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FOSSIL ENERGY

CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES PHASE I

Quarterly Progress Report
January—March 1976

T. F. Yen
I. Schwager

Date Published—1976

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University of Southern California
Los Angeles, California

ENERGY RESEARCH & DEVELOPMENT ADMINISTRATION USA

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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES

Phase I

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T. F. Yen*
I. Schwager*

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

PREPARED FOR
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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ABSTRACT

Coal liquids have been separated by solvent fractionation into three crude fractions: pentane-soluble (gas oil and resin), pentane-insoluble and benzene-soluble (crude asphaltene), and benzene insoluble (carbene and carboid). The crude asphaltene fractions have been further separated by solvent elution chromatography on silica gel into two major fractions (benzene eluted and diethyl ether eluted). The great majority of these materials were characterized as to elemental analyses, molecular weight, metal analyses, color intensity, NMR - hydrogen percentages by proton type, carbon aromaticity by X-ray diffraction, and infared spectral analysis.

The two major asphaltene fractions obtained from Synthoil by elution from silica gel with benzene and diethyl ether compare relatively well with respect to ultimate analysis with the two components isolated by Sternberg et al. (1) by treatment of Sythoil asphaltenes dissolved in toluene with dry HCl. If these components prove to be similar, then silica gel chromatography offers a mild, chlorine free procedure for separating asphaltenes into acidic and basic components.

OBJECTIVE AND SCOPE OF WORK

It is the objective of this project to isolate and separate 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. Once 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 of 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 this quarter the following tasks had been undertaken and/or completed:

(1) Sample acquisition has continued throughout the quarter.
(2) Training of technical assistants has been completed.
(3) Set up of isolation protocol procedures has been completed.
(4) Set up of Duffy's Procedure has been completed on Teflon-silica gel columns.
(5) Preliminary characterizations have been 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.

