DOE/PC/93202--7

DOE Report No. DOE/PC 93202-7

June 1995

Quarterly Report

For

Grant No. DE-FG22-93PC93202

entitled

Molecular Accessibility in Oxidized and Dried Coals

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Lowell D. Kispert, Principal Investigator
Department of Chemistry
The University of Alabama
Tuscaloosa, AL 35487-0336

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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.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-carboxy-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). 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 rank⁴ with increasing pyridine concentration, decreases markedly. The results to date for Upper Freeport and Lewiston-Stockton coals were discussed⁵ 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.

O-alkylation

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 have been used to remove internal hydrogen bonding in APCS coal samples by derivatizing the hydroxyls.⁶ 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 swelled 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. Preliminary results have been obtained for

the O-alkylated APCS coals Beulah-Zap, Illinois #6, Upper Freeport, Blind Canyon, and Pittsburgh #8. The O-alkylation procedure is very tedious and progress has been slow.

SUMMARY OF CURRENT ACTIVITIES

This quarter a talk was given at the University Coal Research Contractors Review Conference held June 13-14, 1995 at Tennessee State University in Nashville, TN entitled "Molecular Accessibility in Oxidized and Dried Coal" (abstract enclosed). In addition an overview of our progress was presented during a 30 minute talk at the Fossil Energy Advanced Research Program Review, June 14, 1995 in Session 18 on Coal Characterization held at the Clubhouse Inn and Conference Center, Nashville, TN.

During the 210th National ACS Meeting Chicago, IL. A talk will be presented entitled "Influence of Binary Swelling Solvents: Mechanism of Action" in the Symposium on Direct Coal Liquefaction to be held Monday, August 21 - at 3:30 p.m. On Aug. 20, 1995 at 2:30 p.m. during a Symposium on New Analytical Methods for Characterizing Fossil Fuels and Derived Products, we will present a paper entitled "Swelling Behavior of O-Alkylated APCS Coals as Examined by the EPR Spin Probe Method."

Further experiments were carried out to check the reproducibility of the relative spin probe concentration in APCS Blind Canyon, Illinois #6 and Pittsburgh #8 before and after O-alkylation. Upon O-alkylation of the coal samples -- the OH groups are replaced by O-alkyl groups, thus removing sites of polar hydrogen bonding. It was observed that upon O-alkylation an increase occurred in spin probe concentration by a factor of 2.5 for Blind Canyon, an increase of 4 for Illinois #6 and 1.5 for Pittsburgh #8. If Illinois #6 coal was exposed to the sunlight for 1.5 hours before it was alkylated -- the retained spin probe concentration doubled over that kept in the dark -- implying that more sites of hydrogen bonding were removed,

giving rise to a larger microporous structure. The strong variation in spin probe concentration as a function of percent pyridine observed when fresh coal samples were exposed to a binary swelling solvent of pyridine in toluene, was eliminated upon O-alkylation. Care taken this last quarter in preparing alkylated coal samples of Illinois #6, Blind canyon and Pittsburgh #8 containing spin probes has reduced some uncertainty in the data previously reported. A more consistent trend has been observed.

STUDIES PLANNED FOR NEXT QUARTER

Since coal is such a heterogeneous material, a number of experiments are planned in which samples of Upper Freeport, Beulah-Zap and Pocohontas #3 will be alkylated and reexamined.

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ABSTRACT AND RESEARCH ACCOMPLISHMENTS OF UNIVERSITY COAL RESEARCH PROJECTS

Managed by:
Pittsburgh Energy Technology Center
Advanced Power and Fundamental Research Division
P.O. Box 10940
Pittsburgh, Pennsylvania 15236

Supported by:
U.S. Department of Energy
Fossil Energy Program

Date Published: June 1995

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TITLE: MOLECULAR ACCESSIBILITY IN OXIDIZED AND
DRIED COALS

DATE: April 14, 1995

PRINCIPAL INVESTIGATOR: Lowell D. Kispert

STUDENT: Y. Hu, Ph.D. Candidate

INSTITUTION: The University of Alabama
Chemistry Department
Tuscaloosa, AL 35487-0336
(205) 348-7134.

DOE GRANT NO.: DE-FG22-93PC93202

PERIOD OF PERFORMANCE: September 1, 1993 to August 31, 1996

I. ABSTRACT

OBJECTIVE: It is the objective of this research to determine the molecular and structural changes that occur in swelled Argonne Premium Coal Samples (APCS) as a result of oxidation and moisture loss both in the presence and absence of light using the EPR-spin probe method that we have developed. The method makes use of nitroxide spin probes of different shapes, sizes or molecular reactivity from which the relative acidic or basic reactive site distribution, the role of hydrogen bonding, and the changes in the size and shape distribution of the accessible regions of the oxidized coal as a function of swelling solvents can be deduced.

