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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES:
PHASE II

Quarterly Progress Report, October--December 1976

MASTER

Work performed under Contract No. E(49-18)-2031

University of Southern California
Los Angeles, California

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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COAL-DERIVED ASPHALTENES
Phase II

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Quarterly Progress Report for the Period
October - December 1976

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Abstract

Plots of H/C atomic ratios versus aromaticity, f_a , for coal liquid fractions suggest that aromatization is responsible for the highly aromatic nature of the carbene and carboid fractions, and that hydrogenation of intermediate fractions tends to reduce f_a values to that of chainlike saturated species.

Infrared analysis of asphaltenes, and asphaltene chromatography fractions confirms the generality that phenolic OH is found in both the neutral and basic asphaltene fractions but predominates in the neutral fraction.

Proton NMR structural analyses indicates that coal asphaltanes are highly aromatic species, moderately substituted with short chain or naphthenic groups, and condensed in kata-systems.

Preliminary VPO molecular weight studies indicate that coal asphaltenes are progressively associated in benzene, but probably unassociated or only slightly associated in tetrahydrofuran over the concentration range 4-40 g/l.

Asphaltene-iodine donor-acceptor complexes have been synthesized which afford charge-transfer ultraviolet-visible absorption bands. Conductivity and x-ray diffraction studies of these complexes do not support an ordered asphaltene-iodine layered structure.

Silylation of asphaltenes indicates that essentially all the oxygen in SRC produced asphaltenes is phenolic oxygen. Asphaltenes produced in staged pyrolysis or catalytic hydrogenation appear to have only about 50% of the oxygen present as phenolic oxygen.

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

The objective of Phase II is to continue the characterization of coal asphaltenes and other coal liquid fractions by the 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 is being carried out.
- (5-11) Characterization of coal liquid fractions by various physical and instrumental methods is continuing.
- (12) Asphaltene donor-acceptor complexes are being studied by a variety of techniques.

Fig. 1 - Milestone Chart

- (13) 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) Establishment of Sample Data Bank

Work accomplished:

The results of solvent fractionation of all currently available coal liquid products, carried out by the standard method (1), are presented in Figure 2. Table I shows the analyses of HRI H-Coal liquid, and the various solvent fractions obtained from this material.

H/C - Aromaticity Relationship

One of the purposes of assemblage of data for characterization is that, hopefully, the structure of asphaltenes can be revealed by a combination of several methods using different chemical or physical approaches. To test this hypothesis, the aromaticity values determined by a variety of techniques (^{13}C -NMR, ^1H -NMR and x-ray diffraction) for coal liquid fractions are plotted against the H/C atomic ratios (Fig. 3). The upper and lower limits of H/C for fully aromatic condensed systems are shown at the top of the figure, and the limiting H/C values for peri condensed naphthenic, and unbranched paraffin systems are shown at the bottom. The intercepts at $f_a=1$, and $f_a=0$ are calculated on the basis of peri, kata, and polyphenyl R[m,n] model systems of ≈ 50 aromatic carbons (2,3). The dashed line in the center is an indication that aromatization is responsible for the highly aromatic content of carbene and carboid and probably coke. The lower portion of the line indicates that hydrogenation will reduce f_a toward the chainlike species. If a molecular weight decrease is considered, then it is anticipated that the 2.0 point will shift to even higher values.

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, instrumental and chemical analyses.

TABLE I

HRI H-Coal 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>
Coal***	69.76	4.63	1.28	3.51	9.86	10.9
Coal Liquid****	89.82	8.33	0.87	0.14	0.84	—
Oil	89.54	9.18	0.45	<0.05	0.83	0.17
Resin	89.39	7.07	1.13	0.14	2.27	<0.05
Asphaltene	86.88	5.91	1.61	0.64	4.96	0.38
Carbene	87.18	5.05	1.93	0.94	4.90	0.32
Carboid	86.09	4.87	1.51	0.97	6.56	0.55

* Moisture and ash free

** By difference

*** Ill. No. 6, Burning Star Mine—Bituminous

**** 400°F + Fuel Oil Product.

FIG. 2 SOLVENT FRACTIONATION ANALYSIS
OF COAL LIQUID PRODUCTS

FIG. 3 PLOT OF AROMATICITY VS. H/C FOR COAL LIQUID FRACTIONS

(2) Separation of Asphaltenes by Solvent Elution Chromatography

In previous quarterly reports several different types of adsorbents (silica gel, alumina, Amberlyst-15 resin) were examined for utility in further purifying crude asphaltenes, and to separate them according to basicity (1, 4, 5). Silica gel and Amberlyst-15 (an acidic sulfonated polystyrene resin) were found to be useful, and separation on acidic adsorbents was suggested as an alternative procedure to precipitation of basic asphaltene by dry HCl gas (6).

