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CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES
PHASE I

Quarterly Progress Report
October—December 1975

T. F. Yen

Work Performed Under Contract No. EX-76-C-01-2031

University of Southern California
Los Angeles, California

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

MASTER

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

PREPARED FOR
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

University of Southern California
Los Angeles, California 90007

ABSTRACT

We have developed a method for characterizing coals and coal-derived asphaltenes based on x-ray diffraction. The parameter thus obtained is termed aromaticity, an indicator for the amount of carbon atoms in the skeleton which is being aromatic.

Provisional data indicate fairly large amounts of polar resin are still occluded in the crude asphaltene (separated by conventional pentane precipitation). This resin is more aromatic than the asphaltene from which the occluded resin has been removed. The extent of aromaticity has been estimated by both x-ray and color intensity methods.

SUMMARY OF PROGRESS TO DATE

During this quarter the following tasks have been undertaken:

- (1) Training of research associate, research fellows and research assistants.
- (2) Protocol procedure of solvent elution chromatography of asphaltenes.
- (3) Setup of automated SARA column.
- (4) Characterization of asphaltenes by x-ray diffraction.
- (5) Data Bank of asphaltenes.

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

DETAILED DISCUSSION OF TECHNICAL PROGRESS

(1) Training of Research Associate, Research Fellows and Research Assistants

Work Accomplished:

Beginning September 15, 1975, Dr. Yu-Ping Hsia, Associate Professor of Chemistry from California State Polytechnic University at Pomona, joined our shale-coal group as a research associate. Since during this academic year he was on his sabbatical leave, he would only partially be involved in the coal project. He has begun to investigate the energy and kinetics of coal liquefaction processes. Notably he has computed, for each rank of coal, the percentage of coal which can undergo liquefaction assuming that the same coal is used to provide all the energy required for conversion and all the hydrogen needed for upgrading. A manuscript has been prepared and a report entitled "Liquefaction Efficiency for Various Coal Ranks" completed.

Beginning this quarter, Dr. W.K.T. Gleim joined us as a senior research associate. He has recently been retired from UOP from the position of associate research director. He would only be involved on a part time basis in this project. His extensive experience in developing the UOP's solvent extractive coal liquefaction process would definitely be of value to this project. His more than 100 patents in the field of catalysis, refining and asphaltenes would provide indispensable guidance to the students who were working on the coal project.

Fig. 1. Milestone Chart

During the last quarter, Edith Chow, an honor high school senior of NSF Training Program, spent a summer with our group. She has successfully isolated the asphaltenes from a variety of shale oils with the help from our assistants and technicians. She has also characterized the structure of shale oil asphaltenes by infrared spectrophotometry. This is another example indicating our effort in gradually shifting shale research toward coal research. She has completed a manuscript entitled "Investigation of the Structure of Shale Oil Asphaltenes".

During this quarter, four coal chemists have spent time visiting our laboratory and holding discussions with our students.

Professor H. Hasegawa of the Nihon University, Japan --- Catalysis

Dr. Takashi Miyazu of Nippon Kokan K., Japan --- Coal Asphaltenes and Coke

Dr. H.W. Sternberg of Laurence Livermore Laboratory of University of California, Berkeley (former USBM) --- Coal Asphaltenes

Professor Keith Hall of the University of Wisconsin at Milwaukee --- Catalysis

Work Forecast:

The P.I. has interviewed a number of candidates for research associate in coal chemistry. We believe one of the candidates, Dr. Irving Schwager, who has had experience in asphaltene and separation, would be able to start working in January, 1976.

(2) Protocol Procedure of Solvent Elution Chromatography of Asphaltenes

Work Accomplished:

Dr. Gleim together with his technicians has worked out a set of procedures for the solvent elution chromatography of asphaltenes. The method was used for different types of asphaltenes. Silica gel is being used in this procedure. The detailed information is as follows:

1. Dissolve 3.00 grams (weighed 0.1 mg) of sample in 150 ml of chloroform warmed to 50°C in an evaporating dish.
2. Add 14.0 grams of Fluoropak 80 to the sample solution.
3. Evaporate the chloroform with mild heat under a N₂ blanket to dryness.
4. Transfer the asphaltene-coated Fluoropak to a beaker and redissolve any residue with chloroform.

