SURFACE PROPERTIES OF PHOTO-OXIDIZED BITUMINOUS COALS

Quarterly Technical Report

Reporting Period: October 1, 1996 - December 31, 1996

Authors: Gareth Mitchell
Alan Davis

Report Issue Date: February, 1997

DE-FG22-93PC93223

Coal and Organic Petrology Laboratories
The Pennsylvania State University
105 Academic Projects Building
University Park, PA 16802

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.

ABSTRACT

During this report period, three vitrain concentrate samples crushed to -200 mesh were irradiated (photo-oxidized) for different time periods (0, 10, 50 and 100 min) using the BLAK-RAY ultraviolet lamp to obtain samples suitable for pyrolysis GC/MS. These samples will be used to investigate whether the levels of photo-oxidation induced with increasing UV irradiation can be detected and measured in bulk vitrains using the technique. The analyses have not been fully completed. Further, additional analysis of reflectance-mode FTIR results obtained from polished blocks of vitrain is currently under way. This evaluation involves calculating the second derivative of the spectra in an attempt to better identify the spectral regions of most significant change resulting from photo-oxidation. These analyses, along with final analytical tests that will destroy the irradiated surfaces, including electron microprobe analysis for near-surface oxygen concentration and x-ray mapping, and measurement of reflectance in oil immersion, are under way and will be completed by the end of February, 1997.

During this report period we have begun the preparation of a manuscript tentatively entitled, "Time Resolved C-NEXAFS Analysis of the Chemistry of Photochemical Alteration of Vitrinite". This publication will discuss our efforts in utilizing Scanning Transmission X-ray Microscopy as a tool to better define the kinetics of photo-oxidation of vitrinite from coals of three different ranks by measuring changes in regions near the carbon-edge absorption.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
EXECUTIVE SUMMARY	iv
<u>INTRODUCTION</u>	1
<u>RESULTS AND DISCUSSION</u>	1
Irradiation and Pyrolysis GC/MS of Powdered Vitrains	1
<u>Introduction</u>	1
<u>Experimental Procedure</u>	2
Photo-Oxidation Studies	4
<u>CONCLUSIONS</u>	5
<u>REFERENCES</u>	6

EXECUTIVE SUMMARY

The ultimate objective of this project is to develop new luminescence techniques that will measure quantitatively changes in surface properties as a function of oxidation and relate them to cleanability of bituminous rank coals. The general objectives to achieve this goal are 1) to measure the changes in functional group concentration as a function of the duration of photo-oxidation using FTIR and flash pyrolysis GC/MS techniques, 2) to identify the influence of photo-oxidation on coal floatability by measuring contact angles from polished surfaces as well as by film flotation of powdered vitrains, and 3) to correlate the changes in surface chemistry with measurements of luminescence intensity and alteration.

This progress report describes details of the final analytical work to be performed in the study including our efforts to evaluate photo-oxidized powdered vitrains using Py-GC/MS as well as a further evaluation of the FTIR spectra collected from irradiated polished blocks. In addition, plans have been made for some limited electron microprobe analyses of near-surface oxygen concentration in the irradiated areas compared to non-photo-oxidized regions. With the completion of these analyses, a more comprehensive understanding of the changes of oxygen functionality and concentration at or near the surface of vitrain resulting from photo-oxidation should be obtained for comparison of changes in luminescence intensity and surface hydrophobicity.

INTRODUCTION

During this performance period photo-oxidation of three powdered vitrains was completed for periods of 0, 10, 50 and 100 min using a longwave ultraviolet light source for analysis by flash pyrolysis gas chromatography and mass spectrometry (Py-GC/MS). These times correspond to irradiation periods of 0, 1, 5 and 10 minutes, respectively, using our optical microscope system. Also, further processing of FTIR spectra collected from irradiated polished surfaces of vitrain was begun as a means of more fully evaluating the changes in functional group chemistry resulting from photo-oxidation. In addition, arrangements have been made to utilize the electron microprobe as a means of determining quantitatively the extent of near-surface oxidation of photo-oxidized surfaces. Finally, with Dr. G. Cody of the Carnegie Institution of Washington we have begun preparing a manuscript concerning the use of Carbon Near-Edge X-ray Absorption Fluorescence Spectroscopy obtained from Scanning Transmission X-ray Microscopy. This article will discuss the kinetics of time-resolved photo-oxidation. The following report summarizes our progress.