In our last quarterly report we presented weight percent recovery, and nitrogen balance data for such chromatographic separations. The results were straightforward for silica gel from which recoveries of greater than 84 weight% could be obtained with observed nitrogen balances within 20% of the expected values (5). The Amberlyst-15 results were clouded due to the necessity of using pyridine to elute the basic fraction. High recoveries, 100% or greater, and high nitrogen balances, >100%, were sometimes obtained. These results suggested that all the pyridine had not been removed from the basic fraction. Several procedures were tried in order to remove adsorbed pyridine. These were long term heating in a vacuum oven, reprecipitation from pentane, and rechromatographing from silica gel. These procedures did apparently result in removal of adsorbed pyridine, but they also resulted in a substantial loss in asphaltene which probably resulted in the final basic fraction not being closely representative of the initial basic fraction. Therefore, we have abandoned the Amberlyst-15 procedure for use in obtaining a highly representative basic fraction although it may still be used for obtaining representative neutral fractions which are eluted with benzene. Silica gel will therefore be the support which we shall use in the future to obtain representative purified chromatography fractions.

We previously reported on the analyses and some of the physical properties of the separated chromatography fractions. We now wish to present additional infrared evidence showing the relative distribution of -OH and -NH functions on the starting asphaltenes and the chromatography fractions. The infrared analysis in dilute CS₂ solutions (Fig. 4), shows a typical series of asphaltene products. The starting asphaltene shows -OH absorptions at 3590, 3540 and 3400-3200, and -NH absorption at 3460 cm⁻¹. The trimethyl silyl derivative shows essentially no OH absorptions. Asphaltenes eluted from either silica gel, with diethyl ether, or Amberlyst-15, with pyridine, show small relative decreases in OH absorption. However, asphaltenes eluted from either silica gel or Amberlyst-15 with benzene show relatively large increases in the 3590

FIG. 4 INFRARED ANALYSIS OF PAMCO ASPHALTENE

cm⁻¹ monomeric OH absorption band. These results confirm the generality that phenolic OH in asphaltenes is not found exclusively in the nonbasic fractions although it does predominate in those fractions.

Work forecast:

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

Exploratory work will be carried out with high pressure liquid chromatography utilizing gel permeation chromatography to isolate selected fractions from crude asphaltenes for further characterization.

(3) Characterization of Coal Liquid Fractions by Physical Methods:

Work accomplished:

(a) NMR Spectroscopy

(1) ¹H Spectroscopy

In the last quarterly report (5) Brown-Ladner structural parameters were presented for various asphaltenes and asphaltene fractions. These calculations were based on directly determined hydrogen percentages. Since hydrogen bonded phenolic OH resonance are also believed to be shifted under the aromatic envelope (7), we now wish to present refined calculations corrected for phenolic OH resonances determined from silylation of phenolic OH groups. The calculations were modified to make use of the most reliable molecular weight data which is presented in section (3-c) of this report. The following additional average structural parameters are also presented in Table II:

R_S, number of substituted aromatic ring carbons;

n, number of carbon atoms per saturated substituent;

C_A, total number of aromatic carbons;

R_A, number of aromatic rings. For a description of these modified Brown-Ladner equations see Table III.

These results indicate that the average coal asphaltene molecules produced from various liquefaction processes, and coals of differing origin, are highly aromatic species having from 67 to 81 percent of the carbon as aromatic carbon. These molecules are moderately substituted with 32-54 percent of the available aromatic edge carbons being substituted. The average number of carbon atoms per saturated substituent is between 1.4 and 1.6. The hydrogen to carbon ratios of the hypothetically-unsubstituted aromatic systems range from 0.63 to 0.76 which suggests only kata systems of small ring number are likely. The average number of aromatic rings was found to vary from 3.5 to 6.6.

Table II . - Average Molar Properties of Asphaltenes

	PNC-CCED	Synthoil	HRI-H-Coal	Catalytic Inc. SRC	PAMCO SRC
Molecular Formula	C _{31.32} H _{29.40} N _{0.56} O _{2.03} S _{0.37}	C _{43.95} H _{39.40} N _{0.93} O _{1.41} S _{0.09}	C _{36.60} H _{27.57} N _{0.53} O _{1.42} S _{0.09}	C _{36.60} H _{27.57} N _{0.44} O _{1.31} S _{0.02}	C _{28.39} H _{24.11} N _{0.42} O _{1.22} S _{0.14}
Molecular Weight ^a	458	606	457	495	395
H _{ar} ^a	24.8	31.4	46	45.7	40.1
H _{OH} ^a	4.2	1.6	--b	4.3	4.9
H _a ^a	45	42	36	34	38
H _o ^a	26	25	18	15	17
f _a	0.57	0.70	0.78	0.81	0.77
H _{aru} /Car	0.76	0.72	0.72	0.63	0.71
σ	0.54	0.44	0.34	0.32	0.38
R _S	8.7	9.7	6.3	5.0	5.8
n	1.6	1.6	1.5	1.5	1.4
C _A	20.9	30.8	25.9	29.7	21.8
R _a	3.5	5.3	4.6	5.6	4.1

