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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES, PHASE 3

Quarterly Progress Report, July—September 1977

By
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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES
Phase III

Quarterly Progress Report for the Period
July - September 1977

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ABSTRACT

The major benzene insoluble fraction, carboid, solvent separated from Synthoil coal liquid, was found to be 90 wt. % soluble in pyridine. This fraction, which contains about 50% of the ash present in Synthoil coal liquid, could be 96% de-ashed by dissolution in pyridine.

A hypothetical average structure for Synthoil asphaltene has been derived from analytical, VPO MW, x-ray, NMR and chemical functionality data.

A self-association model has been developed for calculating molecular weights, and fractions of monomeric, dimeric and trimeric asphaltene species present as a function of concentration in benzene solution.

ESR measurements of Landé g-values and spin intensities have been made for coal liquid solvent fractions and asphaltene derived products. The observed g-values fall within the narrow range. 2.0028-2.0036, previously reported for asphaltic fractions of petroleum and neutral radicals.

TGA measurements of coal liquid fractions have been carried out, and % char values determined. Synthoil asphaltene has been found to undergo oxygen induced reactions which stabilize it toward volatilization vis-a-vis the Synthoil carboid fraction.

Silylation studies on carboid coal-liquid fractions afforded % OH/O_{total} values: Synthoil, 47; HRI H-Coal, 64; FMC-COED, 52; Catalytic Inc., 36; PAMCO, 53.

Methylation studies of Synthoil asphaltene, with methyl iodide, indicate that about 67% of the asphaltene nitrogen is non-basic, and that about 33% of the nitrogen in molecules containing basic nitrogen is non-basic.

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 III is to continue the characterization of coal asphaltenes and other coal liquid fractions by the use of physical, instrumental and chemical methods. The structural parameters 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) Solvent Separations.

(2) Training of new technical personnel is underway.

(3) Establishment of sample data bank.

(4) Chromatography of asphaltenes is being carried out.

(5-13) Characterization of coal liquid fractions by various physical and instrumental methods is continuing.

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

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

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

Detailed Discussion of Technical Progress

(1) Sample Acquisition and Separation

Work Accomplished:

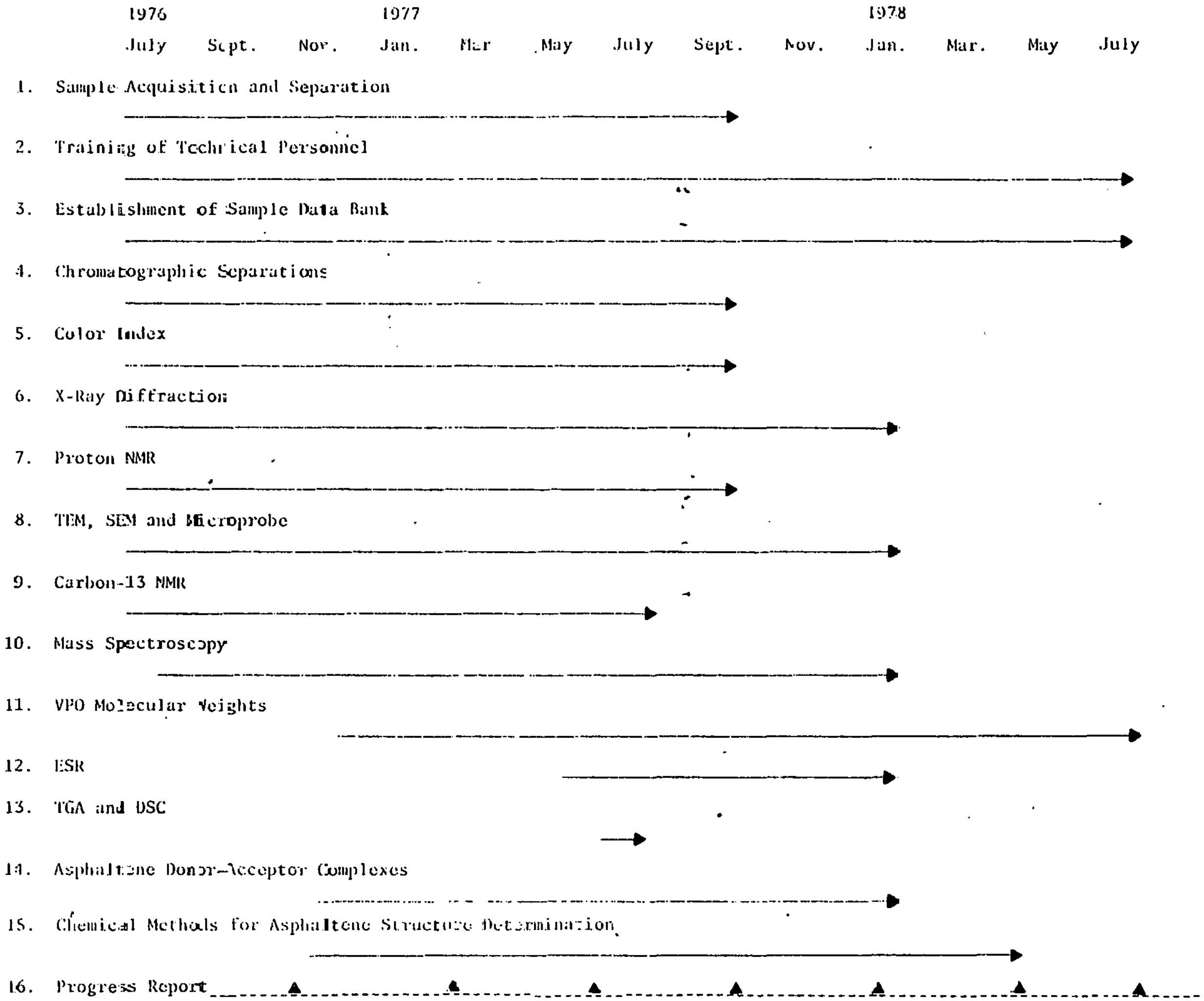
(a) Solvent Separation of Coal Liquids

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

(b) Solvent Separations of Carbene and Carboid Fractions

In previous reports we have described a solvent fractionation scheme for separating coal liquid products into five fractions: oil, resin, asphaltene, carbene, and carboid (1 , 2). 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 fraction. Sternberg et al. (3) have treated the benzene insoluble material with pyridine in order to obtain a pyridine insoluble fraction containing unreacted coal and mineral matter, and pyridine soluble, benzene in-

Fig. 1. Milestone Chart



soluble fraction, which they designated pre-asphaltenes*. More recently Schweighardt et al. (4) 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 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.

(c). Solubility Parameters of Coal Liquid Fractions

Solvent fractionation has long been used to separate the fractions of the coal liquefaction product. In an attempt to more clearly define the coal liquid fractions, the solubility limits of the asphaltene and carbene fractions were obtained as a function of solubility parameters (5).

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*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 (6 ,7).

Table I. Solubility and Ash Distribution of Synthoil Carboid in THF and Pyridine

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

The solubility parameter, δ, is given in equation (1):

$$\delta = \left(\frac{\Delta E}{V} \right)^{\frac{1}{2}} \qquad (1)$$

where ΔE is the internal energy and V is the molar volume. When two miscible liquids are mixed, the effective solubility parameter (δm) of the mixture is given by equation (2):

$$\delta m = V_1\delta_1 + V_2\delta_2 \qquad (2)$$

where δ_1 and δ_2 are the solubility parameters of the liquids,and V_1 and V_2 are the volume fractions. The solubility limits of a coal liquefaction product can be evaluated by using a number of overlapping mixed solvent systems with δm ranging from 8.19 to 23.5 hildebrands and measuring percent dissolved in each solvent mixture.

Solvent mixtures of four liquids of increasing Hildebrand values and decreasing molar volumes were used. These are given in Table II.

The solubility limits were determined for the asphaltenes and carbene fractions. Asphaltene is defined as pentane insoluble and benzene soluble. Carbene is defined as benzene insoluble and carbon disulfide soluble. Solubility parameters of these solvents are given in Table II.

Results of the solubility experiments are shown in Fig. 2. Solubility limits for the asphaltene are between 9 and 12 hildebrands. Solubility limits for carbene are between 10 and 11 hildebrands.

Additional samples will be solvent fractionated by the standard methods as required to obtain samples for further physical, instrumental and chemical testing and analyses. Solubility parameter studies will be extended to study coal liquid derived carboid fractions.

Table II. Hildebrand Values, δ, of Solvents

Solvent	δ
Pentane	7.02
Cyclohexane	8.19
Benzene	9.16
CS_2	9.92
HEMA*	12.45
Water	23.50

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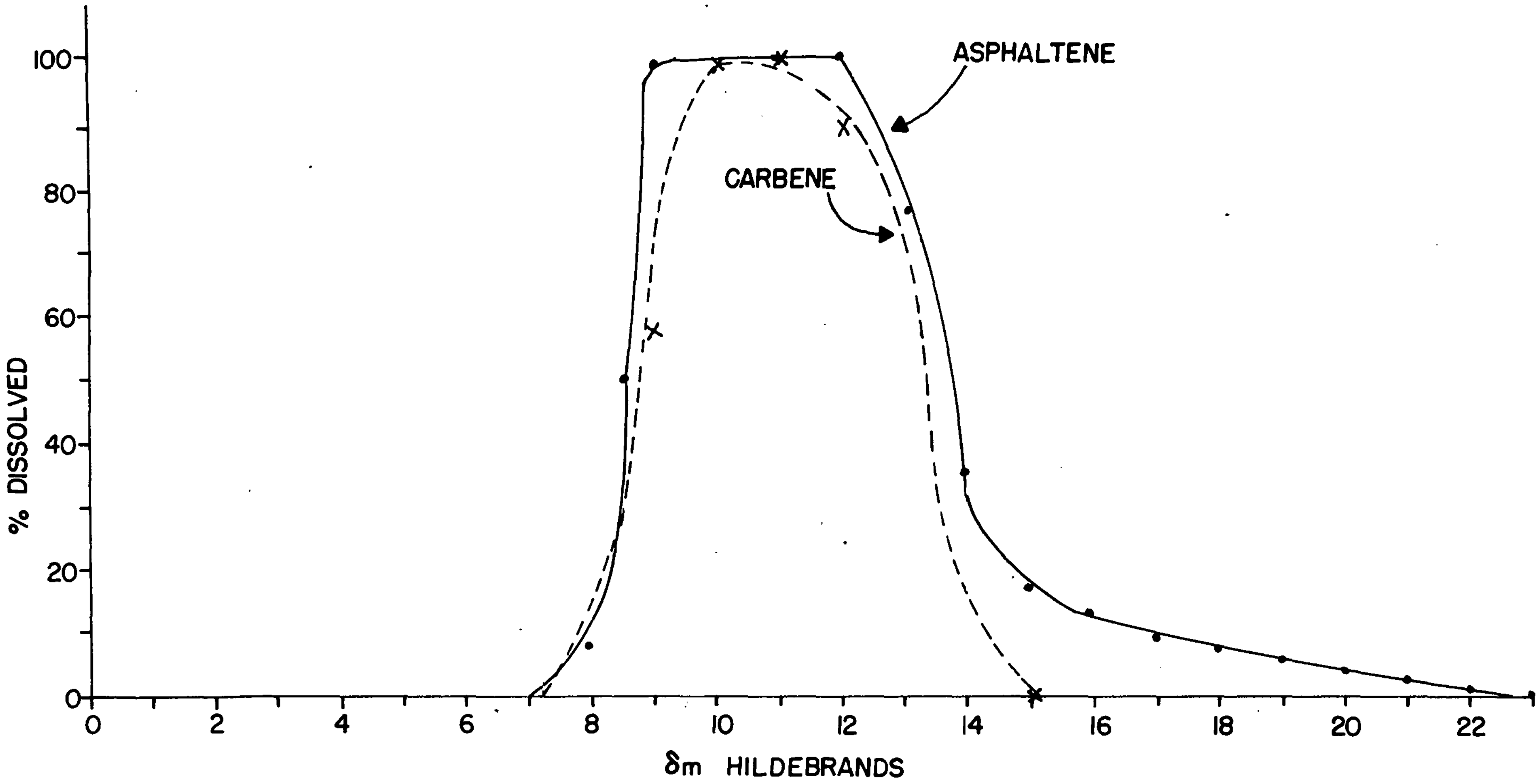
*2-Hydroxyethyl Methacrylate.