RESULTS AND DISCUSSION

Irradiation and Pyrolysis GC/MS of Powdered Vitrains

Introduction

The BLAK-RAY, 100 watt long wavelength ultraviolet spotlight which was used to irradiate powdered vitrain concentrates for film flotation studies earlier in this research program (1) has been used to generate samples suitable for Py-GC/MS. Vitrains from three different ranks of coal were crushed to an appropriate particle size and irradiated for 0, 10, 50 and 100 min. At this point, however, results still are being collected and evaluated.

Experimental Procedures

Vitrain concentrate samples of the hvCb Illinois #6 (DECS-24-Vit), hvAb Lower Kittanning (PSOC-1562-Vit) and mvb Splash Dam (DECS-30-Vit) which were set aside from samples irradiated for film flotation were prepared for Py-GC/MS. These samples were crushed with an agate mortar and pestle to a fine powder (-200 mesh or $<74\ \mu\text{m}$) and irradiated in the same manner as discussed in previous progress reports (2,3). Briefly, a monolayer of powdered vitrain was spread on the outside bottom half of a glass Petri dish and exposed to the UV light for the desired time period. Then, the top half of the Petri dish was placed over the bottom half to secure the particles while they were inverted. Then the undersides of the particles were irradiated for the same time period. These steps were repeated on successive layers until approximately 100 mg of irradiated vitrain was produced.

Flash pyrolysis gas chromatography and mass spectrometry will be performed using a Varian 2700 gas chromatograph and a DuPont 21-490B mass spectrometer equipped with a Chemical Data Systems Pyroprobe 1000 according to the method outlined by Hatcher et al. (4). The pyroprobe pyrolyzes samples at any fixed heating rate ranging from 10 to 20,000°C/s to a desired final temperature (max. 1400°C), and holds at the final temperature for a given time (0.01 - 99.99 s). In this project a flash pyrolysis temperature of 610°C will be employed. Lower temperatures produce smaller fragments of low molecular weight which would provide little structural detail and obscure the information on the exact structural features present in the sample. A heating rate of 10°C/s will be used because this relatively rapid heating minimizes the potential for secondary reactions and enhances the detection of pyrolysis fragments characteristic of the original macromolecular nature of the vitrain. The

time of pyrolysis is 10 s to ensure complete expulsion of the volatile pyrolyzates from the capillary tube into the gas chromatograph - mass spectrometer.

It is important to carefully prepare the finely powdered sample and properly select the sample weight to minimize the effects of thermal gradients in the sample and to ensure that the representative sample is completely pyrolyzed. A sample weight of about 0.5 mg will be used. Samples are weighed with a microbalance and loaded into a quartz capillary tube as evenly as possible to minimize thermal gradients. The quartz tube is placed inside the platinum heating coil of the pyroprobe; this assembly is then inserted into the injection port (temperature maintained at 280°C) of a Varian 2700 gas chromatograph and the sample pyrolyzed. The pyrolyzate is cryotrapped with liquid nitrogen prior to being subjected to gas chromatography in a J&W DB-17 capillary column (25 m in length, 0.25 mm in diameter, made of 50% phenyl methyl silicone). The chromatograph temperature is programmed from 30°C (0 min) to 280°C (20 min) at a rate of 4°C/min. The effluent is swept into the source of a DuPont 21-490B mass spectrometer fitted with a Teknivent Vector/One data system for detection and compound identification. Compounds are identified by a combination of methods including comparison of mass spectra to the NBS/Wiley library and other published mass spectra and to authentic standards. This Py-GC/MS technique has been found to be very reproducible for repetitive analysis of the same sample.

Our preliminary evaluation of these samples should be completed by the end of February, in time for inclusion into the final project report.

