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FOSSIL ENERGY

CHEMISTRY AND STRUCTURES OF COAL-DERIVED ASPHALTENES
PHASE I

Quarterly Progress Report, April—June 1976

I. Schwager

1976

Work Performed Under Contract No. E(49-18)-2031

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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES
Phase I

Quarterly Progress Report for the Period April-June 1976

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ABSTRACT

Coal liquids from the three direct general processes for converting coal to liquid fuels, catalyzed hydrogenation, staged pyrolysis, and solvent refining, have been separated by solvent fractionation into five fractions. These fractions are: propane-soluble (oil); propane-insoluble and pentane-soluble (resin); pentane-insoluble and benzene-soluble (asphaltene); benzene-insoluble and carbon disulfide-soluble (carbene); carbon disulfide-insoluble (carboid). The great majority of the suitable fractions were characterized as to elemental analyses, molecular weight, metal analyses, color intensity, NMR-hydrogen percentages by proton type, infrared spectral analysis, structural parameter determination by x-ray diffraction, and particle size determination by transmittance electron microscopy.

Selected crude asphaltene fractions have been chromatographed on alumina and acidic ion-exchange resins. The two major fractions obtained from Synthoil by elution from an acidic ion-exchange resin with benzene and pyridine compare relatively well with respect to ultimate analysis with previously isolated acidic and basic components of asphaltenes (1,1a).

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 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 U. S.

The objective of Phase I is to complete the isolation and separation of coal asphaltenes and to initiate their characterization.

SUMMARY OF PROGRESS TO DATE

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

(1) Sample acquisition has continued throughout the quarter.
(2) Training of new technical assistants is underway.
(3) Solvent fractionation according to the standard procedure has been extended to include separation of oils, resins, carbenes and carboids.
(4) Chromatography of asphaltenes on alumina and acidic ion exchange resins is being carried out.
(5) Preliminary characterizations are being carried out on solvent separated fractions.
(6) Data bank of asphaltenes.

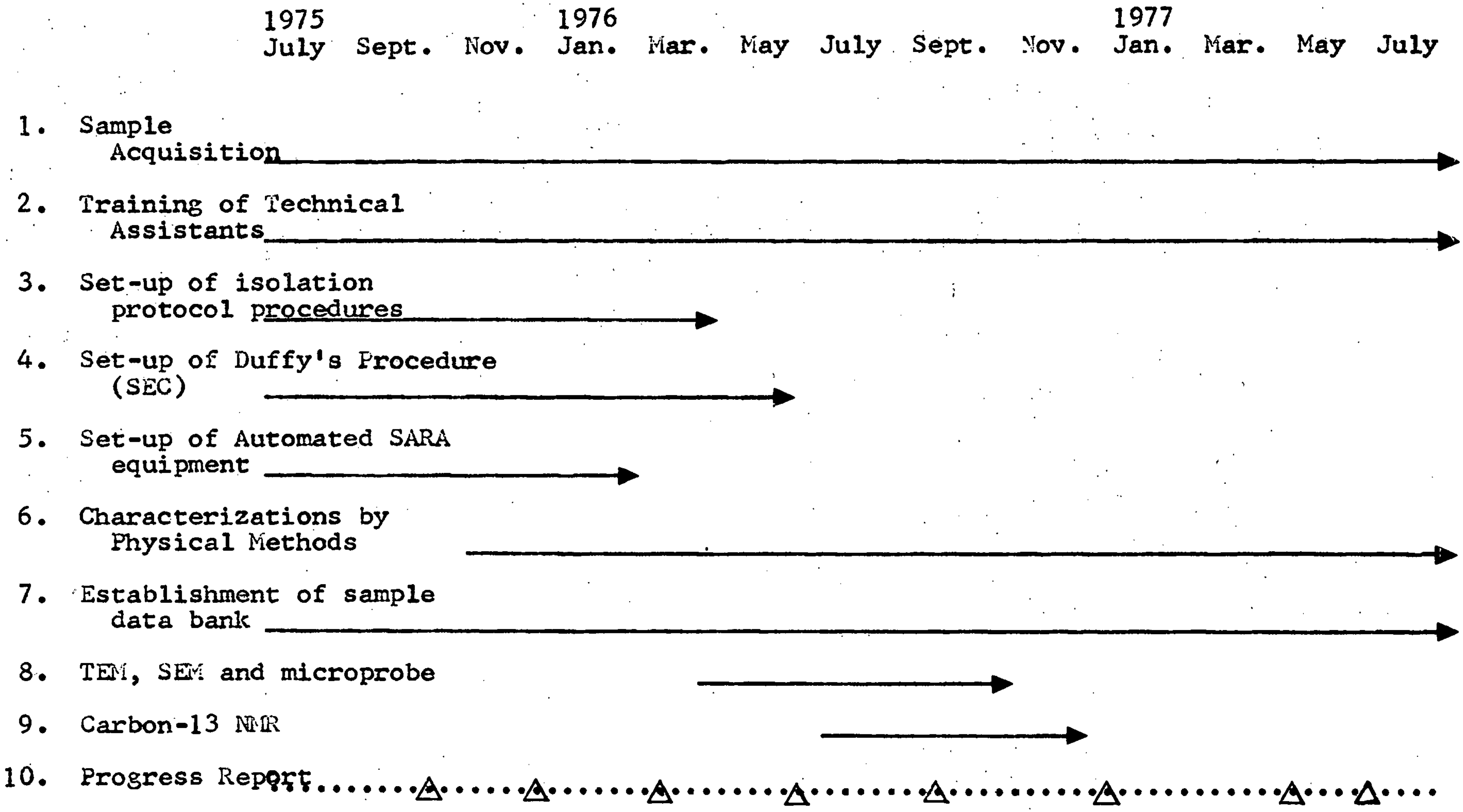
These tasks are listed in the milestone chart in Fig. 1. Detailed discussion is found in the next section.

DETAILED DISCUSSION OF TECHNICAL PROGRESS

(1) Separation of Coal Liquid Products by Solvent Fractionation

Work accomplished:

Fig. 1 Milestone Chart



Coal liquids were previously separated into three crude fractions: pentane-soluble (oil and resin); pentane-insoluble and benzene-soluble (crude asphaltene); benzene-insoluble (carbene and carboid)(1). During the present quarter the solvent fractionation scheme was extended to include the separation of the pentane-soluble fraction into oils (soluble in liquid propane) and resins (pentane-soluble and propane-insoluble). The benzene-insoluble fraction was further separated into carbenes (benzene-insoluble and carbon disulfide-soluble) and carboids (carbon disulfide-insoluble).*

The complete solvent fractionation scheme for separating coal liquid products into five fractions (oil, resin, asphaltene, carbene, and carboid) is shown in Fig. 2. Representative coal liquid samples produced via the three direct coal liquefaction processes were separated into the five fractions described above. The results are presented in Fig. 3. For the catalyzed hydrogenation product produced in the Synthoil process (2), the product composition is about 61% oil, 22% resin, 13% asphaltene, 0.6% carbene, and 3% carboid. The staged pyrolysis filtered product** from the FMC Corporation's COED process (3) has a product composition of about 26% oil, 48% resin, 15% asphaltene, 1% carbene and 10% carboid. The solvent refined coal (SRC) produced by Catalytic Inc. based on PAMCO's SRC process (4) affords about 4% oil, 15% resin, 45% asphaltene, 2% carbene, and 34% carboid.

