

CONF-950801--24

# AMERICAN CHEMICAL SOCIETY

Division of Fuel Chemistry

Michael A. Serio, Chairman  
Advanced Fuel Research, Inc.  
P.O. Box 380379  
E. Hartford, CT 06138-0379

Frank J. Derbyshire, Program Chairman  
Center for Applied Energy Research  
3572 Iron Works Pike  
Lexington, KY 40511-8433



Karl S. Vorres  
Director of Publications  
Chemistry Division, Bldg. 211  
Argonne National Laboratory  
Argonne, IL 60439

John C. Crelling  
Director of Preprint Subscriptions  
Department of Geology  
Southern Illinois Univ. at Carbondale  
Carbondale, IL 62901-4324

Volume 40, No. 3  
Preprints of Papers Presented at the  
210th ACS National Meeting  
Chicago, IL  
August 20-25, 1995

New Analytical Methods for Characterizing  
Fossil Fuels and Derived Products  
Direct Coal Liquefaction  
Biomass Fuels

NOV 30 1995  
41:01 AM 2-NOV 95

0134/00050  
DEAL/00301

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

## SWELLING BEHAVIOR OF O-ALKYLATED APCS COALS AS EXAMINED BY THE EPR SPIN PROBE METHOD

Ruisong Ding, David Tucker and Lowell D. Kispert  
Department of Chemistry, Box 870336  
The University of Alabama  
Tuscaloosa, AL 35487-0336

KEYWORDS: O-Alkylated Coal, EPR Spin Probe, Hydrogen Bonding

### ABSTRACT

Known O-alkylation procedures have been used to derivatize the carboxyl and hydroxyl groups in the APCS coals Lewiston-Stockton, Wyodak-Anderson, Beulah-Zap, Illinois #6, Upper Freeport, and Pittsburgh #8. In general the resulting decrease in hydrogen bonding reduced the cyclical variation in nitroxide spin probe retention observed for nonalkylated coals when small amounts (<1%) of pyridine are present in the toluene swelling solvent. An increase in spin probe retention by the O-alkylated coals relative to the undervatized coals indicates a more open arrangement in the coal due to a decrease in attractive forces, confirming that microporosity increases with increasing rank.

### INTRODUCTION

A recent study of Tucker,<sup>1</sup> using an EPR spin probe method we have developed, and an earlier study by Green and Larsen<sup>2</sup> showed that an unexpectedly large number of guest molecules could be included in the swelled macromolecular structure of coal by spiking a "poor" swelling solvent such as toluene (or chlorobenzene) with as little as 100 ppm of a strong swelling solvent such as pyridine. The specific amount of included guest material depends on the rank of the coal undergoing swelling, but all ranks showed reproducible fluctuations in the number of trapped guest molecules as the pyridine content was increased by increments of 100 ppm. This oscillatory uptake behavior was explained as follows. At low ppm pyridine, weak hydrogen bonds which isolate interconnected micropore systems are disrupted. As the concentration of pyridine increases, disruption of weak hydrogen bonds which protect individual micropores will occur, followed at 1-5% pyridine by disruption of stronger hydrogen bonds within the macromolecular structure resulting in an opening of the structure. The cartoon given in Figure 1 emphasizes the active sites that can hydrogen bond (OH) with guest molecules, the interconnected micropore system, the hydrogen bonds of individual micropores and the stronger hydrogen bonds within the macromolecular structure.

In an effort to examine the integrity of the proposed swelling model for the action of binary solvents composed of less than 1% strong swelling solute in a poor swelling solvent, the Argonne Premium Coal Samples (APCS)<sup>3,4</sup> of Lewiston-Stockton (LS), Wyodak-Anderson (WA), Beulah-Zap (BZ), Illinois #6 (I6), Upper Freeport (UF) and Pittsburgh #8 (P8) were O-alkylated by a published procedure.<sup>5</sup> Due to space limitations, only the results for BZ, WA and LS coals will be presented here. The O-alkylated coal differs from the undervatized coal because interactions involving the acidic protons of the hydroxyl and carboxylic groups are no longer possible. Helium density and mercury porosimetry measurements revealed that the secondary structure (intermolecular associations) of the O-alkylated coals is significantly altered.<sup>5</sup> Furthermore, it is known that lower rank coals have lower microporosity (pores smaller than 18 Å) and largely consist of macropores, while higher rank coals have higher microporosity. Microporosity is a measure of the short-range intermolecular forces which contribute to the secondary structure of coal. Upon O-methylation the total porosity (<2200 Å) increases, and the increase is more pronounced for the higher ranked coals. The dramatic increase in the microporosity of O-methylated coals indicates a more open arrangement in the regions where short-range attractive molecular interactions are affective.<sup>4</sup> Since higher rank coals lack the very polar carboxylic acid functionalities and also have a low total concentration of polar functional groups, relative to subbituminous rank coals, microporosity increases with rank.

