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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES

Phase III

Quarterly Progress Report, April-June 1978

By
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Work Performed Under Contract No. EX-76-C-01-2031

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MASTER

U. S. DEPARTMENT OF ENERGY

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CHEMISTRY AND STRUCTURE OF
COAL-DERIVED ASPHALTENES

Phase III

Quarterly Progress Report For the Period
April — June 1978

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Solubility parameters may be calculated for coal liquid derived products by use of a semi-empirical relationship between solubility parameter and refractive index:

$$\delta \cong \sqrt{C \frac{n^2 - 1}{n^2 + 1}}$$

Thermal treatment of Synthoil coal liquid oil + resin solvent fraction at 235-300 °C resulted in the transformation of oil and resin into asphaltene.

Further support of structural characterizations was obtained by use of a combined x-ray and NMR structural characterization procedure which relies on the important x-ray structural parameter L_a (average layer diameter of the aromatic sheet). L_a values of $\approx 8-10 \text{ \AA}$ for asphaltenes, $\approx 13.4-14 \text{ \AA}$ for carbenes, and $\approx 14-16.5 \text{ \AA}$ for carboids were obtained by the x-ray procedure. These data were used to calculate C_{Au} (aromatic carbons per structural unit) and N (number of structural units per molecule) values. For asphaltenes the results agree with those previously deduced from NMR and other techniques. The C_{Au} values are generally close to 14 which is the number of aromatic carbons present in a 3-ring kata-system such as anthracene or phenanthrene. The number of structural units per molecule is close to two for all the asphaltenes.

Additional data were used to improve the correlation equation between weight percent OH, determined by the silylation method, and the absorbance of the monomeric OH infrared stretching band at 3600 cm^{-1} for asphaltenes:

$$\text{Wt. \% OH} = 10.0 A_{OH} \text{ at } C = 25 \text{ g/l, and } l = 1.0 \text{ mm, in } \text{CDCl}_3.$$

A similar correlation between weight percent NH, from elemental analysis of asphaltene samples containing essentially all nitrogen as pyrrolic N-H, and the infrared absorbance of the N-H stretching band at 3470 cm^{-1} afforded the equation below for asphaltenes:

$$\text{Wt. \% NH} = 9.0 A_{NH} \text{ at } C = 25 \text{ g/l, } l = 1.0 \text{ mm, in } \text{CDCl}_3.$$

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.

These 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 United States.

The objective of Phase III 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 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 separations and interconversions.
- (2) Training of new technical personnel is continuing.
- (3) Establishment of sample data bank.
- (4) Chromatography of asphaltenes is being carried out.

(5-16) Characterization of coal liquid fractions by various physical and instrumental methods is continuing.

(17) Characterization of asphaltenes by densimetric methods.

(19) 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

Work Accomplished:

(a) Solvent Separation of Coal Liquids

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

(b) Solubility Parameters of Coal Liquid Fractions

In previous Quarterly Reports we discussed the rationale of using solubility parameters to more clearly define coal liquid fractions⁽¹⁾, and reported experimentally measured solubility spectra determined as a function of solubility parameters⁽²⁾. During the present Quarter we used a semi-empirical correlation between solubility parameters and refractive index values to calculate solubility parameter values. The correlation is:

$$\delta \cong \sqrt{C \frac{n^2 - 1}{n^2 + 1}} \quad (1)$$

where δ is solubility parameter, n is refractive index, and C is constant.

The constant, C , depends on the type of compound. An average value of C , obtained from 57 hydrocarbons⁽³⁾, of 305 was used in equation (1).

Fig. 1. Milestone Chart

The refractive indices of Synthoil coal liquid solvent fractions have been determined as a function of concentration in dilute solutions. THF and pyridine were used as solvents. The extrapolated values to 100% concentration and the average values are shown in Table I. The results show that the extrapolated refractive indices of Synthoil coal liquid solvent fractions, obtained from these two solvents, THF, and pyridine, are in close agreement. The % deviation is less than 1% in 3 cases.

Based on the average values, the solubility parameters of those fractions have been estimated from Eq. (1), and are shown in Tables I, II. The calculated solubility parameters of five asphaltenes and all Synthoil coal liquid solvent fractions are in very good agreement with the results of the solubility experiments in Reference (1). This suggests a very convenient method for quickly estimating δ values of coal-derived asphaltenes and solvent fractions. Next quarter the refractive index data of coal liquid solvent fractions from other processes will be obtained, and this correlation Eq. (1) will also be tested.

(c). Thermal Interconversion of Coal Liquid Fractions

When coal is liquefied, regardless of the process used, three major fractions are obtained: pentane-soluble, pentane-insoluble and benzene soluble, and benzene-insoluble and pyridine soluble (Fig. 2). The pentane soluble fraction is generally designated as "oil," and contains saturated and aromatic hydrocarbons plus nonpolar and polar nonhydrocarbons. The pentane-insoluble and benzene soluble fraction is called "asphaltene." The third fraction, benzene-insoluble and pyridine soluble has been variously designated as "carbene and carboid," (4, 5), "pre-asphaltene (6), and "asphaltol" (7). As illustrated in Fig. 2, the composition of coal liquids depends on coal type to be liquefied, the process utilized, and the conditions employed. The benzene insolubles can

Table I. Extrapclated Refractive Indices and Calculated Solubility Parameters* of Synthoil Coal Liquid Solvent Fractions

<u>Fraction</u>	<u>n</u>				<u>δ^*</u>	<u>δ^{**}</u>
	<u>THF</u>	<u>Pyridine</u>	<u>Av</u>	<u>% Dev.</u>		
Oil	1.5920	1.5521	1.5721	1.3	10.0	—
Resin	1.5856	1.6056	1.5956	0.6	10.2	—
Asphaltene	1.5361	1.6233	1.6297	0.4	10.4	9-12
Carbene	1.5352	1.5642	1.5497	0.9	9.9	10-12
Carboid	—	1.7536	—		11.2	10.62

*Calculated from Eq. (1).

