

COAL: MACROMOLECULAR STRUCTURE AND REACTIVITY

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This paper will tie together results from two disparate studies of coal reactivity, studies whose only uniting feature is the reactant coal. They will be discussed in terms of a model for the macromolecular structure of coal. Two very different reactions have been chosen to illustrate the utility and appropriateness of the model under very different circumstances. Not all of the predictions made are correct, we have very far to go. The ability to make a definite prediction about coal reactivity from a model is an advance. I hope the power and utility of viewing coal as a macromolecular solid will be made apparent by the selected examples.

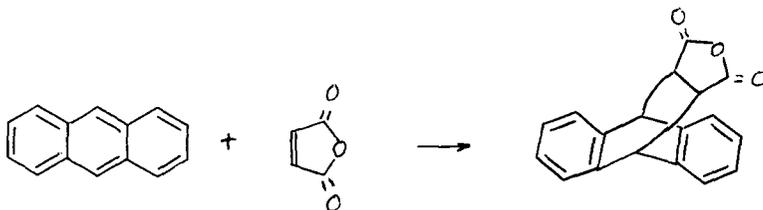
Coals are extraordinarily difficult materials to study, and, more than in most areas of science, progress is general and due to the efforts of the whole, rather than a few. Progress has been rapid recently, due in part to new ideas and approaches rising from the general realization that coals are macromolecular gels and the concepts and techniques of polymer science apply.

A tiny beginning has been made in relating coal macromolecular structure to reactivity. The importance of macromolecular structure can be made clear by a consideration of the general factors which are important in the conversion of coals to soluble materials. The overall conversion rate will be a function of the number of bonds which must be broken to produce a soluble material, some mass transport terms, and the rates at which the individual chemical bond breakings occur. The first term is a simple function of the macromolecular structure. In principal, knowledge of the macromolecular structure will lead to a reasonable understanding of mass transport rates. Systematic study of mass transport in coals is just now beginning, despite the very important role it plays in many, if not most, coal reactions. The intrinsic chemical reactivity of individual bonds or groups, the third term, is not a function of the network containing those groups. Any attempt to understand coal reactivity in a fundamental way must include a macromolecular structure model of sufficient specificity to be useful for predictions. Neither the model nor the necessary theoretical framework yet exist, but progress is being made^{1,6}. In this short paper a structural model will be presented and related to coal reactivity at both low and high temperatures. The discussion will cover important issues which we do not understand as well as a few we are beginning to understand.

The structural model is shown in Figure 1, and is for an Ill. No. 6 coal having the following composition (dmwf) $C_{100}H_{84}O_{11}S_{1.8}N_{1.4}$ and five hydroxyl groups per 100 carbon atoms. In drawing this model, we arbitrarily assumed a cluster molecular weight of 300. The extractable material, that not bonded to the network, has an average molecular weight of 900, close to experimental value for this coal⁷. The number average molecular weight between cross links (M_c) is 3000, higher than that given by our experiments⁸. There exists

evidence that the use of the Kovac model⁸ underestimates M_c . The clusters which are network branch points, which are linked to more than two other clusters, are circled. The most startling feature of the model is the large number of network active hydrogen bonds, denoted by hash marks. In this native coal, hydrogen bond cross links (branch points) exceed covalent ones by a factor of four. This value was derived from solvent swelling measurements published elsewhere.

We will first use this model to make some qualitative predictions about the rate of the low temperature diffusion controlled reaction between maleic anhydride and coal. This has been established as a Diels-Alder reaction^{9,10}. A consideration of the known reactivity of maleic anhydride in Diels-Alder reactions and current coal structural models leads to the conclusion that the reaction must be occurring between anthracene structure units and maleic anhydride. Neither benzene, naphthalene, or phenanthrene react. The linear anthracene structure reacts readily, either as anthracene itself as shown below or when this structure is imbedded in a larger polynuclear aromatic system (PNA). The evidence that the reaction is mass transport limited is: the reaction of coals is much slower than the reaction of anthracene itself, the reaction kinetics follow $t^{1/2}$, and the activation energy for the reaction in *o*-dichlorobenzene is 7.5 kcal/mole.



We anticipated that swelling the coal would increase the reaction rate. Particularly, as hydrogen bonds were broken by solvents like dioxane, the network would become more flexible and diffusion rates would increase. This did not happen as shown by the data in Table 1. We do not understand this, and plan further studies.

