. - Analysis of Cat. Inc. SRC Asphaltene Chromatography Fractions

<u>Column</u>	<u>SOLVENT</u>	<u>% Composition*</u>						<u>MW***</u>
		<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>O**</u>	<u>Ash</u>	
(Starting Asphaltene)		88.80	5.61	1.25	0.12	4.22	0.78	560
Amberlyst 15	Benzene	87.65	6.44	0.78	0.42	4.71	1.38	511
Amberlyst 15	Pyridine	85.33	5.83	2.76	0.18	5.90	<0.01	780
Silica Gel	Benzene	87.66	6.40	0.65	0.65	4.64	1.01	467
Silica Gel	Et ₂ O	84.73	6.33	1.67	0.79	6.48	1.78	490

*Moisture and Ash Free

**By Difference

***VPO in Benzene

Table IX. - Analysis of PAMCO SRC Asphaltene Chromatography Fractions

Column	SOLVENT	% Composition*						
		C	H	N	S	O**	Ash	MW***
(Starting Asphaltene)		85.22	6.64	2.71	0.75	4.68	0.48	510
Amberlyst-15	Benzene	85.73	6.10	1.20	0.77	6.20	0.07	475
Amberlyst-15	Pyridine	84.62	6.11	3.69	0.62	4.96	0.40	582
(Starting Asphaltene)		85.03	6.06	1.45	1.11	4.85	1.50	426****
Silica Gel	Benzene	85.67	6.09	0.67	1.18	4.56	1.83	400****
Silica Gel	Et ₂ O	81.31	6.39	1.95	0.99	7.33	2.03	490****

*Moisture and Ash Free
**By Difference
***VPO in Benzene
****VPO inDMF

Table X. - Nitrogen Balances on Chromatography Fractions

<u>Asphaltene</u>	<u>$\frac{N_{found*}}{N_{starting}}$</u>	<u>$\frac{N/C_{found}}{N/C_{starting}}$</u>
<u>SILICA GEL</u>		
Cat. Inc. SRC	0.80	0.82
Synthoil***	0.63	0.63
FMC-COED	0.79	0.80
PAMCO	0.90	0.91
<u>AMBERLYST-15</u>		
Cat. Inc. SRC	1.42**	1.46**
Synthoil	0.85	0.85
FMC-COED	1.23**	1.14**
PAMCO	0.92	0.92

*All results based on normalized percentages.

**Being repeated--all pyridine probably not removed.

***A more polar fraction, 5% by wt., could be eluted with CH₃CN from Synthoil.

involved in nitrogen analysis, and the fact that 100% recovery of samples could not be obtained. Therefore, it seems that chromatography offers a general method of separating asphaltenes into basic and non-basic components without the use of dry HCl (1) which may introduce chlorine chemically into at least one of the separated components.

Work forecast:

Chromatography of selected asphaltene samples will continue on suitable adsorbents. The major chromatographic fractions will be characterized by the same methods that are being used for the characterization of the asphaltenes.

(3) Characterization of Coal Liquid Fractions

Work accomplished:

(a) Color Index

Color Index values for a variety of asphaltenes and solvent fractions have been reported previously (3,4). In this report we wish to present a preliminary correlation between color index values, and the number of aromatic carbons per average molecule (See Table XI and Fig. 2). The color index of a substance is defined as the integrated absorption of a species between 750 nm and 400 nm. As such, it should be a function of the size of the aromatic π -system of the observed species. The number of aromatic carbon atoms per average molecule should be a good measure of the size of the aromatic π -network if these aromatic carbons are present in condensed systems rather than dispersed in smaller aromatic rings.

(b) Structural Parameters by X-Ray Diffraction

Carbon aromaticity values, f_a , determined by the x-ray method (5) were reported previously for asphaltenes (4). These values are now compared with aromaticity values determined by the ^1H (6) and ^{13}C -NMR methods. The results, presented in Table XII, indicate that the x-ray aromaticity values are all lower than the f_a values determined by the other methods. If we assume that the ^{13}C values, determined directly from the ^{13}C -NMR, are more reliable than the values obtained using the ^1H -NMR method which requires the use of several assumptions, then the x-ray values are seen to be 0.07 ± 0.01 lower than the ^{13}C values.

Additional f_a values determined for the carbene and carboid fractions (Table XIII) indicate that these materials have a larger fraction of aromatic carbons than the asphaltenes derived from the same coal liquid product. The use of the x-ray method is of particular importance in the case of the carboid, as these materials are not sufficiently soluble in solvents suitable for use in determining f_a directly by the ^{13}C -NMR method.