**From solubility experiments in Ref. 1.

Table II. Calculated Solubility Parameters of Coal-Derived Asphaltenes from Refractive Index Data

	<u>n*</u>	<u>δ</u>
Synthoil Asphaltene	1.6668	10.7
HRI Asphaltene	1.6979	10.8
Cat. Inc.SEC Asphaltene	1.70C9	10.9
PAMCO SRC Asphaltene	1.7282	11.0
FMC-COED Asphaltene	1.6373**	10.5

* From Reference (2) .

**Extrapolated to 100% in THF.

Fig. 2. THREE MAJOR FRACTIONS OF COAL LIQUIDS

be converted into asphaltene during the course of liquefaction, hence the name of "pre-asphaltene". It is essential to study the generation and elimination of this fraction (Fig.3). The benzene-insolubles can be converted to asphaltene, and subsequently end in the oil fraction. Of course there is also a probability that the benzene insolubles may ultimately be changed irreversibly to coke. In order to study the above transformations as a function of temperature, pressure and time, an autoclave system equipped with injection loading and withdrawal systems for introducing and removing samples without disturbing the reaction under study is being constructed.

During the present Quarter preliminary interconversion studies on coal liquid fractions were carried out in glass systems. The Synthoil pentane-soluble fraction (oil + resin) was refluxed at atmospheric pressure, and under vacuum (0.4 mm Hg). The products were then distilled in order to concentrate any asphaltenes or benzene insoluble products produced by the thermal treatment. The residue was then separated by the standard solvent separation procedure (5).

The results in Table III show that when mixtures of oil and resin are heated, asphaltene is formed, and this formation is temperature dependent. However, whether this asphaltene is formed directly from resin, or from oil through resin is not yet clear. In future runs separate samples of oil and resin will be thermally treated to test this point. It is also planned to thermally treat asphaltenes and the benzene insoluble fraction.

Fig. 3. HYPOTHETICAL COAL LIQUID COMPOSITION AS A FUNCTION OF TIME (T,P=CONSTANT)

Table III. Analysis of Thermally Treated Synthoil Oil+Resin Fraction

<u>Thermal Treatment</u>	<u>Wt.% Recovery</u>	<u>-----Wt.% Normalized-----</u>		<u>-----Wt.% Distribution of Residue-----</u>			
		<u>% Distillate^a</u>	<u>% Residue</u>	<u>Oil</u>	<u>Resin</u>	<u>Asphaltene</u>	<u>Benzene Insoluble</u>
None	—	—	—	73	27	0	0
235 ^o	97	78 (-235 ^o C/0.4mmHg)	22 (+235 ^o C)	5.5	78.8	15.7	0
300 ^o	96	41 (-300 ^o C/1 Atm)	59 (+300 ^o C)	46.7	47.6	5.7	0

^aDistillation carried out with 5 plate perforated bubble plate Oldershaw column.

(2). Characterization of Coal Liquids by Physical Methods

Work Accomplished:

(a). Infrared

We previously reported the infrared spectrum, and band assignments for a typical coal-derived asphaltene taken as a KBr mull. The OH and NH absorption region from $3400\text{--}3600\text{ cm}^{-1}$ is generally obscured in KBr mulls by the presence of a large water contamination band which is difficult to eliminate. Because of the utility of infrared spectroscopy for analyzing the concentrations of OH and NH in asphaltene fractions we present the typical spectra of an asphaltene, Synthoil, and the silica gel chromatography fractions obtained from this material in the OH and NH regions (Fig. 4).

The assignments of the various peaks are shown in Table IV. The large 3600 cm^{-1} peak is assigned to monomeric phenolic OH. The small 3540 cm^{-1} peak has not been unequivocally assigned as yet. Workers at PERC (8) report that this band was not completely removed from the infrared spectrum of the TMS derivative of a Synthoil acid/neutral asphaltene fraction although the free phenolic OH stretching band at 3600 cm^{-1} was completely removed on silylation. They suggest, therefore, that this band belongs to an independent species, and may be due to carboxylic acid structures. We, on the other hand, have observed the essentially complete loss of this band on silylation of many asphaltenes (Fig. 5), which suggests that this band could be from an intramolecular associated phenolic OH. Others have assigned this band to an intramolecular associated phenolic OH (plus weaker carboxylic

^a The CDCl_3 spectra contain, in addition to asphaltene OH and NH bands, two water bands at 3690 and 3600 cm^{-1} from adventitious water contamination of the CDCl_3 . Because the 3600 cm^{-1} H_2O band appears at the same position as the asphaltene monomeric OH band it must be subtracted from the asphaltene OH band. Since the absorbance ratio of the 3600 cm^{-1} band to the 3690 cm^{-1} band is 0.32 , this factor is used to correct for H_2O absorbance when quantitative measurements are carried out.

