

Understanding the chemistry and physics of coal structure (A Review)

(coal reactivity/physical properties of coal/coal pore structure)

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ABSTRACT This article outlines our current understanding of the structure of coal in terms of both the chemical and physical bonding processes responsible for its structural integrity and the extensive network of pores that permeate the organic material. Information on the microscopic chemistry of coal and its relationship to coal's physical structure and reactivity is an essential component in the successful development of the next generation of coal conversion technologies. Although coal is an extremely complex and heterogeneous material, many of its fundamental properties can be determined by the coordinated efforts of organic and physical chemists, solid state physicists, and chemical engineers. The scientific questions that emerge from these efforts lie at the frontiers of chemistry and physics research.

Coal and coal products will play an increasingly important role in fulfilling the energy needs of our society. Future applications will extend far beyond the present major uses for power generation, metals processing, and chemicals production. A key feature in these extensions will be the development of means to convert coal from its native form into useful gases and liquids in ways that are energy efficient, nonpolluting, and economical. The design of this next generation of conversion processes will require a deeper understanding of coal's intrinsic properties and the ways in which it is chemically transformed under process conditions. Coal properties—such as the chemical form of the organic material, the types and distribution of organics, the nature of the pore structure, and the mechanical properties—must be determined for coals of different ranks (or degrees of coalification) in order to use each coal type most effectively (1).

A second and more subtle challenge is to identify the chemical pathways followed during the thermal conversion of coal to liquids or gases. This is accomplished by tracing the conversion of specific chemical functional groups in the coal and studying the effects of various inorganic compounds on the conversion process. Significant progress has been made in this area by combining test reactions with a battery of characterization techniques. The ultimate goal is to relate the structure of the native coal to the resulting conversion products.

A brief description of coal from three different points of view illustrates the dimensions of the problem. Structurally, coal is a complex system (Fig. 1). Organic material dominates, typically representing 85–95% (wt/wt) of a dry coal. These organic materials occur in various different petrographic types, called “macerals,” which reflect the nature of the precursor plant material. Various inorganic materials, particularly aluminosilicates and pyrites (especially in high-sulfur coals), comprise 5–15% of the coal. A third structural element, and perhaps its most distinctive feature when compared to other solid fossil fuel sources like petroleum and oil shale, is an extensive network

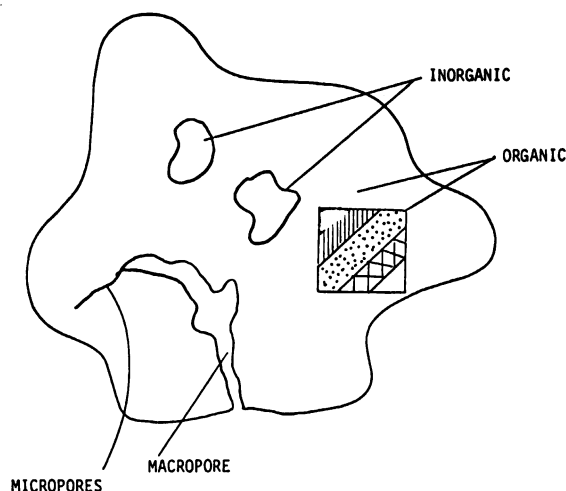


FIG. 1. Diagram of the major constituents in coal: organic material, fragments of plant debris (macerals), inorganic inclusions, and an extensive pore network.

of pores. These pores give coal a high surface area ($>100 \text{ m}^2/\text{g}$ for bituminous and sub-bituminous coals and lignites) and an appreciable volume of pore space, allowing access to a significant fraction of the organic material.

Elemental analysis provides a second perspective of coal: its macrochemical form. The analysis of a relatively low rank, sub-bituminous coal from the Rawhide mine in Wyoming is shown as an example in Table 1. Organic material represents 95% of this coal, the balance being aluminosilicate and iron minerals. The low level of sulfur ($<1\%$) makes it particularly desirable for power generation and the synthesis of “clean” conversion products. Coal is hydrogen deficient, the atomic hydrogen-to-carbon ratio (≈ 0.9) being roughly half that for petroleum and oil shales. This suggests a very different chemical structure, with higher levels of aromatic and other unsaturated species than found in petroleum. A second dominant feature is the high level of organic oxygen in coal—one oxygen for every five carbon atoms—more than 10 times the oxygen levels in petroleum. These abundant oxygen forms strongly influence coal's structure and reactivity.

