Chemistry of Coal Utilization

SECOND SUPPLEMENTARY VOLUME

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To Homer H. Lowry, an outstanding coal scientist, who brought into being the first three volumes of this work so extensively used and greatly appreciated by workers in coal science and coal technology

for design and scaleup, and a mechanistic understanding of the controlling phenomena is essential for efficient progress toward full realization of the potential advantages.

12.2.2 Coal Composition

12.2.2.1 *Coal Petrography*

The organic material in coal is a heterogeneous mixture of "organic minerals" known as macerals. Coal petrographers have identified numerous types of maceral components by microscopic analysis with reflected and transmitted light.[19] The precise chemical nature of the macerals is not well established, but their botanical origins seem to be rather well understood.[20]

For ease of discussion, the various types of maceral component are often combined into three principal groups: vitrinite, exinite, and inertinite. With regard to physical and chemical properties, exinite is characterized by the highest hydrogen content, volatile matter content, and heating value: inertinite has the least. Inertinite has the highest density and the greatest degree of aromaticity, whereas exinite is the lowest in both these properties. Thus vitrinite, by far the most abundant of the three maceral groups as can be seen in Table 12.2, usually exhibts chemical and physical properties between those of the other two.[22]

The different maceral groups exhibit markedly different behaviors under pyrolysis conditions,[2] and the same would presumably hold for hydropyrolysis. As might be expected from the order of volatile matter contents, the total yield of volatiles is usually in the order exinite > vitrinite > inertinite. There are also compositional differences among the products. For example, liquids from exinite have been characterized as primarily neutral oils, but those from vitrinite tend to be lighter and more phenolic.

The discussion of petrographic constituents points up the approximate character of available descriptions of pyrolysis and hydropyrolysis that treat coal as a single material. If extensive rate and yield data on the different maceral groups eventually become available, it should be possible to describe the behavior of different coals in terms of their petrographic compositions and kinetic parameters evaluated for each maceral group.

12.2.2.2 *Coal Chemistry*

The organic matter in coal consists primarily of carbon, hydrogen, oxygen, nitrogen, and sulfur, although trace quantities of other elements are also found. Typical elemental or so-called ultimate analyses of some American coals are given in Table 12.2, where organic and inorganic sulfur contents are lumped together in accordance with ASTM standards. In proximate analysis coal is divided into moisture, volatile matter, fixed carbon, and ash. Either volatile matter or fixed carbon on a moisture-free, ash-free (maf) basis, and the maf calorific value of the coal, permit classification of coals in the ASTM system[23] in decreasing rank as anthracitic, bituminous, or lignitic or brown. The rank of a coal is directly related to its carbon content, with a highly graphitic material representing the ultimate product of the coalification process. Unfortunately this information provides very little direct insight into chemical structure or petrographic composition.

There have been substantial efforts to elucidate the molecular structure of coal, but the task is exceedingly difficult because of the variety of coal types, the heterogeneity of a single coal, and the complexity of individual coal constituents. The results of numerous diverse measurements have been synthesized in attempts to develop a consistent picture (see Van Krevelen,[20] and Dryden[22]) but much work remains to be done. Given[24] presented the hypothetical structure shown in Fig. 12.1 for bituminous coal vitrinite possessing 82% carbon as one possible arrangement of the atoms consistent with most of the facts available at that time.

[19] W. Spackman, "The Nature of Coal and Coal Seams," in *Short Course in Coal Characteristics and Coal Conversion Processes,* Pennsylvania State University, University Park, May 19–23, 1975.

[20] D. W. Van Krevelen, *Coal,* Elsevier Publishing Company, Amsterdam, 1961.

[21] H. Gan, S. P. Nandi, and P. L. Walker, Jr., "Nature of the Porosity in American Coals," in *Short Course on Characterization and Characteristics of U.S. Coals for Practical Use,* Pennsylvania State University, University Park, October 25–28, 1971.

[22] I. G. C. Dryden, "Chemical Constitution and Reactions of Coal," in *Chemistry of Coal Utilization,* Supplementary Volume, H. H. Lowry, Ed., John Wiley and Sons, New York, 1963, pp. 232–295.