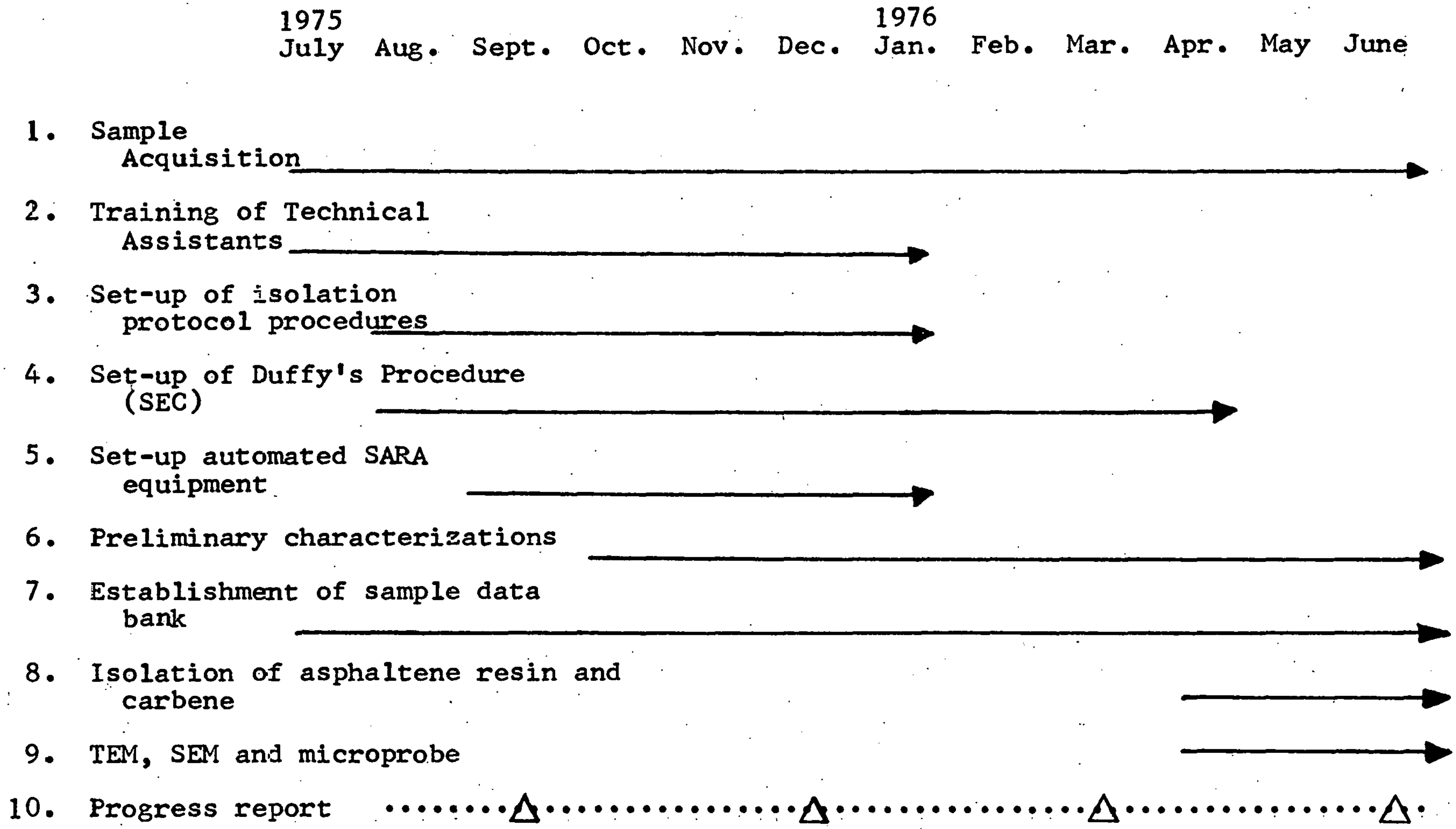
DETAILED DISCUSSION OF TECHNICAL PROGRESS

(1) Isolation of Crude Asphaltenes by Standard Method

Work Accomplished:

Efforts were continued to improve and standardize the crude asphaltene preparation by solvent fractionation. The general procedure involves precipitation of the crude asphaltene by addition of the "as received" coal liquid to a 20-fold (volume to weight) excess of pentane.[a] The precipitate is filtered, washed with pentane, and Soxhlet-extracted until no color is observed in the out-flowing extract. The Soxhlet thimble is then allowed to drain and the solids air dried. The pentane soluble materials (gas oil and resin) are recovered by evaporating off the pentane in a rotary evaporator.

Fig. 1 Milestone Chart



The pentane insoluble material is then Soxhlet-extracted with benzene until the out-flowing extracts are clear. This benzene-soluble, pentane-insoluble solution is then filtered while hot, and concentrated by rotary evaporation. The concentrated benzene solution is freeze-dried overnight to obtain the crude asphaltene as a powder. The benzene-insoluble residues (carbene and carboid) from the various steps are then dried and weighed.

The quantified results for fractionation of several coal liquids are presented in Table I. The results, where comparisons are possible, indicate reasonable reproductibility. Subsequent measurement of the physical properties of these crude asphaltenes indicate that they are of higher purity than materials obtained previously.

Table II shows the analysis and VPO molecular weights of most of these fractions.

The semiquantitative metal analysis of the crude asphaltenes and the benzene-insoluble fractions are presented in Table III.

Work Forecast:

Additonal samples will be solvent fractionated by the standard method, and analyzed as above, as they are received. The pentane-soluble fractions, gas oil and resin, will be further separated into propane soluble (gas oil) and pentane-soluble (resin) fractions. The benzene-insoluble fractions will be further separated into carbon disulfide-soluble (carbene), and carbon disulfide-insoluble (carboid) fractions.

(2) Separation of Crude Asphaltenes by Solvent Elution Chromatography

Work Accomplished:

In previous quarterly reports (2, 3), it was suggested that solvent elution chromatography might be useful for further purifying crude asphaltenes contaminated with small amounts of resin and/or carbene fractions. Solvent elution chromatography was carried out on a dual column of Teflon and alumina, and a procedure was suggested for chromatography on a column of Teflon and silica gel. During the present quarter, separation of crude asphaltenes on silica gel has been carried out, and the major solvent fracitons examined by a variety of analytical and physical techniques.

The quantitative results from chromatography of various crude asphaltenes on silica gel using benzene, diethyl ether and acetonitrile as eluents are presented in Table IV. Total recovery is generally in the range of 80-98%, and the majority of the crude asphaltenes may be recovered with the mobile phases of benzene and diethyl ether. Additional small amounts of material retained on the column after diethyl ether extraction may be recovered with acetonitrile elution.

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[a]Where the "coal liquid" has been solidified, as is the case for the Southern Services-SRC sample, the solid is first dissolved in a small volume of hot benzene before precipitation from pentane. For a sample such as the FMC-COED Syncrude which is too dilute, as received, to precipitate from pentane, a vacuum distillation is carried out to concentrate the asphaltenes, and to remove some of the volatile components.

