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CHEMISTRY AND STRUCTURE OF COAL DERIVED ASPHALTENES AND
PREASPHALTENES

Interim Report

By
T. F. Yen

MASTER

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

University of Southern California
University Park
Los Angeles, California

U. S. DEPARTMENT OF ENERGY

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CHEMISTRY AND STRUCTURE OF COAL DERIVED ASPHALTENES AND PREASPHALTENES

Interim Report

University of Southern California

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OBJECTIVE AND SCOPE OF WORK

It is the objective of this project to isolate the asphaltene and preasphaltene fractions from coal liquids from a number of liquefaction processes. These processes consist of in general: catalytic hydrogenation, staged pyrolysis and solvent refining. 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 and preasphaltene 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 asphaltenes in liquefaction processes will enable engineers to both improve existing processes, and to make recommendations for operational changes in planned liquefaction units in the United States.

The objective of Phase 1 was to complete the isolation and separation of coal liquid fractions and to initiate their characterization.

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

The objective of Phase 3 is to concentrate on the characterization of the preasphaltene (benzene insoluble fraction) of coal liquid fraction by the available physical and chemical methods to obtain a number of structural parameters.

TABLE OF CONTENTS

	<u>Page</u>
OBJECTIVE AND SCOPE OF WORK	
DETAILED DESCRIPTION OF TECHNICAL PROGRESS	
I. DESCRIPTION OF COAL LIQUIDS	1
II. SOLVENT FRACTIONATION OF COAL LIQUIDS	5
1. General Solvent Fractionation Scheme	5
2. Solvent Separation of Carbene and Carboid	5
3. Comparison of Solvent Fractionation Procedure with Separation by High Pressure Liquid Chromatography	6
III. CHROMATOGRAPHIC FRACTIONATION OF ASPHALTENES	12
A. Solvent Elution Chromatography (SEC)	12
B. Gel Permeation Chromatography (GPC)	23
1. Analytical Scale (GPC)	23
2. Preparative Scale (GPC)	23
3. GPC of SEC Fractions	24
IV. CHARACTERIZATION OF COAL LIQUID FRACTIONS BY ANALYTICAL, PHYSICAL, AND CHEMICAL METHODS	30
A. Elemental Analyses	30
B. Semiquantitative Metal Analysis	36
C. Molecular Weights and Association	38
1. Vapor Pressure Osmometry	38
a. Coal Liquid Solvent Fractions	38
b. Coal-Derived Asphaltenes	38
c. Silica Gel Separated Asphaltenes	39

TABLE OF CONTENTS (cont.)

d. Miscellaneous Asphaltene Products	39
e. Synthoil GPC Fractions	39
f. Mixtures of Asphaltenes and Resins	39
2. Gel Permeation Chromatography	40
D. X-Ray Diffraction	52
E. Nuclear Magnetic Resonance	72
1. Proton Nuclear Magnetic Resonance	72
2. Carbon-13 Nuclear Magnetic Resonance	74
F. X-Ray-NMR Analysis	88
G. Infrared Spectroscopy	93
H. Polarography	106
I. Thermogravimetric Analysis	114
J. Electron Spin Resonance	119
K. Ultraviolet-Visible Spectroscopy	129
L. Mass Spectroscopy	133
M. Donor-Acceptor Complexes	138
N. Oxidation	151
O. Self-Association	161
P. Densimetric Methods	173
1. Refractive Index	173
2. n-d-M Method	173
3. Compactness	174
4. Correlation of Solubility Parameters	175
5. Structural Correlations	176
Q. Solubility Parameters	196
R. Transmittance Electron Microscopy	217
1. Image Processing	217

TABLE OF CONTENTS (cont.)

2. Metal Shadowing Technique	218
S. Mesophase Formation	227
T. Transformation Curve	238
U. Thermal Interconversion	243

I. DESCRIPTION OF COAL LIQUID SAMPLES

Representative coal liquefaction samples were obtained from the following sources:

1. Pittsburgh Energy Research Center -- Synthoil Process (1).
2. Hydrocarbon Research Inc. ----- H-Coal Process (2).
3. FMC Corp. ----- COED Process (3).
4. PAMCO, Fort Lewis, Wash. ----- Solvent Refined Coal Process (4).
5. Catalytic Inc., Wilsonville, Ala. -- Solvent Refined Coal Process (5).

The analyses of the coals, and the coal liquid samples are given in Tables I-I and I-II, respectively, along with a history of the samples.

Table I-I. Data on Coal Used for Producing Coal Liquids

	<u>Synthoil</u>	<u>HRI H-Coal</u>	<u>FMC-COED</u>	<u>PAMCO SRC</u>	<u>Cat. Inc. SRC</u>
<u>Location</u>	W. Ky.	Ill. #6	W. Ky.	W. Ky.	Wy.
<u>Rank</u>	hvAb	bituminous	hvBb	hvBb	sub-bituminous
<u>Seam (mine)</u>	Homestead 9, 11, 12 & 13	Burning Star Mine	Colonial 9 + 14	Colonial 9 + 14	Bellicup Roland-Smith Mine
<u>Analyses</u>					
% C	60.7	69.76	70.0	70.79	67.82
% H	4.8	4.63	4.7	5.06	4.83
% N	1.2	1.28	1.6	1.56	1.08
% S	5.5	3.51	3.3	3.92	0.64
% O	11.3	9.86	8.9	7.14	17.86
% Ash	16.5	10.9	11.5	10.78	7.25

Table 1-II. Coal Liquids Data

	<u>Synthoil</u>	<u>HRI H-Coal</u>	<u>FMG-COED</u>		<u>PAMCO SRC</u>		<u>Cat. Inc. SRC</u>
<u>Description</u>	<u>Centrifuged Product Oil</u>	<u>400°F⁺ Fuel Oil Product</u>	<u>Filtered Product</u>	<u>Vac. Dist. Residue</u>	<u>Stripper Bottoms</u>	<u>Filter Feed Product</u>	<u>SR Coal</u>
<u>Prod. Temp.</u> <u>(°C)</u>	450	455	185-705	450	450	450	455
<u>Pressure</u> <u>(psig)</u>	4000	2500	—	1500	1499	1766	2390
<u>Analyses</u>							
%C	86.67	89.32	82.81	86.64	87.94	87.37	88.45
%H	8.38	8.33	7.66	5.91	6.77	7.37	5.51
%N	0.93	0.87	1.09	2.14	1.37	0.84	1.26
%S	0.09	0.14	1.10	0.62	1.26	0.17	0.19
%O	3.24	0.84	7.06	4.54	1.40	4.25	4.30
%Ash	0.69	—	0.28	0.15	4.75	0.10	0.29

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3. FMC Corporation, Char Oil Energy Development, Research and Development Report No. 56, Interim Report No. 1, Office of Coal Research, U.S. Department of the Interior 1970.
4. Pittsburgh and Midway Coal Mining Co., Economics of a Process to Produce Ashless, Low Sulfur Fuel from Coal, Research and Development Report No. 53, Interim Report No. 1, Office of Coal Research, U.S. Department of the Interior 1970.
5. Catalytic Inc., SRC Process. Operation of SRC Pilot Plant at Wilsonville, Ala., ERDA Report No. FE-2270-3, August 1976.

II. SOLVENT FRACTIONATION OF COAL LIQUIDS

1. General Solvent Fractionation Scheme. The general procedure for solvent fractionation is shown in Fig. II-1 and consists of the following steps: the "as received" coal liquid (100 g thinned with benzene if necessary) is added dropwise to a well stirred 20-fold (volume to weight) excess of pentane. The precipitate is filtered, washed with pentane, and Soxhlet-extracted until no color is observed in the out-flowing extract. The Soxhlet thimble is then allowed to drain and the pentane insoluble solids air dried. The pentane soluble materials, after removal of pentane in a rotary evaporator, are further separated into oil and resin fractions by shaking with 500 ml of liquefied propane, at room temperature, in a 1 liter cylinder. The undissolved resin fraction is removed first from the bottom of the cylinder through a valve and short length of tubing, then the propane solution of the oil fraction is obtained. Propane is removed by evaporation under vacuum. The pentane-insoluble material is Soxhlet-extracted with benzene until the out flowing extracts are clear. This solution of benzene-soluble, and pentane-insoluble material is filtered, concentrated by rotary evaporation, and freeze dried to obtain the asphaltene as a powder. The benzene-insoluble residue is Soxhlet extracted with carbon disulfide to obtain a carbon disulfide-soluble fraction (carbene) and a carbon disulfide-insoluble fraction (carboid). The results of the solvent fractionation of the various coal liquefaction process products are shown in Fig. II-2.

2. Solvent Separations of Carbene and Carboid Fractions. Above we described the solvent fractionation scheme for separating coal liquid products into five fractions: oil, resin, asphaltene, carbene, and carboid. The benzene-insoluble fractions, carbene and carboid, are carbon disulfide-soluble and insoluble, respectively. Other workers have proposed alternative solvent separations for the benzene-insoluble material with pyridine in order to obtain a pyridine-insoluble fraction containing unreacted coal and mineral matter, and a pyridine-soluble, benzene-insoluble fraction, which they designated pre-asphaltenes^{*}(1). More recently Schweighardt et al. (3) substituted tetrahydrofuran for pyridine in order to separate the benzene-insoluble fraction of a Synthoil coal liquid into a THF-soluble fraction (designated pre-asphaltenes) and a THF-insoluble fraction (designated coal-derived ash). Because of the widespread interest in the solubility and constitution of the benzene-insoluble fraction of coal liquids, we felt it was important to examine the solubility of this material, and the ash distribution of the various soluble and insoluble fractions obtained in such separations.

The results shown in Table II-I indicate that Synthoil carboid may be almost completely de-ashed by extraction with either THF or pyridine. However, pyridine is more effective in dissolving the carboid 90 wt. % vs 63 wt. % for THF, and therefore should be used to achieve maximum separation of ash from benzene-insoluble coal liquid fractions.

* We have designated this fraction carbene and carboid, and have presented evidence suggesting that this material may be post-asphaltene. It may also be composed of pre- and/or post-asphaltenes depending on the coal liquefaction processing conditions (2).

II-3. Comparison of Solvent Fractionation Procedure with Separation by High Pressure Liquid Chromatography. Liquid chromatography has been suggested as an alternative procedure to solvent fractionation for separation of coal liquefaction products (4,5). In order to compare and evaluate such a procedure vis-a-vis the solvent fractionation procedure we arranged to employ a Waters System 500 high pressure preparative liquid chromatography system with disposable Prep PAK-500 silica gel cartridges.* The separation scheme used was that reported in reference (4) for separation of Synthoil liquid product (CLP). The column was consecutively and exhaustively eluted with hexane, hexane/benzene (1:1, v/v), and tetrahydrofuran (THF). The weight percent yields and comparison with reported results, and typical solvent fractionation results are shown in Table II-II.

It may be seen that liquid chromatography permits separation of coal liquid into various fractions in high (96.9 wt. %) yield. The procedure is rapid; twenty grams of coal liquid could be separated in less than one hour. However, the fractions obtained by using the recommended eluting solvents were not clearly delineated, and do not appear, to us, to be as distinctive as those obtained by use of the solvent fractionation procedure. A particularly uncharacteristic fraction was the THF eluted fraction. This was reported to closely resemble asphaltene (4). We found it to be a mixture of resin, asphaltene, and carbene and carboid. Further solvent fractionation, using our standard procedures, was required to isolate pure asphaltene, carbene and carboid, and resin from this material. Therefore, we feel that additional work with more complex chromatographic solvents will be required to obtain characteristic fractions similar to those obtained with the solvent fractionation procedure.

* Obtained with technical operators through the generosity of Waters Associates, Inc., Milford, Mass.

Table II-I

Solubility and Ash Distribution of Synthoil Carboid
in THF and Pyridine

Solvent	Starting Ash	Solvent-Soluble		Solvent-Insoluble	
		wt. %	% Ash	wt. %	% Ash
THF	8.8	63	0.39	37	27.2
Pyridine	11.4	90	0.52	10	65.2

Table II-II - Comparison of Solvent and Silica Gel Chromatographic Fractionation of Synthoil

-----Weight%-----					
<u>Fraction</u>	<u>Standard Solvent Fractionation</u>	<u>Chromatographic Eluting Solvent</u>	<u>Normalized Waters System 500</u>	<u>After Solvent Fraction of THF Eluted Fraction</u>	<u>Chromatographic Fractionation Reference (2)</u>
Oil	61	Hexane	49.0		52.6
Resin	22	Hexane/Benzene	12.5		16.7
Asphaltene	13	THF	38.5		30.7
Carbene + Carboid	4	—			
Actual Total Recovery	96		96.9		(100)

Fig. II-1. SOLVENT FRACTIONATION SCHEME FOR COAL LIQUID PRODUCT

Fig. II-2. SOLVENT FRACTIONATION ANALYSIS
OF COAL LIQUID PRODUCTS

REFERENCESII. Solvent Fractionation of Coal Liquids2. Solvent Separations of Carbene and Carboid Fractions

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3. Comparison of Solvent Fractionation Procedure with Separation by High Pressure Liquid Chromatography

4. F.K. Schweighardt, H.C. Retcofsky, and R.A. Friedel, Fuel, 55, 313 (1976).
5. Mobil R & D Corp., EPRI AF-252, Project 410-1, Annual Report, Feb. 1976.

III. CHROMATOGRAPHIC FRACTIONATION OF ASPHALTENES

A. Solvent Elution Chromatography. In order to better understand the chemistry and structure of coal-derived asphaltenes, a simple, rapid, chromatographic procedure was required to separate asphaltenes into a limited number of acid/neutral and basic fractions, which contain high concentrations of the major functional groups O-H, N-H, O, and N. The adsorbents evaluated were: activated alumina, Amberlyst 15 (a sulfonated styrene-divinylbenzene copolymer cation exchange resin in the hydrogen form) and silica gel. The first two adsorbents proved unsatisfactory, due to non-quantitative recovery of samples, and difficulty in quantitatively removing highly polar solvents such as pyridine, which were required to elute the basic asphaltene fractions from these adsorbents. Therefore, silica gel was selected as the adsorbent of choice because of its mildly acidic, hydrogen bonding properties, and because asphaltenes could be recovered essentially quantitatively by exhaustive elution with three solvents: benzene, diethyl ether, and tetrahydrofuran (1).

Baker-analyzed reagent grade silica gel (60-200 mesh) was used as obtained after initial work showed no significant improvements in results could be obtained by thermally activating the silica gel. Reagent grade benzene was used as obtained. Diethyl ether and tetrahydrofuran were either obtained from Burdick and Jackson Co., Muskegon, Michigan, without inhibitors, and passed through activated alumina just prior to use, or were reagent grade solvents which were distilled from sodium just prior to use.

Preliminary experiments were carried out with analytical columns, at high adsorbent to sample ratios, in order to select solvent combinations which afforded the desired separation and recovery of the asphaltenes. Preparative scale operations were then carried out with a large 50 x 500 mm column. The column was slurry packed with 400 ml of silica gel in benzene, and topped with layers of 60-80 mesh non-polar Fluoropak 80 (The Fluorocarbon Co., Anaheim, California) and sand. Accurately weighed samples (4 - 5 g) of asphaltenes, dissolved in a minimum volume of benzene, were carefully charged to the top of the column, and the columns exhaustively eluted with benzene ($\approx 4\ell$), diethyl ether ($\approx 2\ell$), and THF ($\approx 1\ell$). Solvents were removed by rotary evaporations, and powders were obtained directly, or by freeze-drying the samples from benzene.

Weight percent distribution and recovery data for the five asphaltenes studied are presented in Table III-A-I. Recoveries from 95-100 percent are obtained with this chromatography procedure. Recovery and precision data for four different runs are presented in Table IV-A-II for a typical asphaltene - Synthoil. The average deviation for each of the fractions is seen to be in the range of 1 - 2 percent. The ultimate analyses, molecular weights, and weight percentages of the Synthoil chromatographic fractions are presented in Table III-A-III. When the values for the separated asphaltenes are arithmetically combined, the calculated total asphaltene values obtained are in good agreement with the values obtained experimentally for the original unseparated asphaltene. The analyses and molecular weight values for the entire set of asphaltenes along with molecular formulas, and modified Brown-Ladner (Section IV-E) average molecular structural parameters are presented in Tables (III-A-IV - III-A-VIII)

The recovery and analytical results indicate that coal-derived asphaltenes may be reproducibly separated into three distinct fractions, in high yields, by solvent elution chromatography with benzene, diethyl ether, and tetra-

hydrofuran on silica gel. The benzene- and diethyl ether-eluted fractions are brown powders which retain their solubility in benzene. Furthermore, when each of these fractions from Synthoil asphaltene was rechromatographed on silica gel with the original eluant, that fraction was recovered essentially quantitatively (97%). This demonstrates that these asphaltene fractions are stable toward silica gel chromatography. The benzene-eluted fraction of this asphaltene has also become 61 weight percent soluble in pentane. This suggests that the chromatographic fractionation has separated components which could form associated complexes in nonpolar solvents, such as pentane, which would normally then precipitate from solution. It was suggested previously that such complexes are hydrogen bonded acid-base complexes (2).

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 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.

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 ~70 % of the originally insoluble material in benzene. These results suggest that part of the THF-eluted 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 this fraction, it becomes practically insoluble in benzene.

Comparisons of these chromatography fractions with the original asphaltene molecules are presented in Tables III-A-IV to III-A-VIII. Molecular Formulas, ^1H NMR structural parameters (IV - E) atomic C/H ratios, and color index (I)(IV-K) 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 suggest fewer larger aromatic π -systems. In addition, the atomic C/H values are usually lowest, indicating the highest degree of saturation for these fractions. The Et_2O -eluted fractions have a higher percentage of the heteroatoms nitrogen and oxygen. 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. They generally have lower f_a and C/H values and relatively high $\text{H}_{\text{aru}}/\text{C}_{\text{ar}}$ values, which indicates greater saturation and smaller average ring systems than the other asphaltene fractions.

Table III-A-I.
Silica Gel Chromatography of Asphaltenes

Asphaltene	- - - Wt. % Normalized - -			Actual Wt. % Recovery
	Benzene	Et ₂ O	THF *	
Synthoil	45	37	18 ^a	98
HRI H-Coal	47	33	20 ^b	99
FMC-COED	41	46	13 ^c	95
Cat. Inc., SRC	54	35	11 ^d	99
PAMCO SRC	47	40	13 ^e	99

* Solubility in Benzene: (a) 22% ; (b) 25% ; (c) Small; (d) 19% ; (e) 24%.

Table III-A-II.

Silica Gel Chromatography of Synthoil Asphaltene - Recovery
and Precision Data

Solvent Fraction	Weight Percentage				Mean $\pm$ Av. Dev.
	Run 1	Run 2	Run 3	Run 4	
Benzene	44	45	46	50	46 $\pm$ 2
Et ₂ O	36	38	37	35	37 $\pm$ 1
THF	18	16	17	17	17 $\pm$ 1
Recovery	98	99	100	102	100 $\pm$ 1

Table III-A-III.

Synthoil Asphaltene and Silica Gel Chromatograph Fractions Ultimate Analysis^a, MW, and Wt%

	----- % -----							
	C	H	N	S	O ^b	Ash	MW ^c	Wt% Fraction
Benzene-Eluted	89.54	6.50	0.95	0.62	2.39	0.50	534	45
Et ₂ O-Eluted	85.38	6.71	2.30	0.21	5.40	0.51	521	37
THF-Eluted	84.23	6.33	2.86	0.70	5.97 ^d	0.50	612 ^e	18
Original Asphaltene	87.65	6.31	1.74	0.41	3.89	0.46	561	100
Calculated Total Asphaltene	87.04	6.55	1.79	0.49	4.15	0.50	541	100

^aMoisture and ash free.

^bBy difference.

^cAverage of VPO infinite dilution values in THF and benzene.

^dDetermined directly.

^eVPO infinite dilution value in THF.

Table III-A-IV.

Comparison of Synthoil Asphaltene and Silica Gel Chromatography Fractions

	Starting Asphaltene	Benzene-Eluted	Et ₂ O-Eluted	THF-Eluted
Molecular Formula	C _{40.94} H _{35.12} N _{0.70} O _{1.36} S _{0.07}	C _{39.81} H _{34.43} N _{0.36} O _{0.80} S _{0.10}	C _{37.04} H _{34.68} N _{0.86} O _{1.76} S _{0.03}	C _{42.92} H _{38.43} N _{1.24} O _{2.28} S _{0.13}
Molecular Weight ^a	561	534	521	612
H ^a _{ar} ^b	33	35	34	25
H ^a _a	42	42	41	45
H ^a _o	25	23	25	30
f _a	0.71	0.72	0.69	0.66
H _{aru} /C _{ar}	0.70	0.70	0.81	0.72
σ	0.43	0.40	0.43	0.53
R _S	8.7	8.0	8.9	10.9
n	1.6	1.5	1.6	1.7
C _A	29.2	28.6	25.6	28.5
R _A	5.4	5.3	3.5	5.0
C/H	1.17	1.16	1.07	1.13
I	15.9 ^c	17.8	9.3	38.5

a. Extrapolated infinite dilution values measured in THF.

b. Uncorrected for phenolic absorption.

c. Average of six samples, ±1.4 (9% deviation).

Table III-A-V.

Comparison of HPL II-Coal Asphaltene and Silica Gel Chromatography Fractions

	Starting Asphaltene	Benzene-Eluted	Et ₂ O-Eluted	THF-Eluted
Molecular Formula	C _{35.59} H _{28.86} N _{0.56} O _{1.52} S _{0.10}	C _{40.62} 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 [*] _a	36	37	39	40
H [*] _o	18	15	19	30
f _a	0.78	0.80	0.74	0.66
H _{aru} /C _{ar}	0.72	0.69	0.81	0.84
σ	0.34	0.32	0.39	0.47
R _s	6.7	7.2	8.4	13.0
n	1.5	1.4	1.5	1.8
C _A	27.8	32.4	26.9	32.6
R _A	4.9	6.0	3.5	3.6
C/H	1.22	1.27	1.12	1.02
I	29.4	30.2	14.7	30.3

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-A-VI.

Comparison of FMC-COED Asphaltene and Silica Gel Chromatography Fractions

	Starting Asphaltene					Benzene-Eluted					Et ₂ O-Eluted					THF-Eluted				
Molecular Formula	C _{26.06}	H _{24.07}	N _{0.33}	O _{2.20}	S _{0.15}	C _{23.00}	H _{20.60}	N _{0.25}	O _{1.13}	S _{0.20}	C _{26.53}	H _{25.71}	N _{0.44}	O _{2.44}	S _{0.17}	C _{25.49}	H _{25.39}	N _{0.92}	O _{2.32}	S _{0.23}
Molecular Weight ^a		382					325					395					389			
I _{ar} ^b		39					40.4					37					32			
H _a [*]		40					39.4					42					47			
H _o [*]		21					20.2					21					21			
f _a		0.72					0.73					0.69					0.66			
H _{aru} /C _{ar}		0.88					0.80					0.94					0.97			
σ		0.43					0.39					0.45					0.51			
R _s		7.0					5.3					7.8					8.3			
n		1.5					1.5					1.5					1.5			
C _A		18.7					16.8					18.4					16.9			
R _A		2.2					2.7					1.5					1.2			
C/H		1.08					1.12					1.03					1.00			
I		4.1					5.1					3.5					11.8			

a. Extrapolated infinite dilution values measured in THF.

b. Uncorrected for phenolic OH absorption.

Table III-A-VII.

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

	Starting Asphaltene	Benzene-Eluted	Et ₂ O-Eluted	THF-Eluted
Molecular Formula	C _{35.64} H _{28.20} N _{0.48} O _{1.30} 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 [*] _α	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

a. Extrapolated infinite dilution values measured in THF.

b. Uncorrected for phenolic OH absorption.

Table III-A-VIII.

Comparison of PAMCO SRC Asphaltene and Silica-Gel Chromatography Fractions

	Starting Asphaltene	Benzene-Eluted	Et ₂ O-Eluted	THF-Eluted
Molecular Formula	C _{36.39} H _{30.05} N _{0.56} O _{1.47} 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	502	464	503	607
H ^a _{ar} ^b	42	41.0	41	41
H ^a _a	38	38.5	37	41
H ^a _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	7.2	6.5	7.5	9.6
n	1.5	1.5	1.6	1.4
C _A	27.7	26.1	26.8	32.3
R _A	4.9	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

a. Extrapolated infinite dilution values measured in THF.

b. Uncorrected for phenolic OH absorption.

REFERENCESIII. Chromatographic Fractionation of AsphaltenesA. Solvent Elution Chromatography (SEC)

1. I. Schwager and T.F. Yen, Fuel, 58, 219 (1979).
2. H.W. Sternberg, R. Raymond, and F.K. Schweighardt, Science, 188, 49 (1975).

III-B. Gel Permeation Chromatography (GPC) (1).

1. Analytical Scale GPC. Analytical scale high performance liquid chromatography (HPLC) was carried out using a Waters L.C. system comprised of the following equipment:

1. Waters Asso. Model 6000A Solvent Delivery System
2. Waters Asso. Model 440 Absorbance Detector (254 nm)
3. Waters Asso. Model R401 Differential Refractometer
4. Houston Omniscribe 2 pen recorder

Three μ -Styragel columns (two 100 Å and one 500 Å, 7 mm ID x 30 cm length, $\approx$ 3000 plates each) were connected in series. Uninhibited THF was used as solvent. Samples were prepared as 2% solutions in THF which had been degassed by sonic bath stirring. The samples were filtered across a 0.45 μ m millipore filter, and the flow rate adjusted to 1.0 ml/min.

Fig. III-B-1 gives examples of the asphaltene separation obtainable with this system. Resolution of individual peaks is not possible due to the complexity, and wide molecular weight distribution of the asphaltene fraction. However, some fractionation of asphaltenes by molecular size may be accomplished by arbitrarily cutting narrow fractions. The average molecular weight of such fractions can then be determined by vapor phase osmometry.

2. Preparative Scale GPC. Preparative scale GPC separations were carried out with an Alltech Associates 25 mm ID x 1 m glass column, slurry packed with Bio-Rad, S-X8, Bio-Beads (200-400 mesh, 8% crosslinked, styrene-divinyl benzene). The column was connected to the Waters Associates HPLC system described previously. Tetrahydrofuran (THF) (freshly distilled from sodium) was used as solvent. A typical GPC run is presented in Fig. III-B-2. Generally a 3 ml sample, containing $\approx$ 1 g of asphaltene, was loaded onto the top of the column, and a flow rate of $\approx$ 2 ml/min was used to elute the sample. Pressures of 5-10 psia were sufficient to obtain reasonable flow rates. The progress of the chromatograph was generally followed by use of the differential refractive index detector, because UV absorption was too strong except at the beginning and final stages of elution. The fractionated GPC samples were stripped of solvent on a rotary evaporator and freeze dried to powders from benzene. The last trace of benzene was removed by heating the powders overnight in a vacuum oven.

The manufacturer reports Bio-Beads, S-X8 to have a molecular weight exclusion limit of 1,000. We found that a polypropylene oxide standard of MW 2,000 was excluded, whereas a similar standard of MW 800 was not excluded. At the lower molecular weight separation range anthracene could be separated from benzene, but tetralin and toluene could not be separated. In the mid-range aromatics such as 9,10-diphenyl-anthracene could be separated (almost to baseline) from 1,2-benzanthracene on our column. Reinjection of fraction two afforded only a relatively narrow peak indicating that the sample size was sufficiently small to avoid overloading the column.