[23] ASTM 1974, Standards on Coal and Coke.

[24] P. H. Given, "The Distribution of Hydrogen in Coals and Its Relations to Coal Structure," *Fuel,* **39,** 147 (1960).

Table 12.2 Composition of Some American Coals[21]

Number[a]	Location	ASTM Rank	Ultimate Analysis (wt %, maf) C	H	N	S	O[b]	Vitrinite Content (vol %)[c]
85	Pennsylvania	Anthracite	91.2	3.8	0.60	1.1	3.1	97.5
80	Pennsylvania	Anthracite	90.8	2.6	0.75	0.64	5.1	96.3
130	West Virginia	lvb	90.5	4.3	1.1	0.55	3.4	72.7
127	Pennsylvania	lvb	89.5	5.0	1.0	0.83	3.6	77.7
135	Alabama	mvb	88.3	4.9	0.25	0.65	5.7	83.1
142	Oklahoma	mvb	88.2	4.5	0.20	1.0	6.4	—
4	Kentucky	hvAb	83.8	5.7	1.5	0.88	7.9	67.3
95	Washington	hvAb	81.6	6.0	1.0	1.7	9.4	89.6
105A	Indiana	hvBb	81.3	5.7	1.0	1.8	9.9	62.5
24	Illinois	hvCb	80.0	5.5	1.0	4.5	8.8	88.1
213	Kentucky	hvCb	78.8	5.6	1.7	4.2	9.4	73.4
22	Illinois	hvCb	78.7	5.8	1.5	2.8	11.0	88.3
26	Illinois	hvCb	77.2	5.6	1.1	7.4	8.3	88.5
197	Pennsylvania	hvBb	76.5	5.6	1.2	4.5	12.2	85.3
64	Missouri	hvBb	76.4	4.2	1.2	7.3	11.4	—
190	Illinois	hvCb	75.5	5.3	1.0	3.3	14.6	88.9
97	Wyoming	Subbituminous	75.0	5.5	0.58	1.3	17.5	86.7
138	Texas	Lignite	74.3	4.9	0.37	0.75	19.6	75.1
100	Wyoming	Subbituminous	72.0	5.2	0.81	0.55	21.2	86.0
141	Texas	Lignite	71.7	5.2	1.3	0.90	20.8	75.3
90	Montana	Lignite	71.5	4.8	0.83	0.50	22.2	60.9
89	North Dakota	Lignite	63.3	4.6	0.47	1.5	29.9	70.3

[a] PSOC numbers employed in Pennsylvania State University–Office of Coal Research (now ERDA) coal characterization study.
[b] Determined by difference.
[c] Mineral-matter-containing basis.

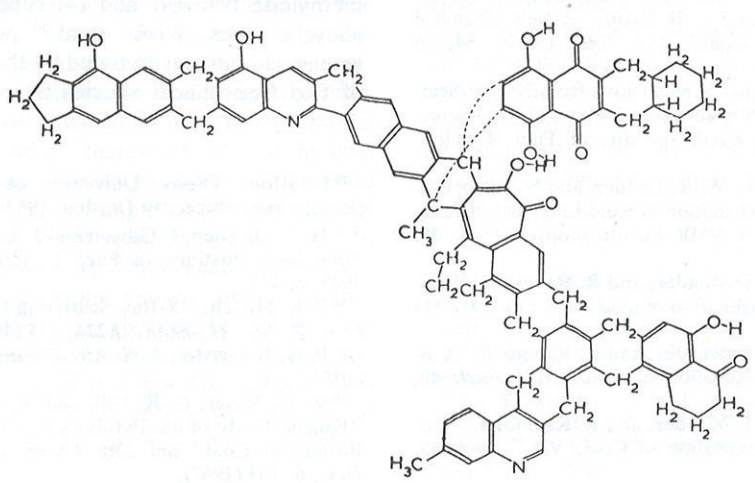

Figure 12.1 The Given model for molecular structure of coal (a vitrinite of 82% C (dmmf); $C_{102}H_{78}O_{10}N_2$).[24]

Although other structures have been proposed—some less complicated than Given's and clearly not in accord with recent findings,[25] and others including a larger variety of possible arrangements[26]—the Given model is generally accepted as a reasonable working hypothesis. This model is certainly suitable for the present discussion of pyrolysis behavior.