A third level of understanding coal chemistry is provided by attempts to determine the microscopic relationship among the aromatic and aliphatic hydrocarbons and heteroatom forms in the coal structure. One convenient means of expressing the available information from a large number of experiments is in terms of a representative organic structure. Fig. 2 shows one such model of the types and arrangements of the organic groups in a bituminous coal.* Relatively small “nuclei” of aromatic and

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* Wisner, W. H. *Proceedings of the Electric Power Research Institute Conference on “Coal Catalysis,”* Santa Monica, CA, September 1973.

Table 1. Chemical composition of a low-rank coal*

Compound	Content, % (wt/wt)
Organic	95
C	73
H	5.2
O	20
N	1
S	<1
Inorganic†	5

* Sub-bituminous coal from the Rawhide mine (Wyoming):

 $C_{100}H_{85}O_{21}N_1S_{0.3}$

† Includes Si, Al, Fe, Ca, and Na.

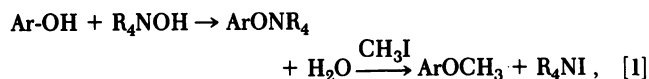
naphthenic rings are coupled to one another by "bridges" of aliphatic chains or heteroatoms. In addition to these covalent bridges, there are a significant number of polar groups such as hydroxyls (-OH) that can contribute to the integrity of the coal structure via electrostatic binding. Oxygen appears in this structure in various chemical forms. Some oxygens occur as substituents, such as carboxyl or phenol groups, attached at the edge of the nuclei. Others are buried as heteroatoms in aromatic or naphthenic rings. Still others occur as bridges between the nuclei as ethers or, to a lesser extent, as esters. These types of oxygen functional groups strongly influence coal reactivity (2), and their relative numbers vary significantly as a function of coal rank (3). What this model cannot convey is the three-dimensional arrangement of these chemical constituents to form the system of micropores and macropores that permeate the solid.

A material of this complexity can only be understood by a broadly based research effort involving various disciplines (4). Selective chemical reactions must quantify the different classes of chemical groups. This information must be related to the observed behavior of the same coal samples under conditions typically encountered in coal conversion processes. An entire spectrum of physical characterization techniques is needed to

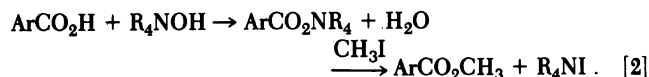
examine the native coals and their products. These different approaches will be illustrated with three examples taken from current research programs: (i) the use of selective chemical reactions to differentiate oxygen functional groups in coal, (ii) model process studies to trace the thermal chemistry of more reactive oxygen forms, and (iii) heat capacity and NMR studies of water molecules residing in coal pores.

OXYGEN FUNCTIONAL GROUPS IN COAL

To clarify oxygen chemistry in coal, one must determine how many oxygen functional groups of a given type exist and how accessible they are for different reagents—two questions that lie at the frontier of coal science. A reaction scheme has recently been discovered which measures coal's acidic oxygen functional groups (phenols and carboxylic acids) quantitatively (5). Phenols can be converted to ethers and carboxylic acids can be converted to esters selectively and under mild conditions by using methyl iodide (or any primary alkyl iodide or bromide) as the alkylating agent in the presence of a quaternary ammonium hydroxide:



and



The hydroxide serves as a coal-soluble base that brings species from two phases (solid coal and liquid CH_3I) rapidly into contact in a solvent (e.g., tetrahydrofuran) and enhances the rate of chemical reaction between them. Experience indicates that CH_3I and (*n*-butyl) $_4\text{NOH}$ is the preferred reagent pair for quantification studies (5).

Infrared spectroscopy is used to follow the alkylation process.