The weight fraction recovery and VPO molecular weights of the fractions are shown on Fig. III-B-2. The average molar properties of the fractions, derived from elemental analyses, VPO molecular weight determination and Brown-Ladner NMR analyses, are presented in Table III-B-I. The elution took place in the order of high to low molecular weight. The C/H ratio generally increases as the MW decreases, and the percent oxygen shows a large decrease in Cut 5. The aromaticity, f_a , shows a steady increase from 0.58 to 0.76 with fraction number, while the number of carbon atoms per saturated substituent, n , decreases from 2.5 to 1.5. The fraction of available aromatic edge atoms occupied by substituents, σ , also decreases from

0.69 to 0.37 as the elution volume increases. These results can be interpreted in terms of aromatic ring systems, with large saturated substituents eluting first. As the elution volume increases the saturated substituents decrease in number and size resulting in the molecules becoming smaller and more aromatic. The size of the average aromatic ring system, as measured by the ratio of substitutable aromatic edge atoms to total aromatic atoms, H_{aru}/C_{ar} , appears to go through a minimum at Cut 3.

The weight average molecular weight:

$$\bar{M}_w = \frac{\sum_i W_i M_{wi}}{\sum_i W_i}$$

(where M_{wi} = the molecular weight of the i th molecular weight state, and W_i = the weight of material in the i th molecular weight state) was calculated to be 641. This value is very close to the $\bar{M}_w$ value of 633 obtained by mass spectroscopy (Section IV-G). The number average molecular weight:

$$\bar{M}_n = \frac{\sum_i N_i M_{wi}}{\sum_i N_i}$$

(where N_i = the number of molecules in the i th molecular weight state) was calculated to be 548. This value is very close to the value 561 calculated independently by VPO in the solvent THF (Section IV-C).

3. Gel Permeation Chromatography of SEC Fractions. Exhaustive solvent elution chromatography with silica gel to obtain major fractions has been described in Section III-A of this report. In order to separate asphaltenes into smaller, more easily identifiable fractions, the benzene-eluted fraction from silica gel was rechromatographed on a preparative Waters System 500 high pressure liquid chromatographic system. Seventeen fractions were collected with the solvent system 90% hexane/10% CH_2Cl_2 , and then seven fractions were collected with benzene. Some of these fractions were then rechromatographed on the Waters analytical high pressure liquid chromatographic system described previously. Three μ -Styragel columns (two 100 Å and one 500 Å, 7 mm IDX 30 cm length, $\approx$ 3000 plates each) were connected in series. Uninhibited THF was used as solvent.

The results for selected fractions are shown in Fig. III-B-3. It appears that each of the solvent elution chromatography fractions may be further fractionated on μ -Styragel to obtain several subfractions based on molecular size. Fractions 1, and 15-21 appear to have comparatively large amounts of high molecular size materials, and fractions 2-6 appear to contain comparatively large amounts of low molecular size materials.

Fraction 1 was isolated and analyzed: %C, 88.33; %H, 7.94; %N, 0.16. Mass spectroscopic analyses at low resolution-low voltage, and high resolution - 30 eV conditions were carried out. The observed mass spectra were complex, and are discussed in Section IV-L of this report.

Table TII-B-I.

Average Molar Properties^a of Synthoil GPC Fractions^b

	Cut 1	Cut 2	Cut 3	Cut 4	Cut 5
Molecular Formula	C _{89.01} H _{84.33} N _{1.96} O _{5.61} S _{0.27}	C _{68.00} H _{61.03} N _{1.69} O _{3.51} S _{0.19}	C _{35.98} H _{33.78} N _{0.81} O _{2.18} S _{0.08}	C _{29.04} H _{25.27} N _{0.68} O _{1.62} S _{0.11}	C _{25.96} H _{21.00} N _{0.65} O _{0.75} S _{0.15}
Molecular Weight	(1280) ^c	964 ^d	515 ^d	413 ^d	359 ^d
H _{ar} ^a	11	25	30	32	42
H _a ^a	35	42	45	46	40
H _o ^a	54	33	25	22	18
f _a	0.58	0.66	0.67	0.70	0.76
H _{aru} /C _{ar}	0.57	0.70	0.83	0.76	0.69
σ	0.69	0.52	0.50	0.48	0.37
R _S	20.5	16.3	9.9	7.5	5.0
n	2.5	1.8	1.5	1.5	1.5
C _A	51.4	45.0	24.1	20.5	19.8
R _a	11.9	7.8	3.1	3.5	4.1
Weight %	3.2	31.6	32.0	20.5	12.7

a. Brown-Ladner Method X=Y=2.

b. Collected from Bio-Heads SX-3, THF solvent.

c. VPO THF (Single point).

d. VPO THF (Extrapolated to infinite dilution).

COLUMN: μ Styragel $1 \times 500 \text{ \AA}$,
 $2 \times 100 \text{ \AA}$

SOLVENT: THF

FLOW: 1 ml/min

CHART: 0.25 cm/min

UV: 1 A at 254nm

Fig. III-B-1. GPC CHROMATOGRAMS OF ASPHALTENES

Fig. III-B-2

NOTE:

1 to 17: 90% Hexane
10% CH₂Cl₂ Cuts

19 to 23: Benzene Cuts

Fig. III-B-3. GPC CHROMATOGRAPHS OF SYNTHOIL ASPHALTENE SILICA GEL CUTS

REFERENCESB. Gel Permeation Chromatography (GPC)

1. I. Schwager, J.T. Kwan, W.C. Lee, S. Meng, and T.F. Yen, "Separation and Characterization of Synthoil Asphaltene by Gel Permeation Chromatography and Proton Nuclear Magnetic Resonance Spectrometry", *Anal. Chem.*, 51, (9), 1803-1806 (1979).

IV. CHARACTERIZATION OF COAL LIQUID FRACTIONS by ANALYTICAL, PHYSICAL and CHEMICAL METHODS

IV-A. Elemental Analyses. Elemental analyses of carbon, hydrogen, nitrogen, oxygen, sulfur and ash were carried out with standard procedures by the ELEK Microanalytical Labs., Torrance, California, and Huffman Labs., Wheatridge, Colorado: Carbon and hydrogen ($\pm 0.3\%$) were measured by combustion followed by CO_2 and H_2O determination; nitrogen ($\pm 0.3\%$) by the Dumas method; oxygen ($\pm 0.5\%$) by pyrolysis followed by oxidation over C; sulfur ($\pm 0.3\%$) by combustion to SO_2 followed by titration; ash ($\pm 0.3\%$) gravimetrically after combustion at 750°C . Most molecular weights were determined by extrapolation to infinite dilution in our laboratory with a Mechrolab Model 301 A Vapor Pressure Osmometer as described in Section IV-C. A few VPO molecular weights were determined at finite concentrations by Galbraith Labs. Inc., Knoxville, Tennessee. The analyses of the starting coals, coal liquids, and the various solvent fractions are given in Tables IV-A-I to IV-A-V, along with the VPO molecular weights of the solvent fractions.

Table IV-A-I.

Synthoil Solvent Fractions Ultimate Analysis, %^a

Fraction	C	H	N	S	O ^b	Ash	MW ^c
Coal ^d	60.7	4.8	1.2	5.5	11.3	16.5	
Coal liquid ^e	87.26	8.44	0.94	0.10	3.26	0.69	
Oil	87.74	9.58	0.60	0.43	1.65	0.02	243
Resin	87.27	7.77	1.30	0.14	3.52	0.30	305
Asphaltene	87.27	6.51	1.63	0.66	3.93	0.48	552 (565) ^f
Carbene	87.04	6.07	2.14	1.25	3.50	0.06	861 ^f
Carboid	88.32	5.69	1.64	2.07	2.28	8.80	938 ^g
Carboid ^h	84.72	5.58	0.89 ⁱ	0.88	7.94 ⁱ	0.52	

a. Moisture and ash free except coal.

b. By difference.

c. VPO in benzene.

d. West Kentucky, hvAb, Homestead Seams 9, 11, 12, 13.

e. Centrifuged product oil produced at 450°C, 4000 psig.

f. VPO in THF.

g. VPO in DMF.

h. Deashed with pyridine.

i. Nitrogen by difference, oxygen determined directly due to pyridine contamination of extracted carboid.

Table IV-A-II.

HRI-H-Coal Solvent Fractions Ultimate Analysis, %^a

Fraction	C	H	N	S	O ^b	Ash	MW ^c
Coal ^d	69.76	4.63	1.28	3.51	9.86	10.9	
Coal liquid ^e	89.82	8.33	0.87	0.14	0.84	---	
Oil	89.54	9.18	0.45	<0.05	0.83	0.17	222
Resin	89.39	7.07	1.13	0.14	2.27	<0.05	270
Asphaltene	86.88	5.91	1.61	0.64	4.96	0.38	513 (471) ^f
Carbene	87.18	5.05	1.93	0.94	4.90	0.32	1260 ^f
Carboid	86.09	4.87	1.51	0.97	6.56	0.55	1020 ^g

a. Moisture and ash free except coal.

b. By difference.

c. VPO in Benzene.

d. Ill. No. 6, Burning Star Mine-Bituminous.

e. 400°F + Fuel Oil Product produced at 455°C, 2500 psig.

f. VPO in THF.

g. VPO in DMF.

Table IV-A-III.

FMC-COED Solvent Fractions Ultimate Analysis, %^a

Fraction	C	H	N	S	O ^b	Ash	MW ^c
Coal ^d	70.0	4.7	1.6	3.3	8.9	11.5	
Coal liquid ^e	83.04	7.68	1.09	1.11	7.08	0.28	
Oil	85.88	9.75	0.42	1.08	2.87	0.01	267
Resin	83.25	7.25	1.06	1.26	7.18	0.39	325
Asphaltene	82.14	6.47	1.70	2.58	7.11	0.79	375
Carbene	81.17	6.01	1.69	1.31	9.82	0.11	326 ^g
Carboid	78.47	5.65	1.95	1.85	12.08	1.31	394 ^f

a. Moisture and ash free except for coal.

b. By difference.

c. VPC in benzene.

d. West Kentucky, hvBb, Colonial Seams 9 + 14.

e. Filtered product from staged pyrolysis at 182-705°C.

f. VPO in DMF.

g. VPO in THF.

Table IV-A-IV.

Cat. Inc. SRC Solvent Fractions Ultimate Analysis, %^a

Fraction	C	H	N	S	O ^b	Ash	MW ^c
Coal ^d	67.82	4.83	1.08	0.64	17.86	7.25	
SRC ^e	88.71	5.53	1.26	0.19	4.31	0.29	
Oil	90.99	6.94	0.41	0.57	1.09	0.25	264
Resin	89.88	6.64	0.84	0.00	2.64	0.05	370
Asphaltene	88.79	5.61	1.25	0.12	4.23	0.78	481 (486) ^f
Carbene	89.77	5.03	1.11	0.26	3.83	0.40	1228 ^f
Carboid	87.08	4.70	0.96	0.34	6.92	0.71	1026 ^g

a. Moisture and ash free except for coal.

b. By difference.

c. VPO in benzene.

d. Wyoming, sub-bituminous, Bellicup Seam, Roland-Smith mine.

e. Solvent Refined Coal produced at 455°C, 2390 psig.

f. VPO in THF.

g. VPO in DMF.

Table IV-A-V.

PAMCO Solvent Fractions Ultimate Analysis, %^a

35

Fraction	C	H	N	S	O ^b	Ash	MW ^c
Coal ^d	70.79	5.06	1.56	3.92	7.17	10.78	
Coal liquid ^e	87.94	6.77	1.37	1.26	1.40	4.75	
Coal liquid ^f	87.37	7.37	0.84	0.17	4.25	0.10	
Coal liquid ^j	86.64	5.91	2.14	0.62	4.54	0.15	
Oil ^e	89.81	7.60	0.83	0.23	1.53	0.21	
Oil ^f	90.12	8.14	0.54	0.34	0.86	0.52	202
Oil ^j	89.96	7.35	0.42	0.14	2.13	0.20	307
Resin ^e	88.40	6.60	1.65	0.40	2.95	0.03	
Resin ^f	86.39	7.08	1.40	0.13	5.00	0.01	226
Resin ^j	88.94	7.30	0.92	0.31	2.54	0.51	352
Asphaltene ^e	86.07	6.17	1.75	0.47	5.54	0.05	
Asphaltene ^f	85.03	6.06	1.45	1.11	6.35	1.50	471 ^g (426) ^h (395) ⁱ
Asphaltene ^j	86.72	6.01	1.57	0.64	4.67	0.39	563
Carbene ^e	87.56	5.42	1.70	0.92	4.40	0.29	
Carbene ^f	87.60	5.70	1.49	0.67	4.54	0.47	
Carbene ^j	86.07	5.70	2.18	2.10	3.68 ^k	0.16	1051 ⁱ
Carboid ^e	80.25	4.61	1.12	8.27	5.75	31.41	
Carboid ^f	85.30	4.92	1.00	1.19	7.50	1.65	(600) ^h
Carboid ^j	84.55	5.43	2.72	1.23	5.79 ^k	0.58	

a. Moisture and ash free except for coal.

b. By difference.

c. VPO in benzene.

d. West Kentucky, hvBb, Colonial Seams 9 + 14.

e. Stripper bottoms produced at 450°C, 14⁹psig. Process solvent included.

f. Filter feed produced at 450°C, 1766 psig. Contains light oil, wash solvent, process solvent and 2.8% Dowtherm A heat transfer fluid contaminant as received.

g. Average of two different samples MW 510, 432.

h. VPO in DMF (may not be completely soluble).

i. VPO in THF.

j. SRC - Vacuum distillation residue.

k. Determined directly.

IV-B. Semiquantitative Metal Analysis

Semiquantitative metal analysis ($\pm 50\%$) was carried out by emission spectrography by the Pacific Spectrochemical Lab. Inc., Los Angeles, California. Samples of the coal liquid asphaltene, and the benzene insoluble fractions were analyzed because they contain the most ash. In general, the benzene insoluble fractions contain higher percentages of metals than the asphaltene. The major elements found are: Si, Fe, Al, Ti, B, Ca and Mg (Table IV-B-I).

Semiquantitative Metal Analysis⁸

* Results in ppm ND - Not detected TR - Trace

IV-C. Molecular Weights and Association (1,2)

1. Vapor Pressure Osmometry (VPO). A limited number of molecular weights were determined by Galbraith Labs. Inc., Knoxville, Tenn. These samples were generally run in benzene at finite concentrations ranging from ≈ 2 -10 g/l. Such molecular weights were often found to be high for asphaltenes or other coal liquid fractions which could associate in solution. A few measurements were repeated in the solvent tetrahydrofuran (THF) at finite concentrations, and lower apparent molecular weight values were found. Therefore, we repeated most measurements, in our own lab, with a Mechrolab Model 301 A vapor phase osmometer 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, chloroform, or tetrahydrofuran for extrapolation to infinite dilution. A plot of the data for a sample of Synthoil asphaltene is shown in Fig. IV-C-1. 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 Tbls. IV-C-I-IV-C-VII. The only class of compounds whose molecular weights have not been redetermined by use of the infinite dilution technique are the carboids. The molecular weights of these materials were determined, at finite concentrations (≈ 5 -10 g/l) in *n,n*-dimethylformamide (DMF) by Galbraith Labs, Inc. These finite values are reported in Table IV-C-I. We intend to redetermine these molecular weights in the solvent pyridine in the future.

a. Coal Liquid Solvent Fractions. The molecular weight determinations of the coal liquid solvent fractions are presented in Table IV-C-I. The general trend indicates increasing molecular weights in going from oil to resin to asphaltene to carbene-carboid. The carboid values are least reliable due to the fact that these values were determined at finite concentrations. The slopes of the linear correlation lines increase in the same order, which suggests that association follows the same trend as size although these two properties are probably not related.

b. Coal-Derived Asphaltenes. Table IV-C-II shows the molecular weights of asphaltenes vs. concentration in the solvents THF, chloroform and benzene. These results and those shown in Fig. IV-C-I, for a typical asphaltene, indicate that association of coal-derived asphaltenes takes place in all three solvents over a wide range of concentrations (4-60 g/l). All of the asphaltenes afford positive linear correlations between concentration and molecular weight in dilute solution. The correlation coefficients of 12 of the 16 least squares equations, presented in Table IV-C-II are ≥ 0.95 , which indicates that the simplifying assumption that molecular weights vs. concentration may be reasonably approximated as linear in dilute solution is valid. The slopes of the linear correlation lines increase as the polarity of the solvents decrease, i.e., slope in benzene $> \text{CHCl}_3 > \text{THF}$, but the molecular weight values obtained by extrapolating the plots to infinite dilution are in very good agreement. The percent deviations of the molecular weights for the five asphaltenes measured in the three solvents range from 2.5-7.8%. The arithmetic average of these 5 deviations is $\pm 4.5\%$. This suggests that association becomes more significant as the polarity of the solvent decreases, but that coal-derived asphaltene dissociation tends to go to completion in all the solvent

used at infinite dilution. This behavior of coal-derived asphaltenes is different from that observed for petroleum-derived asphaltenes which are apparently not dissociated in either benzene (3), or THF (4) over the range 2-7 wt. % and 1.2-2.4 wt. %, respectively. For the former case, with Athabasca asphaltenes, a solvent of higher polarity, such as pyridine, was required to cause significant variation in the observed molecular weight as a function of concentration.

c. Silica Gel Separated Asphaltenes. The molecular weights of asphaltene silica gel chromatography fraction vs. concentration in benzene and THF are presented in Table IV-C-III. The molecular weights of the THF-eluted fractions were not determined in benzene because these materials were not completely soluble in that solvent. Once again, significant correlation coefficients were generally observed, and the average deviation between molecular weights determined in the two solvents was only $\pm 1.8\%$ for the 10 asphaltenes measured.

The slopes of the equations are generally significantly lower in THF than in benzene. If one considers the slope of the MW vs. concentration curves as a measure of association, then it is instructive to consider which mechanism of the association would be consistent with the observed variations among the different asphaltene products. Since the slopes are greater, and show more differences in benzene, we will consider only that series. In every case the benzene-eluted fractions have reduced slopes, whereas, the Et₂O-eluted fractions have either smaller decreases in slopes, or increases in slopes compared with the starting unseparated asphaltenes. Two additional cases, presented in Table IV-C-IV the silylated- and HCl-soluble Synthoil asphaltenes show decreases of slope in benzene from 11.1 in the starting asphaltene to 4.9 and 4.6, respectively. We feel that these results tend to support a hydrogen bonding donor-acceptor (5, 6) model of coal-derived asphaltene association (7, 8, 9). The reasoning for this is as follows: silylation eliminates phenolic OH functions and would be expected to reduce H-bonding; the benzene-eluted fractions from silica gel, and the HCl-soluble fraction are known to have reduced basic nitrogen concentrations (Section IV-G) which would also reduce the hydrogen bonding possibilities; the Et₂O-eluted fraction, which contains the major portion of both basic nitrogen and oxygen, still contains substantial phenolic OH (Section IV-G), and therefore would be expected to show the smallest change in associative properties relative to starting asphaltene.

d. Miscellaneous Asphaltene Products. Molecular weight equations for miscellaneous coal asphaltene products are presented in Table IV-C-IV. The average value for the completely silylated Synthoil asphaltene, 620, is in excellent agreement with a calculated value of 624 for a Synthoil asphaltene with 64 % of its oxygen silylated (Section IV-G-1). The average value of 466 for an HCl-soluble Synthoil asphaltene fraction is in reasonable agreement with the values recently reported for similar fractions produced in different ways (10). The other asphaltene values are discussed in appropriate sections of this report.

e. Synthoil GPC Fractions. Table IV-C-V gives the molecular weight vs. concentrations for Synthoil GPC cuts (Section III-B.2) as measured in the solvent THF.

f. Mixtures of Asphaltenes and Resins. The VPO molecular weights of mixtures of coal-derived resins and asphaltenes vs. concentration in THF have also been determined and are shown in Table IV-C-VI. The results indicate that

reduced association takes place for those mixtures in THF over the concentration range of 6-60 g/l. All of the mixtures afforded positive linear correlations between concentration and molecular weight except for the mixture of Synthoil resin and asphaltene. The observed molecular weights of all the mixtures, obtained by extrapolating the plots to infinite dilution, are close to the calculated molecular weights of the arithmetically combined molecular weights of resin and asphaltene (average deviation +5%). This suggests that the dissociation of those mixtures tends to go to completion in THF at infinite dilution.

The slopes of the linear correlation lines of the mixtures are almost always significantly lower than those of either the pure resin or pure asphaltene. Since the slope of the MW vs. concentration curve is a measure of association, this indicates that mixtures of resins and asphaltenes associate less as a function of concentration than do the unmixed materials.

2. Gel-Permeation Chromatography - Correlation Between Molecular Weights and GPC Retention Times. Representative GPC chromatograms of several asphaltenes, carried out on the above described series of μ -styragel columns, are shown in Fig. IV-C-2. The elution volume corresponding to the maximum detector response was obtained for various Synthoil coal liquid fractions, Synthoil asphaltene SEC and GPC fractions, and a set of standard compounds (Table IV-C-VII). Those retention volumes were plotted vs. the known molecular weights, and the VPO number average molecular weights (Fig. IV-C-3). The results show a relatively smooth curve which may be used for obtaining number average molecular weights rapidly for unknown coal liquid fractions.

Table IV-C-I.

Molecular Weights of Coal Liquid Products vs. Concentration^a in THF

41

		Least Squares Equation	Cor. Coeff.	MW at Infinite Dilution Zero Conc. Finite Conc.	
Synthoill	Oil	MW = $0.26 \pm 0.05C + 245 \pm 0.8$	0.87	245	243 ^e
	Resin	MW = $0.86 \pm 0.30C + 252 \pm 5.1$	0.61	252	305 ^e
	Asphaltene ^b	MW = $2.85 \pm 0.96C + 568 \pm 17.5$	0.83	567 ^c	---
	Carbene	MW = $2.42 \pm 0.10C + 562 \pm 2.2$	0.99	---	---
	Carboid ^f	MW = $5.97 \pm 0.28C + 861 \pm 6.5$	0.989	861	---
HRI	Oil	MW = $0.71 \pm 0.06C + 190 \pm 1.1$	0.96	190	222 ^e
	Resin	MW = $1.00 \pm 0.14C + 255 \pm 8.1$	0.87	255	270 ^e
	Asphaltene	MW = $3.02 \pm 0.36C + 471 \pm 6.0$	0.95	502 ^c	---
	Carbene	MW = $16.84 \pm 5.48C + 1260 \pm 112.9$	0.74	1260	---
	Carboid ^f	---	---	---	1020 ^f
FMC-COED	Oil	MW = $0.13 \pm 0.17C + 276 \pm 2.8$	0.24	276	267 ^e
	Resin	MW = $0.50 \pm 0.14C + 298 \pm 2.5$	0.62	298	325 ^e
	Asphaltene	MW = $0.56 \pm 0.10C + 382 \pm 1.9$	0.89	370 ^c	---
	Carbene	MW = $1.30 \pm 0.15C + 326 \pm 3.0$	0.93	326	---
	Carboid ^f	---	---	---	394 ^f
Cat. Inc. SRC	Oil	MW = $0.68 \pm 0.09C + 235 \pm 1.6$	0.92	235	264
	Resin	MW = $0.53 \pm 0.18C + 326 \pm 3.1$	0.60	326	370
	Asphaltene ^b	MW = $1.11 \pm 0.38C + 486 \pm 7.6$	0.77	477 ^c	---
	Carbene	MW = $2.25 \pm 0.27C + 502 \pm 4.5$	0.95	---	---
	Carboid ^f	MW = $4.08 \pm 0.47C + 1228 \pm 9.1$	0.97	1228	---
PAMCO SRC ^d	Oil	MW = $0.64 \pm 0.09C + 248 \pm 1.9$	0.93	248	307
	Resin	MW = $1.22 \pm 0.39C + 320 \pm 6.1$	0.58	320	352
	Asphaltene	MW = $1.8 \pm 0.16C + 502 \pm 3.3$	0.96	545 ^c	---
	Carbene	MW = $4.8 \pm 1.67C + 1051 \pm 38.4$	0.69	1051	---
	Carboid ^f	---	---	---	---

^a Conc., g/l^b Results from two samples prepared independently.^c Avg. MW at zero concentration in three different solvents: benzene, chloroform and THF.^d Vacuum distillation residue.^e Finite concentration values measured in benzene.^f Finite concentration values measured in DMF.

Table IV-C-II.

Molecular Weight of Asphaltenes vs. Concentration* in the Solvents THF, Chloroform and Benzene

Asphaltene	Solvent	Least Squares Equation	Corr. Coeff.	Av. MW at Zero Conc.	% Dev.
Synthoil	THF**	MW = $2.85 \pm 0.96C + 568 \pm 17.5$	0.83	567	3.2
		MW = $2.42 \pm 0.10C + 562 \pm 2.2$	0.99		
	Chloroform	MW = $5.9 \pm 0.30C + 585 \pm 8.8$	0.99		
	Benzene	MW = $11.1 \pm 0.60C + 552 \pm 10.4$	0.99		
HRI H-Coal	THF	MW = $3.02 \pm 0.36C + 471 \pm 6.0$	0.95	502	6.2
	Chloroform	MW = $4.31 \pm 0.56C + 523 \pm 11.0$	0.91		
	Benzene	MW = $6.27 \pm 0.30C + 513 \pm 7.6$	0.99		
FMC-COED	THF	MW = $0.56 \pm 0.10C + 382 \pm 1.9$	0.89	370	2.9
	Chloroform	MW = $3.38 \pm 0.21C + 359 \pm 3.6$	0.99		
	Benzene	MW = $5.61 \pm 0.26C + 368 \pm 4.5$	0.99		
Cat. Inc. SRC	THF	MW = $1.11 \pm 0.38C + 486 \pm 7.6$	0.77	477	2.5
	Chloroform	MW = $4.36 \pm 0.19C + 465 \pm 3.8$	0.99		
	Benzene	MW = $4.74 \pm 0.58C + 481 \pm 12.1$	0.95		
PAMCO SRC	THF	MW = $1.83 \pm 0.16C + 502 \pm 3.3$	0.96	545	7.8
	Chloroform	MW = $5.35 \pm 0.26C + 569 \pm 4.9$	0.99		
	Benzene	MW = $7.26 \pm 0.51C + 563 \pm 10.1$	0.98		

* Conc. g/l.

**Results from two asphaltene samples prepared independently.

Table IV-C-III.
Molecular Weights of Asphaltene Silica Gel Chromatography Products
vs. Concentration* in Benzene and THF

Asphaltene	Eluant	VPO Solvent	Least Squares Equation	Corr. Coeff.	Av. MW at Zero Conc.	% Dev.
Synthoil	Benzene	THF**	MW = $2.03 \pm 0.09C + 521 \pm 1.8$	0.99	534	2.3
		Benzene	MW = $3.71 \pm 0.27C + 546 \pm 6.5$	0.97		
	Et ₂ O	THF**	MW = $2.68 \pm 0.30C + 512 \pm 7.6$	0.95	522	1.8
		Benzene	MW = $7.98 \pm 0.20C + 531 \pm 4.9$	0.997		
	THF (Benzene Soluble)	THF	MW = $1.16 \pm 0.09C + 472 \pm 3.0$	0.98	472	---
	THF (Benzene Insoluble)	THF	MW = $6.84 \pm 0.70C + 869 \pm 21$	0.98	869	---
HRI H-Coal	Benzene	THF	MW = $1.61 \pm 0.22C + 549 \pm 6.2$	0.93	554	0.9
		Benzene	MW = $5.39 \pm 0.22C + 560 \pm 6.1$	0.992		
	Et ₂ O	THF	MW = $0.89 \pm 0.11C + 514 \pm 2.9$	0.93	496	3.5
		Benzene***	MW = $12.18 \pm 0.28C + 479 \pm 7.4$	0.998		
FMC-COED	THF	THF	MW = $3.54 \pm 0.40C + 698 \pm 12.7$	0.95	698	---
	Benzene	THF	MW = $1.69 \pm 0.45C + 325 \pm 7.8$	0.79	331	1.7
		Benzene	MW = $2.24 \pm 0.47C + 337 \pm 7.8$	0.85		
	Et ₂ O	THF	MW = $-0.92 \pm 0.13C + 395 \pm 2.3$	0.92	383	3.1
		Benzene	MW = $4.82 \pm 0.66C + 371 \pm 9.4$	0.96		
	THF	THF	MW = $2.04 \pm 0.13C + 389 \pm 3.5$	0.98	389	---
Cat. Inc. SRC	Benzene	THF	MW = $0.88 \pm 0.12C + 505 \pm 2.9$	0.93	489	3.4
		Benzene	MW = $4.36 \pm 0.24C + 472 \pm 5.9$	0.98		
	Et ₂ O	THF	MW = $1.75 \pm 0.20C + 463 \pm 4.5$	0.94	459	0.9
		Benzene	MW = $10.17 \pm 0.49C + 454 \pm 11.5$	0.99		
	THF	THF****	---	---	822	---
PAMCO SRC	Benzene	THF	MW = $2.83 \pm 0.19C + 464 \pm 4.2$	0.98	464	0.0
		Benzene	MW = $5.18 \pm 0.60C + 464 \pm 14.1$	0.95		
	Et ₂ O	THF	MW = $1.39 \pm 0.20C + 503 \pm 3.5$	0.92	501	0.2
		Benzene***	MW = $8.55 \pm 4.81C + 500 \pm 76.4$	0.66		
	THF	THF	MW = $7.49 \pm 0.58C + 607 \pm 10.3$	0.97	607	---

* Conc. g/l

** Repeated with a new sample

*** Not completely soluble

**** Determined at Finite Conc. only

Table IV-C-IV.

Molecular Weights of Miscellaneous Coal Asphaltene Products vs. Concentration

Sample	VPO Solvent	Least Squares Equation	Corr. Coeff.	Average MW at Zero Conc.	% Dev.
Silylated Synthoil Asph.	THF	$1.35 \pm 0.13C + 639 \pm 2.5$	0.97	620	3.1
	Benzene	$4.93 \pm 0.95C + 600 \pm 21.9$	0.87		
Synthoil HCl-Soluble Asphaltene*	THF	$1.21 \pm 0.15C + 475 \pm 3.88$	0.96	466	2.0
	Benzene	$4.62 \pm 0.64C + 456 \pm 16.7$	0.92		
Synthoil Asphaltene K reduction product	THF	$5.45 \pm 1.01C + 1133 \pm 29.2$	0.92	1133	---
Synthoil Asphaltene KMnO ₄ oxidation product	THF	$4.36 \pm 4.7C + 1670 \pm 85.3$	0.40	1670	---

Table IV-C-V.
Molecular Weights of Synthoil GPC Cuts vs. Concentration* in THF

Cut	Least Squares Equation	Corr. Coeff.	MW at Zero Conc.
1	---	---	1280**
2	MW = $1.79 \pm 1.7C + 964 \pm 3.2$	0.40	964
3	MW = $0.65 \pm 0.79C + 515 \pm 12$	0.30	515
4	MW = $0.93 \pm 0.22C + 413 \pm 4.0$	0.88	413
5	MW = $4.09 \pm 0.95C + 359 \pm 11$	0.82	359

* Conc. g/l.

** Measured at finite conc. 8.25 g/l.

Table IV-C-VI.

Molecular Weight of Mixtures^c of Coal-Derived Resin and Asphaltene vs. Concentration^a in THF

Sample		Least Squares Equation	Corr. Coeff.	Observed MW at I.D. ^b	Calculated MW at I.D.	% Dev. ^c
PANCO SRC ^d	Resin	$MW = 1.22 \pm 0.39C + 320 \pm 6.1$	0.58	320	---	---
	5/6Resin+1/6Asphaltene	$MW = 0.29 \pm 0.04C + 324 \pm 1.5$	0.87	324	341	-5.0
	2/3Resin+1/3Asphaltene	$MW = 0.33 \pm 0.19C + 362 \pm 6.7$	0.34	362	364	-0.5
	1/2Resin+1/2Asphaltene	$MW = 0.54 \pm 0.06C + 427 \pm 1.9$	0.91	427	391	+9.2
	1/3Resin+2/3Asphaltene	$MW = 0.58 \pm 0.06C + 441 \pm 2.0$	0.93	441	422	+4.5
	Asphaltene	$MW = 1.8 \pm 0.16C + 502 \pm 3.3$	0.96	502	---	---
Synthoil	Resin	$MW = 0.86 \pm 0.30C + 252 \pm 5.1$	0.61	252	---	---
	1/4Resin+3/4Asphaltene	$MW = -1.10 \pm 0.28C + 410 \pm 9.6$	0.63	410	348	+18
	Asphaltene	$MW = 2.42 \pm 0.10C + 562 \pm 2.2$	0.99	562	---	---
HRI H-Coal	Resin	$MW = 1.00 \pm 0.14C + 255 \pm 8.1$	0.87	255	---	---
	1/4Resin+3/4Asphaltene	$MW = 1.02 \pm 0.07C + 332 \pm 2.3$	0.95	332	331	+0.3
	Asphaltene	$MW = 3.02 \pm 0.36C + 471 \pm 6.0$	0.95	471	---	---
FMC-COED	Resin	$MW = 0.50 \pm 0.14C + 298 \pm 2.5$	0.62	298	---	---
	1/4Resin+3/4Asphaltene	$MW = 0.09 \pm 0.02C + 309 \pm 0.8$	0.68	309	335	-8.8
	Asphaltene	$MW = 0.56 \pm 0.10C + 382 \pm 1.9$	0.89	382	---	---
Cat. Inc. SRC	Resin	$MW = 0.53 \pm 0.18C + 326 \pm 3.1$	0.60	326	---	---
	1/4Resin+3/4Asphaltene	$MW = 0.22 \pm 0.19C + 466 \pm 6.9$	0.23	466	395	+18
	Asphaltene	$MW = 2.25 \pm 0.47C + 502 \pm 4.5$	0.95	502	---	---
		$1.11 \pm 0.38C + 486 \pm 7.6$	0.77	486	---	---

a. Conc., g/l.

b. I.D. means infinite dilution.

c. % Dev. = (Observed MW - Calculated MW)/Calculated MW, Average Dev. + 5%

d. Vacuum distillation residue.

e. Resin and asphaltene are mixed in weight percentage.

Table IV-C-VII. Standard Compounds Used to Obtain GPC Correlation Curve*

<u>Standards</u>	<u>M.W.</u>
1. Benzene	78
2. Cyclohexane	84
3. Naphthalene	128
4. Pentamethylbenzene	148
5. Anthracene	178
6. Benzanthracene	228
7. 9-phenylanthracene	254
8. 1,1'-Bi (acenaphthenylidene)	304
9. 9,10-Diphenylanthracene	330
10. 1,2,8,9-Dibenzpentacene	378
11. Squalene	411
12. Pressure Chemical Standard	600
13. tetra-meso-4 methylphenylporphin	670
14. Polypropylene glycol	800
15. tetra-meso-2-naphthylporphin	818
16. tetra-meso-biphenylporphin	918
17. Polypropylene glycol	1200

*Columns used: Waters Associates μ -Styragel: 1 x 500 $\text{\AA}$, 2 x 100 $\text{\AA}$ (each 7.8mm, 30cm length).

FIG. IV-C-1. MW OF SYNTHOIL ASPHALTENE VS. CONCENTRATION IN DIFFERENT SOLVENTS

Fig. IV-C-2. Analytical GPC chromatograms of Synthoil asphaltene and Synthoil asphaltene fractions; gel, μ -Styragel, two 100 Å and one 500 Å columns, each 30 cm length; THF flow rate, 1.0 mL/min; UV, 1 Å at 254 nm.

Fig. IV-C-3. MOLECULAR WEIGHTS AND GPC ELUTION VOLUMES FOR STANDARDS, AND SYNTHOIL COAL LIQUID FRACTIONS

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IV-D. X-Ray Diffraction

1. Introduction. X-ray diffraction methods developed by Warren (1), Franklin (2) and Diamond (3, 4) have been utilized by many workers to study the structure of coal (5, 6, 7), carbon black structures (8), small aromatic systems in non-crystalline polymers (9), petroleum asphaltenes (10), pitch fractions (11,12), and oil shale kerogen (13). Most of the early workers (6), focused their attention on scattering at medium and large angles. Scattering patterns obtained by those workers revealed two (or more) diffuse peaks at the positions of the most prominent graphite bands; and the peaks became less diffuse as carbon content of the coal increased. These observations led most of them to suggest that small graphite ring clusters exist in coal and that coals become more graphite-like as coalification proceeds. Though supported by later work, these deductions were regarded by crystallographers as tentative explanations rather than established facts. Because of the orientation and periodicity of an ideal crystal, the x-ray diffraction pattern is sharp. In a mesomorphic or semicrystalline substance including polymers, carbon blacks, coals, pitches, asphaltites, such intra- and intermolecular order is limited in extent with the result that the x-ray diffraction pattern is diffuse. Suitably interpreted, the area and shape of the bands provide an insight into certain interesting structural features. By using blends of low crystallinity polyethylene and carbon black, it may be demonstrated that the aromaticity can be determined semiquantitatively by the x-ray diffraction method (10).

2. Experimental

a. General Procedure. A General Electric XRD-6 X-ray Diffractometer was used with copper as x-ray target, and settings of 35 kv and 18 ma for all the data run. Samples were ground to a 200 mesh size. An aluminum sample holder was used initially, but was subsequently replaced by a glass holder to reduce background interference. A balanced filter system of nickel (0.0068 mm) and cobalt (0.0075 mm) filters was used to obtain monochromatic radiation from the copper source. The standard procedure was to run the initial scan through the Ni filter, and then to repeat the scan through the Co filter. The differential intensity curve data, I , was corrected for polarization effects, normalized to electron units, A , and corrected for incoherent scattering, C , and converted to reduced intensity, I' , in the following way:

- Correction for Polarization, P. The theoretical calculation of the diffracted intensity rests on the assumption that there is a single polarized incident wave. An actual beam, on the other hand, is not uniquely polarized as a whole, but consists of waves with all possible directions of polarization within a plane perpendicular to the propagation direction.

To develop a correction for the effects of polarization, one should confine oneself to the case of a rotating sample and detector with the following geometry (shown in Fig. IV-D-1).

The intensity of the incoming radiation is constant for all angles 2θ . The intensity of the radiation perpendicular to the plane of the paper is also constant. The amplitude of that part of the incoming radiation that is in the plane of the paper appears to the detector to be reduced by the factor $\cos 2\theta$ before it gets to the sample. Let the intensity of the incoming wave be I_0 so that the amplitudes of the x and y components are $I_0/\sqrt{2}$. The amplitudes of the x and y components as seen by the detector are $I_0/\sqrt{2}$ and $I_0/\sqrt{2} \cos 2\theta$; so the incoming intensity as seen by the detector is $(I_0/\sqrt{2})^2 + (I_0/\sqrt{2} \cos 2\theta)^2$. In order to have an intensity independent of this effect we must, therefore, divide each measured intensity by the polarization factor $(1 + \cos^2 2\theta)/2$.

• Electron Unit, A, Normalization. When x-rays strike an electron, scattered x-rays of the same wavelength are produced. Such Thomson (coherent) scattering; i.e., scattering with no change in wavelength, gives rise to interference. The independent coherent scattering for carbon, E, is computed in the literature (14,15). This independent scattering data may be used to normalize the observed intensity data to electron units, A. The problems associated with this procedure, and the rationale for its use are as follows:

If we had data out to very large values of 2θ , we would have no problem. We could look at intensities at angles so large that the corresponding interatomic spacings were much smaller than the separation between the nearest atoms. When we use long wavelength radiation like the typical CuK we do not get data at large enough angles for this. There is a historical basis (8,10) for interpreting data as follows: One recognizes that some published data taken with shorter wavelength radiation (16) show that the ratio of the sum of intensities in the region $0.08 \leq \sin/\lambda \leq 0.34$ is proportional to the sum in the region $0.56 \leq \sin/\lambda \leq 0.90$ where the corresponding interatomic spacings are so small that no interference effects are possible (this is based on data taken on some carbon blacks). With a little faith, one can assume that the relationship holds for other structures and can use the accessible range to normalize the data.

• Correction for Incoherent Scattering, C. Electrons bombarded by x-rays also emit radiation whose phase and frequency are independent of those of the incoming radiation called Compton (incoherent) scattering, which does not give rise to interference. In the case where x-rays of wavelength λ give rise to Compton scattering of wavelength λ' ; we may put $\lambda' = \lambda + \delta\lambda$, where $\delta\lambda$ corresponds to the increase in wavelength of the center of the Compton spectrum. Where $\delta\lambda$ is small we have:

$$\delta\lambda = 2h/mc \sin^2 \theta = 0.024 (1 - \cos 2\theta)$$

The value of $\delta\lambda$ is in fact very small, and the intensity is only a few percent of that of the Thomson scattering (14,15). Compton scattering does not cause diffraction, but is observed as a weak background scattering over the whole angular range. Therefore, it may be subtracted from the normalized curve to give the corrected coherent scattering.

• Conversion to Reduced Intensity, I'. The corrected coherent scattering may then be divided by the independent carbon coherent scattering, E, to yield the reduced intensity, I',

$$I' = \frac{A - C}{E}$$

In summary, a usable procedure for handling the data is the following:

1. Obtain data values from the difference between the Ni and Co filter measurements.
2. Adjust the data for polarization by dividing each intensity by $(1 + \cos^2 2\theta)/2$.
3. Adjust the data to electron units by normalizing the amplitudes so that the sum of the amplitudes in the region $0.08 \leq \sin \theta/\lambda \leq 0.34$ is equal to the sum of the coherent and incoherent scattering expected in that range.
4. Subtract tabulated values of the incoherent scattering, C.
5. Divide each value by the proper value of the independent coherent scattering, E.

A computer program was written to do all the above steps, and to have the results plotted on paper (Fig. IV-D-2). One example of the print out is in Table IV-D-VI (23).

3. Interpretation of Data. The interpretation of x-ray diffraction results from noncrystalline carbon compounds is based largely on extrapolation of knowledge gained from model compounds such as graphite (carbon black), and paraffin or polyethylene (10). The reduced intensity values in the region $\sin \theta/\lambda < 0.2$ represent the data which are most precise and least subject to errors in calibration. This region of the x-ray spectrum has not been investigated theoretically (17), and hence the interpretation involves superposition of information gained from the diffraction spectra of substances supposedly understood. In the development of quantitative methods, some assumptions were made concerning carbon atoms: they were regarded as either belonging to aromatic ring clusters or randomly distributed; the ring clusters were presumed to be perfect in their internal structure; and, except for a tendency of neighboring planar units to align parallel, the planes were assumed to be randomly distributed in space. These assumptions appear to be only partially true, for it has not been possible to fit the observed intensity curves with those calculated over a wide angular range. Now we have to define the two peaks in the range of $\sin \theta/\lambda < 0.2$, namely, the (002) peak and the gamma peak (Fig. IV-D-2.).

a. The (002) Peak. The (002) band is attributed to the interplanar spacing of condensed aromatic rings. In natural graphite, the spacing corresponds to the (002) band is 3.35 Å, which corresponds to $\sin \theta/\lambda = 0.15$. Different compounds will have different interplanar spacings as shown in Fig. IV-D-3. The shifts observed in the (002) band in some compounds are shifts toward larger spacings and are attributed to actual change in interatomic spacing or to buckling of planes due to substitution of heteroatoms.

Blayden et al. (18) studied carbonization products of various coals and their banded constituents and of some pure organic compounds. They contended that the asymmetry of (002) peak is due to the gamma peak even when a peak at its position was absent. Therefore, this peak was resolved into a symmetrical (002) band and a gamma band. The method of plotting was entirely arbitrary and no valid conclusions can be drawn for the symmetry of the (002) peaks in the curves.

b. The Gamma Band. A band centered around spacing of 4.0 to 5.5 Å is observed in melted paraffin. It is attributed to the spacing between disordered aliphatic chains or alicyclic rings. There seems to be no published criterion for distinguishing between saturated rings and saturated chains based on the shape of the gamma band. The gamma band has been found to be symmetric (10); this becomes a very important point when one separates the gamma band from the (002) aromatic band by arguments that defend this symmetry.

c. Aromaticity. Aromaticity, f_a , is the fraction of the total carbon atoms in the sample present in aromatic rings. If A_γ and A_{002} are the area under the gamma and (002) peaks, the aromaticity is taken (19) to be:

$$f_a = A_{(002)} / (A_{(002)} + A_\gamma)$$

Implicit in this equation is the assumption that the area under the peaks is proportional to the concentration of each type structure and that the fraction of layers stacked is constant. The first assumption is based on runs made on 35 noncrystalline compounds in 1950 (20) and the second on the observation that the shape of the (002) band does not change much. The most convincing evidence for the usefulness of this computed aromaticity is from the experiment (10), in which a mixture of half polyethylene and half carbon black was shown to have an aromaticity of about 1/2 (Table IV-D-I).

d. High Angle Region: (10) and (11) Peaks (Fig. IV-D-2). The peaks in the high angle region at $(\sin \theta)/\lambda \approx 0.25$ and 0.425 can be indexed as the (10)-reflection and the (11)-reflection respectively. These bands correspond to the first and second nearest neighbors in ringed compounds, and the shapes of the bands have been studied theoretically (3,17).

e. Crystallite Parameters. An x-ray diffraction method, previously used to investigate the structure of petroleum asphaltenes (10) was employed to determine the crystallite parameters of these coal-derived asphaltenes. The repeat distance, representing the spacing between aromatic sheets, d_m , was calculated from the maximum of the (002)-band by the Bragg relation:

$$d_m = \frac{\lambda}{2 \sin \theta}$$

The repeat distance representing the spacing between saturated structures, d_γ , was calculated similarly from the maximum of the γ -band.

The average size of the aromatic clusters perpendicular to the plane of the sheet, L_c , was calculated from the width of the (002)-band at half maximum by use of the Scherrer crystallite size formula: (21)

$$L_c = \frac{0.45}{B_{1/2}}$$

where $B_{1/2}$ is the width of the band at half maximum expressed in terms of $(\sin \theta)/\lambda$.

The number of aromatic sheets associated in a stacked cluster, M , may be calculated from the values of L_c and d_m :

$$M = \frac{L_c}{d_m} + 1$$

The average layer diameter of the sheets, L_a , was evaluated by a procedure developed by Yen and coworkers (10) which makes use of Diamond's computed intensities of x-rays diffracted from randomly oriented perfect aromatic molecules of varying sizes, and the Debye radial distribution function (22).

By use of the Debye radial distribution function, the (10) and (11) peak intensities, $J(s)$, in atomic units can be calculated directly.

$$J(s) = \sum_r n(r)/N \sin 2\pi rs/2\pi rs$$

$n(r)$ = number of interatomic distances; r = length of interatomic distances; N = total number of atoms in layer; $s = 2 \sin \theta/\lambda$. Such calculations were made by Diamond on a series of aromatic molecules having from 11 to 288 carbon atoms, i.e., ranging in size from $5.8 - 30 \text{ \AA}$, in order to obtain the values of $J(s)$ (3). The width of the (10) peak, $\Delta \sin \theta/\lambda$, is shown in Figs. IV-D-4, IV-D-5 as a function of L_a according to Diamond's procedure. The observed intensity curves and the curves obtained using the calculated size distribution always shows a horizontal shift in coal samples. This is due mainly to the fact that the band lengths used in the calculations generally do not coincide with the mean band lengths of coal. The displacement is related to the deviation of the true band length from the assumed.

In an alternate procedure, based on Scherrer's equation, it was suggested that the size of a crystallite or random layer lattices could be calculated from the width of the (10) or (11) bands at half intensity (21).

$$\beta = c\lambda/L \cos \theta$$

β = band width; λ = wavelength of the x-ray target; L = crystallite diameter; θ = Bragg angle; c = constant. This equation was used in the calculation of some crystallite parameters in petroleum asphaltene (10).

Yen and coworkers (10) tested their procedure on both the (10) and (11)-bands with a model blend, and found that the (11)-band afforded better agreement. We also found the (11) band to be more reliable, and have therefore calculated L_a values from the correlation curve between the width at half maximum of the (11)-band and Diamond's data. We have also utilized Scherrer's equation in conjunction with the (11)-band to make a second set of calculations.

4. Results and Discussions. The x-ray crystallite parameters, and f_a results for asphaltenes, carbenes, carboids, and Synthoil asphaltene silica gel chromatography fractions are presented in Tables IV-D-II - IV-D-V. A comparison between aromaticity results obtained by the x-ray method, and those obtained by ^1H and ^{13}C NMR methods is presented in Table IV-E-VII, Section IV-E.

The aromaticity values are seen to generally increase in going from asphaltenes, to carbenes, to carboids which suggests larger aromatic ring systems in the order cited. The comparison between the x-ray method of f_a determination and the other methods shows that, on the average, the x-ray f_a value for asphaltenes is 0.054 lower than the direct ^{13}C value. This aromaticity difference may be attributed to the simplifying assumption, involved in the above method, that carbon atoms in coals or coal-derivatives are either in aromatic ring clusters or are distributed randomly, i.e., gas-like scatters. It appears that there are arrangements of nonaromatic carbons that lead to some diffuse x-ray interference pattern affecting the curves. Another problem is the resolution of the (002) and the gamma bands. The high angle side of the broad peak is used as a guide to delineate the unresolved slopes of the (002) band, and the remaining intensity is attributed to the gamma band. However, in addition to using the high angle side as a guide, it is necessary to determine a peak for the (002) band. This can be done completely randomly or, as has been done in recent x-ray work, by fixing a location for the peak. The (002) band peaks have been fixed as $\sin \theta/\lambda = 0.140$ if there is no definite and clear break in the combination (002) and gamma peaks at a different point. If aromaticities were determined completely randomly, the error would be approximately 20%. This points out the fact that aromaticities determined by x-ray may be relative as determined at a particular location. Error may be involved in converting scattering from arbitrary into electron units. Some layers may be separated by a greater distance so that the small stacks would give rise to an enhancement of the low angle side of the (002) band at the expense of the high angle side. However, despite these possible sources of error, the x-ray method is still extremely useful in determining f_a values of insoluble materials, such as carbenes and carboids, for which no simple solvent is available to measure ^{13}C NMR spectra. The use of recently developed solid state NMR techniques is limited, at present, due to the general inaccessibility of the equipment necessary to carry out that type of experiment.

X-ray crystallite parameters such as L_a , L_c , and M are seen to generally increase along the series asphaltene < carbene < carboid.

It has been reported that a progressive sharpening of the (10) and (11) bands is observed in coal as carbonization temperature is raised (6). The progressive sharpening of these bands is believed to be due to the recombination and parallel orientation of aromatic nuclei which accompanies thermal destruction of peripheral groups in carbonization. Therefore, it was of interest to investigate a series of coal liquefaction products; asphaltenes, carbenes, and carboids, which are also

believed to be formed progressively by a mechanism analogous to carbonization of coal, by the x-ray diffraction method.

The x-ray diffraction patterns for the HRI H-Coal asphaltene, carbene, and carbooid solvent fractions are shown in Fig. IV-D-6. It may be seen that the (002) + (γ) band, and the (11) band become increasingly sharpened as one progresses from asphaltene to carbene to carbooid. This supports the proposition that these materials are formed by mechanisms similar to carbonization of coal. However, the (10) band shows only minimal sharpening in going from asphaltene to carbooid. The failure to observe completely systematic results may be due to experimental problems in data measuring and processing. The difficulty in measuring bands precisely comes from the fact that the radiation detected at the corresponding angles is interfered with by polarization, x-ray fluorescence and by band broadening due to heterocyclic atoms. Therefore, the results are sensitive to small errors in data processing. The intensity analysis is good for a system composed of aromatic ring clusters and completely amorphous carbon. Also, the internal structure of the aromatic ring clusters should be perfectly regular. In coal liquid asphaltenes, these assumptions are to be regarded as only partially true. If both aromatic and aliphatic ring compounds are present, this technique loses effectiveness because of the similarity between a broad peak and the superposition of two narrow peaks. Theoretical considerations (1) shows that each peak extends indefinitely towards the high angle side so that the intensity never falls to background between peaks; therefore, definitions of the widths of these bands become ambiguous. The discrepancy observed in the region of the (10) band points to either irregularities in the layers, or to the fact that the layers are part of a larger imperfect unit. Also, oxygen atoms directly attached to aromatic carbons are expected to contribute heavily to the size of the cluster.

Despite these difficulties, x-ray crystallite parameters may be used to derive hypothetical cross-sectional model structures for coal-derived products (Fig. IV-D-7). Condensed aromatic sheets are postulated to be stacked on top of each other with the sheets parallel, and with aliphatic chains or naphthenic rings protruding from the edges. The results for asphaltenes indicate that the average interlayer distance, d_m , ranges from 3.6-3.7 Å; the average interchain distance, d_γ , is between 4.4 and 5.4 Å; and the average diameter of the aromatic clusters perpendicular to the plane of the sheets, L_c , ranges between 10.6 and 13.6 Å. The average effective number of aromatic sheets associated in a stacked cluster is between 3.9 and 4.8. The average layer diameter of the sheets generally falls between 8.0 and 10.3 Å when the (11)-band is used in conjunction with Diamond's curve.

Table IV-D-I.

Make-up Composition of Polyethylene-Carbon Black Blends

	1:1 Mixture by Weight	1:1 Mixture Based on Carbon Content
$C_{A\gamma}/C_{sat}$	1.17	1.00
$f_{A_{calc}} = \frac{C_{Ar}}{C_{Ar} + C_{sat}}$	0.54	0.50
$f_{A_{obs}} = \frac{A_{002}}{A_{\gamma} + A_{002}}$	0.48	0.43

A_{002} = Integrated intensity under 002 band at $2\theta = 26^{\circ}$

A_{γ} = Integrated intensity under γ band at $2\theta = 18^{\circ}$

Table IV-D-II.

Asphaltene X-ray Crystallite Parameters and Aromaticity, f_a

Asphaltene	L_a^a	L_c^b	d_m^c	d_γ^d	M^e	f_a^f
Synthoil	10.3 (12.3) ^g	12.2	3.7	5.4	4.3	0.63
HRI H-Coal	8.2 (9.2)	13.6	3.6	4.4	4.8	0.67
FMC-COED	8.0 (9.1)	10.6	3.6	4.9	3.9	0.58
PAMCO SRC	10.0 (10.9)	12.1	3.6	5.1	4.3	0.69
Cat. Inc. SRC	9.4 (10.3)	10.6	3.6	5.2	3.9	0.68

a_{L_a} = Diameter of aromatic sheet + α carbons of side chains, from Diamond's curve (11) band, Å.

b_{L_c} = Diameter of the aromatic clusters perpendicular to the plane of the sheets, Å.

c_{d_m} = Inter-aromatic layer distance, Å.

d_{d_γ} = Inter-chain or inter-naphthene layer distance, Å.

e_M = Average number of aromatic sheets associated in a stacked cluster.

f_{f_a} = $C_A/C_{total} = A_{002}/(A_{002} + A_\gamma)$.

g_{L_a} = value from Scherrer's Equation (11) band, Å.

Table IV-D-III.

Carbene X-ray Crystallite Parameters and Aromaticity, f_a^*

Carbene	L_a^a	L_c^b	d_m^c	d_γ^d	M^e	f_a^f
Synthoil	13.5 (14.5) ^g	10.9	3.47	4.80	4	0.63
HRI H-Coal	14.0 (15.2)	13.6	3.48	4.69	5	0.70
FMC-COED	10.0 (11.0)	12.7	3.41	4.57	5	0.81
PAMCO SRC	13.4 (14.5)	11.7	3.5	5.1	4	0.74
Cat. Inc. SRC	13.0 (14.2)	13.9	3.38	4.37	5	0.72

*Footnotes same as in Table IV-D-II.

Table IV-D-IV.

Carboid X-ray Crystallite Parameters and Aromaticity, f_a^*

Carboid	L_a^a	L_c^b	d_m^c	d_γ^d	M^e	f_a^f
Synthoil	14.5 (15.9) ^g	11.3	3.42	4.59	4	0.71
HRI H-Coal	16.5 (18.4)	14.1	3.40	5.00	5	0.75
FMC-COED	11.0 (12.2)	10.9	3.37	4.45	4	0.78
PAMCO SRC	14.0 (15.2)	13.0	3.52	4.67	5	0.76
Cat. Inc. SRC	15.0 (15.8)	15.3	3.30	4.44	6	0.83

*Footnotes same as in Table IV-D-II.

Table IV-D-V.

Aromaticity, f_a , and Crystallite Parameters for Synthoil Asphaltene and Synthoil Asphaltene Silica Gel Chromatography Fractions

	Asphaltene	Benzene- Eluted	Et ₂ O- Eluted	THF- Eluted
f_a^1	0.63	0.67	0.62	0.71
d_m^2 (Å)	3.68	3.76	3.62	3.57
d_γ^2 (Å)	5.35	4.85	4.81	5.10
L_c^2 (Å)	12.2	11.8	9.4	11.5
M^3	4.	4.	4.	4.
L_a^4 (Å) (11) band	12.3	11.7	11.6	15.3
L_a^5 (Å) (11) band	10.3	11.0	10.0	13.6

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

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

3 Effective number of aromatic sheets associated in a stacked cluster.

4L_a = diameter of the aromatic sheets from Scherrer's Eq. Ref. 10.

5L_a = diameter of the aromatic sheets from Diamond's Curve. Ref. 10

Table IV-D-VI.

SAMPLE NUMBER= 72.200

ELU=0.006003

SUM=75803.3125

DATA IN	P	CAL	C	E	REDUCE INT	SIN
3800.0000	1.0100	3837.9971	0.3300	33.7000	0.6739	0.0460
3250.0000	1.0150	3293.7478	0.4500	32.6500	0.5927	0.0570
3000.0000	1.0220	3065.9580	0.5800	31.4200	0.5673	0.0680
2800.0000	1.0310	2836.7576	0.7400	30.0000	0.5530	0.0790
2700.0000	1.0390	2805.2586	0.9200	28.5000	0.5586	0.0900
2650.0000	1.0440	2766.5991	1.0000	27.8000	0.5615	0.0950
2650.0000	1.0500	2782.4578	1.0800	27.0000	0.5787	0.1010
2900.0000	1.0670	3094.2583	1.2800	25.2500	0.6850	0.1130
3400.0000	1.0760	3658.3575	1.4500	23.7000	0.8655	0.1240
3750.0000	1.0820	4057.4990	1.5300	22.8000	1.0012	0.1290
4150.0000	1.0900	4523.4961	1.6200	22.0000	1.1607	0.1350
4560.0000	1.0980	5006.8750	1.6900	21.2500	1.3349	0.1400
4650.0000	1.1020	5124.2930	1.7400	20.8000	1.3953	0.1430
4600.0000	1.1060	5087.5977	1.7800	20.4000	1.4099	0.1460
4000.0000	1.1150	4459.9961	1.8500	19.7500	1.2620	0.1510
3250.0000	1.1240	3652.9585	1.9400	18.8500	1.0605	0.1570
1900.0000	1.1430	2171.6592	2.0800	17.3500	0.6315	0.1680
1450.0000	1.1640	1687.7593	2.2300	15.9000	0.4970	0.1790
1170.0000	1.2090	1414.5295	2.0500	13.3500	0.4825	0.2000
1180.0000	1.2350	1457.2956	2.6300	12.1500	0.5036	0.2110
1250.0000	1.2600	1574.9590	2.7700	11.1500	0.5995	0.2220
1350.0000	1.2740	1719.8989	2.8300	10.6500	0.7037	0.2270
1550.0000	1.2880	1996.3587	2.8800	10.1500	0.8970	0.2320
1640.0000	1.3040	2138.5558	2.9500	9.7500	1.0142	0.2370
1600.0000	1.3170	2107.1990	3.0200	9.3000	1.0355	0.2430
1530.0000	1.3340	2041.0193	3.0600	8.8500	1.0387	0.2480
1400.0000	1.3500	1889.9990	3.1100	8.5000	0.9689	0.2540
1250.0000	1.3820	1727.4598	3.1900	7.8500	0.9147	0.2640
1120.0000	1.4160	1585.9192	3.2700	7.3500	0.8504	0.2740
1050.0000	1.4500	1522.4598	3.3600	6.8500	0.8438	0.2840
900.0000	1.5250	1372.4555	3.5000	6.1000	0.7769	0.3040
770.0000	1.6000	1231.9555	3.6500	5.3500	0.7002	0.3240
650.0000	1.6580	1144.0198	3.7500	4.9000	0.6363	0.3390
680.0000	1.6780	1141.0396	3.7700	4.7500	0.6484	0.3440
600.0000	1.7540	1052.3997	3.9000	4.2500	0.5689	0.3630
600.0000	1.8260	1095.5994	4.0100	3.9000	0.6582	0.3810
620.0000	1.8590	1152.5753	4.0700	3.7500	0.7598	0.3900
650.0000	1.8900	1228.4995	4.1200	3.7000	0.8797	0.3990
750.0000	1.9160	1436.9595	4.1600	3.5500	1.2582	0.4080
750.0000	1.9300	1447.4555	4.1800	3.5300	1.2775	0.4120
740.0000	1.9420	1437.0793	4.2000	3.4700	1.2758	0.4170
720.0000	1.9520	1405.4357	4.2200	3.4200	1.2331	0.4210
700.0000	1.9620	1373.3999	4.2300	3.3700	1.1913	0.4250
660.0000	1.9800	1306.7596	4.2700	3.2700	1.0933	0.4340
620.0000	1.9910	1234.4194	4.2900	3.2500	0.9601	0.4420
550.0000	2.0000	1100.0000	4.3400	3.0300	0.7470	0.4580
550.0000	1.9910	1095.0496	4.3800	2.9100	0.7539	0.4740
540.0000	1.9620	1059.4757	4.4300	2.8200	0.6845	0.4890
540.0000	1.9420	1048.6797	4.4500	2.7300	0.6760	0.4970

Data printout

Fig. IV-D-1. X-Ray Diffraction Arrangement

Fig. IV-D-2. CATALYTIC INC. SRC ASPHALTENE

FIG. IV-D-3

INTERLAYER DISTANCES OF AROMATIC SYSTEMS

Fig. IV-D-4. Calibration curve of diameter of aromatic sheets vs. width at half maximum of (10) band based on data published by Diamond.

Fig. IV-D-5. Calibration Curve of Corrected Diameter of Aromatic Sheets Based on the Width at Half Maximum of the (11) - Band of the Curves Calculated by Diamond.

ASPHALTENE

69

Fig. IV-D-6. X-RAY DIFFRACTION PATTERNS FOR HRI H-COAL
COAL LIQUID SOLVENT FRACTIONS

Fig. IV-D-7. Cross-sectional view of coal derived product.

D. X-Ray Diffraction

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IV-E. Nuclear Magnetic Resonance

1. Proton Nuclear Magnetic Resonance

a. Introduction. High resolution ^1H NMR spectrometry was used first by Brown and Ladner for structural characterization of coal pyrolysis products (1). Other workers have extended this type of analysis to coal extracts (2) and coal hydrogenation products (3-7). A recently published comparison between f_a values determined from ^{13}C NMR spectra, and those estimated from ^1H NMR data demonstrated that the use of the ^1H NMR method is reasonably reliable for coal-derived materials (8). The structural parameters calculated are: f_a , fraction of total carbon which is aromatic carbon; H_{ar}/C_{ar} , ratio of substitutable edge atoms to total aromatic atoms; σ , fraction of the available aromatic edge atoms occupied by substituents; R_s , number of substituted aromatic ring carbons; n , number of carbon atoms per saturated substituent; C_A , total number of aromatic carbon atoms; R_A , number of aromatic rings (Table IV-E-I).

b. Experimental. ^1H NMR spectra were run on a Varian T-60 spectrometer. The solvent used ordinarily was 99.8% DCCl_3 + 1% tetramethylsilane (TMS), but because of solubility limitations, the carboids were run in 99.5% dimethylformamide (DMF)- d_7 or pyridine- d_5 . The concentrations were generally 10-20 wt/vol %. For asphaltenes, $\text{OH}/\text{O}_{\text{total}}$ and $\text{NH}/\text{N}_{\text{total}}$ values were determined as described in Section IV-G.

c. Results and Discussion. The ^1H NMR spectrum of a typical coal asphaltene is shown in Fig. IV-E-1. The centers of absorption for different types of protons are marked with arrows: $\delta = 7.25$, H_{ar} = aromatic protons; $\delta = 2.40$, H_α = protons α to aromatic rings; $\delta = 1.58$, H_N = naphthenic protons; $\delta = 1.25$, H_R = methylenic protons; $\delta = 0.9$, H_{SMe} = saturated methyl protons. Brown-Ladner analysis requires that the three areas of absorption centered at $\delta = 7.3$, 2.4, and 1.2 ppm be assigned to aromatic ring hydrogens (H_{ar}), aliphatic hydrogens adjacent to aromatic rings (H_α), and aliphatic hydrogens not adjacent to aromatic rings (H_0). The separation point between the H_α and H_0 protons was chosen at $\delta = 1.73$ ppm. Because hydrogen-bonded phenolic OH resonances also are believed to be shifted under the aromatic envelope (9, 10), it is necessary to determine the % of phenolic OH in order to correct the H_{ar} value. Therefore, for asphaltenes, silylation was carried out, and phenolic OH values were determined as described in Section IV-G. These values were used to make corrected average molecular property calculations for asphaltenes (Table IV-E-IV).

The average molar properties of the oils, resins, asphaltenes, carbenes, and carboids are presented in Tables IV-E-II - IV-E-VI. The oils are fairly aromatic ring having from 43-54% of the carbon as aromatic carbon. They have ~one aromatic ring per average molecule, and contain only small amounts of the heteroatoms nitrogen, oxygen, and sulfur. These molecules are moderately substituted with 41-52% of the available aromatic edge carbons being substituted. The average number of carbon atoms per saturated substituent ranges from 2.3-2.8. The oil fractions from the two SRC fractions contain average molecules which are larger and more aromatic than those found in the other oil fractions from the pyrolysis and catalyzed hydrogenation processes. This suggests less breakdown of coal and coal liquefaction intermediates to small molecules in SRC processes than in the other types of processes studied. Another contributing factor in the higher aromaticity and aromatic ring size in SRC oil and resin fractions is that SRC products are vacuum flash tower bottoms, and might have had a higher percentage of more saturated oil and resin molecules removed in the distillation.

The resins show an increase in heteroatoms and small decreases in substitution, and in the number of carbon atoms per saturated substituent. Again SRC resins appear to have larger percentages of aromatic carbons and a larger average aromatic ring system.

The average coal-derived asphaltenes generally have number-average molecular weights in the 400-550 range, and are highly aromatic species having from 71 to 79 percent of their carbon as aromatic carbon. These molecules are moderately substituted with 34 to 48 percent of the available aromatic edge carbons being substituted. Saturated substituents are small; the average number of carbon atoms per saturated substituent is between 1.4 and 1.6. The fraction of O as OH ranges from 0.56 to 0.78, and the fraction of N as pyrrolic NH from 0.28 to 0.74. These OH/O total values are more reliable than those reported previously (6) due to the more rigorous silylation procedure used, and the use of proton NMR analysis (11) instead of the direct silicon analysis method (12).

Carbenes afford f_a values from 0.74 to 0.82 which fall between the ranges calculated for asphaltenes (0.71-0.79) and those calculated for carboids (0.76-0.84). The H_{aru}/C_{ar} values 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, 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 H_{aru}/C_{ar} 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 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.

Average molecules of carboids (Table IV-E-VI) generally have the largest molecular weights and the largest aromatic ring systems. They contain the most heteroatoms found in any of the solvent fractions. The degree of substitution is less than in the asphaltenes, and the number of carbon atoms per saturated substituents is about the same as is found in the asphaltene fractions.

The structural parameter H_{aru}/C_{ar} , which gives the ratio of substitutable edge atoms to total aromatic atoms, is important because it is a measure of the average aromatic ring system which is independent of molecular weight measurements. Fig. IV-E-2 shows the H_{aru}/C_{ar} values for some typical 1-7 cata-condensed aromatic ring systems. When the H_{aru}/C_{ar} values of the coal liquid fractions are plotted vs. the atomic C/H ratios of the same fractions (Fig. IV-E-3), a smooth decrease in H_{aru}/C_{ar} vs. C/H is obtained. This indicates that the increase in C/H values is caused by an increase in the size of the average polynuclear condensed aromatic ring systems in going from oils to carboids. The number of kata-condensed aromatic rings of the H_{aru}/C_{ar} values is shown on the left side of the figure. This comparison indicates that oils contain ~1 aromatic ring; resins, ~ 2-3 aromatic rings; asphaltenes, ~ 3-5 aromatic rings; and carbenes and carboids ~ 4-7 aromatic rings per aromatic ring system.

It is interesting to note that the atomic C/H values of coals fall generally into the range of 1.16-1.26 which would correspond to ~ 3 aromatic rings per average aromatic unit in coals if coal followed the curve. This further suggests that carboids, which are more unsaturated than coal, and which apparently have a larger size aromatic unit than coal, are formed either by dehydrogenation of coal or coal liquefaction intermediates, or by polymerization of such reactive coal depolymerization species which have not been stabilized by addition of hydrogen. A general mechanism consistent with such observations for coal liquefaction product is:

2. Carbon-13 Nuclear Magnetic Resonance

The technique of ^{13}C nmr spectroscopy can be applied directly on the determination of the values of carbon aromaticities, and can provide, in combination with proton nmr spectroscopy, a series of parameters for detailed characterization of coal liquid samples (13).

Aside from practical problems, ^{13}C nmr has greater potential than ^1H nmr for the study of organic systems. In spite of the advantages of the direct observation of the molecular carbon skeleton, carbon resonances of organic compounds are found over a chemical shift range of 600 ppm, compared with that under 20 ppm for proton nuclei. ^{13}C nmr spectra are however more difficult to obtain than proton spectra. The most abundant isotope of carbon, atomic weight 12, has no nuclear spin and is not observable in nmr experiments. The natural abundance of carbon-13 is only 1.1%. The magnetogyric ratio, γ , of ^{13}C nucleus is about 1/4 that of ^1H nucleus. The sensitivity of a nucleus in a magnetic resonance experiment is proportional to the cube of γ . The result of the 1.1% natural abundance and lower γ is a lowering of the sensitivity in a ^{13}C nmr experiment by a factor of ≈ 6000 relative to a proton nmr experiment.

The development of the pulsed Fourier Transform (FT) nmr technique (14) has made the ^{13}C nmr studies practical. There are two major concerns in the use of integrated intensities for quantitative analysis in ^{13}C nmr experiments. First, since different carbons have different relaxation times, complete relaxation between pulses for all the carbon nuclei in the sample is required in order to obtain accurate relative intensities. The second problem is that different carbons exhibit different values of Nuclear Overhauser Enhancement (NOE) effects in the broadband proton decoupling experiments. The above two problems can, however, be eliminated by the addition of a paramagnetic relaxation agent such as chromium acetyl acetonate ($\text{Cr}(\text{acac})_3$) which has been shown to effectively shorten the relaxation times and quench the NOE effects (15).

The ^{13}C nmr spectra were run on a Varian GFT-20 nmr, with built-in mini-computer, operated at 20 MHz. Asphaltenes were run at concentrations of 10-40 wt/vol % in $\text{CS}_2 + \text{CDCl}_3$ (1% TMS) with $\text{Cr}(\text{acac})_3$ concentrations ranging from 0.05 - 0.10 M. Figure IV-E-4 shows a comparison of spectra run under similar conditions except that proton decoupling is on in trace a and off in trace b. The increase in sensitivity and the decrease in complexity in the broad-band proton decoupling spectrum were observed (16). The f_a values obtained for the asphaltenes are given in Table IV-E-VII. A comparison of carbon aromaticities of the three methods obtained is made.

Carbon aromaticities have been used for characterizing a number of asphaltic fractions, e.g., Table IV-E-VIII.

Table IV-E-I.

Modified Brown-Ladner Equations

$$f_a = \frac{\frac{C}{H} - \frac{H_\alpha^*}{x} - \frac{H_o^*}{y}}{\frac{C}{H}} = \text{fraction of total carbon which is aromatic carbon}$$

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

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

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

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

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

$$R_A = C_A \frac{1 - H_{aru} / C_{ar}}{2} + 1 = \text{number of aromatic rings}$$

Table IV-E-I. Continued

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, $x = y = 2$.

Table IV-E-II.
Average Molecular Properties of Oils^a

	FMC-COED	Synthoil	HRI H-Coal	Catalytic Inc. SRC	PANCO SRC
Molecular Formula	C _{19.11} H _{26.03} N _{0.08} O _{0.48} S _{0.09}	C _{17.77} H _{23.28} N _{0.10} O _{0.25} S _{0.03}	C _{16.58} H _{20.25} N _{0.07} O _{0.09} S _{0.00}	C _{20.02} H _{18.32} N _{0.08} O _{0.18} S _{0.05}	C _{23.00} H _{22.40} N _{0.09} O _{0.41} S _{0.01}
Molecular Weight ^b	267	243	222	264	307
H _{ar} ^a	0.16	0.17	0.24	0.48	0.40
H _a ^a	0.30	0.35	0.33	0.28	0.37
H _O ^a	0.54	0.48	0.42	0.24	0.23
f _a	0.43	0.46	0.54	0.76	0.71
H _{aru} /C _{ar}	1.03	1.01	0.94	0.75	0.82
σ	0.51	0.52	0.41	0.24	0.34
R _S	4.4	4.3	3.5	2.7	4.6
n	2.8	2.4	2.3	1.9	1.6
C _A	8.3	8.2	8.9	15.3	16.3
R _A	0.9	1.0	1.3	2.9	2.5

^aBrown and Ladner Method $x - y = 2$

^bVPO in benzene

Table IV-E-III.
Average Molecular Properties of Resins^a

	FMC-COED	Synthoil	HRI H-Coal	Catalytic Inc. SRC	PAMCO SRC
Molecular Formula	C _{22.55} H _{23.50} N _{0.25} O _{0.22} S _{0.73}	C _{22.18} H _{23.70} N _{0.28} O _{0.67} S _{0.01}	C _{20.10} H _{18.94} N _{0.22} O _{0.38} S _{0.01}	C _{27.71} H _{24.57} N _{0.22} O _{0.61} S _{0.00}	C _{26.07} H _{25.48} N _{0.23} O _{0.56} S _{0.03}
Molecular Weight ^b	325	305	270	370	352
H _{ar} [*]	0.28	0.29	0.40	0.43	0.37
H _a [*]	0.37	0.35	0.35	0.30	0.39
H _o [*]	0.35	0.36	0.25	0.27	0.25
f _a	0.63	0.62	0.72	0.75	0.69
H _{aru} /C _{ar}	0.87	0.84	0.77	0.71	0.82
σ	0.47	0.41	0.33	0.29	0.38
R _S	5.8	4.8	3.7	4.3	5.5
n	2.0	2.0	1.7	1.9	1.6
C _A	14.1	13.8	14.4	20.8	17.9
R _A	1.9	2.1	2.7	4.0	2.6

^aBrown and Ladner Method x = y = 2

^bVPO in benzene

Table IV-E-IV.
Average Molar Properties of Asphaltenes^a

	Synthoil	HRI H-Coal	FMC-COED	PAMCO SRC	Cat. Inc. SRC
Molecular Formula	$C_{40.9}H_{35.1}N_{0.70}O_{1.36}S_{0.07}$	$C_{35.6}H_{28.8}N_{0.56}O_{1.52}S_{0.10}$	$C_{26.1}H_{24.1}N_{0.33}O_{2.20}S_{0.15}$	$C_{36.4}H_{30.1}N_{0.56}O_{1.47}S_{0.10}$	$C_{35.6}H_{28.2}N_{0.48}O_{1.39}S_{0.02}$
Molecular Weight ^b	561	492	382	502	486
H^*_{ar} ^c	30.5	43	32	39	44.3
H^*_a	42	36	40	38	36
H^*_o	25	18	21	20	16
f_a	0.71	0.78	0.72	0.76	0.79
H_{aru}/C_{ar}	0.67	0.69	0.79	0.68	0.67
σ	0.45	0.35	0.48	0.38	0.34
R_s	8.8	6.7	7.0	7.2	6.5
n	1.6	1.5	1.5	1.5	1.4
C_A	29.2	27.8	18.7	27.7	28.3
R_A	5.9	5.3	3.0	5.4	5.7
OH/O_{total}	0.64	0.56	0.78	0.60	0.75
NH/N_{total}	0.53	0.55	0.28	0.74	0.58

^a Brown-Ladner method $x = y = 2$.

^b Extrapolated infinite dilution values measured in THF.

^c $H^*_{ar} = H^*_{ar} \text{ (observed)} - O_{OH}/H$

Table IV-E-V.
Average Molar Properties of Carbenes^a

	FMC-COED	Synthoil	Catalytic Inc. SRC	HRI H-Coal	PAMCO 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} ^a	42	40	51	47	45
H _a ^a	42	37	28	36	37
H _o ^a	16	23	21	17	18
f _a	0.74	0.75	0.78	0.82	0.78
H _{aru} /C _{ar}	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 _a	2.1	8.3	14.1	16.0	10.4

^aBrown-Ladner Method $x = y = 2$

^bVPO in THF Extrapolated to Infinite Dilution.

Table IV-E-VI.
Average Molecular Properties of Carboids^a

	FMC-COED	Synthoil	HRI H-Coal	Catalytic Inc. SRC	PAMCO SRC
Molecular Formula	C _{25.76} H _{22.26} N _{0.55} O _{2.98} S _{0.23}	C _{69.64} H _{53.37} N _{1.10} O _{1.34} S _{0.61}	C _{73.52} H _{49.55} N _{1.11} O _{4.21} S _{0.31}	C _{74.45} H _{48.22} N _{0.70} O _{4.44} S _{0.11}	C _{42.66} H _{29.29} N _{0.43} O _{2.81} S _{0.22}
Molecular Weight ^b	394	938	1020	1026	600
H _{ar} ^a	0.43	0.49	0.52	0.51	0.485
H _a ^a	0.39	0.35	0.31	0.34	0.31
H _o ^a	0.18	0.16	0.17	0.15	0.205
f _a	0.76	0.80	0.84	0.84	0.82
H _{aru} /C _{ar}	0.86	0.66	0.61	0.59	0.61
σ	0.43	0.29	0.33	0.34	0.34
R _S	7.3	10.6	11.9	12.6	7.4
n _D	1.5	1.5	1.5	1.4	1.7
C _A	19.5	55.5	61.8	62.7	35.1
R _A	2.3	10.5	12.9	14.0	7.8

^aBrown and Ladner Method $x = y = 2$

^bVPO in UMF

Table IV-E-VII.

Asphaltene Carbon Aromaticity, f_a Comparison

Method	Synthoil	HRI H-Coal	FMC-COED	Cat. Inc. SRC	PAMCO SRC
^1H NMR*	0.71	0.78	0.72	0.79	0.76
^{13}C NMR**	0.66	0.72	0.66	0.76	0.73
X-Ray***	0.63	0.67	0.58	0.68	0.69

$$*f_a = \frac{\frac{C}{H} - \frac{H_{\alpha} + H_{\text{sat}}}{2}}{\frac{C}{H}}, \text{ Section IV-E}$$

$$**f_a = \frac{C_{\text{aromatic}}}{C_{\text{aromatic}} + C_{\text{sat}}}, \text{ Section IV-E}$$

$$***f_a = \frac{\text{Area}_{002}}{\text{Area}_{002} + \text{Area}_{\gamma}}, \text{ Section IV-D}$$

Table IV-E-VIII. ^{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	--	0.72	0.63
Amberlyst-15 Pyridine Eluted	0.76	0.67	--	0.73	0.72

Fig. IV-E-1.

Fig. IV-E-2. $\frac{H_{ARU}}{C_{AR}}$ VALUES FOR SELECTED AROMATIC RING SYSTEMS

Fig. IV-E-3. VARIATION IN AROMATIC RING SIZE VS. ATOMIC C/H RATIO

Fig. IV-E-4. ^{13}C NMR SPECTRUM OF SYNTHOIL ASPHALTENE

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IV-F. X-Ray-NMR Analysis

From the x-ray diffraction analysis (section IV-D) it is possible to obtain L_a , the average layer diameter of the sheets, which is one of the most important structural parameters. Although L_a is generally considered to be the diameter of the aromatic sheet, this is only strictly correct for wholly aromatic molecules. For such systems, which are kata-condensed, L_a is related to the number of carbons per aromatic structural unit (C_{Au}) by the equation (1):

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

However, the aromatic systems in coal liquid fractions contain some heteroatoms in place of carbons, and contain some rings which may be partially or completely saturated. Therefore, the dimensions of the sheet may be considered to include heteroatoms and carbons of side chains which are also restricted to the plane of the sheet. In order to correct the above equation for the latter effect it is necessary to multiply L_a by the factor $\frac{C_A}{C_A + R_S}$ which may be obtained from the pre-

ceeding NMR analysis. The structural parameter C_{Au} may be divided into the total number of aromatic carbons per molecule, C_A , to obtain the number of aromatic structural units per molecule, N . The results of such calculations are presented in Table IV-F-I. For asphaltenes the results agree with those previously deduced from NMR alone. The C_{Au} values are generally close to 14 except for FMC-COED which is 11.5. These values are close to 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 except the FMC-COED asphaltene which has an N value of 1.6.

The N values of a variety of coal-derived liquid products are determined and listed in Table IV-F-III. For the coal liquid product, N value is approximately 2 (2).

Hypothetical Average Structures. By combining the structural information obtained by NMR and functional group analyses (Table IV-F-II) with that obtained by the x-ray method (Table IV-F-I), it is possible to derive hypothetical average structures for asphaltene molecules. Examples of such molecules, for Synthoil asphaltene, are shown in Fig. IV-F-1. A comparison of the average molecular parameters obtained experimentally with those calculated for the hypothetical structures shown in Fig. IV-F-1 is presented in Table IV-F-II. The results are seen to agree reasonably well in most cases.

Table IV-F-I.

Asphaltene Structural Parameters Calculated From X-Ray and NMR Data

Asphaltenes	L_a^a	L_a^{*b}	C_{Au}^c	N^d
Synthoil	10.3	7.9	14.9	2.0
HRI H-Coal	8.2	6.6	12.7	2.2
FMC-COED	8.0	5.8	11.5	1.6
PAMCO SRC	10.0	7.9	14.9	1.9
Cat. Inc. SRC	9.4	7.6	14.4	2.0

aL_a = X-ray diameter of the aromatic sheet + α carbons of side chains, Å, from Diamond's curve (11) band.

$$^bL_a^* = L_a \left(\frac{C_A}{C_A + R_S} \right)$$

$$^cC_{Au} = \text{aromatic carbons per structural unit} = \frac{L_a^* + 1.23}{0.615}$$

$$^dN = \text{Number of aromatic structural units per molecule} = \frac{C_A}{C_{Au}}$$

Table IV-F-II.
Comparison of Average Molecular Parameters for Synthoil Asphaltene

	Experimentally Determined	From Hypothetical Amphoteric	Average Structures Acid/Neutral
Molecular Formula	$C_{41}H_{35}N_{0.7}O_{1.4}S_{0.07}$	$C_{39}H_{35}N_1O_2S_0$	$C_{41}H_{37}O_1N_1S_0$
Molecular Weight	561	549	559
H_{ar}^*	0.31	0.29	0.30
H_a^*	0.42	0.40	0.43
H_o^*	0.25	0.29	0.27
f_a	0.71	0.69	0.68
H_{aru}/C_{ar}	0.67	0.71	0.66
σ	0.45	0.47	0.47
R_S	8.8	9	9
n	1.6	1.5	1.6
C_A	29.1	28	28
R_A	5.9	6	7
C/H	1.16	1.11	1.11
$\alpha\text{-CH}^a$	1.93	2	2
$\geq\beta\text{-CH}^a$	1.31	1	1
C_{Au}^b	14.9	14	14.5
N^b	2.0	2	2

^aDetermined from ^{13}C NMR analysis.

^bFrom X-ray-NMR analysis-considering aromatic ring nitrogen as carbon.

Table IV-F-III. Structural Parameters Calculated From X-Ray and NMR Data

Asphaltenes	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
PANCO	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	75.03	11.35	19.87	3.77
FMC-COED	10.0	16.30	4.09	12.97	1.26
PANCO	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
PANCO	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, $\text{\AA}$, 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. 16

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.

Fig. IV-F-1.

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1. Introduction. Infrared spectra of coal-derived products are generally very similar. A typical infrared spectrum of a coal-derived asphaltene, taken as a KBr mull, is presented in Fig. IV-G-1. Identification of the various bands is given (1). Infrared analysis has been used to determine qualitatively certain structural parameters such as: saturated hydrogen to carbon ratio (2), methyl content (3), aromatic/aliphatic, CH/CH_2 ratio and methyl/methylene, CH_3/CH_2 ratio (3). However, ^1H and ^{13}C NMR methods are now believed to afford more reliable structural parameters. The one area in which infrared methods still are very useful is in the determination of nitrogen and oxygen functional groups.

2. Experimental. Infrared spectra were obtained in dilute solution of deuteriochloroform or carbon disulfide on a Beckman Acculab 6 IR or as KBr discs. The solution spectra were obtained in either sodium chloride cells, or in 1-cm matched near-infrared silica cells. 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 and/or the asphaltene. Because the 3600 cm^{-1} H_2O band appears at the same position as the asphaltene monomeric OH band, it was 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 was used to correct for H_2O absorbance when quantitative measurements were carried out.

Trimethyl silyl ethers of asphaltenes were synthesized by refluxing the asphaltene with excess 1,1,1,3,3,3-hexamethyldisilazane (HMDS), and catalytic amounts of trimethylchlorosilane and pyridine in either benzene or tetrahydrofuran (4). After removal of liquids by rotary evaporation, the silyl-derivatives were freeze-dried to powders from benzene, and dried under vacuum to constant weight. The number of trimethylsilyl groups introduced was determined by proton NMR analysis (5) after the silyl derivative was checked by infrared in dilute solution to ensure complete removal of hydroxyl groups. Under the conditions used to silylate the asphaltenes, nitrogen-containing functional groups in coal have been reported not to react to form derivatives (6). We found no evidence for NH silylation by examining the asphaltenes before and after silylation by infrared.

The non-basic benzene-eluted chromatographic fractions (Section III-A), and in one case a non-basic fraction, obtained by HCl precipitation of basic asphaltenes were further treated to remove any residual basic compounds by methylation. Methylations were carried out in benzene with a large excess (35/1) of methyl iodide. The reaction solutions were refluxed for one week, and any benzene insoluble product was removed by filtration. The benzene soluble products were recovered by freeze drying the concentrated benzene solutions.

3. Results and Discussion. Assignments for the various peaks in the OH and NH region, shown in Fig. IV-G-2 and Table IV-G-I, are well established from earlier work on petroleum fractions (7,8) and coal-derived asphaltenes (9) with the exception of the small 3540 cm^{-1} band. A band at 3540 cm^{-1} was assigned to a hydrogen bonded phenolic OH for phenolic species in petroleum distillates (7). For Synthoil asphaltene it was reported that temperature studies indicate that the 3590 cm^{-1} and 3560 cm^{-1} bands do not change relative to one another. This was taken to mean that the second band was not from an intramolecularly H-bonded phenolic hydroxyl group (9). Workers at PERC (10) report that this band at 3600 cm^{-1} was 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. IV-G-2), which suggests that this band could be from a species capable of being silylated. Others have assigned this band to an intramolecular associated phenolic OH (plus weaker carbonylic acid OH) (11).

Infrared spectra were obtained in dilute CDCl_3 solution down to 0.3 g/ where self-association between asphaltenes is not significant (12). Plots of absorbance vs. concentrations were generally linear below concentrations of 10 g/ and could be extrapolated to a value of zero at infinite dilution (Figs IV-G-3, IV-G-4). However, some of the asphaltenes (FMC-COED, Cat. Inc. SRC) afforded deviations from linearity at concentrations approaching 5 g/. Such deviations support the general premise that asphaltene association via hydrogen bonding (12-15) and concomitant loss of monomeric OH absorption are related. The extrapolated slopes of the linear portion of such plots were used to obtain absorptivity values (Table IV-G-II). These values for a_{OH} afforded a good linear correlation vs. weight percent OH, determined by the silylation method (Fig. IV-G-5), and a fair correlation between a_{NH} and weight percent pyrrolic nitrogen obtained from elemental analysis of chromatographically separated or HCl-treated asphaltenes which were also subjected to methylation to remove remaining basic nitrogen (Fig. IV-G-6). These methods for determining phenolic oxygen and pyrrolic nitrogen are believed to be superior to methods which require the use of low molecular weight model compounds. Snyder (16) has shown that molar absorptivity values show a decrease with increasing molecular weight for carbazoles and sulfoxides from petroleum. He attributes the decrease to increased crowding of the infrared active groups by adjacent alkyl groups within the same molecule as the extent of alkyl substitution is increased.

These results may then be used to calculate ether oxygen and basic nitrogen by difference from total oxygen and nitrogen. This method was applicable to all cases except for the FMC-COED asphaltene where IR absorption bands were observed at 3400 cm^{-1} and 1650 cm^{-1} which may be assigned to the NH and C=O stretches of the amide nitrogen (8). In such cases a correlation would have to be developed for calculating separate amide and basic nitrogen concentrations. The results for Synthoil asphaltene and its silica gel chromatography fractions are presented in Table IV-G-III. When the values for the separated asphaltene are arithmetically combined, the calculated total asphaltene values obtained are in good agreement with the values obtained experimentally for the original unseparated asphaltene. The results indicate that the benzene eluted fraction contains high proportions of OH and NH ($\text{OH}/\text{O}_{\text{total}} = 0.67$, $\text{NH}/\text{total} \sim 1$). The diethyl ether eluted fraction contains a large proportion of OH and a small fraction of NH ($\text{OH}/\text{O}_{\text{total}} = 0.76$, $\text{NH}/\text{N}_{\text{total}} = 0.20$). The THF fraction contains only small proportions of OH and NH (~ 0.20 each). The starting unseparated asphaltene contains a majority of both OH and NH (0.69 and 0.53 respectively). The presence of phenolic and pyrrolic species in the basic fractions tends to support the idea that asphaltenes are made up of amphoteric molecules containing both acid/neutral and basic groups as well as acid/neutral, and basic molecules.

The oxygen and nitrogen analyses for asphaltenes from five demonstration processes are presented in Table IV-G-IV. The results show that the $\text{OH}/\text{O}_{\text{total}}$ values range from 0.59 to 0.83, and the pyrrolic $\text{NH}/\text{N}_{\text{total}}$ values range from 0.53 to 0.74. The FMC-COED pyrrolic NH could not be determined unambiguously due to the presence of possible amide type NH functional groups. (17)

Table. IV-G-I.

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

Wave Number, cm^{-1}	Assignment
3690	Water
3600	Water
3600	Free phenolic OH
3540	Associated phenolic OH or OH independent of phenolic OH
3470	Pyrrolic NH
3400	Other NH, possibly amines and/or amides
3400 - 3200 (broad)	H-bonded acidic components

Table IV-G-II.

Infrared Absorptivity Values for Asphaltene
OH and NH Stretches

Asphaltene	----- Absorptivity, a -----	
	OH _{STR} (3600 cm ⁻¹) (1/g-cm)	NH _{STR} (3470 cm ⁻¹) (1/g-cm)
	a	b
Synthoil	0.15	0.045
Synthoil Benzene Eluted	0.10	0.062
Synthoil ET ₂ O Eluted	0.26	0.023
Synthoil THF Eluted	0.06	0.026
HRI H-Coal	0.18	0.044
FMC-COED	0.39	0.024
PAMCO SRC	0.19	0.058
CAT. INC. SRC	0.22	0.037

^aTypical least squares equation $A_{OH} = 0.145 \pm 0.003g - cm/l + 0.037 \pm 0.012$,
correlation coefficient 0.999

^bTypical least squares equation $A_{NH} = 0.0454 \pm 0.0005g - cm/l + 0.0047 \pm 0.0005$,
correlation coefficient 0.999

Table IV-G-III.

Synthoil Asphaltene and Silica Gel Chromatography Fractions
Nitrogen and Oxygen Analyses

Sample	----- % Oxygen -----			----- % Nitrogen -----			% Wt. Fraction
	Total ^a	Hydroxyl ^b	Ether ^c	Total ^d	Pyrrolic ^e	Basic ^f	
Benzene Eluted	2.39	1.61	0.78	1.07	1.24	(0)	45
ET ₂ O Eluted	5.40	4.11	1.29	2.30	0.45	1.85	37
THF Eluted	5.97	1.19	4.78	2.86	0.52	2.34	18
Original Asphaltene	3.89	2.67	1.22	1.74	0.93	0.81	100
Calculated Total Asphaltene	4.15	2.45	1.69	1.84	0.82	1.02	100

^aBy difference from ultimate analysis, Error $\pm$ 1.5%, estimated sum of all errors

^bFrom NMR analysis of trimethylsilylated asphaltene TMS area, Error $\pm$ 3%, as determined by replicate measurement

^cTotal Oxygen-Hydroxyl = Ether

^dFrom ultimate analysis

^eFrom IR Absorbitivity NH stretch, Error $\pm$ 12%, as determined from least squares standard deviation of slope of correlation line.

^fTotal Nitrogen-Pyrrolic = Basic

Table IV-G-IV.
Asphaltene Oxygen and Nitrogen Analyses

Asphaltene	% Oxygen			% Nitrogen		
	Total ^a	Hydroxyl ^b	Ether ^c	Total ^d	Pyrrolic ^e	Basic ^f
Synthoil	3.89	2.67	1.22	1.74	0.93	0.81
HRI H-Coal	4.96	2.92	2.04	1.61	0.88	0.73
FMC-COED	7.11	5.88	1.23	1.70	0.47	(1.23) ^g
PAMCO SRC	4.67	2.96	1.71	1.57	1.16	0.41
CAT. INC. SRC	4.58	3.65	0.93	1.25	0.73	0.52

^aBy difference from ultimate analysis, Error $\pm$ 1.5%, estimated sum of all errors

^bFrom NMR analysis of trimethylsilylated asphaltene TMS area, Error $\pm$ 3%, as determined by replicate measurement

^cTotal Oxygen-Hydroxyl = Ether

^dFrom ultimate analysis

^eFrom IR Absorbitivity NH stretch, Error $\pm$ 12%, as determined from least squares standard deviation of slope of correlation line

^fTotal Nitrogen-Pyrrolic = Basic

^gThis sample showed IR absorption at 3400 cm^{-1} which may belong to amide type NH, therefore, Total Nitrogen-Pyrrolic = Basic + Amide Nitrogen

Fig. IV-G-1. Typical IR Spectrum. FMC-COED Crude.
Asphaltene, KBr Mull

Fig. 1V-G-2. Partial IR spectra of Synthoil asphaltene and silylated Synthoil asphaltene in the OH and NH region(CDCl₃, 1-mm path)

Fig. IV-G-3. Correlation of Synthoil Asphaltene OH Absorbance vs. Concentration in CDCl_3 .

Fig. IV-G-4. Correlation of Synthoil Asphaltene NH Absorbance vs. Concentration in CDCl₃.

Fig. IV-G-5. Correlation of Asphaltene Absorbivity of OH Stretch (3600 cm^{-1}) vs. Wt. % OH from NMR Analysis of Silylated Asphaltenes.

Fig. IV-G-6. Correlation of Asphaltene Absorbivity of NH Stretch (3470 cm^{-1}) vs. Wt. % Pyrrolic Nitrogen from Elemental Analysis.

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IV-H. Polarography

Polarography has been used for the determination of aromaticity type in coals and SRC coal liquefaction products (1). Crude estimates of reducible aromatic species in SRC solvent elution chromatography fractions have been made. The concentration of polycondensed aromatic structures produced in an SRC process was found to increase as a function of temperature and time. Polarographic analyses were carried out on Synthoil solvent fractions, Synthoil asphaltene chromatography fractions, and asphaltenes obtained from the other coal liquefaction products under study.

The current-potential curves were recorded with a Princeton Applied Research (PAR) Model 174A Polarographic Analyzer. The mode of operation employed was current-sampled DC polarography (Tast polarography). In this mode of operation the current is measured for a very short period of time (16.7 ms) just before the drop is dislodged by a drop timer. The use of slow scan rates and fairly rapid drop times produces a curve having the change in current from one step to the next so small as to produce a smooth curve. A comparison between ordinary DC polarography and current-sampled DC polarography is shown for the substrate anthracene in Fig. IV-H-1.

All potentials were measured with reference to an internal mercury pool anode in 0.1 M tetra-n-butylammonium iodide in dimethylformamide (which is -0.55 V vs. a standard calomel electrode). The Hg pool cell was thermostated at $25.0 \pm 0.5^\circ\text{C}$. The decomposition potential of the supporting electrolyte solution is approximately -2.40 volts versus the Hg pool anode. Solutions of the coal liquid solvent and chromatography fractions were run at standard concentrations of 5×10^{-4} M in deoxygenated supporting electrolyte solutions under an inert gas.

The Ilkovic equation is generally used to describe the relationship between the diffusion current and the concentration of the reducible species when polarographic measurements are carried out with a dropping mercury electrode (2):

$$i_d = knD^{1/2} C m^{2/3} t^{1/6}$$

where i_d = diffusion current in amps

$k = 607$

n = number of electrons/molecule taking part in the process

D = diffusion coefficient in cm²/sec

C = concentration of active substance in m mole/l

m = mercury drop time in sec

When m and t are measured, or held constant, and D values are approximately equal then the quantity i_d/C (diffusion constant) may be assumed to be proportional to the number of electrons per molecule involved in the reduction.

In solvents of low protonating power, such as DMF, the radical anion formed by the addition of an electron to many aromatic hydrocarbons may become long lived enough to diffuse away from the mercury drop without undergoing addition of a second electron. At more negative potentials, however, two electrons may be added. For example, in DMF, naphthalene is reduced in a single

however, in protic media naphthalene shows a single wave corresponding to a two-electron reduction:

Anthracene affords two one electron waves in aprotic media:

but only one two-electron wave in protic media (3):

Hoijsink (4) has explained results in protic media on the basis of the following mechanism: (S = substrate = aromatic hydrocarbon)

The half-wave potentials for a number of polycyclic aromatic compounds are shown in Fig. IV-H-2. The polarograms of Synthoil coal liquid solvent fractions are presented in Fig. IV-H-3. The maximum half-wave potentials and diffusion constants of coal liquid solvent fractions and asphaltenes are given in Table IV-H-I.

The results may be interpreted in a qualitative way only because of the complexity of the materials under study. Half-wave potentials of aromatic hydrocarbons are known to be related to the energy of the lowest vacant molecular orbital (5). This MO parameter is crudely related to the number and structural configuration of the individual aromatic rings which make up the condensed polycyclic aromatic ring system. Benzene, the $E^{\frac{1}{2}}$ of which is estimated to be - 3.0 V, cannot be reduced because this voltage is greater than that of any supporting electrolyte solution presently known. Small, 2-3 ring systems such as phenanthrene, naphthalene and biphenyl are reduced in the range - 1.92 to - 2.05 V. Anthracene and larger condensed ring systems undergo initial reduction in the range of - 1.0 to - 1.77 V. Inspection of Fig. IV-H-3 and Table IV-H-I reveals most of the reduction of coal liquid fractions occurs above - 1.8 V. Almost all of the major half-wave reduction waves take place at about - 2.0 volts. This trend becomes less pronounced as one proceeds along the series: oil resin asphaltene carbene carboid. The total reduction per average molecule, as measured by i_d/C , also increases along the same series. The

oil fraction which has an i_d/C value approximately equal to that of naphthalene (2.6) also undergoes almost all reduction around -2.0 V. (Substitution of aromatic rings by alkyl groups is known to raise the $E^{1/2}$ (6)). The asphaltene fractions show relatively more reduction below -1.8 V, indicative of the presence of larger ring systems. They also afford i_d/C in the range 5.4-6.4 (except FMC-COED, $i_d/C = 2.6$) which suggests addition of 2-3 electrons per molecule. This trend suggests larger aromatic ring systems and molecules which have more than one aromatic ring system. For example, the average hypothetical Synthoil asphaltene molecule could contain two 3-ring aromatic systems condensed within the naphthenic system or, possibly some 2-ring + 4-ring systems. These trends, more reduction at lower $E^{1/2}$, and higher i_d/C values, are seen to increase in going to the carbene and carboid fractions which have been shown to be comprised of larger and more aromatic systems (Sections IV-D,E,F).

Table IV-H-I.

Half-Wave Potentials and Diffusion Constants of Coal Liquid
Solvent Fractions and Asphaltenes

Sample	$-E_{\frac{1}{2}}$ Max. (volts)	$\frac{i_d^*}{C}$
Synthoil Oil	2.0	2.6
Synthoil Resin	1.9	3.9
Synthoil Asphaltene	2.0	5.4
Synthoil Carbene	2.0	6.7
Synthoil Carboid	2.0	7.8
FMC COED Asphaltene	2.0	2.6
Synthoil Asphaltene	2.0	5.4
HRI Asphaltene	2.0	5.8
PAMCO SRC Asphaltene	2.0	6.4
Cat. Inc. SRC Asphaltene	2.0	6.4
Synthoil Asphaltene	2.0	5.4
Benzene Eluted**	2.0	6.8
Diethyl Ether Eluted	2.0	4.6
THF Eluted	2.0	5.8

* At -2.20 V. i_d/C for Naphthalene = 2.4.

** Silica Gel Chromatography Fractions.

Fig. IV-H-1
POLAROGRAM OF ANTHRACENE
(1.1 mM in 0.1M tetra-n-butylammonium
iodide in dimethylformamide)

Fig. IV-H-2. Halfwave Potentials ($E_{1/2}$) of Aromatic Compounds
(In 0.1M tetra-n-butylammonium iodide - DMF)

AROMATIC COMPOUND

Fig. IV-H-3. Polarograms of Synthoil Coal Liquid Fractions..

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IV-I. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) may be used to determine the percent volatile matter, fixed carbon or char, and ash of coal liquid products. When TGA is carried out in the presence of oxygen, useful information about the oxygen sensitivity of various materials may be obtained.

All samples were run with a DuPont Model 990 Thermal Analyzer coupled with a Model 951 Thermogravimetric Analyzer. Samples were heated to $\approx 700^{\circ}\text{C}$ at $20^{\circ}\text{C}/\text{min}$ with a constant nitrogen flow, and then in a few selected cases further heated to 900°C with air. Alternatively, some samples were heated separately from room temperature to 700°C in both nitrogen and air. The percent char was calculated from the difference between the percent weight left after heating in nitrogen and the percent ash remaining. For all samples, except Synthoil carboid (ash $\approx 9\%$) less than 1% ash was present. Because such small values were difficult to measure accurately with TGA, ash values determined independently by dry ash determination were used to calculate percent char.

Thermogravimetric analysis results are presented in Table IV-I-I. Initial weight loss temperatures range from $200\text{--}250^{\circ}\text{C}$; maximum rate of weight loss is about 500°C , and the temperature at which weight loss becomes small and constant is about 600°C for all samples.

Comparison of the thermograms for Synthoil asphaltene and carboid carried out in nitrogen and air (Figs. IV-I-1 and IV-I-2) reveals that, in air, Synthoil asphaltene begins to be stabilized toward volatilization vis-a-vis Synthoil carboid at $\approx 460^{\circ}\text{C}$. At $\approx 600^{\circ}\text{C}$ the carboid is essentially completely volatilized. This behavior indicates that the asphaltene undergoes oxygen catalyzed reactions on heating which stabilize it toward further volatilization. Such reactions could be oxidative polymerization or crosslinking. In Section IV-N we report the observation that partially oxidized Synthoil asphaltene (alkaline KMnO_4 at 75°C) underwent a three-fold increase in both oxygen content and VPO molecular weight. This also was suggestive of oxidative polymerization.

Another interesting correlation observed from the TGA data related the % char formed with the color intensity values of the various materials (integrated intensity obtained by absorption spectrometry over the $400\text{--}750\text{ mm}$ range). It may be seen in Fig. IV-I-3 that the wt. % char increases as the color intensity increases. This is consistent with the idea that both visible absorption and char formation, in the various fractions, are related to the content of polyaromatic π -system molecules present in these fractions. A similar relationship is described in Section IV-J of this report between the color intensity and the ESR spin intensity of the various materials.

Table IV-I-I.
Thermogravimetric Analysis of Coal Liquid Solvent Fractions
and Asphaltene Derivatives

Sample Designation	Initial Wt. Loss Temp.	Max. Rate Wt. Loss Temp.	Constant Wt. Temp.	Wt. % ^a Char	Wt. % ^b Ash
Synthoil Oil	64	241	438	0	0.02
Synthoil Asphaltene	246	499	593	39	0.48
Synthoil Carbene	256	513	602	45	0.56
Synthoil Carboid	251	506	673	66	8.8 (9.4) ^c
HRI H-Coal Asphaltene	241	471	597	44	0.38
FMC-COED Asphaltene	178	385	532	16	0.79
PAMCO SRC Asphaltene	258	473	614	35	0.39
Cat. Inc. SRC Asphaltene	261	475	602	41	0.78
Synthoil Benzene-Eluted ^d	244	494	598	43	0.50
Synthoil Diethyl Ether-Eluted	202	494	579	23	0.51
Synthoil THF-Eluted	197	490	626	57	0.67

^a Wt. % char = (wt. % remaining N₂ - wt. % ash).

^b Determined independently by dry ashing method.

^c Determined from TGA curve.

^d Asphaltene solvent elution chromatography fractions from silica gel column.

Fig. IV-I-1. THERMOGRAVIMETRIC ANALYSIS OF SYNTHOIL ASPHALTENE

Fig. IV-I-2. THERMOGRAVIMETRIC ANALYSIS OF SYNTHOIL CARBOID

Fig. IV-I-3. RELATIONSHIP BETWEEN TGA WT. % CHAR. AND COLOR INDEX OF SOLVENT FRACTIONS ASPHALTENE DERIVATIVES

IV-J. Electron Spin Resonance

1. Introduction. Electron spin resonance (ESR) has been used in the past to study the structure and state of association of native petroleum asphaltenes (1-3). It was therefore of interest to study the ESR of coal-derived products in order to learn more about the structure, and state of association of these materials (12).

2. Experimental. ESR spectra were measured with a Varian E-12 dual cavity spectrometer operating at a microwave frequency of about 9.5 GHz. A microwave power of 1 milliwatt was used to avoid saturation effects, and a modulation amplitude of 1 gauss was used to minimize distortion.

A standard strong pitch sample, supplied by Varian Associates (0.1% pitch in KCl, $N_S = 3 \times 10^{15}$ spins per cm, $g = 2.0028$), was used as a reference standard for determining g-factors and spin intensities of liquid and solution samples. Since the microwave frequency and the Q-factor for the two channels of the dual cavity are identical, the g-values and the N_S values may be calculated from the following formulas:

$$(1) \quad g = 2.0028 \left(1 - \frac{\Delta H}{H} \right)$$

where ΔH = the field spacing between the field at resonance for the sample and the reference.

$$(2) \quad N_S = N_R \frac{(\Delta H_S)^2}{(\Delta H_R)^2} \frac{I_S}{I_R}$$

where I is the intensity and ΔH is the line-width. Samples were measured as solids in evacuated tubes in pyridine and benzene solutions.

3. Results and Discussion

a. General. For a typical asphaltene, or asphaltene derivative (Fig. IV-J-1), 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 co-workers (4):

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

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

Lande g-values, spin intensities, line widths, MW and spin/molecules values are reported in Table IV-J-I for coal liquid solvent fractions and asphaltene derived products. The g-values for all the coal liquid derived materials fall in the narrow range of 2.0028-2.0036. These g-values fall within the range previously reported for asphaltic fractions of petroleum, are close to those observed for neutral radicals rather than to those observed for either radical ions or semiquinones (5). Spin intensities have been converted into free spin per molecules values. The Synthoil carboid fraction and the THF eluted fraction from Synthoil asphaltene are seen to have maximum values of about one free spin per 80 and 90 molecules, respectively. The Synthoil oil fraction has the lowest values, about one free spin per 50,000 molecules. The spin intensity has been plotted against the color

intensity of the various samples (integrated intensity obtained by absorption spectrometry over the 400-750 nm range (Fig. IV-J-2). It may be seen that the spin intensity increases as the color intensity increases. Since absorption in the visible region is most likely due to the mobile electrons of the polyaromatic π -system, it appears likely that only those molecules possessing large delocalized aromatic π -systems possess free spins in solutions.

b. Association Studies. Previously it was suggested that coal-derived asphaltene association could be explained on the basis of a hydrogen bonding donor-acceptor model (6-7). However, because of published reports support charge transfer complexation in petroleum asphaltenes (8-9), we decided to study coal-derived asphaltene to see if any evidence could be found to support this type of association mechanism. ESR studies were carried out on Synthoil asphaltene dissolved in benzene and pyridine, and also on solid samples of this asphaltene and its chromatographically separated components.

The dependence of the ESR signal intensity vs. the concentration of asphaltene in benzene solution is presented in Fig. IV-J-3. Despite the scatter in the experimental points, no discernible trend is evident. One point, determined in the solvent pyridine, is also presented. A second series of measurements was made on solid samples of Synthoil asphaltene and its chromatographically separated components, and on Synthoil asphaltene-TCNE, and I_2 charge transfer complexes. The temperature dependence of the signal intensity was studied. The results are presented in Figs. IV-J-4 - IV-J-6.

The association of Synthoil asphaltenes in benzene has been studied by VPO. The associated asphaltenes are believed to approach complete dissociation as their concentrations approach infinite dilution (7). As a concentration of 1 g/l the asphaltene is believed to be present almost completely as the monomer. At ≈ 20 g/l the monomer fraction is about 0.5, and above this concentration higher oligomers predominate. In some cases charge transfer complexes may be formed which have a triplet state which lies not far above the ground state (10). If this were the case such association complexes might have triplet states which were sufficiently populated at room temperature so that these complexes would show increased spin intensity. The fact that we observed no increase in spin intensity with concentration rules out the possibility, but does not rule out the possibility of complex formation in which the paramagnetic triplet state is energetically too high to be populated at room temperature.

In the solid state Synthoil asphaltene is believed to be associated in stacked clusters containing ≈ 4 aromatic sheets per cluster (IV-D). Such systems, if they were formed by charge transfer association might be expected to show ESR intensity-temperature dependence curves containing both $1/T$ (Curie-Weiss doublet) and exponential (singlet-triplet) components (8-9). The results presented in Figs. IV-J-3 - IV-J-6 indicate no exponential component down to 95°K for either Synthoil asphaltene, or for charge transfer complexes formed between a basic Synthoil asphaltene fraction and the acceptors TCNE and I_2 . This suggests that coal derived asphaltene complexes contain little or no triplet states with energies low enough to be populated at our experimental temperatures. These findings do not preclude the possibility of weak charge transfer complexes being formed, but they suggest that the ESR method of confirming the presence of such complexes may not be applicable in such cases.

As alternative procedure, previously employed by Retcofsky et al. (11), involves determining the temperature variation of the ESR intensities of asphaltenes and some of the separated components of the asphaltenes. They found, for their acid/neutral and base components, that the weighted averages of these two components reproduce the temperature dependence of the total asphaltene before separation. We carried out the same type of study on our silica gel chromatography fractions, Fig. IV-J-4, and also found that the weighted averages of the benzene, diethyl ether, and THF eluted fractions reproduce the temperature dependence of the total asphaltene before separation. This suggests that charge transfer interactions if present, may not be major binding forces between asphaltene components.

Table IV-J-I.

Lande g-Values, Intensity and Line Width of Coal Liquid Solvent Fractions^a
and Asphaltene Derived Products

Sample	g-Value	Intensity, Ng ($\times 10^{18}$) Spins/g	Line Width ΔH , Gauss	VPO MW ^b	Spin / Molecules
Synthoil Asphaltene	2.0028	4	5.6	567	300
HRI H-Coal Asphaltene	2.0029	3	5.2	502	400
FMC-COED Asphaltene	2.0036	0.4	5.1	370	5,000
PAMCO SRC Asphaltene	2.0030	1.7	5.8	545	800
Cat. Inc. SRC Asphaltene	2.0030	1.7	5.1	477	700
Synthoil Oil ^f	2.0034	0.05	5.6	243 ^c	50,000
Synthoil Resin	2.0032	0.7	6.5	305 ^c	3,000
Synthoil Carbene	2.0029	6	5.2	861	80
Synthoil Carboid	2.0029	9	5.2	(844) ^d	80
Synthoil Benzene-Eluted	2.0029	1.0	6.7	534	1,100
Synthoil Et ₂ O-Eluted	2.0030	1.5	6.5	522	800
Synthoil THF-Eluted	2.0030	10	5.8	(612) ^e	90
Synthoil Sternberg Acid/Neutral	2.0032	0.4	6.2	466	3,000

^a Measured in pyridine solution

^b Extrapolated infinite dilution average value in benzene, CHCl₃, and THF unless otherwise cited.

^c Average finite concentration value in benzene.

^d Average finite concentration value in DMF, corrected for 8.8% ash.

^e Infinite dilution value in THF obtained by combining values for two THF eluted fractions.

^f ESR run on neat liquid.

Fig. IV-J-1—ESR SPECTRUM OF SYNTHOIL ASPHALTENE

Fig. IV-J-2 PLOT OF COLOR INDEX (I) VS SPINS/g (Ng) FOR COAL LIQUID SOLVENT FRACTIONS AND ASPHALTENE DERIVED PRODUCTS

Fig. IV-J-3

ESR SPIN INTENSITY OF SYNTHOIL ASPHALTENE VS CONCENTRATION
IN BENZENE SOLUTION

Fig. IV-J-4.

VARIABLE ESR TEMPERATURE DATA FOR SYNTHOIL ASPHALTENE
AND SYNTHOIL ASPHALTENE CHROMATOGRAPHY FRACTIONS

Fig. IV-J-5.
VARIABLE ESR TEMPERATURE DATA FOR SYNTHOIL ASPHALTENE
(Et₂O ELUTED CHROMATOGRAPHY FRACTION)-TCNE CHARGE TRANSFER
COMPLEX

Fig. IV-J-6. VARIABLE ESR TEMPERATURE DATA FOR SYNTHOIL ASPHALTENE
(Et_2O ELUTED CHROMATOGRAPHY FRACTION)- I_2 CHARGE TRANSFER
COMPLEX

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IV-K. Ultraviolet-Visible Spectroscopy

The UV-visible spectra for most asphaltene fractions do not exhibit distinctive features. They usually absorb strongly at the 220nm and slowly decrease to 700nm indicating a glass spectrum feature. This may be derived from the different sizes of aromatic systems which they contain. For verification an equimolar mixture of 12 polynuclear hydrocarbons are determined in the KBr-solid state. The features of the most aromatic absorption have been lost (Fig. IV-K-1).

Color intensities or color indices can be determined as a relative arbitrary unit in a solvent such as tetrahydrofuran (1). This is a simple method and the parameter can be used to follow the reaction or conversion of any fossil energy sources.

Table IV-K-I shows the color indices (integrated absorption of a species between 750nm and 400nm) of the various solvent fractions for different coal liquids. Since the color index of an aromatic molecule is a function of the size of the aromatic π -system, it appears reasonable to assume that the increase in the color indices in going from oil, to resin to asphaltene to carbene, reflects an increase in the size of the respective π -systems.

Other correlation of color indices are discussed in Sections IV-I and IV-P, for example, Figures IV-I-3 and IV-P-8.

Table IV-K-I- Color Indices, I* of Solvent Fractions

Fraction	Synthoil	FMC-COED	PAMCO-SRC***	Cat. Inc.-SRC
Oil	0.1	0.1	0.0	0.4
Resin	1.7	1.8	0.6	1.5
Asphaltene	12.7	4.1	10.4	16.6
Carbene	24.7	5.3	25.6	48.5
Carboid**	33.3	14.2	50.7	56.3

* $I = \int_{400\text{nm}}^{750\text{nm}} \text{Ad}\lambda \text{ in THF} \times 10^{-1} \text{ (relative) (mm}^2, \text{cm}^{-1}, \text{ml/mg)}$

** Due to insolubility in THF, the I values had to be measured in pyridine.

*** Filter feed.

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IV-L. Mass Spectroscopy

An Allied Electrical Industries Model MS-9 was used in this work. A direct insertion probe held at 240°C was used to introduce the solid samples into the region of ionization. Ionizing voltages of 16 eV and 70 eV were used. The 16 eV spectra is believed to represent the broad envelopes of molecular ions. The 70 eV spectra consists of two broad envelopes of peaks corresponding to the singularly and doubly charged aromatic species, which are believed to represent fragment peaks due to β -cleavage of aliphatic and naphthenic portions of the asphaltene molecules. A test run was done on polynuclear mixture of 19 components, the observed and calculated intensities are comparable as shown in Fig. IV-L-1 (1,2).

Figure IV-L-2 shows the low and high eV spectra of the Synthoil asphaltene. The weight average molecular weight of the Synthoil asphaltene, calculated from the 16 eV mass spectrum, assuming equal sensitivity factors, was 633.^a This value may be compared with the number average molecular weight of 552 determined by vapor phase osmometry in benzene.

Also, 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 investigated.

The low resolution 16 eV spectrum is presented as a bar graph in Fig. IV-L-3. The spectrum suggests the presence of series, differing by 14 mass units, of structurally related parent peaks (3).

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.

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

Fig. IV-L-1. Polynuclear Mixture of 19 Components

70 eV

16 eV

MASS (M/E)

Fig. IV-L-2. Mass Spectrograph of Synthoil Asphaltene

Fig. IV-L-3: Mass Spectrograph of Synthoil Asphaltene
Silica Gel Chromatographic Cut 16 eV

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IV-M. Donor-Acceptor Complexes

Coal-derived asphaltenes are thought to be key intermediates in the conversion of coal to oil (1). A model, based on X-ray diffraction studies (2), has been proposed to describe the macrostructure of associated asphaltenes in the solid state (3). The state of association of these species in benzene and tetrahydrofuran solution has been studied by vapor pressure osmometry, and molecular weights have been reported as a function of concentration (4). Evidence has been presented recently in the literature supporting a hydrogen-bonding donor-acceptor association in solution (5-7). Previously the mechanism of association of petroleum asphaltenes (8-10), and coal and chars (11) was described in terms of charge transfer donor-acceptor forces. A study of the properties of iodine-petroleum asphaltene complexes was carried out, and led to useful information on the structure of petroleum asphaltenes (12). It was therefore decided to synthesize donor-acceptor complexes of coal-derived asphaltenes, and to study their properties by a variety of physical and analytical techniques (19).

1. Experimental. Coal-derived asphaltenes were separated by solvent fractionation (13,14) from coal liquids produced in five major demonstration liquefaction processes: Synthoil, HRI H-Coal, FMC-COED, Catalytic Inc. SRC, and PAMCO SRC. The asphaltenes were further separated into three fractions by exhaustive solvent elution chromatography on silica gel using the solvents: benzene, diethyl ether, and tetrahydrofuran. The benzene and diethyl ether eluted fractions, known to contain a higher and lower proportion of basic asphaltene molecules (13), were used in addition to starting asphaltene to form some of the complexes.

Complexes were formed by mixing benzene solutions of the asphaltenes (~ 50 g/l) with benzene solutions of either iodine or tetracyanoethylene (freshly sublimed reagent grade) in the approximate mole ratios, asphaltene/acceptor = 0.7 - 1.0/1. A precipitate forms rapidly. It was filtered, washed with benzene and dried overnight at 40°C/2mm Hg.

The dark brown to black I₂-asphaltene complexes are relatively insoluble in benzene, carbon disulfide, and pentane, and slightly to moderately soluble in chloroform and tetrahydrofuran. The brown-black TCNE-asphaltene complexes are only moderately soluble in THF.

Analyses were performed by the ELEK Microanalytical Laboratories, Torrance, California. Iodine was determined gravimetrically after nitric acid oxidation in the presence of silver nitrate; nitrogen was determined by the Dumas procedure. Molecular weights were measured in THF with a Mechrolab Model 301A Vapor Pressure Osmometer. Infrared spectra were determined as KBr disks on a Beckman Acculab 6 IR. Ultraviolet-visible spectra were run in either chloroform or tetrahydrofuran solution on a Beckman Model 25 Spectrophotometer, X-ray diffraction measurements were made with a General Electric XRD-6 X-ray diffractometer with a CuK α radiation source (15). Electron spin resonance spectra were taken with a Varian E-12 x-band spectrometer. Resistivity measurements were carried out at 25°C over the pressure range 10-3000 atmospheres by use of a cell and procedure described by Hadek (16).

2. Results and Discussion.

Composition of Complexes. Analytical data for I₂-asphaltene and TCNE-asphaltene complexes are presented in Tables IV M-I & IV M-II. The mole ratios of asphaltene to iodine are approximately 1 to 1 with the exception of the FMC-COED-I₂

complex which afforded a tar-like material initially instead of a precipitate. The mole ratios of asphaltene to TCNE are more widespread, but are closer to 2 to 1. The mole ratio calculations are based on the assumption that the molecular weight of the asphaltene portion of the complex is the same as the molecular weight of the starting asphaltene, which may not be strictly correct.

Ultraviolet-Visible Spectra of Complexes. Measurement of the UV-Visible spectrum of I₂-asphaltene complexes in THF or CHCl₃ (Fig. IV-M-1) 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. 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.

Measurement of the UV-Visible spectrum of TCNE-asphaltene complexes in THF (Fig. IV-M-2) 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-transfer absorption bands of the donor asphaltene molecules and the π -acceptor TCNE.

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 400-600 cm⁻¹ region, and no aromatic-I₂ bands in the 992 cm⁻¹ to 1200 cm⁻¹ region (17, 18).

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.

X-Ray Diffraction. The X-ray diffraction patterns of asphaltenes show diffuse bands typical of mesomorphic or semicrystalline substances (2): the (002) band is attributed to the interplanar spacing between condensed aromatic rings of ≈ 3.5 Å; the gamma band is attributed to the spacing between disordered aliphatic chains or alicyclic rings of ≈ 4.6 Å (Fig. IV-M-3).

X-ray analysis of petroleum asphaltene-iodine complexes indicates a low degree of order exists within these complexes (12). The (002) band disappears on forming a petroleum asphaltene-iodine complex, and a new band at 8.7 Å appears. These observations were rationalized by assuming that the layered structure of the asphaltene was expanded from 3.5 Å to 8.7 Å by intercalation of a molecule of iodine between the aromatic layers of the asphaltene.

In the case of coal-derived 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 ≈ 8.7 Å. 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.

The X-ray diffraction patterns of asphaltene-TCNE complexes have been measured. 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 Å. The X-ray diffraction patterns were analyzed, and aromaticity and X-ray crystallite parameters determined (Table IV-M III). The results indicate structural differences between the asphaltene base fractions (Et₂O 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, may be rationalized in terms of asphaltene-TCNE complex clusters such as the ones shown in Fig. IV-M-4. 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 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.

ESR Spectra. ESR parameters of Synthoil asphaltenes and their I_2 and TCNE complexes are presented in Table IV-M-IV. Spin intensity is seen to be significantly larger in the complexes than in the uncomplexed asphaltenes. This may be indicative of low lying triplet states in the complexes which can be populated at room temperature.

Conductivity. The resistivities of a series of asphaltenes and their I_2 and TCNE complexes have been measured, and range between about 3×10^9 - 3×10^{10} ohm-cm at 25°C and 10 atm. pressure. In each case the resistivity of the complex is lower than that of the parent asphaltene, but not by more than an order of magnitude. These resistivities may be contrasted with those obtained for petroleum asphaltenes which exhibit higher values, in the insulator range, of 10^{16} - 10^{17} ohm-cm at 25°C, but upon addition of iodine, the resistivities of the complexes formed decrease by about the million-fold (12).

The effect of pressure, over the range 10-3000 atm., on resistivity is shown in Fig. IV-M-5. The resistivity of the uncomplexed asphaltenes is seen to remain essentially constant, however, two of the asphaltene- I_2 complexes afford a decrease in resistivity over the same pressure range. This is consistent with electric conduction.

Table IV-M-I
Analytical Data for I₂-Asphaltene Complexes

<u>Asphaltene</u>	<u>VPO^a MW</u>	<u>% Iodine</u>	<u>Asphaltene^b / I₂</u>
Synthoil	560	35.02	0.84
HRI H-Coal	492	28.13	1.33
FMC-COED ^c	375	22.00	2.38
PAMCO SRC ^d	363	38.36	1.12
CAT. INC. SRC	483	32.72	1.08
CAT. INC. Benzene Eluted	511	30.34	1.15
CAT. INC. Et ₂ O Eluted ^e	459	34.03	1.08

^aAverage of infinite dilution MW's in benzene and tetrahydrofuran of starting asphaltenes. ^bMole ratios calculated assuming MW of asphaltene portion of complex is the same as the MW of the starting asphaltene. ^cA tar formed on mixing the asphaltene/I₂ solutions. ^dFrom Filter Feed. ^eEluted from Silica Gel.

Table IV-M-II

Analytical Data for TCNE-Asphaltene Complexes

<u>Asphaltene^a</u>	<u>VPO^b MW</u>	<u>%N Complex - %N Starting Asphaltene</u>	<u>Asphaltene^c/ TCNE</u>
Synthoil	522	5.08 ^d , 5.21	1.87, 1.82
HRI H-Coal	496	5.13	1.95
FMC-COED	383	5.48	2.34
PAMCO SRC	532	3.76	2.56
CAT. INC. SRC	459	7.61	1.33

^aAsphaltene eluted from Silica Gel with Et₂O after exhaustive elution of asphaltene with benzene. ^bAverage of infinite dilution MW's in benzene and tetrahydrofuran of starting asphaltenes. ^cMole ratios calculated assuming MW of asphaltene portion of complex is the same as the MW of the starting asphaltene. ^dTwo different preparations.

Table IV-M-III

X-Ray Analysis of Synthoil Asphaltene Basic Fraction and Synthoil
Asphaltene-TCNE Complex

	Synthoil Asphaltene Et ₂ O Eluted	Synthoil Asphaltene Et ₂ O Eluted-TCNE Complex
f_a^1	0.64	0.72
d_m^2	3.47	3.46
d_γ^2	4.52	4.52
L_c^2	12.1	13.8
L_a^3 (11) band	10.0	10.1
L_a^4 (11) band	11.4	11.9
M^5	4	5

$f_a^1 = C_A / C_{\text{total}} = A_{002} / A_{002} + A_\gamma$. d_m^2 = interlayer distance, d_γ = interchain distance, L_c^2 = diameter of the aromatic clusters perpendicular to the plane of the sheets. L_a^3 = diameter of the aromatic sheets from Diamond's Curve. L_a^4 = diameter of the aromatic sheets from Scherrer's Eq., all values in Å. M^5 = Effective number of aromatic sheets associated in a stacked cluster.

Table IV-M-IV

ESR Parameters of Asphaltenes and Asphaltene Complexes^a

<u>Sample</u>	<u>g-Value^b</u>	<u>Intensity, N^b (x10¹⁸) Spins/g</u>	<u>Line Width ΔH, Gauss</u>
Synthoil Asphaltene	2.0030	1.4	6.4
Synthoil Asph. Et ₂ O Eluted	2.0031	0.8	6.8
Synthoil Asph.-I ₂ Complex	2.0032	28.8	9.8
Synthoil Asph. Et ₂ O Eluted- TCNE Complex	2.0029	5.5	8.2

^aSolid samples. ^bMeasured relative to DPPH.

Fig. IV-M-1
UV-VIS. SPECTRA OF I_2 , SYNTHOIL ASPHALTENE, AND
SYNTHOIL ASPHALTENE- I_2 COMPLEX IN $CHCl_3$

Fig. IV-M-2

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

146

Fig. IV-M-3

Fig. IV-M-4

Fig. IV-M-5

Conductivity of Cat. Inc. SRC Asphaltene and
Asphaltene-I₂ Complexes

BASIC ASPHALTENE CUT AMB.-15-I₂ COMPLEX

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IV-N. Oxidation

Oxidation has been used widely as a means of characterizing naturally occurring complex molecules such as coals(1-4), oil shale (5-8), and petroleum asphaltenes(6,7). 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 $\text{Na}_2\text{Cr}_2\text{O}_7$ (4). Young et al. (5) 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 (7) have described the effects of a variety of oxidizing agents on Athabasca asphaltenes 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 IV-N-1 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 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 are given in Table IV-N-2. 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.

A mild, stepwise oxidation procedure was also used in order to avoid extensive degradation of the oxidized asphaltene intermediate products (Fig. IV-N-1). Approximately 4 g. of asphaltene was subjected to the stepwise alkaline permanganate oxidation procedure. In each step, 100 ml of preheated KMnO_4 -KOH solution (1% KMnO_4 in 0.1% KOH by weight) was added to the asphaltene. The mixture was allowed to react, with stirring, under nitrogen at a temperature of $75 \pm 2^\circ\text{C}$ until the violet color of the permanganate disappeared. The product mixture was then filtered to separate the aqueous phase from the solid residue of unreacted asphaltene and MnO_2 precipitate. The MnO_2 precipitate was removed by treatment with hot acidified oxalic acid solution, followed by filtration and thorough washing with water and alkaline water. The unreacted asphaltene, after drying and weighing, was subjected to the next oxidation step.

The aqueous oxidized asphaltene solution was acidified and filtered. The more highly oxidized filtrate was extracted with diethyl ether, and after removal of the Et_2O and weighing, this material was esterified with BF_3/MeOH . The esterified product was extracted into diethyl ether and examined by gas chromatography (Fig. IV-N-2).

The rate of oxidation of Synthoil asphaltene is shown in Fig. IV-N-3, for duplicate runs. It requires 8-10 steps to oxidize 90-95% of the asphaltene under the stated conditions. After an early induction period, probably caused by the difficulty of initially wetting the asphaltene, the asphaltene oxidation appears to proceed at a constant rate until near the end of the oxidation.

The highly oxidized product of Synthoil asphaltene, which was esterified with BF_3/MeOH , was examined by GC-MS analysis.* A Finnigan high performance system, equipped with the INCOS automated library search system for matching unknowns with library spectra was used. The column used was a 6 foot, 3% Dexsil, held at 50°C for 2 minutes, then programmed at $10^\circ/\text{minute}$ to 260°C , then held for 15 minutes. The GC spectrum is shown in Fig. IV-N-4. The probable identification of the separated peaks by mass spectrometry is presented in Table IV-N-III.

The complexity of the observed benzene aromatic acid type products could be indicative of a high degree of aliphatic or alicyclic linkages between aromatic units. Alternatively, it may be that our oxidation conditions are producing degradation of larger aromatic rings such as naphthalene, anthracene and phenanthrene.

The results of our oxidation studies indicate that the rates of oxidation of asphaltenes, and other liquefied coal derived products may be measured. It also appears likely that esterified oxidized asphaltene fragments, which have been separated by gas chromatography, could be identified by the GC-MS technique. This information should be useful for characterizing the basic structures of asphaltenes.

*GC-MS analysis was carried out by the California Analytical Laboratories, Inc., Sacramento, California.

Table IV-N-I
Oxidation of Synthoil Asphaltene

<u>Oxidant</u>	<u>Medium</u>	----- Product % -----			
		<u>OH₂ sol</u>	<u>OH₂ insol</u>	<u>Aq. H⁺ soluble</u>	<u>Aq. H⁺ insoluble</u>
Potassium permanganate	Alkaline 95°/1hr	10	37*	(14)	(3)
	95°/4hrs	0	0	?	?
Sodium Peroxide	Alkaline 80°/16hrs	74	23	(1)	?
Potassium Dichromate	Neutral 100°/5hrs	88	9	(3)	?

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

Table IV-N-II
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.

Table IV-N-III

Mass Spectrometric Identification of GC Separated Esterified
KMnO₄ Oxidized Synthoil Asphaltene

<u>Peak No.</u>	<u>Assignment^a</u>	<u>Parent Peak</u>
1	2-Acetylbut-1-ene	98
2	(C ₃ -benzene)	120
3	Methylbenzoate	136
4	Adipic Acid,-dimethyl ester	157
5	Phthalic anhydride	148
6	Dimethylphthalate	194
7	(Methylphthalic anhydride)	162
8	(Methyl dimethylphthalate)	208
9	(Methyl dimethylphthalate)	208
10	(C ₆ H ₄ (CH ₂ COOCH ₃) ₂ , C ₆ H ₂ (CH ₃) ₂ (COOCH ₃) ₂)	222
11	(CH ₃ OCO-C ₆ H ₄ (CO) ₂ O)	206
12	(C ₆ H ₄ (COOCH ₃) ₃)	252
13	(C ₆ H ₃ (CH ₃)(COOCH ₃) ₃)	266

^aCompounds listed without parentheses were identified by comparison with spectra found in the INCOS library of spectra. Compounds in parentheses were tentatively identified from parent peak and cracking pattern.

Fig. IV-N-1

Stepwise Oxidation of Synthoil Asphaltene

Fig. IV-N-4. GC OF ESTERIFIED KMnO_4 OXIDIZED SYNTHOIL ASPHALTENE

Reference

N. Oxidation

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IV-0. Self-Association

Vapor Pressure Osmometry (VPO) molecular weights of coal-derived asphaltenes obtained from coal liquids produced in five major coal-liquefaction demonstration processes have been determined as a function of concentration in the solvents tetrahydrofuran (THF), chloroform, and benzene. In those three solvents over the dilute concentration range of 4 - 36g/l, it was shown that association of coal-derived asphaltenes takes place, but the dissociation tends to go to completion at infinite dilution. In order to study the self-association of the asphaltenes, the VPO molecular weights of the same asphaltenes have been determined over a wider concentration range of 4 - 60g/l and a self-association model of asphaltenes in solution has been derived and the dissociation constants; one for the dissociation of dimeric complexes and one for the dissociation of higher order complexes, have been calculated with the aid of a modern computer.

This is the first time that VPO has been used to quantitatively correlate the degree of association of coal-derived asphaltenes in solution, although a number of other techniques have been used in the past (2-8, 13, 14).

1. Theoretical

In order to investigate the self-association of phenol in carbon tetrachloride solution, Coggeshall and Saier (2) carried out an IR study of the hydroxyl stretching region of phenol and obtained very good agreement between theory and experiment by using two equilibrium constants. They derived the following two expressions:

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

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

where

n = integer

α_n = fraction of monomer bound in nth 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 $= K_2 = K_3 \dots$

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

If C is the initial concentration of monomer before any association, at equilibrium the concentrations of monomer, dimer, trimer, etc., are αC ,

$\frac{\alpha_2 C}{2}, \frac{\alpha_3 C}{3}, \dots, \frac{\alpha_n C}{n}$ and the molecular weights are $Mo, 2Mo, 3Mo, \dots$ and nMo .