FIG. 4. IR SPECTRA OF SYNTHOIL ASPHALTENE AND SILICA GEL CHROMATOGRAPHY FRACTIONS IN THE OH AND NH REGION

Table IV. Assignment of IR Bands for Asphaltene Spectra in CDCl_3 in the OH and NH Region

<u>Wavenumber, cm^{-1}</u>	<u>Assignment</u>
3690	Water
3600	Water
3600	Free phenolic OH
3540	Associated phenolic OH
3470	Pyrrolic NH
3400	Other NH, possibly amines and/or amides
3400-3200 (broad)	H-bonded OH

FIGURE 5 . PARTIAL IR SPECTRA OF SYNTHOIL ASPHALTENE AND TMS DERIVATIVE

acid OH) (9). We plan to investigate this band as a function of substrate concentration to see whether it belongs to an intramolecular band which will be unaffected by dilution.

The medium size 3470 cm^{-1} band is assigned to pyrrolic N-H, and is seen to be largest in the benzene eluted fraction. The fourth small band at 3400 cm^{-1} may be assigned to other NH bands (amines and/or amides), and generally increases in the order: benzene eluted < Et_2O eluted < THF eluted. Finally, the band absorption between $3200\text{--}3400\text{ cm}^{-1}$ is generally assigned to hydrogen bonded OH absorption bands. In the case of asphaltenes such bands are generally assumed to be related to the hydrogen-bonded complexes of acid/neutral and basic components. Such absorption is seen to be minimal (Fig. 4) for the benzene eluted fraction which has been chromatographically separated from any basic components.

(b). VPO Investigation of Coal Liquid Molecular Weight

The VPO molecular weights of coal-derived resins and carbenes vs. concentration in THF have been determined and are shown in Table V . The results show that association of resins takes place in THF over the concentration range of 4-30 g/l, whereas that of carbene takes place in THF over the concentration range of 9-32 g/l. Within these two concentration ranges all of the resins and carbenes afford positive linear correlations of molecular weight, and most of the correlation coefficients are reasonably significant. Generally, the slopes of the linear correlation lines of asphaltenes are greater than those of resins, but smaller than those of carbenes. This does not hold for the FMC-COED process, and experiments need to be repeated. Despite this exception, it is clear that the molecular weights of carbenes are generally higher than those of asphaltenes, whereas the molecular weights of resins are lower. Also, the results show that the self-association of carbenes is stronger than that of asphaltene, while the self-association of resin is weaker.

Table V . Molecular Weight of Coal Liquid Products vs. Concentrations^a in THF

		Least Squares Equation	Cor. Coeff.	MW at Infinite Dilution
Synthoil	Resin	MW = $0.86 \pm 0.30 C + 252 \pm 5.1$	0.82	252
	Asphaltene ^b	MW = $2.85 \pm 0.96 C + 568 \pm 17.5$	0.83	
		MW = $2.42 \pm 0.10 C + 562 \pm 2.2$	0.99	567 ^c
	Carbene	MW = $5.97 \pm 0.28 C + 861 \pm 6.5$	0.989	861
HRI	Resin	MW = $0.77 \pm 0.57 C + 252 \pm 5.1$	0.61	252
	Asphaltene	MW = $3.02 \pm 0.36 C + 471 \pm 6.0$	0.95	502 ^c
	Carbene	MW = $16.84 \pm 5.48 C + 1260 \pm 112.9$	0.74	1260
FMC-COED	Resin	MW = $2.43 \pm 0.43 C + 224 \pm 7.7$	0.82	224
	Asphaltene	MW = $0.56 \pm 0.10 C + 382 \pm 4.5$	0.89	370 ^c
	Carbene	MW = $1.30 \pm 0.15 C + 326 \pm 3.0$	0.93	326
Cat. Inc. SRC	Resin	MW = $0.53 \pm 0.18 C + 326 \pm 3.1$	0.60	326
	Asphaltene ^b	MW = $1.11 \pm 0.38 C + 486 \pm 7.6$	0.77	
		MW = $2.25 \pm 0.27 C + 502 \pm 4.5$	0.95	477 ^c
	Carbene	MW = $4.08 \pm 0.47 C + 1228 \pm 9.1$	0.97	1227
PAMCO SRC	Resin	MW = $1.22 \pm 0.39 C + 320 \pm 6.1$	0.58	320
	Asphaltene	MW = $1.83 \pm 0.16 C + 502 \pm 3.3$	0.96	545 ^c
	Carbene	MW = $4.83 \pm 1.67 C + 1051 \pm 38.4$	0.69	1051

^a Conc., g/l.

^b Results from two samples prepared independently.

^c Ave. MW at zero concentration in three different solvents, Benzene, Chloroform and THF.

^d Vacuum distillation residue.