In other respects, the reaction seems normal. The effect of bulky groups on the reaction is to slow the rate, as illustrated by the data for fumarate esters shown in Table 2. Di-neopentyl fumarate does not undergo a Diels-Alder reaction with anthracene or with the coal.

This reaction can be used as an interesting probe of coal structure since it is limited to structures containing the anthracene nucleus. The analysis of the Bruceton coal used is 78.6% C, 5.0% H, 1.6% N, 8.3% O (diff), 1.2% S, and 5.4% mineral matter. For every 78.6 g of carbon, 18 g of maleic anhydride were added. Since a minimum of 14 carbon atoms are required for the reaction, at least 39% of this coal's carbon atoms are in reactive PNA structures. With an f (measured by Dr. Ron Pugmire, Univ. of Utah) of 0.73, a bit more than half of the aromatic carbons must be contained in reactive PNA systems. This is a startling result, and deserves both further checking and elaboration. Work on this reaction continues.

The next reaction to be discussed is pyrolysis of a lignite and a bituminous coal. Details are to be published elsewhere¹¹. We studied the emission of volatile products from coals rapidly pyrolyzed (1000 K/sec) and cooled (200 - 400 K/sec) on a wire mesh. These data were combined with measurements of the cross-link density of the chars by solvent swelling with pyridine. As shown in Fig. 2, the cross-link densities of the chars increase parallel with the loss of CO and CO₂. With no more evidence than this, we cannot say that the pyrolytic loss of the carboxyl groups leads directly to the formation of new cross-links in the coal. The data certainly are consistent with this.

The situation is very different with the bituminous coal. As shown in Figure 3, the pyridine swelling does not begin to decrease due to cross-link formation until about 2/3 of the tar formation has occurred. Cross linking occurs at a late stage of pyrolysis, as must be true if a coal is to melt and form a good metallurgical coke. The measurement of char cross-link densities makes the very different pyrolysis behavior of lignites and bituminous coals very clear and allows a quantitative comparison between them.

Coals are macromolecular solids; this has long been known. But only recently has the systematic application of classical polymer physics and chemistry techniques to coals occurred. All of the hopes we had for the power and success of these techniques have been exceeded. We are a very long way from a fundamental understanding of the relationships between coal structure and reactivity, but progress is being made and the problem can be solved.

Acknowledgements. I am grateful to the Department of Energy, the Gas Research Institute, and the Exxon Education Foundation for financial support of the research described. The names of my collaborators and students appear in the references. Their contributions have often been crucial and I could not wish for a finer group of associates.

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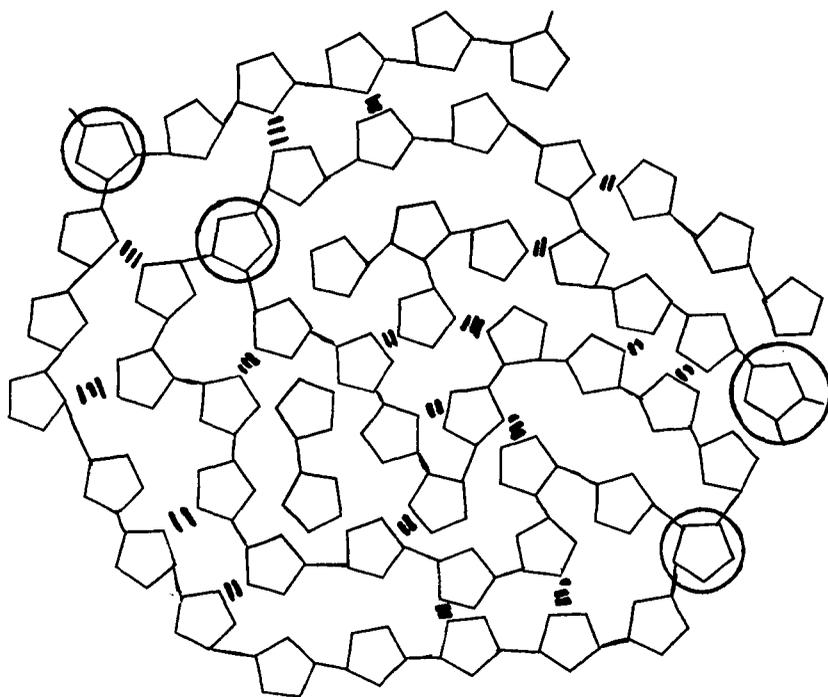


