Molecular Accessibility in Oxidized and Dried Coals

entitled

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INTRODUCTION

The objective of this research project is to determine the molecular and structural changes that occur in swelled coal as a result of oxidation and moisture loss both in the presence and absence of light using our newly developed EPR spin probe method. The proposed study will make it possible to deduce the molecular accessibility distribution in swelled, oxidized APCS coal for each rank as a function of (1) size (up to 6 nm) and shape, (2) the relative acidic/basic reactive site distributions, and (3) the role of hydrogen bonding as a function of swelling solvents. The advantage of the EPR method is that it permits molecules of selected shape, size and chemical reactivity to be used as probes of molecular accessible regions of swelled coal. From such data an optimum catalyst can be designed to convert oxidized coal into a more convenient form and methods can be devised to lessen the detrimental weathering processes.

PREVIOUS WORK

Long-Term Weathering of APCS coal

A detailed study of long term weathering of 8 APCS coals using spin probe VII in toluene has been carried out. Preliminary results were given at the Symposium on Coal Conversion at the 45th ACS Southeast Regional meeting held in Johnson City Tennessee, October 17-20, 1993.1

The intercalation of potential catalysts in APCS coal Illinois #6 during the swelling process in binary solvent mixtures2 was studied using spin probes with various functionalities as model guest compounds. Samples of Illinois #6 coal were swelled in spin probe solutions of toluene spiked with various amounts of pyridine (1000:1 to 10:1). The spin probe retention was measured after solvent removal by Electron Paramagnetic Resonance (EPR) spectroscopy. Our work showed that spiked toluene leads to a larger uptake of the spin probe TEMPAMINE than when pure
toluene is used as the solvent. To study the effect of OH hydrogen bonding, alkylated samples of Illinois #6 and Beulah Zap coals were prepared.

An invited paper on the current status of spectroscopic techniques used to study the porous structure of coal with emphasis placed on the recent application of the EPR spin probe method to the study of Argonne Premium Coal Samples (APCS) was given by the principal investigator at the National ACS Meeting, Division of Fuel Chemistry, Symposium on Recent Advances in Coal Chemistry in San Diego, CA March 13-17, 1994.

Results of long term weathering for periods up to six months of exposure to air have been analyzed for spin probes VI (3-carboxy-2,2,5,5-tetramethylpiperidine-1-oxyl) and VIII (TEMPO). It was determined that the medium ranked coals (Illinois #6 at 80.7% carbon and Blind Canyon at 81.3% carbon) are effected to a greater extent than the low or high ranked coals. Careful comparison of these results to the data obtained for vacuum dried coals oxidized in a pure oxygen environment has led to conclusions that the oxidative process for coals proceeds very similarly to autoxidation observed in polymers. The oxidative degradation of polymers proceeds by a method called hydroperoxide autoxidation and is shown in the following three steps.

If termination of radicals does not occur, the formation of hydroperoxides prevails. Hydroperoxides are not very stable and their decomposition results in the formation of alcohols, aldehydes, ketones and acids. These reaction products are then subject to further oxidation and polymerization. The formation of these oxygenated functional groups in coal results in additional hydrogen bonding sites so that a larger amount of polar spin probes can be retained. This presents us with two processes which can be monitored by following the molecular accessibility of spin probes in coal. It is further possible to determine which types of oxygenated
products are being formed during the oxidation process because their hydrogen bonding character is greatly varied.

Looking at the over-all picture of the oxidation process in coal, the data supports the model that initially a decrease in retention would be observed because of the increased cross-linking and lack of structural accessibility of the spin probes. This decrease would be observed in coals swelled in both toluene and pyridine since neither solvent is known to disrupt covalent cross-linking in coal. As the concentration of free radicals in the coal is decreased, this process would become less significant, and the production of hydroperoxides would become more important. As the oxidation process continued, production of hydroxides would cause both polar spin probes to be more strongly retained. As the hydroxyls were oxidized further to ketones, the retention of spin probe VI would become stronger than spin probe VII. However, as the ketones and hydroxyls are further oxidized to carboxylic groups, this trend would be reversed and spin probe VII would be retained more strongly than spin probe VI. Of course, since the reaction products can form cross-links with other sections of the coal, this process would much more convoluted. It is apparent that the EPR spin probe method is very sensitive to the oxidation process in coal.

