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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES

Phase II

Quarterly Progress Report, April–June 1977

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COAL-DERIVED ASPHALTENES
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Quarterly Progress Report for the Period
April - June 1977

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Abstract

Separation of coal asphaltenes by solvent elution chromatography with benzene, diethyl ether, and tetrahydrofuran, on silica gel, may be carried out to obtain distinct fractions with 98-99% recovery of starting asphaltene. These three fractions have been characterized by a variety of analytical, physical and chemical methods. The diethyl ether eluted fraction is found to be more basic and polar, to have a higher degree of saturation, and to contain smaller average aromatic π -systems than the benzene eluted asphaltene fraction. The third fraction (THF-eluted) has the highest molecular weights, and the largest percentages of nitrogen and oxygen. It is believed to be solubilized originally in benzene by association with the other two fractions.

Donor-acceptor complexes between coal asphaltenes and the π -acceptor tetracyanoethylene have been synthesized. UV-visible spectra of these species show new charge-transfer absorption bands not found in the free components. Electron spin resonance measurements show enhanced spin signals for these complexes. X-ray diffraction measurements indicate solid state clusters of asphaltene/TCNE in the range of 3/2 to 4/2.

Electron spin resonance spectra of asphaltenes, asphaltene chromatography fractions, and asphaltene charge transfer complexes afford relative ESR signal intensity values which are consistent with a picture of donor-acceptor properties holding alternate layers together.

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 denitrification will also be correlated. It is anticipated that understanding the role of asphaltene 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 II is to continue the characterization of coal asphaltenes and other coal liquid fractions by the use of physical, instrumental and chemical 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) Separation.
- (2) Training of new technical personnel is underway.

- (3) Establishment of sample data bank.
- (4) Chromatography of asphaltenes is being carried out.
- (5-12) Characterization of coal liquid fractions by various physical and instrumental methods in continuing.
- (13) Asphaltene donor-acceptor complexes are being studied by a variety of techniques.
- (14) Characterization of asphaltenes by chemical methods is being carried out.

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

DETAILED DISCUSSION OF TECHNICAL PROGRESS

(1) Sample Acquisition and Separation

Coal liquid samples were solvent fractionated by the standard method in order to obtain stockpiles of the various solvent fractions.

(2) Separation of Asphaltenes by Chromatography

In previous quarterly reports (1-5), chromatographic separation of asphaltenes on silica gel has been described. Three major fractions are generally obtained in 98-99% recovery by exhaustive elution with benzene, diethyl ether, and THF. The third fraction (THF-eluted) represents 10-20% of material, and contains varying amounts of black char-like material of high molecular weight which is not soluble in benzene. This material may have been present originally in the starting asphaltene, and could have been solubilized in benzene by association with other molecules; alternatively, this material could have been formed from labile asphaltene molecules while passing through the silica gel column.

Fig. 1. Milestone Chart

In order to investigate the source of this material the following experiments were carried out:

(1) A sample of Synthoil asphaltene was dissolved in THF, and exhaustively eluted from silica gel with this solvent.

(2) Samples of THF eluted, benzene insoluble, chromatography fractions were dissolved with samples of benzene and diethyl ether eluted fractions in THF; the solvent was evaporated, and the residues mixed with benzene.

The first test resulted in the recovery of 97% asphaltene which was completely benzene soluble. In the second case, mixing the THF fractions with either the benzene or diethyl ether fractions, resulted in solubilizing $\approx 70\%$ of the originally insoluble material in benzene. These results suggest that the THF eluted fraction is stable to the chromatography conditions, and that this fraction was originally solubilized in benzene by association with the other two fractions present in the asphaltene. However, when these two fractions are separated from the THF eluted fraction, that fraction becomes practically insoluble in benzene.

Comparison of these chromatography fractions with the original asphaltene molecules is presented in Tables I-IV. Molecular formulas, ^1H NMR structural parameters, atomic C/H ratios, and color index (2, 3) values are given. The benzene and diethyl ether fractions generally possess molecular weights and structural parameters which are not too far removed from the starting asphaltene. The Et_2O eluted fractions tend to have lower f_a , and higher $\text{H}_{\text{aru}}/\text{C}_{\text{ar}}$ values indicative of smaller aromatic ring systems. The color index values for these fractions are invariably the lowest of any of the fractions, which also suggests smaller aromatic π -systems (3). In addition the atomic C/H values are usually lowest, indicating the highest degree of saturation for these fractions. The Et_2O eluted fraction has a

Table I Comparison of Synthoil Asphaltene and Silica Gel Chromatography Fractions

	Starting Asphaltene	Benzene Eluted	Et ₂ O Eluted	THF Eluted
Molecular Formula	C _{40.87} H _{25.05} N _{0.65} O _{1.36} S _{0.07}	C _{40.93} H _{35.94} N _{0.23} O _{0.60} S _{0.17}	C _{37.68} H _{35.09} N _{0.65} O _{2.15} S _{0.03}	C _{59.97} H _{50.17} N _{1.19} O _{5.14} S _{0.16}
Molecular Weight	560 ^a	546 ^e	530 ^a	869 ^a
H _{ar} [*]	31 ^c	34 ^c	31 ^c	42 ^d
H _a [*]	42	42	41	39
H _o [*]	25	23	25	19
f _a	0.71	0.72	0.69	0.76
H _{aru} /C _{ar}	0.67	0.70	0.78	0.79
σ	0.45	0.40	0.46	0.42
R _S	8.7	8.2	9.4	14.9
n	1.6	1.6	1.6	1.5
C _A	29.1	29.3	26.1	45.5
R _A	5.8	5.4	3.9	5.7
C/H	1.16	1.18	1.07	1.19
I	17.4	17.8	9.3	36.1

^a Average extrapolated infinite dilution values measured in benzene and THF.

