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**CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES
PHASE I**

Quarterly Progress Report
July–September 1975

T. F. Yen

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University of Southern California
Los Angeles, California

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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T. F. Yen

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

PREPARED FOR
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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ABSTRACT

The first phase of a project for the investigation of the chemistry and structure of coal-derived asphaltenes has been initiated. Asphaltenes have been isolated from the products originated from three different coal liquefaction processes. Duffy's procedure has been applied to these crude asphaltenes to remove the contaminated resin. Updated results indicate that the asphaltene as obtained conventionally from solvent fractionation still contains fair amounts of polar resin.

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 are further purified 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 are 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 the understanding of the role of asphaltene in liquefaction process will enable improvement in the methodology and recommendations for operational changes for the existing and planned liquefaction units in the U.S.

SUMMARY OF PROGRESS TO DATE

The final contract of this project was signed by ERDA's officer on June 30, 1975, hence the starting date of this project has been delayed to July 15, 1975. Nevertheless, a few important tasks of Phase I have been completed during this quarter. As depicted by the milestone chart in Fig. 1, the following tasks have been undertaken:

- (1) Acquisition of coal liquids.
- (2) Training of research associate, research fellows and research assistants.
- (3) Isolation of asphaltenes by standard method.
- (4) Establishment of Duffy's procedure on asphaltene purification.
- (5) Data bank of asphaltenes.

Detailed discussion and projection for the next quarter is included in the next section.

Fig. 1. Milestone Chart

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

(1) Acquisition of Coal Liquids

Work Accomplished:

Representative samples of liquid products from major coal liquefaction projects in the U.S. have been requested. These coal liquid samples as indicated in Table I, represent generic categories of all the major processes.

TABLE I
Coal liquids to be Studied

<u>Generic categories</u>	<u>Process</u>	<u>Sources</u>
Pyrolysis	COED	FMC
Solvent refining	SRG	PAMCO
	"	Southern Service
Catalytic hydrogenation		
Hydrofining	H-Coal	HRI
"	Synthoil	USBM
Alkali metal H_2 or CO/H_2	$CO-NaHCO_3$	MSU
Molten halides	CONSOL	CONOCO
Fischer-Tropsch		
Misc.		
Disproportionation		
Reduction alkylation		

Samples of coal liquids shall include but not be restricted to those from the following processes: COED, Synthoil, H-Coal, CONSOL and SRC (PAMCO and Southern Service). At present we have obtained the following coal liquids: Synthoil (1 gal.), COED (10 gal. or filtered Western Kentucky oil and 10 gal. of Syncrude derived from that oil) and a sample of Alkali Metal ($CO-NaHCO_3$) process. Ten gallons of coal liquid is ample for the purpose of isolation of asphaltene fractions. The contacts were made from the person whose name is listed in Table II.

TABLE II
Sample Acquisition

<u>Sample Sources</u>	<u>Contacts</u>
COED	Frank Schoemann
Synthoil	Sayeed Akhtar

TABLE II
(continued)

H-Coal	William Volk
CONSOL	Everette Gorin
PAMCO	Harold Fisher
Southern Service	Zy Taylor

Work Forecast:

It is anticipated shortly that the remaining samples will be collected for the use of this project.

(2) Training of Research Associate, Research Fellow and Research Assistants

Work Accomplished:

Most of the research associates and students the P.I. work with are much experienced in oil shale or bioengineering areas. It will take quite some time to orient them toward the coal field. In order to accomplish this, every Friday during our regular weekly meeting, we scheduled lectures in the coal chemistry area. Occasionally we have had visitors invited to give lectures in the coal field. The P.I. has launched a series of discussions on the asphaltene characterizations for this quarter and the upcoming quarters.

Dr. Moshen Moussavi, a research associate with the P.I., trained in chemical engineering and environmental engineering, is leaving us (end of July) to accept a teaching position in Iran. Dr. John Findley, a microbiologist, will not be involved in this project. At the present time, we are attempting to hire a research associate, either in the field of synthetic organic chemistry or analytical chemistry.

Two graduate students, David Young and Jonathon Kwan, are gradually being trained to shift their interest from shales to coals. During this transition period David Young was given a problem concerning the structural investigation of liquite by oxidative degradation. Jonathan Kwan was assigned to use x-ray diffraction as a means for obtaining aromaticity. These are the first steps in implementing the stage for the full assault on the structural elucidation of coal asphaltenes. Both projects are

proceeding well.

During this quarter, two research assistants, Raymond Leung and Sam Louie, were assigned to work on the isolation of asphaltene from coal liquids under the close guidance of the P.I.

Work Forecast:

Beginning in September, Dr. Yu-Ping Hsia, Associate Professor of Chemistry from California State Polytechnic University at Pomona, will visit this group during his sabbatical year. His interest is in coal liquefaction. Since his experience is in theoretical chemistry he will be involved in our effort in the modeling of liquefaction process.