5. Add 4.0 grams of Fluoropak 80 to the asphaltene in chloroform solution and evaporate to dryness.
6. Transfer the asphaltene-coated Fluoropak to the beaker and redissolve any residue with chloroform.
7. Add 0.5 grams of Fluoropak 80 and evaporate to dryness. Transfer the dry Fluoropak to the beaker containing asphaltene-coated Fluoropak.
8. Attach a stopcock assembly containing a fritted glass plate to a 15 cm X 2.5 cm O.D. column using a Teflon seal and clamp.
9. Add Fluoropak 80 to the column until the top of the Fluoropak layer is 1 cm above the bottom joint of the 15 cm column.
10. Slurry 25 gms of Davis Grade 62 silica gel with n-hexane and transfer the slurry to the 15 cm X 2.5 cm O.D. column.
11. Connect a 25 cm column to the 15 cm column using a Teflon seal and clamp.
12. Add Fluoropak 80 to the joint columns until the top of the Fluoropak 80 layer is 1 cm above the bottom joint of the 25 cm column.
13. Using a powder funnel to quantitatively transfer the asphaltene-coated Fluoropak to the column.
14. Add a 2 cm thick layer of Fluoropak 80 to the top of the asphaltene-coated Fluoropak layer.
15. With the stopcock closed, fill the column with n-hexane until all the Fluoropak layers are saturated with n-hexane.
16. While the n-hexane is saturated, the Fluoropak layer four 150-ml beakers are marked with the sample identification and cut numbers 1 through 4 (cut number 4 is a spare one in case that the beaker breaks during the elutions). Four large boiling chips are weighed to 0.1 mg.

CUT #1 - OILS CUT

17. Elute the column with 800 ml of n-hexane and collect the effluent in a 1000-ml beaker which has been identified as cut #1.
18. After collecting 800 ml of n-hexane effluent, the boiling chips are transferred from the 150-ml beaker marked "Cut #1" to the 1000-ml beaker and the beaker is placed on the steam bath. The n-hexane is allowed to evaporate to 75 ml. The 75 ml of oils in n-hexane and the boiling chips are then transferred to the 150-ml beaker mark "Cut #1".

The beaker is then placed on the steam bath with N_2 purge to be evaporated to dryness. The dry beaker is placed in vacuum oven at $60^\circ C$ for 30 min. After 30 min. the beaker is placed in a desiccator to cool.

19. While the n-hexane is evaporating, separate the column at Teflon joint between the 15-cm silica gel column and the 25-cm asphaltene-coated Fluoropak column.
20. Add a fritted glass plate to a stopcock assembly and attach the assembly to the 25-cm column using a Teflon seal and clamp. Attach a 25-cm column to the 15-cm column using a Teflon seal and clamp.
21. Prepare 1 liter of ether-ethanol solution in a separatory funnel (9 parts ether with 1 part of 95% ethanol and 5% water).
22. Fill the silica gel column with the ether-ethanol solution and elute the yellow-colored oil into a 400 ml beaker. Collect the yellow effluent until the darker brown band reaches the bottom of the silica gel but is not eluted from the column.
23. The yellow color ether-ethanol solution is added to the 1000 ml beaker containing the evaporating n-hexane effluent. If the effluent initially has a brown color, it is added to the Resin Cut #2 (See Step 25).

CUT #2 - RESIN CUT

24. A 1000-ml beaker is marked "Cut #2" and is placed under the silica gel column. The dark colored resins are then collected into the beaker using approximately 250 ml of ether-ethanol solution to elute the resins.
25. While the silica gel column is eluting, the column containing the Fluoropak is placed over the 1000-ml beaker and eluted into the beaker with the ethanol-ether. The Fluoropak column is eluted until the effluent is clear.