Table XI. - Color Index and No. of Aromatic Carbon Atoms Per Molecule for Coal Liquid Products

<u>Sample</u>	<u>I*</u>	<u>No. Ar. Carbon Atoms**</u>
FMC-COED Asphaltene	4.5	20.5
PAMCO Asphaltene	12.5	26.3
Cat. Inc. Asphaltene	14.6	31.0
Synthoil Asphaltene	15.3	35.7
Synthoil Carboid***	35.3	57.4

$$*I = \int_{400 \text{ nm}}^{750 \text{ nm}} A d\lambda, \quad (\text{mm}^2 \cdot \text{ml/mg}) \times 10^{-3}$$

**No. aromatic carbons per molecule = $(f_a)(MW)(C)$

f_a = fraction of aromatic carbons per average molecule

MW = no. average molecular weight

C = fraction of carbon atoms per average molecule

*** MW determined in DMF = 938, corrected to 1000 for comparison with other values determined in benzene.

f_a determined by x-ray method = 0.71, corrected to 0.78 for comparison with other values determined by ^{13}C method.

Table XII.- Asphaltene Carbon Aromaticity, f_a

<u>Method</u>	<u>Synthoil</u>	<u>FMC-COED</u>	<u>Cat. Inc. SRC</u>	<u>PAMCO SRC</u>
^1H NMR*	0.70	0.70	0.81	0.77
^{13}C NMR**	0.69	0.66	0.76	0.73
X-Ray***	0.63	0.58	0.69	0.66

$$*f_a = \frac{\frac{C}{H} - \frac{H_a + H_{sat}}{2}}{\frac{C}{H}}$$

$$**f_a = \frac{C_{aromatic}}{C_{aromatic} + C_{sat}}$$

$$***f_a = \frac{Area_{002}}{Area_{002} + Area_{\gamma}}$$

Table XIII. - Aromaticity, f_a , for Asphaltenes, Carbenes and Carboids by X-Ray Diffraction

<u>Sample</u>	<u>f_a</u>		
	<u>Asphaltene</u>	<u>Carbene</u>	<u>Carboid</u>
Synthoil	0.63 ^a	0.63 ^a	0.71 ^a
FMC-COED	0.58 ^a	0.81	0.84
Cat. Inc. SRC	0.67	0.72	0.83
PAMCO SRC	0.66 ^a	0.74	0.77

^aThese values are less reliable due to overlap of background because of use of aluminum sample holder. Other values determined by use of glass sample holder.

(c) NMR H-Percentages by Proton Type

The NMR H-percentages by proton type for the "oil" and the "carboid" coal liquid fractions are presented in Tables XIV and XV. It is interesting to note the apparently large hydroxyl resonances observed for the PAMCO and Cat. Inc. SRC carboids. These bands ≈ 5.4 ppm from TMS disappear when D_2O is added to the sample, and a new band at around 5.1 ppm appears. However, the H_{OH} percentages reported are not completely representative of the whole carboid fraction as the carboids were not completely soluble in DMF.

Structural parameters may be calculated from the NMR data by use of equations derived by Brown and Ladner (6). The results of such calculations for the various asphaltenes and the major chromatographic products obtained from these asphaltenes on silica gel and Amberlyst-15 are presented in Table XVI.

The Brown and Ladner parameters f_a , σ , and H_{aru}/C_{ar} do not generally differ grossly for series of asphaltenes derived from the same asphaltene by chromatographic separation. However, some differences are observed. The similarity of the Brown-Ladner structural parameters among related asphaltenes may be rationalized by assuming relatively little fractionation on silica gel or Amberlyst-15 due to variation in asphaltene structure. The major type of fractionation observed is believed to be related to the basicity of the asphaltenes as has been discussed earlier in this report.

(d) Transmittance Electron Microscopic Examination of Coal Liquid Fractions

Transmittance electron microscopy pictures, at 910,000 magnification, were obtained for all the solvent fractionated asphaltenes and carboids during this quarter. Efforts have been initiated, in cooperation with the USC Image Processing Institute, to obtain computer processed digitized analysis of the particle sizes.

(e) ^{13}C -NMR Spectroscopy

The technique of ^{13}C -NMR spectroscopy allows the determination of direct and accurate values of carbon aromaticities, and may provide, in conjunction with proton NMR spectroscopy, a series of parameters for detailed characterization of coal liquid fractions (7).

Carbon-13 NMR spectra is more difficult to obtain than proton spectra because of the lower magnetic moment, and the lower abundance of ^{13}C . These factors result in a 5700-fold reduction in signal for ^{13}C compared to an equal number of protons. This reduced sensitivity may be compensated for by use of the Fourier Transform technique (8), which permits accumulation of pulses in a computer memory before

Table XIV. - Oil NMR H-Percentages by Proton Type*

	<u>H_{aromatic}</u>	<u>H_{benzyl}</u>	<u>H_{sat}</u>
Synthoil	17	35	48
FMC-COED	16	30	54
PAMCO SRC	43	31	26
Cat. Inc. SRC	48	28	24

*Run on Varian T-60 NMR. Solvent 99.8% DCCl₃ + 1% TMS.