Photo-Oxidation Studies

In an attempt to further evaluate changes in oxygen functional groups as a result of time-resolved photo-oxidation, reflectance-mode FTIR spectra obtained from polished blocks of vitrain and that were photo-oxidized for contact-angle measurements are being studied in more detail. Second derivative plots of spectra from three of the coals, namely the hvCb Illinois #6 (DECS-24), hvAb Lower Kittanning (PSOC-1562) and the mvb Splash Dam (DECS-30) have been generated for each level of photo-oxidation. The reason for this is to obtain further resolution of peaks in the C-H stretching region between 3000 and 2800 cm^{-1} , the carbonyl region between 1835 and 1560 cm^{-1} , as well as the O-H band near 3450 cm^{-1} (5). Of particular interest will be analysis of the carbonyl region which broadens with increasing photo-oxidation and resolution of the multiple peaks that are shown by the second derivative plots. These analyses currently are being performed.

In addition, the photo-oxidized areas of the same coal blocks used to measure contact angle and generate FTIR spectra are being evaluated for visual changes in surface properties by photomicroscopy and measurement of changes in vitrinite reflectance as a result of photo-oxidation. Following this evaluation, which must be performed using oil immersion, the samples will be cleaned and dried under vacuum, and then carbon coated for X-ray mapping of oxygen and other heteroatoms (S and N) as well as quantitative measurement of near surface oxygen concentration using the electron microprobe. This work is scheduled and will be completed by the end of February.

Finally, a manuscript for work conducted early in the project is being prepared concerning an investigation of the use of Scanning Transmission X-ray Microscopy (STXM)

of photo-oxidized thin sections of vitrinite from three different ranks of coal and the evaluation of Carbon Near-Edge X-ray Absorption Fluorescence spectra (C-NEXAFS). Analysis of absorption energies in the range of 280-300 eV show variations in energy bands assigned to methyl, hydroxyl and carbonyl functional groups attached to aromatic rings. For vitrinite of subbituminous and hvAb rank, changes in concentration of methyl and carbonyl groups with duration of photo-oxidation agree well with published results from weathered bituminous coals. Results show that hydroxyl and carbonyl functionalities increase in concentration with increasing time of photo-oxidation accompanied by an overall decrease in methyl group concentration. The publication will discuss these results based on the kinetics of photo-oxidation and will include new results from the evaluation of vitrinite from a medium volatile rank coal.

CONCLUSIONS

Details of the final analytical work to be performed in the study are provided in this report which includes our efforts to evaluate photo-oxidized powdered vitrains using Py-GC/MS, as well as a further evaluation of the FTIR spectra collected from irradiated polished blocks. In addition, some limited electron microprobe analyses of near-surface oxygen concentration in the irradiated areas will be compared to non-photo-oxidized regions. With the completion of these analyses, we should have more comprehensive quantitative information on the changes of oxygen functionality and concentration at or near the surface of vitrain that result from photo-oxidation and the influence of surface hydrophobicity.

REFERENCES

1. Mitchell, G.D., Werner, D., Davis A. and Chander, S. (1996). Surface Properties of Photo-Oxidized Bituminous Coals, DOE Technical Progress Report for the Period July to September, 1996, No. DOE/PC/93223--12.
2. Mitchell, G.D., Davis A. and Chander, S. (1996). Surface Properties of Photo-Oxidized Bituminous Coals, DOE Technical Progress Report for the Period January to March, 1996, No. DOE/PC/93223--10.
3. Mitchell, G.D., Werner, D., Davis A. and Chander, S. (1996). Surface Properties of Photo-Oxidized Bituminous Coals, DOE Technical Progress Report for the Period April to June, 1996, No. DOE/PC/93223--11.
4. Hatcher, P.G., Lerch, H.E., III, Kotra, R.K., and Verheyen, T.V. (1988). Pyrolysis/gc-ms of a Series of Degraded Woods and Coalified Logs that Increase in Rank from Peat to Subbituminous Coal. Fuel. v. 67, pp. 1069-1075.
5. