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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES, PHASE II

Quarterly Progress Report, January—March 1977

T. F. Yen

1977

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University of Southern California
Los Angeles, California

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES
Phase II

Quarterly Progress Report for the Period
January-March 1977

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Under contract no. E(49-18)-2031

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EP

Abstract

Separations of Synthoil liquefied coal by solvent fractionation and high pressure liquid chromatography have been compared. Solvent fractionation is believed to give more distinctive fractions. The asphaltene fraction obtained by use of hplc was found to be a mixture of resin, asphaltene, carbene and carboid.

Solvent elution chromatography of asphaltenes on silica gel has been scaled up, and recoveries of 98-99 wt. % are generally obtained.

VPO molecular weight studies of coal asphaltenes, as a function of concentration, in the solvents benzene and THF indicate that association of asphaltenes takes place in both solvents, but is more significant in benzene.

Structural parameters obtained from modified Brown-Ladner treatment of proton NMR data suggest that solvent fractions: oil, resin, asphaltene and carboid have structural characteristics which are sequentially related.

X-ray diffraction patterns for asphaltene, carbene, and carboid fractions reveal progressively sharpened (002) and (11) bands indicative of increasing carbonization in this series.

Methyl iodide addition to a basic fraction of Synthoil asphaltene (diethyl ether-eluted from silica gel) suggests, in conjunction with infrared results, that essentially all of the nitrogen in this fraction is present in basic pyridine-like compounds.

OBJECTIVE AND SCOPE OF WORK

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

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

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

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

SUMMARY OF PROGRESS TO DATE

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

(1) Sample acquisition has continued throughout the quarter.

(2) Training of new technical personnel is underway.

(3) Establishment of sample data bank.

(4) Chromatography of asphaltenes is being carried out.

(5-11) Characterization of coal liquid fractions by various physical and instrumental methods is continuing.

(12) Asphaltene donor-acceptor complexes are being studied by a variety of techniques.

(13) Characterization of asphaltenes by chemical methods is being carried out.

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

DETAILED DISCUSSION OF TECHNICAL PROGRESS

(1) Sample Acquisition and Separation

Work accomplished:

(a) Solvent Fractionation

During the past quarter a sample of PAMCO vacuum flash tower bottoms was received. The solid SRC product was solvent fractionated by the standard method (1). The results are presented in Fig. 2 along with those previously obtained for the other coal liquefaction products. Table I shows the analyses of the oil and resin solvent fractions obtained for this product.

(b) Separation by High Pressure Liquid Chromatography

Liquid chromatography has been suggested as an alternative procedure to solvent frationation for separation of coal liquefaction products (2 , 3). 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 (2) for separation of Synthoil centifuged liquid product (CLP). The column was consecutively and exhaustively eluted with hexane, hexane/benzene (1:1, v/v), and tetrahydrofuron (THF) elution. The weight percent yields and comparison with reported results, and typical solvent fractionation results are shown in Table 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