Since the molecular weight measured in VPO is the number average molecular weight, it is given that

$$MW_{obs} = \frac{Mo \alpha C + 2Mo \cdot \frac{\alpha_2 C}{2} + 3Mo \cdot \frac{\alpha_3 C}{3} + \dots + nMo \cdot \frac{\alpha_n C}{n}}{C \cdot \left[\alpha + \frac{\alpha_2}{2} + \frac{\alpha_3}{3} + \frac{\alpha_n}{n} \right]} \quad 3)$$

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

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

In theory, the equilibrium constants K and K_1 can be obtained by solving Equations 2 and 4 simultaneously at two different concentrations. The approach will be discussed in the next section.

2. Experimental

Coal-derived asphaltenes were separated by solvent fractionation (9,10) from coal liquids produced in five major demonstration liquefaction processes: Synthoil, HRI H-Coal, FMC-COED, Catalytic Inc. SRC, and PAMCO SRC.

A Mechrolab Model 301A Vapor Pressure Osmometer was used to determine molecular weights with benzil employed as a standard. Both the non-aqueous probe and the thermostat were designed for 37°C. In normal runs, 6-8 molecular weights over the range 4-60 g/l were measured in the solvents benzene or THF.

A modern computer was used to solve the calculation problem according to the following steps:

- Assume values of K and K_1 .
- Calculate for α and β at two concentrations, C_1 and C_2 , from Equation 4 where MW_{obs} is the molecular weight from VPO. When the concentration is C_1 , the fraction of monomer unassociated at equilibrium is α , and when the concentration is C_2 , it is β .
- Substituting C_1, C_2, α and β into Equation 2 and get

$$K = \frac{C_1 \alpha}{2(K_1 - \bar{K}_1)} \left[2K_1 - \frac{\bar{K}_1}{2} + \sqrt{2K_1 \bar{K}_1 + \frac{\bar{K}_1^2}{4}} \right] \quad 5)$$

$$K = \frac{C_2 \beta}{2(K_1 - \bar{K}_2)} \left[2K_1 - \frac{\bar{K}_2}{2} + \sqrt{2K_1 \bar{K}_2 + \frac{\bar{K}_2^2}{4}} \right] \quad 6)$$

where $\bar{K}_1 = 2\alpha^2 C_1 / (1 - \alpha)$
 $\bar{K}_2 = 2\beta^2 C_2 / (1 - \beta)$

Since K is independent of concentration, by combining Equations 5 and 6, it is given that

$$= \frac{\frac{\alpha C_1}{2(K_1 - \bar{K}_1)}}{\frac{C_2 \beta}{2(K_1 - \bar{K}_2)}} \left[\frac{2K_1 - \frac{\bar{K}_1}{2} + \sqrt{2K_1 \bar{K}_1 + \frac{\bar{K}_1^2}{4}}}{2K_1 - \frac{\bar{K}_2}{2} + \sqrt{2K_1 \bar{K}_2 + \frac{\bar{K}_2^2}{4}}} \right] \quad 7)$$

- (d) Solve Equation 7 for K_1 by the Newton-Raphson method.
- (e) Calculate K from Equation 5 or 6.
- (f) Repeat the same procedures until the calculated values of K and K_1 are close enough to the assumed values.
- (g) Using the equilibrium constants obtained above the molecular weights over the concentration range of 4-65 g/l can be calculated based on this model. The fraction of monomer unassociated at each concentration is obtained by solving Equation 2 and the fraction of monomer bound in any degree of polymer can be also obtained from Equation 1.

A number of different equilibrium constant pairs, K and K_1 , have been tried for five asphaltenes in benzene. The ones which afford the minimum standard deviations between the experimental and calculated molecular weights have been chosen.

3. Results and Discussion

The VPO molecular weights for all five coal-derived asphaltenes in benzene, chloroform, and THF are shown in Figs. IV-O-1 to IV-O-5. The results indicate that association of coal-derived asphaltene takes place in all three solvents over the concentration range of 4-60 g/l. The calculated equilibrium constants, together with the standard deviations are summarized in Table IV-O-I where the % Dev. is defined as:

$$\frac{\text{Standard Deviation of MW}}{\text{MW of Monomer}} \times 100\%$$

All % Dev. values are less than 7.8%. This suggests that this two parameter model is efficient in describing the self-association of asphaltenes from five different processes in benzene, chloroform, and THF. The calculated molecular weights, fraction of monomer and monomer bound in dimer and trimer are also plotted in Figs. IV-O-1 to IV-O-5 for the five asphaltenes.

It is interesting to note from Equation 4 that $MW_{obs} \doteq Mo/\alpha$ as $C \rightarrow 0$ and $Mo/\alpha \doteq Mo$ since $\alpha \rightarrow 1$ as $C \rightarrow 0$. This agrees with the experimental results obtained from VPO and reported in Reference (1) 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 and were used as M_0 throughout this study.

The association of petroleum asphaltenes has been studied by a variety of techniques (3-8) and the mechanism of self-association has been described largely in terms of electronic association. The mechanism of bonding in coal-derived asphaltenes is important and is under study (11). The association of these species has been reported in terms of hydrogen bonded complexes which can be separated into acidic and basic components (12). The hydrogen bonding of these two components and some model complexes has been further studied by NMR (13,14). Unfortunately, all of the reports on coal-derived asphaltenes contain only qualitative results. However, these studies tend to support the self-association model derived here, since it is very likely that in solution dimer could be formed through the bondings between the acidic proton and basic nitrogen or oxygen of two molecules or trimer could be formed through the bondings between those of three molecules. The association of monomer into dimer, trimer in solution depends on the solvent used. It is more significant in the less polar solvent benzene than chloroform and THF, so the variation of molecular weights vs. concentration in benzene is the greatest.

This study is significant because, based on this model, the heat of formation of the polymers can be calculated from equilibrium constants at various temperatures and the mechanism of the bonding can be studied. This is the first time that VPO has been used to quantitatively correlate the degree of association of coal-derived asphaltenes in solution.

Comparing the equilibrium constants K_1 and K of these five different asphaltenes in benzene, chloroform and THF, it is found that Synthoil and PAMCO SRC asphaltenes have stronger association between molecules while FMC-COED and Cat. Inc. SRC asphaltenes have less. This suggests that more energy may be needed in upgrading heavy fractions of coal liquid from Synthoil and PAMCO SRC than those from FMC-COED and Cat. Inc. SRC.

The equilibrium constants in THF are generally larger than in benzene and chloroform, since THF is more polar and tends to dissociate the asphaltene molecules as they are dissolved. However, this dissociation tends to go to completion in all three solvents at infinite dilution.

In Figures 1 to 5 the distributions of asphaltene among monomer, dimer and trimer as a function of total asphaltene concentration are represented by the solid curves labeled 1, 2, 3 in benzene, a, b, c in chloroform, and A, B, C in THF. For example, if 20 gm of Cat. Inc. SRC asphaltene is dissolved in 1ℓ benzene at 37°C, the fractions of monomer, dimer and trimer are 0.70, 0.18, 0.07 (from Fig. 1, curves 1, 2, 3), while the remaining 0.05 is contained as polymers higher than trimer. The concentrations of monomer, dimer and trimer can be calculated and are:

$$\text{concentration of monomer (moles/ℓ)} = \frac{20}{483} \times 0.7 = 2.9 \times 10^{-2} M$$

$$\text{concentration of dimer (moles/ℓ)} = \frac{20}{483} \times 0.18 \times 1/2 = 3.7 \times 10^{-3} M$$

$$\text{concentration of trimer (moles/ℓ)} = \frac{20}{483} \times 0.07 \times 1/3 = 9.7 \times 10^{-4} M$$

If the rest is assumed tetramer then concentration of tetramer (moles/l) = $\frac{20}{483} \times 0.05 \times 1/4 = 5.2 \times 10^{-4}$ M where the number 483 is the molecular weight of monomer.

Since the degree of association in benzene is larger, the fraction of monomer in benzene should be less than in the other two solvents, and these results can be seen very clearly in Figures 1 to 5 when curves of 1, a, A are compared. In benzene solution, as the concentration increases, the fraction of asphaltene, existing as a dimer reaches a maximum, and then decreases, and higher multimers become increasingly important. Since the association in chloroform and THF is less, more concentrated solutions are needed for dimer to reach maxima and are not shown. In highly concentrated solutions these larger multimers become dominant and start to precipitate. Evidence for association of monomeric asphaltenes into 4-6 average layers in the solid state has been found by x-ray diffraction spectroscopy (15).

Table IV-O-I. Calculated Equilibrium Constants and Standard Deviations of Coal-Derived Asphaltenes

Process	Monomer MW **	Solvent	K ₁	K	Standard Deviation	%Dev.
Synthoil Asphaltene	567	Benzene	0.0762	0.0671	13.7	2.4
		Chloroform	0.0764	0.2275	23.5	4.1
		THF	0.7799	0.6848	9.5	1.7
HRI Asphaltene	502	Benzene	0.118	0.0866	9.0	1.8
		Chloroform	0.2048	0.2275	27.7	5.5
		THF	0.4560	1.0989	8.1	1.6
FMC-COED Asphaltene	370	Benzene	0.210	0.0813	20.7	5.6
		Chloroform	0.2645	0.1779	29.0	7.8
		THF	2.9946	0.2591	25.5	6.9
Cat. Inc. SRC Asphaltene	477	Benzene	0.225	0.109	12.2	2.6
		Chloroform	0.2151	0.1497	10.2	2.1
		THF	0.3426	0.4994	10.4	2.2
*PAMCO SRC Asphaltene	545	Benzene	0.061	0.0971	18.6	3.4
		Chloroform	0.180	0.1239	12.7	2.3
		THF	0.3157	0.7978	16.5	3.0

* Isolated form vacuum distilled bottom product.

** Molecular Weights at infinite dilution.

Fig. IV-0-1. FRACTIONS OF MONOMER AND VPO MW VS. CONCENTRATION
CAT. INC. ASPHALTENE

Fig. IV-0-2.

FRACTIONS OF MONOMER AND VPO MW VS. CONCENTRATION
 PAMCO ASPHALTENE

Fig. IV-0-3.

FRACTIONS OF MONOMER AND MW OF SYNTHOIL ASPHALTENE
 VS. CONCENTRATION

Fig. IV-0-4.

FRACTIONS OF MONOMER AND VPO MW VS. CONCENTRATION
 HRI ASPHALTENE

Fig. IV-0-5.
 FRACTIONS OF MONOMER AND VPO MW VS. CONCENTRATION
 FMC-COED ASPHALTENE

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IV-P. Densimetric Methods

1. Refractive Index. We are developing methods to measure the refractive index of an unknown in the solid state. Our first attempt was designed to verify the linear relationship between refraction index and concentration as proposed by O. Merz (2).

$$n = \frac{v_1 n_1 + v_2 n_2}{100}$$

where n is the refractive index of the mixture and n_1, n_2 are the refractive index of the components of volume percentage v_1 and v_2 .

Two solution systems were used: One ideal solution (benzene-toluene), and one non-ideal solution (chloroform-acetone) in the sense of Rault's Law. Each sample was made of 10 ml solution. The concentrations of the solutions were 25%, 50%, 75%, and 100% by volume respectively.

The refractive index at 25°C for the two model solution systems as a function of solution concentration is shown in Table IV-P-I and Figure IV-P-1. The linear correlation is calculated by least square method. n_D^{25} is expressed as a function of percent volume fraction, v . Correlation coefficients of both linear lines are good.

All the refractive indexes were measured at 25°C with a Bausch & Lomb Co., thermostated, refractometer. A few minutes were allowed to let the solution come to 25°C in the refractometer before measurements were made. In order to check for accuracy, a number of solvents was used for the determination of the n_D^{25} values. Table IV-P-II lists the experimental and literature value of n_D^{25} of several solvents. The last column is the difference of these two values which may be used as an indication of the existence of impurity.

In order to check for the validity by the extrapolation to 100% solid, we have used a standard polystyrene sample, the literature value is $n=1.59$. As shown by Fig. IV-P-2, the extrapolated value is very close to 1.59.

The refractive indexes of coal-derived asphaltenes were determined as a function of concentration in dilute solutions. Several different solvents were used, and the index of refraction of each asphaltene was determined by extrapolation to 100% concentration. The solvent systems included benzene, chloroform, dimethyl formamide (DMF) and tetrahydrofuran (THF). The concentrations of the solutions were 0.05, 0.1, 0.2 and 0.4% by weight. An example of a SRC asphaltene is illustrated by Fig. IV-P-3.

In general, refractive indices of coal fractions are slightly different according to solvents used. The determination in pyridine solution for various fractions are listed in Table IV-P-III.

2. n-d-M Method. The n-d-M method is an empirical method, and has long been used in petrochemical analysis for determining carbon distribution and ring content of olefin free petroleum portions boiling about the gasoline range (1). The n stands for refractive index, d , for density, and M for molecular weight. By utilizing these three parameters one may determine the percentage of carbon atoms in aromatic ring structures ($\%C_A$); in naphthenic ring structures ($\%C_N$), and in paraffinic structures ($\%C_P$). By applying this method the mean number of naphthenic rings R_N can also be estimated.

The powder density of Synthoil asphaltene was measured by a helium displacement method. The densitometer used was based on the basic design proposed by Schumb (3) with same improvements, as shown in Fig. IV-P-4. The density was measured at room temperature and atmospheric pressure.

A preliminary value for the density of Synthoil asphaltene, obtained by the helium displacement method, is 1.1756 g/ml. This datum, together with the refractive index, and molecular weight, 561 g/mole (4), may be used to calculate the carbon distribution of Synthoil asphaltene according to the n-d-M method. The procedure is outlined in Table IV-P-IV. The calculated carbon distribution of Synthoil asphaltene according to this method is: %C_A, 74; %C_N, 34; %C_P, -8; the aromatic ring content R_A is 5, and the naphthenic ring content R_N is 5. The aromaticity f_a, obtained previously from an NMR study was 0.70 (5), which is close to the result obtained here. The hypothetical molecular structure of Synthoil asphaltene proposed previously (6) contained six aromatic rings and three naphthenic rings. The negative percentage of paraffinic carbon is not too unreasonable because the paraffinic content consists of only a few methyl groups. Therefore, one may assume that the negative value obtained (-8%) actually represents a result close to zero.

Densimetric methods of structural analysis have been widely used for determining the average structural character of molecules in a complex mixture. Also using refractive index, density, and elementary analysis van Krevelen and coworkers (7) developed methods for studying the structure of coal. Van Nes and van Westen (1) 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 (9,10). At this time, we do not know if n-d-M method is suitable for coal-derived products.

Therefore, we have 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 (1) by making calculations of the percent deviation of the carbon distribution and ring content as a function of the percent deviation of the variable: n (refractive index), d (powder density), M (molecular weight), S (% sulfur). The results, shown in Table IV-P-V, indicate that the refractive index value is the most critical variable. 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 may not be generally applicable to coal liquid products as they are too sensitive to deviations in the refractive index, and density values.

3. Compactness. 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 (10). 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 (9). 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 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 IV-P-VI. 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.

4. Correlation to Solubility Parameters. We have developed 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 the 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 by Lawson and Ingham (11), of 305 was used in equation (1).

Based on the average values, the solubility parameters of the asphaltenes have been estimated from Eq. (1), and are shown in Tables IV-P-VII. 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 (12). This suggests a very convenient method for quickly estimating δ values of coal-derived asphaltenes and solvent fractions.

We now present extended and improved calculations of solubility parameters. Instead of using the average value of C , (305) in Eq. (1), we calculate weighted values of C_{AV} depending on the ratio of aromatic to aliphatic carbons in each coal liquid fraction and the value of C given by Lawson and Ingham for aromatic compounds (287.6) and branched aliphatic hydrocarbons (230.9).

$$\begin{aligned} C_{AV} &= C_{Ar} f_a + C_{BP} (1 - f_a) \\ C_{Ar} &= 287.6 \\ C_{BP} &= 230.9 \end{aligned} \quad (2)$$

The calculated δ values based on Eq. (2) in Table IV-P-VIII, and are seen to be in

reasonable agreement with experimentally determined δ values. This suggests a convenient method for rapidly estimating δ values of coal-derived products.

5. Structural Correlations. Molar refraction is generally useful in aiding in structural determination. The Lorenz-Lorentz formula may be used to express molar refraction:

$$R_M = \frac{(n^2 - 1) M}{(n^2 + 2) d}$$

n = refractive index
 M = MW
 d = density

The molar refraction of saturated organic compounds is usually accurately given by the sum of atomic interactions ($R'_M = \sum a_i r_i$, where a_i is the number of atoms of type i in the molecule and r_i are the corresponding atomic refractions). For unsaturated molecules increments due to double bonds are included. However, for compounds having conjugated double bonds an extra increment has to be added. This increment generally rises with increasing degree of condensation for aromatic compounds. R_m is always greater than R'_M and the difference between the two is known as the molar refractometric increment I_M :

$$I_M = R_M - R'_M$$

The refractometric increment has been shown theoretically and experimentally to be a function of the number of carbon atoms in the aromatic cluster C_{Au} (13). Even when R_M cannot be calculated as in cases such as coal, because the molecular weight is not known, it is still possible to obtain the size of aromatic clusters by plotting I_M/C_A vs. the aromatic surface area, S :

$$\frac{I_M}{C_A} = f(1/S)$$

and relating S to C_{Au} (Fig. IV-P-5). We have calculated I_M/C_A values by use of M , d , n , elemental analyses, and f values. We then utilized these values in conjunction with Schuyer and Van Krevelen's curve (Fig. IV-P-5) to determine average aromatic cluster sizes. The preliminary results for C_{Au} , shown in Table IV-P-IX for the asphaltenes and the Synthoil carbene, appear generally to be too low. Only the Synthoil asphaltene, $C_{Au} = 14$, and the Synthoil carbene, $C_{Au} = 18$, values agree with the more reasonable values previously determined by the X-Ray - NMR procedure (3). It appears that either our experimental data are not accurate enough, or that the Schuyer and Van Krevelen refractometric structural parameter method is not generally applicable to coal sliquid products.

When refractive indices are plotted vs. the Brown-Ladner parameters s_{fa} , (ratio of aromatic carbons to total carbons), H_{aru} / C_{ar} (ratio of substitutable edge atoms to total aromatic atoms) or other parameters I (color intensity) and C/R (ring condensation index), rough correlations are observed (Figs. IV-P-6, IV-P-7, IV-P-8, IV-P-9). Such correlations could be used as a simple means of obtaining f_a , or H_{aru} / C_{ar} values or other parameters from index of refraction measurements. (8)

Figure IV-P-1 N_D^{25} VS. CONC. FOR ACETONE-CHLOROFORM AND BENZENE-TOLUENE.

Fig. IV-P-2. REFRACTIVE INDEX OF POLYSTYRENE

Fig. IV-P-3.

N_D^{25} OF PAMCO ASPHALTENE FROM SRC (IS-74-7) IN SEVERAL SOLVENTS.

Figure IV-P-4 HELIUM DENSITOMETER

Figure IV-P-5. MOLAR INCREMENT PER GRAM ATOM AROMATIC CARBON VS AROMATIC SURFACE AREA AND CARBON ATOMS PER AROMATIC CLUSTER

Figure IV-P-6. REFRACTIVE INDEX VS. AROMATICITY FOR COAL LIQUID PRODUCTS

Fig. IV-P-7. REFRACTIVE INDEX VS. H_{ARU}/C_{AR} FOR COAL LIQUID PRODUCTS.

Fig. IV-P-8.

Fig. IV-P-9.

Table IV-P-I. n_D^{25} of two model solutions.

solution systems	volume fraction (% v.)				
	0	25	50	75	100
Benzene - Toluene	1.4981	1.4969	1.4960	1.4953	1.4946
Acetone - Chloroform	1.3566	1.3786	1.4011	1.4220	1.4427

*For Benzene - Toluene solution, $n_D^{25} = 1.4979 - 3.440 \times 10^{-5}v$, $r = 0.993$

For Acetone - Chloroform solution, $n_D^{25} = 1.3571 + 8.624 \times 10^{-4}v$, $r = 1.000$

Table IV-P-II. n_D^{25} of several solvents.

solvent	$(n_D^{25})_{lit.}$	$(n_D^{25})_{exp.}$	$(n_D^{25})_{exp.} - (n_D^{25})_{lit.}$
Acetone	1.3560	1.3566	0.0006
Benzene	1.4979	1.4981	0.0002
Chloroform	1.4429	1.4427	-0.0002
DMF	1.4282	1.4288	0.0006
THF	1.4050	1.4051	0.0001
Toluene	1.4941	1.4946	0.0005

Table IV-P-III Refractive Indices (n_D) of Coal Liquid Products^a

<u>Solvent Fraction</u>	<u>Synthoil</u>	<u>HRI</u>	<u>CAT. INC.</u>	<u>PAMCO</u>	<u>FMC -COED</u>
Oil	1.55	1.59	1.66	1.55	1.56
Resin	1.61	1.61	1.70	1.77	1.62
Asphaltene	1.62	1.67	1.73	1.73	1.63
Carbene	1.74	1.78	1.88	1.86	1.68
Carboid	1.76	1.78	1.77	1.88	1.71

^aExtrapolated to 100% in pyridine solution.

Table IV-P-IV. Structural Calculation Formulas Used in the n-d-M Method

Calculate	
	$v = 2.501 (n-1.4735) - (d-0.8487)$ $w = (d-0.8487) - 1.11 (n-1.4735)$
$\%C_A$	$v > 0$
	$\%C_A = 428v + 3660/M$
	$v < 0$
	$\%C_A = 575v + 3660/M$
$\%C_T$	$w > 0$
	$\%C_T = 815.5w - 3S + 10150/M$
	$w < 0$
	$\%C_T = 1436w - 3S + 10750/M$
$\%C_N$	$\%C_N = \%C_R - \%C_A$
$\%C_P$	$\%C_P = 100 - C_R$
R_A	$v > 0$
	$R_A = 0.437 + 0.055Mv$
	$v < 0$
	$R_A = 0.437 + 0.080Mv$
R_T	$w > 0$
	$R_T = 1.352 + 0.146M (w-0.005S)$
	$w < 0$
	$R_T = 1.352 + 0.180M (w-0.005S)$
R_N	$R_N = R_T - R_A$

Table IV-P-V. 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 (1).

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.

Table IV-P-VI. Ring Compactness of Coal-Derived Asphaltenes

Process	d^a	$\sum_i^n V_i / C$	V_M / C	C/R	f_a^b	C_A	F/C_A
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.

Table IV-P-VII. Calculated Solubility Parameters of Coal-Derived Asphaltenes from Refractive Index Data

	<u>n</u>	<u>δ</u>
Synthoil Asphaltene	1.6668 a	10.7
HRI Asphaltene	1.6979 b	10.8
Cat. Inc.SRC Asphaltene	1.7009 c	10.9
PAMCO SRC Asphaltene	1.7282 c	11.0
FMC-COED Asphaltene	1.6373 d	10.5

a Average Extrapolated to 100% values measured in benzene, DMF, and THF

b Average Extrapolated to 100% values measured in benzene, chloroform, DMF, and THF

c Average Extrapolated to 100% values measured in DMF, and THF

d Extrapolated to 100% in THF

Table IV-P-VIII. Estimated Solubility Parameter, δ_{calc} , For CoalLiquid Products

<u>Solvent Fractions</u>	----- Coal Liquid Process -----				
	<u>Synthoil</u>	<u>HRI</u>	<u>CAT, INC.</u>	<u>PAMCO</u>	<u>FMC</u>
Oil	9.0	9.4	10.1	9.3	9.1
Resin	9.6	9.7	10.3	10.6	9.7
Asphaltene	9.8 ^a	10.1	10.5	10.5 ^b	9.8
Carbene	10.5 ^a	10.8	11.2	11.1	10.2
Carboid	10.7 ^a	10.8	10.8	11.3 ^b	10.4

^aExperimentally measured maximum solubility range δ values: Asphaltene, 9-12; Carbene, 10-12; Carboid, 10.6-12. (see ref. 12)

^bExperimentally measured maximum solubility range δ values: Asphaltene, 8-12; Carboid, 9-12. (see ref. 12)

Table IV-P-IX.

Aromatic Carbons Per Structural Unit, C_{Au} , By Molar Refraction Method^a

Sample	M^b	d^c	n^d	R_M	R'_M	I_M	f_a	I_M/C_A	C_{Au}
Synthoil Asphaltene	561	1.18	1.67 ^d	177.7	145.6	32.1	0.71	1.11	14
HRI H-Coal Asphaltene	492	1.27	1.70 ^d	149.7	125.1	24.6	0.78	0.88	10
FMC-COED Asphaltene	375	1.24	1.63 ^e	107.7	96.9	10.8	0.67	0.63	<<10
PAMCO SRC Asphaltene	563	1.32	1.73 ^d	170.1	144.5	25.6	0.76	0.83	<10
Cat-Inc SRC Asphaltene	483	1.23	1.70 ^d	151.8	125.8	26	0.80	0.89	10
Synthoil Carbene	861	1.23	1.74 ^e	282.5	222.7	59.8	0.75	1.28	18

a. Schuyer and van Krevelen, Ref. 26

b. VPO infinite dilution value in THF.

c. Helium displacement method.

d. Average value extrapolated to 100% solute concentration in solvents benzene, THF, and DMF.

e. Extrapolated to 100% solute concentration in solvent pyridine.

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IV-Q. Solubility Parameters

a. Introduction. Solubility parameter spectra have been used in polymer research to determine the solubility characteristics of cross-linked polymer systems. Cross-linked systems are not soluble in any solvent. Instead, solvent is imbibed by the cross-linked polymer and causes it to swell. The solubility parameter of the solvent which causes maximum swelling is defined as the solubility parameter of the cross-linked material. Coal can be thought of as having some characteristics of a cross-linked system (1, 2). That is, when immersed in a solvent with which it interacts, it will swell. In addition, coal contains soluble matter which can be thought of as the uncross-linked portion of the coal. The aim of this research is to find a type of solvent that will both induce break-down of the coal through swelling and dissolve the the soluble portion.

b. Theory of Solubility Parameters. The basic assumption in the solubility parameter concept is that there is a correlation between the cohesive-energy density (potential energy per unit volume) and mutual solubility. The cohesive-energy density, C is defined as :

$$C = \frac{\Delta U^V}{V^L}$$

where ΔU^V is the energy change for complete isothermal vaporization of the saturated liquid to the ideal gas state and V^L is the molar volume of the liquid. The solubility parameter, δ , is defined as the positive square root of the cohesive-energy density:

$$\delta = \frac{\Delta U^V}{V^L}^{\frac{1}{2}}$$

The dimensions of the solubility parameter are $\text{cal}^{\frac{1}{2}} \text{cm}^{-3/2}$ or "hildebrands".

For a material to dissolve in a solvent, the free energy change, ΔG_m , of the process must be negative; $\Delta G_m = \Delta H_m - T\Delta S_m$. Since the entropy change, ΔS_m , is always positive, the heat of mixing, ΔH_m , determines whether dissolution occurs or not. Experimentally, it has been found that, for most polymer systems, the heat of mixing is either positive or zero. According to the Hildebrand-Scatchard (3, 4) theory, the heat of mixing is given by:

$$\Delta H_m = V_m (\delta_1 - \delta_2)^2 \phi_1 \phi_2$$

where V_m is the total volume of the mixture, ϕ_1, ϕ_2 are the volume fractions and δ_1, δ_2 are the solubility parameters of the solvent and solute respectively. Therefore, the heat of mixing will be small or zero and the free energy change negative when $\delta_1 = \delta_2$. The assumptions in the above are: 1) forces of attraction are due primarily to dispersion forces, 2) molar volumes of the solute and the solvent are not significantly different, 3) no volume change occurs on mixing, 4) mixing is random. These assumptions are not generally valid and many more sophisticated theories have been developed (5, 6, 7). However, the relationship produced is a simple one and is easy to use as a rough guideline.