Immediately evident in the structure is the high degree of aromaticity involving about two-thirds of the carbon and about 20% of the hydrogen. Condensed aromatic clusters each comprised of one to three rings are in line with Hirsch's[27] X-ray scattering studies, which also showed that the number of rings per cluster increased with increasing rank of the coal, ultimately approaching a fully condensed graphitic structure. The linkages between clusters represent an area of considerable debate. The Given model is built around a 9,10-dihydroanthracene module. Dryden[22] recommended a dihydrophenanthrene module as being more compatible with the absence of methylene bridges, which was reported by Brown et al.[28] based on nuclear magnetic resonance (NMR) studies. In addition, other types of linkage such as short-chain aliphatics several carbons long, ethers, sulfides, and disulfides, are certainly possible. Much of the linkage structure, however, is hydroaromatic according to the results of Reggel et al.[29–31] Aliphatic side chains such as the methyl groups in the Given model are also distributed throughout the coal matrix. Oxygen appears predominantly in hydroxyl and carbonyl groups in all types of coal.[32] Carboxylic acid groups and ether linkages are common to lower rank coals only. The nitrogen in coal is shown in the Given model as a ring-substituted azine structure. Organic sulfur, although not shown, will also appear in heterocyclic aromatic rings as well as sulfide functional groups.

Blayden et al.[33] found that interatomic distances in coal are approximately 2–3 times greater in one dimension than in the other two. This result indicates a highly planar polymeric molecule in a layered structure with considerable internal pore volume and surface area. In fact, this layering phenomenon persists even in the intertwined and highly cross-linked structures of the less-ordered lower rank coals.[34] Internal surface areas of up to several hundred square meters per gram are typically found in all ranks of coal.[22] The porosity of various coals is reported by Sevenster[35] as ranging from 8 to 20%. Extensive data on the pore structure of numerous American coals are being generated at Pennsylvania State University.[12,21]

12.2.2.3 *Relationship to Pyrolysis Reactions*

Given[24] speculated that the course of pyrolysis anticipated from his model would consist of four steps: (1) a low-temperature (400–500°C) loss of hydroxyl groups, (2) dehydrogenation of some of the hydroaromatic structures, (3) scission of the molecule at the methylene bridges, and (4) rupture of the alicyclic rings. Wiser et al.[36] postulated a sequence of events initiated by the formation of two free radical species from a thermal cracking of the linkages forming the aromatic clusters. These free radical species would then stabilize, either through a rearrangement of atoms within a fragment or by collision with another species. The resultant stabilized structure, depending on its vapor pressure, would either evolve as volatile material or remain as part of the residual char.

The amount of hydrogen in coal, if allocated appropriately to the carbon, would be sufficient to permit nearly complete volatilization, at least for medium- and low-rank coals. Unfortunately the structure of coal preferentially evolves hydrogen as chemical water (probably from the hydroxyl groups) and light, highly stable aliphatics (such as methane and ethane), depleting the remaining carbon of much needed hydrogen. Because of this inefficent use of intrinsic hydrogen, pyrolysis, even under the most favorable conditions, includes the formation of heavy tarry compounds and residual char. In the absence of external hydrogen, the aromatic clusters appear to be immune to internal rupture. In fact, prolonged heating at high temperatures results in only a slow dehydrogenation and further condensation of the clusters.

When the rate of reaction is considered, the free radical secondary reactions described by Wiser et al.[36] will be fast compared to the thermally invoked bond ruptures as radical formation steps. Given has already indicated the presence of a hierarchy of bond susceptibilities to scission within the original molecule. Intermediate char structures formed by free radical recombinations similarly will be subject to thermal bond rupture at high temperatures thus assuring a virtual continuum of rate-determining bond energies. This structural observation is the basis for the distributed activation energy model described later. Increased interest in coal research and the accessibility of powerful computers has prompted reexamination of more fundamental reaction mechanisms. In the past, however, a manageable set of fundamental reactions usually proved inadequate to describe experimental results, and a larger, more complete set resulted in too many degrees of freedom for useful modeling, since it was impossible to specify coal reaction rates a priori or to determine them independently.

