

CHANGES IN ORGANIC OXYGEN CONTENTS OF ILLINOIS #6 COAL DURING COAL LIQUEFACTION

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INTRODUCTION

The initial stage of direct coal liquefaction is generally presumed to involve the cleavage of the weak bonds in coal. While these weak bonds have not been identified, it appeared possible that they are ether oxygen bonds, and probably benzylic ether bonds because of their low bond strength, and the low activation energies observed in coal liquefaction (1). This view has been strengthened by the observation that coal liquefaction products frequently contain more phenolic components than do the coals from which they were derived (2), suggesting the cleavage of ethers to form phenols. To check this hypothesis, it would be of interest to follow the oxygen content of coal at very low liquefaction conversions, even before much of the coal actually becomes liquid. To do this requires a liquefaction reactor system capable of sampling at very short contact times and low conversions. This system must be such that temperatures and pressures are carefully controlled, and reaction times and reaction time distributions are known. Such a liquefaction reactor has been constructed in our laboratory (3). A preliminary report of the aromaticity of such low conversion products have already been reported (4). In this paper, we present a preliminary report on the total organic oxygen and organic oxygen species in these low conversion solid products.

EXPERIMENTAL

Reactor and Sampling System. The reactor system used is a 1 liter CSTR (continuous stirred tank reactor) described previously (3). A constant flow of tetralin (7 liters/hour) is maintained in a 900 psig nitrogen atmosphere (450 sccm nitrogen) at a temperature of 390°C. 50 gram charges of coal in a tetralin slurry (1:2 coal to solvent) are injected through a rupture disk almost instantaneously by diverting solvent into the charging bomb. Product samples taken in an automated sampling manifold (in this study at 2, 23, 55, 87, 119, and 151 seconds) after injection are quenched to 150°C with a countercurrent water heat exchanger. The system was tested with samples of dibenzylether to check the behavior of a compound with well-known kinetics in the system (5).

Sample Work-Up. The solids were filtered and washed with methylene chloride at room temperature, to remove residual tetralin and coal liquids, and dried in a vacuum oven.

Conversion. Conversion of the coal was determined by measuring the low-temperature ash content of the solid residue and comparing it to that of the unreacted coal (6). A low-temperature ashier (LFE Corporation, LTA-302) was operated at 100 watts. The oxygen flow rate was kept at 100 cc/min. Samples were ashed to constant weight.

Organic Oxygen Content. Fast neutron activation analysis (FNAA) was used to determine the oxygen content of the dried reactor sample and the derived low temperature ash. The total

organic oxygen content was determined by correcting the FNAA value of the dried reactor sample for the oxygen content of the mineral matter in the ash (7,8).

Organic Oxygen Speciation. The organic oxygen species (carboxyl, hydroxyl and carbonyl) in the dried reactor samples were determined by the chemical methods of Blom and Schafer (9,10). The organic ether contents of the samples were determined by the difference of the total organic oxygen by FNAA and the oxygen species determined by the chemical methods mentioned above.

Coal Sample. The coal studied was Illinois #6 obtained from AMOCO Corporation. The entire sample was finer than 200 mesh. The analysis of this coal is summarized in Table 1.

RESULTS AND DISCUSSION

The changes in the solid coal at various reaction times are shown in Table 2.

It is apparent from the kinetics of coal conversion (Fig. 1) that a portion of the coal is liquefied more rapidly than the bulk of the coal. That this is not due to the conversion of a particularly reactive maceral is shown by the petrographic analysis summarized in Table 3. Fusinite and semifusinite are generally less reactive than vitrinite (11).

Moreover, these differences are not likely due to particle size effect since the entire sample was extremely fine. In short, a portion of the vitrinite appears to be more reactive than other parts of the vitrinite.

The data gathered thus far suggest that only a relatively small change in the total organic oxygen content occurred (perhaps 10%), even though up to 20% of the coal went into solution. The carboxyl or carbonyl contents of the solid coal are very low to begin with and show little or no change. On the other hand, the hydroxyl content dropped significantly (30-35%) and the ether groups, determined by difference, therefore increased. The explanation for the change in hydroxyl is not clear at this point. However, these results are consistent with the condensation of phenolic groups within the coal to form furane type ring structures (12).

SUMMARY AND CONCLUSIONS

Previous NMR results (4) and the present experiments show clearly that chemical changes occur in solid coal before it becomes a liquid. Further and more extensive measurements will be required before the details of these changes can be resolved. These experiments also show significant conversion of solid to liquid 390°C even at very short contact times. If the formation of these liquid products occurs by cleavage of benzyl ether bonds, they must have occurred in components of the coal having quite different reactivities than the rest of the coal, and to represent only a small proportion of the original ether groups present.

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Table 1. Elemental Analysis of Illinois #6 Coal Used.

Carbon	67.18	
Hydrogen	5.00	
Nitrogen	0.98	
Sulfur	3.63	
Chlorine	0.19	
Oxygen (by diff)	12.34	
Ash (ASTM D3174)	10.68	(High Temperature)

Table 2. Total Organic Oxygen Content and Oxygen Functional Groups in the Coal Liquefaction Residues as a Function of Reaction Time at 390°C.

Reaction Time (sec)	0	23	55	87	119	155
% Conversion	0	9.5	16.4	19.5	17.6	20.1
% Organic Oxygen	10.5	10.0	9.6	9.1	10.3	
% Oxygen as Hydroxyl	7.5	5.3		4.7		
% Oxygen as Carboxyl	0.6	0.4		.5	0.65	
% Oxygen as Carbonyl	0.6	0.9		0.6	0.7	
% Oxygen as Ether	2.1	3.3		3.4		

Table 3. Petrographic Analysis of Illinois #6 (AMOCO)

maceral	Volume %	
	Southern Ill. Univ.	Argonne National Laboratory
Vitrinite	86	85
Semifusinite	10.4	10
Fusinite	2.0	
Liptinite	1.6	5

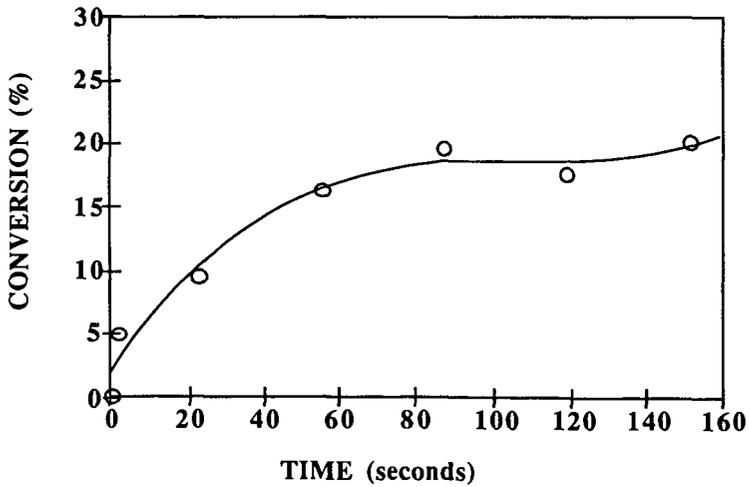


Figure 1. Conversion vs. Time