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

Fig. 1 - Milestone Chart

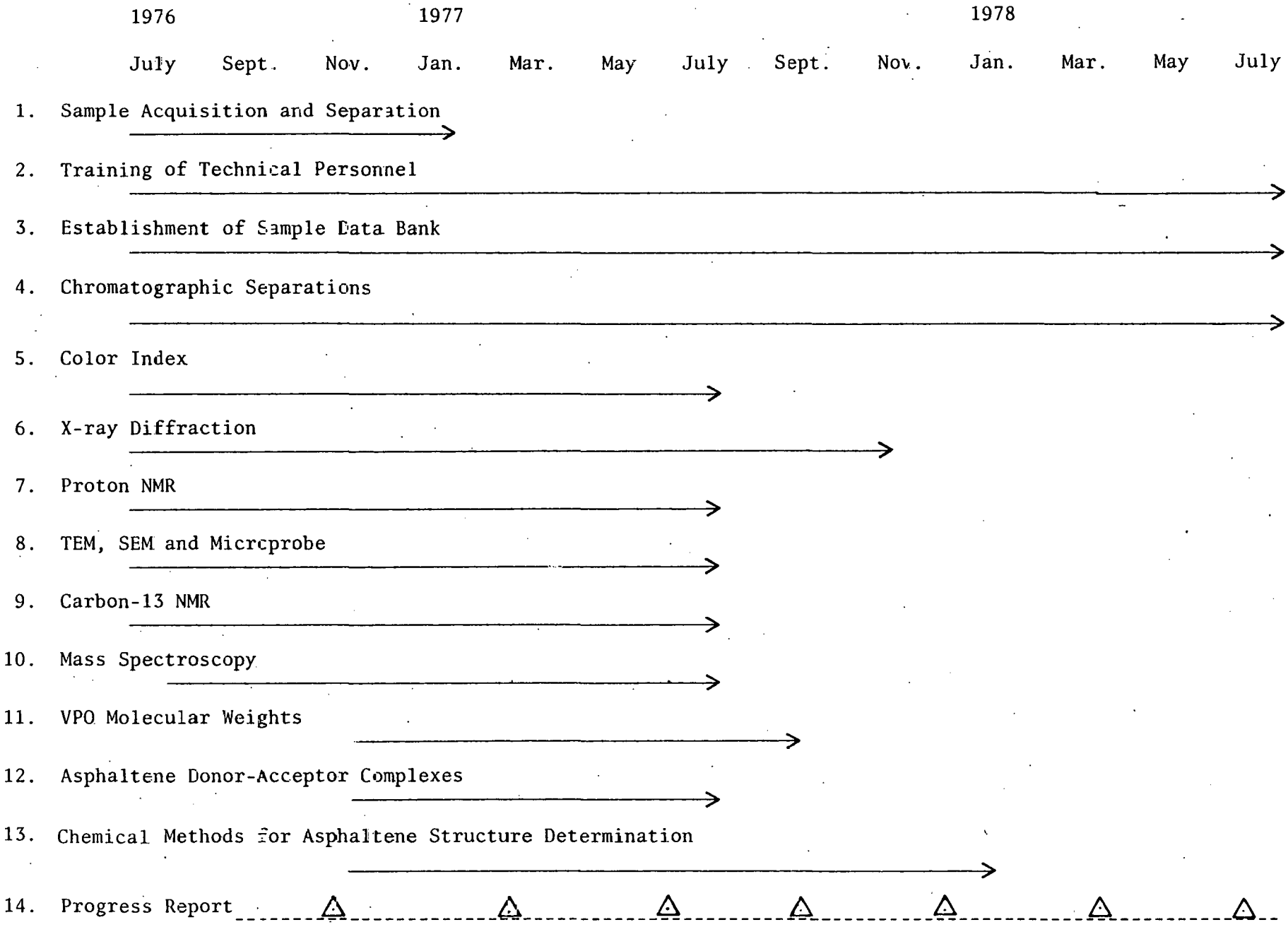


FIG. 2 SOLVENT FRACTIONATION ANALYSIS
OF COAL LIQUID PRODUCTS

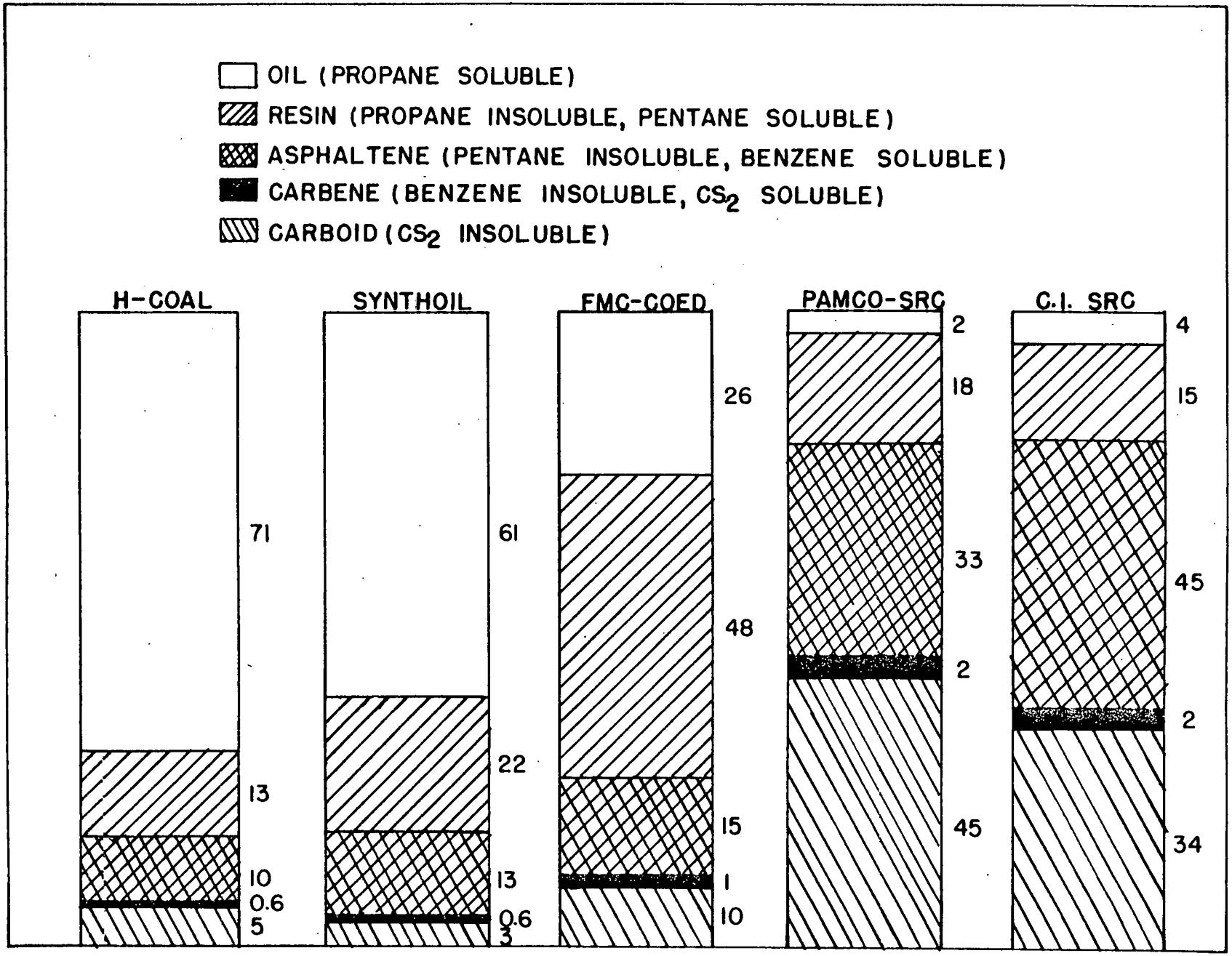


Table I. PAMCO SRC* Solvent Fractions Ultimate Analysis, % **

Fraction	C	H	N	S	O***	Ash
Oil	89.95	7.35	0.42	0.14	2.14	0.20
Resin	88.94	7.30	0.92	0.31	2.53	0.51

* Flash tower bottoms from West Kentucky, hvBb, Colonial Seams 9 + 14 coal.

** Moisture and ash free.

*** By difference.

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

Fraction	Standard Solvent Fractionation (Weight%)	Chromatographic Eluting Solvent	Normalized Waters System 500 (Weight%)	After Solvent Fraction of THF Eluted Fraction (Weight%)	Chromatographic Fractionation Reference (2) (Weight%)
Oil	61	Hexane	49.0		52.6
	83		86		69.3
Resin	22	Hexane/Benzene	12.5		16.7
Asphaltene	13 — 13	THF	38.5 — 10.5		30.7 — 30.7
Carbene + Carboid	4 — 4	—	3.5		—
Actual Total Recovery	96		96.9		(100)

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 (2). 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.

Work forecast:

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

(2) Separation of Asphaltenes by Chromatography

(a) Solvent Elution Chromatography

In previous quarterly reports (1, 4, 5, 6),chromatography with different types of adsorbents (silica gel, alumina, Amberlyst-15 resin) was described. Silica gel was found to be the most useful adsorbent for separating asphaltenes. Two major fractions were obtained by exhaustive solvent elution chromatography with benzene and diethyl ether. In the present quarter, we were able to scale up our chromatographic separations to a 4-5 gram preparative scale by employing a large 50x500 mm column. The preparative scale operations enabled us to improve our material recovery by use of a third solvent, tetrahydrofuran, to elute the small residue not generally obtained previously. We have also begun studies on asphaltene fractions obtained by use of the dry HCl precipitation procedure (7). We hope to learn if there is any correlation between these fractions and our solvent eluted fractions.

The results of the silica gel chromatographic separations are presented in Table III. It may be seen that essentially complete recoveries, 98-99%, are generally obtained. In each case the THF fraction contains some black char-like material which is not soluble in benzene. This material may have originally been present in the starting asphaltene, and could have been solubilized in benzene by association with other molecules. However, it is also likely that this material, which resembles carboid solvent fractions, was formed from labile asphaltene molecules in passing through the silica gel column. The benzene and diethyl ether eluted fractions are brown powders which retain their benzene solubility. Furthermore, when each of these fractions was rechromatographed on silica gel with the original eluting solvent, that fraction was recovered essentially quantitatively (97%). This demonstrates that these asphaltene fractions are stable toward silica gel chromatography.

An attempt was made to separate synthoil asphaltene into two fractions by precipitation with dry HCl from benzene. The precipitate was filtered and the benzene soluble fraction (acid and neutral molecules) was obtained in 48% yield. However, after the HCl adduct of the basic fraction was treated with dilute aqueous alkali, it was found that most of the material in this fraction was black, char-like, and insoluble in benzene. Therefore, we are repeating this preparation in order to obtain a basic fraction which will retain its solubility in benzene.

Molecular weights of the various synthoil asphaltene products in benzene and THF are presented in Table

(b) Gel Permeation Chromatography

Exhaustive solvent elution chromatography with silica gel to obtain major fractions has been described in section (2) (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

TableIII. - Silica Gel Chromatography of Asphaltenes

Asphaltene	Weight % Recovered by Solvent Normalized: Benzene	Et_2O	THF*	Actual Wt.% Recovery
Synthoil	45	37	18[a]	98
HRI H-Coal	47	33	20[b]	99
FMC-COED	41	46	13[b]	95
Cat. Inc.SRC	51	35	14[c]	99
	56	35	9[d]	100
PAMCO SRC	47	40	13[e]	99

*Solubility in benzene: (a) 50%; (b) small; (c) 15%; (d) 22%; (e) 24%.

the Waters analytical high pressure liquid chromatographic system described previously (1). Three μ-Styrogel columns (two 100Å and one 500Å, 7 mm IDX 30cm length, ≈ 3000 plates each) were connected in series. Uninhibited THF was used as solvent.

The results for selected fractions are shown in Fig. 3 . It appears that each of the solvent elution chromatography fractions may be further fractionated on μ-Styrogel to obtain several subfractions based on molecular size. Fractions 1 and 15 appear to have comparatively large amounts of high molecular size materials, and fractions 4, 6 and 23 appear to contain comparatively large amounts of low molecular size materials.

Work Forecast:

Asphaltene fractions, separated by solvent elution chromatography on the basis of group type, polarity, and aromaticity, and further separated according to size by gel permeation chromatography will be examined by a variety of analytical techniques in order to further characterize the asphaltene fraction of coal liquids. Mass spectroscopy may be a particularly useful technique with these samples.