FIGURE 1. Macromolecular Structural Model for An Illinois No. 6 Coal

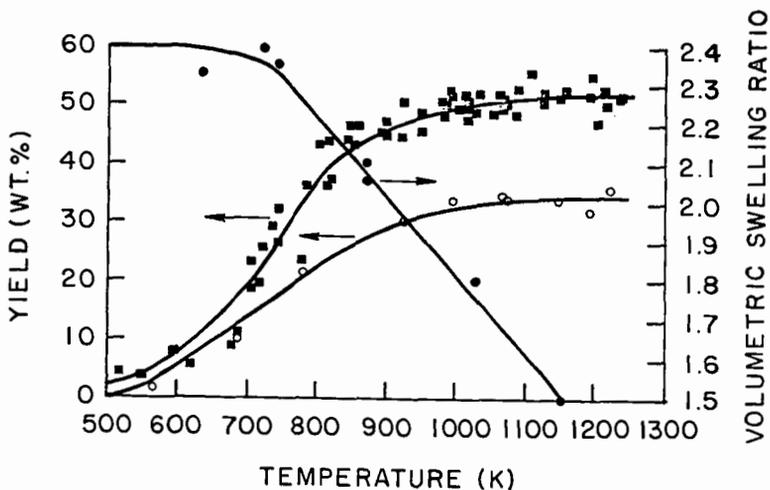


FIGURE 2. Yields of Carbon Monoxide (o), Carbon Dioxide (o), and the Ratio of Initial to Final Number Average Molecular Weights Between Crosslinks (M_0/M) in North Dakota Lignite Char

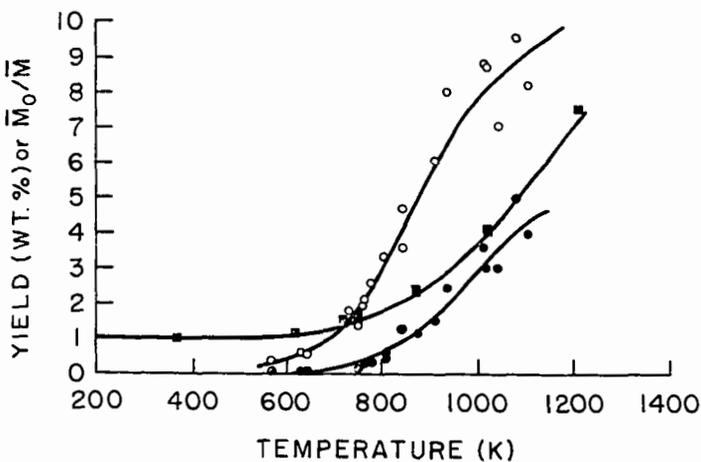


FIGURE 3. Total Volatiles Yield (), Tar Yield (o), and Char Volumetric Swelling Ratio in Pyridine (o) as a Function of Pyrolysis Peak Temperature for Bruceton Coal

TABLE 1. Influence of the solvent on the rate of addition of maleic anhydride to Bruceton coal at $90 \pm 3^\circ\text{C}$

Solvent	Slope ^a (g h ^{1/2})	Swelling ratio
1,2,4-trichlorobenzene (TCB)	0.0018	1.16
o-dichlorobenzene (oDCB)	0.0018	1.22
m-dichlorobenzene (mDCB)	0.0018	1.42
p-dichlorobenzene (pDCB)	0.0025	1.06
Nitrobenzene (ϕNO_2)	0.0016	1.56
o-xylene	0.0015	1.33
Dioxane	0.0015	1.62
Chlorobenzene	0.0017	1.43

^aSlope of a plot of mass of coal product versus \sqrt{t} (h)

TABLE 2. Ratio and extent of reaction of fumarate esters with Bruceton coal swollen with xylene at 200°C

Dineophile	Slope ($\Delta\text{g/hr}^{1/2}$, $\times 10^{-4}$)	Rel. Rate ^a
Dimethylfumarate	22	1
Diethylfumarate	25	0.95
Di-n-hexylfumarate	32	0.73
Diphenylfumarate	36	0.87
Dineopentylfumarate	0	0
Maleic Anhydride	80	5.3

^aNormalized to a moles $\text{hr}^{-1/2}$ basis. All reactions are diffusion controlled