TABLE I

SOLVENT FRACTIONATION OF COAL LIQUIDS

——— Weight Percent ———

Sample	Crude Asphaltene (Pentane Insoluble/Benzene Soluble)	Gas Oil + Resin (Pentane Soluble)	Carbene + Carboid (Benzene Insol.)	Total Recovered
FMC-COED (Filtered)	(18)[a]	(52)[a]	(11)[a]	(81)[a]
Synthoil (Product Oil)	11 13	82 76	3 4	96 93
PAMCO (Filter Feed)	9 6	81 75	9 7	99 88
Southern Services (Solvent Refined Coal)	44	18	35	97

[a]Early Run will be repeated under Standard Conditions

TABLE II

ANALYSIS - MOLECULAR WEIGHT

Sample	VPO MW	COMPOSITION % C	H	N	S	Ash	O Diff
EMC-COED (Filtered)							
Crude Asphaltene (C.A.)	458[c]	81.49	6.42	1.69	2.56	0.79	7.05
Benzene Eluted C.A. from Silica Gel	445[c]	82.67	6.21	1.05	1.90	1.38	6.79
Diethyl Ether Eluted C.A. from Silica Gel	340[c]	78.69	6.40	1.52	1.31	1.23	10.85
Pentane Soluble (Gas Oil + Resin)	310[c]	84.72	8.77	0.70	1.13	0.25	4.43
Benzene Insoluble (Carbene + Carboid)	-[a]	78.44	5.93	1.76	0.93	1.55	11.39
Synthoil (Product Oil)							
Crude Asphaltene (C.A.)	500[d]	86.85	6.48	1.63	0.66	(0.35)[b]	(4.03)
Benzene Eluted C.A. from Silica Gel	550[d]	88.29	6.51	0.57	0.98	0.97	2.68
Diethyl Ether Eluted C.A. from Silica Gel	560[c]	84.16	6.78	1.58	0.72	1.19	5.57
Pentane Soluble	260[c]	87.69	9.06	0.82	0.16	0.29	1.98
Benzene Insoluble	-[a]	85.49	5.72	1.50	0.67	1.33	5.29
PAMCO (Filter Feed)							
Crude Asphaltene (C.A.)	426[d]	85.03	6.06	1.45	1.11	1.50	4.85
Benzene Eluted C.A. from Silica Gel	400[d]	85.67	6.09	0.67	1.18	1.88	4.51
Diethyl Ether Eluted C.A. from Silica Gel	490[d]	81.31	6.39	1.95	0.99	2.03	7.33
Pentane Soluble		88.36	7.17	0.66	0.27	0.41	3.13
Benzene Insoluble	-[a]	85.08	5.00	0.63	1.37	2.23	5.69

[a] Insoluble in available solvents

[b] Value appears to be low. Analysis being repeated.

[c] MW determined in benzene

[d] MW determined in n,n-dimethyl formamide

TABLE III

SEMIQUANTITATIVE METAL ANALYSIS[a]

Element	FMC-COED (Filtered) Crude Asphaltene	FMC-COED (Filtered) Benzene Insoluble	SYNTHOIL (Product Oil) Crude Asphaltene	SYNTHOIL (Product Oil) Benzene Insoluble	PAMCO (Filter Feed) Crude Asphaltene	PAMCO (Filter Feed) Benzene Insoluble
Si	210	100	180	1800	150	1800
Fe	20	270	130	420	11	650
Al	57	140	7.6	760	17	710
Ti	12	9.5	69	130	1.6	220
Mg	5.4	14	1.3	29	2.9	39
Ca	39	280	3.4	69	2.9	92
Cd		1.2		1.1		1.3
Ba		ND<10		ND<10		ND<10
Be		ND< 0.04		TR< 0.04		3.2
B	81	72	69	77	11	120
Mn		6.0		4.9	1.0	34
Pb		4.8		18		31
Sn		0.64		0.50		7.5
Ga		ND< 0.30		TR< 0.30		2.1
Na		TR<10		86	67	TR<10
Ni		3.3		2.1		4.7
Mo		ND< 0.30		TR< 0.30		ND< 0.30
V		0.42		0.51		3.3
Cu	1.0	1.6	0.55	2.3	0.35	3.2
Ag		0.15		TR< 0.02		ND< 0.02
Zn		6.5		ND< 4.0		19
Zr		ND< 0.30		0.65		2.5
Co		0.36		0.34		0.60
Yb		ND< 0.40		ND< 0.40		1.3
K		ND<10		ND<10		ND<10
Sr		0.86		2.3		2.4
Cr	TR<1.0	1.5		3.8		6.6
Other elements	Nil	Nil	Nil	Nil	Nil	Nil
Loss on ignition (sulf. ash):	99.841%	99.709%	99.902%	98.969%	99.930%	98.936%

[a]Results in ppm ND - Not detected TR - Trace

TABLE IV

SILICA GEL CHROMATOGRAPHY

Sample	Benzene	Diethyl Ether	Acetonitrile	Total Weight % Recovered
	Weight % Recovered Material with Solvent			
FMC-COED (Filtered)	39	61	—	80
	38	62	—	88
Synthoil (Product Oil)	49	46	5	70[a]
	57	43	—	84
PAMCO (Filter Feed)	43	48	9	82

[a]Crude Asphaltene Contaminated with some Benzene Insoluble Material.