(c). Proton NMR

Previously we reported average molar properties of asphaltenes (10), oils, resins and carboids (11), and asphaltene chromatography fractions (12). We now wish to report average molar properties of the carbene solvent fractions (benzene insoluble and carbon disulfide soluble), which were obtained by use of modified brown-Ladner structural parameter equations (10,13). The results (Table VI) are consistent with the previously discussed trends. Number average molecular weight values, obtained by extrapolating to infinite dilution in THF, are higher than those reported for asphaltenes, and about the same order of magnitude as the less precise values obtained earlier for incompletely soluble carboids in DMF. (Carboid molecular weight determination will be carried out in pyridine in the future.) The f_a values (fraction of carbons which are aromatic) range from 0.74 to 0.82 which falls between the ranges calculated for asphaltenes (0.67-0.81) and those calculated for carboids (0.76-0.84). The Haru/Car values (ratio of substitutable edge atoms to total aromatic atoms) also fall generally between the values calculated for asphaltenes and carboids. The values generally range from 0.60 to 0.69 which is consistent with average aromatic kata-condensed ring systems of 4-6 aromatic rings, with 31-36 percent of the available aromatic edge atoms occupied by substituents (σ values), and joined together by naphthenic, methylenic or etheric bridges. The FMC-COED carbene fraction appears to deviate from the others in that it has a relatively low molecular weight (326) and a relatively high Haru/Car value of 0.87, which suggests an average aromatic ring system of 1-2 aromatic rings. However, the FMC-COED process is a staged pyrolysis process which affords ≈ 60 percent char. The coal liquid represents only that portion of the

Table VI Average Molar Properties of Carbenes^a

	— FMC-COED —					— Synthoil —					— Catalytic Inc. SRC —					— HRI H-Coal —					— PANCO SRC —				
Molecular Formula	C _{22.03}	H _{19.46}	N _{0.39}	O _{2.00}	S _{0.13}	C _{62.44}	H _{51.88}	N _{1.32}	O _{1.85}	S _{0.34}	C _{91.80}	H _{61.28}	N _{0.98}	O _{2.93}	S _{0.10}	C _{91.47}	H _{63.08}	N _{1.74}	O _{3.85}	S _{0.37}	C _{75.32}	H _{59.42}	N _{1.64}	O _{2.41}	S _{0.69}
Molecular Weight	326					861					1228					1260					1051				
H _{ar}	42					40					51					47					45				
H _a	42					37					28					36					37				
H _o	16					23					21					17					18				
f _a	0.74					0.75					0.78					0.82					0.78				
H _{aru} /Car	0.87					0.69					0.64					0.60					0.68				
σ	0.43					0.36					0.31					0.34					0.33				
R _s	6.1					11.5					14.4					15.2					13.4				
n	1.4					1.6					1.8					1.5					1.5				
C _A	16.4					46.9					71.8					74.8					59.0				
R _J	2.1					8.3					14.1					16.0					10.4				

^a Brown-Ladner Method $x = y = 2$

^b VPO in THF Extrapolated to Infinite Dilution.

product which is volatile enough to be vaporized, condensed and filtered. Therefore higher molecular weight, more aromatic coal constituents are probably lost to char formation, and the resulting coal liquefaction fractions would be expected to have relatively lower molecular weights and aromaticities.

(d). X-Ray and NMR Structural Characterization

In previous reports (10 , 13) we have described the modified Brown-Ladner NMR structural parameter calculations, which we utilized to calculate average molar properties of coal liquid derived fractions. We have also described in detail the X-ray procedure for obtaining crystallite parameter data (14,15). During the present Quarter we completed the X-ray crystallite parameter determinations on our complete set of asphaltenes, carbenes and carboids.

One of the most critical structural parameters is the average layer diameter of the sheets (L_a). The most reliable procedure for evaluating L_a is a procedure developed by Yen and coworkers (16) which makes use of Diamond's computed intensities of X-rays diffracted from randomly oriented perfect aromatic molecules of varying sizes using the Debye radial distribution function (17). Yen and coworkers tested their procedure on both the (10) and (11)-bands with a model blend, and found that the-(11) band afforded better agreement. Therefore, we have reported L_a values based on the width at half maximum of the (11)-band calculated from Diamond's curve (Table VII).

Although L_a is generally considered to be the diameter of the aromatic sheet, this may only be strictly correct for perfect aromatic molecules. For such systems, which are kata-condensed, L_a is related to the number of aromatic carbons per structural unit (C_{Au}) by the equation (18):

Table VII. Structural Parameters Calculated From X-Ray and NMR Data

<u>Asphaltenes</u>	L_a ¹	$C_A = C_T f_a$ ²	$C_\alpha = H_\alpha^* H/2$ ³	$C_{Au} = (L_a + 1.23)/(0.615 + C_\alpha/C_A)$ ⁴	$N = C_A/C_{Au}$ ⁵
Synthoil	10.3	29.07	7.38	13.27	2.2
HRI H-Coal	8.2	27.76	5.20	11.75	2.4
FMC-COED	8.0	18.76	4.81	10.59	1.8
PAMCO	10.0	27.66	5.71	13.67	2.0
Cat. Inc.	9.4	28.16	5.08	13.36	2.1
<u>Carbenes</u>					
Synthoil	13.5	46.83	9.60	17.96	2.61
HRI H-Coal	14.0	75.00	11.35	19.87	3.77
FMC-COED	10.0	16.30	4.09	12.97	1.26
PAMCO	13.4	58.75	10.99	18.24	3.22
Cat. Inc.	14.0	71.60	8.58	20.73	3.45
<u>Carboids</u>					
Synthoil	14.5	55.23	9.34	20.06	2.75
HRI H-Coal	16.5	61.76	7.68	23.98	2.58
FMC-COED	11.0	19.58	4.34	14.62	1.34
PAMCO	14.0	34.98	4.54	20.45	1.71
Cat. Inc.	15.0	62.54	8.20	21.75	2.87

¹ L_a = X-Ray Diameter of the aromatic sheet + α carbons of side chains, Å, from Diamond's Curve (11) band.

