

The Effect of Reagent Access in Coal Reactivity

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Hypothesis: The reactivity of bituminous coals under mild conditions is dominated by the accessibility of the reacting groups in the coal to reagents and not by the intrinsic reactivity of those groups. Evidence for this hypothesis will be presented. It is not conclusive evidence, but it is sufficient to warrant further exploration of this idea.

Bituminous coals contain cross linked, three dimensional macromolecular networks. Perhaps the best evidence for this comes from experiments in which the coal is swollen by solvents (1). The weight increase in several coals which have been exhaustively extracted with pyridine are shown in Table 1. These coals can be swollen to about twice their original volume by absorbing solvent. The solvent-coal interactions responsible for this inhibition are strong enough so that if the coal "molecules" were not covalently linked together, they would dissolve. The observed behavior is characteristic of a cross linked macromolecular network (2,3,4).

Coal is a highly porous, insoluble material. An attacking reagent has access to those parts of the surface of the coal which form the walls of the pores into which it can diffuse. Any solvent which expands the pore structure will enhance a coal's reactivity by increasing the surface area accessible to the reagents. One limitation on coal reactivity is the ability of reagents to penetrate the pore structure.

However, even ready penetration of the pores only gives access to the surface of the coal. For complete reaction, the reagent must diffuse into the coal network and penetrate to the bonds or groups with which it will react. It would seem that this diffusion process is likely to be very slow, and indeed may limit not only the rate of reaction but also the number of groups which ultimately react. Some examples of access limited reactions follow.

Analysis for Phenolic Hydroxyl. Maher and O'Shea (5) measured the phenolic hydroxyl content of Greta coal (DAF 82.4%C, 6.2%H, 1.7%N, 1.0%S) by titration in ethylenediamine solvent. They also extracted the coal with various solvents and measured the OH content of the extract and the residue. The data are shown in Table 2 and it is obvious that the results with the extracted coals are greater than that obtained with the whole coal. Precautions were taken to prevent oxidation and the generation of new phenolic OH groups by depolymerization seems unlikely. An increase in the accessibility of OH groups is the most reasonable explanation.

Friedel-Crafts Acylation. The Friedel-Crafts acylation of coals give products whose "solubility" increases with the size of the acyl group (6). These products are of very high (10^5 - 10^6) molecular weight (7). The proton nmr and ^{13}C nmr of octanoylated Bruceton coal are shown in Figs. 1 and 2. Peaks due to aromatic protons are absent from the proton nmr. The peaks due to the methylene α and β to the carbonyl group are broadened, while the methylene peaks at the terminal end of the chain show normal line widths. These data can be explained if acylation occurred at the coal surface and the resulting substance was solubilized, micelle like, by the interactions of the long chain with the solvent. The aromatic protons would still be in a solid environment, and their absorption would be too broad to detect. The motion of the portion of the acyl chain close to the coal surface would be hindered by close packing, giving rise to broad lines. The other end would have free motion and normal line widths as observed.

Heredy-Neuworth Depolymerization. Using currently accepted models for bituminous coal, it is clear that any reaction which cleaves the bonds between aromatic carbons and methylene groups should result in destruction of the coal and the products of low molecular weight products. The Heredy-Neuworth depolymerization is one such reaction (8,9). When applied to coal it gives mostly high molecular weight products, 80% greater than 3000. The colloidal material from a depolymerization can be further depolymerized if reacted again. The cleavage of these bonds in model compounds is not a slow reaction. These results can be explained by postulating limited access of the necessary reagents to the interior of the coal.

There are reactions which produce low molecular weight products from coals. Heat has ready access to the interior of coal, so pyrolysis would be expected to, and does, rapidly destroy the network and produce low molecular weight products. Vigorous reactions, such as oxidation, can chew their way into the coal by cutting small molecules off of the surface. This requires vigorous, unselective reactions. The attempts to use mild, selective reactions to solubilize coal lead to high molecular weight products.

If the hypothesis stated here is correct, its consequences for coal chemistry and processing will be enormous. Methods for gaining ready, rapid access to the interior of the coal network should be sought. The discovery of such methods will allow rapid, mild processing of coals. If rapid access cannot be obtained, pyrolysis may be the necessary first step of any process rapid enough to be commercially attracted.