FIG. 2 SOLUBILITY OF SYNTHOIL ASPHALTENE AND CARBENE VS HILDEBRAND SOLUBILITY PARAMETER δ_m



(2) Separation of Asphaltenes

(a) Chromatography

Asphaltene samples were separated by solvent elution chromatography on silica gel by the standard method in order to obtain stockpiles of the various chromatographic fractions. Additonal VPO molecular weight data, x-ray crystallite parameters, ESR, and TGA data on these fractions are reported in Sections 3(a), 3(c), 3(d) and 3(e) of this report.

(b) HCl Precipitation

Additional attempts were made to separate Synthoil asphaltene quantitatively into two fractions by precipitation with dry HCl from benzene ([8,9]). The non-basic, benzene soluble fraction was easily isolated. However, once again, back titration of the basic asphaltene-HCl precipitate, suspended in benzene, with 0.5N NaOH led to difficulties. It was not possible to cleanly separate the organic and aqueous layers so as to obtain a quantitative yield of the basic asphaltene fraction. The back titrated basic asphaltene seemed to be composed of two fractions:

(a) a brown material which is readily soluble in benzene;

(b) a dark brown material which is difficultly soluble or insoluble in benzene.

Our best yield to date is 83 weight percent. The normalized yields are: acid/neutral-benzene soluble 37%, basic-benzene soluble 29%, basic-benzene insoluble 34%. Analytical and physical comparisons are being carried out on these materials.

(3) Characterization of Coal Liquid Fractions by Physical Methods

Work Accomplished:

(a). X-Ray Diffraction

In previous Quarterly Reports (10, 2), we discussed the procedure for analyzing X-ray diffraction patterns in order to obtain aromaticity, f_a, and crystallite parameter data for asphaltenes (2), and other coal liquid derived products (7, 9, 11). We now wish to report f_a values, and crystallite parameters for the Synthoil asphaltene silica gel chromatography fractions. The results are presented in Table III. These results, obtained by the X-ray diffraction method, may be compared with the average molecular properties reported previously for the same series of asphaltene derivatives (11). The average f_a obtained by the X-ray method is 0.06 lower, but the order THF eluted > benzene eluted > starting asphaltene > Et_2O eluted is followed. The diameter of the aromatic sheets obtained by using the (10) band in conjunction with Diamond's curve yields values of 8.0 to 8.6 Å for the starting asphaltene and the first two solvent eluted fractions. These results are close to what one would expect for an average asphaltene aromatic system of 3-4 condensed rings, and agree with the previously reported asphaltene aromatic ring system size calculated from Brown-Ladner NMR parameters. The infinite dilution molecular weight values found for these fractions were also close: 560, 546 and 530 respectively. The greater aromatic sheet diameter found for the THF eluted fraction is also consistent with the higher MW found for this fraction, 869.

Table III. 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 (Å)[2]	3.68	3.76	3.62	3.57
d_γ (Å)[2]	5.35	4.85	4.81	5.10
L_c (Å)[2]	12.2	11.8	9.4	11.5
M[3]	4.	4.	4.	4.
L_a[4] (Å) (10) band	13.9	13.4	14.1	18.7
(11) band	12.3	11.7	11.6	15.3
L_a[5] (Å) (10) band	8.5	8.0	8.6	12.0
(11) band	10.3	11.0	10.0	13.6

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[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. (9)

[5] L_a = diameter of the aromatic sheets from Diamond's Curve (9).

(b) Proton NMR

In previous Quarterly Reports, NMR, analytical, VPO molecular weight, and chemical functionality data have been reported for solvent fractionation products. Average molar properties have been calculated by use of modified Brown-Ladner structural parameter equations. These accumulated experimental results may be used to build working models for the average structures of the various fractions. As an example, we have derived a hypothetical average structure for Synthoil asphaltene, shown in Fig.3 , based on a set of average molecular parameters. In this structure, the substituents may be located in any position along the ring system. The assignment of one phenolic and one ether oxygen was based on the finding, by silylation, that ≈50% of the total asphaltene oxygen is phenolic. The assignment of only one nitrogen as a basic pyridine-like nitrogen was made arbitrarily although it is known that a substantial amount of the nitrogen present in asphaltene is non-basic and pyrrole-like.

A comparison of the average molecular parameters for Synthoil asphaltene obtained experimentally with those calculated for the hypothetical structure shown in Fig.3 is presented in Table IV. The results are seen to agree reasonably well in most cases.

FIGURE 3 HYPOTHETICAL AVERAGE STRUCTURE FOR SYNTHOIL ASPHALTENE

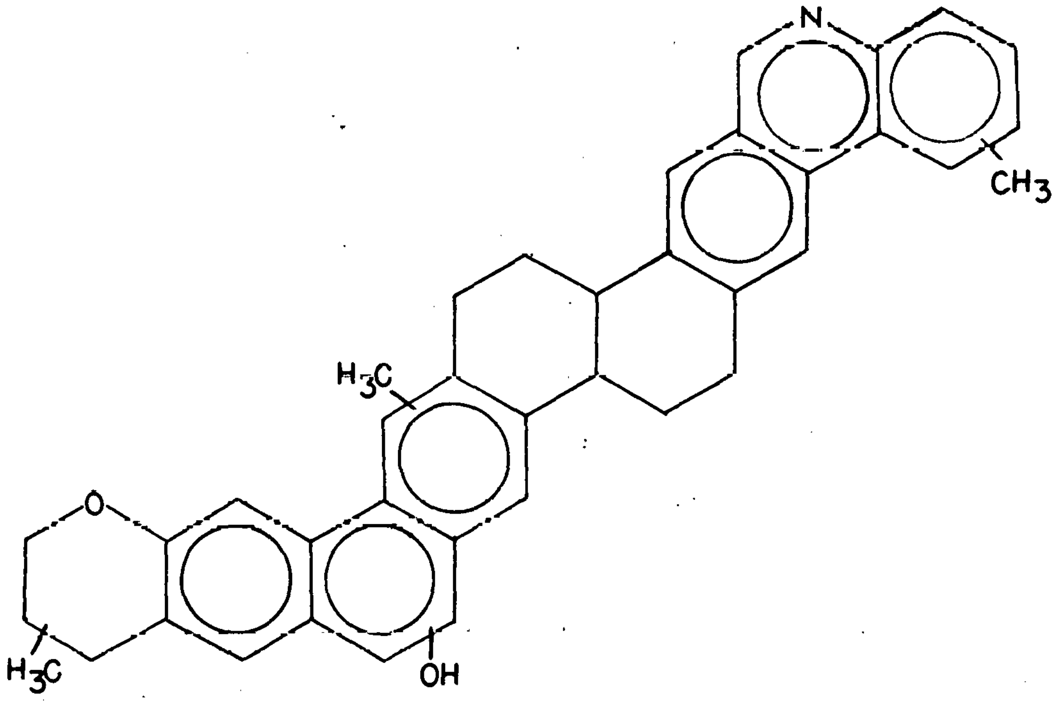

TABLE IV. COMPARISON OF AVERAGE MOLECULAR PARAMETERS FOR SYNTHOIL ASPHALTENE

	EXPERIMENTAL ANALYSIS	HYPOTHETICAL AVERAGE STRUCTURE
MOLECULAR FORMULA	$C_{41}H_{35}N_{0.7}O_{1.4}S_{0.07}$	$C_{39}H_{35}N_{1}O_{2}S_{0}$
MOLECULAR WEIGHT	560	549
H^*_{AR}	0.31	0.29
H_α	0.42	0.40
H^*_0	0.25	0.29
F_α	0.71	0.69
H_{ARU}/C_{AR}	0.67	0.71
σ	0.45	0.47
R_S	8.7	9
N	1.6	1.5
C_A	29.1	28
R_A	5.8	6
C/H	1.16	1.11
α-CH_3 ^{A}	1.93	2
$\geq\beta$-CH_3 ^{A}	1.31	1

^{A}DETERMINED FROM ^{13}C NMR ANALYSIS.

(c) VPO Investigation of Asphaltene Molecular Weight

The VPO molecular weights of coal-derived asphaltene chromatography products vs. concentration in benzene and THF have been determined and are shown in Table V. The results show that association of asphaltene products takes place in a manner similar to that observed for starting asphaltenes in both solvents. A positive correlation is observed between concentration and molecular weight, and the slopes of the linear correlation lines are greater in benzene than in THF. The agreement between the extrapolated molecular weights at infinite dilution in both solutions is very good (average deviation for 11 samples is 2.1%).

These silica gel solvent elution chromatography fractions represent the majority of the starting asphaltenes (80-90%). As previously reported for Synthoil asphaltene chromatography fractions (9), the slopes of the MW vs. concentration curves are greater for the diethyl ether eluted fractions than for the benzene eluted fractions when the VPO measurements are carried out in the less polar solvent benzene. The former fraction is known to contain basic nitrogen and phenolic OH, and, therefore, would be expected to show greater association if the mechanism for association was via hydrogen bonding donor-acceptor complexation.