[25] W. Fuchs and A. G. Sandhoff, "Theory of Coal Pyrolysis," *Ind. Eng. Chem.*, **34**, 587 (1942).
[26] G. R. Hill and L. B. Lyon, "A New Chemical Structure for Coal," *Ind. Eng. Chem.* **54**, 36 (1962).
[27] P. B. Hirsch, "Conclusions from X-Ray Scattering Data on Vitrain Coals," *Proc. Conf. Science in the Use of Coal,* Institute of Fuel, London, 1958, p. A29.
[28] J. K. Brown, W. R. Ladner, and N. Sheppard, "Hydrogen Distribution in Coal-Like Materials by High-Resolution NMR Spectroscopy," *Fuel,* **39**, 79 (1960).
[29] L. Reggel, I. Wender, and R. Raymond, "Catalytic Dehydrogenation of Coal, II," *Fuel,* **47**, 373 (1968).
[30] L. Reggel, I. Wender, and R. Raymond, "Catalytic Dehydrogenation of Coal, III," *Fuel,* **49**, 281 (1970).
[31] L. Reggel, I. Wender, and R. Raymond, "Catalytic Dehydrogenation of Coal, VII," *Fuel,* **52**, 162 (1973).
[32] L. Blom, Thesis, University of Delft, 1960 (Results reproduced by Dryden, 1963.)
[33] H. E. Blayden, I. Gibson and J. L. Riley, *War-Time Bull.*, Institute of Fuel, London, February 1945, p. 117.
[34] P. B. Hirsch, "X-Ray Scattering from Coals," *Proc. R. Soc. (London),* **A226**, 143 (1954).
[35] P. G. Sevenster, *J. S. Afr. Chem. Inst.*, **7**, 41 (1954).
[36] W. H. Wiser, G. R. Hill, and N. J. Kertamus, "Kinetic Study of the Pyrolysis of a High-Volatile Bituminous Coal," *Ind. Eng. Chem., Process Des. Dev.*, **6**, 133 (1967).

12.2.3 Physical Factors

12.2.3.1 *Plastic Behavior*

A coal is characterized as plastic or nonplastic depending on whether it exhibits thermoplastic behavior, that is, softening and becoming deformable followed by resolidification to form a char, on being heated either through a certain temperature range or to a temperature above the softening point and there maintained for a certain period of time. Plastic coals are also referred to as caking coals because coal particles in the plastic state are viscous liquid masses capable of coalescence and, on resolidification, formation of a cake.

The macerals discussed above differ in physical behavior as well as in chemical composition. Neavel[37] states that plasticity is exhibited only by the macerals exinite (a minor constituent of typical coals) and vitrinite, of which only vitrinite has plastic capability in bituminous coals, except for a few very unusual coals. A plastic coal ground fine enough to effect substantial liberation of macerals may exhibit, under a given set of heating conditions, a wide range of individual particle behavior including no softening or swelling, moderate swelling with formation of approximately uniformly distributed macroscopic pores, and extreme cenosphere formation. In the present discussion the behavior attributed to a given plastic coal represents that of the dominant maceral, vitrinite.

The occurrence of the plastic state is associated with and kinetically similar in many ways to pyrolysis. The temperature limits and time duration of plasticity depend on heating rate and other conditions. At a constant heating rate of about 0.05 °C/s the plastic region is typically 420–500°C[38] with some variation among different coals. The plastic region moves to higher temperatures as heat-

[37] R. C. Neavel, "Coal Plasticity Mechanism: Inferences from Liquefaction Studies," *Symp. Plasticity and Agglomeration of Coal,* U.S. Energy Research and Development Administration, Morgantown, W. Va., May 5–6, 1975.
[38] D. W. Van Krevelen, F. J. Huntjens, and H. N. M. Dormans, "Chemical Structure and Properties of Coal, XVI, Plastic Behavior on Heating," *Fuel,* **35**, 462 (1956).

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Second Supplementary Volume

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