^aVPO in THF^bSilylation in progress H_{OH} not yet available

Table III - Modified Brown-Ladner Equations

$$f_a = \frac{\frac{C}{H} - \left(\frac{H^*_\alpha}{x} + \frac{H^*_O}{y} \right)}{\frac{C}{H}} = \text{fraction of total carbon which is aromatic carbon}$$

$$\frac{H_{aru}}{C_{ar}} = \frac{\frac{H^*}{x} + H^*_{ar} + \frac{O-O_{OH}}{H}}{\frac{C}{H} - \frac{H^*_\alpha}{x} - \frac{H^*_O}{y}} = \text{ratio of substitutable edge atoms to total aromatic atoms}$$

$$\sigma = \frac{\left(\frac{H^*_\alpha}{x} + \frac{O}{H} \right)}{H^*_{ar} + \frac{H^*_\alpha}{x} + \frac{O-O_{OH}}{H}} = \text{fraction of the available aromatic edge atoms occupied by substituents}$$

$$R_S = \sigma C_A \frac{H_{aru}}{C_{ar}} = \text{number of substituted aromatic ring carbons}$$

$$n = \frac{H^*_O}{H^*_\alpha} + 1 = \text{number of carbon atoms per saturated substituent}$$

$$C_A = \frac{f_a(C)(M)}{100} = \text{total number of aromatic carbon atoms}$$

$$R_a = C_A \left(\frac{1 - H_{aru}/C_{ar}}{2} \right) + 1 = \text{number of aromatic rings}$$

C = mole % carbon

H = mole % hydrogen

O = mole % oxygen

O_{OH} = mole % phenolic oxygen

H^{*}_{ar} = mole fraction aromatic hydrogen

H^{*}_α = mole fraction hydrogen α to aromatic ring

H^{*}_O = mole fraction of aliphatic hydrogen not α to aryl ring

x = average ratio of hydrogen to carbon on carbons α to aryl ring

y = average ratio of hydrogen to carbon on aliphatic carbons not α to aryl ring

Assumptions: All oxygen is attached to aryl rings in either phenol or aryl ether groups. All phenolic hydrogens found by the TMS derivative method are under the aryl absorption. x=y=2.

(2) ^{13}C Spectroscopy

The technique of ^{13}C -NMR spectroscopy is valuable because it allows the determination of different types of carbon atoms directly. Structural parameters such as aromaticity, f_a , and others identical with those obtained from proton NMR spectroscopy may be calculated. In addition, under favorable conditions, other structural parameters not available from proton spectra may be obtained from ^{13}C spectra. In Table IV, we present ^{13}C aromaticity values for various solvent and chromatography fractions. For asphaltenes, these values compare reasonably well with those obtained from ^1H spectra (Table II). The range of difference is from 0.01 to 0.06 with the average deviation being 0.036. If one assumes that ^{13}C values of f_a , which are obtained directly, are more reliable than f_a values calculated using the Brown-Ladner equation, and the assumption that $x=y=2$, then one may fit the values of $x=y$ to give Brown-Ladner f_a values which are the same as ^{13}C f_a values. This procedure will be carried out in the future and should result in a more reliable set of structural parameters.

(b) Particle Size Determination by Transmittance Electron Microscopy

The aromatic sheet dimensions of coal asphaltenes have been determined previously by the x-ray diffraction method (4), and found to be within the range of observation of Transmission Electron Microscopy (TEM). Preliminary measurements for asphaltenes, sprayed onto a carbon film, were made manually, and discussed previously (4). Manual measurement was found to be a time consuming, and imprecise means of obtaining particle dimensions. Therefore, a method, which is rapid and precise, was sought to efficiently handle TEM data. In recent years modern digital computers have been used to process images, to emphasize details, to sharpen picture and to modify various aspects of pictures in order to enhance the ability of the human photo interpreter to extract information. The technique of image processing was initially developed for processing pictures returned from NASA space vehicles. However, these same techniques have been utilized to process pictures from many other sources such as electron and light microscopes, and medical and industrial radiographs.

