SHORT TIME REACTION PRODUCTS OF COAL LIQUEFACTION AND THEIR RELEVANCE TO THE STRUCTURE OF COAL

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INTRODUCTION

The subject of the chemical structure of coal is almost as controversial as it is complex. The complexity of this problem is partially due to the lack of homogeneity and solubility of coals, as well as to the large variety of organic rocks labeled as coals.

A fundamental question is whether we can even consider a chemical structure for a specific coal. Experimental data indicates that there are similarities in the physical properties of some groups of coal and in their behavior toward different chemical reactions; this at least allows us to speak of elements of structure in coal.

Traditionally, both physical and chemical data have been used to study coals. Both kinds of methods require a large amount of experimental work and highly specialized competence in the understanding and application of the method itself. This makes it quite difficult for any individual to master all the aspects of this kind of research. Fully aware of this reality, I will try to present some of our present concepts on coal structure. These concepts are based on data available in the literature as well as from our own experiments. The main idea is to use as much information as possible, which has been obtained by methods as different as possible, and to question all the data, expecially those which can be proven by a single method only. One should mention that previous work by Given [1] and Wiser [2] was based on a similar approach. In this paper we will discuss some new data, which was not available to them when they proposed several representative coal average structures.

RESULTS AND DISCUSSION

The first step in the chemical analysis of a coal is the determination of its moisture-ash-free elemental composition. For example, for two coals which have been extensively studied for liquefaction behavior the elemental composition, calculated for 100 atoms is:

Coal	Elemental Composition
Illinois #6 (Monterey)	$C_{50.8}H_{43}O_{4.8}S_{0.8}N_{0.6}$
Wyodak	$C_{48.4}H_{42.4}O_{8.6}S_{0.07}N_{0.5}$

A look at the above data gives several hints about coal structure:

1. For each 100 atoms in coal over 90 are atoms of carbon and hydrogen. Stoichiometry dictates that the majority of the chemical bonds in coal will be carbon-carbon and carbon-hydrogen.

2. Oxygen is the main heteroatom and understanding its chemistry during any coal transformation is essential. For each reaction performed for the usual purpose of removing sulfur and nitrogen, understanding what happens to oxygen is very important, as well as how its reactivity affects those of N and S functions.

Looking at possible coal structures, two aspects are relevant:

a) the chemical functions in which the heteroatoms appear,

b) the carbon skeleton of the rest.

The most important chemical functionalities in coal are [3]: for oxygen: phenols, ethers, carboxylic acids, quinones; for nitrogen: pyrrole and pyridine derivatives.

These functionalities can be present in larger or smaller relative amounts in a given coal, but, qualitatively, all the coals contain the same kind of chemical functions.

The carbon skeleton of coal is perhaps the most controversial aspect of the research on coal structure. Three major questions are of interest in this field:

1. What is the percentage of aromatic carbons?

2. How condensed are the aromatic ring structures?

3. What is the carbon skeleton of the aliphatic portion of the coal?

The percentage of aromatic carbon can now be determined by solid-state ^{13}C-NMR. Alex Pines from the University of California at Berkeley made the quantitative measurements for the coals discussed in this paper.

To answer the other two questions related to the carbon skeleton, several approaches can be taken.

One of them is a careful structure determination of the short time reaction products of the thermal liquefaction of coal [4]. During the last four years we worked on a research project supported in part by the Electric Power Research Institute. One of the purposes of this project was to establish the chemical composition of short contact time thermal liquefaction products (including structure). We will now discuss how this data can be used to obtain information about coal structure.

In the short time of 2-5 minutes, coal dissolves in the presence of an H-donor; in the absence of an added catalyst only a few bonds are actually broken. Work at Mobil [4], Exxon [5] and Oakridge National Laboratory [6] indicates that none of the following reactions take place:

- Hydrogenation of aromatic polycyclic hydrocarbons,
- Destruction or formation of polycyclic saturated structures.

A corollary of this is: if these polyaromatic or polycyclic saturated structures are present in coal, they should be identified in the thermal liquefaction products.

Many of the chemical functionalities are also stable in these conditions, especially the O,S,N heterocyclic structures. Water formation by phenol dehydrogenation is also minimal. We found that in coal conversions even at long reaction times (up to 90 minutes) in the absence of an added catalyst, the -OH bonded to a monoaromatic ring is stable. In the same conditions, dehydroxylation of naphthenic phenols does occur [7].

The degree of ring condensation of the aromatic part can be semi-quantitatively determined in coal liquids [4]. It has been found that in the short time liquefaction products, the majority of the aromatic rings are as in benzene and naphthalene. These data are consistent with the data obtained by Hayatsu, Scott, Moore and Studier [9], using an oxidative method and with the uv-visible spectroscopy data reported by Friedel and Queiser [10]. I conclude then that in the subbituminous and bituminous coals studied by us and others, the aromatic carbons are not present in significant amounts as highly condensed rings.