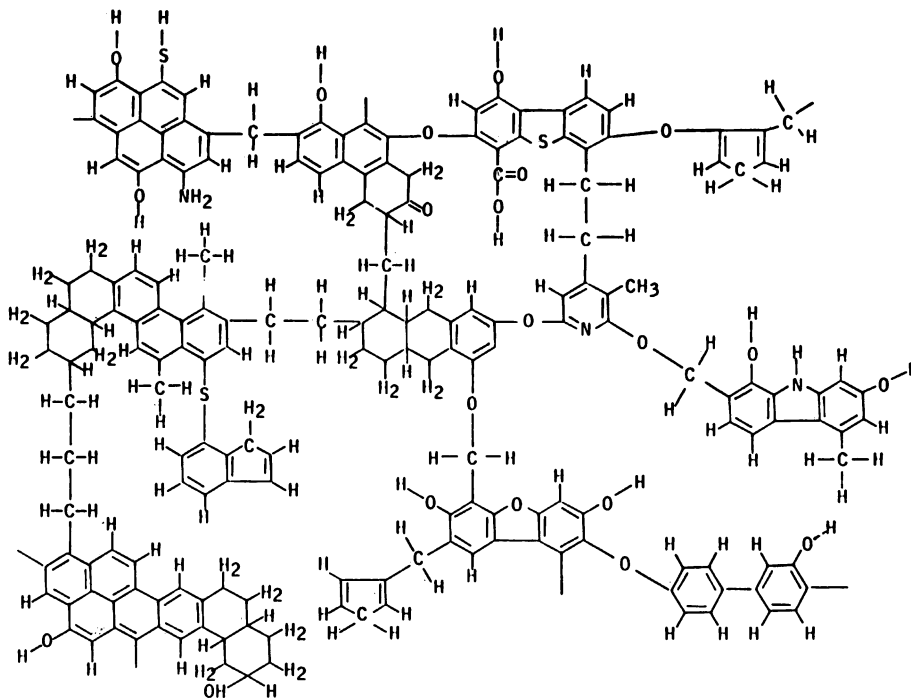


FIG. 2. A representative structure of the chemical groups in a bituminous coal (as proposed by W. H. Wiser).

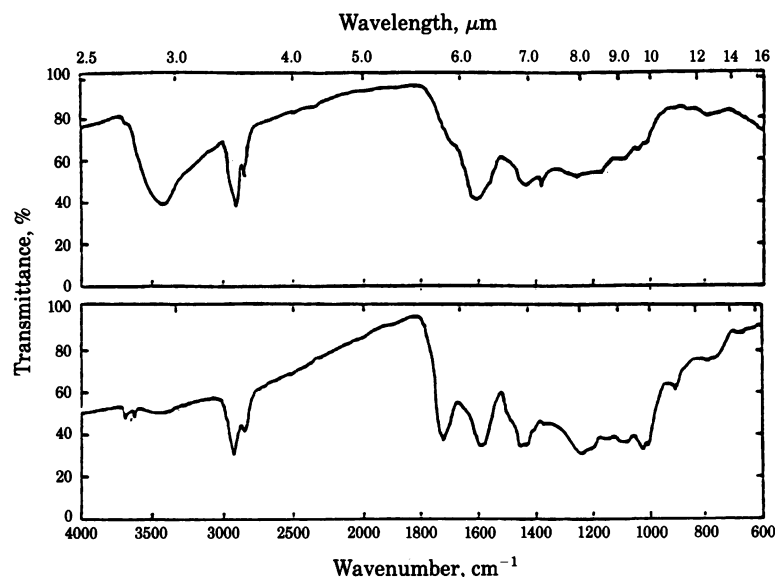


FIG. 3. Fourier-transform infrared spectroscopic studies of the alkylation process showing the loss of -OH and the increase in -OCH₃ upon alkylation (6). (Upper) As received. (Lower) After alkylation.

The infrared spectra in Fig. 3 show the disappearance of the -OH stretch absorption near 3,500 cm^{-1} and the enhancement of an O—C stretch near 1,100 cm^{-1} associated with the replacement of acidic protons with alkyl groups. The disappearance of the -OH stretch suggests that this mild, room-temperature, chemical reaction has completely alkylated the acidic protons in the coal. The number of such alkylated sites is determined by using isotopically enriched C²H₃I as the reagent. Combustion of the C²H₃I-alkylated material followed by mass spectroscopic analysis of the ²H₂O in the combustion products provides a quantitative measure of the number of -OH groups present (5).

These data, combined with macrochemical analysis, show how coal microchemistry varies with rank. Table 2 shows the organic distribution of oxygen functional groups in Illinois bituminous and Rawhide (Wyoming) sub-bituminous coals. The total numbers of -OH and -COOH groups were determined by alkylation techniques, the hydroxyl/carboxyl ratio by ¹³C NMR, and the ether oxygen by difference from the total amount of organic oxygen as determined by neutron activation techniques. Perhaps the most prominent functional difference is the much higher level of carboxylic acids in the Rawhide coal, which reflects its lower rank and lesser age (≈ 50 million years for Rawhide sub-bituminous, opposed to ≈ 300 million years for Illinois bituminous). Hydroxyl levels are comparable in the two coals, but Rawhide coal has twice the level of ether oxygen. A most important observation from the point of view of reactivity is that nearly one-quarter of the organic mass of Rawhide coal occurs as the O, C, and H in these oxygen functional groups.