The TEM image intensity of exposure at a particular point on the film depends primarily on the object density and the microscope source-object-film geometry. The electron gun has a finite focal spot which also limits resolution. The information content of the picture depends upon the absorption characteristics of the object which are determined by the thickness, density and material properties of the

Table IV. - ^{13}C Aromaticity Values, f_a , for Solvent and Chromatography Fractions

	FMC-COED	Synthoil	HRI-H-Coal	Catalytic Inc. SRC	PAMCO SRC
Oil	0.50	0.53	0.44	0.83	0.60
Resin	0.68	0.57	0.59	0.84	0.73
Asphaltene	0.66	0.65	0.72	0.76	0.76
Amberlyst-15 ØH Eluted	0.71	0.66	-- ^a	0.72	0.63
Amberlyst-15 Pyridine Eluted	0.76	0.67	-- ^a	0.73	0.72

^aChromatography in progress.

object. Thus, TEM pictures are more quantum limited than most photographic images, and therefore, exhibit lower resolution and smaller contrast ratios. This is both an advantage and a disadvantage for computer image analysis. The advantage is the fidelity requirement for digitization is not as great as for other images. But the noise level and low image contrast will be a limiting factor.

Image Processing

A flow diagram of the overall TEM picture analysis, including image processing is shown in Fig. 5. The TEM picture image is first digitized to a 512x512 point matrix. Each point is represented by an 8-bit binary word which is equivalent to an integer between 1 to 256. The number associated with each point represents the brightness of the point. The darkest shade is 256, and the lightest is 1. Since, in the original picture, different shades of grey are present, and our interest is only in the dark particles, a threshold has to be set to allow processing of the picture in a simple form represented by only 1's and 0's. This threshold is selected for each individual picture by use of the on-line interactive Aerojet General Color Display. The digitized picture can be stored on a magnetic tape, and then transferred to the DEC 10 system where the conversion to a binary picture takes place. A computer program was written to differentiate individual particles, and an algorithm was developed to minimize the occupancy of the computer memory. In the algorithm, only two lines of the digitized picture must be in the core memory each time during data processing. The whole picture does not have to be in the active memory, the algorithm will take two lines each time and compare them, then it will drop the first line and pick up the third line and compare, etc.. This algorithm can minimize computer cost and provide a potential for small computer operation. An artificial picture was made up to test the program, the result is very encouraging and is shown in Fig. 6. After the size determination, which is done by counting the 1's in a particle, a size distribution can be printed out. The procedure of image processing can operate much faster and more efficiently than the manual method.

The above description details the development of the technique. The quality of the TEM pictures needs to be improved. Background interference due to the supporting carbon film should be eliminated, and optimum concentrations of asphaltenes and carboids in benzene and pyridine must be determined. Depositions will be made on silicon monoxide films at various concentrations in the next quarter.

(c) VPO Investigation of Asphaltene Molecular Weights Work accomplished:

A Mechrolab Model 301A Vapor Phase Osmometer was

Fig. 5

FLOW DIAGRAM OF TEM
PICTURE ANALYSIS BY
IMAGE PROCESSING

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Fig. 6 - Image Processed Particle Size Distribution

I(1) =	3
I(2) =	3
I(3) =	5
I(4) =	4
I(5) =	7
I(6) =	4
I(7) =	5
I(8) =	1
I(9) =	4
I(10) =	3
I(11) =	1
I(12) =	1
I(13) =	2
I(14) =	2
I(15) =	2
I(17) =	2
I(18) =	2
I(20) =	1
I(22) =	1
I(33) =	1
I(40) =	2
I(41) =	1

used to determine molecular weights with benzil employed as a standard. In normal runs, 6-8 concentrations over the range 4-36 g/l were employed in the solvents benzene or tetrahydrofuran for extrapolation to infinite dilution. A plot of the data for a sample of Synthoil asphaltene is shown in Fig. 7. Computer assisted least squares analysis was carried out for the linear portions of each curve. The resulting lines, with accompanying standard deviations of the lines, slopes and intercepts of the lines along with correlation coefficients, are presented in Table V.

A great deal of work has been carried out on the study of petroleum asphaltene molecular weights (8). Recently it was found that the observed VPO molecular weights for Athabasca asphaltenes increase as the dielectric constant of the solvent is decreased (9). In addition, different molecular weight vs. concentration behavior was observed for different solvents. For the low dielectric constant solvent benzene, no variation in molecular weight was observed when the concentration of the asphaltene was varied over the range $0.37-1.28 \times 10^{-2}$ M. However, use of pyridine, a solvent of higher dielectric constant, resulted in approximately a 1.6 fold increase in the observed molecular weight over the same concentration range. These results were interpreted in terms of association in solvents of low dielectric constant and dissociation in solvents of high dielectric constant.