Table XV. - Carboid NMR H-Percentages by Proton Type*

	<u>H_{aromatic}</u>	<u>H_{OH}</u>	<u>H_{benzyl}</u>	<u>H_{sat.}</u>
Synthoil**	49	--	35	16
FMC-COED	43	--	39	18
PAMCO SRC**	33	33	21	14
Cat. Inc. SRC**	41	20	27	12

*Run on Varian T-60 NMR.

**Carboids not completely soluble in 99.5% DMF-d₇ + TMS.

Table XVI. - Hydrogen Distribution and Structural Parameters for Asphaltenes and Chromatography Fractions

Sample	H_{ar}^*	H_a^*	H_o^*	f_a	σ	H_{aru}/C_{ar}
<u>Synthoil</u> (Asph.)	0.33	0.42	0.25	0.70	0.43	0.74
Amberlyst-15(benzene)	0.33	0.38	0.26	0.70	0.41	0.74
Amberlyst-15(pyridine)	0.33	0.42	0.26	0.69	0.42	0.75
Silica Gel(benzene)	0.38	0.34	0.28	0.73	0.38	0.75
Silica Gel(Et ₂ O)	0.31	0.38	0.30	0.68	0.45	0.78
<u>FMC-COED</u> (Asph.)	0.29	0.45	0.26	0.66	0.51	0.83
Amberlyst-15(benzene)	0.32	0.43	0.25	0.67	0.47	0.89
Amberlyst-15(pyridine)	0.37	0.40	0.23	-- ^a	-- ^a	-- ^a
Silica Gel(benzene)	0.40	0.40	0.20	0.73	0.40	0.81
Silica Gel(Et ₂ O)	0.37	0.42	0.21	0.70	0.46	0.95
<u>PAMCO</u> (Asph.)	0.45	0.37	0.18	0.74	0.34	0.86
Amberlyst-15(benzene)	0.40	0.36	0.24	0.74	0.37	0.73
Amberlyst-15(pyridine)	0.43	0.36	0.22	0.75	0.35	0.76
Silica Gel(benzene)	0.43	0.35	0.22	0.75	0.35	0.74
Silica Gel(Et ₂ O)	0.43	0.35	0.22	0.73	0.37	0.87
<u>Cat. Inc.</u> (Asph.)	0.50	0.34	0.16	0.81	0.30	0.66
Amberlyst-15(benzene)	0.47	0.35	0.18	0.76	0.33	0.80

^aAnalysis being repeated

Table XVI. - Hydrogen Distribution and Structural Parameters for Asphaltenes and Chromatography Fractions (cont'd)

<u>Sample</u>	<u>H_{ar}*</u>	<u>H_a*</u>	<u>H_O*</u>	<u>f_a</u>	<u>σ</u>	<u>H_{aru}/C_{ar}</u>
Cat. Inc. (asph.)	0.50	0.34	0.16	0.81	0.30	0.66
Amberlyst-15(benzene)	0.47	0.35	0.18	0.76	0.33	0.80
Amberlyst-15(pyridine)	0.43	0.32	0.21	0.78	0.32	0.72
Silica Gel(benzene)	0.43	0.33	0.24	0.74	0.35	0.80
Silica Gel(Et ₂ O)	0.46	0.32	0.22	0.77	0.30	0.77

transforming to the spectrum. A second technique, broad-band proton decoupling, results in an increase in signal sensitivity by eliminating spin-spin coupling between ^{13}C and ^1H , and by increasing the excess population of ^{13}C in the lower energy state [Nuclear Overhauser Enhancement (NOE)]. There are two problems associated with these techniques: one is that different carbons have different relaxation times, T_1 , and that $5T_1$ seconds are required to assure complete relaxation. The second problem is that the NOE may vary for different carbons. However, the use of a paramagnetic reagent such as chromium acetyl acetonate (CrAcAc) has been shown to shorten the T_1 's and quench the NOE's without unduly broadening the observed peaks (9). This method also permits spectra to be run at a considerable time saving over other methods which require long pulse delays to overcome the T_1 problem.

The ^{13}C spectra were run on a Varian CFT-20 NMR, with built-in minicomputer, operated at 20 MHz. Asphaltenes were run at concentrations of 10-40 wt/vol % in $\text{CS}_2 + \text{CDCl}_3$ (1% TMS) with CrAcAc concentrations ranging from 0.05-0.10 M. Figure 3 shows a comparison of spectra run under similar conditions except that proton decoupling is on in trace a and off in trace b. The f_a values obtained for the asphaltenes are given in Table XII.