However, if the effluent has a golden color, a maximum of 800 ml of Et_2O -EtOH solution should be used. This will require a second 1000-ml beaker to contain the larger volume of solvent.

26. The boiling chips from the 150-ml beaker marked "Cut #2" are transferred to the 1000-ml beaker marked "Resin Cut #2". The 1000-ml beaker is then placed on the steam bath with N_2 purge to be evaporated and dried as described under "Cut #1 - OIL CUT" Step #18.
27. If the silica gel is colorless, it can be discarded after it is dry; otherwise, it is retained for the sample requestor.

CUT #3 - ASPHALTENES CUT

28. The asphaltenes are eluted with chloroform. Initially, 2-propanol is added to the Fluoropak column until its height is 1 cm above the Fluoropak layer. Then the remaining column space is filled with chloroform. The two liquids are mixed with a glass stirring rod. The 2-propanol and chloroform solution is eluted into a 600-ml beaker marked "Cut #3". After the solution is eluted the column is filled with chloroform only to elute the remaining asphaltenes. 350 ml of chloroform is usually required to elute the asphaltenes from the column.
29. The boiling chips are transferred from the 150-ml beaker marked "Cut #3" to the 600-ml asphaltenes beaker. The 600-ml beaker is then placed on the steam bath with N₂ purge to be evaporated and dried as described in Step #18.
30. The Fluoropak is then placed in a beaker and returned to the requestor along with the final oils.

WEIGHINGS

31. The cool 150-ml beakers are removed from the desiccator and weighed to 0.1 mg.
32. The beakers are replaced in the vacuum oven at 60°C for 30 min and re-cooled in a desiccator.

CALCULATIONS

34. The weight percent of oils, resins and asphaltenes are calculated using the following equation:

$$\text{Wt \%} = A/B \times 1000$$

where A = weight of material in cut, and
B = original weight of sample.

The approach as outlined above still requires modifications. We believe the gradient elution is important, i.e., to be able to partition the polar resin into perhaps further fractions.

Work Forecast:

We will devise a modified version of the universal procedure which is applicable to coal asphaltenes.

Figure 2 - A SARA column for the separation of coal asphaltene I

Figure 3. G E C Separation Schematic
(After Jewell)

(3) Setup of Automated SARA Column

Work Accomplished:

The SARA column (1, 2) was originally intended to separate the asphaltic fractions of heavy oils by both ion-exchange chromatography (IEC) and gradient elution chromatography (GEC). In our case, the SARA column is used for purification purposes. An actual design is illustrated in Fig. 2. We have constructed and tested such a column (the IEC portion). We are now in the process of assembling an automated GEC system which includes a UV-visible spectrophotometer and a fraction collector (Fig. 3).

Work Forecast:

We will complete the automated SARA system so that asphaltenes can be further purified.

(4) Characterization of Asphaltenes by X-Ray Diffraction

Work Accomplished:

We are trying to reactivate the x-ray diffraction method for aromaticity measurement of the asphaltene. The following is a summary of the present progress. In order to obtain meaningful values for asphaltenes, coals and other fuel-related materials are also studied.

Most of the early workers (3-5) focused their attention on scattering at medium and large angles. Scattering patterns obtained by those workers revealed two (or more) diffuse peaks at the positions of the most prominent graphite bands; and the peaks became less diffuse as carbon content of the coal increased. Those observations led most of them to suggest that small graphite ring clusters exist in coal and that coals become more graphite-like as coalification proceeds. Though supported by later work, these deductions were regarded by crystallographers as tentative explanations rather than established facts. Because of the orientation and periodicity of an ideal crystal, the x-ray diffraction pattern is sharp. In a mesomorphic or semicrystalline substance including polymers, carbon blacks, coals, pitches, asphaltites, such intra- and intermolecular order is limited in extent with the result that the x-ray diffraction pattern is diffuse. Suitably interpreted, the area and shape of the bands provide an insight into certain interesting structural features. By using blends of low crystallinity polyethylene and carbon black, it was demonstrated that the aromaticity can be determined semiquantitatively by the x-ray diffraction method (6, 7).