The analyses of the starting coal liquids and the various solvent fractions are given in Tables I, II, and III. Semiquantitative Metal Analyses are presented in Table IV. It may be seen that heteroatoms and metals are generally concentrated in the asphaltene and carboid fractions.

Work forecast:

Additional samples will be solvent fractionated by the standard method, and analyzed as above, as they are received. Additional quantities of samples currently available will be separated in order to build up stockpiles of the various solvent fractions.

(2) Separation of Crude Asphaltenes by Solvent Elution Chromatography

Work accomplished:

In a previous quarterly report (1) results were presented for the solvent elution chromatography of crude asphaltenes on silica gel columns. During the present quarter, separations of crude asphaltenes have been carried out on an acidic ion exchange resin (Amberlyst 15), and on alumina.

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*The combined carbenes and carboids are pyridine-soluble.

**The filtered product is the pyrolysis product produced prior to the final hydrotreating reaction. The FMC-COED Syncrude produced by hydrotreating the filtered product at 3100 psi, 775°F consists of about 99% oil, 0.8% resin, and 0.2% asphaltene.

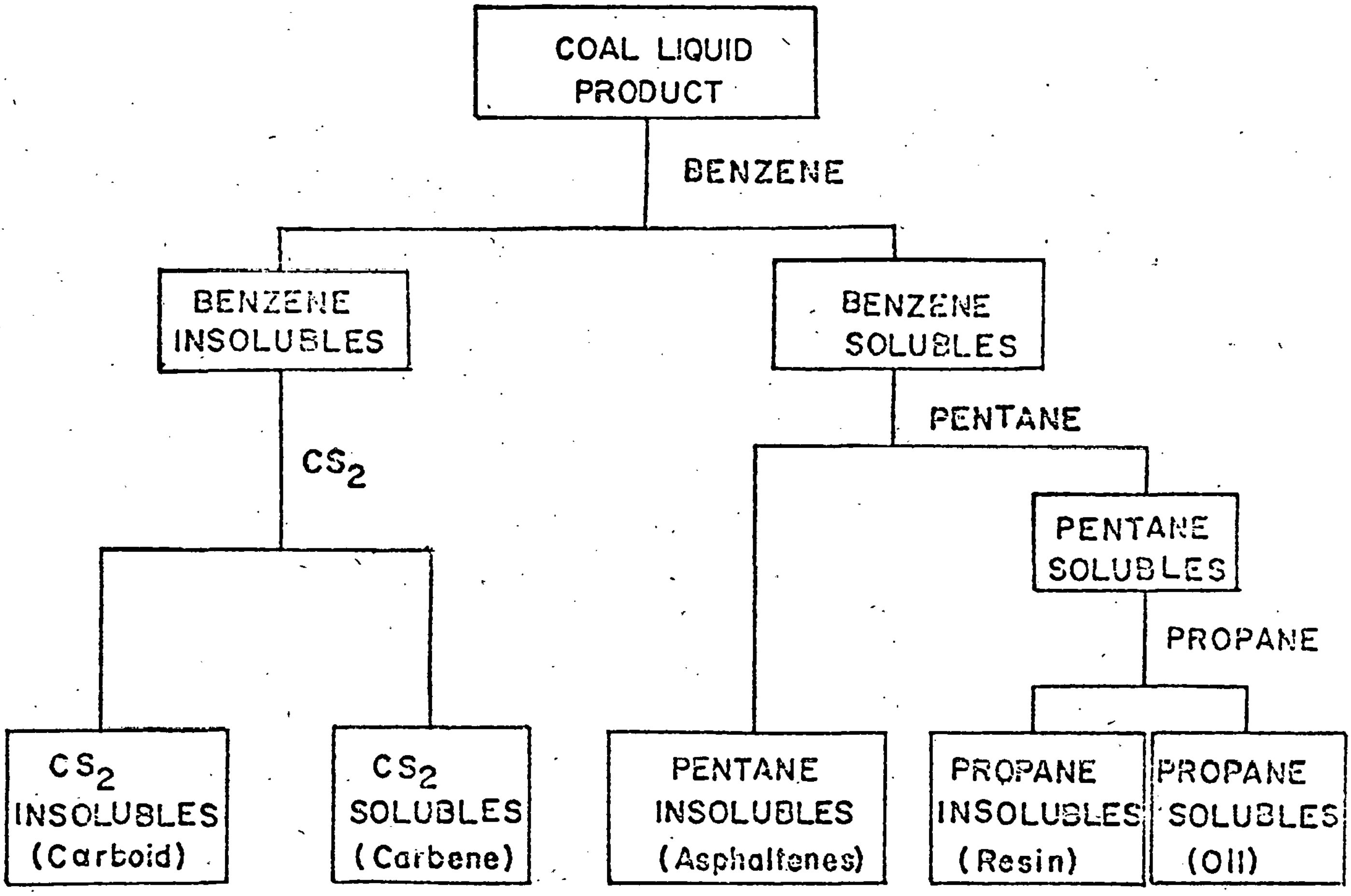

FIGURE 2 SOLVENT FRACTIONATION SCHEME FOR COAL LIQUID PRODUCT

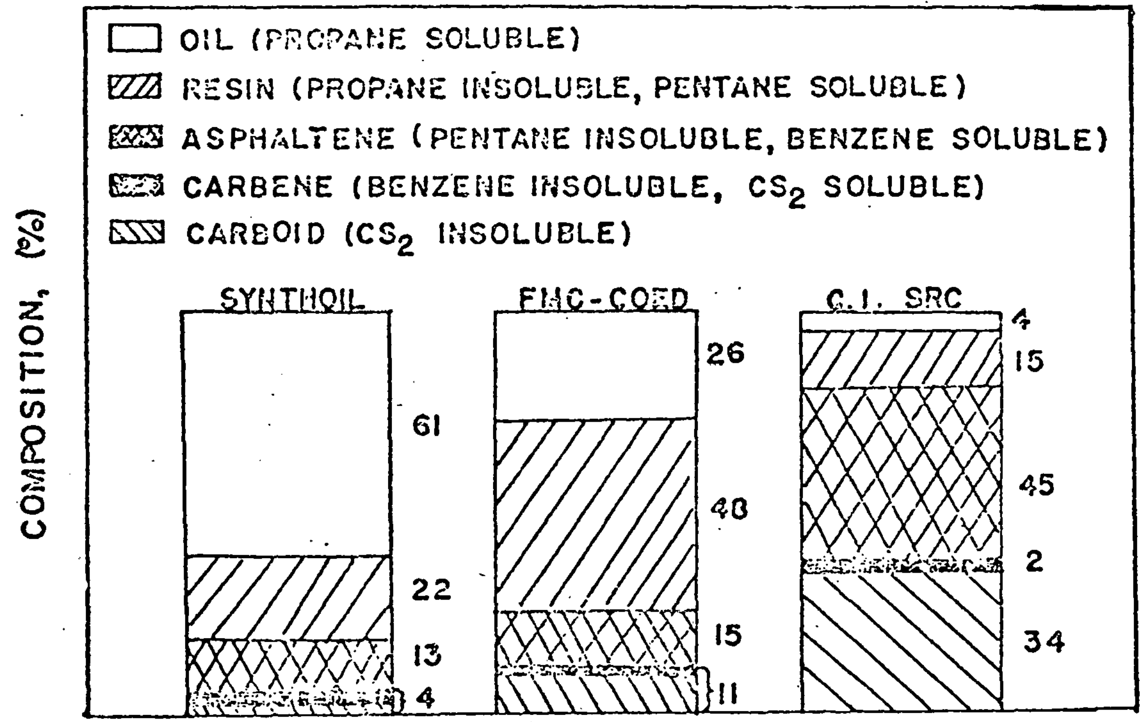

FIGURE 3 SOLVENT FRACTIONATION ANALYSIS OF COAL LIQUID PRODUCTS

Table I. - Synthoil Solvent Fractions Ultimate Analysis, %*

Fraction	C	H	N	S	O**	Ash	MW***
Coal Liquid	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	260
Resin	87.27	7.77	1.30	0.14	3.52	0.30	
Asphaltene	87.27	6.51	1.63	0.66	3.93	0.48	738
Carbene	87.96	5.94	1.72	0.74	3.64	0.56	
Carboid	88.32	5.69	1.64	2.07	2.28	8.80	

*Moisture and ash free
**By difference
***VPO in benzene

Table II. - FMC-COED Solvent Fractions Ultimate Analysis, %*, MW

Fraction	C	H	N	S	O**	Ash	MW***
Coal Liquid	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	310
Resin	83.25	7.25	1.06	1.26	7.18	0.39	
Asphaltene	82.14	6.47	1.70	2.58	7.11	0.79	458
Carbene	81.17	6.01	1.69	1.31	9.82	0.11	
Carboid	78.47	5.65	1.95	1.85	12.08	1.31	

*Moisture and ash free
**By difference
***VPO in benzene

Table III. - Cat. Inc. SRC Solvent Fractions Ultimate Analysis, %*

Fraction	C	H	N	S	O**	Ash	MW***
Coal liquid	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	
Resin	89.88	6.64	0.84	0.00	2.64	0.05	
Asphaltene	88.79	5.61	1.25	0.12	4.23	0.78	747
Carbene	89.77	5.03	1.11	0.26	3.83	0.40	
Carboid	87.08	4.70	0.96	0.34	6.92	0.71	

*Moisture and ash free
**By difference
***VPO in benzene

Table IV. - Semiquantitative Metal Analysis*

Major Elements	SYNTHOIL Asphaltene	SYNTHOIL Benzene Insoluble	FMC-COED Asphaltene	FMC-COED Benzene Insoluble	CAT. INC. SRC Asphaltene	CAT. INC. SRC Benzene Insoluble
Si	180	1800	210	100	55	130
Fe	130	420	20	270	7	58
Al	8	760	57	140	6	420
Ti	69	130	12	10	1	71
B	60	77	81	72	5	18
Ca	3	69	39	280	26	96
Mg	1	29	5	14	10	140

*Results in ppm

(a) Cation-Exchange Chromatography

(1) Preparation of the cation-exchange resin

Amberlyst 15 was washed four times with a methanolic hydroxide solution (10% weight potassium hydroxide in methanol) then rinsed and Soxhlet extracted with methanol. The resin was activated by adding it slowly to a stirred solution of 10% volume HCl in methanol. The resin was then washed with distilled water until the washings were neutral to litmus paper. Final preparation was made by 24 hour Soxhlet extraction of the resin with each of the following solvents: methanol, benzene, and pentane. The resin was then dried in an oven at 100°C.