WORK DONE AND CONCLUSIONS: Internal hydrogen bonding, especially in the bedding planes, plays an important role in determining the swelling characteristics in variously ranked coal. To further examine the swelling behavior using the EPR spin probe technique developed in this lab, known O-alkylation procedures have been used to derivatize the hydroxyl groups in APCS coal samples. Reduction of the extent of hydrogen bonding altered the amount of polar spin probe retention. Furthermore, an increase in coal swelling by nonpolar solvents such as toluene has been observed. By swelling O-alkylated APCS coals with nonplanar as well as polar solvents, using amine substituted nitroxide spin probes has yielded spin probe retention as a function of rank when internal hydrogen bonding due to hydroxyl groups is removed in the APCS coals; Wyodak Anderson (WA), Blind Canyon (BC), Lewiston-Stockton (LS), and Pocahontas (P). The sharp variation in spin probe uptake as a function of trace amounts of pyridine in toluene has disappeared, demonstrating the fact that localized hydrogen bonding is disrupted upon adding a trace (ppm) of a good swelling solvent like pyridine.

Green and Larsen had previously reported that the up-take of chlorobenzene by coal is dramatically increased if small amounts of a good swelling solvent like pyridine are added. In efforts to understand how a small amount (ppm) of a good swelling solvent can exert such a pronounced effect, we have used our newly developed EPR spin probe method to examine the structural changes in binary solvent swelled (up to 5% pyridine) Argonne Premium Coal Samples (APCS). Results to date show that the unexpected up-take can be explained in terms of four different processes: (1) disruption of weak hydrogen bonds which isolate the interconnected micropore system; (2) disruption of weak hydrogen bonds which protect individual micropores; (3) competition of pyridine for the active sites involved in the hydrogen bonds or the "poisoning" of active site; (4) disruption of stronger hydrogen bonds within the macromolecules which causes an opening of the structure. Less dramatic effects are observed when more than 5% pyridine is used. Mr. David Tucker successfully defended his Ph.D. dissertation and has completed all the

requirements for the Ph.D. degree. He will officially graduate in May. He has started his own venture capital company where a working pilot plant turns paper mill wastes into useful products like carbon black etc.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Molecular accessibility of catalysts to the coal structure is an important consideration in the chemical conversion of this resource to other valuable chemicals. Weathering of coal causes oxidation and a loss of water from coal, and these changes have a significant effect on the accessibility of catalysts to its structure.

PLANS FOR THE COMING YEAR: We plan to complete the effect of O-alkylation on the swelling characteristics of the remaining 4 APCS coals, Upper Freeport (UF), Pittsburgh #8 (P8), Illinois (IL) #6 and Beulah-Zap (BZ). The effect of light on the oxidation of coal is now in the initial stage of study and an extensive effort will be made in this area.

II. HIGHLIGHT ACCOMPLISHMENTS

The physical or hydrogen bonded structure of coals swelled in toluene can be significantly altered upon the addition of pyridine in amounts as small as 100 ppm. These changes are detected by the dramatic increases and decreases in spin probe retention by hydrogen bonding as a function of pyridine concentration observed up to 5%. The structural change is most severe at $\leq 0.1\%$ pyridine for LS, at $\leq 0.5\%$ for IL, at $\leq 1\%$ for BZ, WA, BC, UF, and P8 coals. This dramatic effect is not observed above 5% pyridine in a toluene solution. It is however noteworthy that O-alkylated WA and BC coals shows complete disappearance of the large variation in spin probe uptake at less than 1% pyridine. These results show that destruction of local variations in hydrogen bonding sites in the pores are responsible for the observed large increase in uptake of a poor swelling solvent upon the addition of $<1\%$ pyridine.

III. ARTICLES AND PRESENTATIONS

1. L. D. Kispert, D. Tucker and W. Sady, "Porosity of APCS Coals: The Accessible Nature of Coal in The Presence of Swelling Solvents," *Am. Chem. Soc. Div. Fuel Chem. Preprints*, **39**, 54 (1994). Presented at the Symposium on "Recent Advances in Coal Chemistry" at The National ACS Meeting, Division of Fuel Chemistry, San Diego, CA, March 13-17, 1994.
2. D. Tucker, Ph.D. Dissertation, University of Alabama, Dec., 1994.
3. D. Tucker and L. Kispert, "An EPR Spin Probe Study of the Use of Binary Swelling Solvent Systems in Coal Conversion," Abstract 36, 45th ACS Southeast Regional Meeting, Johnson City, Tennessee, October 17-20, 1993.
4. R. Ding, D. Tucker and L. D. Kispert, "Swelling Behavior of O-Alkylated APCS Coals as Examined by the EPR Spin Probe Method," *Am. Chem. Soc. Div. Fuel. Chem. Preprints*, **40**, 0000 (1995). Presentation at the 210th National ACS Meeting, Div. of Fuel Chemistry, Chicago, IL Aug. 20-25, 1995.
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