(a) Procedure

The General Electric XRD-6 X-ray Diffractometer was used with copper as x-ray target, and settings on 35 kv and 18 ma for all the data run. Samples were grounded to a 200 mesh size. An aluminum sample holder was especially made. The chart recorder was calibrated to read out exact counts per second from the proportional counter.

The data on the recorder must be corrected for polarization effects, normalized to electron units, corrected for incoherent scattering, and examined for the effects of background radiation.

A. Correction for Polarization

The theoretical calculation of the diffracted intensity rests on the assumption that there is a single polarized incident wave. An actual beam, on the other hand, is not uniquely polarized as a whole, but consists of waves with all possible directions of polarization within a plane perpendicular to the propagation direction.

To develop a correction for the effects of polarization, one should confine oneself to the case of a rotating sample and detector with the following geometry shown in Fig. 4.

The intensity of the incoming radiation is constant for all angles 2θ . The intensity of the radiation perpendicular to the plane of the paper is also constant. The amplitude of that part of the incoming radiation that is in the plane of the paper appears to the detector to be reduced by the factor $\cos 2\theta$ before it gets to the sample. Let the intensity of the incoming wave be I_0 so that the amplitudes of the x and y components are $I_0/\sqrt{2}$. The amplitudes of the x and y components as seen by the detector are $I_0/\sqrt{2}$ and $I_0/\sqrt{2} \cos 2\theta$; so the incoming intensity as seen by the detector is $(I_0/\sqrt{2})^2 + (I_0/\sqrt{2} \cos 2\theta)^2$. In order to have an intensity independent of this effect we must, therefore, divide each measured intensity by the polarization factor $(1 + \cos^2 2\theta)/2$.

B. Electron Unit Normalization

When x-rays strike an electron, scattered x-rays of the same wavelength are produced. Such Thomson (coherent) scattering; i.e., scattering with no change in wavelength, gives rise to interference. The coherent scattering is computed in the literature (8, 9). It also emits radiation whose phase and frequency are independent of those of the incoming radiation called Compton (incoherent) scattering, which does not give rise to interference. In the case where x-rays of wavelength λ give rise to Compton scattering of wavelength λ' ; we may put $\lambda' = \lambda + \delta\lambda$, where $\delta\lambda$ corresponds to the increase in wavelength of the center of the Compton spectrum. Where $\delta\lambda$ is small we have:

$$\delta\lambda = 2h/mc \sin^2 \theta = 0.024 (1 - \cos 2\theta)$$

The value of $\delta\lambda$ is in fact very small, and the intensity is only a few percent of that of the Thomson scattering (8, 9). Compton scattering does not cause diffraction, but is observed as a weak background scattering over the whole angular range. We shall now inspect two basically similar approaches for using tabulated values of the incoherent scattering c and the coherent scattering E to normalize the observed intensity to electron units.

If we had data out to very large values of 2θ , we would have no problem. We could look at intensities at angles so large that the corresponding interatomic spacings were much smaller than the separation between the nearest atoms. When we use long wavelength radiation like the typical CuK we do not get data at large enough angles for this. There is historical basis (11, 6) for interpreting data as follows: One recognizes that some

Fig. 4. X-Ray Diffraction Arrangement

published data taken with shorter wavelength radiation (12) show that the ratio of the sum of intensities in the region $.08 \leq \sin\lambda \leq .34$ is proportional to the sum in the region $0.56 \leq \sin\lambda \leq 0.90$ where the corresponding interatomic spacings are so small that no interference effects are possible (this is based on data taken on some carbon blacks). With a little faith, one can assume that the relationship holds for other structures and can use the accessible range to normalize the data.

