Molecular Weight Distribution of Depolymerized Bruceton Coal

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Bruceton coal was depolymerized by using refluxing phenol and *p*-toluenesulfonic acid. The resulting pyridine extractables had a number-average molecular weight of 400, in agreement with the literature, but consisted primarily of colloidal material and polymers having molecular weights greater than 3000. The colloidal material was removed by using ultracentrifugation and subjected to a second depolymerization. It did react further. The structural implications of these observations are discussed.

Bituminous coals are solid, insoluble, inhomogeneous mixtures composed chiefly of macromolecular organics.[1] While they have received much attention from chemists, the amount of study they have received is not commensurate with their importance. Because bituminous coals are nearly insoluble in nearly everything, most organic analytical techniques are of little value; they require dissolved molecules. Since coals are noncrystalline, X-ray studies provide little detailed structural information. In this situation, degradation schemes have been used. Vigorous reactions such as oxidation produce small molecules from coal. These molecules can be identified and provide useful insights into the structure of the parent coal.[2] Another pathway is to use the mildest possible degradation conditions in hopes of isolating structural fragments of the parent coal. One of the reactions developed for this purpose, the Heredy–Neuworth depolymerization, is the subject of this paper.

It is widely, though not universally,[3] accepted that bituminous coals consist of largely aromatic "clusters" which are linked together to form macromolecules.[1,4,5] Ether linkages and short methylene chains are thought to be important linkages between the clusters.[1,4,5] Thus any reaction which cleaves the aromatic-methylene carbon–carbon bond should destroy the coal's macromolecular structure and liberate a collection of small molecules, the molecules which are linked together to form the coal macromolecules. A procedure for accomplishing this was devised by Heredy and Neuworth.[6-8]

Heredy and Neuworth showed that methylene-linked aromatics would undergo a facile acid-catalyzed transalkylation reaction with phenol (eq 1). When coals were

$$\mathrm{Ar(CH_2)_nAr' + C_6H_5OH \xrightarrow{H^+} ArH + Ar'H + HOC_6H_4(CH_2)_nC_6H_4OH} \quad (1)$$

heated with phenol–BF_3 mixtures, a soluble "depolymerized coal" was produced. Ouchi and co-workers studied the efficiency of a variety of acid catalysts for this reaction and concluded that the best conditions were *p*-toluenesulfonic acid catalyst used in refluxing phenol.[9] Using the weight increase of the products due to phenol uptake as the criterion, they showed that ca. 20 h was required for complete reaction. A review of the early development of this reaction is available.[10] More recently, a variety of phenols have been used without obtaining large differences in reactivity.[11] Also, a large number of coals of different ranks have been examined, and it is clear that maximum reactivity is achieved with low-rank bituminous and subbituminous coals.[12]

A number of research groups have measured the number-average molecular weight ($\bar{M}_N$) of the products of this depolymerization reaction carried out on a variety of coals under a variety of conditions. Their results are contained in Table I. In all cases, these molecular weights are number-average molecular weights measured by vapor pressure osmometry. Most of the values are quite low, and it has been generally assumed that the depolymerization reaction was proceeding to cleave all of the aromatic methylene bridges and coals were being thoroughly depolymerized. We became interested in the molecular weight distribution of the "molecules" which are linked together to form the coal's macromolecular network. We therefore depolymerized coals by using Ouchi's modification of the Heredy–Neuworth technique and determined the molecular weight distribution of the products. That study is the subject of this paper.

Gel permeation chromatography (GPC) coupled with vapor pressure osmometry (VPO) was used to measure the molecular weight distributions. Gel permeation chromatography gives a separation based on molecular size and shape, not molecular weight. There is always the possibility of adsorption phenomena complicating the separation. For these reasons, if a calibrated GPC column is to be used, the calibrating molecules must be related in shape and absorption characteristics to the unknown mixture.[13] The depolymerized coals have been so poorly characterized that it is impossible to safely choose a set of calibration standards, although a calibration curve derived for some asphaltenes[14] is tempting. Accordingly, we used GPC only for separation. Fractions were collected, and the number-average molecular weight for each fraction was measured by vapor pressure osmometry. While column calibration complications can be avoided by using vapor pressure osmometry, VPO on these complex systems is not straightforward, as will become obvious.