Table V, Molecular Weight of Asphaltene Products vs Concentration* in Benzene and THF

	Solvent	Least Squares Equation	Corr. Coeff.	Av. MW at Zero Conc.	% Dev.
Benzene Eluted Synthoil Asphaltene	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_2O Eluted Synthoil Asphaltene	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		
Benzene Eluted HRI Asphaltene	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_2O Eluted HRI Asphaltene	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		
Benzene Eluted FMC-COED Asphaltene	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_2O Eluted FMC-COED Asphaltene	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		
Benzene Eluted Cat. Inc. SRC Asph.	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_2O Eluted Cat. Inc. SRC Asph.	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		
Benzene Eluted PAMCO SRC Asphaltene	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_2O Eluted PAMCO SRC Asphaltene	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		
PAMCO SRC**** Asphaltene	THF	$MW = 1.83 \pm 0.16C + 502 \pm 3.3$	0.96	532	5.7
	Benzene	$MW = 7.26 \pm 0.51C + 563 \pm 10.1$	0.98		

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*Conc. g/l

**Repeated with a new sample

***Not completely soluble

****Vacuum distillation residue

Asphaltene Self-Association Model

A theoretical model of self-association of asphaltenes in solution was derived last quarter (11). It was based on Coggeshall and Saier's (12) two equilibrium constants model; one for the formation of dimer (K_1), and the other for the successive addition of monomeric units to form higher polymers (K). A concentration term C was missing in the denominator of equation (3) on page 15 in that report. The correct form should be:

$$MW_{obs} = \frac{M_o \alpha C + 2\, M_o \cdot \frac{\alpha 2 C}{2} + 3\, M_o \cdot \frac{\alpha 3 C}{3} + \ldots + nM_o \frac{\alpha n C}{n} + \ldots}{C \cdot \left[\alpha + \frac{\alpha 2}{2} + \frac{\alpha 3}{3} + \ldots + \frac{\alpha n}{n} + \ldots \right]}$$

Instead of solving two nonlinear equations simultaneously, a different approach has been tried based on the same model in this quarter, and only one non-linear equation has to be solved, making the calculation simpler. The approach is as follows:

(a) Assume values of K and K_1.

(b) 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.

(c) Substituting C_1, C_2, α and β into equation (2) and get

$$K = \frac{C_{1\alpha}}{2(K_1 - \bar{K}_1)} \left[2K_1 - \frac{\bar{K}_1}{2} + \sqrt{2K_1\bar{K}_1 + \frac{\bar{K}_1^{\,2}}{4}} \right] \quad \ldots \qquad (5)$$

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

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

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

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

(d) Solve equation (7) for K_1 by 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. The calculated equilibrium constants, together with the standard deviations, are summarized in Table VI where the % Dev. is defined as:

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

and it is within 5.5%. This suggests that this two parameter model is efficient in describing the self-association of asphaltenes from five different processes in benzene. The calculated molecular weights, fraction of monomer, and monomer bound in dimer and trimer are plotted in Figs. 4 to 8 for the five asphaltenes.

In the future we will measure VPO molecular weights as a function of concentration for the carboid fractions in the solvent DMF. We will also study asphaltene self-association in other more and less polar solvents than benzene and THF, and test the association model in these solvents.

Table VI. Calculated Equilibrium Constants and Standard Deviations of Coal - Derived Asphaltenes in Benzene

Process	Monomer MW	K_1	K	Standard Deviation	% Dev.
Synthoil Asphaltene	560	0.0762	0.0671	13.7	2.4
HRI Asphaltene	492	0.118	0.0866	9.0	1.8
FMC-COED Asphaltene	375	0.210	0.0813	20.7	5.5
Cat. Inc. SRC * Asphaltene	483	0.225	0.109	12.2	2.5
PAMCO SRC * Asphaltene	532	0.0610	0.0971	18.6	3.5

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*Isolated from vacuum distillated bottom product.

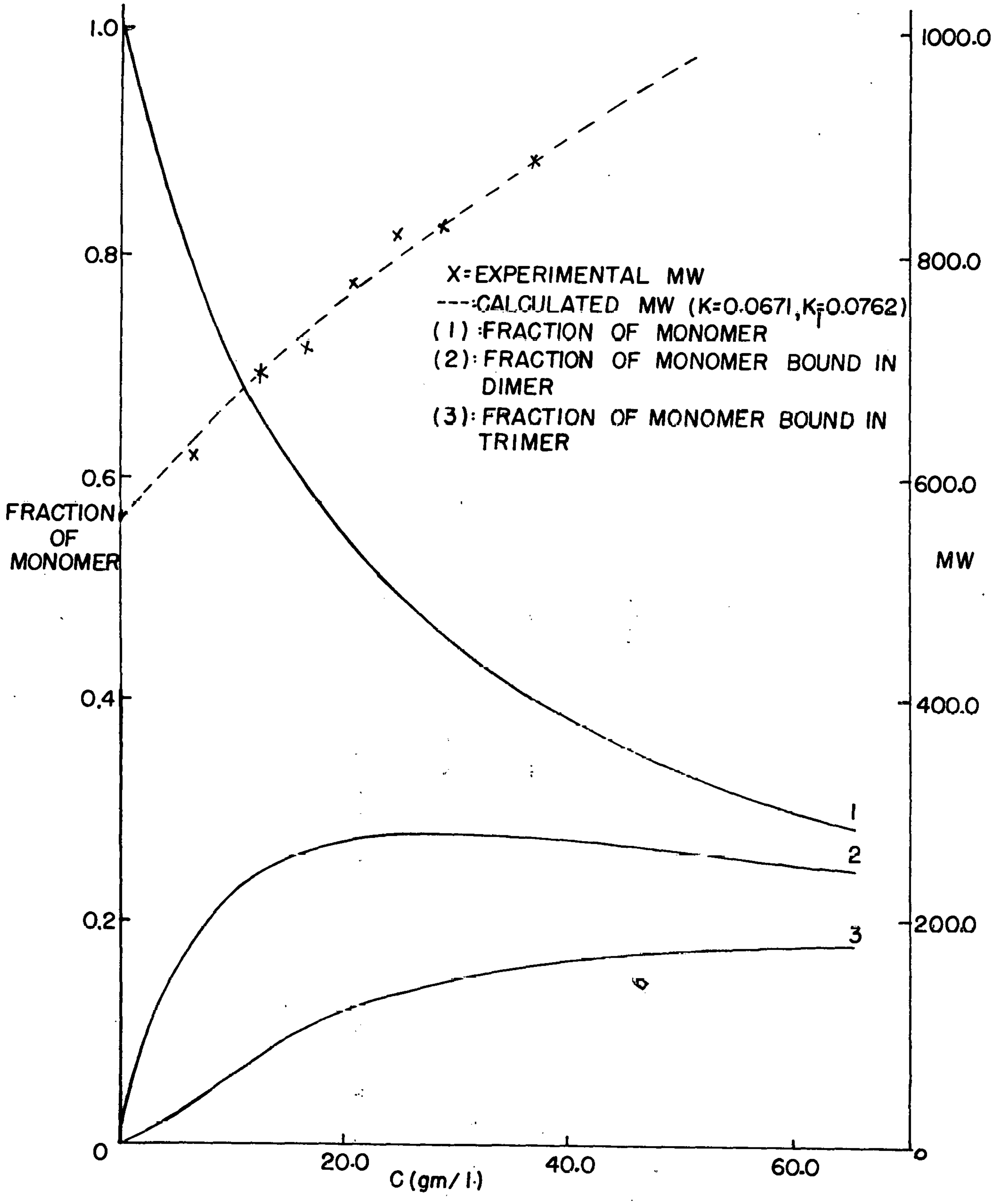

FIG. 4 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION SYNTHOIL ASPHALTENE IN BENZENE

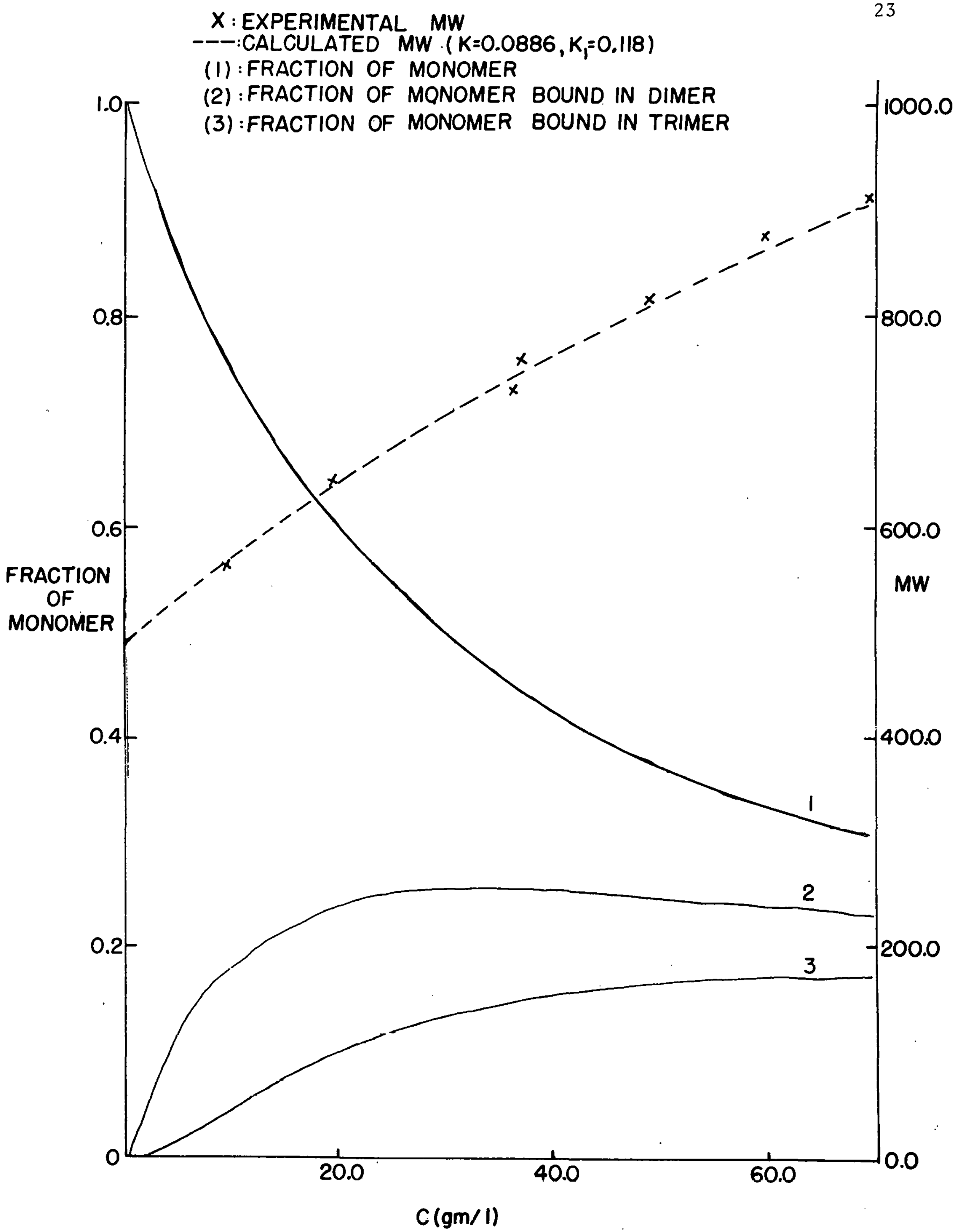

FIG. 5 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION HRI ASPHALTENE IN BENZENE

