THE CHEMISTRY OF COAL LIQUEFACTION

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This progress report presents a working hypothesis for our study of coal liquefaction with Illinois No. 6 coal and indicates the kinds of evidence on which our hypothesis is based and which are desirable for its substantiation.

Coal is considered to be mostly a crosslinked high polymer with condensed aromatic aggregates that are difficult to cleave and connecting links that are relatively easy to cleave (scissile bonds). A range of soluble materials is mixed with the predominantly insoluble material. Associated with these primary bond relations are significant interactions between phenolic groups and pyridine-type bases (1). Thus, relatively small polyfunctional molecules, even if not incorporated in the network, need complexing solvents to dissolve them. Our 1976 Coal Workshop paper related the molecular weight, and presumably the functionality, of the fractions that would dissolve in certain solvents (2), as revised and summarized in Table I. Recent experiments indicate that ethylene diamine will extract from coal much more and higher molecular weight materials at 120°C. An effort to relate the amount of soluble material extracted by solvents to the amount of solvent used and to the extent of swelling of the undissolved residue at 100° is in progress.

The extracted coal in the upper series of fractions in Table I is a preferred material for liquefaction studies, uncomplicated by admixed soluble materials. Progress in breaking bonds can be followed by formation of soluble materials and probably also by increased swelling of the insoluble material in a chosen solvent. The pyridine-soluble, toluene-insoluble fractions of both coal extract and SRC are preferred materials for following the upgrading of syncrudes. They have fairly high molecular weights and rather narrow molecular weight distributions. Both the extracted coal and the pyridine-soluble fraction have elementary analyses (dry, mineral free) and nuclear magnetic resonance (nmr) spectra (3) that are very similar; they apparently differ significantly only in molecular size.

Table I

Comparison of Fractions from Extraction and Solvent-Refining of Illinois No. 6 Coal

		Fractions				
	Insoluble extracted Coal	Soluble in Insoluble in	Pyridine Toluene	Toluene Hexane	Hexane	
Coal (78.6% C, 5.1% H, 12.4% O) — Pyridine extraction	78.0	% C	79.5	83.0	84.0	More O
	4.8	% H	5.4	6.3	8.7	
	12.6	% O	10.8	7.3	5.0	
		Increasing C + H, decreasing O →				
Coal — Solvent refining	All soluble	% C	86.1	87.4	89.9	More C + H
		% H	4.9	6.1	6.6	
		% O	5.7	4.0	2.0	
	Common designations		Preasphaltenes, asphaltols, polar Compounds	Asphaltenes	Oils	
	Average moleculer weight		~ 1200	~ 600	~ 300	

Figure 1 summarizes our data on retention times in gel permeation chromatography (gpc) as a function of average molecular weights by vapor phase osmometry (vpo) of fractions derived from both coal extract and the solvent-refined product from the same coal. Even though the SRC fractions contain about 10% more oxygen and 10% less carbon than the extract fractions, the points are well fitted by a single curve. Individual gpc curves show that fractionations into pyridine, toluene, and hexane-soluble fractions give products with fairly narrow and symmetrical gpc peaks. Two pairs of points in Figure 1 correspond to double peaks with special fractions.

Listed below are all the scissile bonds that we now think are important in the liquefaction of bituminous coal under common operating conditions. The same types of bonds are probably involved in scissions under strongly acidic conditions, as with phenol plus boron trifluoride etherate.

$$\mathrm{Ar\text{-}CH_2Ar}$$
$$\mathrm{Ar\text{-}(CH_2)_n Ar}$$
$$\left.\begin{array}{l}\mathrm{Ar\text{-}OAr}\\ \mathrm{R\text{-}OAr}\\ \mathrm{R\text{-}OR}\end{array}\right\}\ \text{and S analogs}$$

We now consider current high-temperature, high-pressure liquefaction processes in terms of Table I and the scissile bonds listed above. The solvent-refining process consists mostly of conversion of insoluble coal to the pyridine-soluble, toluene-insoluble fraction of SRC. The net result approximates loss of some hydrogen and more oxygen, formation of a more aromatic aggregate, and some bond breakage. Because the solubility-molecular weight relations are the same in the extract and SRC series (2), the net phenol-base relations have changed little, and so the required bond breakage appears to be associated with net loss of ethers and some bibenzyl type bonds. The conversion of SRC to "oil" or distillate requires a large hydrogen input and a considerable reduction in molecular weight and heteroatom content. Part of the hydrogen requirement is to cap the fragments left when heteroatoms are removed as water, H_2S, and NH_3, but much of the hydrogen requirement may be to reduce condensed aromatic systems that cannot be cleaved to partially hydroaromatic systems that can be cleaved, especially by reforming catalysts.