Our preliminary results indicate that association is taking place with the asphaltenes studied to date, Synthoil and HRI-H-Coal, in the solvent benzene over the range 4-40 g/l ($\approx 0.8-4 \times 10^{-2}$ M). However, the interpretation of our results in the solvent THF is still uncertain. The plots of MW vs. concentration for the five asphaltenes studied (Table V.), with the exception of FMC-COED, show small increases of MW with increasing concentration. But the correlation coefficients for the least squares lines are not significant, and if one eliminates the low and high concentration points from these runs, it is possible to obtain a nearly constant MW value for each asphaltene within the approximate concentration range of 8-24 g/l. These approximate values in THF are: Synthoil 606 $\pm$ 4; HRI-H-Coal 457 $\pm$ 25; FMC-COED 332 $\pm$ 8; Cat. Inc. SRC 495 $\pm$ 6; PAMCO SRC 395 $\pm$ 8. More work will be done over broader concentration ranges in the next quarter in an effort to clearly establish whether association is taking place with asphaltenes, and with other solvent fractions of interest.

Work forecast:

Characterization will continue on all applicable fractions by the analytical and physical methods described in this report.

FIG. 7 MOLECULAR WEIGHT VS. CONCENTRATION
SYNTHOIL ASPHALTENE

Table v. - Molecular Weight of Asphaltenes vs. Concentration*in
Benzene and THF

		St. Dev. MW	Corr. Coeff.
<hr/>			
<u>THF</u>			
Synthoil	MW = $2.85 \pm 0.96(\text{Conc}) + 567.7 \pm 17.5$	20.2	0.83
HRI-H-Coal	MW = $6.90 \pm 3.0(\text{Conc}) + 394.1 \pm 35.2$	33.8	0.76
FMC-COED	MW = $-0.095 \pm 0.25(\text{Conc}) + 333.2 \pm 5.1$	6.5	0.76
Cat. Inc. SRC	MW = $1.11 \pm 0.38(\text{Conc}) + 485.6 \pm 7.6$	9.7	0.77
PAMCO SRC	MW = $2.26 \pm 0.48(\text{Conc}) + 362.7 \pm 10.4$	13.8	0.87
 <u>BENZENE</u>			
Synthoil	MW = $11.1 \pm 0.6(\text{Conc}) + 552.3 \pm 10.4$	8.6	0.995
HRI-H-Coal	MW = $11.5 \pm 0.9(\text{Conc}) + 598.2 \pm 14.7$	18.4	0.986

*Concentration g/l.

(4) Asphaltene Donor-Acceptor Complexes

Work accomplished:

Evidence has been presented recently in the literature concerning the acid-base nature of coal asphaltenes (6). A more recent publication presents additional evidence suggesting that acid and base components of asphaltenes form hydrogen-bonded complexes in solution (7). An alternative explanation for the associative behavior of asphaltenes, based on acceptor (π -deficient) and donor (π -abundant) charge transfer complexation, was previously suggested for petroleum asphaltenes (10, 11, 12).

Preliminary studies were carried out during the past quarter on iodine complexes of asphaltenes. Complexes were formed by mixing benzene solutions of iodine and the individual asphaltenes (approximate mole ratios, I_2 /Asphaltene=1.1-1.5/1). A precipitate forms rapidly. It was filtered, washed with benzene and dried overnight at 40°C/2mm Hg. The yields and mole ratios of the asphaltene: I_2 complexes are presented in Table VI.

The dark brown to black I_2 -asphaltene complexes are relatively insoluble in benzene, carbon disulfide and pentane, and slightly to moderately soluble in chloroform and tetrahydrofuran. The complexes have small equilibrium constants for dissociation to their components. Soxhlet extraction of a Cat. Inc. SRC I_2 -asphaltene with pentane for 5 days led to only a small decrease in the % iodine of the complex from 32.72 to 26.00 percent.

a) Ultraviolet-Visible Spectra of Complexes

Measurement of the UV-Visible spectrum of I_2 /asphaltene complexes in THF or $CHCl_3$ (Fig. 8) leads to the observation of a new band at ≈ 295 nm and new shoulder at ≈ 355 nm. Neither of these absorptions is observed in the free components. The differential spectrum presented in Fig. 9 shows these two bands clearly. These bands are presumed to be charge-transfer absorption bands of the iodine:asphaltene complex. The nature of the donor interaction of the asphaltene may be either via the electrons of the π -orbitals, or via the non-bonded, lone pair electrons in atomic orbitals of n donors such as nitrogen or oxygen bases.

b) Infrared Spectra

Asphaltene-iodine samples were run as KBr disks, and infrared spectra were obtained directly, and differentially of asphaltene-iodine complexes versus reference asphaltene. No C-I stretching frequencies were observed in the 400-

Table VI. - I_2 :Asphaltene Complexes

Sample	% Yield Complex	% Iodine	I_2 /Asphaltene ^a
Synthoil	60	35.02	1.21
PAMCO SRC	64	38.36	0.89
Cat. Inc. SRC	61	32.72 ^e	0.83
HRI H-Coal ^b	69	28.13	0.61
FMC-COED ^c	28	22.00	0.37
Cat. Inc. (benzene eluted from Amberlyst-15) ^d	44	30.34	0.86
Cat. Inc. (pyridine eluted from Amberlyst-15) ^d	76	37.06	1.16

^aMole ratios calculated assuming MW of asphaltene portion of complex is the same as the MW of the starting asphaltene.