Also during the next quarter, Dr. W.K.T. Gleim, former associate director of research at UOP, will join us as a senior research associate. Dr. Gleim has extensive knowledge and experience in catalysis and refining of heavy asphaltic oil as well as coal liquids. He has more than 100 publications in this field alone. His help will be invaluable to this project.

(3) Isolation of Asphaltene by Standard Method

Work Accomplished:

The traditional method for isolation of asphaltene from heavy oil was applied to coal liquids. The asphaltene is defined as a solvent fraction which is soluble in benzene and insoluble in n-pentane. The conventional definitions of some of the asphaltic fractions are as follows:

- (a) gas oil - propane-soluble fraction of a topped resid.
- (b) resin-propane-insoluble and n-pentane-soluble fraction.
- (c) asphaltene - n-pentane-insoluble fraction.
- (d) maltene - the combined resin and asphaltene fractions.
- (e) carbene - benzene-insoluble and carbon disulfide-soluble fraction.
- (f) carboid - carbon disulfide-insoluble fraction.
- (g) polar resin - the fraction of resin which can be dissolved by polar solvents.
- (h) neutral resin - the fraction of resin which can be dissolved by non-polar solvents.

The interrelations of the different asphaltic fractions can be demonstrated by the chart below (Fig. 2). In this sense, the line between fuel oil and coke is only arbitrary.

Figure 2. Interrelations of Different Asphaltic Fractions

Our methodology is such that the asphaltene isolated from coal liquids still contains an appreciable amount of resin or carbene. Therefore, this cut of asphaltene as isolated from the traditional method still can be called "crude". A purification step such as Duffy's method is required.

The sequence of the solvent separation procedures can be illustrated by the graph shown in Fig. 3. The solubility parameters form the basis for the solvent fractionation.

The general procedure used for isolating asphaltene is as follows:

Ca. 420g. of Synthoil (Western Kentucky, Code No. AmA 103) was dissolved in 500 ml. of hot benzene. This solution was slowly added to a large volume of n-pentane (1.5 gal.) with stirring. The precipitate was washed with fresh n-pentane and loaded in Soxhlet thimbles for continuous extraction by n-pentane. Extraction was continued until no color was indicated by the out flowing extract. The solid was vacuum dried overnight. This solid was redissolved in benzene, filtered and freeze-dried. The solid yields 90 g. corresponding to 20%.

Elementary analysis of the various asphaltenes isolated thus far having this result is shown in Table III.

TABLE III
Elemental Analysis of Some Crude Asphaltene

<u>Coal liquid</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%S</u>	<u>% Ash</u>	<u>H/C ratio</u>
Synthoil	72.34	6.66	1.08	3.43	9.58	1.104
HCO ₃ ⁻ /CO	80.32	6.48	1.03	0.86	2.22	0.968
COED	78.31	6.26	1.37	1.75	2.46	0.959

FIGURE 3

TABLE III

Elemental Analysis of Some Crude Asphaltenes

<u>Coal liquid</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%S</u>	<u>% Ash</u>	<u>H/C ratio</u>
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COED	78.31	6.26	1.37	1.75	2.46	0.959

Work Forecast:

We are also recovering the resin and the gas oil fractions. Also, in the meantime, we are proceeding to prepare a large amount of crude asphaltene.

(4) Establishment of Duffy's Procedure on Asphaltene PurificationWork Accomplished:

As indicated in the last section, the asphaltene thus obtained is not "pure" and is still contaminated with resin or carbene fractions. A more efficient method for separation is to employ a better surface for the spreading of asphaltic component. Even in benzene the asphaltene is not a true solution, but appears to be full of suspended particles. The surface substrate selected will be able to interact with these particles. The best surface chosen was Teflon powder.

Traditionally this is called Duffy's procedure (1). The configuration of the setup for column chromatography may be slightly different. The basis for separation is polarity. For example, neutral resin can be removed by cyclohexane, polar resin can be removed by dioxide-ether, asphaltene by benzene-chloroform and carbene by pyridine. The classification system is shown in Fig. 4. Again the solubility parameters play an important role.

Since Duffy's procedure was only developed for the petroleum asphaltenes, its application to coal asphaltenes may require modification.

The following example is a case of using a dual column of Teflon and alumina.

FIG. 4 - PROPOSED SCHEME FOR THE PURIFICATION OF COAL ASPHALTENE

Materials for the Separation of Crude Asphaltenes Using Duffy's Procedure

1. Activated alumina (80-325 Mesh), chromatographic grade; AX611; L1174 from Matheson, Coleman and Bell (MCB).
2. Fluropak 80, nonpolar chromatograph solid support from the Fluropak Co., 60-80 Mesh.
3. Standard Ottawa sand, SX70, CB666 from MCB.
4. Chromaflex 20 chromatographic column, 20 mm. (I.D.) x 500 mm. from Kontes Glass Co.
5. Benzene, ethyl ether, chloroform, dioxide, pyridine, cyclohexane.
6. Crude asphaltene sample i.e., Synthoil crude asphaltenes.