Table 2. Oxygen functional group distribution reflects coal rank

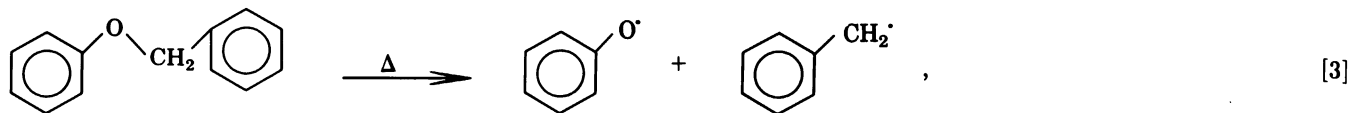
Functional group	Functional groups, no./100 C atoms	
	Illinois no.6 (C ₁₀₀ H ₈₆ O ₁₁ N _{1.6} S _{1.6})	Rawhide (C ₁₀₀ H ₈₅ O ₂₁ N ₁ S _{0.3})
Ether (—O—)	5.5	9.8
Hydroxyl (—OH)	4.5	4.8
Carboxylic acid or ester O (—CO—)	0.5	3.2
Total oxygen	11.0	21.0

THERMAL CONVERSION OF OXYGEN FUNCTIONAL GROUPS

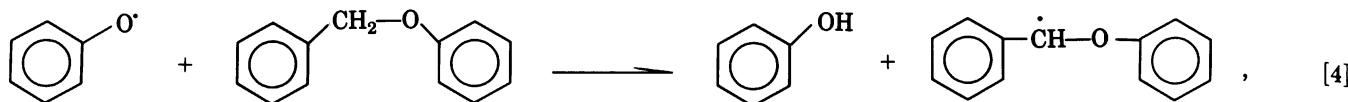
A second major chemical issue concerns the important role oxygen plays in bridges connecting nuclei of the coal structure. Both oxygen and alkyl chains are major bridging elements (Fig. 2). Several workers have studied the chemical breakdown of aliphatic linkages (6–8), and further information is provided by the study of model compounds containing oxygen bridges under reaction conditions similar to those used in coal conversion processes (9, 10).

As in the aliphatic bridging studies, the appropriate starting place is the careful analysis of the thermal transformation of model systems in which the detailed chemical character of the starting molecule is known and the type and amount of various transformation products can be quantified. For example, benzyl phenyl ether is a reactive organic oxygenate containing an aryl-alkyl ether function of the type expected as a bridge in bituminous and sub-bituminous coals. It reacts readily, being $\approx 30\%$ converted by reaction in a batch autoclave (tubing bomb) system at 375°C for 1 min. The course of the reaction and the final products are sensitive to the availability of hydrogen. In excess hydrogen, its pyrolysis products are toluene and phenol (11). In the absence of hydrogen, a 1-min pyrolysis produces toluene, phenol, and $\approx 30\%$ (wt/wt) of material with molecular weights between 200 and 700 as determined by gas chromatographic/mass spectroscopic analyses. An identical experiment carried out with the addition of a small amount of a very efficient hydrogen donor solvent (1,2,3,4-tetrahydroquinoline) produces $<1\%$ of these heavier species (9).

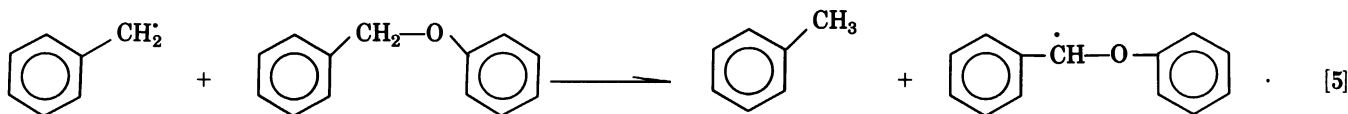
The mechanism of benzyl phenyl ether pyrolysis is similar to that observed for dibenzyl (8). This cleavage reaction is a radical process in which termination is particularly important. The relative amounts of phenol and toluene in the products of short-time reactions suggest that phenoxy radicals are more involved in the hydrogen abstraction mechanism. In a 1-min experiment at 375°C in the absence of hydrogen, 17% of the product is phenol and only 6% is toluene. The rapid conversion rates observed for benzyl phenyl ether (in contrast to dibenzyl, for example) suggest that these materials have bond dissociation



followed by



and



energies significantly less than the 235 kJ/mol reported for the benzylic C—C bond in dibenzyl (8).