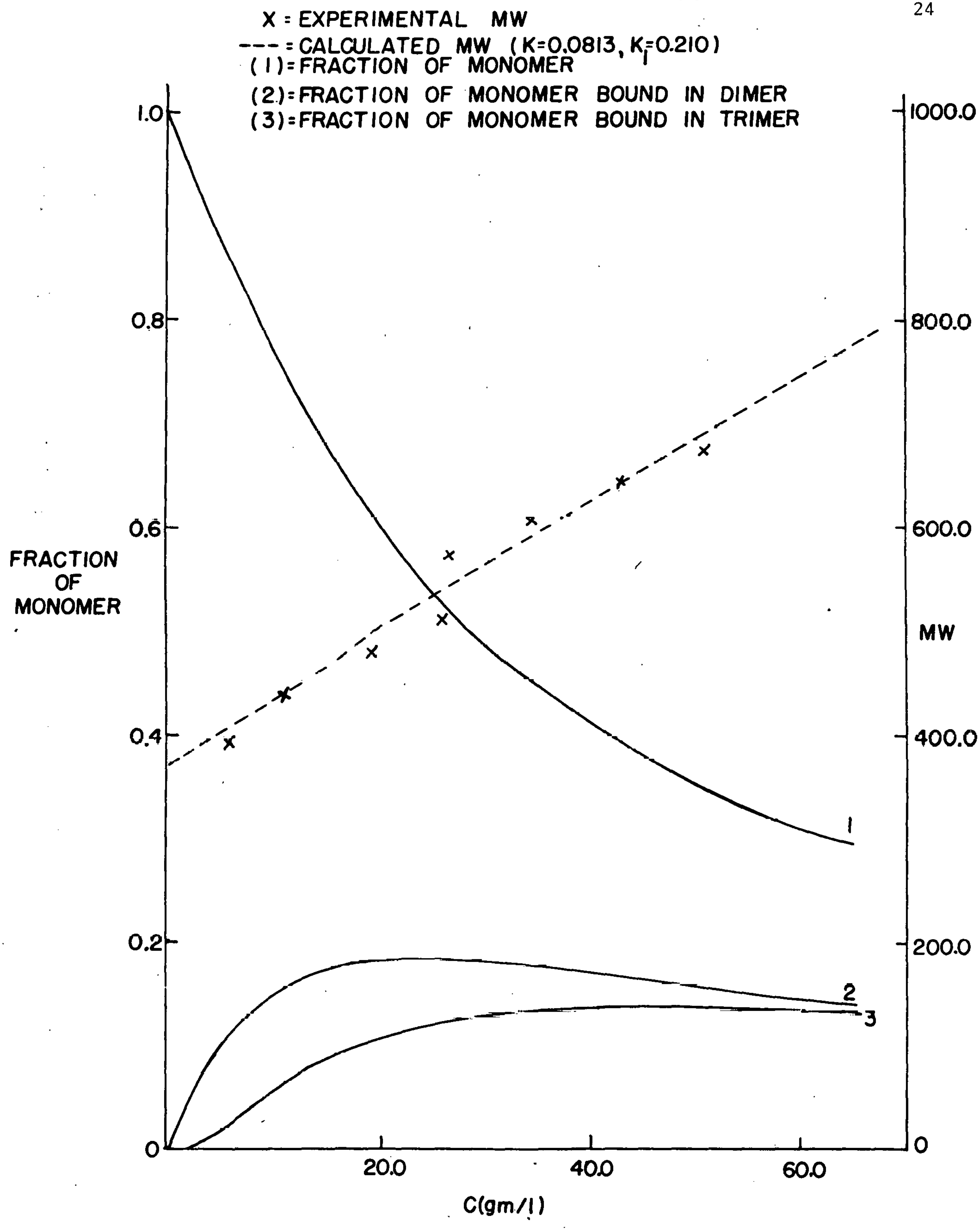

FIG. 6 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION FMC-COED ASPHALTENE IN BENZENE

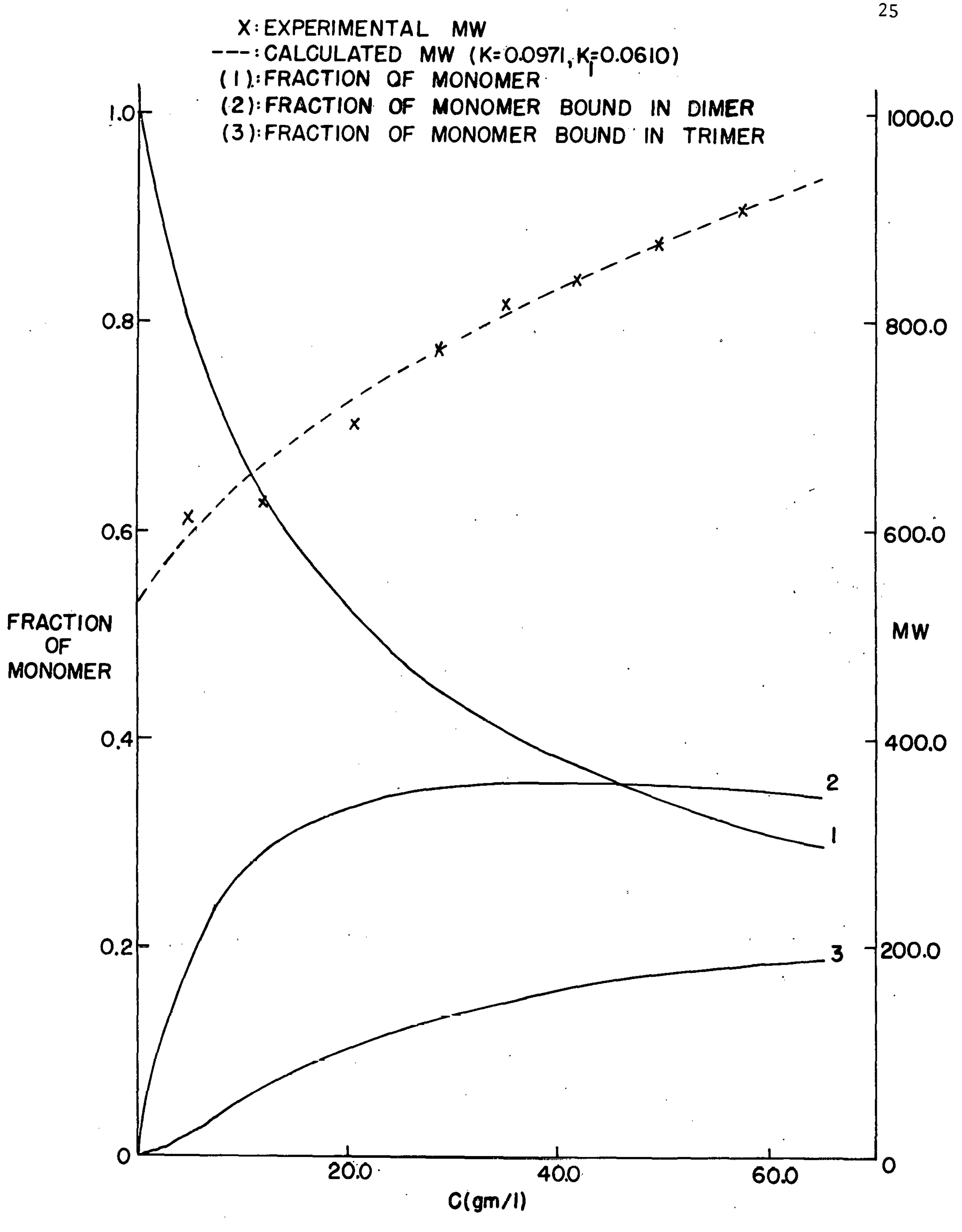

FIG. 7 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION PAMCO ASPHALTENE IN BENZENE