(2) Separation of crude Synthoil asphaltene

100 gms. of the prepared Amberlyst 15 was mixed with benzene, and the resulting slurry was added to a column (500mm x 20mm ID). Crude Synthoil Asphaltene (3 gms) was dissolved in benzene and charged to the column. The column was eluted with benzene (5 liters). The initial fraction was dark brown with the latter portion of the fraction being light yellow. After elution with benzene, the column was eluted with pyridine (1 liter). The pyridine fraction was dark brown. The asphaltene recovered from the benzene elution is referred to as the 'acid cut' and the asphaltene recovered from the pyridine elution is referred to as the 'basic cut'. The following percent yields were reported: acid cut, 36%; basic cut, 50%. Both cuts were lyophilized from benzene, and then dried in a drying tube (2mm Hg, 56°C) for 12 hours.

The results of various analyses on the above chromatography fractions are presented in Table V. It may be seen that the benzene eluted fraction contains substantially reduced % nitrogen, while the pyridine eluted fraction contains a substantially increased % nitrogen. The observation that nitrogen-containing, and probably basic, species are absorbed by the acidic resin is in agreement with the observations of Sternberg et al. (1a) who were able to precipitate a basic component from a solution of Synthoil asphaltene dissolved in toluene by passing dry HCl gas through the solution.

The weight ratio (acidic/basic components) observed in this work, 42/58, from a 450°C/4000psig product, is in good agreement with the ratios 42/58 found by Sternberg et al. for a 415°C/4000psig product, and 37/63 for a 450°C/2000psig product. The observed MW of 540 for the acidic fraction is also in good agreement with our previously found MW of 614 from silica gel chromatography (1) and Sternberg et al.'s value of 550. However, the basic fraction affords a grossly different MW value. Our value from Amberlyst 15 is 906, while Sternberg et al.'s value from HCl/toluene is 368.

(b) Alumina Chromatography

Alumina columns were prepared as described previously (5). Elution of Synthoil crude asphaltene, from alumina, with benzene led to only about 4% by weight recovery of asphaltene. Diethyl ether elution removed an additional 7% of the charged asphaltene. Tetrahydrofuran eluted an additional 43% of the starting asphaltene. The use of methanol as an elutant led to anomalous results. The product asphaltene was contaminated with a non-volatile liquid that was difficult to remove by rotary evaporation, so that a reliable weight % yield could not be obtained. After freeze-drying, the methanol eluted asphaltene was subjected to the usual analyses. The results of these analyses show that the asphaltene was affected by methanol elution from an alumina column. The carbon % decreased from 86.85 to 76.79; the infrared showed the appearance of a strong carbonyl type band at 1720 cm^{-1}; and the color index decreased from 12.7 to 4.6. In a later run, using the solvents THF and pyridine, two major fractions of 51 and 37 weight % respectively were obtained. These fractions appear to be normal. Preliminary characterizations are shown in Table V. Further analyses are pending.

The results of various analyses of Synthoil chromatography fractions are presented in Table V.

Work forecast:

Chromatography of selected crude asphaltene samples will continue on ion exchange resins, alumina, and other suitable chromatographic separatory systems. The major chromatographic fractions will be characterized by the same methods that are being used for characterization of crude asphaltenes.

