

## **<sup>13</sup>C NMR SPECTROSCOPIC STUDIES OF ILLINOIS #6 COAL AND THE PRODUCTS OF ITS LIQUEFACTION**

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### **INTRODUCTION**

The direct liquefaction of coal involves the cleavage of a variety of bonds, both covalent and otherwise, having a wide range of activation energies.<sup>1,2</sup> The weaker bonds of lower activation energy are expected to break first, forming somewhat different products than are formed later in the process. As the coal becomes liquefied, the liquid products are also subject to further reaction. A practical application of these concepts is the observation that higher yields of liquids are obtained when the liquefaction process is carried out in two or more stages under somewhat different conditions.<sup>3</sup> While the specific bonds that are first broken is still not known, examination of the process at very low conversions even before the coal has become a liquid should be of great interest. To do this, one requires a sampling system capable of providing samples at very short, well-defined reaction times (low conversions) of less than one minute to perhaps 5 to 15 minutes with mass and heat transfer not limiting and temperature and residence times accurately known. It is to report the preliminary results of such a study using solid-state NMR spectroscopy that this paper is presented.

### **EXPERIMENTAL**

*Reactor and sampling system.* The system selected for study is a 1 liter CSTR (continuous stirred tank reactor) [Fig. 1] with a constant flow of tetralin (7 liters/hour) as a hydrogen-donor solvent in a 900psig nitrogen atmosphere (450 sccm nitrogen) at a selected temperature (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 the pressurized solvent into the charging bomb. Isothermal and isobaric conditions are achieved within 20s after injection. Product samples taken in an automated sampling manifold at 2, 23, 55, 87, 119, and 155s after injection are quenched to

150°C with a countercurrent water heat exchanger. The system was tested with samples of dibenzylether (with the inert biphenyl run as a blank) to check the behavior of a compound with well-known kinetics in the system and to determine the distribution of residence times. More details about the reactor system can be found in another paper.<sup>4</sup>

*Sample work-up.* The solids were filtered and washed with methylene chloride and dried in a vacuum oven. The liquefaction products were placed in a rotary evaporator to remove tetralin and lower-boiling products. The light fraction was analyzed by GC/MS and the heavy fraction by NMR spectroscopy.

*Ash measurements.* 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. A low-temperature asher [LFE Corporation, LTA-302] was operated around 75-100 watts. The oxygen flow rate was kept at 100 cc/min.

*NMR spectroscopic experiments.* Residual solids were analyzed by variable-contact-time solid-state <sup>13</sup>C CPMAS NMR spectroscopy,<sup>5</sup> with a Chemagnetics m100S spectrometer operating at 25.1 MHz for carbon. Samples were kept in Kel-F<sup>®</sup> spinners to avoid spurious resonances from spinner material. Typical spinning speeds were about 3 kHz. The acquisition time was 50 ms with a <sup>1</sup>H 90° pulse width of 6.5 μs and a pulse delay of 1 s. Carbon aromaticities were derived by fitting integrated signal intensities for the aliphatic and aromatic carbon bands to the magnetization-recovery equation.<sup>6</sup> We checked this procedure on known model compounds (hexamethylbenzene, adamantane and high-molecular-weight polystyrene), and in each case found that we could determine the relative fraction of intensity in one NMR peak to within ±0.01 of the known stoichiometric value. The Bloch-decay experiments were done with pulse delays of 5 s, 20 s and 120 s.

*ESR experiments.* ESR spectra were recorded on a Varian E-109 spectrometer at 9.1 GHz with 100 kHz modulation. All spectra were recorded at ambient temperature (295 ± 2 K) and DPPH was used as an external spin standard.

## RESULTS

All of the experiments reported here were carried out on an Illinois #6 coal obtained from AMOCO Corporation.

One point of concern in measurements with NMR spectroscopy of solids is that the presence of paramagnetic centers may render some of the carbon NMR-invisible.<sup>6</sup> If that process affected one carbon type more than another, aromaticities determined with NMR techniques could be skewed so that they do not reflect actual changes in the carbon, but rather the increase in paramagnetic centers. To address this point, we determined the paramagnetic concentrations in a set of residual solids as a function of residence time, as well as the aromaticity. These data are plotted against each other in Figure 2. As can be seen, the concentration of paramagnetic centers did change by more than a factor of four with processing. [The spin density is reported as the ratio of that in the residue to that of the unprocessed Illinois #6 coal.] The comparison of the <sup>13</sup>C-derived aromatic fractions with the spin densities shows that there is very little, if any, correlation between these two variables. We assume,

therefore, that for this system the changes in aromaticity with residence time are not attributable to changes in paramagnetic concentrations.

Another issue regarding quantitation is the contention that Bloch-decay experiments give reliably quantitative information on the aromaticity of coal as compared to the variable-contact-time CPMAS experiments. When a Bloch-decay experiment was performed with a pulse delay of 20 s, the aromaticity value obtained was 0.77, whereas with a pulse delay of 120 s, the aromaticity value obtained was 0.66. The larger relative aromaticity value obtained in the experiment with a shorter pulse delay may be due to insufficient aromatic carbon nuclear relaxation toward equilibrium magnetization. The value of 0.66 is within experimental error, the same value found by fitting the entire build-up and decay curve in a CPMAS experiment.