Electron paramagnetic resonance (EPR) techniques have been used previously to follow the inclusion of molecular probes in the micropore structure of coal in order to determine the changes in pore size, shape characteristics, pore wall chemistry, and hydrogen bonding which occur during the swelling process.<sup>6</sup>

The most common molecular probes are stable cyclic nitroxyl free radicals (depicted in Figure 2) which contain a ring nitrogen that is also singly bonded to oxygen and flanked by four methyl groups which sterically stabilize the radical. The unpaired electron density is distributed over both the nitrogen (40%) and the oxygen (60%) atoms. Reactive substituents (R) on the ring allow for chemical reactions to be studied, and varying the size and shape of a non-reactive substituent, allows evaluation of the effect on shape or size of the structural features of coal. The spin probe technique has been described in detail.<sup>6</sup> Briefly the coal sample is swelled in a mM nitroxide spin probe solution for approximately 18 h until equilibrium is reached. The coal slurry is then filtered and the solid is vacuum dried to remove the swelling solvent. The samples are then washed with cyclohexane, a non-swelling solvent, to remove any spin probes not trapped in the coal structure. The samples are again vacuum dried and then sealed in evacuated EPR tubes for subsequent measurement of the concentration of the nitroxide radicals trapped in the coal structure.

## EXPERIMENTAL

Spin probe VII (Tempamine) was obtained from Aldrich and used as received. This probe contains an amino group which can react with acidic sites in the coal, or in the absence of such sites, it can be trapped in small pores. Ca. 4 g of APCS coal samples, obtained from the Argonne Premium Coal Sample program,<sup>3,4</sup> were O-alkylated according to a literature method,<sup>5</sup> although the work-up procedure was modified as follows. Warm water (100 mL) was added to the reaction mixture and the pH was adjusted to 7. Volatiles were removed by distillation under vacuum for 2 h at 22°C and then at 40°C for 3 h. The residue was treated with hot water (500 mL) to dissolve ammonium salts. The mixture was left to stand overnight; the aqueous layer was decanted, and the procedure was repeated 5 times. The product was isolated by filtration and washed with hot water (4-6 L) until the washings were devoid of halide ions. The alkylated coal was first dried over CaCl<sub>2</sub> under N<sub>2</sub>, then under vacuum for 2 days and finally at 110°C for 3 days. The alkylated coal was sealed under N<sub>2</sub>. Infrared analysis was used to follow the decrease in adsorption in the 3300-3600 cm<sup>-1</sup> region (loss of hydroxyl groups) and the adsorption increase in the 1730 cm<sup>-1</sup> region (esterification of the carboxylic acids).

## RESULTS AND DISCUSSION

The retention of spin probe VII in BZ APCS lignite is given in Figure 3 as a function of percent pyridine present in toluene swelling solvent. The important feature to note is that large variations occur in the spin probe retention. In the absence of pyridine 1.2 x 10<sup>18</sup> spins/g of probe VII is retained in the BZ lignite. When very small amounts of pyridine are present the spin probe retention drops to 0.8 x 10<sup>18</sup> and then increases to 1.8 x 10<sup>18</sup> with 0.1% pyridine. A decreasing variation in the amount of spin probe retained occurs as the percent pyridine in toluene is increased, becoming more or less constant near 0.4 x 10<sup>18</sup> spins/g.

Totally different behavior shown in Figure 4, of spin probe VII retention as the percent pyridine is increased occurs with O-alkylated BZ. The highest spin probe retention (4.1 x 10<sup>18</sup> spins/g) is obtained in the absence of pyridine and this then decreases without any evidence of oscillation to ca. 2.4 x 10<sup>18</sup> spins/g with a pyridine content of ≥ 0.5%.