² C_A = Aromatic carbon, C_T = Total carbon, f_a = fractions of carbon which is aromatic from Brown-Ladner ¹H NMR analysis.

³ C_α = Carbons α to aromatic rings, H_α^* = fraction of protons on carbons α to aromatic rings, H = total hydrogen.

⁴ C_{Au} = Aromatic carbons per structural unit. ⁵ N = Number of structural units per molecule.

$$C_{Au} = (L_a + 1.23) / 0.615 \quad (1)$$

However, the aromatic systems in coal liquid fractions may contain some heteroatoms in place of carbons, and contain some rings which may be partially or completely saturated (19). In addition, the dimensions of the sheet may be considered to include α carbons of side chains which are also restricted to the plane of the sheet. In order to correct equation (1) for the latter effect it is necessary to increase the denominator by the factor C_α/C_A , where C_α represents the carbons α to the aromatic rings, and C_A equals the total number of aromatic carbons:

$$C_{Au} = (L_a + 1.23) / (0.615 + C_\alpha/C_A) \quad (2)$$

The structural parameter C_{Au} may be divided into the total number of aromatic carbons per molecule, C_A , to obtain the number of structural units per molecule (N). The results of such calculations are presented in Table VII. For asphaltenes the results agree with those previously deduced from NMR and other techniques. The C_{Au} values are generally close to 14 which is the number of aromatic carbons present in a 3-ring kata system such as anthracene or phenanthrene. The number of structural units per molecule is close to two for all the asphaltenes. Carbene C_{Au} values, with the exception of FMC-COED, range from 18 to 21 aromatic carbons per molecule which represents around 4-5 kata condensed rings per aromatic system. The carbenes generally have from 2.6 to 3.8 of these structural units per molecule. Carboids generally have the largest C_{Au} values which range from 20 to 24 aromatic carbons per structural unit. This represents around 4.5-5.5 kata condensed rings. The N values generally range from 1.7 to 2.9 structural units per molecule. (However, these values depend on C_A values which were obtained from VPO molecular weight values measured at finite concentrations in the solvent DMF. We intend to obtain more reliable

carboid molecular weights by the technique of extrapolating MW values to infinite dilution in the solvent pyridine.)

In the future we intend to determine X-ray crystallite parameter data for resins and oils, and to calculate additional structural parameters.

(e) Electron Spin Resonance

Previously we discussed the experimental procedures for obtaining ESR data (20), and reported g-value, intensity, and line width data for coal liquid solvent fractions and asphaltene-derived products (1,2). We have now measured the ESR spectrum of the Synthoil carboid fraction at high microwave power (40 mw), and high modulation amplitude in order to see if signals corresponding to paramagnetic metal-containing species are detectable. The sample contained $\approx 9\%$ ash. The semiquantitative metal analysis was reported previously (5). Iron (≈ 400 ppm) and titanium (≈ 100 ppm) were the major transition metals present. The ESR spectrum (Fig. 6) shows, in addition to the usual major asphaltic signal at $g=2.00$, a small peak around $g=2.05$ and a dip around $g=2.08$. A background sample of weak pitch, run under the same conditions, is also shown. No signals other than the $g=2.00$ signal are observed in the background which means that the signals cannot be attributed to cavity contamination. It is known that transition metals afford g-values higher than 2.00. Baggaley (21) has reported a ferromagnetic resonance centered at $g=2.06 \pm 0.02$ for a colloidal suspension of pure metallic iron particles. Also low spin complexes of cobalt (II) and nickel (II) are found with isotropic g-factors in the range of $g=2.08$. Although the high g-value of the ESR line suggests metal origin, such an explanation must be considered tentative at this time.

It is also interesting that the $g=2.00$ line shows no microwave saturation up to a microwave power of 60 mw at room temperature. Such fast spin relaxation can be caused by association with metal species. However, further study will be needed to confirm this possibility.

FIG. 6. ESR SPECTRUM OF SYNTHOIL CARBOND

(f). Densimetric Methods of Structural Analysis

Densimetric methods of structural analysis have been widely used for determining the average structural character of molecules in a complex mixture. Using refractive index, density, and elementary analysis van Krevelen and coworkers (22) developed methods for studying the structure of coal. Van Nes and van Westen (23) continued work in this area, and developed the n-d-M method primarily for petroleum oils. Yen and coworkers discussed densimetric methods of ring analysis for petroleum asphaltenes and related bitumens (24, 25). In the last Quarter we began determining the refractive indices and densities of coal-derived asphaltenes, and other coal liquid solvent fractions in order to obtain these generally useful parameters, and also to utilize them in structural analyses and in other applications. In Section 1(b) of this report we discuss the utilization of refractive index values for calculating solubility parameter data. In this section we shall discuss the use of such parameters in structural analysis calculations.