(3) Characterization of Coal Liquid Fractions by Physical Methods

Work accomplished:

(a) NMR Spectroscopy

In the last quarterly report (6) average molar properties of asphaltenes were reported. These properties were obtained by use of modified Brown-Ladner structural parameter equations. The derivation of the following structural parameters was given previously:

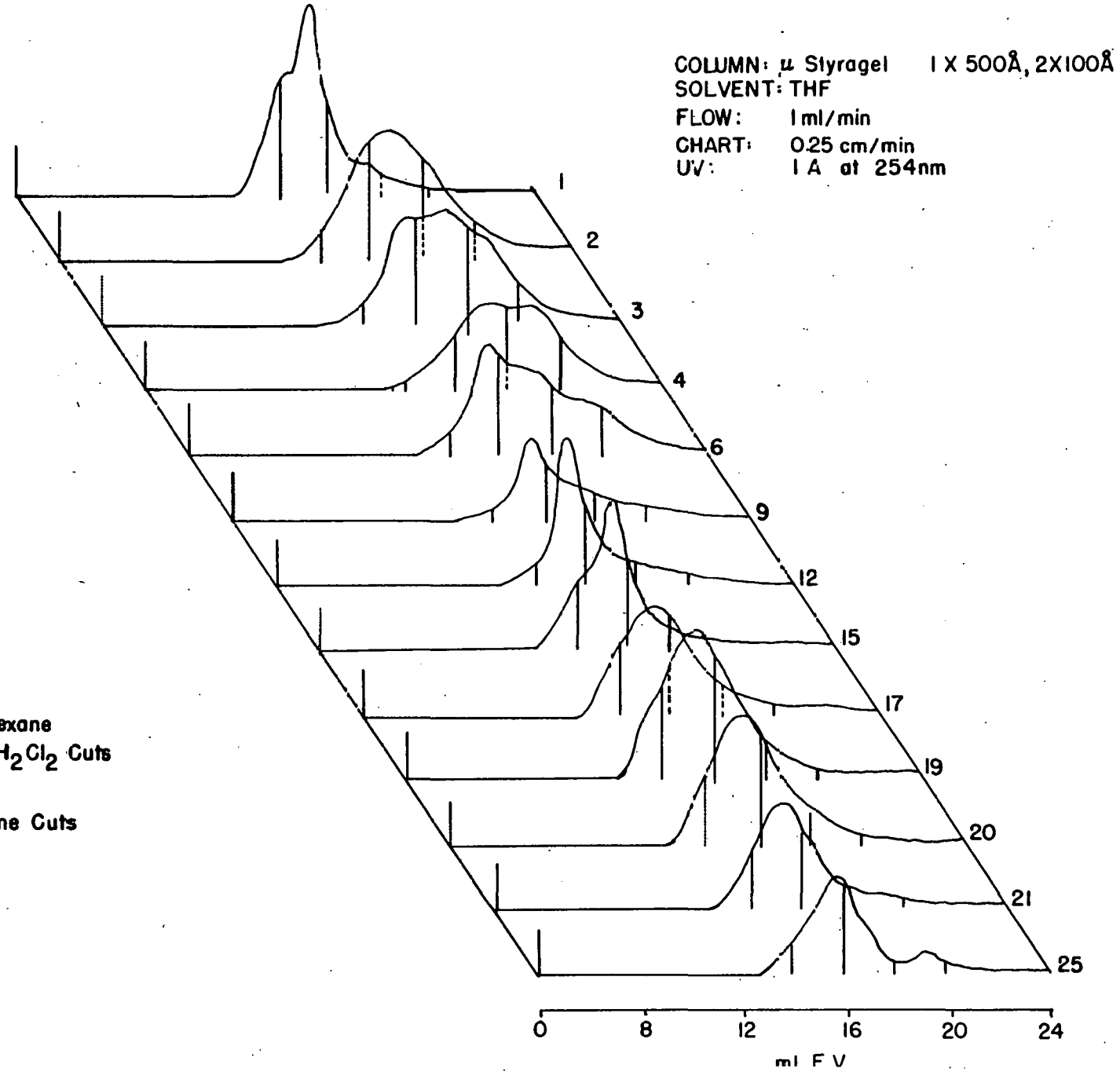
f_a = fraction of total carbon which is aromatic carbon

$\frac{H_{aru}}{C_{ar}}$ = ratio of substitutable edge atoms to total aromatic atoms

σ = fraction of the available aromatic edge atoms occupied by substituents

R_s = number of sustituted aromatic ring carbons

FIG. 3 GPC CHROMATOGRAPHS OF SYNTHOIL ASPHALTENE SILICAGEL CUTS



NOTE:

1 to 17: 90% Hexane
10% CH_2Cl_2 Cuts

19 to 23: Benzene Cuts

n = number of carbon atoms per saturated substituent

C_A = total number of aromatic carbon atoms

R_A = number of aromatic rings

We now report, Tables IV, V, VI, average molar properties for three of the other major coal liquid solvent fractions: oil, resin, and carboid (1).

The oils, with the exception of the SRC products, are seen to be fairly aromatic species having from 43 to 54 percent of the carbon as aromatic carbon. They have about one aromatic ring per average molecule, and contain only small amounts of the heteroatoms N, O, and S. These molecules are moderately substituted with 41-52 percent of the available aromatic edge carbons being substituted. The average number of carbon atoms per saturated substituent ranges from 2.3 to 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 percentage of aromatic carbons and a larger average aromatic ring system.

The trends cited above continue in the average asphaltene molecules, and were discussed previously (6).

Average molecules of carboids, Table VI, are seen, in general, to have the largest molecular weights, and the largest aromatic rings systems. They contain the most heteroatoms found in any of the solvent fractions. The degree of substitution and the number of carbon atoms per saturated substituent are about the same as is found in the asphaltene fractions.

TABLE IV

AVERAGE MOLAR PROPERTIES OF OILS[A]

	FMC-COED	SYNTHOIL	CATALYTIC INC. SRC	HEI H-COAL	PAMCO SRC
MOLECULAR FORMULA	$C_{19.11}H_{26.03}N_{0.38}O_{0.48}S_{0.09}$	$C_{17.77}H_{23.28}N_{0.1}O_{0.25}S_{0.03}$	$C_{20.02}H_{18.32}N_{0.08}O_{0.18}S_{0.05}$	$C_{16.58}H_{20.25}N_{0.07}O_{0.09}S_{0.00}$	$C_{23.00}H_{22.40}N_{0.09}O_{0.41}S_{0.01}$
MOLECULAR WEIGHT[B]	267	243	264	222	307
H^*_{AR}	0.16	0.17	0.48	0.24	0.40
H^*_{α}	0.30	0.35	0.28	0.33	0.37
H^*_{O}	0.54	0.48	0.24	0.42	0.23
F_A	0.43	0.46	0.76	0.54	0.71
H_{ARU}/C_{AR}	1.03	1.01	0.75	0.94	0.82
σ	0.51	0.52	0.24	0.41	0.34
R_S	4.4	4.3	2.7	3.5	4.6
N	2.8	2.4	1.9	2.3	1.6
C_A	8.3	8.2	15.3	8.9	16.3
R_A	0.9	1.0	2.9	1.3	2.5

[A] BROWN AND LADNER METHOD $x = y - 2$, $H^{*\prime}_{AR} = H^*_{AR} = 0.5\ O/H$

[B] VPO IN BENZENE

TABLE V

AVERAGE MOLECULAR PROPERTIES OF RESINS[A]

	FMC-COED	SYNTHOIL	CATALYTIC INC. SRC	HRI H-COAL	PAMCO SRC
MOLECULAR FORMULA	$C_{22.55}H_{23.56}N_{0.25}O_{0.22}S_{0.73}$	$C_{22.18}H_{23.70}N_{0.28}O_{0.67}S_{0.01}$	$C_{27.71}H_{24.57}N_{0.22}O_{0.61}S_{0.00}$	$C_{20.10}H_{18.94}N_{0.22}O_{0.38}S_{0.01}$	$C_{26.07}H_{25.48}N_{0.23}O_{0.56}S_{0.03}$
MOLECULAR WEIGHT[B]	325	305	370	270	352
H^*_{AR}	0.28	0.29	0.43	0.40	0.37
H^*_u	0.37	0.35	0.30	0.35	0.39
H^*_O	0.35	0.36	0.27	0.25	0.25
F_A	0.63	0.62	0.75	0.72	0.69
H_{ARU}/C_{AR}	0.87	0.84	0.71	0.77	0.82
σ	0.47	0.41	0.29	0.33	0.38
R_S	5.8	4.8	4.3	3.7	5.5
N	2.0	2.0	1.9	1.7	1.6
C_A	14.1	13.8	20.8	14.4	17.9
R_A	1.9	2.1	4.0	2.7	2.6