Similar plots for Wyodak-Anderson coal and alkylated Wyodak-Anderson coal are given in Figures 5 and 6, respectively. As the percent pyridine increases from 0% to 0.01% (Figure 5) the retained spin probe concentration in units of 10<sup>18</sup> spins/g drops from 6.1 to 4.8, then rises to 5.5 at 0.02%, drops to 3.6 at 0.08%, rises to 4.9 at 0.1%, drops to 3.2 at 0.2%, rises to 5.5 at 0.6%, and drops to 3.1 at 1%. Further variation is observed as the pyridine content increases to 5%. Above 5% the retained spin concentration equals approximately 3.7 ± 0.5. For the alkylated coal (Figure 6), the spin concentration is nearly constant at 9.0 ± 0.2 x 10<sup>18</sup> spins/g with the variation close to the relative error of ±0.1.

Figures 7 and 8 show the results of a similar study for Lewiston-Stockton and alkylated Lewiston-Stockton coal, respectively. The spin probe concentration in units of 10<sup>18</sup> spin/g (Figure 7) varies from 2.2 at 0% pyridine to 1.8 at 0.06%, increases to 2.1 at 0.08%, decreases to 1.7 at 0.4%, increases to 2.0 at 0.6%, and then decreases to 1.6 at 1%, 1.4 at 2% and 1.2 at 4%. In contrast, the spin probe retention in the alkylated coal (Figure 8) decreases from 7.6 at 0% pyridine to 6.9 at 0.2% and then gradually increases to 7.4 at 2%.

In all three coals, the absolute value of the spin probe concentration increased upon alkylation (a factor of 4 for Beulah-Zap lignite; 2.5 for Wyodak-Anderson subbituminous and 5.4 for Lewiston-Stockton high volatile bituminous coal). Previous porosity measurements<sup>5</sup> indicated that an increase in microporosity occurs upon alkylation and that this increase is more pronounced in high ranked coals than in the lower ranked coal. This is confirmed by this study. It is also clear that upon alkylation the cyclical variation is nearly eliminated, confirming the role of the hydrogen-bonding scheme outlined in the introduction. The largest variation in spin concentration with % pyridine occurred for Wyodak-Anderson coal suggesting more extensive changes in local structure with pyridine at less than 1% than for the high ranked Lewiston-Stockton coal. Beulah-Zap, which loses water upon exposure to air, has a lower tendency to retain the spin probe than the high rank Lewiston-Stockton coal.

## ACKNOWLEDGMENT

This work was supported by the U. S. Department of Energy, University Coal Grant program, Grant no. DE-FC22-93PC 93302.

## REFERENCES

1. Tucker, D. Ph.D. dissertation, University of Alabama, 1994 Entitled, "The Use of the EPR Spin Probe Method to Study Structural Changes in Solvent Swelled, Weathered Coal."
2. Green, T. K.; Larsen, J. W. *Fuel* 1984, 63, 1538.
3. Vortres, K. S. "User's Handbook for the Argonne Premium Coal Sample Program," 1989, ANL/JCSP-89/1.
4. Vortres, K. S. *Energy and Fuels* 1990, 4, 420.
5. Liotta, R.; Rose, K.; Hippo, E. J. *Org. Chem.* 1981, 46, 277.
6. Kispert, L. D.; Tucker, D.; Sady, W. *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem.* 1994, 39, 54 and references cited therein.

Figure 1  
A cartoon depicting a possible pore structure with the location of (OH) sites that can hydrogen bond with guest molecules and localized hydrogen bonding (---).

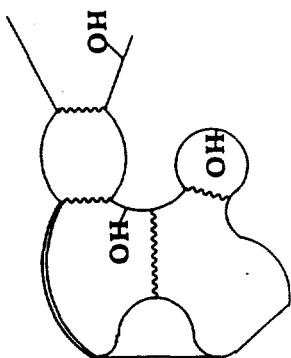


Figure 2

- (a) General structure of a nitroxide spin probe,  
(b) Structure of spin probe VII (TEMPAMINE)

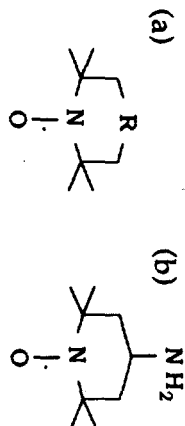


Figure 3  
Retention of spin probe VII in Beulah-Zap APCS lignite after swelling with toluene spiked with pyridine.