Results

Fractionation of the Depolymerized Coal. Bruceton coal was depolymerized by using the procedure developed by Ouchi.[9] The depolymerized coal was fractionated by both chemical and physical means as outlined in Figure

(1) D. W. van Krevelen, "Coal", Elsevier, New York, N.Y., 1961.
(2) For example, see R. Hayatsu, R. E. Winans, R. G. Scott, L. P. Moore, and M. H. Studier, *ACS Symp. Ser.*, **No. 71** (1978).
(3) S. K. Chakrabartty and N. Berkowitz, *Fuel*, **53**, 240 (1974).
(4) D. D. Whitehurst, *ACS Symp. Ser.*, **No. 71** (1978).
(5) J. W. Larsen and J. Kovac, *ACS Symp. Ser.*, **No. 71** (1978).
(6) L. A. Heredy and M. B. Neuworth, *Fuel*, **41**, 221 (1962).
(7) (a) L. A. Heredy, A. E. Kostyo, and M. B. Neuworth, *Fuel*, **42**, 182 (1963); (b) *ibid.*, **43**, 414 (1964); (c) *ibid.*, **44**, 125 (1965).
(8) L. A. Heredy, A. Y. Kostyo, and M. B. Neuworth, *Adv. Chem. Ser.*, **No. 55**, 493 (1966).
(9) K. Ouchi, K. Imuta, and Y. Yamashita, *Fuel*, **52**, 156 (1973).
(10) J. W. Larsen and E. W. Kuemmerle, *Fuel*, **55**, 162 (1976).
(11) J. Darlage and M. E. Bailey, *Fuel*, **55**, 205 (1976).
(12) R. H. Moore, E. C. Martin, J. L. Cox, and D. C. Elliott, *ACS Symp. Ser.*, **No. 55** (1977).
(13) J. V. Dawkins and M. Hemming, *Polymer*, **16**, 554 (1975).
(14) H. Reerink and J. Lijzenga, *Anal. Chem.*, **47**, 2160 (1975).

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Table I. Phenol-Free Molecular Weight of Depolymerized Coals

coal	C, wt %, daf	alkylation technique	solvent	$\bar{M}_N$	extractability, wt %
W.Va. 1vb[a]	90.6	HNO_3-PhOH/BF_3-Ac_2O	$CHCl_3$	530	14
Clarian hvb[a]	60.0	HNO_3-PhOH/BF_3-Ac_2O	$CHCl_3$	1725	84
Ohio 8 hvAb[a]	80.9	HNO_3-PhOH/BF_3-Ac_2O	$CHCl_3$	645	95
McFarlane hvCb[a]	67.3	HNO_3-PhOH/BF_3-Ac_2O	$CHCl_3$	375	96
Japanese[b]	75.8	PhOH/PTS	pyridine	320	98
	78.0	PhOH/PTS		340	100
	81.7	PhOH/PTS		440	90
	81.9	PhOH/PTS		450	96
	83.1	PhOH/PTS		460	98
	84.6	PhOH/PTS		500	92
	86.2	PhOH/PTS		480	98
	89.6	PhOH/PTS		1100	32
lignite[c]	71	PhOH/BF_3	PhOH	300	21
			PhH-MeOH	300	48
subbituminous[c]	77	PhOH/BF_3	PhOH	350	2
		PhOH/BF_3	PhH-MeOH	290	15
high-volatile[c] vitrain	82	PhOH/BF_3	PhOH	920	13.5
		PhOH/BF_3	PhOH-MeOH	525	25
high-volatile[c] bituminous	85	PhOH/BF_3	PhOH	930	7
		PhOH/BF_3	PhH-MeOH	730	15
high-volatile[c] bituminous	86	PhOH/BF_3	PhOH	750	19
low-volatile[c] bituminous	91	PhOH/BF_3	PhOH	360	5.4

[a] L. J. Darlage, J. P. Widner, and S. S. Block, *Fuel*, **53**, 54 (1974). [b] Reference 11. [c] Reference 7c.