Concerning the carbon skeleton of the aliphatic portion, there are no methods for direct identification. However, for a given formula if the total number of C and H is known, as well as the percentages of aromatic and aliphatic carbon and hydrogen a possible structure for the aliphatic part may be inferred.

Possible average chemical structures present in short time reaction products have been determined by a methodology we have already reported [4,8]. Fractions with average molecular structures as in Figures 1-4 are consistent with the experimental data.

As shown in Figure 1 for a given molecular formula, there is a relationship between the degree of aromatic ring condensation and the degree of aliphatic ring condensation.

The relative number of aliphatic hydrogens and carbons is consistent with the presence of some polycondensed aliphatic structures. The number of the polycondensed aliphatic rings seems quite high in certain Wyodak coal liquids obtained in a thermal process at short reaction time (Figure 4). It is likely that such structures are also present in Wyodak coal. Other experimental data are also in favor of this explanation. For example, the oxidative method used by Deno et al. [11], gives selective oxidation of aromatic structures only if polycondensed aliphatic rings are not present. The results obtained by this method for Wyodak coal are nonreproducible and the oxidation products are difficult to analyze.

Another approach is a direct calculation of the possible number of the aliphatic rings. The calculation is based on the elemental analysis of the coal and the percent of aromatic carbon obtained by ^{13}C-NMR in solid state [4]. Based on this method, the Wyodak coal used in the liquefaction study to obtain data as in Figure 2 contained 44-50% aromatic carbon. This would be consistent with 2 to 8 aliphatic rings for 100 atoms of carbon. We should note that some other samples of Wyodak coal for which we measured the aromatic content were somewhat more aromatic (50-70% aromatic carbon).

The data we presented are based on the similarity of the elements of structure in coal and in the short contact time, noncatalytic liquefaction products. These elements of structure could be bound together with low energy thermally labile bonds. As described in the literature [4,6], these weak bonds could be:

$$ArCH_2\text{——}XAr \text{ bonds } (X = O,S,C\text{-}Ar).$$

An important practical consequence of knowing the coal structure and the structure of its short time liquefaction products is the understanding of the possible limits of reduction of H-consumption for the liquefaction of a particular coal. In Figure 5 we make such correlations. This aspect will be discussed more fully in the future.

ACKNOWLEDGMENTS

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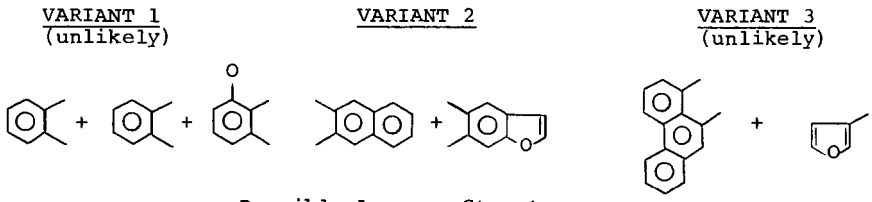
General Formula $C_{31}H_{27}O_2$

Aromatic Moiety $C_{18}H_{10-11}$ (^{1}H-NMR, ^{13}C-NMR)

Aromatic Structures Considered



Possible Average Structures

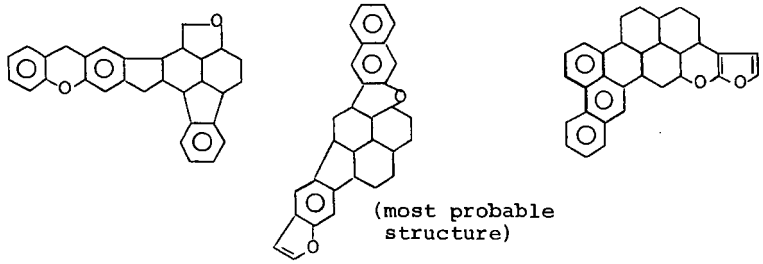


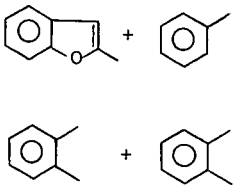
Figure 1: Possible Average Structure for a Short Contact Time Fraction SESC-3 of Monterey Coal.