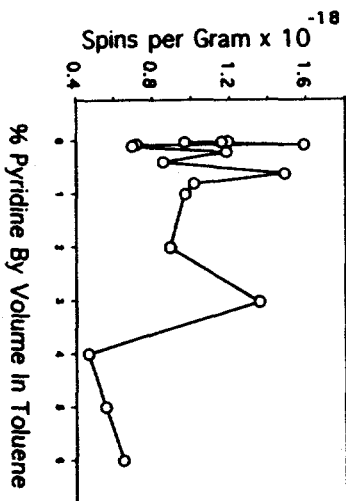


Figure 4  
Retention of spin probe VII in O-alkylated Beulah-ZAP APCS lignite after swelling with toluene spiked with pyridine.

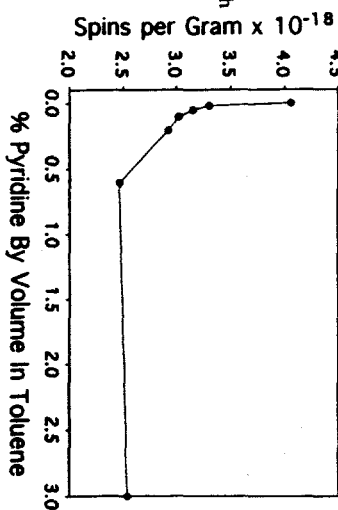


Figure 5  
Retention of spin probe VII in Wyodak-Anderson sub-bituminous APCS coal after swelling with toluene spiked with pyridine.

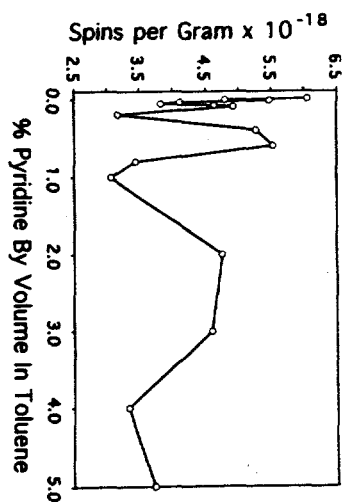


Figure 6  
Same as Figure 5 except with O-alkylated Wyodak-Anderson coal.

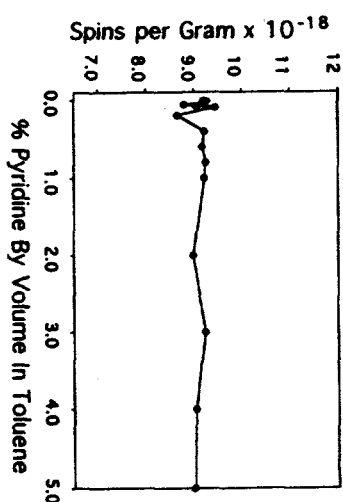


Figure 7  
Same as Figure 5 except with Lewis-Stockton high volatile bituminous APCS coal.

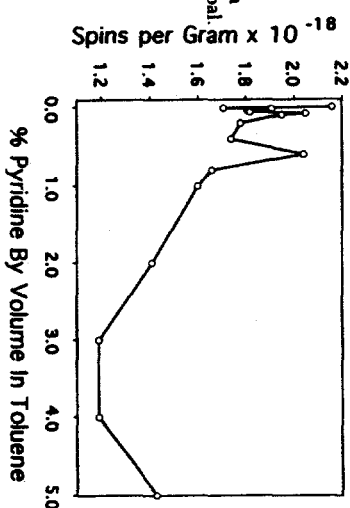
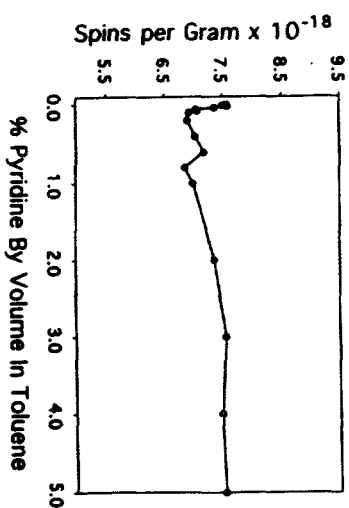


Figure 8  
Same as Figure 5 except with O-alkylated Lewis-Stockton coal.



### **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.