C. Balance Filter for Monochromatic X-Ray

A further correction of the data can be made by being very careful in eliminating radiation of the wrong wavelength. Modern x-ray diffractometers use radiation produced by bombarding a target with electrons and then filtering the radiation produced through a material that absorbs almost all wavelengths longer than the wavelength desired. When radiation from a CuK transistor is passed through a nickel filter, almost all the radiation at wavelengths above that characteristic of the K_α transition is absorbed in the filter. By utilizing balance filter, the exclusion of wavelengths outside the pass band can be made practically complete. It was concluded that most satisfactory balance of nickel and cobalt occurs at thickness of 0.0068 and 0.0075 mm respectively. The standard method involves taking data with CuK radiation through a Ni filter and then repeating the experiment with a Co filter and using the difference.

In summary, a usable procedure for handling the data is the following:

- (1) Obtain data values from the difference between Ni and Co filter experiment.
- (2) Adjust data for polarization by dividing each intensity by $(1 + \cos^2 2\theta)/2$.
- (3) Adjust the data to electron units by normalizing the amplitudes so that the sum of the amplitudes in the region $0.40 \leq \sin\theta/\lambda \leq 0.50$ is equal to the sum of the coherent and incoherent scattering expected in that range.
- (4) Subtract tabulated values of incoherent scatterings c .
- (5) Divide each value by the proper value of the independent coherent scattering E .

A computer program was written to do all the above steps and have the results plotted on paper (Figs. 5-8).

(b) Interpretation of Results

interpretation of the x-ray diffraction results from noncrystalline carbon compounds is based largely on the fact that model compounds such as graphite (carbon black) and paraffin or polyethylene can obtain an x-ray pattern (6). The reduced intensity values in the region $\sin\theta/\lambda < 0.2$ represent the data which are most precise and least subject to errors in calibration. This region of the x-ray spectrum has not been investigated enough theoretically (13), and hence the interpretation involves superposition of

diffraction spectra from substances supposedly understood. In the development of quantitative methods, some assumptions concerning carbon atoms were regarded as either belonging to aromatic ring clusters or randomly distributed; the ring clusters were presumed to be perfect in their internal structure; and, except for a tendency of neighboring planar units aligning parallel, the planes were believed to be randomly distributed in space. These assumptions appear to be only partially true, for it has not been possible to fit the observed intensity curves with those calculated over a wide angular range. Now we have to define the two peaks in the range of $\sin\theta/\lambda = 0.2$, namely, the (002) peak and the gamma peak.

A. The (002) Peak

The (002) band is attributed to the interplanar spacing of condensed aromatic rings. In natural graphite, the spacing corresponds to the (002) band is 3.35 Å, which corresponds to $\sin\theta/\lambda = 0.15$. Different compounds will have different interplanar spacings as shown in Fig. 9. The shifts observed in the (002) band in some compounds are shifts toward larger spacings and are attributed to actual change in interatomic spacing or to buckling of planes due to substitution of heteroatoms.

Blayden et al. (15) studied carbonization products of various coals and their banded constituents and of some pure organic compounds. They contended that the asymmetry of (002) peak is due to the gamma peak even when a peak at its position was absent. Therefore, the peak was resolved into symmetrical (002) band and a gamma band. The method of plotting was entirely arbitrary and no valid conclusions can be drawn for the symmetry of the (002) peaks in the curves.

B. The Gamma Band

The band centered around spacing of 4.0 to 5.5 Å is observed in melted paraffin. It is attributed to the spacing between disordered aliphatic chains or alicyclic rings. There seems to be no published criterion for distinguishing between saturated rings and saturated chains based on the shape of the gamma band. The gamma band has been found to be symmetric (6); this becomes a very important point when one separates the gamma band from the (002) aromatic band by arguments that defend this symmetry. Aromaticity, f_a , is the fraction of the total carbon atoms in the sample present in aromatic rings (Fig. 10). If A_γ and $A_{(002)}$ are the area under the gamma and (002) peaks, the aromaticity is taken (7) to be:

$$f_a = A_{(002)} / (A_{(002)} + A_\gamma)$$

Implicit in this equation is the assumption that the area under the peaks is proportional to the concentration of each type structure and that the fraction of layers stacked is constant. The first assumption is based on runs made on 35 noncrystalline compounds in 1950 (14) and the second on the observation that the shape of the (002) band does not change much. The most convincing evidence for the usefulness of this computed aromaticity is from the experiment (6), in which a mixture of half polyethylene and half carbon black was shown to have an aromaticity of about 1/2 (Table I).