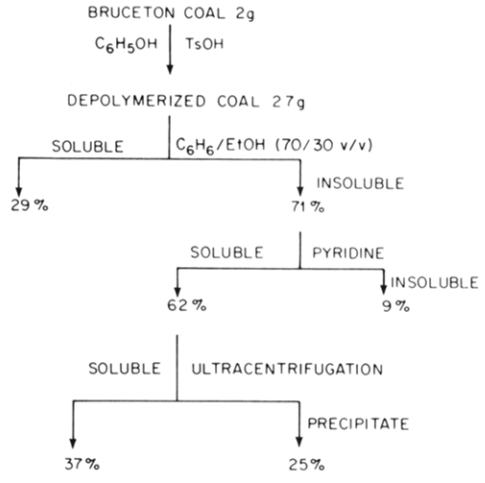

Figure 1. Fractionation of depolymerized Bruceton coal.

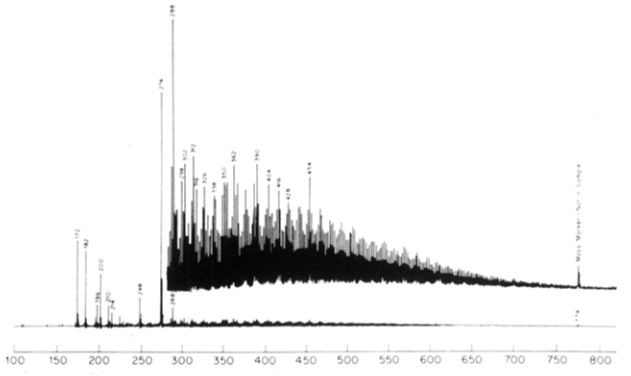

Figure 2. Field ionization mass spectrum of the benzene–ethanol-soluble fraction of depolymerized Bruceton coal.

1. The dried, solid, depolymerized coal was first Soxhlet-extracted with the 70:30 (v/v) benzene–ethanol azeotrope. The solid remaining after this extraction was Soxhlet-extracted with pyridine. All of the material soluble in benzene–ethanol is also soluble in pyridine. In agreement with values of earlier workers, the $\bar{M}_N$ of all of the material extractable into pyridine (i.e., all fractions) was 400 as measured by vapor pressure osmometry.

In preparation for GPC studies, we attempted to filter the pyridine extract through a 0.5-μm Millipore filter. The filter plugged. A glass-fiber fiilter pad designed to pass particles smaller than 7.5 μm removed 8% of the pyridine-extractable material. Clearly the pyridine extract is not a true solution but contains much particulate material of very high molecular weight. This was removed by ultracentrifugation (3 h at ca. 375000*g*. The material remaining dissolved in the pyridine had $\bar{M}_N$ = 1100 by VPO and easily passed a 0.5-μm Millipore filter. Before centrifugation, the evaporation of the pyridine left a solid which would not completely redissolve. After centrifugation, the materials remaining in solution could be dried and redissolved.

Benzene–Ethanol-Soluble Fraction. This material was not separated by mass on μ-Styragel columns. The molecular weight ($\bar{M}_N$) of this solid material was measured by vapor pressure osmometry, first in THF and then in pyridine. The values obtained were 300 in pyridine and 800 in THF. One possible explanation for the higher $\bar{M}_N$ in THF than in pyridine is association in THF but not in pyridine. The most logical type of associative interaction in these phenol-rich systems is hydrogen bonding. Accordingly the trimethylsilyl derivatives of these fractions were prepared and $\bar{M}_N$ was redetermined. The reaction increased the mass of the sample by 29% and the $\bar{M}_N$ in pyridine increased by 30%, from 300 to 400. The increase in $\bar{M}_N$ in THF was much larger, from 800 to 1600. One plausible explanation is that removal of acidic OH groups removes the principle interaction between THF and the solute. The association of the solute then increases since it is now more poorly solvated. The increased association must be due to van der Waals interactions. Finally, this fraction (unsilated) was studied by field ionization mass spectroscopy, and the spectrum obtained is shown in Figure 2. The probe temperature was increased from 60 to 360 °C. Most of the sample apparently consists of a few components having molecular weights between 172 and 288. Superimposed on this is a less intense, broad range of compounds typical of coal-derived materials studied by this technique.[15] This fraction was 67% volatile; presumably some high-mass material is missing from the mass

(15) M. Anbar and G. A. St. John, *Fuel*, **57**, 105 (1978).