^b Extrapolated infinite dilution value measured in THF. (Sample not soluble in benzene.)

^c Corrected for phenolic OH absorption, $H_{ar}^* = H_{ar}^{observed} - H_{OH}^*$

^d Uncorrected for phenolic OH absorption.

Table II Comparison of HRI H-Coal Asphaltene and Silica Gel Chromatography Fractions

	<u>Starting Asphaltene</u>	<u>Benzene Eluted</u>	<u>Et₂O Eluted</u>	<u>THF Eluted</u>
Molecular Formula	C _{35.59} H _{28.86} N _{0.56} O _{1.52} S _{0.10}	C _{40.52} H _{31.76} N _{0.42} O _{1.30} S _{0.11}	C _{36.21} H _{32.03} N _{0.64} O _{2.19} S _{0.09}	C _{49.40} H _{48.05} N _{0.80} O _{3.34} S _{0.15}
Molecular Weight	492 ^a	549 ^b	514 ^b	698 ^b
H _{ar} [*] ^c	46	48	42	30
H _o [*]	36	37	39	40
H _o [*]	18	15	19	0.66
f _a	0.78	0.80	0.74	0.84
H _{aru} /C _{ar}	0.72	0.69	0.81	0.47
σ	0.34	0.32	0.39	13.0
R _S	6.7	7.2	8.4	1.8
n	1.5	1.4	1.5	32.6
C _A	27.8	32.4	26.9	3.6
R _A	4.9	6.0	3.5	1.02
C/H	1.22	1.27	1.12	30.3
I	29.4	30.2	14.7	

^a Average extrapolated infinite dilution values measured in benzene and THF.

^b Extrapolated infinite dilution value measured in THF.

^c Uncorrected for phenolic OH absorption.

Table III Comparison of Cat. Inc. SRC and Silica Gel Chromatography Fractions

	<u>Starting Asphaltene</u>	<u>Benzene Eluted</u>	<u>Et₂O Eluted</u>	<u>THF Eluted</u>
Molecular Formula	C _{35.64} H _{28.20} N _{0.48} O _{1.39} S _{0.02}	C _{36.86} H _{32.09} N _{0.23} O _{1.46} S _{0.10}	C _{29.77} H _{26.51} N _{0.50} O _{1.71} S _{0.10}	C _{57.81} H _{46.96} N _{1.41} O _{3.71} S _{0.04}
Molecular Weight ^a	486	505	422	822
H _{ar} ^b	48	47	43	48
H _a ⁺	36	32	34	36
H _o ⁺	16	21	24	16
f _a	0.79	0.77	0.74	0.79
H _{aru} /C _{ar}	0.71	0.76	0.80	0.76
σ	0.32	0.30	0.35	0.35
R _S	6.5	6.6	6.2	12.2
n	1.4	1.7	1.7	1.4
C _A	28.3	28.4	22.1	45.6
R _A	5.2	4.3	3.2	6.5
C/H	1.26	1.15	1.12	1.23
I	14.6	13.4	10.8	42.4

^aExtrapolated infinite dilution values measured in THF

^bUncorrected for phenolic OH absorption

Table IV Comparison of PAMCO SRC Asphaltene and Silica Gel Chromatography Fractions

	Starting Asphaltene	Benzene Eluted	Et ₂ O Eluted	THF Eluted
Molecular Formula	C _{34.79} H _{28.73} N _{0.54} O _{1.41} S _{0.10}	C _{34.17} H _{27.53} N _{0.33} O _{1.17} S _{0.08}	C _{35.90} H _{30.98} N _{0.69} O _{1.80} S _{0.07}	C _{43.08} H _{36.39} N _{1.03} O _{2.11} S _{0.15}
Molecular Weight ^a	480	464	503	607
H _{ar} ^{*b}	42	41.0	41	41
H _a [*]	38	38.5	37	41
H _o [*]	20	20.5	22	18
f _a	0.76	0.76	0.75	0.75
H _{aru} /C _{ar}	0.72	0.68	0.76	0.76
σ	0.36	0.36	0.37	0.39
R _S	6.9	6.5	7.5	9.6
n	1.5	1.5	1.6	1.4
C _A	26.5	26.1	26.8	32.3
R _A	4.8	5.2	4.3	4.9
C/H	1.21	1.24	1.16	1.18
I	16.5	19.7	12.2	26.2

^aExtrapolated infinite dilution values measured in THF.

^bUncorrected for phenolic OH absorption.

higher percentage of the heteroatoms nitrogen and oxygen. Silylation with hexamethyldisilazane^a indicates 30% of the oxygen in the benzene-eluted fraction, and 64% of the oxygen in the diethyl ether-eluted fraction is phenolic oxygen. Alkylation with methyl iodide indicates most of the nitrogen in the diethyl ether-eluted fraction is basic nitrogen, but that only a small portion of the nitrogen in the benzene-eluted fraction is basic.^a

The THF eluted fractions have the highest molecular weights, and the highest color index values, as well as the largest percentages of nitrogen and oxygen. Silylation indicates 16% of the oxygen is phenolic oxygen.