General Formula $C_{43}H_{38}O_2$

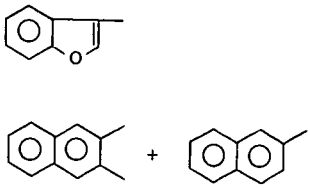
Aromatic Moiety $C_{26}H_{18}$ (^{1}H-NMR, ^{13}C-NMR)

Aromatic Structures Considered:

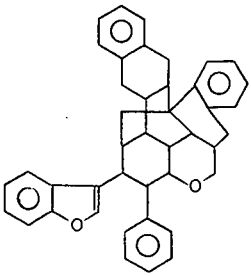
VARIANT 1



VARIANT 2



Possible Average Structures:



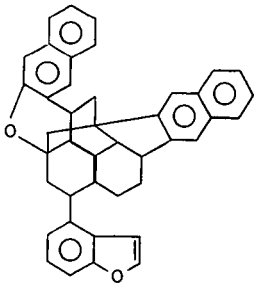


Figure 2: Possible Average Structures for Wyodak SESC-3 Short Contact Time SRC

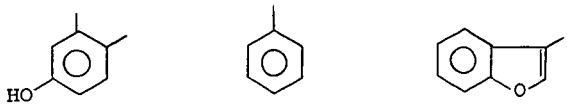
Figure 3: Fraction SESC-4 Monterey Coal Short Contact Time SRC

$C_{34}H_{33}O_{2.55}H_{0.3}S_{0.4}$

% Aromatic C = 59

% Aromatic H = 43

Aromatic Part $C_{20}H_{14}$

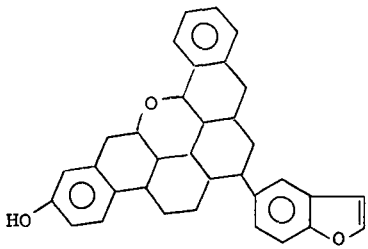


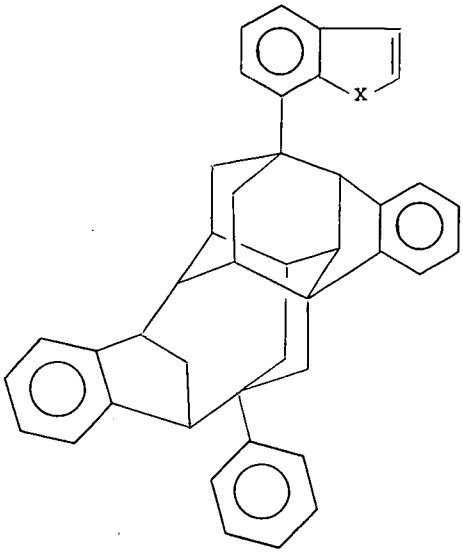
Aliphatic Part $C_{14}H_{19}$

1 Aliphatic Ether + 4 Substitutents

$C_{14}H_{19} + 2 + 4 = C_{14}H_{25}$

$C_{14}H_{26}$ -- 3 Condensed Aliphatic Rings





Calculated Based on Experimental Data:

$C_{43}H_{36}NO_2$ Av. MW = 600

Aromatic $C_{27}H_{18-19}$ (^{1}H-NMR, ^{13}C-NMR) In formula:

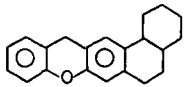
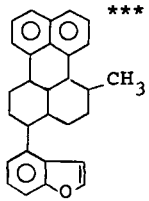
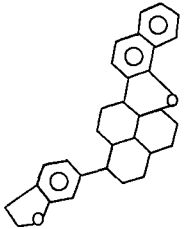
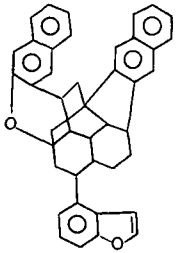
(62% Aromatic C, 52% Aromatic H) $C_{26}H_{18}$

Benzylic (2-3 ppm) C_{16} H_{10} H_3

Aliphatic H_7 C_{16} H? H_{18}

Figure 4: Average Carbon Skeleton Formula for Wyodak SRC

Figure 5: Comparison of Structures and Hydrogen Consumption for Four Coals

Coal		Kentucky	Hiawatha	Monterey	Wyodak
Composition		$C_{100}H_{82}N_{1.7}O_{9.4}$	$C_{100}H_{84}N_2O_{9.5}$	$C_{100}H_{88}N_{1.6}O_{13.2}S_{1.74}$	$C_{100}H_{86}NO_{18}$
No. polycondensed saturated rings/100C	Coal	4		6	10
	SESC-3 SCT*	2		4	5
Structure SESC-3 SCT-SRC			*** 		
g H consumed/ 100g coal during liquefaction (Normalized to 100% conversion)	SCT	0.43		0.63	0.89
	LCT**	0.96		2.03	2.80

*SCT = Short Contact Time <2 min.

**LCT = Long Contact Time >30 min.

***Ca. 30 min. contact time.