The  $f_a$  values for Illinois #6 and the residual solids obtained upon liquefaction are given in Fig. 3 (as determined by fitted carbon magnetization curves) as a function of residence time. Conversions are reported as a function of residence time in Table 1.<sup>7</sup> The graph in Fig. 3 is roughly divided into three regions: (a) a very early, almost instantaneous, decrease in aromatic fraction, (b) an intermediate regime in which the aromatic fraction increases and (c) a regime in which the aromatic fraction again decreases with time. The initial sharp decrease in aromaticity (after a residence time of only 2s) may be attributed to the removal of small aromatic moieties not covalently bound to the coal structure. An increase in the number of condensed aromatic protons in the liquid phase, as determined by NMR, (Fig. 4) is consistent with these results. The light fraction of the liquid products was found by GC/MS to contain only tetralin and its degradation products, to any measureable degree. An explanation for the intermediate regime, in which the aromatic fraction of the solid increases, is not clear. Aliphatic side chains may be removed<sup>8</sup> or internal transfers of protons to liquefying fragments<sup>9</sup> may produce an increase in aromaticity of the solid material. At residence times greater than about 2 minutes, the aromaticity of the residual solids is again seen to decrease. This decrease in aromaticity is probably due to hydrogen transfer from tetralin to the aromatic structures as the dominant process.<sup>10</sup>

## CONCLUSIONS

Preliminary coal liquefaction experiments in a specially designed CSTR using NMR spectroscopy of the residual solid and the liquid products show that the kinetics of this process are very complex. There are at least three regimes that can be distinguished, with several different processes contributing to the overall process. These are readily distinguished by their effects on the aromaticity as determined by NMR techniques. Such processes as the flash desorption of small aromatics not covalently bonded to the framework, disruption of the coal with release of aliphatic material, proton transfer within the coal and from tetralin to the coal all presumably contribute to the observed changes.

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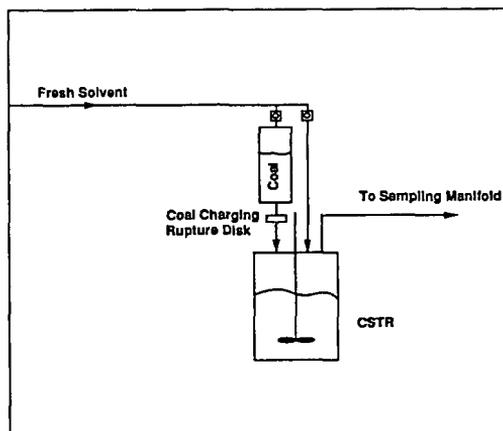


Figure 1 Schematic diagram of the CSTR.

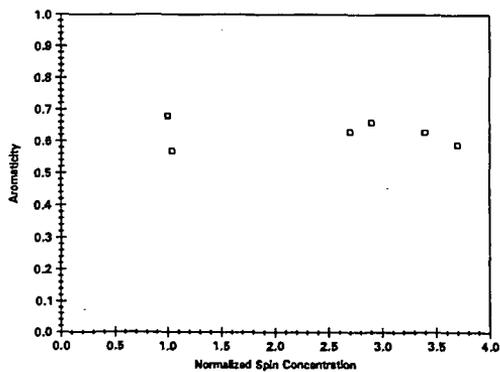


Figure 2 Aromaticity versus spin concentration for several solid residues.

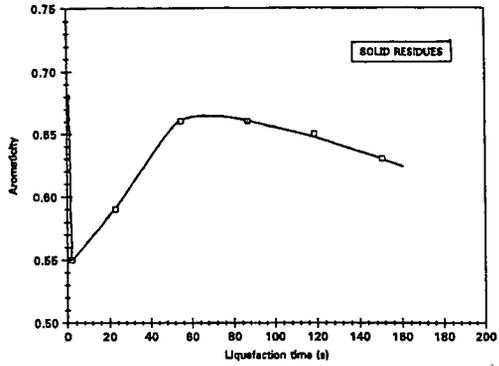


Figure 3 Aromaticity of solid residues as a function of liquefaction time.

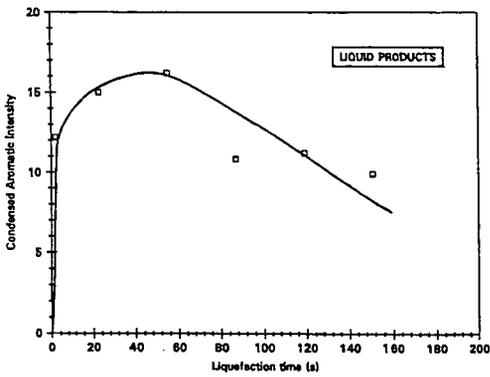


Figure 4 Aromaticity of liquid products as a function of liquefaction time.

Table 1. Weight % Conversion as a Function of Residence Time

Residence time (s)	Weight % Conversion
2	5.0
23	9.5
55	16.4
87	19.5
119	17.6
151	20.1

$$\text{Weight \% Conversion} = \frac{(A_t - A_0)}{A_1(1 - A_0)} \times 100$$

$A_0$  = Ash fraction of coal at time,  $t = 0$

$A_1$  = Ash fraction of coal at time,  $t$