SAMPLE NUMBER= 72.200

ELU=0.006003

SUM=75803.3125

DATA IN	P	CAL	C	E	REDUCE INT	SIN
3800.0000	1.0100	3837.9971	0.3300	33.7000	0.6739	0.0460
3250.0000	1.0150	3298.7478	0.4500	32.6500	0.5927	0.0570
3000.0000	1.0220	3065.9980	0.5800	31.4200	0.5673	0.0680
2800.0000	1.0310	2886.7976	0.7400	30.0000	0.5530	0.0790
2700.0000	1.0390	2805.2986	0.9200	28.5000	0.5586	0.0900
2650.0000	1.0440	2766.5991	1.0000	27.8000	0.5615	0.0950
2650.0000	1.0500	2782.4978	1.0800	27.0000	0.5787	0.1010
2900.0000	1.0670	3094.2983	1.2800	25.2500	0.6850	0.1130
3400.0000	1.0760	3658.3975	1.4500	23.7000	0.8655	0.1240
3750.0000	1.0820	4057.4990	1.5300	22.8000	1.0012	0.1290
4150.0000	1.0900	4523.4961	1.6200	22.0000	1.1607	0.1350
4560.0000	1.0980	5006.8750	1.6900	21.2500	1.3349	0.1400
4650.0000	1.1020	5124.2930	1.7400	20.8000	1.3953	0.1430
4600.0000	1.1060	5087.5977	1.7800	20.4000	1.4099	0.1460
4000.0000	1.1150	4459.9961	1.8500	19.7500	1.2620	0.1510
3250.0000	1.1240	3652.9985	1.9400	18.8500	1.0605	0.1570
1900.0000	1.1430	2171.6992	2.0800	17.3500	0.6315	0.1680
1450.0000	1.1640	1687.7993	2.2300	15.9000	0.4970	0.1790
1170.0000	1.2090	1414.5295	2.0500	13.3500	0.4825	0.2000
1180.0000	1.2350	1457.2996	2.6300	12.1500	0.5036	0.2110
1250.0000	1.2600	1574.9990	2.7700	11.1500	0.5995	0.2220
1350.0000	1.2740	1719.8989	2.8300	10.6500	0.7037	0.2270
1550.0000	1.2880	1996.3987	2.8800	10.1500	0.8970	0.2320
1640.0000	1.3040	2138.5998	2.9500	9.7500	1.0142	0.2370
1600.0000	1.3170	2107.1990	3.0200	9.3000	1.0355	0.2430
1530.0000	1.3340	2041.0193	3.0600	8.8500	1.0387	0.2480
1400.0000	1.3500	1889.9990	3.1100	8.5000	0.9689	0.2540
1250.0000	1.3820	1727.4998	3.1900	7.8500	0.9147	0.2640
1120.0000	1.4160	1585.9192	3.2700	7.3500	0.8504	0.2740
1050.0000	1.4500	1522.4998	3.3600	6.8500	0.8438	0.2840
900.0000	1.5250	1372.4995	3.5000	6.1000	0.7769	0.3040
770.0000	1.6000	1231.9995	3.6500	5.3500	0.7002	0.3240
690.0000	1.6580	1144.0198	3.7500	4.9000	0.6363	0.3390
680.0000	1.6780	1141.0396	3.7700	4.7500	0.6484	0.3440
600.0000	1.7540	1052.3997	3.9000	4.2500	0.5689	0.3630
600.0000	1.8260	1095.5994	4.0100	3.9000	0.6582	0.3810
620.0000	1.8590	1152.5793	4.0700	3.7500	0.7598	0.3900
650.0000	1.8900	1228.4995	4.1200	3.7000	0.8797	0.3990
750.0000	1.9160	1436.9995	4.1600	3.5500	1.2582	0.4080
750.0000	1.9300	1447.4995	4.1800	3.5300	1.2775	0.4120
740.0000	1.9420	1437.0793	4.2000	3.4700	1.2758	0.4170
720.0000	1.9520	1405.4397	4.2200	3.4200	1.2331	0.4210
700.0000	1.9620	1373.3999	4.2300	3.3700	1.1913	0.4250
660.0000	1.9800	1306.7996	4.2700	3.2700	1.0933	0.4340
620.0000	1.9910	1234.4194	4.2900	3.2500	0.9601	0.4420
550.0000	2.0000	1100.0000	4.3400	3.0300	0.7470	0.4580
550.0000	1.9910	1095.0496	4.3800	2.9100	0.7539	0.4740
540.0000	1.9620	1059.4797	4.4300	2.8200	0.6845	0.4890
540.0000	1.9420	1048.6797	4.4500	2.7300	0.6760	0.4970

