The associated molecular nature of bituminous coal

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A cross-linked, three-dimensional macromolecular model has been widely accepted for the structure of coal, but there is no direct evidence to prove this model. In this paper, the conventional coal structure model is reinvestigated because of the importance of relatively strong intra- and intermolecular interactions in bituminous coal. It is reasonable to deduce that significant portions are physically associated after a study of multistep extractions, associative equilibria, the irreversibility and the dependence of coal concentration on solvent swelling, and consideration of the monophase concept. A pretreatment in coal liquefaction is also investigated on the basis of this proposed concept.

(Keywords: bituminous coal; molecular nature; macromolecular model)

Since coal is the most abundant hydrocarbon resource on earth, coal structure should be well understood for its effective utilization. Coal is a complex mixture of organic material and inorganic components. Detailed characterization of the organic material is still impossible, even with today's highly developed analytical techniques. This is primarily due to the amorphous nature of high molecular mass mixtures. The understanding of the physical structure of these materials is an important step in the study of coal structure. The extent to which coal molecules may be covalently cross-linked (model A) and/or physically associated (model B) is illustrated in *Figure 1*.

A series of reviews concerning the molecular nature of coal[1-3] has proposed a cross-linked, three-dimensional macromolecular model (model A) for organic material. This model has been widely accepted, with the framework occluding some solvent-extractable components. Wiser's[4] and Shinn's[5] models are representative examples of model A, and propose that aromatic ring systems are linked by carbon or heteroatom bridges. It is, however, this author's opinion that the evidence is indirect and there is little information to elucidate the real state of the physical structure of coal. van Krevelen[1] was probably the first to suggest that coal has a polymeric character, but the properties he mentions do not provide evidence for model A or B.

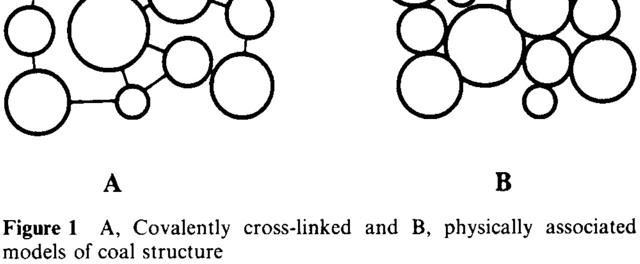
Intra- and intermolecular (secondary) interactions play an important role in model B, but differentiation between covalent bonds and the strong secondary interactions has not been thoroughly studied. Recent work by Painter *et al.*[6-8] has accounted for hydrogen bonding by use of association models in solvent swelling of the coal network, but relatively strong secondary interactions have not been considered. Our recent work[9-14] demonstrated the significance and importance of relatively strong secondary interactions in all ranks of coal. Therefore, the conventional coal structural model A needs to be reinvestigated.

In this paper, our recent results will be summarized and investigated along with relevant past work. From this analysis, it is reasonable to deduce that significant portions (far more than generally believed) of coal molecules are physically associated. To illustrate the importance of understanding coal structure in coal utilization, the preconversion of coal liquefaction will be reconsidered on the basis of the concept derived in this paper.

EXPERIMENTAL

American Chemical Society reagents and h.p.l.c.-grade solvents were used without purification. Coal samples were obtained from the Premium Sample Program at Argonne National Laboratory[15], the Pennsylvania State University Coal Bank and Exxon Research and Engineering Co. Their elemental analyses are given in *Table 1*. Coal particles of -60 to -100 mesh size were generally used. (The symbols given in *Table 1* will be used for the Argonne Premium coal samples).

Most of the experimental procedures have been reported in previous papers[9-14,16]. Soxhlet extraction was carried out under nitrogen with 2–5 g coal and 200 ml pyridine generally for 72 h. Coal residues were



A B

Figure 1 A, Covalently cross-linked and B, physically associated models of coal structure

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