From the Synthoil crude asphaltenes, 0.4986 g. was mixed with 0.500 g. of Fluropak 80 and applied to a dual column of equilibrated with cyclohexane. (See Fig. 5 for column dimensions.)

Exhaustive elution of the column with cyclohexane at a rate of 0.39 ml/min yielded no visible color changes of the fractions collected. A total of 400 ml of cyclohexane was used. Evaporation of the cyclohexane left behind a faint yellow ring inside the evaporating flask, though not identifiable as neutral resins by any analytical tool. Most of the original samples were still retained on the top of the Fluropak 80. The alumina was discolored with a faint yellow-brown.

The column was then eluted with ethyl ether-dioxide (50:50 mixture) to separate the polar resins from the asphaltenes. The flow rate achieved was 0.75 ml/min. The top layer of Synthoil asphaltene migrated down the Fluropak 80 and alumina column. The asphaltene fraction was adsorbed to the alumina. A total of 2,136 ml of the 50:50 ethyl ether-dioxane mixture was used to exhaustively elute the column until the fractions were clear. Evaporation of the ethylether-dioxane was accomplished with a rotary evaporator after which the resins were redissolved in benzene and lyophilized to a brown, flaky powder. The yield was 0.2735 g. or 58.9% of the original crude asphaltene.

The next solvent used was a 50:50 mixture of benzene and chloroform to remove the asphaltenes adsorbed on the alumina. The flow rate was 0.45 ml/min. However, after 500 ml of the solvent mixture was used, no asphaltenes were eluted. Pyridine was then used and the asphaltenes were successfully eluted. The flow rate was 0.47 ml/min. A dark brown color persisted in the alumina while the fluropak 80 was white. The column was disassembled and the alumina was then refluxed with benzene in a Soxhlet extractor. The resulting benzene solution was evaporated to a working volume of 20 ml to which the original pyridine fraction was added. Nitrogen gas was then used to evaporate away the solvents at 60°C. The semi-solid was then redissolved in benzene and lyophilized to a dark brown solid. The yield was 0.0848 g. or 17.0% of the original crude asphaltenes.

For the different samples of asphaltene obtained, a simple characterization procedure was applied. The visible absorption spectra of the asphaltenes from 400-800 nm were obtained. A simple parameter, color intensity (2), was then obtained as indicated by the following table (Table IV).

TABLE IV

Color Intensity of Coal Asphaltene

$$I = \int_{400 \text{ nm}}^{800 \text{ nm}} A d\lambda$$

<u>Samples</u>	<u>Values (Arbitrary Unit)</u>
Synthoil	4.470
COED	5,240
CO-NaHCO ₃	5,970
Synthoil Purified	2,580

It is shown that the "purified" Synthoil asphaltene has less color index than the original "crude" asphaltene. Apparently, removal of the polar resin accounts for the decrease in the color intensity.

Work Forecast:

The conditions of Duffy's Separation will be chosen so that adequate separation of neutral resin, polar resin and asphaltene can be made. A standard protocol procedure will be set up.

(5) Data Bank of Asphaltene

Work Accomplished:

The setup of a useful depository or clearing house of asphaltenes is meaningful only if the sample sources are representative and the data are accurate. Toward this goal the P.I. has discussed with a great number of coal experts including: Dr. Bill Spackman of Pennsylvania State University. Additionally, the P.I. has visited a number of liquefaction units. During September, he had the opportunity to visit the coal chemistry projects in both the USSR and Poland on his official exchange fellowship sponsored by the National Academy of Science of U.S. and the Academy of Science of USSR.

The coal laboratory headed by Dr. V.A. Kushinluk in the Institute of Geology and Geochemistry of Combustible Minerals at Lvov, Ukrania is very interesting. They have an extensive collection of world-wide coal samples and their products. The most impressive assembly is that of the Institute of Carbochemistry of the Central Mining Institute at Katowice, Poland. Dr. Bronislaw Malecki, head of the Institute, had shown the P.I. various coal liquids obtained at different stages from the liquefaction plant.

CONCLUSION

Preliminary phase of isolation and separation of asphaltenes from coal liquids has been accomplished. It is rather surprising to find that the "crude" asphaltene separated by the conventional approach still contains the polar resin in extensive quantity. These resin contaminants can be purified through Duffy's procedure. Maybe this is the reason that asphaltene can be separated into acids and bases (3).

As an initial effort for training the student into the coal field, a technical report entitled "Oxidation of Lignite into Water Soluble Organic Acids" by David Young, has been completed. This report will be revised and modified into publication form.

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