These thermal reaction studies lead to a different picture of coal's chemical reactivity than is often appreciated. Many of the bridging structures in coal are highly reactive—more so than the similar bridge structures in petroleum. The difficulty is that the products of such reactions depend sensitively on the availability of hydrogen to terminate the process, capping off the radicals that are thermally generated. In the presence of hydrogen, from a good donor solvent for example, radical processes are rapidly quenched and small molecules are formed. In a hydrogen-deficient system, these radicals propagate, forming large amounts of high molecular weight products.

HEAT CAPACITY AND NMR STUDIES OF THE COAL PORE STRUCTURE

The thermolysis results emphasize the need for access of reagents such as hydrogen to regions of the coal undergoing conversion. Thus, a key consideration in coal conversion is the mass transfer of reagents and products which occurs by means of coal's extensive pore network. A wide variety of pore types exist in coals of different ranks (Fig. 4), ranging from large ($\geq 300 \text{ \AA}$) macropores to small ($\leq 12 \text{ \AA}$) micropores (12). A knowledge of the total volume of such pores, the pore size distribution, and the effective surface area of the organic material is needed to anticipate coal's potential reactivity. The nature of these pores can be studied by examining the water that normally fills the pore structure of the native coal. Water content is significant in coals from low to medium rank, ranging from $\approx 40\%$ (wt/wt) for a typical lignite (Arkansas) to $\approx 14\%$ for Illinois bituminous coal. The dominant role of water is particularly apparent for lignites: the volume of coal occupied by water ($\approx 0.67 \text{ cm}^3/\text{g}$ of dry coal) is comparable to the volume occupied by the organic material ($\approx 0.75 \text{ cm}^3/\text{g}$ of dry coal).

Heat capacity observations of the water in coal furnish important information about coal's physical structure. It is a simple, quantitative measurement which can be made without the need for any pretreatment of the coal: native coal samples can be examined exactly as they occur in the coal seam. In Fig. 5, the thermal behavior of water molecules in the coal pore structure is contrasted with that of bulk water (13). For bulk water, the heat capacity is nearly independent of temperature above 273 K, a latent heat of fusion of 80 cal/g (1 cal = 4.184 J) is observed at the melting point, and a slow, monotonic variation is observed in the ice phase. The water heat capacity in coal is similar to that of bulk water above the melting point and at low temperatures ($\approx 120 \text{ K}$). Significant deviations from the bulk

water heat capacity behavior at intermediate temperatures reflect the strong effect of the pores on the freezing properties of the water. The sharp heat capacity peak associated with the first-order phase transition of bulk water is no longer present for the water in the coal sample, the peak being broadened and shifted to lower temperatures. When roughly half of the coal's water is removed by room temperature drying, the residual peak seen for the water-saturated coal sample is lost and a smooth, monotonic decrease in heat capacity is observed from 300 to 120 K. This continuous variation is observed in many systems when water or other molecules are in the vicinity of a substrate (13). In Fig. 6 the heat capacity is plotted as a function of temperature for water in coal, for water associated with protein fibers in collagen, for water in the clay mineral endellite, and for water condensed on the surface of an alumina catalyst support. For water contents amounting to roughly two monolayers or less on the substrate, the continuous variation is observed. This general phenomenon can be used to estimate the surface area of the coal probed by water molecules.

The relative amount of water types varies with coal rank (Table 3) (14). There is a liquid-like fraction which occurs at high relative humidity ($>98\%$) for low-rank coals. The amount of substrate water is determined by measuring coal heat capacity as a function of water content and determining the onset of a heat capacity maximum. The rest of the water, exhibiting the modified phase transition properties, is assigned to water residing in coal pores but away from the pore surface. The amount