Analytical and molecular weight data for those benzene- and diethyl ether-eluted fractions are given in Table II. Color intensities, hydrogen aromaticities and carbon aromaticities are presented for those chromatographic fractions in Tables V, VI, and VII respectively.

Discussion:

The major portion of the crude asphaltenes may be eluted from silica gel with a two-solvent system, benzene and diethyl ether. Preliminary analyses indicate that the benzene- and diethyl ether-eluted materials differ in several properties related to composition and structure. In all three of the crude asphaltenes studied so far, the % nitrogen is substantially higher in the diethyl ether eluted fraction (Table I).

The observation that nitrogen-containing species are absorbed more strongly than species with less nitrogen is consistent with the acidic nature of silica gel, and the expectation that silica gel would preferentially absorb basic molecules. These findings are in agreement with observations of Sternberg et. al (1) who were able to precipitate a basic component from a solution of Synthoil asphaltenes dissolved in toluene by passing dry HCl gas through the solution.

Work Forecast:

Additional crude asphaltene samples will be separated by solvent chromatography on silica gel as they become available. Results will be quantified and suitable analytical and physical property values will be ascertained for major fracitons. Selected crude asphaltene samples will be separated by solvent chromatography on alumina. Major fractions will be examined in order to determine whether meaningful separations can be obtained on alumina.

(3) Separation of Crude Asphaltenes by High Performance Liquid Chromatography Utilizing Gel Permeation Chromatography

Work Accomplished:

Preliminary attempts to separate crude asphaltenes by size have been carried out using gel permeation chromatography with μ-Styrogel columns. High performance liquid chromatography was carried out using a Waters L.C. system comprised of the following equipment:

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

Three μ-Styrogel columns (two 100 Å and one 500 Å, 7 mm ID x 30 cm length, ≈3000 plates each) were connected in series. Uninhibited THF* was used as solvent.

Samples were prepared as 2% solutions in THF which had been degased by sonic bath stirring. The samples were filtered across a 0.45 millipore filter, and the flow rate adjusted to 1.0 ml/min.

*THF without inhibitors added.

TABLE V

COLOR INTENSITY, I[a]

Material	FMC-COED (Filtered)	Synthoil (Product Oil)	PAMCO (Filter Feed)
Crude Asphaltene (C.A.)	4.1 ± 0.2	12.7 ± 0.9	14.4 ± 0.1
Benzene Eluted C.A. from Silica Gel	5.1 ± 0.3	12.0 ± 0.1	13.4 ± 0.2
Diethyl Ether Eluted C.A. from Silica Gel	3.5 ± 0.3	8.2 ± 0.2	9.0 ± 0.1
Pentane Soluble (Gas Oil + Resin)	1.0 ± 0.1	0.8 ± 0.1	0.3 ± 0.1
Benzene Insoluble (Carbene + Carboid)	11.2 ± 0.2	27.1 ± 0.6	32.2 ± 0.7

[a]Color Intensity, $I = \int_{400nm}^{750nm} A d\lambda$, $(mm^2 . cm^{-1} . ml/mg) x 10^{-3}$

TABLE VI

NMR H-PERCENTAGES BY PROTON TYPE[a]

	$H_{aromatic}$	H_{benzyl}[b]	H_{sat}[b]
FMC-COED(filtered)			
Crude Asphaltene (C.A.)	42	40	22
Benzene Eluted C.A. from Silica Gel	41	38	21
Diethyl Ether Eluted C.A. from Silica Gel	37	40	23
Pentane Soluble (Gas Oil + Resin)	18	36	46
SYNTHOIL(Product Oil)			
Crude Asphaltene(C.A.)	33	42	25
Benzene Eluted C.A. from Silica Gel	35	42	23
Diethyl Ether Eluted C.A. from Silica Gel	34	41	25
Pentane Soluble (Gas Oil + Resin)	16	33	51
PAMCO(Filter Feed)			
Crude Asphaltene(C.A.)	45	38	17
Benzene Eluted C.A. from Silica Gel	43	35	22
Diethyl Ether Eluted C.A. from Silica Gel	43	33	24
Pentane Soluble (Gas Oil + Resin)	46[c]	32	22

[a]Run on Varian T-60 NMR, Solvent 99.8% $DCCl_3$ + 1% TMS

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

[c]PAMCO Filter Feed contains Dowtherm aromatic-base fluid as received

TABLE VII

AROMATICITY, f_a[a]

MATERIAL	FMC-COED (filtered)	SYNTHOIL (Product oil)	PAMCO (Filter Feed)
Crude Asphaltene (C.A.)	0.5	0.5	0.5
Benzene Eluted C.A. from Silica Gel	0.4	0.4	0.5
Diethyl Ether Eluted C.A. from Silica Gel	0.4	0.4	0.5

[a] $f_a = C_A/C_{total} = A_{002}/A_{002}+A_r$

C_A = number of aromatic carbons

C_{total} = number of total carbons

A_{002} = area under peak for aromatic carbons

A_r = area under peak for saturated carbons

Fig. 2 gives an example of the separation obtainable with this system. Resolution of individual peaks is not possible due to the complexity, and wide molecular weight distribution of the crude asphaltene fraction However, some fractionation of crude asphaltenes by molecular size may be accomplished by arbitrarily cutting narrow fractions. The average molecular weight of such fractions can then be determiend by vapor phase osmometry. Some of these fractions could be further separated by either liquid-solid absorption chromatography or gas chromatography, and individual components identified, where applicable, by comparison with known compounds.