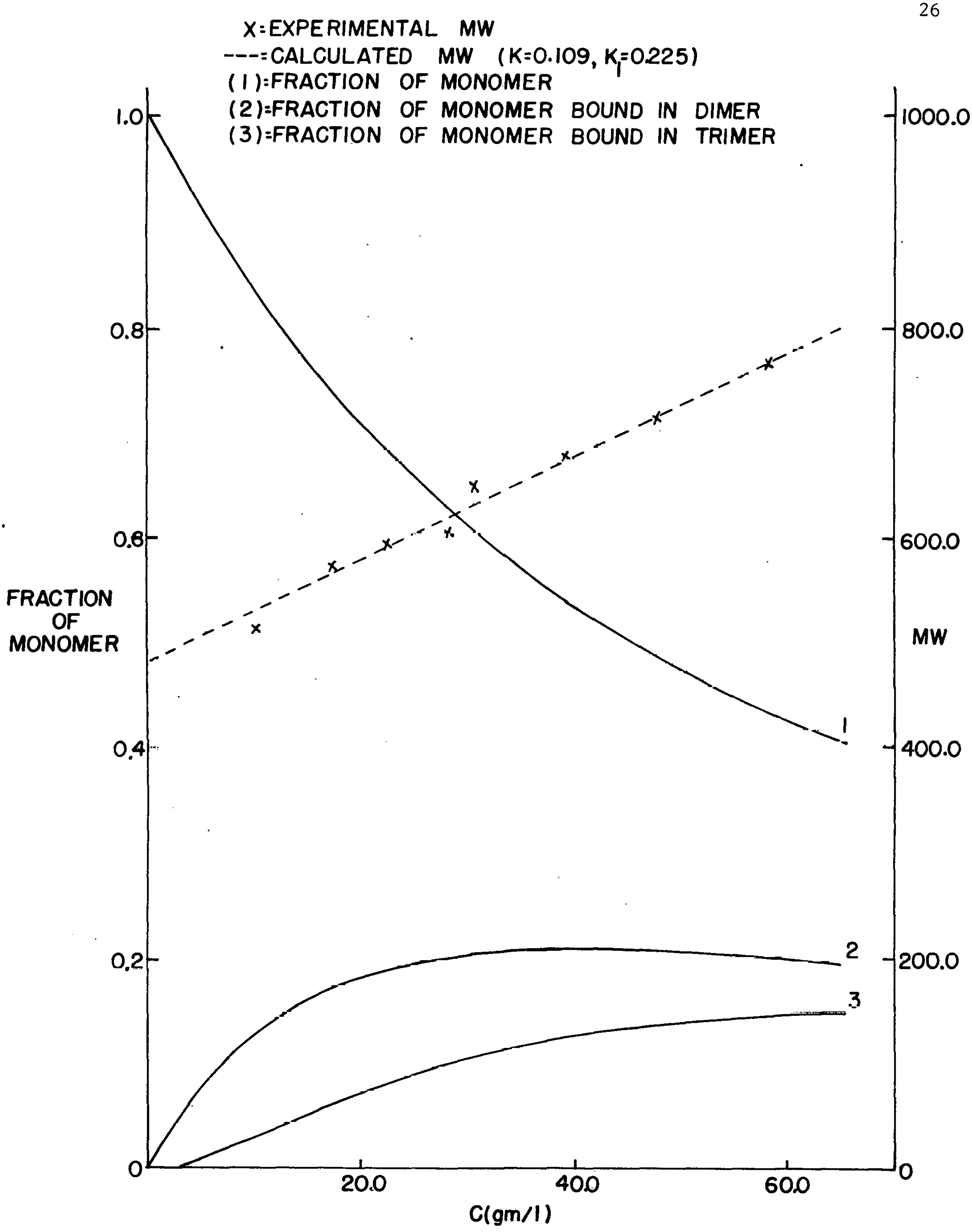

FIG. 8 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION CAT. INC. ASPHALTENE IN BENZENE

(d) Electron Spin Resonance of Asphaltenes

Electron spin resonance (ESR) has been used in the past to study the structure and state of association of native petroleum asphaltenes (13-15). We reported preliminary ESR results obtained with a single cavity spectrometer previously (11). During the past quarter we have improved our measurements by using a Varian E-12 dual cavity spectrometer operating at a microwave frequency of about 9.5 GH z. 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, $N_S=3\times10^{15}$ 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:

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

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

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

where I is the intensity and ΔH is the line width.

Lande g-values, spin intensities, line widths, MW and spin/molecules values are reported in Table VII 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, and are close

Table VII. Lande g-Values, Intensity and Line Width of Coal Liquid Solvent Fractions[a] and Asphaltene Derived Products

Sample	g-Value	Intensity, N_g ($\times 10^{18}$)Spins/g	Line Width ΔH, Gauss	VPO MW[b]	Spin Molecules
Synthoil Asphaltene	2.0028	4	5.6	560	300
HRI H-Coal Asphaltene	2.0029	3	5.2	5.3	400
FMC-COED Asphaltene	2.0036	0.4	5.1	350	5000
PAMCO SRC Asphaltene	2.0030	1.7	5.8	480	800
Cat. Inc. SRC Asphaltene	2.0030	1.7	5.1	486	700
Synthoil Oil[f]	2.0034	0.05	5.6	243[c]	50,000
Synthoil Resin	2.0032	0.7	6.5	305[c]	3000
Synthoil Carbene	2.0029	6	5.2	——	——
Synthoil Carboid	2.0029	9	5.2	(344)[d]	80
Synthoil Benzene Eluted	2.0029	1.0	6.7	546	1100
Synthoil Et_2C Eluted	2.0030	1.5	6.5	530	800
Synthoil THF Eluted	2.0030	10	5.8	(570)[e]	90
Synthoil Sternberg Acid/Neutral	2.0032	0.4	6.2	466	3000

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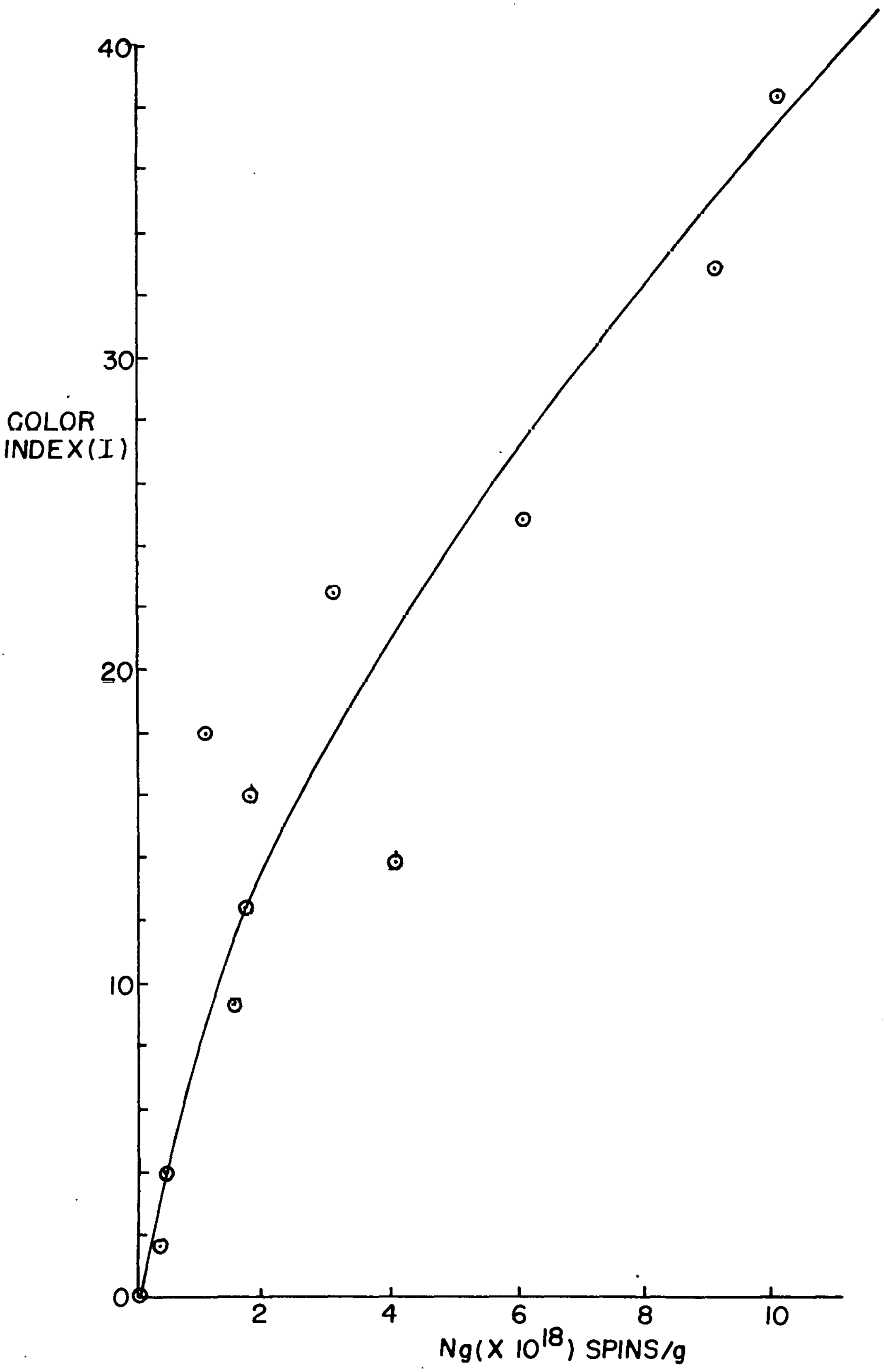
[a] Measured in pyridine solution.
[b] Extrapolated infinite dilution average value in benzene and THF unless otherwise cited.
[c] Average finite concentration value in benzene.
[d] Average finite concentration value in DMF, corrected for 8.8% ash.
[e] Infinite dilution value in THF obtained by combining values for two THF eluted fractions.
[f] ESR run on neat liquid.

to those observed for neutral radicals rather than to those observed for either radical ions or semiquinones (16). 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. 9). 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 solution.

In the next Quarter we will measure spin intensities in solution as a function of substrate concentration. We will also measure spin intensities of solid samples. Parts have been ordered to repair an inoperable variable temperature controller, and it is expected that the variation in sample signal intensities with temperature will also be studied.

FIG. 9 PLOT OF COLOR INDEX (I) VS SPINS/g (Ng) FOR COAL LIQUID SOLVENT FRACTIONS AND ASPHALTENE DERIVED PRODUCTS



(e) Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out in this quarter on Synthoil solvent fractions, Synthoil asphaltene chromatography fractions, and asphaltenes obtained from the other liquefaction processes under study. Thermogravimetric analysis is useful in determining % volatile matter, fixed carbon or char, and ash. 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 $\approx 700^{\circ}$C at 20°C/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 VIII. Figures 10 and 11 show a comparison of the thermograms for Synthoil asphaltene and carboid carried out in nitrogen and air.

Comparison of Figs. 10 and 11 indicates that Synthoil asphaltene begins to be stabilized toward volatilization vis-a-vis Synthoil carboid at $\approx 460^{\circ}$C. At $\approx 600^{\circ}$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

Table VIII. 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

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[a] Wt. % char = (wt. % remaining N_2 - wt. % ash).

[b] Determined independently by dry ashing method.

[c] Determined from TGA curve.

[d] Asphaltene solvent elution chromatography fractions from silica gel column.