During the present Quarter we tested the reliability of the n-d-M method for evaluating coal-derived asphaltenes and other coal liquid solvent fractions. The n-d-M method was developed to handle olefin-free petroleum portions boiling above the gasoline range. For such light liquid materials refractive index and density values may be obtained to a high degree of accuracy ($\pm 0.01\%$). However, coal-derived asphaltenes, and many of the other coal liquid solvent fractions are dark solids. Therefore, an extrapolation method is required to obtain refractive index values, and a helium displacement method is required to obtain powder densities. These methods are less accurate than the direct methods which can be utilized with clear liquids. The best percent deviations obtained to date for our extrapolated refractive index, and helium displacement powder density

values are about ± 1 percent. Because this precision is so much lower than that obtainable for clear liquids ($\pm 0.01\%$), we decided to check the reliability of the n-d-M method (23) by making calculations of the percent deviation of the carbon distribution and ring content as a function of the percent deviation of the variables: n (refractive index), d (powder density), M (molecular weight), S (% sulfur). The results, shown in Table VIII, indicate that the refractive index value is the most critical variable. A ± 1 percent deviation in n affords deviations in carbon distribution and ring content ranging from 41 to 94 percent. The value of d used is also significant. A ± 1 percent deviation in d results in deviations ranging from 10 to 38 percent in the calculated structural parameters. Molecular weight and percent sulfur are not very significant variables. These calculations suggest that the n-d-M formulas will not be applicable to coal liquid products as they are too sensitive to deviations in the refractive index, and density values.

Another useful densimetric structural parameter for aromatic systems is the compactness, F/C_A , which is defined as the ratio of the number of fused carbon atoms, (carbon atoms common to three rings) to the total aromatic carbon atoms (25). The F/C_A calculation was made by the method of Yen and Dickie:

$$F/C_A = 4(C/R)^{-1} f_a^{-1} + 2C_A^{-1} - 1$$

where f_a is the aromaticity; C/R is the reciprocal of the ring condensation index and is expressed as:

$$C/R = V_R / (\sum_i n_i V_i / C - V_M / C)$$

where V_R is the molar contraction per ring and is assumed to be 9.2. The molar volume per carbon atom, V_M/C , is calculated from helium density and percent carbon. The atomic volume sums, $\sum_i n_i V_i$, are calculated from the various atomic

Table VIII. Percentage Deviation of Carbon Distribution and Ring Content Calculated from Structural Calculation Formulas Used in the n-d-M Method^a

Variable	Percent Deviation			
	+1%	+3%	-1%	-3%
n				
C _A %	41.6	124.7	-41.5	-141.2
C _N %	-94.4	-283.3	94.4	303.8
C _P %	52.8	158.4	-52.8	-158.4
R _A	42.3	126.8	-42.3	-149.1
R _N	-69.6	-208.8	69.6	225.7
d				
C _A %	-10.7	-32.1	10.7	32.1
C _N %	38.3	115.0	-38.3	-115.0
C _P %	-30.7	-92.1	30.7	92.0
R _A	-10.9	-32.7	+10.9	32.7
R _N	30.1	90.3	-30.1	-90.3
M				
C _A %	-0.2	-0.7	0.2	0.7
C _N %	-0.5	-1.6	0.5	1.6
C _P %	1.0	2.9	-1.0	-3.0
R _A	0.8	2.3	-0.8	-2.3
R _N	0.6	1.9	-0.6	-1.9
S				
C _A %	0	0	0	0
C _N %	-0.02	-0.05	0.018	0.05
C _P %	-0.1	-1.0	-0.02	-0.07
R _A	0	0	0	0
R _N	-0.02	-0.06	0.02	0.06

^aNorth Borneo heavy cyclic oil Fraction VI (23).

n = 1.5670, d = 1.0105, M = 384.0, S% = 0.20, C_A% = 40.37, C_N% = 32.78, C_P% = 26.86, R_A = 1.96, R_N = 2.59.

ratios as follows:

$$\frac{\sum_i n_i V_i}{C} = 9.9 + 3.1 \text{ H/C} + 1.5 \text{ N/C} + 14 \text{ S/C} + 3.75 \text{ O/C}$$

An F/C_A value close to 0 indicates a kata-condensed aromatic system. A value close to 1 indicates a peri-condensed aromatic system, whereas a negative value (approaching ≈ -0.33) indicates that the system is either a "linked" molecule such as polyphenylene or a "hole" molecule such as annulene. The results of the evaluation of F/C_A for coal-derived asphaltenes are listed in Table IX. It may be seen that practically all of the F/C_A values are very close to zero. This supports the generally accepted hypothesis that coal-derived asphaltenes have kata-condensed aromatic ring systems.

In the future we shall continue to try and improve the precision of the refractive index, and helium displacement density measurement procedures. We shall also extend these measurements to other coal liquid fractions, and test other densimetric structural calculation procedures.

Table IX. Ring Compactness of Coal-Derived Asphaltenes

<u>Process</u>	<u>d^a</u>	<u>$\sum_i n_i V_i / C$</u>	<u>V_M / C</u>	<u>C/R</u>	<u>f_a^b</u>	<u>C_A</u>	<u>F/C_A</u>
Synthoil	1.202	12.84	11.44	6.57	0.71	30.8	-0.08
HRI	1.266	12.63	10.96	5.51	0.78	25.9	0.01
Cat. Inc.	1.261	12.39	10.72	5.51	0.81	29.7	-0.04
PAMCO	1.203	12.67	11.47	7.67	0.76	27.9	-0.24
FMC	1.243	13.24	11.75	6.17	0.67	20.9	0.06

^a Powder densities, measured by helium displacement method.