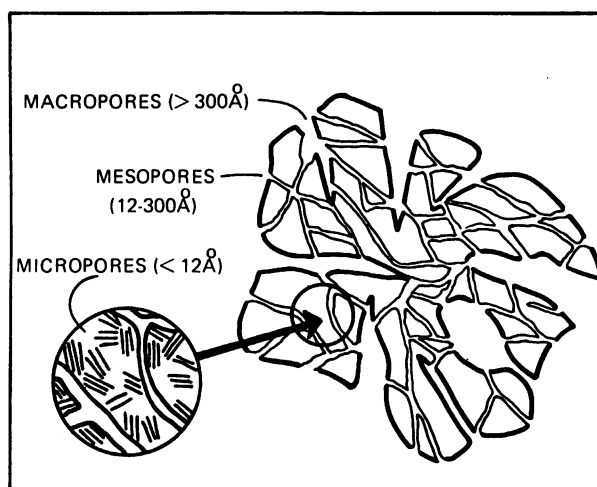


FIG. 4. Different pore types encountered in coals.

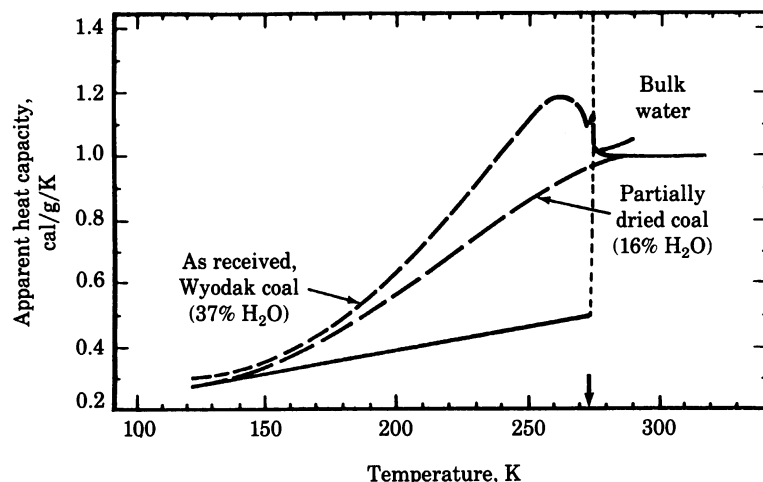


FIG. 5. The heat capacity of pore water is dramatically different from that of bulk water (14). Arrow marks melting point of ice at 273 K. Heat capacity of the organic material has been subtracted for the coal data.

of substrate water provides an estimate of the effective water surface area of the coal: 150 m²/g for Illinois no.6 bituminous; 480 m²/g for Rawhide sub-bituminous; and 530 m²/g for Arkansas lignite. The surface area obtained for the bituminous coal is very close to the values determined by many previous studies using CH₃OH heats of wetting, CO₂ absorption isotherms, and small angle x-ray scattering; these values range from 125 to 150 m²/g (15). By contrast, the high values obtained for the lower-rank coals are significantly larger than those obtained by other techniques (12).

We believe that this difference is associated with the drying step which precedes most surface area determinations and reflects the crucial role that water plays in the structure of low-rank coals. When Illinois no.6 bituminous coal is initially dried at temperatures from 24°C to 100°C and reexposed to water vapor, practically all of the water removed by drying can be replaced. By contrast, ≈60% of the water can be replaced in the Rawhide sub-bituminous coal and only ≈35% in the Arkansas lignite. This loss of water capacity is explained by the following picture (S. C. Mraw and D. F. O'Rourke, personal communication). A significant amount of water is in the organic material during the formation of the coal seam. This water serves to separate the various organic species. When the water is removed, the reactive functional groups, such as the carboxyls

in Rawhide coal, interact and tie the organic structures together. The destruction of reactive functional groups is consistent with loss of oxygen and fairly constant carbon contents during the coalification process (16). This loss of access to the structure of low-rank coals caused by pore collapse during drying has also been documented in nickel ion exchange studies of Wyodak sub-bituminous coal. When dried Wyodak coal is placed in a nickel sulfate solution, it exchanges only 35% as many nickel ions as does the native coal (17). The microscopics of drying may have major implications for future process design. In particular, if a treatment requires access to the internal organic surface of the coal, predrying low-rank coals may have an undesirable effect. More generally, the preparation, storage, and handling of coal will all affect the conversion properties and must be controlled.