[A]BROWN AND LADNER METHOD x = y = 2, $H^{*1}_{AR} = H^*_{AR} - 0.5\ D/H$

[B]VPO IN BENZENE

TABLE VI

AVERAGE MOLECULAR PROPERTIES OF CARBOIDS[A]

	FMC-COED	SYNTHOIL	CATALYTIC INC. SRC	HRI H-COAL	PAMCO SRC
MOLECULAR FORMULA	$C_{25.76}H_{22.26}N_{0.55}O_{2.98}S_{0.23}$	$C_{69.04}H_{53.37}N_{1.10}O_{1.34}S_{0.61}$	$C_{74.45}H_{48.22}N_{0.70}O_{4.44}S_{0.11}$	$C_{73.52}H_{49.55}N_{1.11}O_{4.21}S_{0.31}$	$C_{42.66}H_{29.29}N_{0.43}O_{2.81}S_{0.22}$
MOLECULAR WEIGHT[B]	394	938	1026	1020	600
H^*_{AR}	0.43	0.49	0.51	0.52	0.485
H^*_α	0.39	0.35	0.34	0.31	0.31
H^*_O	0.18	0.16	0.15	0.17	0.205
F_A	0.76	0.80	0.84	0.84	0.82
H_{ARU}/C_{AR}	0.86	0.66	0.59	0.58	0.61
σ	0.43	0.29	0.34	0.33	0.34
R_S	7.3	13.6	12.6	11.9	7.4
N	1.5	1.5	1.4	1.5	1.7
C_A	19.5	55.5	62.7	61.8	35.1
R_A	2.3	13.5	14.0	14.0	7.8

[A] BROWN AND LADNER METHOD $x = y = 2$, $H^*_{AR}{}' = H^*_{AR} - 0.5\ C/H$

[B] VPO IN DMF

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. 4 shows the H_{aru}/C_{ar} values for some typical 1-7 kata condensed aromatic ring systems. Table VII gives the atomic C/H ratios for the original coals and the coal liquid solvent fractions. The H_{aru}/C_{ar} values are plotted vs the atomic C/H ratios in Fig. 5. A smooth decrease in H_{aru}/C_{ar} vs C/H is obtained which 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 representative of the H_{aru}/C_{ar} values is shown on the left side of the figure. This comparison indicates that oils contain $\approx$1 aromatic ring, resins $\approx$ 2-3 aromatic rings, asphaltenes $\approx$ 3-5 aromatic rings, and carboids $\approx$ 4-7 aromatic rings per aromatic ring system.

It is interesting to note that the atomic C/H values of coals generally fall in the range 1.16-1.26 which would correspond to about 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 mechansism consistent with such observations for coal liquefaction products is:

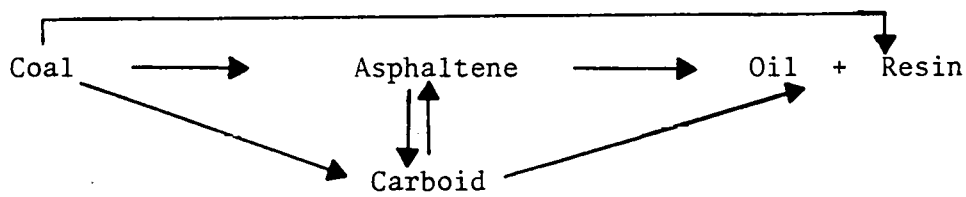


Table VII Atomic C/H Ratios of Coal Liquid Solvent Fractions

Fraction	Synthoil	H-Coal	FMC-COED	Cat.Inc.SRC	PAMCO SRC
Original Coal	1.05	1.26	1.24	1.17	1.16
Coal Liquid	0.86	0.90	0.90	1.34	1.22
Oil	0.76	0.81	0.73	1.09	1.02
Resin	0.94	1.05	0.96	1.13	1.02
Asphaltene	1.12	1.22	1.06	1.32	1.16
Carbene	1.23	1.44	1.13	1.49	1.35
Carboid	1.29	1.47	1.16	1.54	1.45