^b f_a - calculated from NMR by Brown-Ladner method.

(3) 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) Hydroxyl Group Determination by Silylation

In previous Quarterly Reports (1, 2, 10-12) we described the procedure and results for the silylation of asphaltenes and other coal liquid derived products. During the present quarter we repeated many of the silylations of asphaltenes in order to improve the accuracy of the analyses. The results are presented in Table X.

In principle, the chemical shifts of TMS-derivatives could be used to determine the hydroxyl composition of asphaltenes. However, it has been reported that alcoholic and hindered phenolic derivatives have overlapping bands in the 0-0.2 ppm region (26). Simple phenols have been reported to absorb in the 0.18-0.4 ppm region. All of our asphaltene samples except the Synthoil THF eluted fraction show large absorptions in the chemical shift region from 0.22-0.28 ppm, and small absorptions at 0.11-0.13 ppm, and 0.06-0.07 ppm (see Fig. 15, Ref. 2). This suggests that the major hydroxyl components are simple phenolics, and that the minor components are benzylic, alcoholic, or hindered phenolic compounds.

The correlation between weight percent OH determined by the silylation method, and the absorbance of the monomeric OH infrared stretching bands at 3590 cm^{-1} was replotted (Fig. 7). The new correlation line at $C = 25\text{ g/l}$ and $l = 1.0\text{ mm}$ in CDCl_3 is:

$$\text{wt. \% OH} = 10.0 A_{\text{OH}}$$

Table X. NMR Analysis of Silylated Asphaltenes and Synthoil Silica Gel Chromatography Fractions

<u>Asphaltene</u>	<u>Wt.%O^a</u>	<u>At.OH/O_{total}</u>	<u>Wt.%OH^b</u>	<u>δ^c</u>
Synthoil	3.43	0.64 $\pm$ 0.01	2.67 $\pm$ 0.04	(0.26, 0.22)lg., 0.12 sm., (0.09, 0.07)sm.
HRI H-Coal	4.94	0.56 $\pm$ 0.03	2.92 $\pm$ 0.14	0.28 lg., 0.13 sm., 0.08 sm.
PAMCO SRC	4.67	0.60 $\pm$ 0.01	2.96 $\pm$ 0.03	0.27 lg., 0.13 sm., 0.07 sm.
Cat. Inc. SRC	4.58	0.75 $\pm$ 0.01	3.65 $\pm$ 0.05	0.28 lg., 0.12 sm., 0.09 sm.
FMC-COED	7.11	0.78 $\pm$ 0.01	5.88 $\pm$ 0.06	0.27 lg., 0.13 sm., 0.07 sm.
Synthoil Benzene Eluted	2.39	0.63 $\pm$ 0.04	1.61 $\pm$ 0.07	0.28 lg., 0.11 sm., 0.07 sm.
Synthoil Et ₂ O Eluted	5.40	0.72 $\pm$ 0.02	4.11 $\pm$ 0.09	(0.27, 0.22)lg., 0.13 sm., 0.06 sm.
Synthoil THF Eluted	5.97	0.16 $\pm$ 0.02	1.19 $\pm$ 0.11	— 0.13 lg., 0.07 sm.

^aBy difference, from ultimate analysis.

^bFrom analysis of trimethylsilylated asphaltene TMS area.

^c δ = Chemical shift from tetramethylsilane, δ = 0.

FIG. 7. CORRELATION OF ASPHALTENE OH ABSORBANCE FROM IR VS. WT.% OH FROM NMR ANALYSIS OF SILYLATED ASPHALTENES

The plot affords a reasonably linear correlation despite the fact that all the asphaltenes are not completely dissociated at 25 g/l concentration in CDCl_3 . This type of correlation should be useful as a simple means of obtaining the %OH of asphaltenes and other types of coal liquefaction products.

During the next Quarter we intend to repeat the infrared measurements on selective samples in a large path cell (1 cm) in order to obtain absorptivity data in more dilute solution where any hydrogen bonding should be insignificant.

(b) Methylation of Basic Nitrogen Groups

In previous Quarterly Reports we described the procedure for methylation of basic nitrogen containing asphaltenes (11), and reported methylation results (1,12,20). During the present Quarter we carried out methylation reactions on the complete set of benzene eluted silica gel chromatography fractions. This fraction affords little or no benzene insoluble materials on methylation. The observed weight percentages of benzene insoluble materials are:

Synthoil-0, FMC-COED-0, PAMCO-3, Catalytic Inc.-7, HRI-10.

The benzene soluble methylation product from the Synthoil process has been analyzed, and less than 0.3% iodine was found. (The analyses for the other products are pending.) This supports the premise that almost no methyl iodide has been added to this chromatography fraction, and that therefore such fractions do not contain a significant amount of basic nitrogen containing asphaltene. If the non-basic nitrogen is largely pyrrolic nitrogen, as is suggested by infrared analysis (Fig. 4), then it should be possible to estimate the concentration of non-basic pyrrolic nitrogen by analysis of the pyrrolic N-H stretch at 3470 cm^{-1} . A correlation between weight percent NH from elemental analysis (assuming all nitrogen present as pyrrolic N-H), and the infrared absorbance of the 3470 cm^{-1} peak is shown in Fig. 8. This preliminary correlation seems satisfactory, and is expected to be improved when the nitrogen analysis of the benzene

Fig. 8. Correlation of Asphaltene N-H Absorbance vs. Wt.% N-H of Benzene Eluted Silica Gel Chromatography Fractions

soluble methylation products are used. This N-H correlation curve may be used to estimate the weight percent N-H in the starting Synthoil asphaltene, and the other two chromatography fractions. Starting Synthoil asphaltene is calculated to have ≈ 0.8 weight percent N-H, and the diethyl ether and THF eluted fractions ≈ 0.5 and ≈ 0.4 weight percent N-H, respectively. The fraction of nitrogen present as NH may be calculated for the unseparated asphaltenes from all five demonstration processes by this method. Such calculations will be made in the next Quarter when we obtain a large enough path cell to run infrared spectra in highly dilute solution.