Table V. - Analyses of Asphaltene Chromatography Fractions

	% Composition									
	C	H	N	S	O_{diff}	Ash	IR	I^a	MW	$-OH^b$
Crude Asphaltene	86.85	6.48	1.63	0.66	4.03	0.35	Normal	12.7	738	-
Silica Gel(Benzene Eluted)	88.29	6.51	0.57	0.98	2.68	0.97	Normal	12.1	614	+
Silica Gel(Et_2O Eluted)	84.16	6.78	1.58	0.72	5.57	1.19	Normal	8.2	560	
Amberlyst 15(Benzene Eluted)	88.08	6.68	0.50	0.69			Normal	9.1	540	+
Amberlyst 15(Pyridine Eluted)	86.00	6.57	2.76	0.50			Normal	16.3	906	+
Alumina(THF Eluted)	87.21	6.35	1.94	0.61	3.49	0.40	Normal	15.6		
Alumina(MeOH Eluted)	76.79	6.97	1.35	0.17	14.04	0.68	C=O	4.6		
Alumina(THF Eluted)							Normal	18.4		-
Alumina(Pyridine Eluted)							Normal	8.3		+

[a] Color Index

[b] Broad NMR resonance at ≈5ppm downfield from TMS.

(3) Characterization of Coal Liquid Fractions

Work accomplished:

The solvent separated coal liquid fractions obtained in this quarter (oils, resins, carbenes and carboids) are being characterized as to %Composition, Molecular Weight, Metal Analyses (Tables I-IV), Color Intensity (Table VI), NMR H-Percentages by Proton Type (Table VII), Carbon Aromaticity by X-Ray Diffraction (Table VIII), and Infrared Spectra as discussed previously (1). In addition, during the present quarter, asphaltene characterization by physical methods was extended to include structural parameter determination by x-ray diffraction, and particle size determination by transmittance electron microscopy.

(a) Color Indices of Solvent Fractions

Table VI. shows the color indices (8) (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. The color indices, but not the molecular weights of the carboid fractions, have been determined. However, as they are the darkest and most insoluble of the fractions it is expected that they will exhibit high molecular weights.

(b) NMR H-Percentages by Proton Type

The NMR H-percentages by proton type are given in Table VII. The results indicate that coal liquid fractions produced by solvent refining have generally more aromatic protons than coal liquid fractions produced by either high pressure catalyzed hydrogenation or staged pyrolysis. The percentage of aromatic protons generally increase in going from resins to asphaltenes to carbenes. The limited solubility of the carboids in available solvents precluded determining their H-percentages this quarter. In the next quarter a high resolution Varian XL-100 FT NMR spectrometer will become available, and it will be possible to measure the proton spectra of carboids in dilute solutions.

(c) Structural Parameters by X-Ray Diffraction

Carbon aromaticity values, f_a, (6) were recalculated

Table VI. - 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

* $I = \int_{400nm}^{750nm} A d\lambda$ in THF

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

Table VII. - NMR H-Percentages by Proton Type[a]

	$H_{aromatic}$	H_{benzyl}[b]	H_{sat}[b]
Resins[c]			
Synthoil	29	35	36
FMC-COED	28	37	35
PAMCO SRC[e]	47	33	20
Cat. Inc. SRC	43	30	27
Asphaltenes[c]			
Synthoil	33	42	25
FMC-COED	37	42	21
PAMCO SRC	45	38	17
Cat. Inc. SRC	50	34	16
Carbenes[d]			
Synthoil	40	37	23
FMC-COED	42	42	16
PAMCO SRC	50	36	14
Cat. Inc. SRC	51	28	21

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[a] Run on Varian T-60 NMR

[b] Since benzyl and methylene resonances overlap in the naphthenic region, an arbitrary separation point between H_{benzyl} and H_{sat} was chosen at $\tau = 8.27$.

[c] Solvent 99.8% $DCCl_3$ + 1% TMS

[d] Solvent CS_2

[e] PAMCO filter feed sample contained Dowtherm aromatic-base fluid as contaminant.

from more precise x-ray data. The results are presented in Table VIII.

The scope of the x-ray diffraction method was increased so that the following parameters (Fig. 4) could be obtained:

d_m - the interlayer distance
d_γ - the interchain distance
L_c - the diameter of the aromatic clusters perpendicular to the plane of the sheets
L_a - the diameter of the aromatic sheets
M - the effective number of aromatic sheets associated in a stacked cluster

The x-ray diffraction peaks that were utilized in this study are the (002), (gamma), (10), and (11) peaks. The 002 and gamma peaks have already been described in a previous report (6). The (10) and (11) bands correspond to the first and second nearest neighbors in the ring compound; they are located at $\sin\theta/\lambda = 0.25$ or 1.4Å, and $\sin\theta/\lambda = 0.42$ or 2.4Å, respectively. Progressive sharpening of the (10) and (11) peaks was observed with carbonization (7). The sharpening was explained on the basis of destruction of peripheral groups that constitute amorphous material and growth or coalescence of freed aromatic ring clusters. The difficulty in measuring these 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 consideration (8) 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. The (10) and (11) peaks have been handled sufficiently well theoretically so that one can simply compare the shape of an observed spectrum with that of a calculated one, in order to de-