Mass Spectroscopy of a Solvent Elution Chromatography Fraction

A benzene eluted fraction from silica gel was rechromatographed on a preparative Waters System 500 HPLC as described previously (5). Selected fractions from this run were further chromatographed on a Waters HPLC analytical system. The results were shown in Fig. 3, p. 12 of the last Quarterly Report (5). The first cut from this chromatography procedure was analyzed: %C, 83.33; %H, 7.94; %N, 0.16. Mass spectroscopic analysis at low resolution - low voltage, and high resolution-30ev conditions was carried out. The results are reported in Section (3)f of this report.

(3) Characterization of Coal Liquid Fractions by Physical Methods

Work Accomplished:

(a) NMR Spectroscopy

Average molar properties of asphaltene solvent elution chromatography

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^aSee p. 35 of this report.

fractions separated on silica gel are reported in Section (2), p. 6-9, of this report. Similar Brown-Ladner NMR structural parameter values for chemically treated asphaltenes are reported in Section (5), p. 39, 43, of this report.

(b) Particle Size Determination by Transmittance Electron Microscopy (TEM)

In previous Quarterly Reports (2-5) we discussed the development of the TEM particle analysis procedure, and the problems associated with particle deposition and analysis. A revised flow diagram is shown in Fig. 2. The vacuum-deposition technique shown on the left path gives less agglomeration and better particle separation. The best results to date are presented in Fig. 3. These results are promising, but improved resolution will still be required in order to carry out the image processing procedure. It is hoped that future TEM pictures can be printed on high contrast paper in order to obtain the required resolution.

(c) VPO Investigation of Asphaltene Molecular Weights

The results of VPO molecular weights reported in the last two quarterly progress reports indicate that association of asphaltenes takes place in both benzene and tetrahydrofuran (THF) over the concentration range of 4-40 gm/l. In this quarter a theoretical model of the self-association of asphaltenes in solution was derived. The association constants were calculated from the number average molecular weight obtained from VPO.

The self-association of phenol in carbon tetrachloride solution has been studied extensively by a variety of techniques. By examining the second overtone of the free hydroxyl stretching band in phenol, Kempler and Mecke (6) concluded that a series of multimers is formed and that a single constant is sufficient to describe the entire process. In 1951,

FIG. 2 FLOW DIAGRAM OF TEM PARTICLE ANALYSIS ON COAL ASPHALTENE

FIG. 3 TEM IMAGE OF SYNTHOIL CRUDE ASPHALTENE HEAT DEPOSIT ON SiO FILM (910K ...

Coggeshall and Saier (7) carried out a similar IR study of the hydroxyl stretching region of phenol and obtained better agreement between theory and experiment by using two equilibrium constants. Whetsel and Lady, (8) in 1970, reported on the effects of concentration and temperature upon the absorption of the fundamental, and first overtone O-H stretching bands of phenol in carbon tetrachloride and cyclohexane solutions. They tested several self-association models and found that the multiparameter model provides the best fit for the experimental data. In 1958, Saunders and Hyne (9) studied the self association of t-butanol, phenol and methanol in carbon tetrachloride solution by nuclear magnetic resonance. They found that for t-butanol and phenol the model which best fits the experimental data is based upon a monomer-tetramer equilibrium. For methanol the best model is based upon a monomer-tetramer equilibrium.

Recently, Schweighardt, et al (10), studied the model complex of Sternberg's acid or base fractions of coal-derived asphaltene with pyridine in CCl_4 by multi-nuclei magnetic resonance, and they concluded that hydrogen bonding does exist between two separate components of coal-derived asphaltenes. Soon after that, Taylor, et al. (11), reported a similar study by proton magnetic resonance and had a similar conclusion. Unfortunately, both of the reports have only qualitative results.

The self-association model of asphaltene in solution used in this study is based on Coggeshall and Saier's (7) two equilibrium constants model; one for the formation of dimer (K_1) and one for the successive addition of monomeric units to form higher polymers (K). They derived the following two expressions:

$$\alpha_n = n\alpha \frac{K}{K_1} \left[\frac{\alpha C}{K} \right]^{n-1} \quad (1)$$

$$K = \frac{C \alpha}{2(K_1 - \bar{K}_1)} \left[2K_1 - \frac{\bar{K}_1}{2} + \sqrt{2K_1 \bar{K}_1 + \frac{\bar{K}_1^2}{4}} \right] \quad (2)$$

Where

n = Integer

α_n = fraction of monomer bound in n th polymer

α = fraction of monomer unassociated

C = concentration in moles per liter

K_1 = dissociation constant of dimer

K = dissociation constant of all other polymers

$\bar{K} = 2 \alpha^2 C / (1 - \alpha)$

If C is the initial concentration of monomer before any association, at equilibrium the concentrations of monomer, dimer, trimer, etc., are C , $\frac{\alpha_2 C}{2}$, $\frac{\alpha_3 C}{3}$, ..., $\frac{\alpha_n C}{n}$ and the molecular weights are M_o , $2M_o$, $3M_o$, ... and nM_o . Since the molecular weight measured in VPO is the number average molecular weight, it is given that

$$MW_{obs} = \frac{M_o \alpha C + 2M_o \cdot \frac{\alpha_2 C}{2} + 3M_o \cdot \frac{\alpha_3 C}{3} + \dots + nM_o \frac{\alpha_n C}{n}}{\alpha + \frac{\alpha_2}{2} + \frac{\alpha_3}{3} + \dots + \frac{\alpha_n}{n}} \quad (3)$$

where MW_{obs} is the number average molecular weight from VPO.