NMR observations complement the heat capacity measurements because they are sensitive to short-range interactions between the individual water molecules, and they probe molecular motions on short time scales (typically 1 μs–1 ns). Fig. 7 provides one example of these observations. A broadening of the proton NMR line from water molecules in Wyodak sub-bituminous coal is observed near 180 K (14). Onset of this broadening occurs when molecular motion slows down to time scales of ≈10⁻⁶ sec from the 10⁻¹⁰ sec for molecular motion at room temperature. Broadening does not begin until ≈200 K, reflecting a much greater freedom for molecular motion than encountered in ice at such temperatures. The variation of the linewidth is continuous, giving no evidence for a phase transition associated with freezing. The shape and width of the NMR absorption below 150 K are identical to those seen for solid ice, in

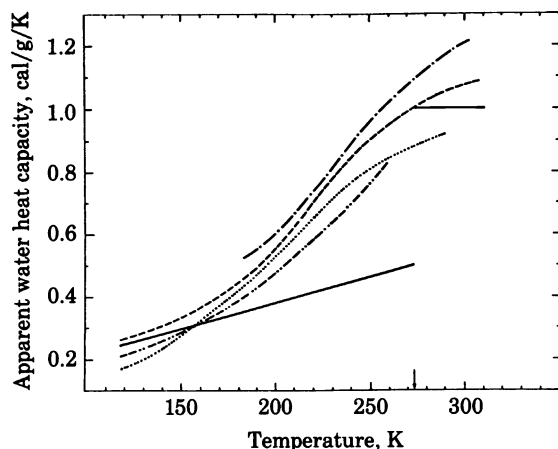


FIG. 6. Suppression of the water freezing transition is quite common in the presence of a substrate (14). —, Collagen; ---, coal; ···, porous ceramic; —·—, endellite; —, water. ↓, Melting point of ice.

Table 3. Different types of water present in raw coals of various rank

	H ₂ O content, g/100 g dry coal		
	Illinois no.6 bituminous	Rawhide sub-bituminous	Arkansas lignite
Total (as received coal)	16	48	67
At >98% relative humidity	≈0	≈3	≈15
Substrate	8	25	28
Pore	8	21	24
Effective H ₂ O surface area, m ² /g	150	480	530

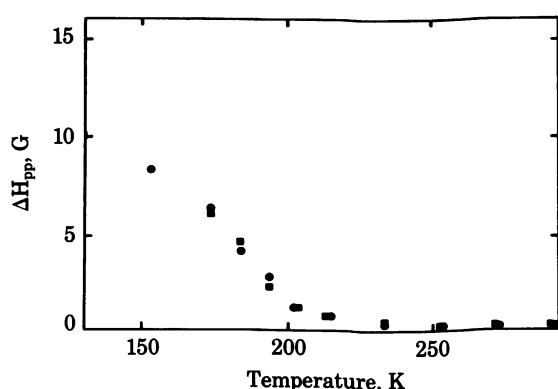


FIG. 7. Wide-line NMR linebroadening shows the high degree of water mobility below the normal freezing transition and little distinction between different water levels in the coal (15). Activation energy, $\Delta = 0.2$ eV = 2,300 K. ●, 0.30 g of H_2O per g of dry coal; ■, 0.18 g/g.

agreement with the heat capacity data at these low temperatures. The behavior of NMR linebroadening for samples nearly saturated with water and those with only half the total possible water are similar, suggesting similar microscopic motions for the substrate and pore waters. The activation energy for water diffusion, determined from the temperature dependence of the linewidth variation, is 4.6 kcal/mol, similar to values determined for diffusion of bulk water.

These heat capacity and NMR observations suggest the following picture of water residing in coal pores. On the microscopic level, the dynamics of individual molecules are similar to those encountered in bulk water and there is little evidence for substrate-related effects. This is expected, because the microscopic molecular dynamics are determined by interactions between the individual molecules. The macroscopic properties of the system are profoundly modified, with the transition shifted and broadened for water in the pores and suppressed for those water molecules in the vicinity of the organic substrate. The finite number of water molecules in the pores and molecule-substrate effects preclude the establishment of the long-range molecular order typical of bulk ice. We believe that the pore water at low temperature exists in a glassy ice form with short-range order between molecules. Recent theoretical cal-

culations suggest that small numbers of water molecules in the pores do lead to a broadening of the transition and a shift of the peak temperature of the type observed in Fig. 5 (18).

SUMMARY

This review of research shows that we are entering a period in which the microscopic chemistry and physics of complicated materials such as coal can be understood. Although these are admittedly difficult problems, the combination of chemistry, characterization, and process studies provide a much deeper insight into coal's properties. This better knowledge of coal should make a significant long-term contribution to advanced coal conversion technology.

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