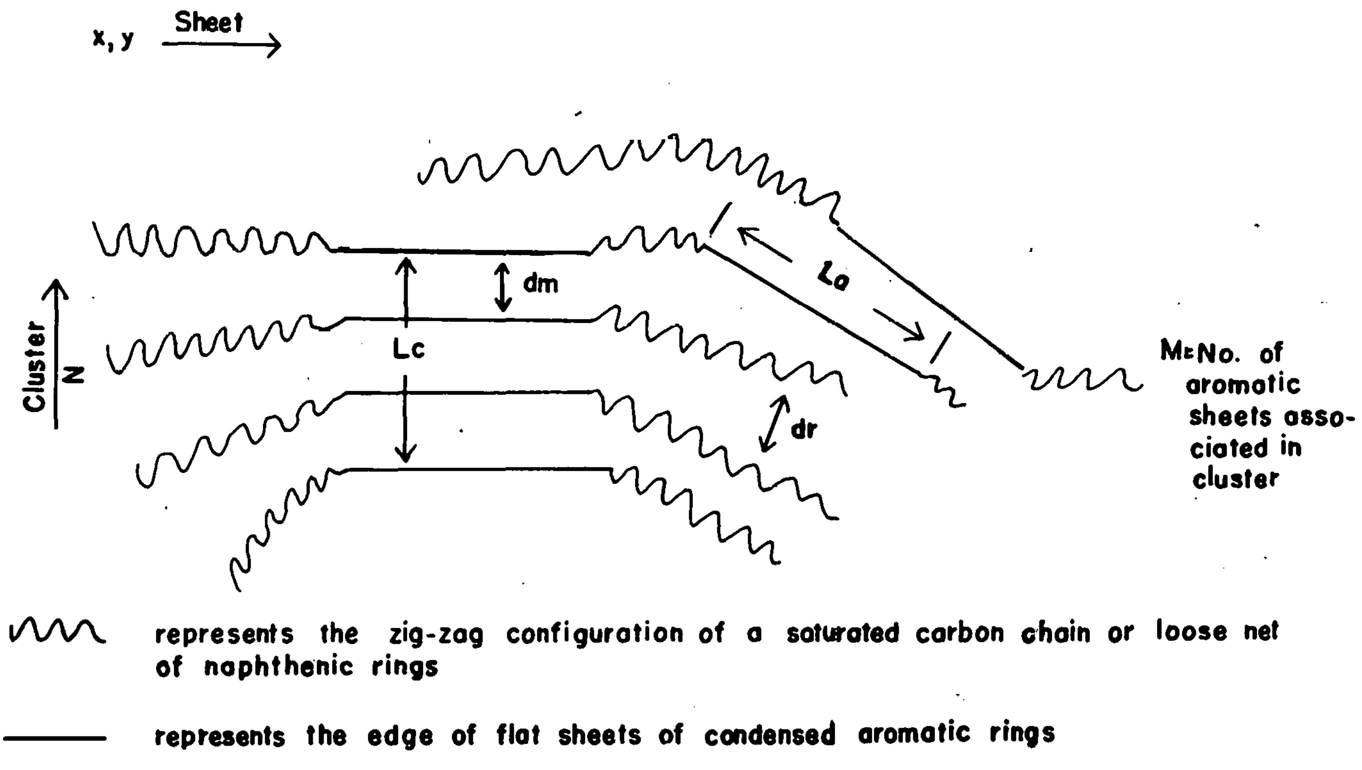

Fig. 4 Cross-sectional view of coal asphaltene model

termine information concerning the size of the ring structure (9).

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

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

n(r) = number of interatomic distance; 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, ie., ranging in size from 5.8-30Å, in order to obtain the values of J(s) (11). The width of the (10) peak, $\Delta\sin\theta/\lambda$, is shown in Fig. 5, as a function of La 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 (12).

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

β = band width; λ = wavelength of the x radiation; L = crystallite diameter; θ = Bragg angle; c = constant. This equation was used in the calculation of some crystallite parameters in petroleum asphaltene (13).

It is generally preferred to use the (10) band rather than the (11) band (12). We also found it preferable to use the (10) band, despite the fact that it overlaps with the (002) band (Figs. 6-9), because the (11) band was not well resolved, and usually weak and broad.

The aromatic sheet diameters, and other crystallite parameters, calculated as described in Ref. 13 are presented in Table VIII

(d) Particle Size Determination by Transmittance Electron Microscopy (14)

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.

Table VIII. - Aromaticity, f_a, and Crystallite Parameters for Coal Liquid Asphaltenes

	CAT. INC. SRC	PAMCO SRC	FMC-COED	SYNTHOIL
f_a[1]	0.69	0.66	0.58	0.63
d_m[2]	3.5	3.7	3.7	3.7
d_γ[2]	4.4	5.0	5.0	5.2
L_c[2]	16.7	12.9	11.3	10.0
L_a[2] (from Scherrer's equation)	12.6	21.7	14.4	15.3
L_a[2] (from Diamond's curve)	6.7	13.8	8.5	9.3
M[3]	6	5	4	4

---

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

[2] dm = interlayer distance; d_γ = interchain distance; L_c = diameter of the aromatic clusters perpendicular to the plane of the sheets; L_a = diameter of the aromatic sheets. All values in Å (See Fig. 3).

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

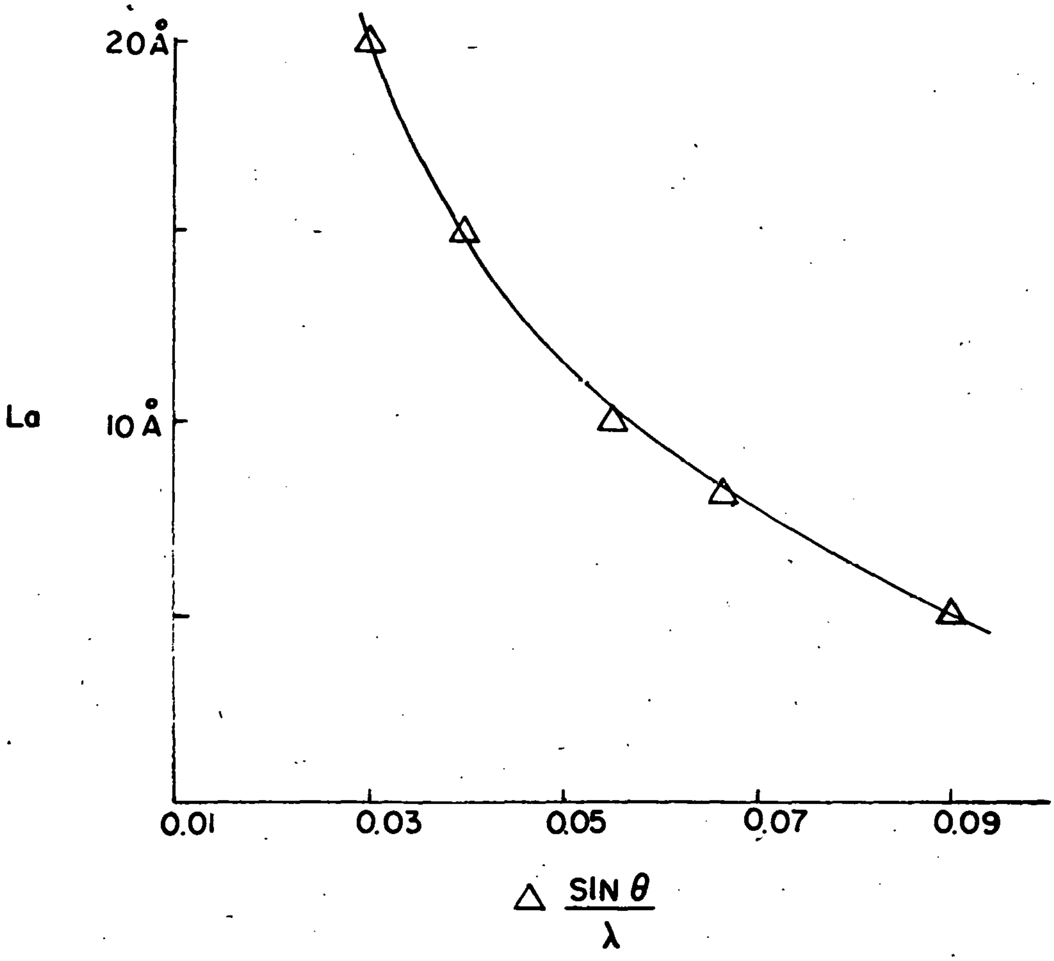

Fig. 5 Calibration curve of diameter of aromatic sheets vs. width at half maximum of (10) band based on data published by Diamond (10).