With the use of the relationship $\sum \alpha_n = 1$, $\frac{1}{1-x} = 1 + x + x^2 + \dots$, and equation (1), one may simplify equation (3) and get

$$MW_{obs} = \frac{M_o}{\alpha \left[1 + \frac{K}{K_1} \frac{1}{\frac{K}{\alpha C} - 1} \right]} \quad (4)$$

It may be shown from equation (4) that $MW_{obs} = M_o/\alpha$ as $C \rightarrow 0$ and $M_o/\alpha = M_o$ since $\alpha \rightarrow 1$ as $C \rightarrow 0$. This agrees with the experimental results obtained from VPO and reported previously, that molecular weight values found

in different solvents, by extrapolating the plots to infinite dilution, are in accordance. These infinite dilution molecular weight values approximate the true monomer molecular weights.

In theory, the equilibrium constants K and K_1 can be obtained by solving equation (2) at two different concentrations. The two α 's are obtained from equation (4) by assuming two values of K and K_1 . This trial and error method was used, and a computer program was written to help solve all these calculation problems. Since two nonlinear equations must be solved simultaneously, the calculation is tedious, only preliminary results for Synthoil asphaltene in benzene and tetrahydrofuran were obtained and are shown in Fig. 4.

The calculated molecular weights in Fig. 4 are obtained from equation (4) where M_0 is the monomer molecular weight obtained by extrapolating to infinite dilution, and K and K_1 are the calculated equilibrium constants. The maximum deviation is 16%. Although the Newton-Raphson method is used to solve the nonlinear equations, the degree of convergence is slow. For the next quarter, other methods for solving systems of non-linear equations will be tried and hopefully a better result will be obtained.

(d) X-ray Diffraction

The x-ray diffraction patterns of asphaltenes and their corresponding tetracyanoethylene (TCNE) complexes have been measured. Figs. 5, 6 show a typical comparison. The diffraction patterns show a large increase in the intensity of the 002-Band of the TCNE complex, which is associated with the interplanar spacing between condensed aromatic rings, and the appearance of a new band for Synthoil-TCNE, which corresponds to a larger distance of ≈ 11 to $14 \text{ \AA}$, and a similar band at 12 - $17.5 \text{ \AA}$ for the HRI-TCNE

FIG. 4 VPO MW vs CONCENTRATION SYNTHOIL ASPHALTENE

BENZENE

$$K_1 = 0.367$$

$$K = 0.0721$$

THF

$$K = 0.466$$

$$K = 0.0540$$

FIG. 5 - X-RAY DIFFRACTION OF SYNTHOIL ASPHALTENE
AND ITS TCNE COMPLEX

FIG. 6- X-RAY DIFFRACTION OF HRI BASE ASPHALTENE TCNE COMPLEX

complex. The x-ray diffraction patterns were analyzed in the usual way (2-5), and aromaticity and x-ray crystallite parameters are presented in Table V. The results indicate structural differences between the asphaltene base fractions (Et_2O eluted from silica gel) and their TCNE complexes. The aromaticity, f_a , increases from asphaltene base fractions to complexed products. The distance through the aromatic sheets, L_c , and the number of layers per cluster M are increased after complexing. However, the diameter of the aromatic sheet, L_a , shows a decrease or no change. The spacing between aliphatic chains or sheets, d_y , and the spacing between the aromatic sheets, d_m , do not show much change. These results, and the appearance of the new bands at 11-14 Å, and 12-17.5 Å may be rationalized in terms of asphaltene-TCNE complex clusters such as the ones shown in Fig. 7. If the TCNE molecules are complexed on top and below the asphaltene sheets, instead of intercalated between the asphaltene sheets, then an increase of L_c would be observed, but an increase in d_m or d_y would not be required. L_a , the average diameter of the aromatic sheet would be expected to be lower if a smaller TCNE molecule in the complex represented a pseudo aromatic sheet. M , the effective number of aromatic sheets would be expected to be larger. The new bands corresponding to an 11-14 Å separation in Synthoil-TCNE and 12-17.5 Å in HRI-TCNE could represent the distance between TCNE molecules in the complexes. The aromaticity, f_a , would be expected to increase in the complexes due to the pseudo-aromatic character of the TCNE π -system.

(e) Electron Spin Resonance of Asphaltenes

Electron spin resonance (ESR) has been used in the past to study the structure and state of association of native petroleum asphaltenes. (12-14).

Table V. X-Ray Analysis on Asphaltene Base Fractions and Their TCNE Complexes

	<u>HRI asphaltene Et₂O eluted</u>	<u>HRI asphaltene Et₂O eluted- TCNE Complex</u>	<u>Synthoil asphaltene Et₂O eluted</u>	<u>Synthoil asphal- tene Et₂O eluted- TCNE Complex</u>
f_a^1	0.54	0.71	0.64	0.72
d_m^2	3.40	3.33	3.47	3.46
d_y^2	4.46	4.52	4.52	4.52
L_c^2	11.4	17.5	12.1	13.8
L_a^3 (11) band	12.7	8.7	10.0	10.1
L_a^4 (11) band	14.5	9.8	11.4	11.9
M^5	4	6	4	5

$$f_a^1 = C_A / C_{\text{total}} = A_{002} / A_{002} + A_{\gamma}$$

d_m^2 = interlayer distance; d_y = interchain distance; L_c = diameter of the aromatic perpendicular to the plane of the sheets; all values in Å.

L_a^3 = diameter of the aromatic sheets from Diamond's Curve.

L_a^4 = diameter of the aromatic sheets from Scherrer's Eq.

M^5 Effective number of aromatic sheets associated in a stacked cluster.

FIG. 7 CROSS-SECTIONAL VIEW OF SYNTHOIL AND HRI ASPHALTENE - TCNE MODEL COMPLEX CLUSTERS

During the past quarter we have carried out preliminary ESR studies on coal asphaltenes, asphaltene chromatography fractions, and charge transfer complexes between asphaltenes and iodine, and TCNE.