^bA low starting ratio of I_2 /asphaltene=0.7/1 was used. This preparation will be repeated.

^cA tar formed on mixing the asphaltene/ I_2 solutions. This preparation will be repeated when a fresh asphaltene sample becomes available.

^dThese asphaltenes were eluted from Amberlyst-15 with the above mentioned solvent.

^eThis I_2 /asphaltene complex was Soxhlet extracted with pentane for 5 days. The % iodine decreased to 26.00.

FIG. 8- UV-VIS. SPECTRA OF I_2 , SYNTHOIL ASPHALTENE, AND SYNTHOIL ASPHALTENE- I_2 COMPLEX IN $CHCl_3$

FIG. 9 UV-VIS SPECTRUM OF SYNTHOIL ASPHALTENE- I_2 COMPLEX VS.
SYNTHOIL ASPHALTENE IN $CHCl_3$

600 cm^{-1} region, and no aromatic- I_2 bands in the 992 cm^{-1} to 1200 cm^{-1} region (13,14). Solution infrared spectra were run in deuteriochloroform. The -OH and -NH bands in the region from 3200-3600 cm^{-1} of the free asphaltenes did not show any significant decrease in vibration frequencies for the CDCl_3 soluble fraction of the I_2 -asphaltene complexes. The soluble portion of the Synthoil I_2 -asphaltene did appear to exhibit a relative decrease in the absorption intensity of the 3460 cm^{-1} , NH band vis-a-vis the 3590 cm^{-1} , OH band, but this could be due to a solvent fractionation effect.

c) X-Ray Diffraction

The x-ray diffraction patterns of asphaltenes show diffuse bands typical of mesomorphic or semicrystalline substances. In previous Quarterly Reports (15, 1, 4) we have discussed the analysis of two of these bands: the (002) band is attributed to the interplanar spacing between condensed aromatic rings of $\approx 3.5 \text{ \AA}$; the gamma band is attributed to the spacing between disordered aliphatic chains or alicyclic rings of $\approx 4.6 \text{ \AA}$ (see Fig. 10).

X-ray analysis of petroleum asphaltene-iodine complexes indicates a low degree of order exists within these complexes (10). The (002) band disappeared on forming a petroleum asphaltene-iodine complex, and a new band at 8.7 $\text{\AA}$ appeared. These observations were rationalized by assuming that the layered structure of the asphaltene was expanded from 3.5 $\text{\AA}$ to 8.7 $\text{\AA}$ by intercalation of a molecule of iodine between the aromatic layers of the asphaltene.

In the case of coal asphaltene-iodine complexes, the x-ray results show the loss of both the (002) and the (γ) bands, but no new peak is formed at $\approx 8.7 \text{ \AA}$ (Fig.10). This result may be interpreted by assuming that iodine molecules are not sandwiched between the aromatic layers, and that the asphaltene-iodine complexes are no longer ordered in the solid state but have become amorphous.

d) Conductivity

Polycyclic aromatic hydrocarbons generally form complexes with halogens, particularly bromine and iodine. Such complex formation usually leads to an increase in the conduction of the complex over that exhibited by the aromatic hydrocarbon alone. If their specific resistivities are lower and vary with temperature according to the equation:

Fig. 10
X-RAY PATTERNS OF ASPHALTENE-IODINE
SYSTEM

$$\rho = \rho_0 e^{\Delta E/2kT}$$

then the complexes may be classed as semiconductors.

Petroleum asphaltenes exhibit resistivities of 10^{-17} to 10^{-16} ohm-cm at 25°C which places them in the insulator range. Upon addition of iodine, the resistivity decreases one million-fold to a minimum corresponding to an iodine: asphaltene ratio of about 1.5:1 (10).

We measured the resistivity of a series of Catalytic Inc. SRC asphaltenes and chromatographic fractions at 25°C over the pressure range 10-3000 atm by the procedure of Hadek (16). The resistivity remained essentially constant as the pressure was increased (Fig. 11). The asphaltene- I_2 complexes formed from these asphaltenes, afforded a decrease in resistivity in two out of the three samples over the same pressure range. The log of the resistivity was found to decrease linearly with increase in pressure. The fact that resistivities of coal asphaltene- I_2 complexes are not significantly lower than those of the original asphaltenes suggests that these complexes may be mesomorphic, and may lack the ordered π -systems necessary to open a path for charge carriers.