Work Forecast:

Additonal exploratory work will be carried out with a large 20 mm ID column packed with 60 Å Styrogel particles in order to scale up the amount of crude asphaltenes being separated.

Exploratory work will be done with suitable μ-Porasil columns in order to further separate selected crude asphaltene fractions on the basis of group type, polarity and aromaticity.

Characterization of selected components of crude apshaltenes may be attempted by comparison with known standard compounds, and by use of other analytical techniques.

(4) Preliminary Characterization of Coal Liquid Fractions

Work Accomplished:

Coal liquids have been separated by solvent fractionation into three crude fractions: pentane-soluble (gas oil and resin), pentane-insoluble, benzene-soluble (crude asphaltene), and benzene-insoluble (carbene and carboid). The crude asphaltene fractions have been further separated by solvent elution chromatography on silica gel into two major fractions (benzene eluted and diethyl ether eluted). The great majority of these samples were characterized as to Analysis and Molecular Weight (Table II), Metal Analysis (Table III), Color Intensity (Table V, Fig. 3), NMR H-Percentages by Proton Type (Table VI, Fig. 4), Carbon Aromaticity by X-Ray Diffraction (Table VII) (3), and Infrared Spectra (Fig. 5).

Work Forecast:

Additional coal liquid samples will be characterized as above as they are received. Additional fractions such as the resin and carbene fractions will be characterized as above as they become available. Selected fractions will be further characterized as to size by transmittance electron microscopy (TEM) and scanning electron microscopy (SEM).

CONCLUSION

It appears that coal liquids can be separated relatively reproducible into three crude fractions: pentane-soluble (gas oil and resin), pentane-insoluble, benzene-soluble (crude asphaltene), and benzene-insoluble (carbene and carboid) with high material recovery by solvent fractionation. Solvent elution chromatography on silica gel appears to offer a means to further