**Binary Swelling Results**

Binary swelling data has been collected for all Argonne Premium Coal Samples (APCS). It appears from preliminary analysis that as the rank of the coal increases, and the presence of interconnected weak hydrogen bonds decreases, that the strong oscillatory behavior observed at low rank with increasing pyridine concentration, decreases markedly. For instance, the amount of included substituted amine nitroxide spin probe (a direct measure of the percent of hydrogen bonding) decreases substantially for swelled Upper Freeport compared to swelled Beulah Zap
coal. An invited paper\textsuperscript{5} was given at the 26th Southeast Regional American Chemical Society meeting held in Birmingham, AL, October 16-17, 1994. The results to date\textsuperscript{5} for Upper Freeport and Lewiston-Stockton coals were discussed in light of the previous study of Wyodak-Anderson and Beulah-Zap coal.

It appears that the observed binary swelling data for the APCS coals studied to date can be explained in terms of four different processes: one, disruption of weak hydrogen bonds which protect or isolate the interconnected micropore system; two, disruption of weak hydrogen bonds which protect individual micropores; three, the competition of pyridine for the active sites capable of establishing hydrogen bonds or the "poisoning" of active sites; four, disruption of stronger hydrogen bonds within the macromolecular structure which cause an opening of the structure. The contributions of each of these factors to the spin probe retention with increasing concentrations of pyridine vary up to 5% pyridine. At concentrations above 5% pyridine, the first factor becomes less significant, and variations in the others require greater changes in pyridine concentration.

**SUMMARY OF CURRENT ACTIVITIES**

The presence of the internal hydrogen bonding, in particular its role in the bedding planes, plays an important role in determining the swelling characteristics in various ranked coal. To further examine the swelling behavior using the EPR spin probe technique, known O-alkylation procedures are being used to remove internal hydrogen bonding in APCS coal samples by derivatizing the hydroxyls.\textsuperscript{6} Removing the internal hydrogen bonding should block the polar spin probe retention. Furthermore, an increase in coal swelling by non-polar solvents such as toluene may be observed. By swelling O-alkylated APCS coals swelled in nonplanar as well as polar solvents using spin probes VII \[
\begin{array}{c}
\text{H}_2\text{N} \\
\text{N=O}
\end{array}
\] and VIII \[
\begin{array}{c}
\text{N=O}
\end{array}
\]
should yield the spin probe retention as a function of rank when internal hydrogen bonding due to hydroxyls is removed.

To date, the APCS coals Beulah-Zap, Illinois #6, Upper Freeport and Pittsburgh #8 have been O-alkylated. The O-alkylation procedure is very tedious and progress has been slow. Also as seen in the attached Figures 1 and 2, the sensitivity of the IR method leaves something to be desired. It is planned that an EPR spin probe study will be completed for O-alkylated Illinois #6 during this next quarter.

Mr. David Tucker successfully defended his Ph.D. dissertation during this quarter and has completed all the requirements for the Ph.D. degree. He will be officially recognized during graduation exercises in May 1995. David Tucker has started his own venture capital company where he has developed a working pilot plant that turns paper mill waste into useful products like carbon black etc.

Replacing David Tucker in January, 1995 on the coal project will be Yongqi Hu, a graduate student working towards a Ph.D. in chemistry. Mr. Hu will be studying the effect of light irradiation in coal oxidation. Currently, Mr. Ding is responsible for the binary solvent swelling studies, the O-alkylated coal preparations, and the EPR spin probe measurements on the O-alkylated coal.

STUDIES PLANNED FOR NEXT QUARTER

An abstract and short paper will be written on our binary swelling solvent study to be presented at the Symposium on new analytical methods for characterizing fossil fuels for the Chicago ACS Meeting, August 20-25, 1995. The first series of EPR spin probe studies will be completed on the effect of O-alkylating Illinois #6 coal. The hydrogen bonds should have been eliminated and a considerable change in swelling characteristics should result. Samples of O-alkylated Lewis-Stockton and Wyodak-Anderson will be prepared this next quarter.
REFERENCES


Fig. 2. Beulah-Zap Coal (O-Alkylation)