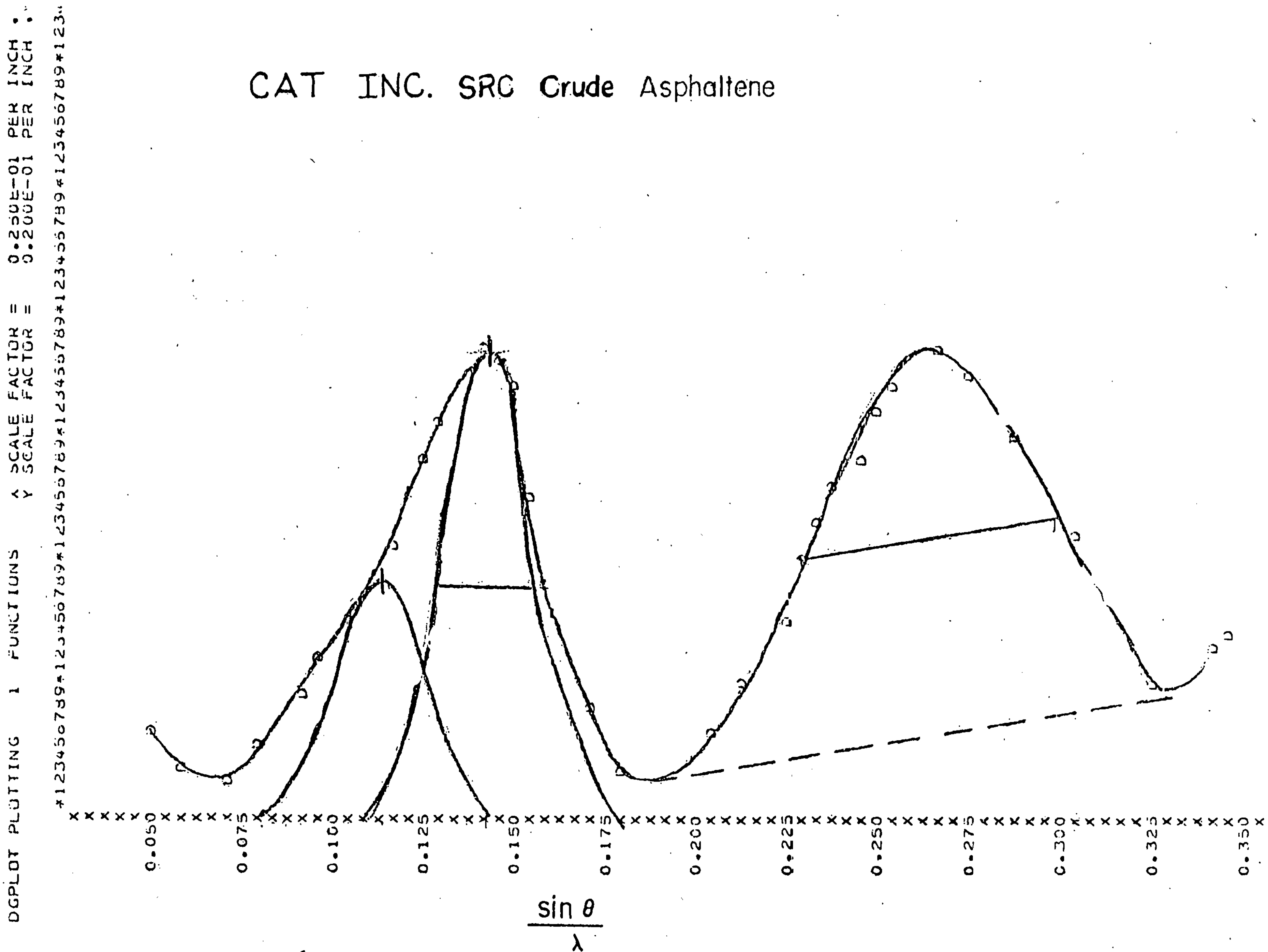

Fig. 6 X-Ray Diffraction Pattern

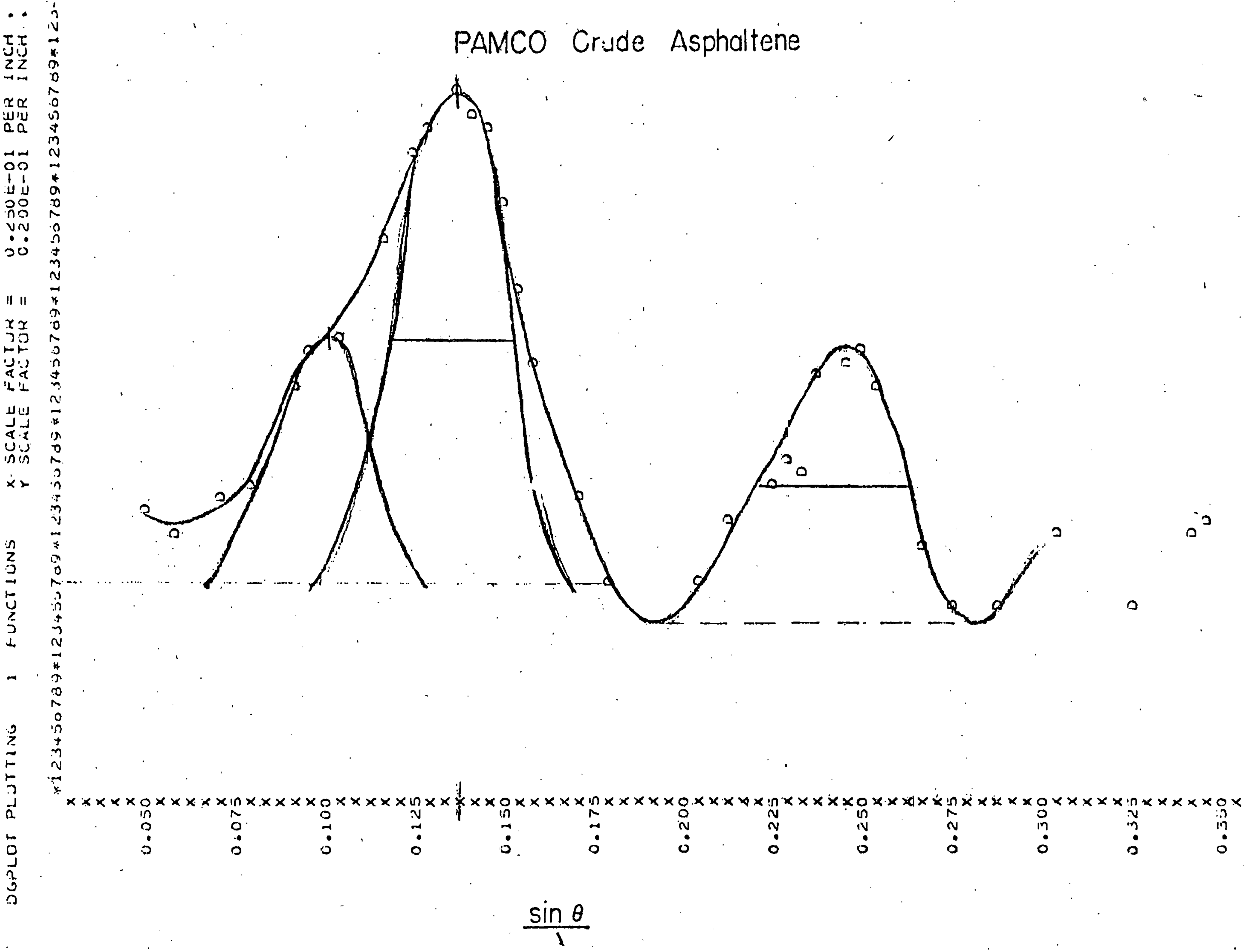

Fig. 7 X-Ray Diffraction Pattern

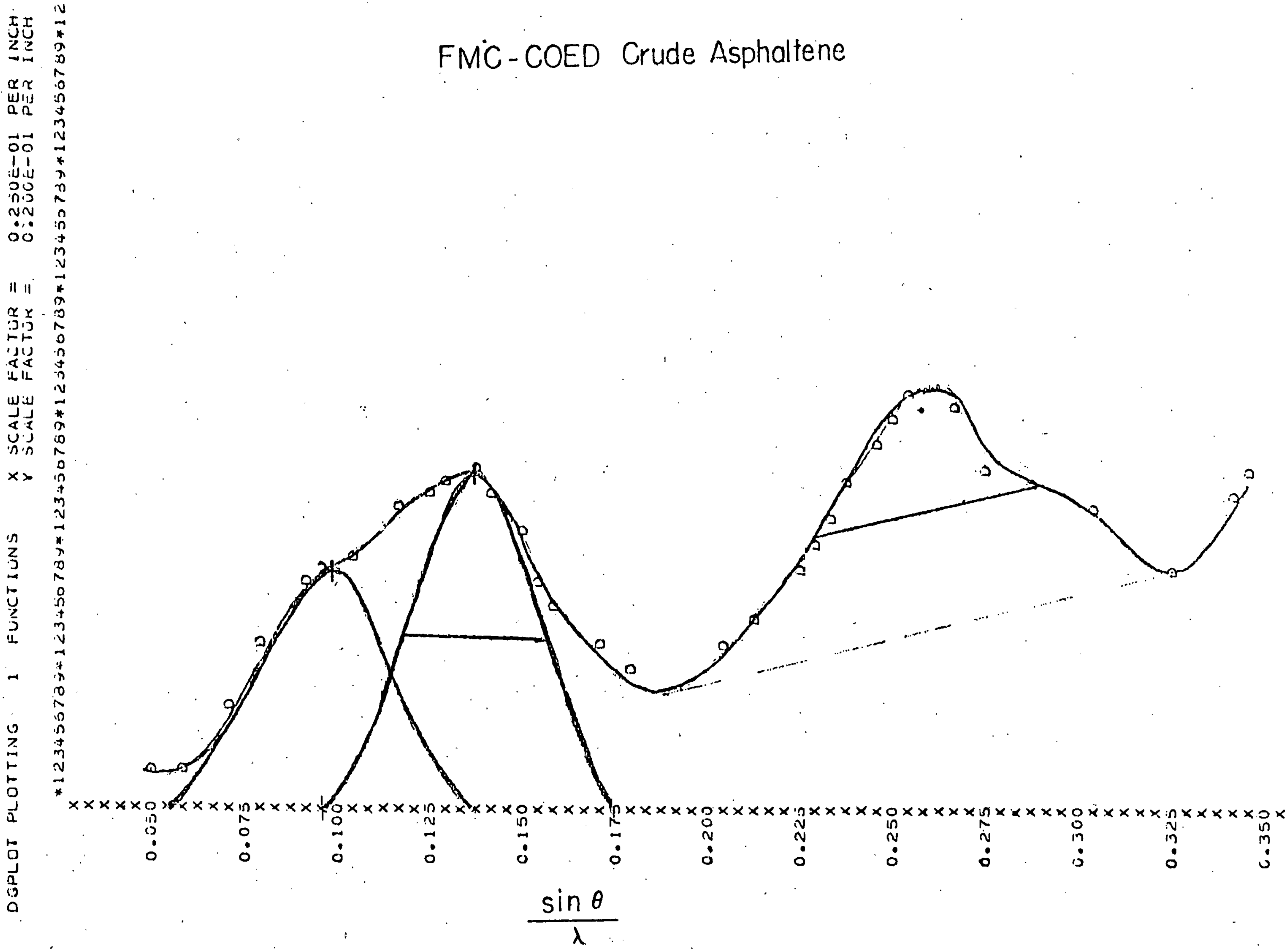

Fig. 8 X-Ray Diffraction Pattern

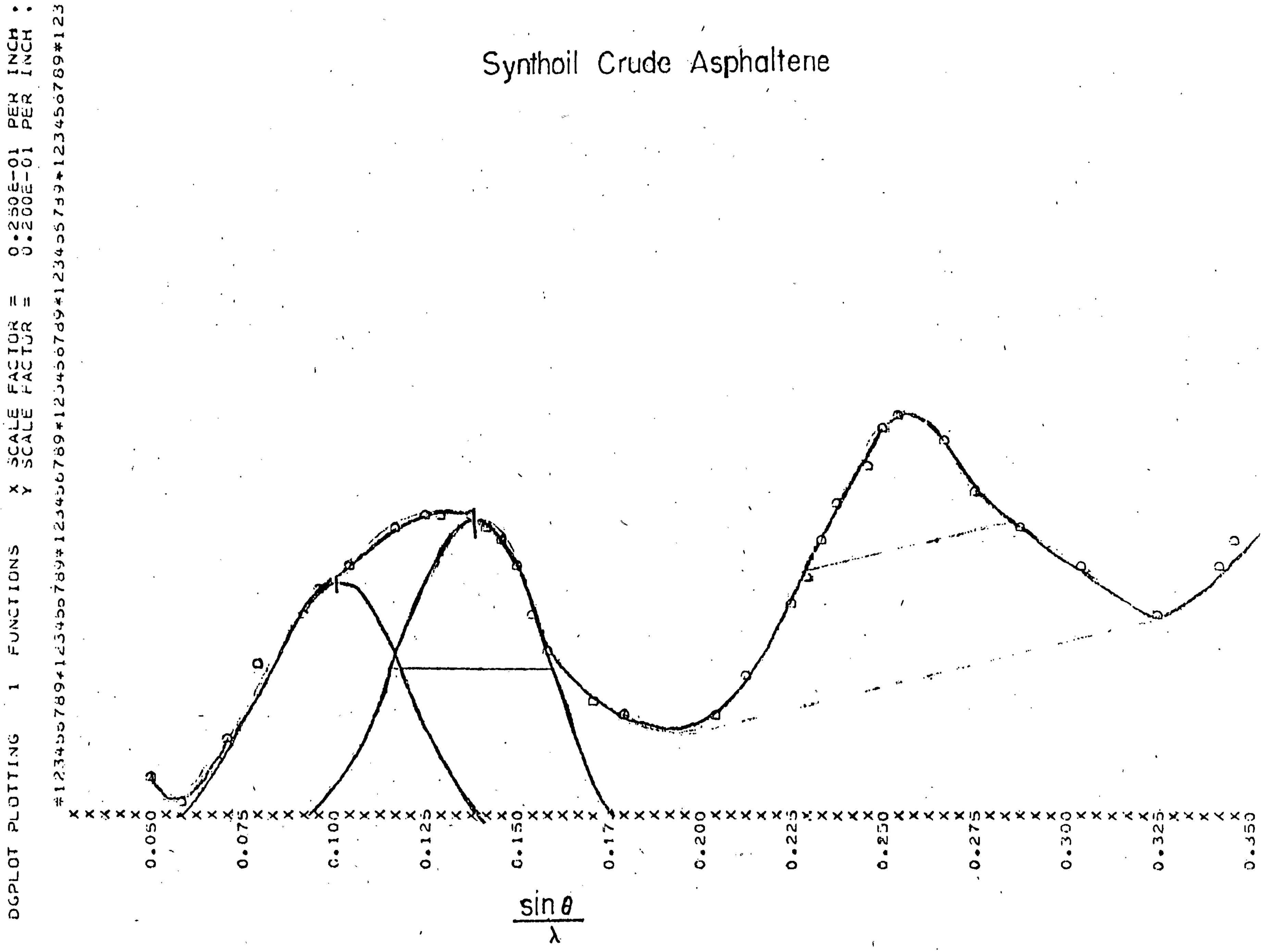

Fig. 9 X-Ray Diffraction Pattern

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 preliminary pictures, Fig.10, indicate that the particles are elliptical for the Synthoil crude asphaltene. The average particle lengths along the long and short axes are reported in Table IX.