Nevertheless, the inverse relationship in Fig. 11 suggests that the conduction is electronic, perhaps through the donor-acceptor properties of iodine with the asphaltene molecules. It is surprising to find that the neutral asphaltene-iodine complex has an inverse relationship following that of the asphaltene-iodine complex; whereas the base-iodine complex is entirely different. Actually the proportional increase of asphaltene base-iodine complex with pressure may indicate an ionic conduction mechanism. Perhaps for the base, functional group interactions become important. An alternative possibility is that this sample of pyridine eluted asphaltene, from Amberlyst-15, was contaminated with traces of pyridine which could have formed traces of ionic conductors with iodine (see Section 2 for discussion of Solvent Elution Chromatography). This conductivity measurement will be repeated with a basic asphaltene fraction eluted from silica gel which does not require the use of pyridine as an eluant.

Work forecast:

Studies will continue on asphaltene donor-acceptor complexes by the same analytical and physical methods described in this report. Donor-acceptor studies will be carried out with π -acceptors such as tetracyanoethylene and polynitroaromatic compounds to see whether such species will give definitive π -complexes with donor asphaltene and resin molecules. ESR studies will be initiated, when equipment becomes available, to study the excitation processes of asphaltene molecules to see if they resemble those of known

donor-acceptor charge transfer complexes (12,17). Conductivity studies will be extended, when equipment becomes available, to study the conductivity of asphaltenes and their complexes as a function of temperature. Seebeck coefficients will be determined for asphaltenes and their complexes.

(5) Chemical Methods for Asphaltene Structure Determination

Work accomplished:

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

(a) Silylation of Hydroxyl Groups

During the past quarter silylation of asphaltenes with 1,1,1,3,3,3-hexamethyldisilazane has been studied. The reaction is:

The silylation procedure entails refluxing a solution of 1 g of asphaltene, and a 3:1 mole ratio of hexamethyldisilazane for 4 hours in dry THF under a nitrogen atmosphere. The reaction solution is then cooled, and stirred under N_2 for 18 hours. The THF is stripped off on a rotary evaporator, and the silylated asphaltene is heated in a vacuum oven (40° and 2 mm Hg) until all unreacted starting material is removed and the product remains at constant weight. The silylated asphaltene is then freeze-dried from benzene.

The hydroxyl content of the original asphaltene may be calculated from the % Si of the silylated asphaltene by the procedure of Friedman, et al. (18) (Table VII). Infrared analysis shows the disappearance of the asphaltene OH bands (Fig. 4) and the appearance of trimethylsilyl ether bands at 1250 and 850 cm^{-1} . Proton NMR spectra show the appearance of new bands in the 0.10-0.12 ppm region typical of trimethylsilyl ethers of simple phenols, and bands in the 0.22-0.26 ppm range which are close to the range of absorptions of more substituted phenols such as chrysin (0.25 ppm), 8-hydroxyquinoline (0.24 ppm), or carboxylic acids such as salicylic acid (0.24 ppm) and 2-naphthoic acid (0.29 ppm) (19).

The results indicate that asphaltenes produced in SRC processes (PAMCO and Catalytic Inc.) contain practically all their oxygen as phenolic oxygen. The analytical results for the catalyzed hydrogenation (Synthoil), and the staged pyrolysis (FMC-COED) product asphaltenes indicate that only about 50% of the oxygen present is phenolic. However,

Table VII - Analysis of Silylated Asphaltenes

Asphaltene	% Si in Silylated Asphaltene	% -OH in Silylated Asphaltene ^a	% O in Starting Asphaltene ^b	% OH/O _{total} in Starting Asphaltene
Synthoil	2.82	1.74	3.93	44
FMC-COED	6.31	4.30	7.11	61
PAMCO SRC	6.53	4.52	4.68	97
Cat. Inc. SRC	6.17	4.19	4.58	92

^aUsing method of Friedman, et al. (18).

^bDetermined by difference.

IR shows that not all the -OH groups have been silylated in the FMC-COED asphaltene. Since a different coal was used in each of the SRC processes (West Kentucky, hvBb and Wyoming, sub-bituminous) and similar coals were used in the Synthoil, FMC-COED and PAMCO processes (West Kentucky, hvAb and hvBb), these results do not appear to be a consequence of the coal employed in the process. The results could be explained by assuming that the relatively mild SRC processes permit retention of phenolic functions in the asphaltenes, whereas the more vigorous Synthoil and FMC-COED processes result in partial conversion of phenolic groups to ether groups in the asphaltenes produced in these processes.

Work forecast:

The silicon analysis will be repeated on the silylated Synthoil asphaltene to verify the low % silicon. The silylation will be repeated on a fresh FMC-COED asphaltene sample to see whether all -OH groups can be silylated. Silylation will be carried out on the HRI H-Coal asphaltene.