Our working hypothesis leads us to suggest cheaper alternative routes to liquefaction. First, there are indications that ether clevage alone, without removal of oxygen or addition of hydrogen, can render coal soluble (4). The alkylation requirement now seems to be associated more with reducing phenol-base interactions (1,2) by O-alkylation (5) than with C-alkylation (4). There should be lower-temperature, low-pressure routes for ether cleavage, as by acids and bases, as well as the alkali metal route. Whether ether cleavage alone will take our coal to preasphaltenes, alphaltenes, or oils, or some of each (Table I) is under investigation (5).

Oxidations of coal models have shown that hydroaromatic rings are likely to be attacked first in free radical chain oxidations. We have therefore tried to dehydrogenate such rings to aromatic rings with two objectives, to direct the oxidation to the scissile bonds and to recover hydrogen for subsequent processing. Our first experiment with ethylene as hydrogen acceptor has given some promise of success.

We are also studying the possibility that selective oxidation will cleave most of the scissile bonds listed above. Oxidation of diarylmethanes should give ketones that can be converted to esters with a peracid. Longer aliphatic chains between aryl groups should be oxidized to pairs of acids. The alkyl ethers should be oxidized to esters. Hydrolysis of esters should then result in cleavage of scissile bonds. Mild oxidations of extracted coal with subsequent base hydrolysis have indeed given marked increases in soluble materials. Oxidation and nmr studies on soluble fractions of coal extract and SRC indicate that the extract is relatively rich in benzyl hydrogen atoms and that these are lost perferentially in oxidation; however, the SRC fractions that have the most aromatic hydrogen are most reactive and this kind of hydrogen is lost preferentially in oxidation.

We have also examined the use of commercial household bleach, $\sim$ 0.8 M sodium hypochlorite, as an oxidizing agent at 30°, where extracted coal is very reactive. By stepwise oxidation, with removal of acids as they form, we have recovered 76% of the carbon reacting as carboxylic acids, mostly black and soluble only in aqueous sodium bicarbonate, with smaller proportions of water-soluble polybasic acids. The susceptibility of some, but not all, substrates to oxidation by sodium hypochlorite is pH dependent.

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References and Notes:

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(3) Kindly supplied by Prof. Alex Pines and Dr. D. E. Wemmer of the University of California, Berkeley.

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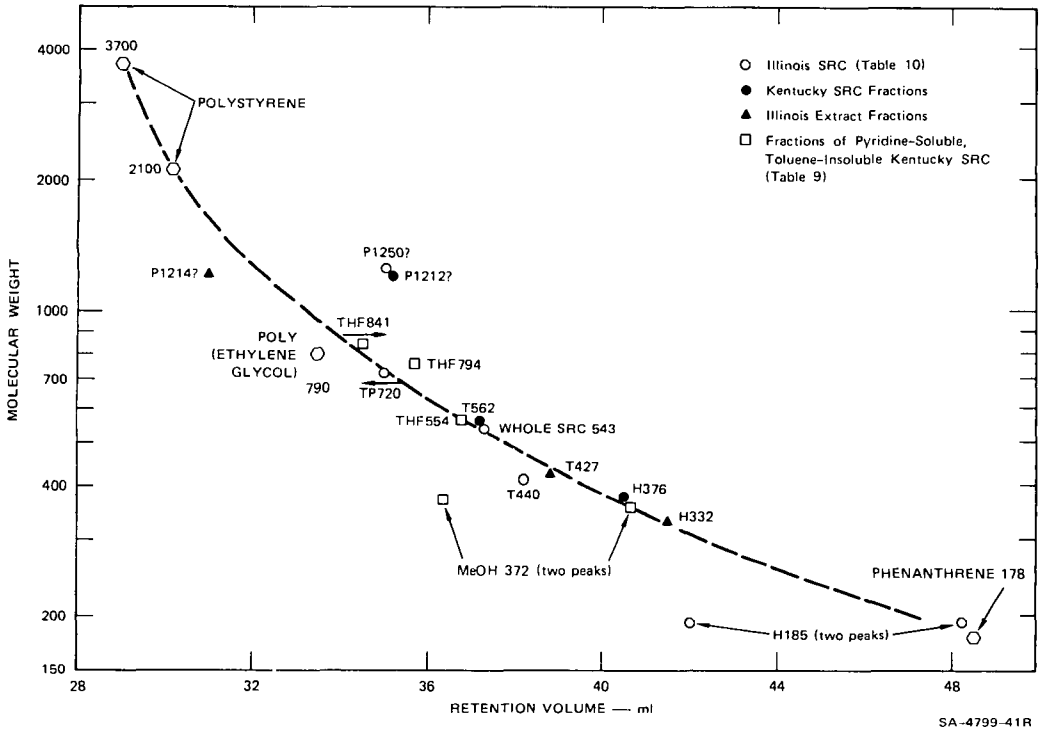

FIGURE 1 MOLECULAR WEIGHTS AND GPC RETENTION VOLUMES FOR FRACTIONS OF EXTRACTS AND SRCs OF ILLINOIS AND KENTUCKY COALS

The letter associated with a point indicates whether the fraction was soluble in pyridine, toluene, or hexane. The number is the $\bar{M}_n$ measured by VPO.