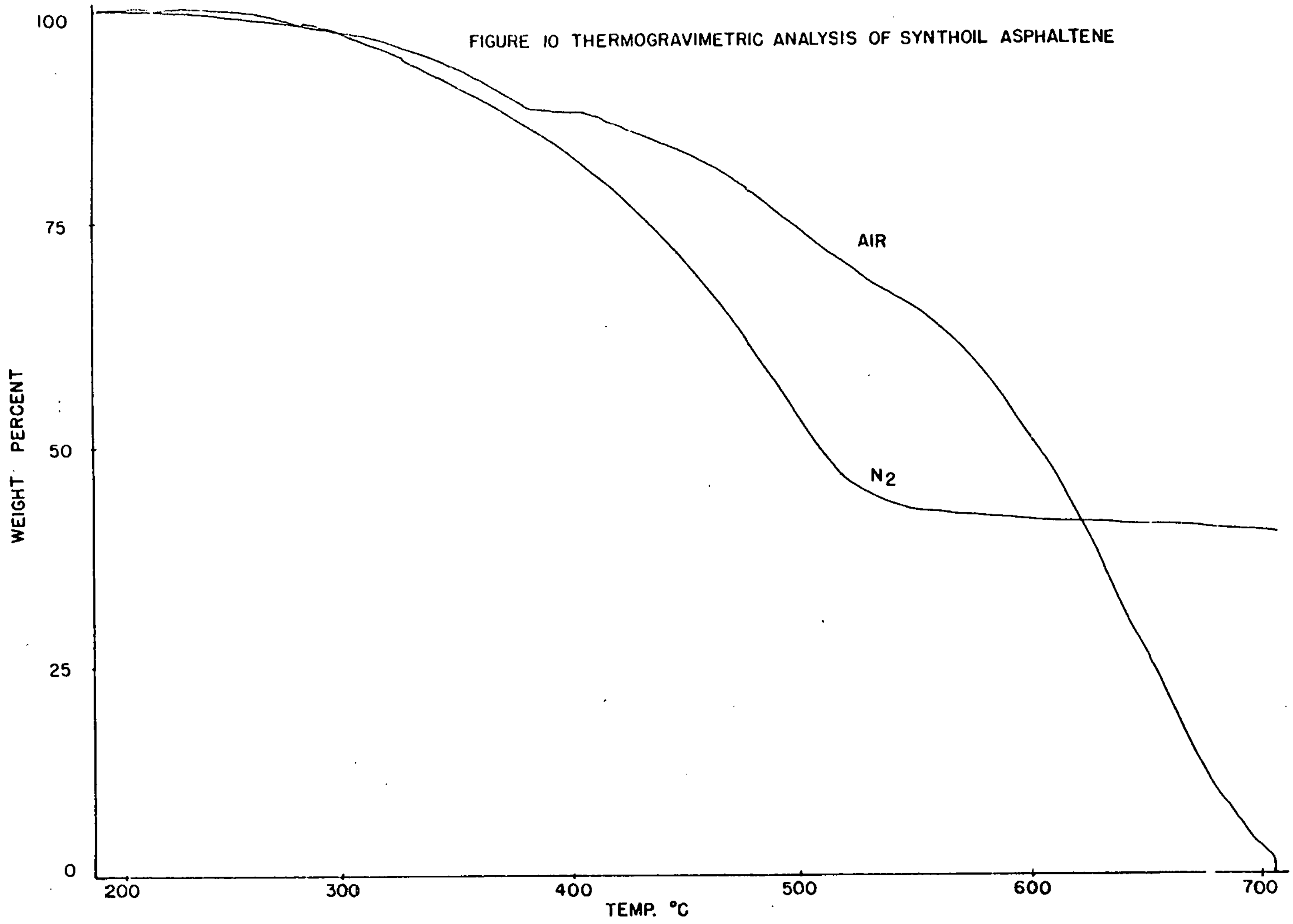
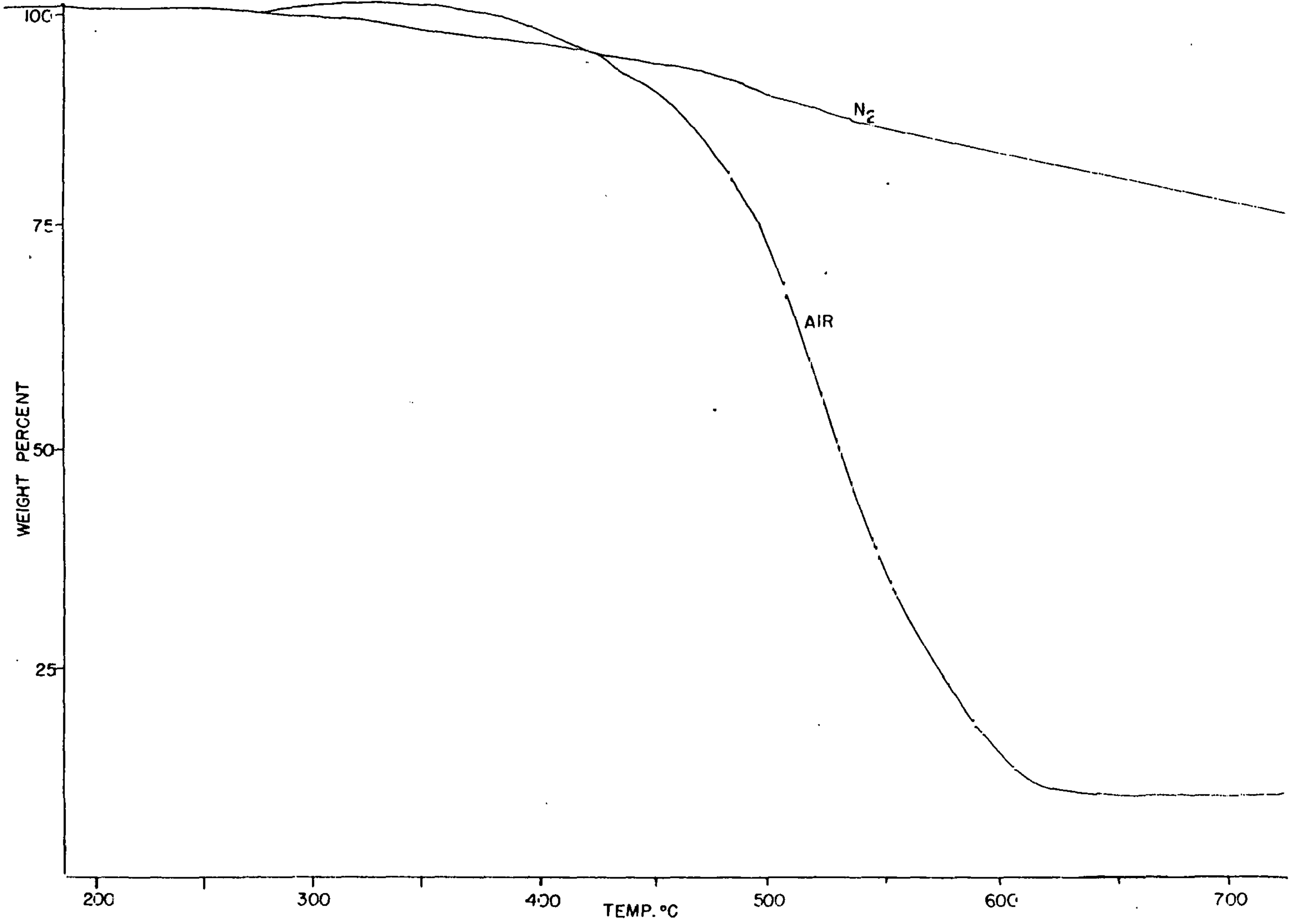


FIGURE 10 THERMOGRAVIMETRIC ANALYSIS OF SYNTHOIL ASPHALTENE

FIG. II THERMOGRAVIMETRIC ANALYSIS OF SYNTHOIL CARBOID



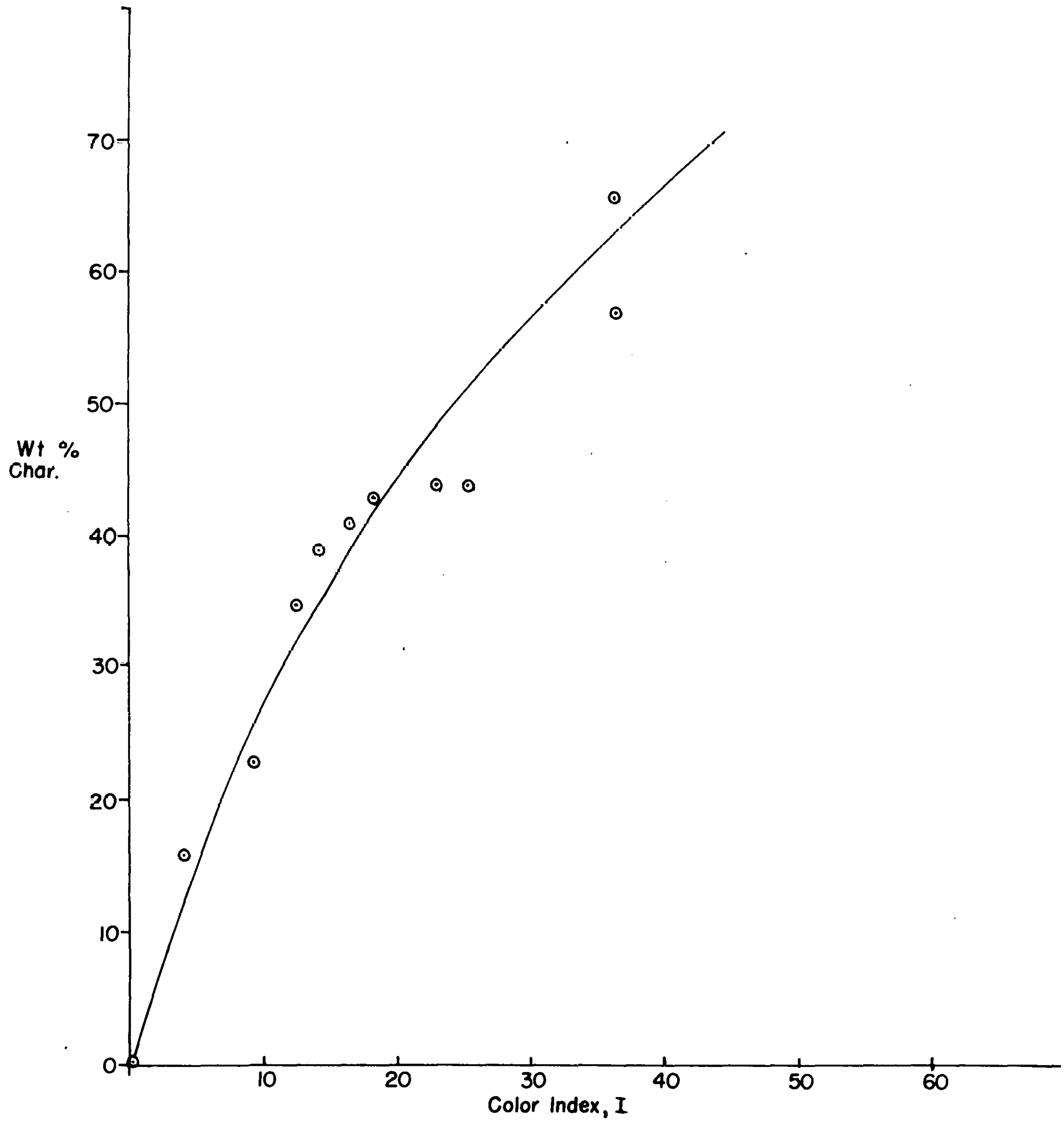
reactions could be oxidative polymerization or crosslinking. In our last Quarterly report,we reported the observation that partially oxidized Sythoil asphaltene (alkaline $KMnO_4$ at 75°C) underwent a three fold increase in both oxygen content and VPO molecular weight (11). This also was suggestive of oxidative polymerization.