This method for estimating pyrrolic nitrogen may be superior to the method in which low molecular weight model pyrrolic compounds are used to obtain molar absorptivity values. Snyder (27) has shown that such molar absorptivity values show a decrease with increasing molecular weight for carbazoles from petroleum.

Conclusion

Solubility parameters may be calculated for coal liquid derived products by use of a semi-empirical relationship between solubility parameter and refractive index:

$$\delta \cong \sqrt{C \frac{n^2 - 1}{n^2 + 1}} \quad (1)$$

The calculated solubility parameters for coal liquid solvent fractions are in good agreement with those values determined experimentally.

Thermal treatment of a Synthoil coal liquid oil + resin solvent fraction at 235-300 °C resulted in the transformation of oil and resin into asphaltene. This supports the proposal reversibility of asphaltene transformation into oil + resin:

VPO molecular weight studies of coal liquid derived resins, asphaltenes and carbenes indicate that both molecular weights and self-association increase in the order:

Modified Brown-Ladner ¹H NMR analyses of the carbene coal liquid solvent fraction show that f_a values (fraction of carbon which is aromatic) range from 0.74 to 0.82 which falls between the ranges calculated for asphaltenes (0.67-0.81) and those calculated for carboids (0.76-0.84). The Haru/Car values (ratio of substitutable edge atoms to total aromatic atoms) also fall generally between the values calculated for asphaltenes and carboids. The values generally range from 0.60 to 0.69 which is consistent with average aromatic kata condensed ring systems of 4-6 aromatic rings, with 31-36 percent of the available aromatic edge atoms occupied by substituents (σ values), and joined together by naphthenic, methylenic or etheric bridges. These NMR

structural parameters are supported by densimetric structural parameter calculations which afforded compactness values (F/C_A) close to zero for asphaltenes. Such values are indicative of kata-condensed aromatic systems. Additional support of structural characterizations was obtained by use of a combined x-ray and NMR structural characterization procedure which relies on the important x-ray structural parameter L_a (average layer diameter of the aromatic sheet). L_a values of $\approx 8-10 \text{ \AA}$ for asphaltenes, $\approx 13.4-14 \text{ \AA}$ for carbenes, and $\approx 14-16.5 \text{ \AA}$ for carboids were obtained by the x-ray procedure. These data were used to calculate C_{Au} (aromatic carbons per structural unit) and N (number of structural units per molecule) values. For asphaltenes the results agree with those previously deduced from NMR and other techniques. The C_{Au} values are generally close to 14 which is the number of aromatic carbons present in a 3-ring kata system such as anthracene or phenanthrene. The number of structural units per molecule is close to two for all the asphaltenes. Carbene C_{Au} values, with the exception of FMC-COED, range from 18 to 21 aromatic carbons per molecule which represents around 4-5 kata-condensed rings per aromatic system. The carbenes generally have from 2.6 to 3.8 of these structural units per molecule. Carboids generally have the largest C_{Au} values which range from 20 to 24 aromatic carbons per structural unit. This represents around 4.5-5.5 kata-condensed rings. The carboid N values generally range from 1.7 to 2.9 structural units per molecule. (However, these N values, which depend on C_A values obtained from VPO molecular weight values measured at finite concentrations in the solvent DMF may be low, and will be recalculated in the future using VPO MW values obtained in the solvent pyridine).

Electron spin resonance measurements were made on the Synthoil carboid fraction at high microwave power (40 MW) and high modulation amplitudes. The ESR spectrum shows, in addition to the usual major asphaltic signal at $g = 2.00$,

a small peak around $g = 2.05$ and a dip around $g = 2.08$ which may be indicative of metals present in the sample.

Additional data were used to improve the correlation equation between weight percent OH, determined by the silylation method, and the absorbance of the monomeric OH infrared stretching band at 3600 cm^{-1} , $\text{wt. \% OH} = 10.0 A_{\text{OH}}$ at $C = 25 \text{ g/l}$, and $l = 1.0 \text{ mm}$, in CDCl_3 .

A similar correlation between weight percent NH, from elemental analysis of asphaltene samples containing essentially all nitrogen as pyrrolic N-H, and the infrared absorbance of the N-H stretching band at 3470 cm^{-1} afforded the equation,

$$\text{wt. \% NH} = 9.0 A_{\text{NH}} \text{ at } C = 25 \text{ g/l}$$

and $l = 1.0 \text{ mm}$, in CDCl_3 . The fraction of nitrogen present as pyrrolic NH may be calculated for asphaltenes containing both basic and pyrrolic nitrogen by use of the above equation and infrared A_{NH} measurements.

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