Experimental

ESR spectra were measured with a Varian model E-12 single cavity spectrometer operating at a nominal frequency of 9.24 GHz. Rough g-values were obtained by alternately scanning a standard strong pitch sample with a g-value of 2.0028 and the asphaltene sample. This procedure was not very satisfactory and only crude values, generally between 2.002-2.003, could be determined. All samples were run as powders in air, and approximate relative intensity data was obtained by dividing the integrated area by the weight of the sample used. A typical ESR spectrum of a Synthoil asphaltene is shown in Fig. 8.

Results and Discussion

For a typical asphaltene, or asphaltene derivative (Fig. 8) a single rather intense signal is observed at about 3284 gauss. This corresponds to a g_{eff} of about 2.003. The linewidth is about 8.5 gauss. This value is in excellent agreement with a calculated value of 8.5 gauss using the relationship of Retcofsky and coworkers (15):

$$\Delta H = 1.6 H - 1.8$$

for correlating ESR linewidth of coals in the solid state with percent hydrogen in the coals.

The relative intensity data for the samples is presented in Table VI. Starting Synthoil asphaltene is seen to have a greater signal intensity than an Et₂O-eluted chromatography fraction. This is consistent with a picture of asphaltenes in which the forces holding the aromatic layers together arise from different donor-acceptor properties of alternate

FIG. 8 — ESR SPECTRUM OF SYNTHOIL ASPHALTENE

Table VI. Relative ESR Signal Intensities for Synthoil Asphaltenes and Asphaltene Complexes

<u>Sample</u>	<u>Intensity/g (Relative)</u>
Synthoil Asphaltene	1
Synthoil - Et ₂ O eluted Asphaltene from Silica Gel	0.24
TCNE	0.029
TCNE - Synthoil (Et ₂ O Eluted Asphaltene) Complex ²	1.47
Iodine - Synthoil Asphaltene Complex	5.73

layers. Electron transfer would be facilitated in the starting asphaltene which has not been separated into donor-acceptor molecules by solvent elution chromatography on silica gel. Both the TCNE and the iodine charge transfer complexes with Synthoil asphaltene show greater signal intensity than the starting asphaltene.

The ESR signal intensity of the starting Synthoil asphaltene, measured over the temperature range 181-297 °K, is shown in Fig. 9. The results appear to follow the Curie-Weiss law (16) over most of the range measured, and if this observation is substantiated in future work, it may be possible to conclude whether or not the free radical signals in such coal asphaltenes arise from excitations typical of charge transfer complexes (13-14).

Work forecast:

Additional quantitative ESR measurements will be made of asphaltenes and asphaltene charge transfer complexes.

(f) Mass Spectroscopy of Asphaltenes

The Synthoil asphaltene chromatography cut discussed in Section (2) of this report was further characterized by mass spectroscopy. An Allied Electrical Industries Model MS-9 was used to measure the low eV, low resolution spectra at 16 eV and 240°C. High resolution spectra were run on an AEI MS - 30, at a resolution of ≈ 9000 with a probe temperature of 250-300°C. The electron energy was 30 eV, which was the lowest eV at which the internal mass standard, perfluorokerosene, gave a sufficiently strong spectrum. Spectra were run as the probe was heated, and some changes in the composition of the ions at different temperatures were observed. The final spectra of the temperature stabilized samples are discussed.

FIG. 9 RELATION OF ESR RELATIVE SIGNAL INTENSITY
TO TEMPERATURE FOR SYNTHOIL ASPHALTENE

The low resolution 16 eV spectrum is presented as a bar graph in Fig. 10. The spectrum suggests the presence of series, differing by 14 mass units, of structurally related parent peaks (17).

The high resolution mass spectrum provided ≈ 400 measured masses in the range 256-590. Possible molecular compositions for each peak have been calculated, allowing up to eight oxygens or nitrogens for each molecule. Additional constraints are being applied to the calculations to eliminate peaks belonging to charged fragments, and peaks falling outside of reasonable ranges of hydrogen, carbon, oxygen, nitrogen and sulfur atoms per molecule. The possible formulas remaining after these operations are carried out will be reported in the next Quarterly report.

(4) Asphaltene Donor-Acceptor Complexes

Work Accomplished:

Research aimed at elucidating the nature of coal asphaltene-iodine complexes was described in previous Quarterly Reports (4, 5). During the present quarter only a limited amount of work was carried out with asphaltene-iodine complexes. The majority of effort was shifted toward synthesis and study of asphaltene-tetracyanoethylene (TCNE) π -acceptor complexes.

(a) Asphaltene I_2 Complexes

Molecular weight studies were carried out on the Synthoil and HRI H-Coal asphaltene - I_2 complexes. The least squares MW vs concentration curves found in THF are:

FIG. 10 MASS SPECTROGRAPH OF SYNTHOIL ASPHALTENE

SILICA GEL CHROMATOGRAPHIC CUT

16 eV

$$\text{Synthoil Asph.} - \text{I}_2 \quad \text{MW} = 12.21 \pm 1.49 \text{ C} + 921 \pm 59$$

$$\text{HRI H-Coal Asph.} - \text{I}_2 \quad \text{MW} = 1.99 \pm 0.53 \text{ C} + 961 \pm 11$$

The extrapolated infinite dilution molecular weight values of 921 and 961 are upper limits because small amounts of the complexes were not soluble in THF. These results indicate that Asphaltene - I_2 complexes are not completely dissociated into asphaltene and I_2 in dilute solutions of THF, and that association to higher molecular weight species does occur at higher concentrations. Conductivity studies on a basic asphaltene - CH_3I complex are still planned to complete the series on conductivity of iodine-asphaltene complexes. It is expected that these measurements will be carried out in the next quarter when suitable equipment and personnel become available.