Another interesting correlation observed from the TGA data relates the % char formed with the color intensity values of the various materials (integrated intensity obtained by absorption spectrometry over the 400-750mm range). It may be seen in Figure 12 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 was described in Section3(d) of this report between the color intensity and the ESR spin intensity of the various materials.

Work forecast:

Characterization will continue on all applicable fractions, as detailed in the body of this report, by the analytical and physical methods developed in this project.

FIG. 12 RELATIONSHIP BETWEEN TGA WT. % CHAR. AND COLOR INDEX OF SOLVENT FRACTIONS ASPHALTENE DERIVATIVES



(4) Chemical Methods for Asphaltene Structure Determination

Work Accomplished:

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

(a) Silylation of Hydroxyl Groups

In previous Quarterly Reports (7,9,11) we described the procedure and results for the silylation of asphaltenes form different coal liquefaction demonstration processes. During the present quarter we carried out the silylation of the carboid solvent fractions (benzene and CS_2 insoluble-pyridine soluble) from the five demonstration processes under study. Because of the poorer solubility, and more intractable nature of the carboids a more vigorous silylation procedure was employed (17). The carboids were dissolved in pyridine and refluxed 24 hours with a 30 to 1 excess of 1,1,1,3,3,3-hexamethyldisilazane and 5 drops of trimethylchlorosilane. The solvent and unreacted starting materials were removed under vacuum, and the product heated in a vacuum oven until its weight remained constant. The preliminary results are reported in Table IX . It may be seen that substantial amounts of the oxygen contained in the carboids is present as phenolic OH. The % OH/O_{total} values for carboids are comparable to those observed for asphaltenes(9) produced in the catalyzed hydrogenation (48-53%) and the staged pyrolysis processes (61%), but differ from those observed for SRC processes. The asphaltenes produced in SRC processes were found to have %OH/O_{total} values of 92 and 97% (9), however, the carboids

Table IX . Analysis of Silylated Carboids

Carboid	% Si in Silylated Carboid	%OH in Silylated Carboid[a]	%O in Starting Carboid[b]	%OH/O_{total} in Starting Carboid
Synthoil	5.56	3.70	7.90	47
HRI H-Coal	6.19	4.20	6.52	64
FMC-COED	8.43	6.14	11.91	52
PAMCO SRC	4.89	3.19	6.04	53
Cat. Inc. SRC	3.89	2.45	6.87	36

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[a] Using method of Friedman, et al. (17).

[b] Determined by difference.

are found to have values of only 36 and 53%, respectively, for Catalytic Inc. and Pamco SRC products. These observations may be rationalized by assuming that the end product carboids from SRC processes have lost a substantial percentage of their phenolic OH- perhaps through conversion of phenolic groups into ether groups.

(b) Methylation of Basic Nitrogen Groups

In previous Quarterly Reports we described the procedure for methylation of basic nitrogen containing asphaltenes (9) and reported preliminary results (11). During the present Quarter methylations of Synthoil asphaltene, and asphaltene-derived silica gel chromatography fractions were repeated in order to check the precision of the methylation procedure. The results are shown in Table X .

The methylation of starting asphaltene is seen to be fairly reproducible in terms of percentages of benzene soluble and insoluble fractions, and %N and atomic I/N ratios of the benzene insoluble fraction. The general premise that no iodine should appear in the benzene soluble fraction, since alkylated asphaltene iodide should precipitate from solution, is violated. It is likely that our simple procedure does not remove all CH_3I decomposition products containing iodine from the benzene soluble fraction. However, we still assume that the nitrogen found in this fraction is not methylated, and, therefore, non-basic nitrogen. The nitrogen found in the benzene insoluble fraction is assumed to be basic nitrogen to the extent that the atomic I/N ratios indicate, i.e., about 0.66 of the nitrogen is methylated and therefore basic. The conclusions which can be reached from these premises are:

Table X. Analysis of CH_3I Alkylated Asphaltenes

		Benzene Soluble Fraction				Benzene Insoluble Fraction			
Sample	(%N)	%	%I	%N	Atomic I/N	%	%I	%N	Atomic I/N
Starting Asphaltene	(1.73)	61	1.82	1.40	0.14	39	13.37	2.35	0.63
		52	2.90	1.29	0.25	48	13.35	2.14	0.68
Benzene Eluted from Silica Gel	(0.95)	(100)	< 0.3	1.14	0.03	(0)	——	——	——
		84	< 0.3	0.93	0.03	16	(12.12)[a]	0.47	(2.78)[a]
Et_2O Eluted from Silica Gel	(1.70)	(0)	——	——	——	(100)	12.74	1.51	0.93
		47	3.13	1.56	0.22	53	14.52	2.31	0.69
		24[b]	——	——	——	76	——	——	——
THF Eluted from Silica Gel	(1.95)	21[c]	< 0.3	2.12	0.02	79	15.42	2.53	0.67

---

[a] Too high. Iodine contamination suspected.

[b] Analyses pending.

[c] Run in THF due to insolubility in benzene. THF stripped off product, and product treated with benzene.

(1) Asphaltene nitrogen is about 67% non-basic.

(2) About 50% of the asphaltene molecules which contain a basic nitrogen atom also contain a second non-basic nitrogen atom on the average.

The asphaltene derived silica gel chromatography fractions were also examined again. The benzene eluted fraction is seen to afford little or no benzene insoluble materials on methylation, and almost no addition of methyl iodide ($< 0.3\%$ iodine on analysis) which supports the assertion that this chromatography fraction does not contain a significant amount of basic nitrogen containing asphaltene.

The diethyl ether eluted fraction was methylated again twice, using different samples, because the first result did not agree with the previously reported result (11) that "the Et_2O eluted asphaltene gives only one fraction which contains practically all basic nitrogen." It now seems likely that this chromatography fraction gives two fractions on methylation: a benzene soluble fraction in $\doteq 24$[a] yield containing little or no basic nitrogen, and a benzene insoluble fraction containing a substantial amount of basic nitrogen (Atomic I/N ratio $\simeq 0.81$[b]). The third chromatography fraction, THF-eluted, affords mostly benzene insoluble material (79 wt. %) which contains a large amount of basic nitrogen (Atomic I/N ratio = 0.67).

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[a] Average of three runs.

[b] Average of two runs-pending analysis on third run.

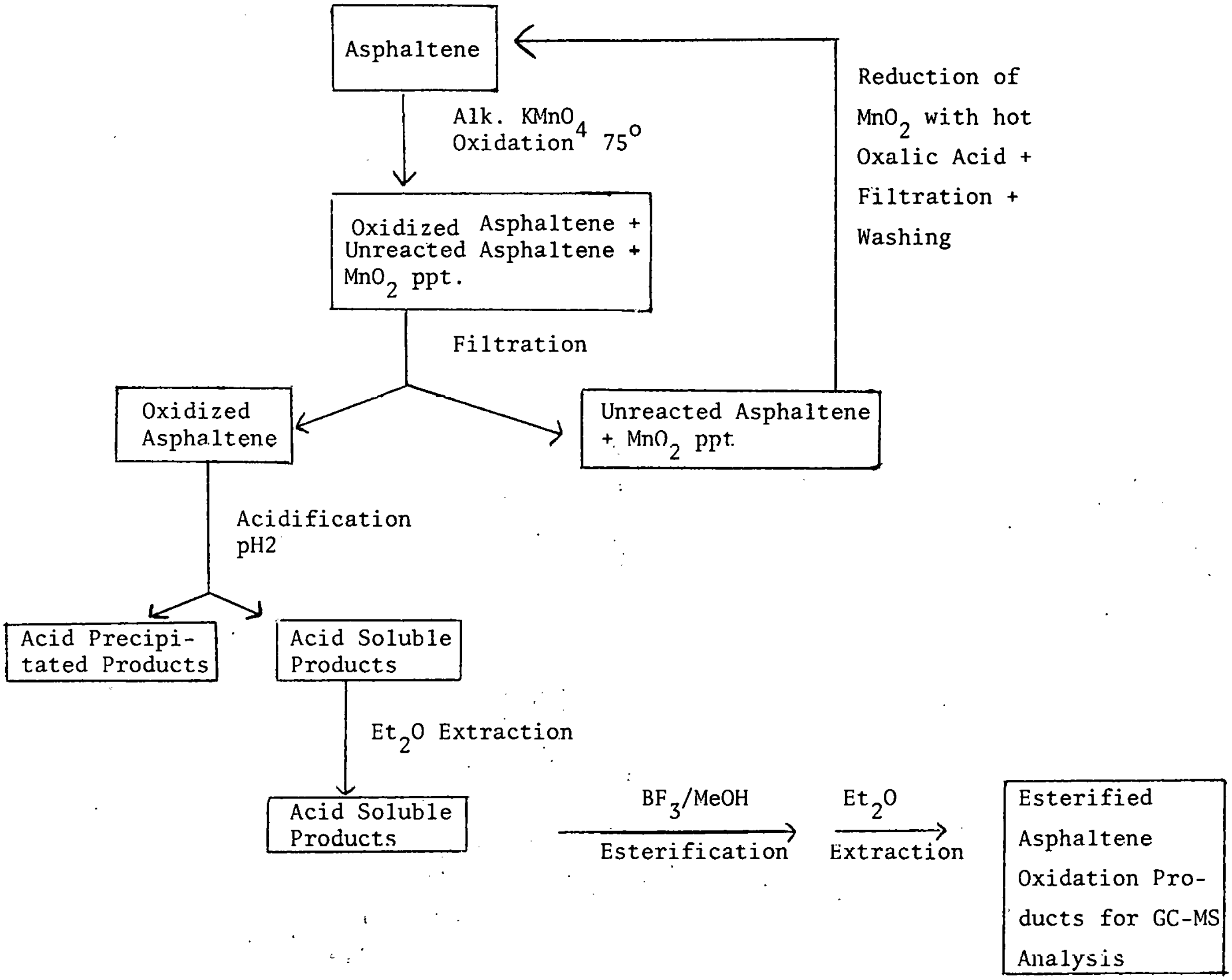
(c) Oxidation

Preliminary results on the oxidation of Synthoil asphaltene were reported earlier (11). During this Quarter a mild, stepwise oxidation procedure was used in order to avoid extensive degradation of the oxidized asphaltene intermediate products (Fig. 13). Approximately 4g 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 ± 2°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. 14). A sample of this material has been submitted for GC-MS analysis.

The rate of oxidation of Synthoil asphaltene is shown in Fig. 15, 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.