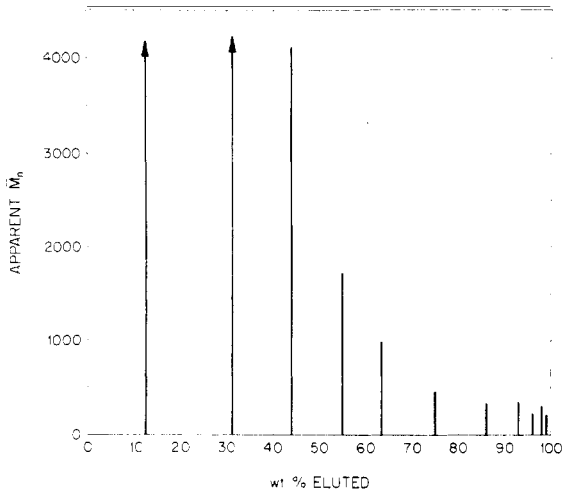

Figure 3. Molecular weight distribution of the total pyridine-soluble fraction of depolymerized Bruceton coal.

spectrum. The $\bar{M}_N$ calculated by using the intense mass spectral peaks is 230. This result will be increased by the many low-intensity peaks at high mass not included in the calculation. The $\bar{M}_N$ values from mass spectroscopy and vapor pressure osmometry in pyridine are in reasonable agreement. It is apparent from the field ionization mass spectrum, which shows only molecular ions, that this fraction consists primarily of about 12 compounds. It is not known whether these derive from the coal or are phenol condensation products. Since it is known that phenol condensation products are produced under our reaction conditions,[16] this is a possible source for the dozen predominant compounds in this fraction.

Pyridine-Soluble Fraction. This fraction was chromatographed on 10^3-, 500-, 100-Å μ-Styragel columns, using pyridine as the eluting solvent. Fractions (1.5 mL each) collected from the column were used for vapor pressure osmometry. Initially, samples for VPO were dried under vacuum at 90 °C. Our concern over the effects of drying led us to carry out VPO measurements on the solutions, as obtained from the chromatograph, without drying. Concentrations were measured by evaporating the solvent to dryness after completing the VPO studies. Results were the same with both techniques. About 80% of this material had $\bar{M}_N$ greater than 2500. In Figure 3 the molecular weight distribution of all of the pyridine-soluble material from depolymerized Bruceton coal is shown. This fraction includes both the benzene–ethanol- and pyridine-soluble fractions.

Solids Removed by Centrifugation. Our chief question regarding these solids was whether or not they were an inert fraction of the coal. Accordingly, they were depolymerized by using the same reaction conditions as were applied to the original coal except for an increase in reaction time from 24 to 43 h. There was an appreciable weight increase, 23%. The product was fractionated as before; the results are shown in Figure 4.

Vapor Pressure Osmometric Measurements. Vapor pressure osmometry has become the standard technique for measuring the molecular weights of coal-derived materials. Very often, experimental details are omitted. Frequently, molecular weights based on one or two measurements are presented. This technique is not very precise, and use of one or two measurements can lead to misleading results. Accordingly, we shall provide some

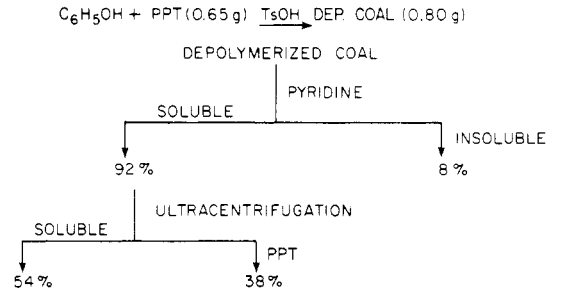

Figure 4. Depolymerization of the precipitate from the ultracentrifugation of the pyridine extractables.

