DOE Report No. DOE/PC 93202-12

September, 1996

DOE/PC/93202--12

Quarterly Report

For

Grant No. DE-FG22-93PC93202

entitled

Molecular Accessibility in Oxidized and Dried Coals

Lowell D. Kispert, Principal Investigator

Department of Chemistry

The University of Alabama

Tuscaloosa, AL 35487-0336

RECEIVED
USDOE/PETC
96 SEP 23 AM 11:10
ACQUISITION & ASSISTANCE DIV.

MASTER

US/DOE Patent clearance is not required prior to the publication of this document.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

mm

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

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.

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 EPR spin probe method. The proposed study will make it possible to deduce the molecular accessibility distribution in swelled, oxidized APCS coal as a function of sunlight 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 reported.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. An invited paper on the current status of spectroscopic techniques used to study the porous structure of coal has been presented.³ Results of long term weathering for periods up to six months of exposure to air have been analyzed for spin probes VI (3-carboxyl-2,2,5,5-tetramethylpiperidine-1-oxyl) and VIII (TEMPO).³

Binary Swelling Results

Binary swelling data has been collected for all Argonne Premium Coal Samples (APCS). As the rank of the coal increased, the presence of interconnected

weak hydrogen bonds decreased and the strong oscillatory up-take of spin probes as a function of percent pyridine in toluene swelling-solvent observed at low rank⁴ with increasing pyridine concentration, decreases markedly. The results to date for Upper Freeport and Lewiston-Stockton coals were presented⁵ in light of the previous study of Wyodak-Anderson and Beulah-Zap coal.

Analysis of the 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.

O-alkylation

To further examine the swelling behavior in the presence or absence of internal hydrogen bonding using the EPR spin probe technique, known O-alkylation procedures⁶ have been used to remove internal hydrogen bonding in APCS coal samples by derivatizing the hydroxyls. Removing the internal hydrogen bonding prevents the polar spin probe retention. On the other hand, an increase in coal swelling by nonpolar solvents such as toluene has been observed. By swelling O-alkylated APCS coals in nonpolar as well as polar solvents using spin probes VII

 and VIII
 yield the spin probe retention as a function of rank when internal hydrogen bonding due to hydroxyls is removed.

Papers have been published on the Influence of Binary Swelling Solvents⁷ and on the Swelling Behavior of O-Alkylated APCS Coal.^{8,9} It was found that upon O-alkylation, the hydrogen bonding is removed and the microporous structure increases in size. The strong oscillatory variation in spin concentration as a function of percent pyridine in a toluene swelling solvent was eliminated. A paper was presented in the coal Liquefaction/Coprocessing Symposium of the National ACS meeting held in Orlando, FL, Aug. 25-29 entitled "Changes in Molecular Accessibility in APCS Coal Oxidized in the Presence of Sunlight." This study was carried out for Pocahontas #3, Lewiston-Stockton and Wyodak-Anderson coal in which the oxygen content varied from 2% to 17%. A paper subsequently published¹⁰ (reprint attached) on the topic examined the reason that sunlight played an important role in the weathering process. One possible reason is the formation of singlet oxygen by energy transfer from the excited singlet states of the naturally occurring naphthalene and phenoxyl anion radical in the coal to the singlet excited state of oxygen.

SUMMARY OF CURRENT ACTIVITIES

The effect of sunlight on the weathering of APCS coal has been carried out for Beulah-Zap (~20% oxygen content), Illinois #6 (~14% oxygen content) and Upper Freeport coal (~8% oxygen content). Plots of spin probe uptake for coal swelled in toluene versus time (0 to 10 hours) of exposure to air and sunlight has been recorded. A decrease in spin probe uptake by a factor of two over that found for exposure to air in the absence of light was observed to occur for Beulah-Zap (Fig. 1). No dependence on sunlight was detected for Illinois #6 and an approximate 50%

increase in spin probe uptake occurred for Upper Freeport (Fig 2) upon exposure to sunlight over a 10 hour period. It appears that the trend as a function of oxygen content in the coal follows the same dependence as found earlier for Pocahontas #3, Lewiston-Stockton and Wyodak-Anderson. Upon alkylation, it was previously deduced that cross-linking by the combination of hydroperoxide radicals with radicals existing in the coal occurred for oxygen rich Wyodak-Anderson and also presumably - Beulah-Zap. As the time of exposure to sunlight increased a decrease in molecular accessibility (decrease in spin probe VII uptake) occurred due to an increase in cross-linking character. However for high rank coal (Pocahontas #3 and also presumably Upper Freeport), this effect was not present to any significant degree and the increase presence of functional groups and subsequent hydrogen bonding caused an increase in the uptake of polar spin Probe VII. These two mechanism essentially counter-balanced each other for Lewiston-Stockton or in the present case of Illinois #6. Further study of this effect will require alkylation of the coal after exposure to sunlight. So far it has been determined that the microporosity depends on the structure of the coal; coals with similar percent oxygen content do not show the same percent increase in microporosity. In oxygen rich coal, evidence exists for crosslinking as a function of exposure to air and sunlight.

STUDIES PLANNED FOR NEXT QUARTER

The uptake of spin probe VII will be measured for Upper Freeport after the sample has been exposed to air and sunlight and then alkylated. This will give some measure of the hydrogen bonding that contributes to the molecular accessibility in high rank coal.

REFERENCES

1. D. Tucker, W. Sady, L. D. Kispert and D. R. Spears, abstract 193, 45th ACS Southeast Regional Meeting, Johnson City, TN, Oct. 17-20, 1993.
2. D. Tucker and L. D. Kispert, abstract #36, 45th ACS-Southeast Regional Meeting, Johnson City, TN, Oct. 17-20, 1993.
3. L. D. Kispert, D. Tucker, W. Sady, *Prepr. Pap. Am. Chem. Soc., Div. Fuel. Chem.* 1994, 39, 54.
4. D. Tucker, Ph.D. Dissertation, University of Alabama, Dec. 1994.
5. R. Ding, D. Tucker and L. D. Kispert, abstract 165, *Am. Chem. Soc.* 46th Southeast Regional Meeting, Birmingham, AL, October 16-19, 1994.
6. R. Liotta, K. Rose and E. Hippo, *J. Org. Chem.* 1981 46, 277.
7. R. Ding, D. Tucker and L. D. Kispert, *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem.* 1995, 40, 590 (1995).
8. R. Ding, D. Tucker and L. D. Kispert, *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem.* 1995, 40, 425 (1995).
9. R. Ding, and L. D. Kispert, "Abstract 550, Joint Southeast-Southwest Regional American Chemical Society Meeting, Nov. 29 - Dec. 1, 1995.
10. R. Ding, L. D. Kispert and A. S. Jeevarajan, *Prepr. Pap. Am. Chem. Soc. Div, Fuel Chem.* 1996, 41, 1094.

Figure 1. Uptake of spin probe VII in Beulah-Zap coal swelled in toluene after exposure to air as a function of sunlight. The dashed line is a straight-line average. Over this same period of time, the uptake in the absence of light decreases by 10%.

Figure 2. Uptake of spin probe VII in Upper Freeport swelled in toluene after exposure to air as a function of sunlight. The dashed line is a straight-line average. Over this same period of time, the uptake in the absence of light decreases by 10%.