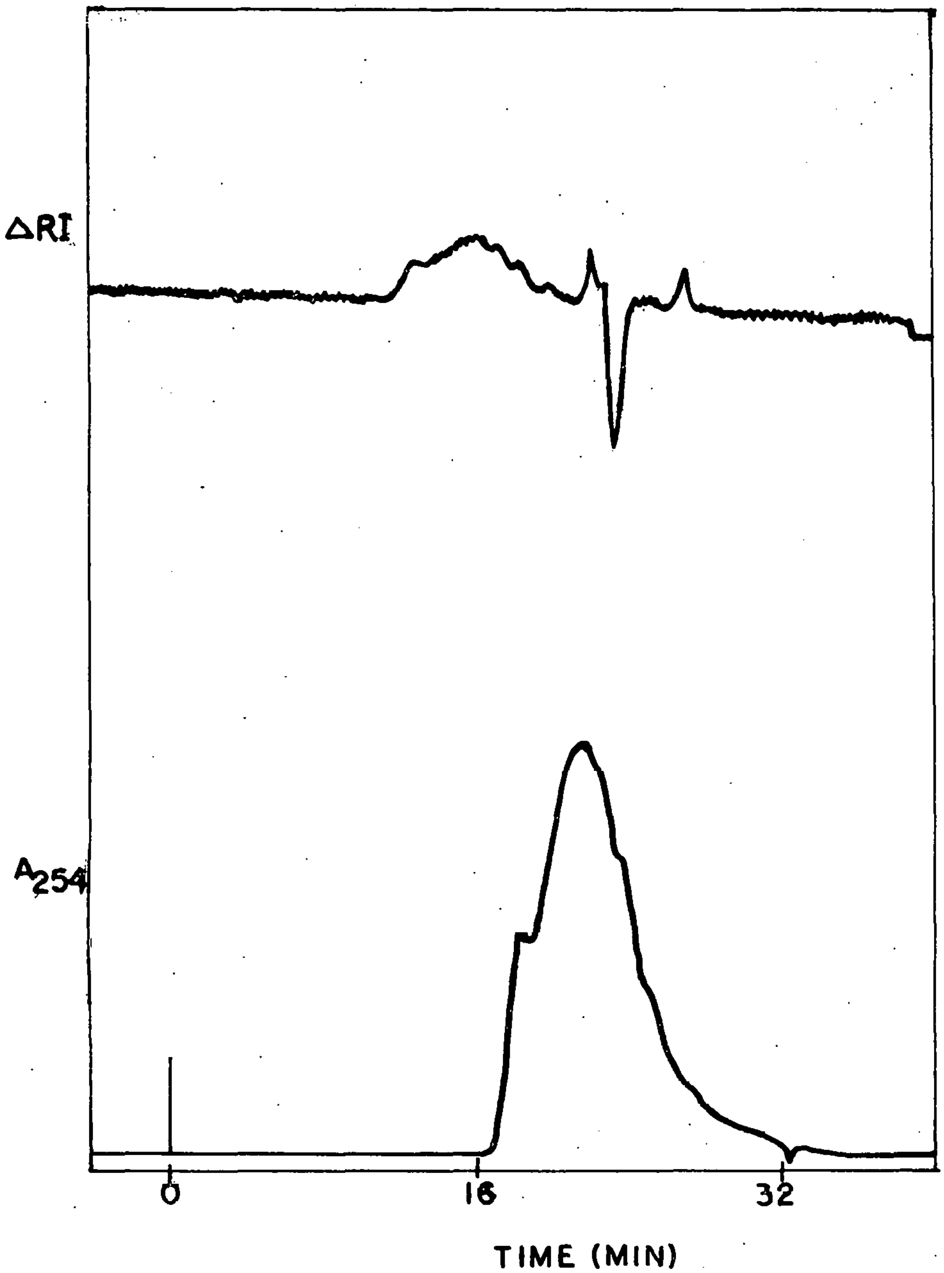

Fig.2 Typical GPC chromatogram. Synthoil Crude Asphaltene.

CONDITIONS
colunms: 60cm-7mm ID 100 Å μStyragel
30cm-7mm ID 500 Å μ Styragel
flow: 1 ml/min ; Solvent: THF

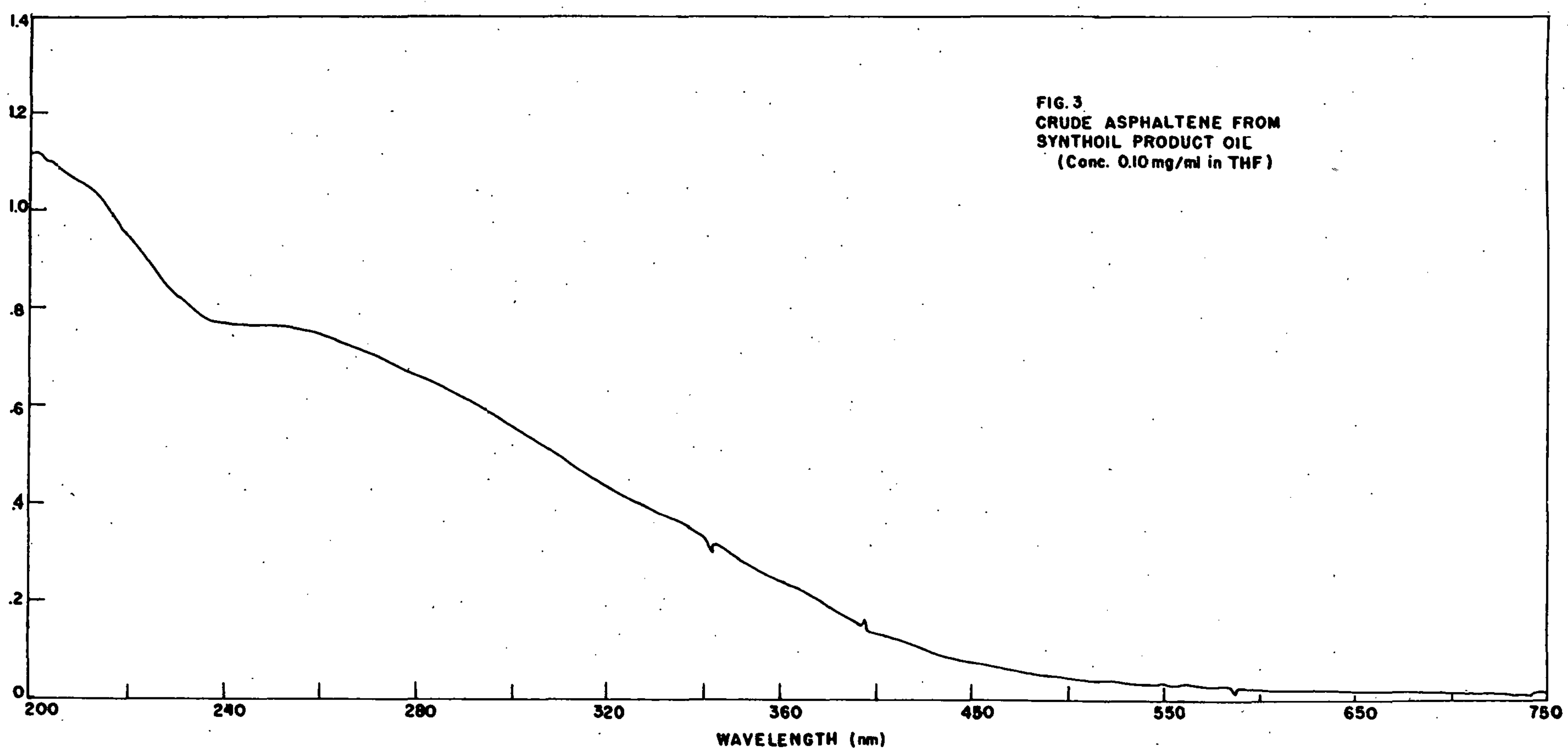
FIG. 3
CRUDE ASPHALTENE FROM
SYNTHOIL PRODUCT OIL
(Conc. 0.10 mg/ml in THF)
ABSORBANCE
1.4
1.2
1.0
.8
.6
.4
.2
0
200
240
280
320
360
450
550
650
750
WAVELENGTH (nm)