Table II. Equations for the Least-Squares Line Obtained from VPO Studies of the Pyridine Solubles from Depolymerized Bruceton Coal

$$\frac{\Delta R}{C} = \frac{K}{\bar{M}_n} + \frac{K\Gamma_2 C}{\bar{M}_n}$$

fraction no.	$10^3 K\Gamma_2 C/\bar{M}_n$	$K/\bar{M}_n$
2	10	0.48 ± 0.63
3	5	0.41 ± 0.27
4	11	0.78 ± 0.20
5	36	1.9 ± 0.3
6	0.87	3.31 ± 0.3
7	171	7.3 ± 0.8
8	120	10.4 ± 0.44
9	29	9.8 ± 0.4
10	440	14.2 ± 1.8
11	550	11.7 ± 0.5
12	580	9.9 ± 1.8
benzyl	0	3260 ± 50

detail about the way in which we treated our data and show that making measurements at a series of concentrations is *necessary* for reliable results. An excellent description of this technique and some of its pitfalls is contained in Billingham's book.[17]

In vapor pressure osmometry, one measures the temperature difference between two thermistors, one immersed in pure solvent and the other in solvent containing the solute. The system is not at equilibrium. The measured temperature difference (ΔR) can be expressed as a function of concentration in the usual virial form of eq 2, where C

$$\Delta R/C = (K/\bar{M}_N)(1 + \Gamma_2 C + \Gamma_3 C^2 ...) \qquad (2)$$

is the concentration, K is a calibration constant, and Γ are the virial coefficients of the solute. In practice, a nonvolatile compound of known molecular weight is run and used to determine the constants in eq 2. Then the unknown is run and those constants, which are often a function of both the instrument and the operator, are used to calculate $\bar{M}_N$. Very often, the series is truncated after the first term, and only one or two points are used.

Plots of ΔR vs. C for the pyridine-soluble fraction were often curved. Plots of $\Delta R/C$ vs. C were straight lines and the data showed more scatter when plotted this way. It is clear that the two-term equation is necessary for this system. In our hands, the data obtainable with a vapor pressure osmometer are too imprecise to justify using more than two terms. Also, basing any conclusions on the value of the second virial coefficient (i.e., the slope of the $\Delta R/C$ vs. C plot) is most unwise. This slope is sometimes interpreted in terms of the association of the solute, even though this is not recommended.[16] In Table II are the constants found for the best least-squares straight line

(16) J. A. Franz, J. R. Morrey, G. L. Tingey, W. E. Skieno, R. J. Pugmire, and E. M. Grant, *Fuel*, **56**, 366 (1977).

(17) N. C. Billingham, "Molar Mass Measurements in Polymer Science", Kogon Poge, London, 1977.

found from a plot of $\Delta R/C$ vs. C and the error in the intercept. The data for the highest molecular weight fractions is the most imprecise and we feel it is safe only to conclude that $\bar{M}_N$ for fractions 2 and 3 is above 4000.

Discussion

It is clear from the data presented here that low molecular weight materials are not the chief products of the Heredy–Neuworth depolymerization of bituminous coals. The material extracted from depolymerized coal by pyridine has $\bar{M}_n$ of 400 measured by vapor pressure osmometry but contains much colloidal and high molecular weight material. One of the consequences of this is that reliable conclusions based on instrumental measurements on these solutions are not possible. Thus structural conclusions based on NMR studies of depolymerized coals[18] are questionable since the NMR will not "see" the colloidal material. If there are large, essentially solid colloidal particles suspended in the NMR tube, the protons in these particles will behave like protons in a solid. Their line widths will be so broad that they are essentially undetectable by a high-resolution instrument. Of course, if the colloidal material and the soluble material have the same composition, the NMR results are reliable.

The weight-average molecular weight of these samples must be much higher than the number-average molecular weights. It is clear that vapor pressure osmometry used alone is not a reliable index of the molecular weights of the products of this and similar reactions. Also, vapor pressure osmometry is not a precise "easy" technique and requires significant care and attention in its execution.