(b) Asphaltene - TCNE Complexes

Complexes of TCNE were formed by mixing benzene - THF solutions of TCNE with benzene solutions of the individual asphaltenes (approximate mole ratios, TCNE/asphaltene = 1.5/1). After several hours stirring at room temperature a black precipitate forms. It was filtered, washed with benzene and dried overnight at $40^\circ\text{C}/2 \text{ mm Hg}$. The analytical data, and estimated mole ratios of asphaltene/TCNE are presented in Table VII. The observed VPO MW at the finite concentration of 15.7 g/l in THF is 1028 for the Sythoil - TCNE complex, which is about 13% lower than the calculated value of 1188 for an asphaltene/TCNE complex of 2.

Ultraviolet - Visible Spectra of Complexes

Measurement of the UV - Visible spectrum of TCNE/asphaltene complexes in THF (Fig. 11) leads to the observation of new bands at 406 and 425 nm not found in the free components. These bands are presumed to be charge-

Table VII. TCNE - Asphaltene Complexes

<u>Sample</u>	Percentage			<u>Asphaltene^a</u>	<u>MW</u>
	<u>C</u>	<u>H</u>	<u>N</u>	<u>TCNE</u>	
Synthoil	80.57	5.55	6.78 ^b	1.84	1028 ^c
	79.47	5.10	6.91	1.79	
HRI H-Coal	79.70	4.97	6.88	1.87	
Cat. Inc. SRC	80.90	4.76	9.25	1.44	

^a Assuming MW of Asphaltene in complex is the same as MW of starting asphaltene.

^b Two different preparations - using different synthoil asphaltene samples.

^c Measured in THF at Conc. of 15.7 g/l.

FIG. 11- UV VIS SPECTRA OF TCNE SYNTHOIL ASPHALTENE, AND
SYNTHOIL ASPHALTENE - TCNE COMPLEX IN THF

transfer absorption bands of the donor asphaltene molecules and the π -acceptor TCNE.

Infrared Spectra

Asphaltene - TCNE complexes were run in KBr disks and the infrared spectra compared with those of the free components, and physical mixtures of the free components. The most obvious changes are in the TCNE doublet at 2200 cm^{-1} which changes to a singlet, and in the appearance of a prominent new band at 1500 cm^{-1} (Fig. 12).

X-Ray Diffraction

X-Ray diffraction studies were carried out on the asphaltene - TCNE complexes, and structural x-ray crystallite parameters were obtained, which could be used to formulate models for the macrostructures of these complexes. The x-ray results are discussed in detail in Section (3)d of this report.

Conductivity

Conductivity studies on these complexes are planned for the next quarter when suitable equipment and personnel should become available.

ESR Spectra

ESR spectra were run on a Synthoil - TCNE complex. A moderate increase in the spin intensity relative to Synthoil asphaltene (1.47/1) was observed. This observation is consistent with increased charge transfer between Synthoil asphaltene molecules and the π -acceptor TCNE. The ESR results are discussed in more detail in Section (3)e of this report.

Work forecast:

Studies will continue on asphaltene donor-acceptor complexes by the same analytical and physical methods described in this report. ESR studies will be carried out in more detail, and conductivity measurements will be

FIG. 12 IR SPECTRA OF SYNTHOIL ASPHALTENE AND SYNTHOIL ASPHALTENE-TCNE COMPLEX

made on asphaltene - TCNE complexes to study the excitation processes of such complexes.

(5) Chemical Methods for Asphaltene Structure Determination

Work accomplished:

Chemical methods which may be useful in the structure elucidation of asphaltene include: hydroxyl oxygen determination by silylation, basic nitrogen determination by methylation with methyl iodide, reduction with potassium and an alcohol or alkyl halide, and mild oxidation with suitable oxidizing agents.

(a) Silylation of Hydroxyl Groups

In a previous Quarterly Report (4) we described the procedure and results for the silylation of asphaltenes from different coal liquefaction demonstration processes. During the present quarter we carried out the silylation of Synthoil asphaltene silica gel chromatography fractions. The results are presented in Table VIII. The benzene eluted fraction is seen to have 30% of the oxygen present in phenolic groups, whereas the diethyl ether eluted fraction contains 64% of the oxygen as phenolic oxygen. These results provide quantitative data on the relative amounts of phenolic OH in asphaltene fractions. Previous infrared analysis of asphaltene and chromatographic fractions showed the presence of both monomeric OH and polymeric or H-bonded OH absorption (4). It is now apparent that the basic components of coal asphaltenes contain a substantial amount of phenolic OH. The THF eluted fraction which contains the largest amount of oxygen contains only 16% phenolic OH.

(b) Methylation of Basic Nitrogen Groups

In the last Quarterly Report (5) we described the methylation procedure. This procedure is useful in determining the amount of basic pyridine-like

Table VIII. Analyses of Silylated Sythoil Asphaltene Silica Gel Chromatography Fractions

<u>Asphaltene</u>	<u>% Si in Silylated Asphaltene</u>	<u>% - OH in Silylated Asphaltene^a</u>	<u>% O in Starting Asphaltene^b</u>	<u>% OH/O_{total} in Starting Asphaltene</u>
Starting	3.02	1.87	3.93	48
Benzene Eluted	1.38	0.81	2.71	30
Diethyl Ether Eluted	4.57	2.93	6.50	64
THF Eluted	2.50	1.53	9.40	16

^aUsing method of S. Friedman, C. Zahn, M. Kaufman, and I. Wender Fuel, 40, 38(1961).