The discussion above holds for non-polar liquids. For polar liquids and solids, it has been assumed that the same principle holds. This assumption has proven fairly satisfactory in practice.

Burrell (9) was the first to deal with hydrogen bonding in solubility parameters. Solvents are divided into three classes according to their hydrogen

bonding capability: poor, including hydrocarbons and nitro-hydrocarbons; moderate, including ketones and ethers; strong, such as alcohols. Again, more complicated theories have been developed (10, 11, 12). However, this simple classification is used in this work as a rough estimate of the hydrogen bonding effect.

c. Experimental. Work was divided into two parts: work on coal and its extract, and work on coal liquids from liquefaction processes. Two solvent systems were used. First, a mixed solvent scheme (13) and then a set of pure solvents, having strong, moderate and poor hydrogen bonding capability. The solvents used in the mixed system are shown in Table IV-Q-I. When two miscible liquids are mixed, the effective solubility parameter (δ_m) of the mixture is given by (14):

$$\delta_m = Y_1\delta_1 + Y_2\delta_2$$

where δ_1 , δ_2 are the solubility parameters of the solvents and Y_1 , Y_2 are the volume fractions. A solubility spectrum is obtained by soaking the coal in a series of mixed solvents with effective solubility parameter ranging from 7.0 to 24.4 hildebrands and measuring the amount of swelling.

When classified according to hydrogen bonding capacity following the system set forth by H. Burrell (9), we see that we are mixing solvents with poor, moderate and strong hydrogen bonding capacity. In order to separate the possible effect of hydrogen bonding, a second series of pure solvents was used and is listed in Table IV-Q-II. These are classified as poor, moderate and strong hydrogen bonding solvents.

The coal used was of high volatile A bituminous rank. It was vacuum dried to remove moisture and sieved. The +35 mesh size was used.

All work was done at room temperature and atmospheric pressure.

d. Results. The solubility spectrum using the mixed solvent system is shown in Fig. IV-Q-1. The swelling is given by $\frac{W_s - W_0}{W_0}$ where W_s is the swollen volume

and W_0 is the initial volume. There are two maxima in the spectrum, at 11 hildebrands and 14 hildebrands. A scanning electron micrograph, Fig. IV-Q-2 of the untreated coal shows it to be fairly smooth. A SEM, Fig. IV-Q-3, of the swollen coal treated in the solvent mixture with effective solubility parameter of 14 hildebrands shows a slight roughening. It is difficult to determine whether the roughening is due to swelling of the coal matrix or to dissolution of soluble matter.

The coal was Soxhlet extracted with pyridine to remove the soluble matter. Pyridine is a strong hydrogen bonding solvent with a solubility parameter of 19.7 hildebrands. A SEM, Fig. IV-Q-4, of the extracted coal shows much cracking and roughening.

A solubility spectrum of the extracted coal, Fig. IV-Q-5 shows that the peak at 15 hildebrands has disappeared but the peak at lower solubility parameter remains. Fig. IV-Q-6 shows the solubility spectra for the pure solvents of varying hydrogen bonding capability. The peak at 15 hildebrands is still absent. However, the peak values for strong, moderate and weak hydrogen bonding solvents vary: for strong at 8 hildebrands, weak at 10 hildebrands and moderate around 12 hildebrands. The interaction for the moderate hydrogen bonding solvents occurs over the widest range.

About 20% of the coal was extracted in to the pyridine. The extract was divided into three fractions by standard solvent fractionation methods; pentane soluble, 8.0%, pentane insoluble but benzene soluble, 32.5%, and benzene insoluble, 59.5%. The pentane soluble fraction contains oils and resins, the benzene insoluble fraction contains molecules akin to preasphaltenes. Fractionation solvents are listed in Table IV-Q-III.

The dissolution range for the benzene solubles and benzene insolubles is shown in Fig. IV-Q-7. Maximum dissolution occurs around 10 hildebrands which is not

too surprising since the extract was obtained in pyridine. However, this range of dissolution occurs in the region of maximum swelling in the original coal. The benzene insoluble fraction is not 100% soluble anywhere. When the pure solvents were used for the benzene insoluble fraction, the same trends found in swelling occur. This is shown in Fig. IV-Q-8. Again, the solvents with moderate hydrogen bonding capability are the most effective.

e. Coal Liquids. In a second set of experiments, solubility limits were obtained for coal liquefaction products from the PAMCO and Synthoil processes. These processes are shown in Table IV-Q-IV. Liquids were again divided into oils and resins, asphaltene and preasphaltene (carbene and carboid) fractions. The asphaltene and preasphaltene fractions are important because they are believed to be intermediates in the liquefaction process. It is desirable to enhance their dissolution to promote hydrogenation. A schematic of the liquefaction process is shown in Fig. IV-Q-9. Solubility ranges for Synthoil products are shown in Fig. IV-Q-10. Here the preasphaltene fraction has been further divided into carbene, CS₂ soluble and carboid, CS₂ insoluble. The effect of hydrogen bonding on Synthoil asphaltene is shown in Fig. IV-Q-11. Again 100% solubility occurs at the lowest solubility parameter for the strong hydrogen bonding solvents followed by the solvent for poor hydrogen bonding capacity. The solvents with moderate hydrogen bonding capability are effective over the widest range. Similar results were obtained for the PAMCO products shown in Fig. IV-Q-12 and IV-Q-13. The effect of hydrogen bonding on the PAMCO preasphaltenes is shown in Fig. IV-Q-14. Again the solvents with moderate hydrogen bonding capability are the most effective.

f. Conclusion. Several conclusions can be drawn from the above results:

- 1) From the swelling experiments we believe that for maximum swelling to occur, the solvent must interact with the soluble matter in the coal. When the soluble material is removed, swelling is suppressed. The extractable portion can be thought of as the uncross-linked coal molecule; its structure can be determined without using destructive chemical methods to break the coal apart.
- 2) Hydrogen bonding is an unsymmetrical interaction, involving a donor and an acceptor. Strong hydrogen bonding solvents appear to compete with specific sites in both the coal (swelling) and the coal liquids (dissolution). The solvents with poor hydrogen bonding capability interact mainly through physical forces. For the moderate hydrogen bonding solvents there may be both kinds of interaction. Since the goal is to interrupt as wide a range of forces as possible in both the coal and coal liquid, it appears that a solvent with moderate hydrogen bonding capability should be selected.
- 3) There is a striking similarity between the behaviors of the coal extract and the coal liquefaction products. We would like to suggest that asphaltene and preasphaltene-like molecules (intermediates in the liquefaction process) already exist in the virgin coal and that hydrogenation products reflect the properties of the starting material. Further work will be done in this area to substantiate this suggestion by hydrogenation experiments on the fractionated coal extract.

Table IV-Q-I. List of Solvents - Mixed

$$\delta_m = \gamma_1 \delta_1 + \gamma_2 \delta_2$$

γ = volume fraction

δ = solubility parameter

<u>Solvent</u>	<u>Solubility Parameter</u>	<u>Hydrogen Bonding (9)</u>
2 Methyl Pentane	7.0	P
cyclohexane	8.2	P
cyclohexanol	9.9	M
HEMA *	12.5	scal ∇
water	23.4	S

* Hydroxyethyl methacrylate

∇ Sum of group contributions to hydrogen bonding capability

Table IV-Q-II.

List of Pure Solvents

<u>Solvent</u>	<u>Solubility Parameter</u>	<u>Hydrogen Bonding (9)</u>
cyclohexane	8.2	P
toluene	8.9	P
chlorobenzene	9.5	P
odichloro benzene	10.0	P
nitro ethane	11.1	P
nitro methane	12.7	P
diethyl ether	7.4	M
ethyl benzoate	8.2	M
dibutyl phthalate	9.3	M
Dioxane	9.9	M
Furfural	11.2	M
Dimethyl formamide	12.1	M
Diethyl amine	8.0	S
pipiridine	8.7	S.
propionic	9.9	S
pentanol	10.9	S
butanol	11.4	S
propanol	11.9	S
ethanol	12.7	S
methanol	14.5	S

Table IV-Q-III.

List of Fractionation Solvents

Solvent	Solubility Parameter	Hydrogen ⁽⁹⁾ Bonding
Pentane	7.0	p
Benzene	9.2	p
Carbon disulfide	10.0	p

Table IV-Q-IV.

COAL LIQUEFACTION PROCESSESDIRECT HYDROGENATION (PERC-SYNTHOIL, HRI-H-COAL) SOLVENT REFINING (PAMCO, CAT. INC, SRC)

Fig. IV-Q-1. Solubility spectrum of the dried untreated coal using the mixed solvent system. W_s is the swollen volume and W_0 is the initial volume.

(*PSOC 102 is the Pennsylvania State designation number for the high volatile A bituminous coal used in this study)

PSOC 102 Untreated Coal 1000X

Fig. IV-Q-2. Scanning electron micrograph of the dried, untreated coal.

PSOC 102 $\delta_m = 14$ 1000X

Fig. IV-Q-3. Scanning electron micrograph of the swollen coal treated with the solvent mixture with effective solubility parameter, δ_m , of 14 hildebrands.

PSOC 102 Pyridine Extracted 1000X : 10µm

Fig. IV-Q-4. Scanning electron micrograph of coal which has been Soxhlet extracted with pyridine.

Fig. IV-Q-5. Solubility spectrum of pyridine extracted coal using mixed solvent system.

Fig. IV-Q-6. Solubility spectrum of pyridine extracted coal using the poor, moderate, and strong hydrogen bonding solvents.

PSOC 102 EXTRACT

Fig. IV-Q-7. Dissolution of benzene soluble and benzene insoluble fractions of coal extract.

Fig. IV-Q-8. Dissolution of benzene insoluble fraction of coal extract, using the pure solvents.

Fig. IV-Q-9.

A general mechanism consistent with observations on coal liquefaction pathways

Fig. IV-Q-10. Solubility ranges for Synthoil products using mixed solvent system.

Fig. IV-Q-11. Dissolution of Synthoil asphaltene in pure solvents

PAMCO ASPHALTENE

Fig. IV-Q-12. Dissolution of PAMCO benzene soluble and benzene insoluble fractions in mixed solvent system.

Fig. IV-Q-13. Dissolution of PAMCO asphaltene in pure solvents.

Fig. IV-Q-14. Effect of hydrogen bonding on dissolution of PAMCO preasphaltene.

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IV-R. Transmittance Electron Microscopy

The asphaltene samples were made up in a 0.1% (wt/vol) solution in benzene, and sprayed onto a carbon film, held on a copper grid, with a low velocity nebulizer as described previously (1). The microscopy was performed with a Philips EM 301. The point-to-point resolution was reported to be 3Å. Micrographs were obtained at about 130,000 diameters on 3 1/4 x 4 inch plates, and subsequently enlarged up to 910,000 diameters for particle size analysis. The average particle lengths along the long and short axes are reported in Table IV-R-I.

The aromatic sheet dimensions of coal asphaltenes have been determined previously by the x-ray diffraction method (2), 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 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 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.

1. Image Processing (3). A flow diagram of the overall TEM picture analysis, including image processing is shown in Fig. IV-R-1. 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 Aeroject 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. IV-R-2. 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.

2. Metal Shadowing Technique. Despite the development of computer assisted image processing techniques, it was not possible to obtain resolvable TEM pictures of isolated asphaltene molecules or clusters. It may be that individual asphaltene molecules, or even small clusters of asphaltenes, are transparent to electron microscopy due to their low densities. Therefore, two modifications of previous experiments were carried out: carboids were used instead of asphaltenes because of their larger size, and a metal shadowing technique was used to enhance resolution.

The metal shadowing technique was developed by Hall (4), and has been used mainly in studies of biomacromolecules such as DNA (4), RNA (5), and proteins (6, 7, 8). In our experiment, a control grid was prepared by metal shadowing a SiO film sprayed only with pyridine (glass distilled grade) (Fig. IV-R-3). The specimen grid, however, was sprayed with a small quantity of a dilute (5 mg/2500 ml) solution of Synthoil carboid in pyridine before the metal was shadowed (Fig. IV-R-4). From the photographs taken at 113,000x we can see a fairly homogeneous (small grains of metal uniformly distributed) control grid, and a specimen grid that shows several distinguishable particles (indicated by dark spots due to piling up of metal on the side facing the metal source) accompanied by shadows (indicated by transparent or white spots due to the absence of metal). The fact that all shadows are in the same direction indicates that they are genuine shadows rather than artifacts on the photoplate. With a shadowing angle of 1:9, the observed shadow lengths of 90-270 Å suggest heights of 10-30 Å for the particles. The width of the shadows is from 100 to 200 Å suggesting particle diameters of 100-200 Å (Fig. IV-R-5). Such dimensions are much larger than the dimensions of individual carboid molecules previously determined by the X-Ray-NMR method. Therefore, it appears that only aggregates of carboid molecules, stacked in 4-8 overlapping sheets are being observed with our present techniques. Calculations based on the weight of carboid sprayed onto a given area of surface, and the average MW of Synthoil carboid (1000), indicate that the upper limit of distinguishable molecules is 0.2 wt.% of the total present. The rest are too small to cast any noticeable shadow. In other words, 99.8% of the carboid deposit may have sizes smaller than the above described average

TEM observable carboid clusters.

To improve the resolution of the technique, less metal should be deposited to give smaller grains in the background. Some bigger reference object of known size may also be introduced to give a more exact calibration. Such an object may also be used as something to focus on during photograph taking. These improvements may allow us to observe species of smaller size, and individual carboid molecules.

Table IV-R-I. TEM Particle Dimensions for Synthoil Crude Asphaltene

	$\frac{D_1^*}{(\text{\AA})}$	$\frac{\sigma_1^{***}}{(\text{\AA})}$	$\frac{\text{Min. Size}}{(\text{\AA})}$	$\frac{\text{Max. Size}}{(\text{\AA})}$	$\frac{D_2^{**}}{(\text{\AA})}$	$\frac{\sigma_2^{***}}{(\text{\AA})}$	$\frac{\text{Min. Size}}{(\text{\AA})}$	$\frac{\text{Max. Size}}{(\text{\AA})}$
Synthoil Asphaltene	15.2	4.7	10.9	24.0	35.9	9.9	21.8	61.0

*Arithmetic mean for short axis

**Arithmetic mean for long axis

***Standard deviation for long and short axes

Fig. IV-R-1. FLOW DIAGRAM OF TEM PARTICLE ANALYSIS ON COAL ASPHALTENE

Fig. IV-R-2 - 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

Fig. IV-R-3. Control: Pyridine Deposited on SiO₂, then Shadowed with Platinum

Fig. IV-R-4. Specimen: Carboide Dissolved in Pyridine, Deposited on SiO₂, then Shadowed With Platinum vapor. (Each particle is pin-pointed by an arrow, the direction of which is that of the incoming platinum vapor. It is characterized by a dark (metal grain piling) leading edge with a white trailing shadow.

Fig. IV-R-5. The Metal Shadowing Technique for EM.

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IV-S. Mesophase Formation

In all coal liquefaction processes varying amounts of organic insoluble matter (IOM) are formed. In a pyrolysis process such as the the FMC-COED process up to 65% of this coke-like material may be formed (1). In an SRC process such as PAMCO SRC II, 6 - 9% of such material is formed (2). Catalyzed hydrogenation processes such as the HRI H-COAL, and the Synthoil process also afford IOM. In addition, these processes suffer from catalyst deactivation due to carbon deposition. A solid residue formed in an SRC plant was found to have anisotropic structures that are characteristic of coalesced mesophase (3). Penn State workers independently produced mesophase from SRC. We have therefore begun to investigate the formation of mesophase from solvent fractionated coal liquid products.

When the organic precursors to coke and synthetic graphite are pyrolyzed, large, flat, polynuclear aromatic molecules are formed by the reactions of aromatic polymerization. As the molecular weight approaches 1500, the molecules condense to form parallel arrays with the structural characteristics of a lamellar liquid crystal. These lamellar liquid crystals are the carbonaceous mesophase. The mesophase transformation usually occurs between 400°C and 500°C. Chemical studies indicate that freshly formed mesophase consists of planar aromatic molecules as shown in Figures IV-S-1 and IV-S-2 (4).

In the early stages of nucleation and growth, the mesophase appears as small anisotropic spherules suspended in an optically isotropic matrix. The structure of the spherules consists of aromatic layer molecules that lie perpendicular to the polar diameter but splay outward to reach the interface with the pyrolyzing matrix normally as shown in Figure IV-S-3.

As pyrolysis proceeds, the mesophase spherules grow at the expense of the fluid matrix and sink through it. When the spherules meet, they coalesce to produce larger droplets of more complex structure (Fig. IV-S-4). This process has been recognized to be the key to the development of graphitizable carbon (5). Materials that go through the mesophase transformation will graphitize and those which do not undergo this transformation will not graphitize.

The formation of the mesophase microstructure follows a systematic pattern which relates primarily to the plasticity of the mesophase and the deformation the plastic mesophase goes through as it hardens into semi coke (6). This effect is shown schematically in Fig. IV-S-5.

Non-Coalescence or fine mosaic isotropic structure results from a fast reacting pyrolyzing mass. The system loses fluidity and the growth of the mesophase is suppressed. In general, fine mosaic structures result from mesophase which is fully transformed below 430°C. A flow-type or coalesced anisotropy results when the mesophase retains sufficient plasticity to respond to thermal convection currents and bubble movement. Mesophase which precipitates above 430°C is extensively deformed to give coarse structures. When the mesophase remains plastic at 455°C to 465°C, a fine, fibrous structure or needle coke morphology results. This type of mesophase is preferred for the production of carbon fiber materials.

The size and chemical reactivity of the precursor molecules control the size and viscosity of the units of growth of the anisotropic mesophase, and it is the viscosity of the mesophase, both before and after coalescence, which determines the character of the final graphite product. The best mesophase is normally formed from planar fused-ring molecules such as naphthalene or anthracene. These materials are usually graphitizable. But if the original molecule is non-planar or if non-planar intermediates are formed as with fluorene or biphenyl, the material will probably not graphitize as well because free rotation inhibits the formation of the ordered planar sheets of the mesophase. Also, phenolic oxygen in the starting material is believed to reduce mesophase growth by inducing cross-linking between molecules.

Asphaltenes from three liquefaction processes, Catalytic Incorporated SRC, Synthoil and FMC-COED, were pyrolyzed under a nitrogen atmosphere to 420°C. The samples were heated at 20°C/hr. to 360°C and at 5°C/hr to 420°C. The weight percent residues, after heat treatment, consisted of 66.7%, 66.66% and 51.84% by weight of the starting Catalytic Incorporated, Synthoil, and FMC-COED samples respectively. Crossed polarized light reflection micrographs were obtained for each of the pyrolyzed samples and are shown in Figures IV-S-6, IV-S-7, IV-S-8. The Catalytic Incorporated asphaltene forms a coarse structure. The Synthoil asphaltene forms a coarse deformed structure and FMC-COED asphaltene forms a fine isotropic structure and is completely transformed at 420°C. These preliminary results can be related to the oxygen content of the starting material. Phenolic oxygen is believed to cause cross-linking and reduce mesophase plasticity. The Synthoil asphaltene has the lowest phenolic oxygen content, 2.71% and forms a mesophase that remains plastic at 420°C giving the coarse, deformed structure. The Catalytic Inc. SRC asphaltene contains slightly more phenolic oxygen, 3.38%, and forms a coarse but not a deformed structure. And the FMC-COED contains 5.90% phenolic oxygen and forms the fine isotropic structure which results from cross-linking and solidification at a temperature below 420°C (7,8,9).

Fig. IV-S-1. Hypothetical Mesophase Molecule (with a molecular weight near 1600. This model includes dangling methyl groups, vacant sites in the aromatic lattice, and a broken bond (free electron)).

Fig. IV-S-2. Model of the carbonaceous mesophase.

Fig. IV-S-3. Mesophase Spherule (sectioned on the polar diameter to display the characteristic Brooks-Taylor sphere).

Before contact

Just after contact

Short time after contact

Type of complex internal structure formed when composite of two or more spheres contracts to one large sphere

Rearrangements which appear to occur when two spheres coalesce.

Fig. IV-S-4. Coalescence of Mesophase Spheres.

Fig. IV-S-5.

Pattern of Formation of Mesophase Microconstituents of Coke (produced from various precursors by pyrolysis at 5° C/hr, The microstructures are defined in terms of the shape and spacing of the polarized-light extinction contours observed under crossed polarizers).

Fig. IV-S-6. Catalytic Inc. SRC Asphaltene Microstructure (Crossed Polarizers 200X)

Fig. IV-S-7. Synthoil Asphaltene Microstructure
(Crossed Polarizers 200X)

Fig. IV-S-8. FMC-COED Asphaltene Microstructure
(Crossed Polarizers 200X)

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IV-T. Transformation Curve

In order to better follow the changes during pyrolysis, a transformation curve was obtained for the Catalytic Inc. asphaltene. The asphaltene was heated at 13°C/hr to 360°C and 5°C/hr to 500°C under nitrogen. Samples were taken at 360°C, 400°C, 425°C, 475°C and 500°C. Crossed polarized micrographs of the samples at the increasing temperatures are shown in Fig. IV-T-1. At 360°C no mesophase has been formed. At 400°C nucleation is just beginning. At 425°C the coarse structure is clearly evident and at 450°C the material shows that flow-type morphology which does not change with further heating. The transformation curve is shown in Fig. IV-T-2. The residues were divided into oil resin (pentane soluble), asphaltene (pentane insoluble-benzene soluble), preasphaltene (benzene insoluble-pyridine soluble) and mesophase (pyridine insoluble) using a Soxhlet extractor. Changes in elemental analysis of the fractions during pyrolysis are shown in Table IV-T-I. The heteroatoms N and O are decreasing during pyrolysis in the oil-resin, asphaltene, and preasphaltene fractions and S is increasing. In the mesophase fraction, the oxygen and sulfur are decreasing and the nitrogen is increasing. From the difference in the elemental analysis of the residues from sample to sample a rough analysis of the volatile composition in the temperature intervals can be made and this is shown in Table IV-T-II.

TABLE IV-T-1.

ELEMENTAL ANALYSIS OF PYROLYSED CATALYTIC INC. ASPHALTENE

	C	H	N	O	S	ASH
Oil-resin						
360°C	88.40	6.20	1.08	4.28	0.26	0.05
Asphaltene						
360°C	87.32	5.96	1.41	5.22	0.08	0.25
400°C	88.35	5.83	1.33	3.63	0.28	0.14
425°C	88.87	5.52	1.32	3.78	0.29	0.25
Preasphaltene						
360°C	86.05	5.30	2.51	6.14	0.23	0.23
400°C	87.15	4.62	2.52	4.84	0.21	0.20
425°C	89.68	4.83	1.68	3.17	0.22	0.28
450°C	90.23	4.85	1.63	3.11	0.42	0.15
Mesophase						
400°C	88.59	4.74	1.67	4.63	0.16	0.27
425°C	90.45	4.09	1.69	3.14	0.13	0.05
450°C	91.23	3.85	1.74	2.69	0.12	0.39
475°C	91.95	3.70	1.81	2.30	0.09	0.35

TABLE IV-T-II.

COMPOSITION OF VOLATILES DURING PYROLYSIS OF CATALYTIC INC. ASPHALTENE

Temperature interval	C	H	N	O	S
360°C-400°C	74.4	9.2	2.3	14.0	--
400°C-425°C	74.8	11.41	1.54	11.57	0.6
425°C-450°C	78.2	10.84	0.61	9.93	0.4
450°C-475°C	82.0	7.48	0.6	8.89	0.9

360°C

400°C

425°C

450°C

475°C

500°C

Fig. IV-T-1. Catalytic Inc. Crossed Polarizer Micrographs

Fig. IV-T-2.
CATALYTIC INC
PYROLYSED
ASPHALTENE

242

IV-U. Thermal Interconversion

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. IV-U-1). 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," (1, 2), "pre-asphaltene (3), and "asphaltol" (4). As illustrated in Fig. IV-U-1, the composition of coal liquids depends on coal type to be liquefied, the process utilized, and the conditions employed. The benzene insolubles can 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. IV-U-2). 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.

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 (2).

The results in Table IV-U-I 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.

To repeat the experiment an autoclave system equipped with injection loading and withdrawal systems for introducing and removing samples without disturbing the reaction was used. Fig. IV-U-3 is a scheme of the whole system. The temperature controller set has been calibrated. It only shows 1.5% error in temperature reading and 5% deviation in constant temperature control.

A preliminary experiment has been run with a mixture of 2:1 ratio of tetralin to Synthoil pentane soluble fraction. About 40 grams of tetralin were charged to the reaction, and a mixture of 40 grams of tetralin and the Synthoil pentane soluble fraction was charged to the liquid feed vessel. After the temperature of the tetralin in the reactor was raised to 450°F (233°C), the mixture in the liquid feed vessel was forced into the reactor, and the reaction began and lasted for about 20 hours. Samples of 10 ml each were taken afterward without disturbing the reaction and were vacuum-distilled to remove unreacted tetralin. The residue was then separated by the standard solvent separation procedures into three fractions: pentane soluble fraction, asphaltene (pentane insoluble-benzene soluble), and benzene insoluble fractions.

The results of this preliminary experiment shows that 3% to 5% of reactant was converted into asphaltene, while less than 1% of benzene insolubles were formed (Table IV-U-II). It seems that either equilibrium has not been achieved or that the equilibrium lies far toward oil and resin. The former means that the rate of reaction is slow under these conditions. The latter could mean that a large portion of asphaltene would be converted to oil and resin.

Table IV-U-I. 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°	97	78 (-235°C/0.4mmHg)	22 (+235°C)	5.5	78.8	15.7	0
300°	96	41 (-300°C/1 Atm)	59 (+300°C)	46.7	47.6	5.7	0

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

Table IV-U-II. Isothermal Reaction Results on SRC II - PS

Temp. = 650° F ; Pressure = 800 psi g , Tetralin to Sample Ration = 2:1 , Reaction Recovery: 91.3%

Run No.	Time (hr.)	Product Distribution (Wt. %)			Separation Recovery %
		PS *	Asphaltene	B.I. **	
2-1	0.5	97.0	1.2	1.8	74.4
2-2	1.0	95.4	1.8	2.8	82.7
2-3	2.0	92.6	4.6	2.9	88.2
2-4	3.0	94.4	4.1	1.5	94.0
2-6	5.0	96.0	2.5	1.5	95.9
2-7	24.0	95.2	3.5	1.3	97.5

* Pentane Solubles (oil & resin)
 ** Benzene Insolubles (preasphaltene)

Fig. IV-U-1. THREE MAJOR FRACTIONS OF COAL LIQUIDS

Fig. IV-U-2. HYPOTHETICAL COAL LIQUID COMPOSITION AS A FUNCTION OF TIME (T,P=CONSTANT)

Fig. IV-U-3. SAMPLE ENTERING AND REMOVING SYSTEM

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