The reactions employed here were carried out for a sufficient time to go to completion, as judged by the weight increase of the coal.[9] That this time is not sufficient for maximum depolymerization is indicated by the further reaction of the precipitate isolated by centrifugation. There is an alternative explanation for this observation, viz., that somehow the acidity of the medium had been decreased so much during the reaction that it would no longer occur. This possibility was investigated by running the reaction for 19 h and then adding additional acid and refluxing for an additional 5 h. The resulting solid was 96% extractable into pyridine, and 12% of the pyridine extractables were precipitated on centrifugation. Clearly more reaction occurred, but significant amounts of colloidal material were still produced.

Since most structural models for bituminous coals include Ar–CH_2 linkages as an important structural feature and since these bonds should be cleaved, predominantly low molecular weight products are anticipated from this depolymerization but this is not observed. There are only two possible explanations: either the Ar–CH_2 linkages are absent or they are not reacting (or reacting very slowly). It seems quite unlikely that current structural models for bituminous coals are seriously in error, and the Ar–CH_2 linkages are almost certainly present. It is more probable that the methylene–aromatic linkages present are unreactive. Their intrinsic chemical reactivity could be low, or access to these bonds buried within the macromolecular network of the coal could be limited. Experiments exploring this point are underway.

(18) See, for example, ref 8 and 9.
(19) K. Ouchi, K. Imuta, and Y. Yamashita, *Fuel*, **44**, 29 (1965).

Experimental Section

Depolymerization. Bruceton coal (C, 82.28; H, 5.24; N, 1.60; S, 1.20; ash, 4.44% dry ash free) was depolymerized by using Ouchi's procedure.[19] Identical results were obtained with 30- or 2-g samples. In a typical run, 2 g of coal was placed in 30 g of phenol, and 1.5 g of *p*-toluenesulfonic acid monohydrate was added. This mixture was refluxed under dry N_2 for 24 h. After the mixture had reacted, 100 mL of water was added and the phenol removed by steam distillation. A small amount (4% of the coal weight) of dark oil separated from the distillate. More than 90% of this oil was diphenyl ether, identified by its GC retention time and its ^{13}C NMR spectrum. The solid residue was isolated by filtration and washed thoroughly with water. A second steam distillation was then carried out to remove the last traces of phenol. The depolymerized coal was dried to constant weight in vacuo at 105 °C; a 33% weight increase was observed.

This dried depolymerized coal was then Soxhlet-extracted with the benzene–ethanol azeotrope under dry N_2 until there was no color observable in the solvent. The undissolved coal was dried and exhaustively Soxhlet-extracted with pyridine. The benzene–ethanol fraction could be dried and redissolved. If the pyridine extract was dried, only 38% redissolved.

The depolymerization of the precipitate obtained by centrifugation was carried out as described except the reaction was run for 43 h.

Vapor Pressure Osmometry. A Knauer osmometer was used. Burdick & Jackson "Distilled-in-Glass" solvents were used without further purification. Pyridine was used at 60 °C and THF at 45 °C.

Centrifugation. A Beckman L5-7-5 ultracentrifuge with a swinging rotor was used. Samples were spun at 60 000 rpm (ca. 375000*g*) for 3 h. The resulting pyridine solution could be evaporated to dryness and redissolved in pyridine.

Gel Permeation Chromatography. A Waters Model 201 high-pressure LC with a refractive index detector was used. The columns were 10^3-, 500-, and 100-Å μ-Styragel in series. A solution of the pyridine solubles after centrifugation (~200 mg/mL) was chromatographed. The initial 15 mL of solvent eluted was discarded. Thereafter 17 1.5-mL samples were collected. Fractions 13–17 contained amounts of material too small to weigh accurately. Fraction 1 contained less than 1% of the total material. Routinely, greater than 99% of the material injected was recovered from the column.

Field Ionization Mass Spectra. The field ionization mass spectra were run by Dr. S. E. Buttrill Jr., at SRI Intrnational.

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