Data printout

Fig. 5

Fig. 6

Anthracite

$$f_a = 0.9$$

Fig. 7

Synthoil Asphaltene

$$f_a = 0.5$$

Fig. 8

Synthoil Polar Resin

$$f_a = 0.6$$

INTERLAYER DISTANCES

Fig. 9

FIG. 10 AROMATICITY, F_A

$$F_A = \frac{C_A}{C_{A_{002}}} = \frac{C_A}{C_A + C_S} = \frac{A_{002}}{A_{002} + A_\gamma}$$

C_i = NO. OF i TH TYPE CARBON
 ATOMS PER STRUCTURAL UNIT
 $i = A$, AROMATIC
 $i = S$, SATURATED

A_i = INTEGRATED INTENSITIES
 UNDER THE i TH TYPE BONDS
 $i = 002$, BANDS AT $2\theta = 26^\circ$
 $i = \gamma$, BANDS AT $2\theta = 18^\circ$

TABLE I.

MAKE-UP COMPOSITION OF POLYETHYLENE-CARBON BLACK BLENDS

	1:1 MIXTURE BY WEIGHT 1.17	1:1 MIXTURE BASED ON CARBON CONTENT 1.00
C_A/C_S		
$\frac{A_{002}}{A}$	0.93	0.76
F_A	0.54	0.50
$\frac{A_{002}}{A + A_{002}}$	0.48	0.43

(c) Data and Results

Several samples in coal, coal asphalt, oil shale and oil shale asphaltene were under investigation. The intensity for a corresponding angle 2θ is read out from the chart paper and input to the IBM 360. The output of reduced intensity is printed and plotted against $\sin\theta/\lambda$. The (002) and gamma peak is then resolved. The calculated aromaticity f_a is shown in Table II.

Table II. Aromaticity Values of Various Coal and Coal-Related Substances

Coal	f_a
Anthracite	0.86
Low volatile bituminous coal	0.83
High volatile bituminous coal	0.58
Oil Shale	
Torbanite	0.13
Green River kerogen	0.15
Appalachian Shale kerogen (LiAlH_4 treated)	0.5
Coal Asphaltene (crude)	
Synthoil	0.62
Montana (alkali process)	0.64
COED (slurry from Kentucky coal)	0.59
Coal Asphaltene (purified)	0.47
Synthoil	0.47
Coal Polar Resin	
Synthoil	0.62
Shale Oil Asphaltene	
Crude asphaltene (upgraded)	0.46
Residual asphaltene (Resid)	0.49

DISCUSSION

The discrepancy of determination of aromaticity may be attributed to a simplifying assumption involved in the above method that carbon atoms in coals or coal derivatives are either in aromatic ring clusters or are distributed randomly, i.e., gas-like scatterers. It appears that there are arrangements of nonaromatic carbons that lead to some diffuse x-ray interference pattern affecting the curves. For example, in the structure of coal, contrary to the classic view that coal is a predominantly aromatic solid, its skeletal carbon arrangement appears to be largely made up of non-aromatic structures. By using sodium hypophalite—a specific agent which clearly differentiates between Sp^2 and Sp^3 carbons—as an oxidation agent for coal, Chakrabarty and Berkowitz had indicated that these structures are modified bridged tricycloalkane systems or polyamantanes (16).