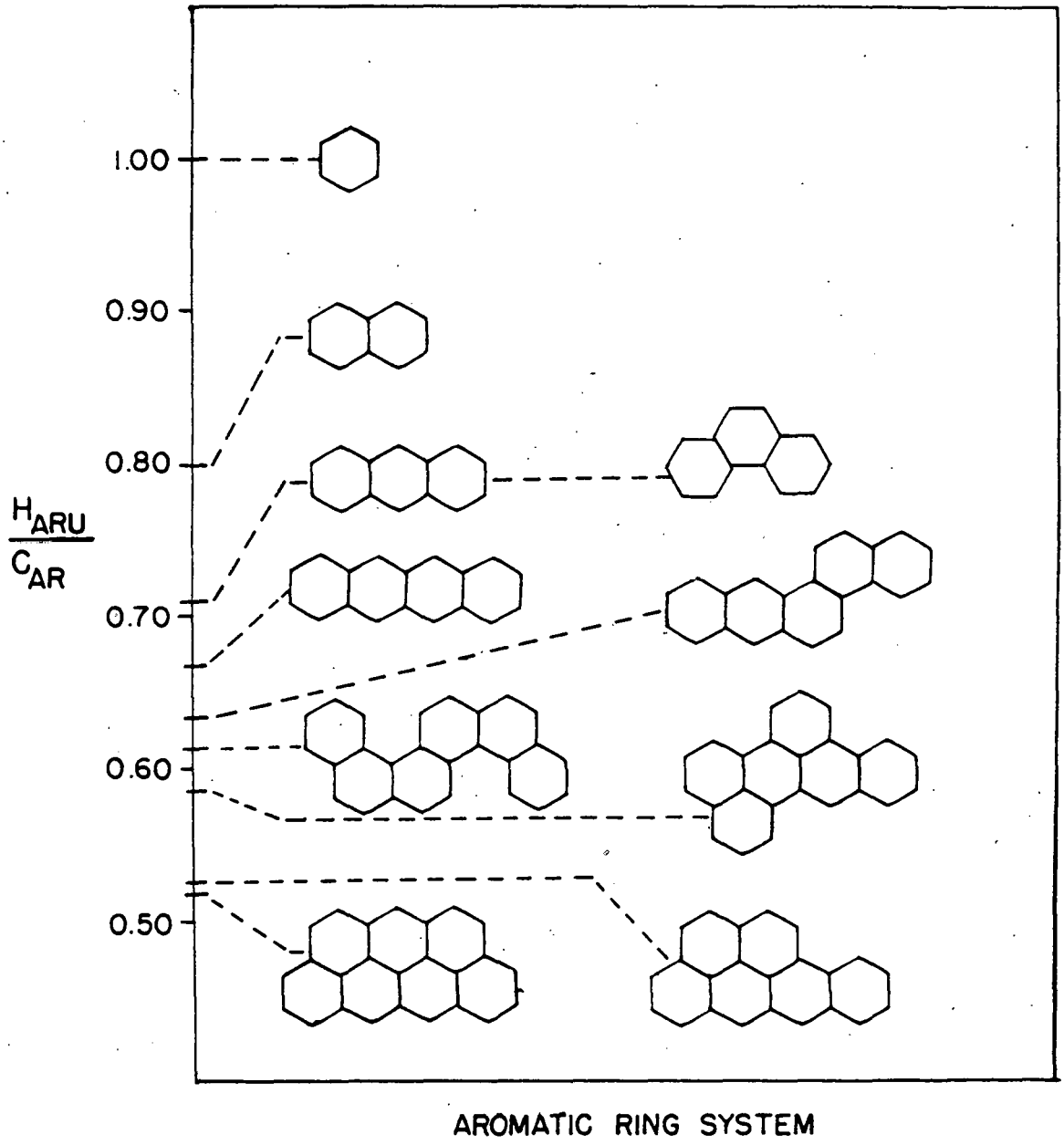


FIG.4 H_{ARU}/C_{AR} VALUES FOR SELECTED AROMATIC RING SYSTEMS

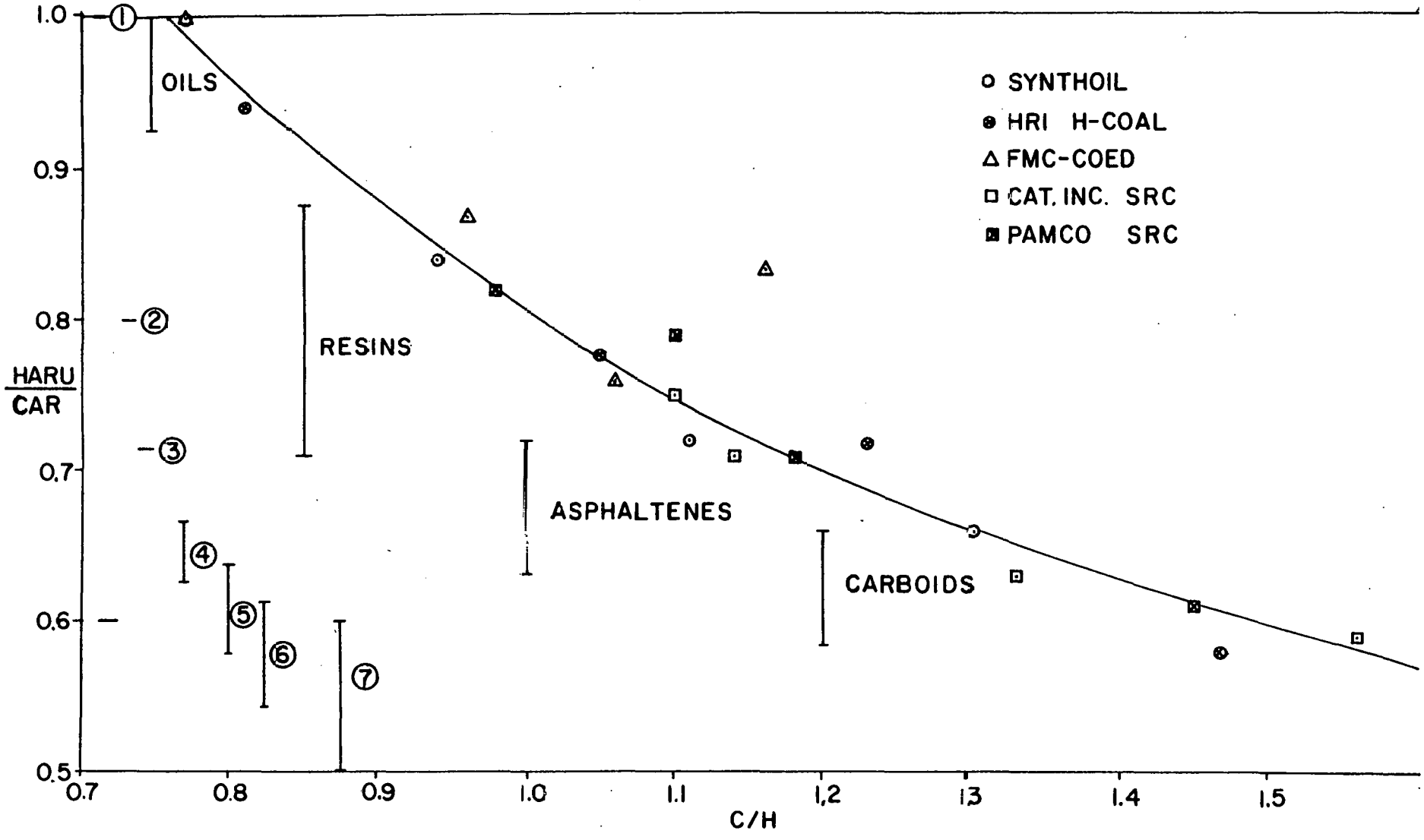


FIG. 5 VARIATION IN AROMATIC RING SIZE VS. ATOMIC C/H RATIO

(b) Particle Size Determination by Transmittance Electron Microscopy

The aromatic sheet dimensions of coal asphaltenes may be determined by the x-ray diffraction method.* These dimensions are found to be within the range of observation of Transmission Electron Microscopy (TEM), which offers a second technique to determine particle and cluster sizes. We previously described the experimental spray deposition technique, and the computerized image processing technique to be used for analyzing the TEM pictures (4, 6).

Because the quality of the TEM pictures was not high enough to permit particle resolution, due to background interference, the supporting carbon film was replaced with silicon monoxide supporting films. However, the atmospheric spray technique still did not result in the preparation of resolvable isolated asphaltene molecules or clusters. Therefore, a new technique, vacuum-deposition, is being explored.

The vacuum-deposition is carried out by dissolving a small sample of asphaltene in excess solvent, and mixing the solution with an inert supporting material such as fire brick. The solvent is then removed by rotary evaporation leaving the sample dispersed in the inert matrix. The mixture is put in a heating boat inside a vacuum chamber, and deposited at 10^{-7} torr onto a thin film ($\approx$150Å) of silicon monoxide. The TEM pictures obtained with this technique showed a uniform distribution of particles, but the particles were too large to represent individual asphaltene molecules. It may be that either the sample concentration and/or the heating rate was too high. Additional vacuum depositions will be carried out in the next quarter in order to optimize the sample concentration, heating temperature, and deposition distance so as to obtain optimum particle depositions.

Additional work was carried out on the computer assisted image processing techniques. More software was added to the DEC-10 computer system in order to improve the statistical analysis of the size distribution and the histogram or graph plotting procedure. The original program for size differentiation has been modified and condensed to handle a larger array of data points with minimal storage space and time.

*See Section (3)(d) of this report.

(c) VPO Investigation of Asphaltene Molecular Weights

Work accomplished:

The probe on the Mechrolab VPO required reconditioning which limited the number of samples that could be run during the past quarter. However, it was possible to obtain molecular weight data for the entire set of asphaltenes in benzene. These results are presented in comparison with the previously reported results (6) in Table VIII. The results indicate that association of asphaltenes takes place in both benzene and tetrahydrofuron over the concentration range of 4-36 g/l. All of the asphaltenes afforded positive linear correlations between concentration and molecular weight except for the FMC-COED in THF. Correlation coefficients were generally reasonably significant. The slopes of the linear correlation lines are greater in benzene than in THF, but the molecular weight values obtained by extrapolating the plots to infinite dilution are in very good agreement. This suggests that association is more significant in the less polar solvent benzene, but that coal asphaltene dissociation tends to go to completion in either solvent at infinite dilution.

The results are significant because the majority of molecular weight data for coal liquefaction products, and coal asphaltenes are reported for molecular weights measured in benzene at finite concentrations. Such values, in many cases, represent the molecular weights of associated species not the molecular weight of the true dissociated monomeric species.

The molecular weights of Synthoil asphaltene products vs concentration in benzene and THF are shown in Table IX . The slopes of the equations generally appear lower in THF than in benzene*, as did the slopes of the other asphaltene equations. The value found for the silylated asphaltene, 620, is in good agreement with a calculated value of 601 for a Synthoil asphaltene which has 50% of its oxygens silylated.