^bBy difference.

asphaltene molecules. Preliminary results and analyses are presented in Table IX. When benzene is used as a solvent for the methylation reaction the general premise is that alkylated asphaltene (asphaltene - $\text{N}^+ \text{I}^-$) will become insoluble and precipitate from solution. The percentage CH_3 of basic nitrogen may then be calculated from analysis data on the percentage of nitrogen and iodine found in the product. This procedure is not quantitatively accurate because small amounts of iodine are also found in the benzene soluble fractions.

The preliminary results indicate that starting asphaltene may be separated into two fractions with grossly different amounts of basic nitrogen. The benzene eluted fraction from silica gel affords a major fraction (84%) which contains essentially no basic nitrogen. The Et_2O eluted fraction gives only one fraction which contains practically all basic nitrogen. Methylation of the THF eluted fraction has been carried out, and analyses are pending.

(c) Reduction of Asphaltene with Potassium

An exploratory run was carried out with Synthoil asphaltene. The asphaltene was stirred with potassium metal, and a small amount of naphthalene in tetrahydrofuran for seven days under argon at room temperature. The asphaltene turned blackish. After filtration, in vacuo, to remove unreacted potassium, the asphaltene radical anion solution was quenched with ethanol. After evaporation of all volatile liquids on a rotary evaporator the solid residue was dissolved in a small amount of THF, and precipitated from pentane. The pentane soluble material was mostly naphthalene. The pentane insoluble and THF soluble fraction was Soxhlet extracted with water to remove any metal salts present. The product was obtained in 70% yield. A comparison of the product with starting asphaltene is given in Table X.

The results suggest that not much reduction took place. The atomic C/H

Table IX. Analysis of CH₃I Alkylated Asphaltenes

	Benzene Soluble Fraction			Benzene Insoluble Fraction		
	%	% I	% N	%	% I	% N
Starting Asphaltene	52	2.90	1.29	48	13.35	2.14
Benzene Eluted Silica Gel	84	<0.3	0.93	16	12.12	--- ^a
Et ₂ O Eluted Silica Gel	---	---	---	(100)	12.74	--- ^a
THF Eluted Silica Gel	---	---	---	(100) ^b	--- ^a	--- ^a

^aAnalysis pending.

^bTHF fraction only slightly soluble in benzene initially.

Table X. Comparison of Synthoil Asphaltene and Potassium/ Naphthalene Treated Asphaltene

	<u>C</u>	<u>H</u>	<u>N</u>	<u>O</u>	<u>S</u>	<u>C/H</u>	<u>Ash</u>
Synthoil Asphaltene	87.65	6.31	1.74	3.89	0.41	1.16	0.46
K/Naphthalene treated Asphaltene	77.82	6.07	1.76	10.45	0.26	1.07	3.64

	<u>Starting Synthoil Asphaltene</u>	<u>K/Naphthalene Treated Synthoil Asphaltene</u>
Mol. Formula	$C_{40.87}H_{35.05}N_{0.69}O_{1.52}S_{0.07}$	$C_{76.19}H_{70.80}N_{1.48}O_{7.68}S_{0.10}$
MW ^a	560	1133
H _{ar} [*]	33	33
H _a [*]	42	39
H _o [*]	25	28
f _a	0.71	0.69
H _{aru} /C _{ar}	0.70	0.86
σ	0.43	0.48
R _s	8.9	21.5
n	1.6	1.7
C _a	29.2	52.5
R _a	5.3	4.8

^aExtrapolated infinite dilution values in THF.

ratio was reduced only from 1.16 to 1.07. Surprisingly the percent oxygen increased from 4.33 to 10.85%, and the molecular weight increased from 560 to 1133. Apparently, under the conditions used to carry out the reaction little or no reductive cleavage of the asphaltene polymeric framework took place. Rather it appears as though some oxidative polymerization, or association of oxidized molecules is taking place.

(d) Oxidation

Oxidation has been used widely as a means of characterizing coals (18 - 21), oil shale (22), and petroleum asphaltenes (23, 24). Many different oxidants such as KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, NaOCl , H_2O_2 , O_3 , and O_2 have been employed. Hayatsu and co-workers identified 35 aromatic carboxylic acids resulting from the oxidation of bituminous coal with aqueous $\text{Na}_2\text{Cr}_2\text{O}_7$ (21). Young et al. (22) confirmed the presence of saturated straight-chain and branched aliphatic mono and di-carboxylic acids in the oxidized products from treated oil shale. Moschopedis and Speight have described the effects of a variety of oxidizing agents on Athabasca asphaltenes (24) and bitumens. By the use of proton NMR analysis they were able to illustrate some of the effects of the oxidation process on the asphaltene aromatic sheets.

In our work with coal asphaltenes we hope to break connecting links by selective oxidation. In this way we may learn more about the basic structure of asphaltenes by characterizing the oxidized fragments and oxidized asphaltene residues.

Table XI shows preliminary oxidation results for Synthoil asphaltene using the oxidizing agents: alkaline permanganate, sodium peroxide and potassium dichromate. Alkaline permanganate appears to be the most effective oxidizing agent under moderate conditions. After one hour only 10% of

Table XI. Oxidation of Synthoil Asphaltene

<u>Oxidant</u>	<u>Medium</u>	----- Product % -----			
		<u>ϕH_{sol}</u>	<u>ϕH_{insol}</u>	<u>Aq. H⁺_{soluble}</u>	<u>Aq. H⁺_{insoluble}</u>
Potassium permanganate	Alkaline	10	37*	(14)	(3)
	95°/1hr 95°/4hrs	0	0	?	?
Sodium Peroxide	Alkaline 80°/16hrs	74	23	(1)	?
Potassium Dichromate	Neutral 100°/5hrs	88	9	(3)	?