It is very interesting to know that large amounts of the diamond-like bond distances exist. One is the graphite-like 1.41 Å and the other is the diamond-like 1.55 Å. It is a three-dimensional network involving the graphite-like and the diamond-like configurations while that of the so-called amorphous carbons is only an aggregate of graphite layers or graphite crystallites.

Probably the most difficult separation is the resolution of the (002) and the gamma band. As discussed in the paper, the high angle side of the broad peak is used as a guide to delineate the unresolved slopes of the (002) band, and the remaining intensity is attributed to the gamma band. However, in addition to using the high angle side as a guide, it is necessary to determine a peak for the (002) band. This can be done completely randomly or, as has been done in late x-ray work, by fixing a location for the peak. The (002) band peaks have been fixed as $\sin \theta / \lambda = 0.140$ if there is no definite and clear break in the combination (002) and gamma peaks at a different point. If aromaticities were determined completely randomly, the error would be approximately 20%. This point out the fact that aromaticities determined by x-ray may be relative as determined at a particular location. Error may be involved in converting scattering from arbitrary into electron units. Some layers may be separated by a greater distance so that the spacing cannot be regarded as constant. Increase in the spacing for the small stacks would give rise to an enhancement of the low angle side of the (002) band at the expense of the high angle side.

This is a very important consideration as it is extremely difficult to remove the last traces of iron (in pyrite or organic form) from coal or oil shale (especially black shale) samples and the fluorescent radiation produced forms a considerable proportion of the total x-ray scattering. That is why the Appalachian shale kerogen has to be treated with $LiAlH_4$ to remove the pyrite before it can give a good spectrum. A better understanding of the structure of coal, oil shale and development of more valid quantitative interpretation of x-ray scattering intensities are more or less interdependent. Systematic investigation of the structure of those materials by other physical and chemical methods and improvement in the techniques and interpretation of amorphous scattering should be pursued simultaneously.

Work Forecast:

A number of asphaltene model compounds will be synthesized and subjected to the x-ray diffraction experiment.

(5) Asphaltene Bank

Work Accomplished:

The P.I. made a trip to Morgantown Energy Research Center and talked to a number of coal scientists there. He has visited the following technical personnel:

Dr. C. Karr, Jr.
Dr. W. E. Wallace, Jr.
Dr. W. K. Overbey, Jr.

He has also examined the Petrocoal process with Dr. Karr. It is anticipated that there will be certain collaboration between U.S.C. and the Morgantown Energy Research Center.

Work Forecast:

We are requesting for different coal liquid samples under a variety of conditions from a number of coal liquefaction plants.

CONCLUSION

During the quarter we have been able to characterize the asphaltene by x-ray method. It is interesting to note that for Synthoil samples, the asphaltene obtained in the traditional manner has a higher aromaticity value than that of the purified asphaltene. The polar resin fraction also has a higher value of aromaticity. The result up-to-date is in agreement with the observation of both the color intensity (see last quarterly report, Ref.) and the preliminary nuclear magnetic resonance (NMR) studies. The results are tabulated in Table III.

In Table III, aromaticity tends to increase with color intensity, which is consistent with the nature of petroleum asphaltene. Further substantiation of the aromaticity has been demonstrated by the preliminary NMR data using a 220 MHz unit.

It appears that the resin fraction which is occluded in the crude asphaltene is more aromatic than the parent asphaltene. This fact has to be further studied.

Table III. Properties of Synthoil Asphaltenes

Synthoil

Crude asphaltene

$$f_a = 0.62$$

NMR spectra give more
aromatic protons

$$I = 4.47 \times 10^3$$

Purified asphaltene

$$f_a = 0.47$$

NMR spectra give little
aromatic protons

$$I = 2.58 \times 10^3$$

Polar resin

$$f_a = 0.62$$

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