15

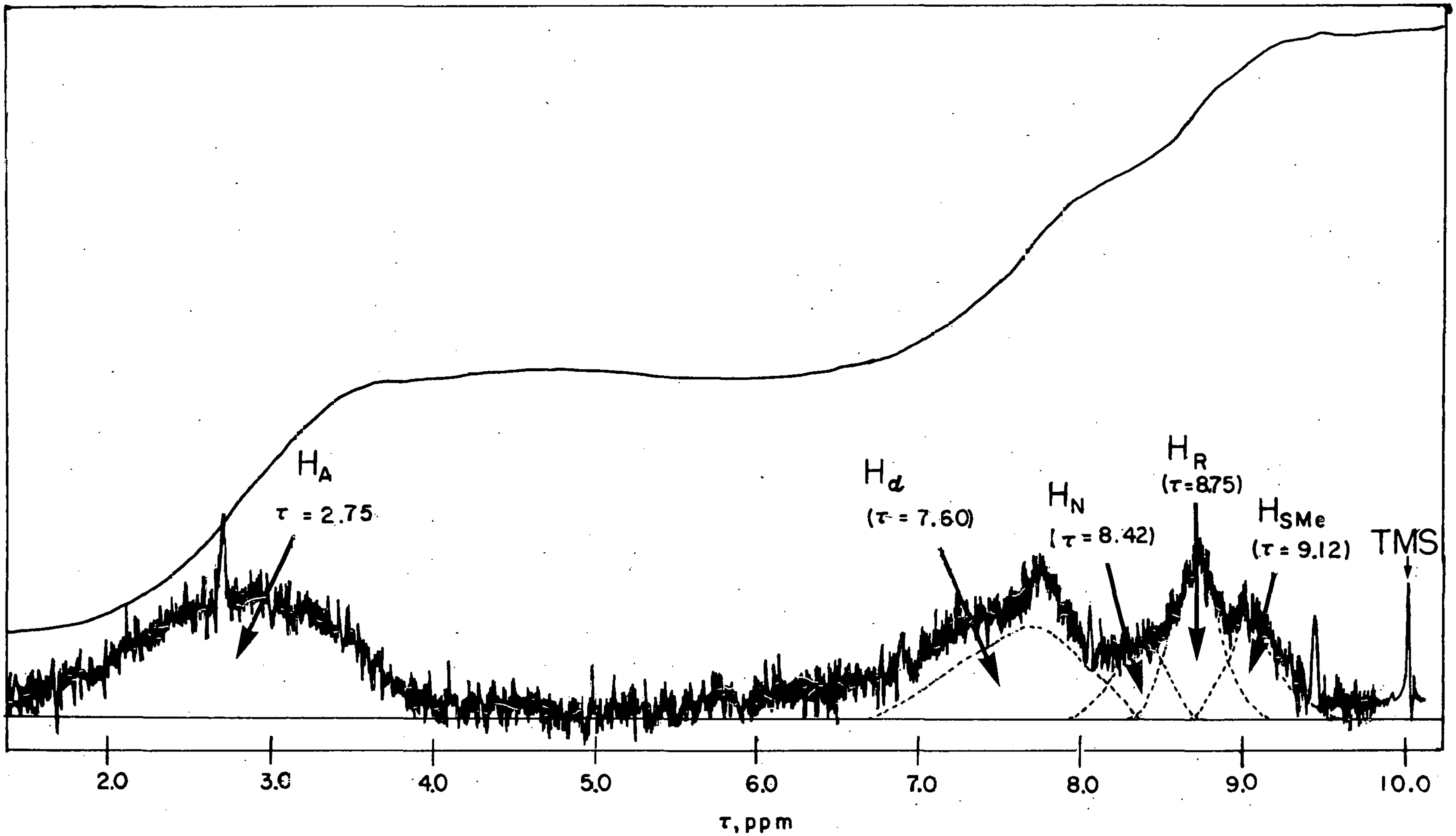

Fig. 4 T-60 Proton NMR Spectrum of PAMCO Diethyl Ether Eluted Asphaltene from Silica Gel, Conc. 0.12/ml