Work forecast:

Characterization will continue on all applicable fractions by the analytical and physical methods described in this report. In addition, other physical and instrumental techniques will be utilized to increase the scope of the characterization procedure. In particular, NMR studies will be extended to carbon-13 NMR by use of a Varian XL-100 Fourier transform NMR spectrometer. This technique allows the determination of direct and accurate values of carbon aromaticities, and in conjunction with proton NMR spectrometry, will provide a series of parameters based entirely upon NMR for detailed characterization of coal liquid fractions.

CONCLUSION

Coal liquids can be separated into five fractions: propane-soluble (oil); propane-insoluble and pentane-soluble (resin); pentane-insoluble and benzene-soluble (asphaltene); benzene-insoluble and carbon disulfide-soluble (carbene); carbon disulfide-insoluble (carboid). The composition of the coal liquids may be correlated with the process conditions used to produce the coal liquids.

Asphaltenes isolated from the coal liquids may be analyzed by a host of physical and analytical techniques in order to determine structural parameters. Asphaltenes may be further separated by chromatographic techniques into major fractions which differ as a function of the acidic or basic nature of the adsorbent used.

Actually, the words 'acid' and 'base' as reported by Sternberg et al (1a,15) do not adequately classify or clarify the coal-derived asphaltene. We would suggest acceptor (π-deficient) and donor (π-abundant), since their association and the nature of charge transfer is well known in asphaltene (16). The asphaltene thus formed is a complex and not a salt in the sense of ionizable species of acid or base. All these phenomena can be explained on the basis of charge-transfer. Actually, the existence of different degrees of association of this charge-transfer makes the task of separation of asphaltene difficult.

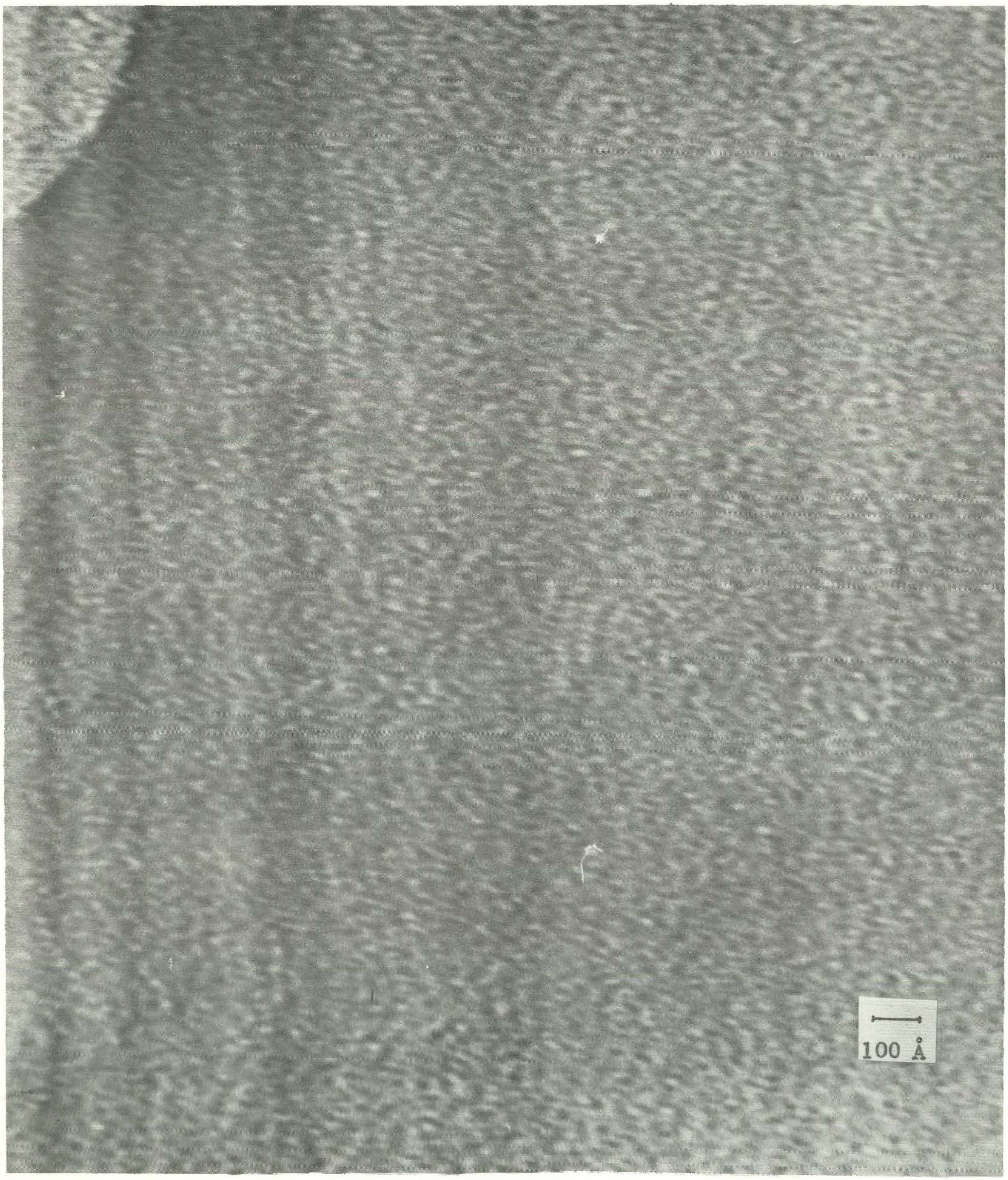

Fig. 10 Synthoil Crude Asphaltene Evaporated Carbon Support Film (910,000x).

Table IX. - TEM Particle Dimensions for Synthoil Crude Asphaltene

	D_1* (Å)	σ_1*** (Å)	Min. Size (Å)	Max. Size (Å)	D_2** (Å)	σ_2*** (Å)	Min. Size (Å)	Max. Size (Å)
Synthoil Asphaltene	15.2	4.7	10.9	24.0	35.9	9.9	21.8	61.0

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*Arithmetic mean for short axis
**Arithmetic mean for long asis
***Standard deviation for long and short axes

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