*The exception, benzene eluted asphaltene from silica gel, has a rather large deviation in infinite dilution values and is being repeated with a new sample.

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

Asphaltene	Solvent	Least Squares Equation	Corr. Coeff.	AV. MV at zero Conc.	% Dev.
Synthoil	THF	$MW = 2.85 \pm 0.96\ C + 568 \pm 17.5$	0.83	560	1.4
	Benzene	$MW = 11.1 \pm 0.60\ C + 552 \pm 10.4$	0.995		
HRI H-Coal	THF	$MW = 3.02 \pm 0.36\ C + 471 \pm 6.0$	0.95	492	4.3
	Benzene	$MW = 6.27 \pm 0.30\ C + 513 \pm 7.6$	0.99		
FMC-COED	THF	$MW = -0.095 \pm 0.25\ C + 333 \pm 5.1$	0.76	351	5.0
	Benzene	$MW = 5.61 \pm 0.26\ C + 368 \pm 4.5$	0.99		
Cat. Inc. SRC	THF	$MW = 1.11 \pm 0.38\ C + 486 \pm 7.6$	0.77	483	0.5
	Benzene	$MW = 4.74 \pm 0.58\ C + 481 \pm 12.1$	0.95		
PAMCO SRC	THF	$MW = 2.26 \pm 0.48\ C + 363 \pm 10.4$	0.87	363	0.0
	Benzene	$MW = 5.81 \pm 0.37\ C + 363 \pm 3.8$	0.99		

*Conc. g/l

Table IX . - Molecular Weight of Synthoil Asphaltene Products vs. Concentration* in Benzene and THF

	Solvent	Least Squares Equation	Corr. Coeff.	Av. MW at Zero Conc.	%Dev
Starting Asphaltene	THF	MW = 2.85 ± 0.96 C + 568 ± 17.5	0.83	560	1.4
	Benzene	MW = 11.1 ± 0.60 C + 552 ± 10.4	0.995		
Silylated Asphaltene	THF	MW = 1.35 ± 0.13 C + 639 ± 2.5	0.97	620	3.1
	Benzene	MW = 4.93 ± 0.95 C + 600 ± 21.9	0.87		
Benzene Eluted Asphaltene from Silica Gel	THF	MW = 5.26 ± 0.50 C + 468 ± 9.8	0.97	507	7.7
	Benzene	MW = 3.71 ± 0.27 C + 546 ± 6.5	0.97		
Et_2O Eluted Asphaltene from Silica Gel	THF	MW = -0.10 ± 0.31 C + 529 ± 7.9	0.11**	530	0.2
	Benzene	MW = 8.0 ± 0.20 C + 531 ± 4.9	0.997		
THF Eluted Asphaltene from Silica Gel (Benzene Soluble)	THF	MW = 1.16 ± 0.09 C + 472 ± 3.0	0.93	472	—
THF Eluted Asphaltene from Silica Gel (Benzene Insoluble)	THF	MW = 6.84 ± 0.70 C + 869 ± 21	0.98	869	—
Sternberg Acid/ Neutral Asphaltene Fraction(7)	THF	MW = 1.21 ± 0.15 C + 475 ± 3.9	0.96	475	—

*Conc. g/l

**This low correlation coefficient is not caused by scatter in the points, but is a consequence of the almost zero slope, of the MW vs Conc. curve for this fraction, i.e., a zero slope would afford zero correlation.

If one considers the slope of the MW vs concentration curve as a measure of association, then it is instructive to consider how association would be expected to vary among the different asphaltene products. Since the slopes are greatest in benzene we will consider only the series:

Asphaltene	Slope
Starting	11.1
50% O - Silylated	4.9
Benzene Eluted from Silica Gel	3.7
Et_2O Eluted from Silica Gel	8.0

We feel that these preliminary results tend to support the hydrogen bonding model of coal asphaltene association (7 , 8) more than the charge transfer complexation model previously suggested as an alternative model. The reasoning for this is as follows: silylation eliminates phenolic OH functions and would be expected to reduce H-bonding; the benzene eluted fraction from silica gel is known to have a reduced basic nitrogen concentration (see section (5) (b) of this report) which would also reduce the hydrogen bonding possibilities; the Et_2O eluted fraction, which contains the major portion of both the basic nitrogen and basic oxygen, still contains some phenolic OH, (see Ref. 6 , Section 2) and therefore would be expected to show the smallest decrease in associative properties relative to starting asphaltene. It will be interesting to see if association is severely reduced in the Sternberg-acid/neutral and basic fractions. These measurements are in progress.

(d) X-Ray Diffraction

The X-ray diffraction patterns of solid coal liquefaction products show diffuse bands typical of mesomorphic or semicrystalline substances. In previous Quarterly Reports (2 , 4 , 6) we discussed the analyses of the (002), (gamma), (10), and (11) peaks for a variety of coal asphaltene samples from different coal liquefaction demonstration projects. Aromaticity, f_a, and crystallite parameters were reported for asphaltenes (4).

It has been reported that a progressive sharpening of the (10) and (11) bands is observed in coal as carbonization temperature is raised (10). 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 carboid solvent fractions are shown in Fig. 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 carboid. This supports the proposition that these materials are formed by mechanisms similar to carbonization of coal.*

The aromaticity values, f_a, and x-ray crystallite parameters are presented in Table X . The f_a values are seen to increase in going from asphaltenes, to carbene, to carboid which suggests larger aromatic ring systems in the order cited. The crystallite parameters also generally increase in the same direction indicating larger aromatic sheet diameters and larger cluster sizes in the same direction.

Work Forecast:

Characterization will continue on all applicable fractions by the analytical and physical methods described in this and previous reports. NMR measurements and VPO molecular weight determinations will be carried out on newly obtained chromatography fractions, and products from various chemical treatments of asphaltenes and other suitable fractions. Additional x-ray diffraction crystallite parameters will be obtained for various solvent and chromatographic fractions. Continued efforts will be made to obtain high quality TEM picture for particle size determination. Various simplified asphaltene fractions obtained by consecutive SEC and GPC chromatographic separations will be examined by mass spectroscopy.

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*The (10) band shows only minimal sharpening in going from asphaltene to carboid. Since this band is related to the separation of the first set of nearest neighbors in the plane of the aromatic ring compounds, it would not necessarily be expected to be sharpened by carbonization changes to the same degree as the (11) band which represents the second set of nearest neighbors in the plane of the ring compounds.