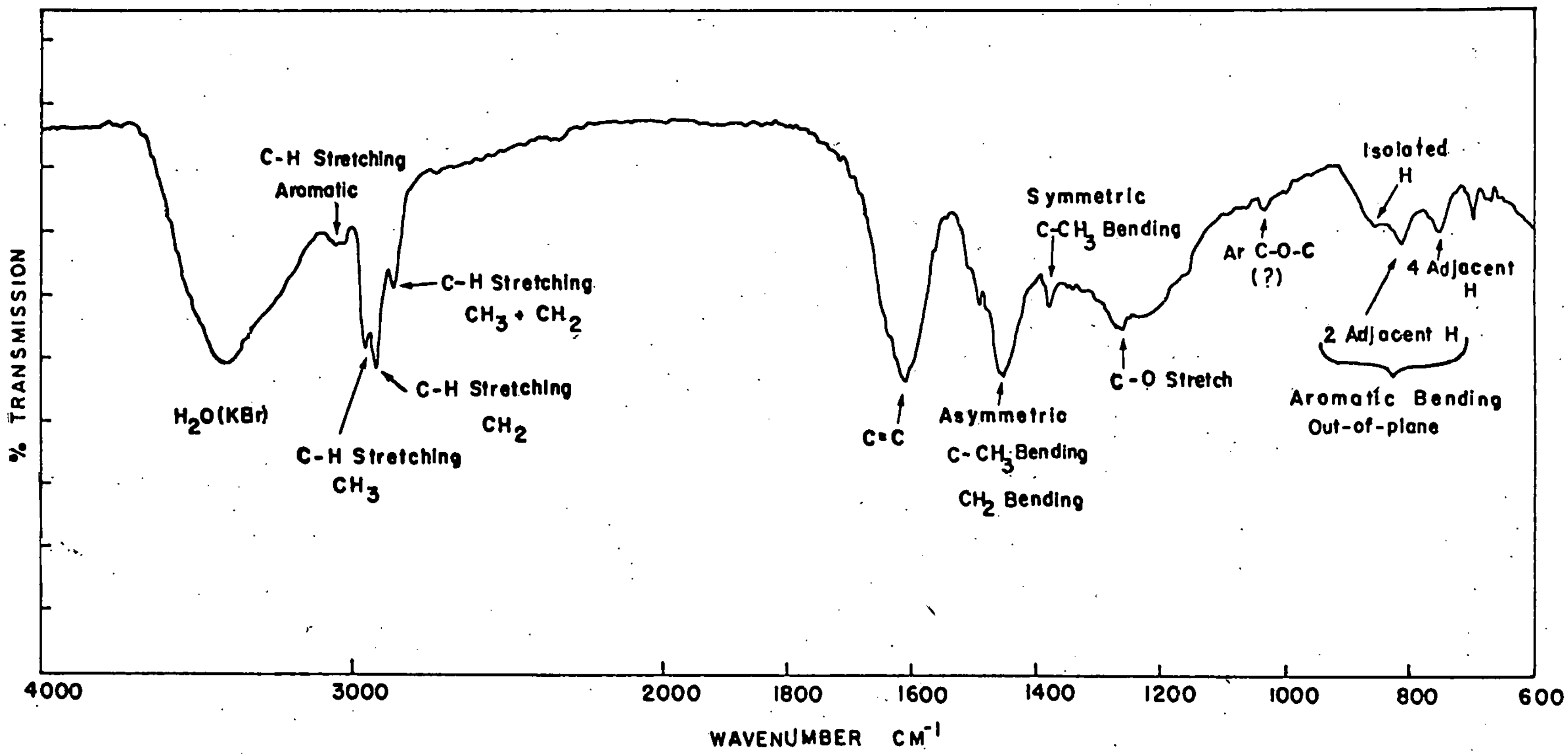

Fig. 5 Typical IR Spectrum. FMC-COED Crude. Asphaltene, KBr Mull

separate crude asphaltenes into acidic and basic components. This method is superior to that of Sternberg (1) because the isolated fractions do not contain chemically bonded chlorine.

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(2) ERDA Report No. FE-2031-1, Sept. 1975.

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