(f) Mass Spectroscopy of Asphaltenes

An Allied Electrical Industries Model MS-9 was used in this work. A direct insertion probe held at 240°C was used to introduce the solid samples into the region of ionization. Ionizing voltages of 16 eV and 70 eV were used. The 16 eV spectra is believed to represent the broad envelope of molecular ions. The 70 eV spectra consist of two broad envelopes of peaks corresponding to the singularly and doubly charged aromatic species, and are believed to represent fragment peaks due to β -cleavage of aliphatic and naphthenic portions of the asphaltene molecules. Figure 4 shows the low and high eV spectra of the Synthoil asphaltene. The weight average molecular weight of the Synthoil asphaltene, calculated from the 16 eV mass spectrum, assuming equal sensitivity factors, was 633.^a This value may be compared with the number average molecular weight of 715 determined by vapor phase osmometry in benzene.

Work forecast:

Characterization will continue on all applicable fractions by the analytical and physical methods described in this report. In addition, ESR studies will be initiated to study the excitation processes of asphaltene molecules to see if they resemble those of known donor-acceptor charge-transfer complexes (10,11). Infrared studies will also be initiated to learn

^aMean MW = $\sum IM / \sum I$, where M is mass number and I is relative intensity.

FIG. 3 C^{13} NMR SPECTRUM OF SYNTHOIL ASPHALTENE

FIG. 4 - MASS SPECTROGRAPH OF SYNTHOIL ASPHALTENE

70 eV

27

16 eV

MASS (M / E)

whether asphaltene molecules are held in stack formation by π - π associations of the donar-acceptor type (12,13). The x-ray diffraction method will be applied to the study of iodine-asphaltene mixtures to determine whether iodine-asphaltene charge transfer complexation is occurring (14).

Mass spectrometric determination of empirical formulas for asphaltene fractions will be carried out when a suitable high resolution mass spectrometer becomes available.

Exploratory feasibility studies will be carried out on chemical methods for use in structure elucidation of asphaltenes. Reagents such as hexamethyldisilazane may be used to differentiate between oxygen present as hydroxyl, and ether oxygen. This reagent converts hydroxyl groups to silyl derivatives. The percentage of hydroxyl present may then be determined simply by silicon analysis, or by the proton NMR intensity of the trimethyl silyl protons added to the asphaltene.

Reduction of asphaltenes by potassium and an alcohol or alkyl halide might be expected to lead to a reduction in molecular weight of asphaltenes or carboids if cleavage of linkage such as ether or activated C-C causes splitting of the polymeric framework of these molecules. However, if the cleaved bonds are part of a ring system, no reduction in MW need necessarily occur.

Mild oxidation of asphaltenes and carboids might be expected to produce identifiable alkyl carboxylic acids, and carboxylated residues. Gas chromatographic analysis of esterified derivatives of the former products could lead to identification of aromatic ring substituents.

CONCLUSION

Elemental analyses on starting coals and coal liquid fractions have shown that the atomic C/H ratios of the carboids are not intermediate between those of the starting coal and those of the asphaltenes produced in the Synthoil and Catalytic Inc. SRC coal liquid product fractions, but rather the atomic C/H ratios are found to increase significantly in the direction carboid > asphaltene > coal. This indicates that these materials, as found in the product liquids, are not pre-asphaltenes (15), in the sense of being intermediate between coal and asphaltenes, in these two processes.

The completed elemental analyses on all chromatographed coal liquid asphaltenes confirms that solvent elution chromatography, on either silica gel or Amberlyst-15, affords two major fractions with high recoveries (greater than 84 weight %), of the starting asphaltene. These fractions differ significantly in their percentage nitrogen, and are believed to represent basic and non-basic asphaltenes. The similarity of the Brown-Ladner, NMR-derived structural parameters among the related chromatographed asphaltenes also suggests that little fractionation based on molecular structure is occurring.

A preliminary correlation observed between color index,

1, and the number of aromatic carbons per average molecule of asphaltene and carboid fractions indicates that the aromatic carbons are probably associated in larger π -networks rather than in smaller discrete non-conjugated aromatic compounds.

Carbon aromaticity values, f_a , for asphaltenes determined directly by carbon-13 NMR are found to be related to those values previously determined by the x-ray diffraction method. The x-ray method gives values 0.07 ± 0.01 lower than those obtained by the ^{13}C method. Additional f_a values determined for the carbenes and carboids show that these materials are all essentially more aromatic than the corresponding asphaltenes. The x-ray method is especially valuable for materials, such as carboids, for which no suitable solvent has been found to carry out ^{13}C NMR measurements.

Mass spectroscopy at 16 eV and 70 eV has been used to obtain spectra believed to represent the envelope of asphaltene parent peaks, and the envelope of asphaltene fragment peaks formed by either α or β elimination with the latter predominant.

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