FIG. 6 X-RAY DIFFRACTION PATTERNS FOR HRI H-COAL COAL LIQUID SOLVENT FRACTIONS

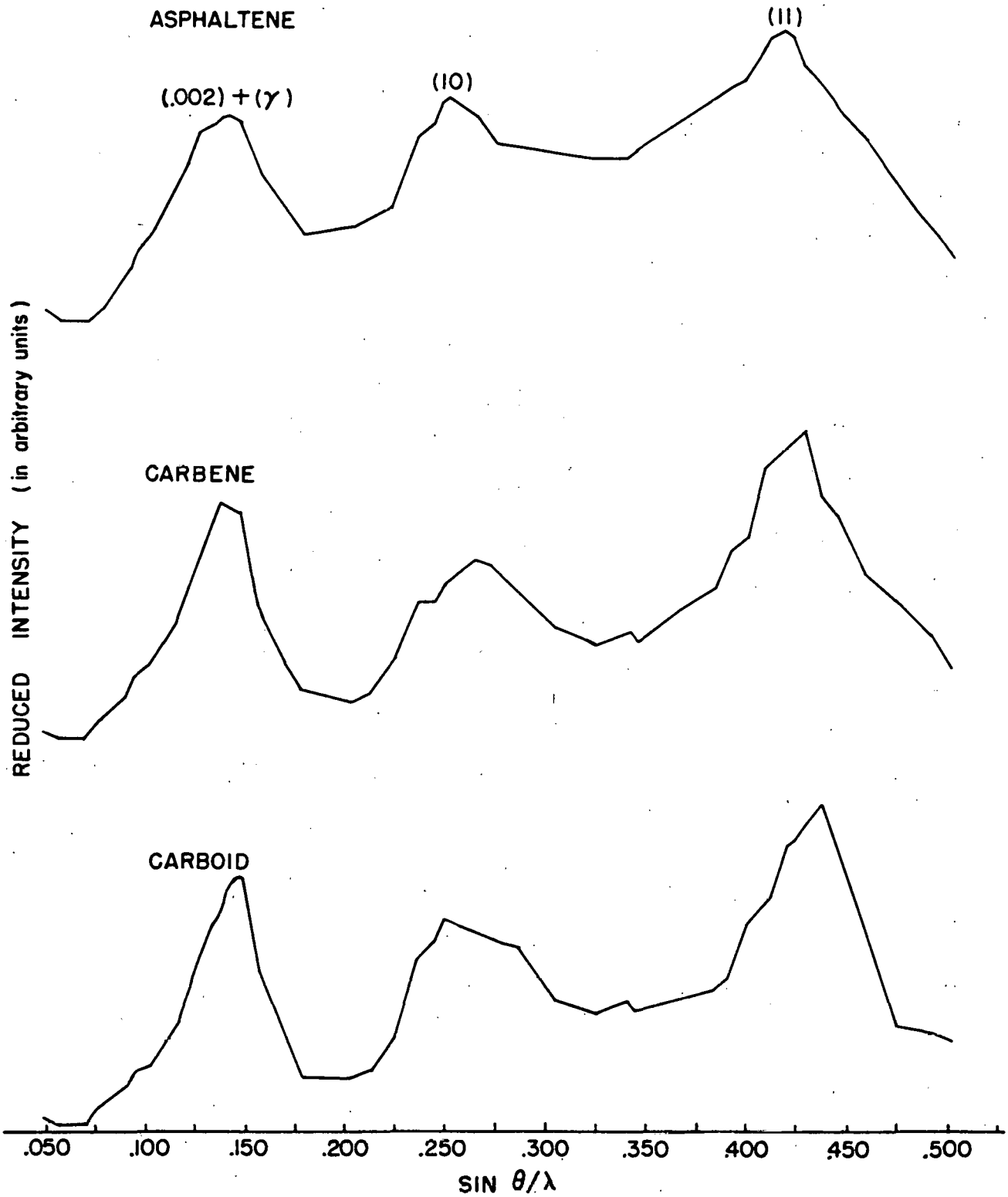


Table X . - Aromaticity, f_a, and Crystallite Parameters for HRI H-Coal Liquid Solvent Fractions

	Asphaltene	Carbene	Carboid
f_a [1]	0.67	0.70	0.75
d_m (Å) [2]	3.57	3.57	3.57
d_γ (Å) [2]	4.42	4.42	5.0
L_c (Å) [2]	13.6	16.1	16.1
M [3]	5	7	7
L_a [4] (Å) (10) band	11.9	12.6	12.6
(11) band	9.2	13.7	16.2
L_a [5] (Å) (10) band	6.7	7.5	7.5
(11) band	8.2	12.5	14.5

[1] $f_a = C_A/C_{total} = A_{002}/A_{002}+A_\gamma$.

[2] d_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.

[4] L_a = diameter of the aromatic sheets from Scherrer's Eq. (11).

[5] L_a = diameter of the aromatic sheets from Diamond's Curve, Fig. (7), Ref 12.

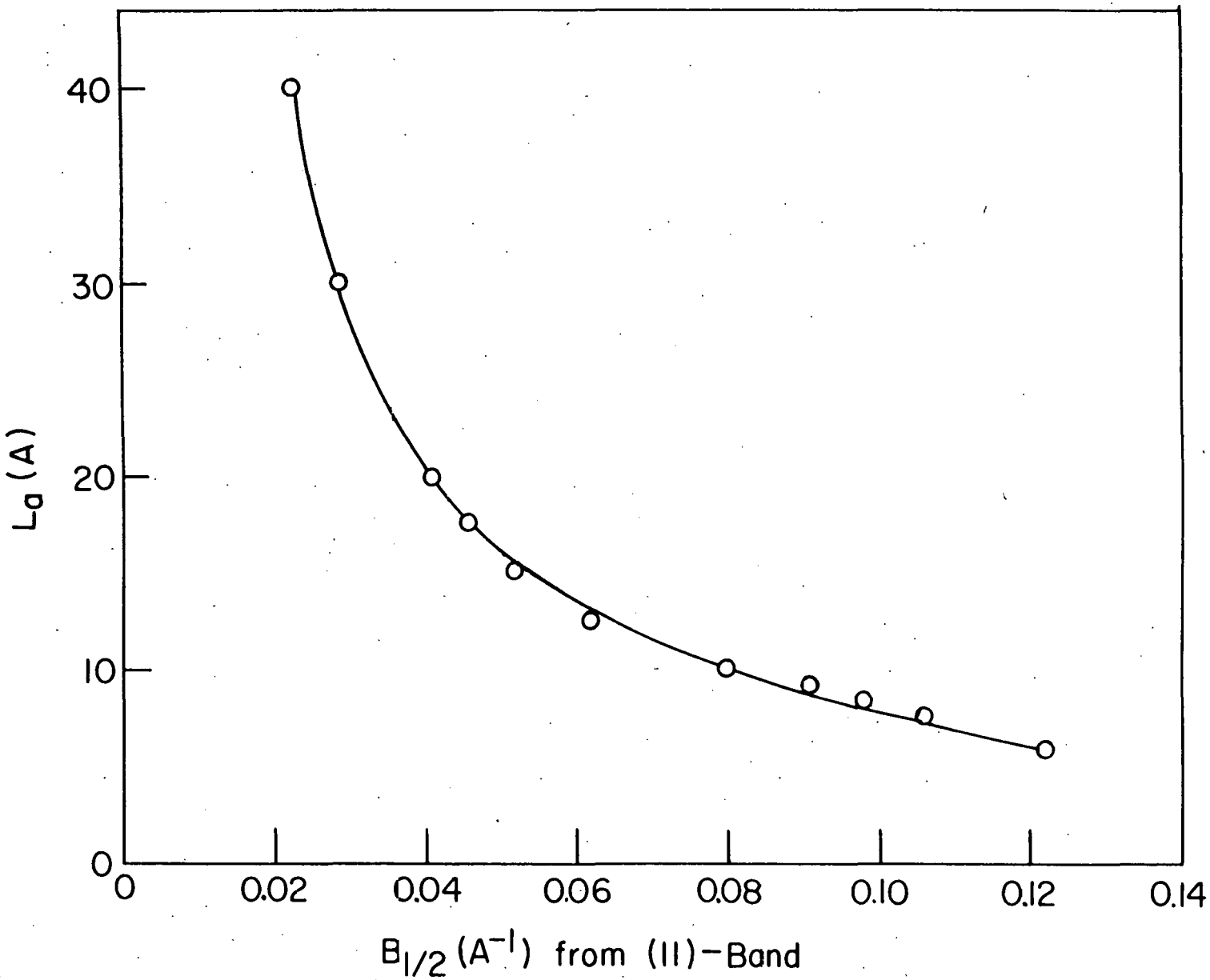


FIG. 7 Calibration Curve of Corrected Diameter of Aromatic Sheets Based on the Width at Half Maximum of the (11)-Band of the Curves Calculated by Diamond.

(4) Asphaltene Donor-Acceptor Complexes

Work accomplished:

Research aimed at elucidating the nature of coal asphaltene-iodine complexes was described in the last Quarterly Report (6). During the present quarter only a limited amount of work was carried out in the area of asphaltene-iodine complex conductivity studies.