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*MW = 1670 in THF (upper limit due to slight amount of insoluble material)

the asphaltene was unattacked, and remained benzene soluble; 37% was partially oxidized; and 17% was soluble in the aqueous alkaline product solution. Some of the material was probably oxidized to CO_2 and volatile acids which were lost in the workup.

The partially oxidized asphaltene showed a carbonyl IR absorption band at $\approx 1700 \text{ cm}^{-1}$. Analysis, molecular weight, and NMR structural parameter calculations (4); are given in Table XII. The oxygen content, and the molecular weight both increased by factor of about three. Apparently either oxidative polymerization of asphaltene is taking place, or the introduction of oxygen functions into the asphaltene molecules has enhanced the ability of these species to undergo inter-molecular association.

A portion of the oxidized material which was soluble in the aqueous alkaline solution was recovered as a precipitate by acidifying the solution. The remainder was obtained by concentrating the aqueous solution by rotary evaporation, and extracting with diethyl ether. This material had IR absorption bands characteristic of acids. It was esterified with methanol/ BF_3 and is currently under investigation.

Work forecast:

Additional silylation, methylation, oxidation, and reduction reactions will be carried out on asphaltenes, and asphaltene derivatives in order to increase our knowledge of the structure, and functional group composition of these materials. These types of chemical methods will be extended to other suitable coal liquid fractions as time and manpower permit.

Table XII. Comparison of Synthoil Asph. & Partially Oxidized Asph.

	<u>C</u>	<u>H</u>	<u>N</u>	<u>O</u>	<u>S</u>	<u>C/H</u>
Synthoil Asph.	87.65	6.31	1.74	3.89	0.41	1.16
KMnO ₄ Part. Ox. Synthoil Asph.	80.31	5.62	1.42	11.68	(0.98)	1.19

	<u>Starting Synthoil Asph.</u>					<u>Partially Oxidized Synthoil Asph.</u>				
Mol. Formula	C _{40.87}	H _{35.05}	N _{0.69}	O _{1.52}	S _{0.07}	C _{111.67}	H _{93.14}	N _{1.69}	O _{12.19}	S _{0.51}
MW ^a	560					1670				
H _{ar} [*]	33					34.3				
H _a [*]	42					41.4				
H _O [*]	25					24.3				
f _a	0.71					0.73				
H _{aru} /C _{ar}	0.70					0.78				
σ	0.43					0.50				
R _S	8.9					31.5				
n	1.6					1.6				
C _A	29.2					81.1				
R _A	5.3					9.8				

^aExtrapolated infinite dilution values in THF.

Conclusion

Separation of coal asphaltenes by solvent elution chromatography with benzene, diethyl ether, and tetrahydrofuran, on silica gel, may be carried out with 98-99% recovery of starting asphaltene. The asphaltenes recovered from the first two solvents comprise 80-90% of the charged asphaltenes. They are brown, benzene soluble powdery materials. They possess molecular weights and structural parameters which are not too different from the starting asphaltene. However, the diethyl ether eluted fractions have higher percentages of the heteroatoms nitrogen and oxygen, and more hydrogen bonded phenolic-OH, and basic nitrogen. These fractions have substantially lower atomic C/H values, and lower color index values. They tend to have lower f_a , and higher H_{aru}/C_{ar} values. This suggests that the diethyl ether eluted asphaltenes are more basic and polar, have a higher degree of saturation, and contain smaller average aromatic π -systems than the benzene eluted asphaltene fractions.

The third fraction (THF-eluted) represents 10-20% of the asphaltene, and contains varying amounts of black char-like material of high molecular weight which is not soluble in benzene. This fraction is probably solubilized originally in benzene by association with the other two fractions. However, when these two fractions are separated from the THF eluted fraction, on the chromatography column, the latter material becomes insoluble in benzene. The THF eluted fractions have the highest molecular weights, and the highest percentages of nitrogen and oxygen. Silylation indicates that only a small percent of the oxygen present is phenolic oxygen.

Donor-acceptor complexes between coal asphaltenes and the π -acceptor tetracyanoethylene have been synthesized. UV-visible spectra of these species show new charge-transfer absorption bands not found in the free components. ESR measurements show enhanced spin signals for these complexes. X-ray diffraction measurements indicate that in the solid state asphaltene/TCNE clusters contain from 3/2 to 4/2 molecules of Synthoil asphaltene and HRI H-Coal asphaltene to TCNE respectively.

Electron spin resonance spectra of asphaltenes, asphaltene chromatography fractions, and charge transfer complexes between asphaltenes and iodine and TCNE show a single, rather intense signal at g_{eff} values of about 2.003. Relative ESR signal intensities are: diethyl ether eluted asphaltene < starting asphaltene < asphaltene-TCNE complex < asphaltene- I_2 complex. This order is consistent with a picture of asphaltenes in which the forces holding the aromatic layers together arise from different donor-acceptor properties of alternate layers. The temperature dependence of the ESR signal may follow the Curie-Weiss law. Quantitative measurements of the temperature dependence of asphaltenes and their derivatives is expected to offer a means of determining whether the observed free radical signals in coal asphaltenes come from excitations typical of charge transfer complexes.

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