

Molecular Weight Distributions of Reductively
Alkylated and Depolymerized Coals

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The intellectual starting point for this work is our belief that bituminous coals consist of largely aromatic "clusters" linked together by various bridges to form a three dimensionally cross-linked macromolecular network in which some extractable molecules are dissolved. The simplest way of making the coal soluble is to cleave enough bridges to destroy the network. Soluble fragments should result. By looking at the molecular weight distribution of these fragments produced by selectively cleaving bridges, the relative importance of the various types of bridges can be determined. Two well developed ways for accomplishing such cleavage are the well known Heredy-Neuwirth depolymerization² and the Sternberg reductive alkylation,³ which cleave methylene bridges and primarily ethers respectively. Their chemistry has been reviewed.⁴ We will concentrate here on the Heredy-Neuwirth depolymerization.

Figure 1 shows the results of depolymerizing Bruceton coal. The fraction soluble in benzene ethanol (70/30 v/v) is stable and passes through a 0.5 μ filter. The pyridine "solution" is stable, in that nothing precipitates on standing. However 6.8% of the "dissolved" material is removed by a 2.7 μ filter. The remaining solution will not pass a 0.5 μ filter. Ultracentrifugation of the pyridine "solution" (60,000 rpm; 3 hrs) results in precipitation of 40% of the pyridine solubles. Before centrifugation, the number average molecular weight (M_N) of the pyridine "solubles" was 400, quite comparable with results reported by others.⁵ After centrifugation, M_N was 1,000. The increase is due to the removal of colloidal material and the latter number is the true M_N for the dissolved material. Similar results have been obtained with a vitrinite sample (PSOC 126). As a result of these observations, all M_N values reported for products of Heredy-Neuwirth depolymerization must be regarded as questionable and probably erroneous. We are currently determining whether the colloidal material emerges from the coal unchanged or whether it is a reaction product.

The molecular weight distribution measured for the benzene-ethanol soluble fraction of depolymerized Bruceton coal by gel permeation chromatography (μ -Styragel columns 10⁵, 500, 100 A^o, THF solvent) followed by vapor pressure osmometry of individual fractions is shown in Fig. 2. Several important points emerge. First, there must be association in THF as indicated by the higher M_N for the fraction in that solvent. Separation on the gpc columns is only partly on the basis of size. Finally, silylation of the depolymerized coal does not decrease its M_N in pyridine, apparently there is little association via hydrogen bonds involving CH groups in that solvent.

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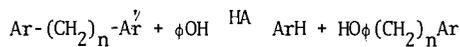


Figure 3. The Depolymerization Reaction

Coal	C (wt %, daf)	Alkylation technique	Solvent	Mol. wt.	Extract- ability (wt %)
W. Va. lvb	90.6	HNO ₃ -φOH/BF ₃ -Ac ₂ O	CHCl ₃	530	14
Clarian hvb	60.0	HNO ₃ -φOH/BF ₃ -Ac ₂ O	CHCl ₃	1725	84
Ohio 8 Hvab	80.9	HNO ₃ -φOH/BF ₃ -Ac ₂ O	CHCl ₃	645	95
McFarlane Hvcb	67.3	HNO ₃ -φOH/BF ₃ -Ac ₂ O	CHCl ₃	375	96
Japanese	75.8	φOH/PTS	Pyridine	320	98
	78.0	φOH/PTS		340	100
	81.7	φOH/PTS		440	90
	81.9	φOH/PTS		450	96
	83.1	φOH/PTS		460	98
	84.6	φOH/PTS		500	92
	86.2	φOH/PTS		480	98
	89.6	φOH/PTS		1100	32
Lignite	71	φOH/BF ₃	φOH	300	21
			φH-MeOH	300	48
Sub-bituminous	77	φOH/BF ₃	φOH	350	2
		φOH/BF ₃	φH-MeOH	290	15
High-volatile vitrain	82	φOH/BF ₃	φOH	920	13.5
		φOH/BF ₃	φH-MeOH	525	25
High-volatile bituminous	85	φOH/BF ₃	φOH	930	7
		φOH/BF ₃	φH-MeOH	730	15
High-volatile bituminous	86	φOH/BF ₃	φOH	750	19
Low-volatile bituminous	91	φOH/BF ₃	φOH	360	5.4

Figure 4. Phenol Free Molecular Weights (Number Average) of Depolymerized Coals (From J.W. Larsen and E.W. Kuemmerle, Fuel, 55, 162 (1976)).

Figure 5. Molecular Weight Distribution of the True Pyridine Solubles After Centrifugation

Fraction No.	Wt. %	Cumulative Wt. %	\bar{M}_N
1	< 0.5		
2	14.7	14.7	> 3000
3	20.3	35.0	> 3000
4	15.2	50.2	> 3000
5	15.5	65.7	2960
6	12.8	78.5	2440
7	7.0	85.5	880
8	5.9	91.4	560
9	4.3	95.7	560
10	2.7	98.4	370
11	1.6	100.0	370

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