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References

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Table 1. Swelling^a of Four Pyridine Extracted Coals with A Series of Organic Solvents.

Coal	Toluene	Ethanol	Acetone	1,4 Dioxane	Pyridine
N.D. Lignite	1.20	1.35	1.44	1.49	1.82
Wyodak	1.33	1.43	1.54	1.71	2.16
Ill. No. 6	1.44	1.41	1.54	1.83	2.18
Bruceston	1.43	1.39	1.46	1.78	2.03

a) Ratio: weight of swollen coal at equilibrium; original weight of coal.

Table 2. Sum of phenolic groups in extracts and residues Basis: 100g of d.a.f. coal: 160 milliequivalents (from ref. 5).

Solvent	Extract		Residue		Total milli-equivalents
	Weight (g)	Total acidity (m.equiv./g)	Weight (g)	Total acidity (m.equiv./g) mean	
Iso-amy1 alcohol	2.2	N.D.	97.8	1.99	>195
Dimethyl formamide	22	3.21	78	1.35	176
Diethylamine	4.1	1.73*	95.9	1.86	185
Pyridine	16	2.51	84	1.75	187
Aniline	15	2.82	85	1.53	172
Ethylenediamine	23	2.88	77	1.24	161
Chloroform	4.7	0.92	95.3	3.03	293
Dichloromethane	2.0	0.30	98	2.32	228

* Approximate figure only, obtained from stirred extractor experiment where yield was 3.5 per cent.

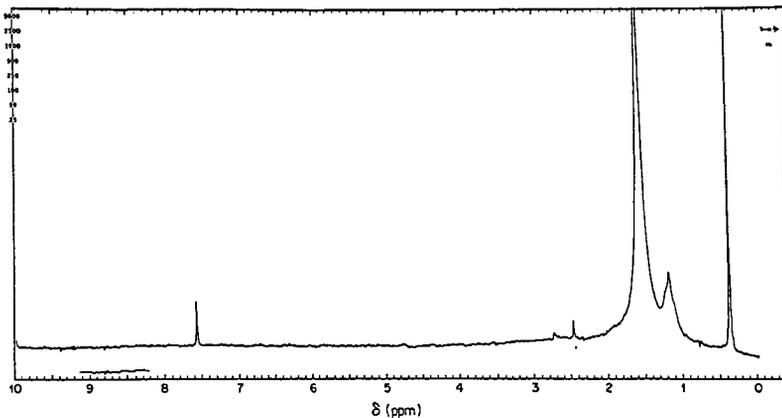


Fig. 1. Proton NMR Spectrum of Octanolyated Bruceton Coal in CCl_3 .

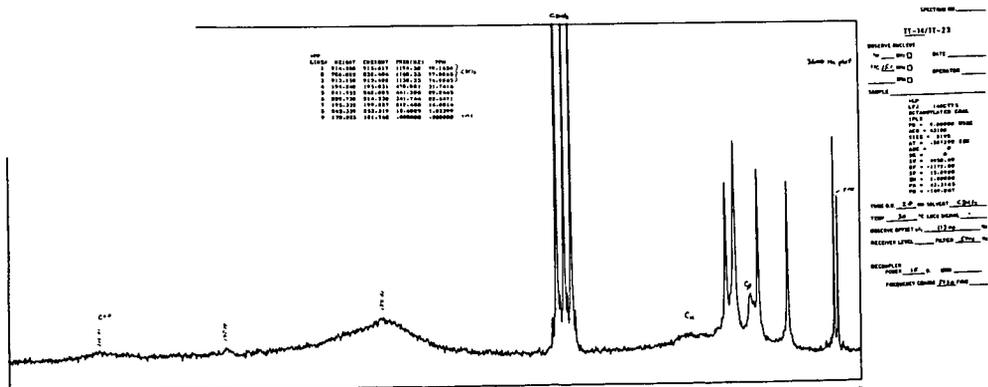


Figure 2. ^{13}C nmr Spectrum of Octanolyated Bruceton Coal (CDCl_3 solvent).