Exploratory feasibility studies will be carried out on reduction of asphaltenes with potassium and an alcohol or alkyl halide to see whether the polymeric framework of these molecules may be cleaved. Mild oxidation of asphaltenes will be carried out to see whether identifiable alkyl carboxylic acid and carboxylic residues can be formed.

Conclusion

Plots of H/C atomic ratios versus aromaticity, f_a , for coal liquid fractions suggest that aromatization is responsible for the highly aromatic content of the carbene and carboid fractions and that hydrogenation of intermediate fractions tends to reduce f_a values to that of chainlike saturated species.

Infrared analysis of asphaltenes, asphaltene basic and neutral chromatographic fractions and silylated asphaltenes confirm the generality that phenolic OH in asphaltenes is found in both the neutral and basic fractions, but predominates in the neutral fraction.

Proton NMR structural parameters derived from modified Brown-Ladner equations indicate that the average coal asphaltene molecules produced from various liquefaction processes, and coals of differing origin, are highly aromatic species having from 67 to 81 percent of the carbon as aromatic carbon. These molecules are moderately substituted with 32 to 54 percent of the available aromatic edge carbons being substituted. The average number of carbon atoms per saturated substituent is between 1.4 and 1.6. The hydrogen to carbon ratios of the hypothetically-unsubstituted aromatic systems range from

0.63 to 0.76 which suggests only kata-systems of small ring number are likely. The average number of aromatic rings was found to vary from 3.5 to 6.6.

Transmission electron microscope pictures of asphaltene particles may be image processed by digital computer techniques and a particle size distribution determined if high resolution TEM pictures can be obtained.

Preliminary VPO molecular weight studies, as a function of concentration, suggest that coal asphaltenees are progressively associated in benzene over the range 4-40 g/l. In the solvent tetrahydrofuran, molecular weights were found to be approximately constant over the range 8-24 g/l for asphaltenes. Less significant measurements on both the low and high end of this range resulted in the observation of lower and higher molecular weight values. If association is taking place in THF, it is not as great as the association observed in benzene.

Asphaltene-iodine donor-acceptor complexes have been synthesized. These complexes afford new ultraviolet-visible bands which are presumed to be charge-transfer absorption bands. The nature of the donor interaction of asphaltenes is under investigation. Conductivity and x-ray diffraction studies on asphaltene-iodine complexes did not give results indicative of ordered asphaltene-iodine layers with iodine molecules sandwiched between the asphaltene layers.

Silylation of asphaltenes with hexamethyldisilazane gave results indicating that asphaltenes produced in SRC processes contain practically all their oxygen as phenolic oxygen. Asphaltenes produced in staged pyrolysis or catalytic hydrogenation appear to have only about 50% of the oxygen present as phenolic oxygen.

References

1. ERDA report No. FE-2031-3, March 1976.
2. T. F. Yen, Theoret. Chim. Acta (Berl.), 20, 399 (1971).
3. T. F. Yen and J. P. Dickie, J. Petrol. Inst., 54, 50 (1968).
4. ERDA Report No. FE-2031-4, June 1976.
5. ERDA Report No. FE-2031-5, September 1976.
6. H. N. Sternberg, R. Raymond and F. K. Schweighardt, Science, 188, 49 (1975).
7. F. K. Schweighardt, R. A. Friedel, and H. L. Retcofsky, Applied Spectroscopy, 30, 291 (1976).
8. J. P. Dickie and T. F. Yen, Anal. Chem., 39, 1847 (1967).
9. S. E. Moschopedis, J. F. Fryer and J. G. Speight, Fuel, 55, 227 (1976).
10. G. A. Sill and T. F. Yen, Fuel, 48, 61 (1969).
11. T. F. Yen, Fuel, 52, 93 (1973).
12. T. F. Yen and D. K. Young, Carbon, 11, 33 (1973).
13. W. Haller, G. Jura, and C. C. Pimentel, J. Chem. Physics, 22, 720 (1954).
14. E. E. Ferguson, Spectrochim. Acta, 10, 123 (1957).
15. ERDA Report No. FE-2031-2, Dec. 1975.
16. V. Hadek, Rev. Sci. Instr., 42, 393 (1971).
17. T. F. Yen, E. C. Tynan, G. B. Vaughan, and L. J. Boucher, in "Spectrometry of Fuels," Ed. R. A. Friedel, Plenum Press, New York (1970), Chapt. 14.
18. S. Friedman, C. Zahn, M. Kaufman and I. Wender, Fuel, 40, 38 (1961).
19. Mobil R & D Corp., EPRI AF-252, Project 410-1, Annual Report, Feb. 1976.