(a) Conductivity

The conductivity of a series of asphaltenes and asphaltene-iodine complexes was reported previously (6). Asphaltene, and asphaltene chromatography fractions, afforded resistivity values which remained constant as pressure was increased from 10-3000 atm. However, two of the asphaltene-iodine complexes, derived from starting asphaltene, and benzene eluted asphaltene, showed an inverse relationship which suggests that the conduction is electronic in those cases. The other asphaltene-iodine complex, a chromatographic fraction eluted from Amberlyst-15 with pyridine, and believed to contain asphaltene with basic nitrogen and oxygen groups showed a linear relationship with a positive slope when log resistivity was plotted vs pressure. An ionic conduction mechanism related to interactions between the basic groups on the asphaltene and iodine was believed possible in this case. An alternative possibility was that this sample of pyridine eluted asphaltene was contaminated with traces of pyridine which could have formed traces of ionic conductors with iodine.

Two experiments were designed to resolve this ambiguity. An ionic quarternary salt of asphaltene was synthesized by methylation of asphaltene with methyl iodide (see section (5) (b) of this report), and a fresh asphaltene-iodine complex was synthesized with a basic asphaltene fraction chromatographed from silica gel with diethyl ether. Conductivity studies were carried out with the former sample, and resistivity values ranging from 9.6×10^9 ohm-cm to 1.08×10^{10} ohm-cm were obtained as the pressure was increased from 10 to 1870 atm. Unfortunately the second sample could not be run during the quarter due to instrument malfunction, and we will have to wait to obtain the result until the next quarter.

Work forecast:

Studies will continue on asphaltene donor-acceptor complexes by the same analytical and physical methods described in this report. Donor-acceptor studies will be carried out with π-acceptors such as tetracyanoethylene and polynitroaromatic compounds to see whether such species will give definite π-complexes with donor asphaltene and resin molecules. ESR studies will be initiated, when equipment becomes available, to study the excitation processes of asphaltene molecules to see if they resemble those of known donor-acceptor charge transfer complexes (13, 14).

(5) Chemical Methods for Asphaltene Structure Determination

Work accomplished:

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

(a) Silylation of Hydroxyl Groups

In the last Quarterly Report (6) we described the procedure and results for the silylation of the Synthoil, FMC-COED, PAMCO SRC, and Catalytic Inc. SRC asphaltenes. The results for the present quarter are included in the updated Table XI . A repeat silylation of Synthoil afforded a result in close agreement with the previous silylation— OH/O_{total} = 51%. The silylation results for the HRI H-Coal asphaltene indicate that the percentage of the total oxygen present as phenolic -OH is 53%. These results indicate a marked difference in the percentage of oxygen present as phenolic oxygen in asphaltenes produced in SRC processes (92-97%), vis-a-vis asphaltenes produced in catalyzed hydrogenation (47-53%) and staged pyrolysis (61%).

(b) Methylation of Basic Nitrogen Groups

Aromatic pyridine-like compounds are known to react with alkyl halides

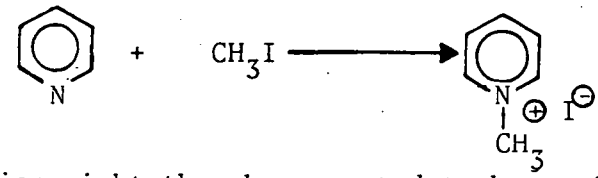
Table XI Analysis of Silylated Asphaltenes

Asphaltene	% Si in Silylated Asphaltene	% -OH in Silylated Asphaltene[a]	% C in Starting Asphaltene[b]	% OH/ ^{O}total in Starting Asphaltene
Synthoil	2.82, 3.22	1.74, 2.00	3.93	44, 51
FMC-COED	6.31	4.30	7.11	61
PAMCO SRC	6.58	4.52	4.68	97
Cat. Inc. SRC	6.17	4.19	4.58	92
HRI H-Coal	4.11	2.62	4.96	53

[a]Using method of Friedman, et al. (15).

[b]Determined by difference.

to form quarternary ammonium salts:



This reaction might then be expected to be useful as a means of determining basic pyridine-like nitrogen in asphaltene molecules. Therefore, alkylation of a Synthoil asphaltene, diethyl ether-eluted fraction from silica gel, was carried out. This material is retained on the silica gel column after elution of an asphaltene fraction with benzene, and is believed to contain a concentrated amount of basic nitrogen containing material.

To a sample of Synthoil, diethyl ether-eluted asphaltene (VPO MW = 530, %N = 1.70), dissolved in benzene was added a large excess (CH_3I/N = 35/1) of methyl iodide. The solution was then refluxed for one week, and the benzene insoluble product filtered, washed with benzene, and dried at 50° in a vacuum oven. The methylated product contained 12.74% iodine.

Analysis of the results indicates that methyl iodide added to the basic nitrogen in the starting asphaltene essentially quantitatively, i.e. for each 0.121 g atoms of nitrogen per 100 g of asphaltene, 0.117 moles of methyliodide added to the asphaltene. This result is substantiated by infrared analysis which shows almost complete loss of the 3460 cm^{-1} N-H stretching band in the diethyl ether-eluted asphaltene fraction.

(c) Reduction of Asphaltene with Potassium

An exploratory run has been carried out with Synthoil asphaltene. The asphaltene was stirred with potassium metal, and a small amount of naphthalene in tetrahydrofuran for seven days under argon at room temperature. The asphaltene turned blackish. After filtration, in vacuo, to remove unreacted potassium, the asphaltene radical anion solution was quenched with ethanol. The work up has been completed and we are now awaiting the results of analysis.

Work forecast:

Additional exploratory chemical prodedures such as silylation, methylation, reduction, and oxidation will be carried out on asphaltenes, asphaltene fractionation products, and other suitable coal liquid solvent fractions as time and manpower permit.

CONCLUSION

Separation of Synthoil coal liquid by high pressure liquid chromatography on silica gel did not permit us to obtain fractions which were as distinctive as those obtained by solvent fractionation. A major fraction, eluted with THF, was found to be a mixture of resin, asphaltene, carbene and carboid.

Solvent elution chromatography of asphaltenes on silica gel has been scaled up, and three major fractions are generally obtained in 98-99 % recovery by exhaustive elution with benzene, diethyl ether, and THF. The third fraction (THF-eluted) represents the 10-20% of material not previously recovered (6), 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.

Proton NMR structural parameters derived for the oil, resin, and carboid solvent fractions suggest that these materials generally fall into a series with the previously reported (6) asphaltene fraction as to molecular weight, aromaticity, ratio of substitutable edge carbon atoms to total aromatic carbon atoms (H_{aru}/C_{ar}), and number of carbon atoms per saturated substituent. A smooth decrease in the H_{aru}/C_{ar} values vs increasing atomic C/H ratios for the various fractions indicates that the increase in C/H values may be caused by an increase in the size of the average polynuclear condensed aromatic ring systems in going from oils to carboids.

Additional VPO molecular weight studies of asphaltenes, as a function of concentration, in the solvents benzene and THF indicate that association of asphaltenes takes place in both solvents over the concentration range 4-36 g/l. The slopes of the correlation lines are greater in benzene than in THF, but the molecualr weight values obtained by extrapolating the plots to infinite dilution are in good agreement.

This suggests that association is more significant in the less polar solvent benzene, but that coal asphaltene dissociation tends to go to completion in either solvent at infinite dilution.

The x-ray diffraction patterns for the HRI H-Coal asphaltene, carbene and carboid solvent fractions show progressive sharpening of the (002) and (11) bands. This is similar to what is observed in coal as carbonization temperature is raised (10), and therefore supports the idea that these materials are formed sequentially by mechanisms similar to those occurring in carbonization of coal.

Methyl iodide addition to a basic fraction of Synthoil asphaltene (diethyl ether-eluted from silica gel) appears to take place in a nearly 1 to 1 molar ratio with asphaltene nitrogen. This implies that essentially all the nitrogen present in this fraction is basic. Infrared examination of this fraction shows little N-H stretching absorption indicating that the basic nitrogens are probably present in pyridine-like compounds.

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