Fig. 13 Stepwise Oxidation of Synthoil Asphaltene



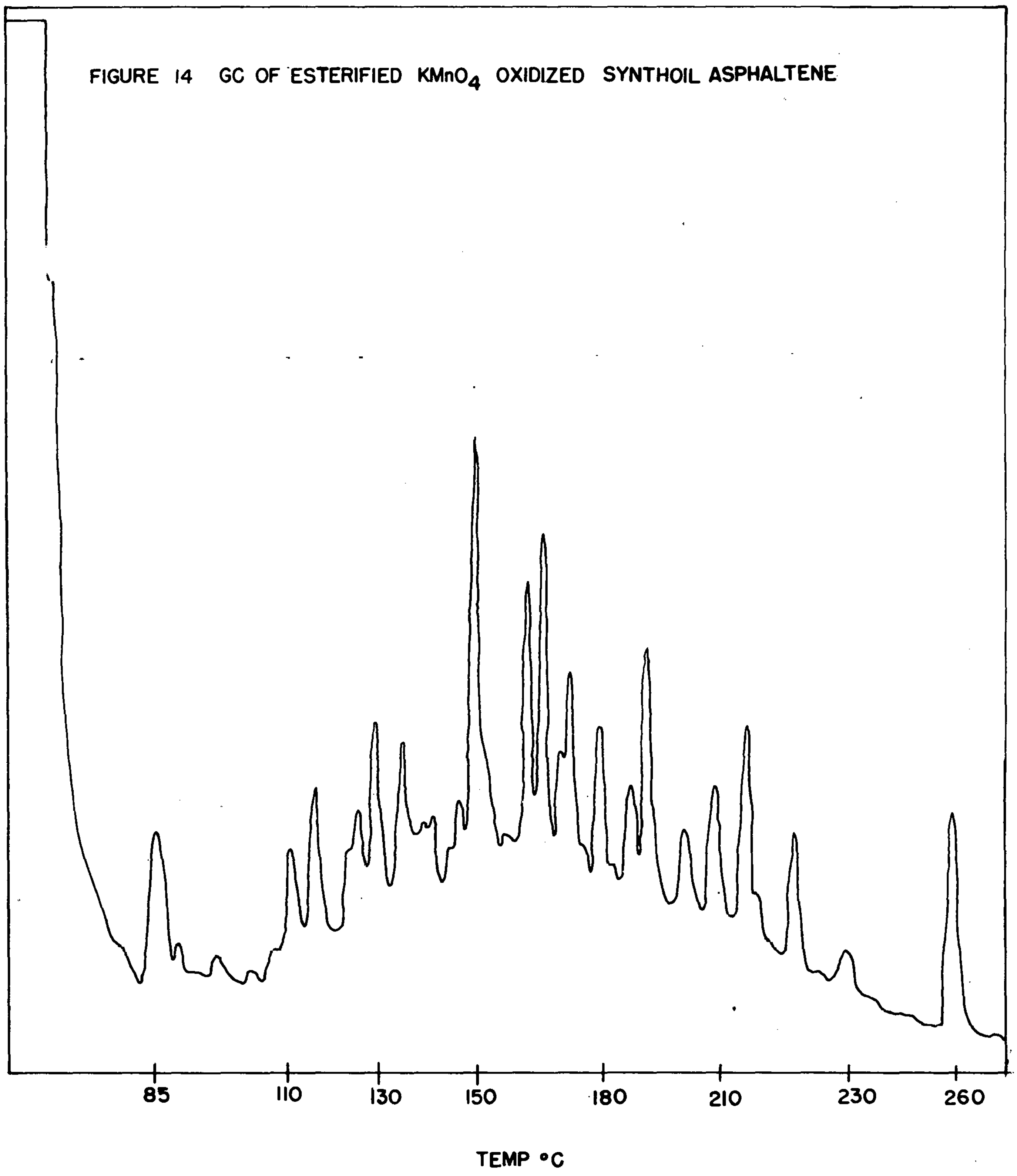


FIGURE 14 GC OF ESTERIFIED $KMnO_4$ OXIDIZED SYNTHOIL ASPHALTENE

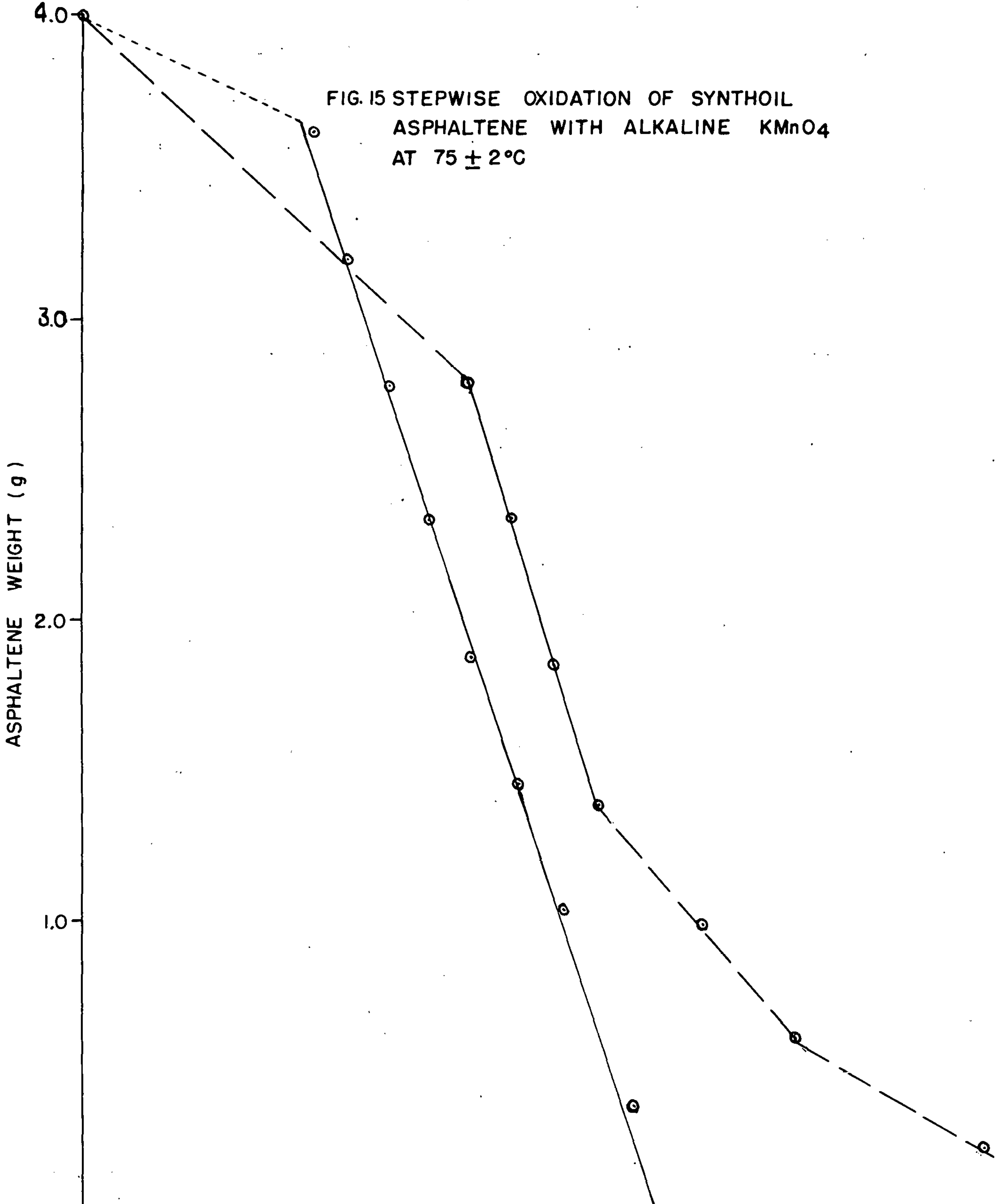


FIG. 15 STEPWISE OXIDATION OF SYNTHOIL ASPHALTENE WITH ALKALINE KMnO4 AT 75 ± 2°C

The results of our oxidation studies to date 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, may be identified by the GC-MS technique. This information should be useful for characterizing the basic structures of asphaltenes.

Work forecast:

Additional chemical reactions such as silylation, methylation and oxidation will be carried out on coal liquid solvent and chromatography fractions as time and man power permit.

CONCLUSION

The major benzene insoluble fraction, carboid, from Synthoil coal liquid was found to be 63 wt. % soluble in THF and 90 wt. % soluble in pyridine. This fraction may be almost completely de-ashed by dissolution in either of these solvents (97% in THF, 96% in pyridine), however, pyridine appears preferable because of the greater solubility of carboid in this solvent. Solubility limits of Synthoil asphaltene, and carbene fractions have been measured as a function of Hildebrand solubility parameters, and found to fall within the range 9-12 hildebrands and 10-11 hildebrands, respectively.

Analytical, VPO molecular weight, x-ray, NMR, and chemical functionality data have been used to derive a hypothetical average structure for Synthoil asphaltene. The average molecular parameters calculated from the hypothetical structure agree reasonably well with those values obtained experimentally for Synthoil asphaltene.

A theoretical model of self-association of asphaltenes in benzene solution, based on a two equilibrium constants model: one for the formation of dimer, and the other for the successive addition of monomeric units to form higher polymers, has been found to be efficient in describing the self-association of asphaltenes from five different coal liquefaction demonstration processes. Molecular weights, and fraction of monomeric, dimeric and trimeric asphaltene have been calculated as a function of concentration.

Landé g-values, and spin intensities have been measured for coal liquid solvent fractions and asphaltene derived products. The g-values for all coal liquid derived materials fall in the narrow range of 2.0028-2.0036. These g-values fall within the range previously reported for asphaltene fractions of petroleum, and are close to those observed for neutral radicals rather than those observed for either radical ions or semiquinones. Spin intensities are related to the color intensity of the various samples (integrated intensity obtained by absorption spectrometry over the 400-750 nm range), and it therefore appears likely that only those molecules possessing large delocalized aromatic π systems possess free spins in solution.

Thermogravimetric analysis of coal liquid fractions has been carried out, and the % char formed has been found to be related to the color intensities of the various samples. Thermograms for Synthoil asphaltene and carboid, carried out in air and nitrogen, indicate that Synthoil asphaltene undergoes oxygen catalyzed reactions on heating which stabilize it toward volatilization vis-a-vis the carboid. Such reactions could be oxidative polymerization or crosslinking.

Silylation of carboids from SRC processes (Catalytic Inc. and PAMCO) indicates that these material have % OH/O_{total} values of 36 and 53% respectively as compared to values of 92 and 97% for the asphaltenes from the same processes. These observations may be rationalized by assuming that the end product carboids from SRC processes have lost a substantial percentage of their phenolic OH - perhaps through conversion of phenolic groups into ether groups.

Methylation of Synthoil asphaltene with methyl iodide indicates that about 67% of the asphaltene nitrogen is non-basic, and that about 33% of the nitrogen in molecules containing basic nitrogen is non-basic.

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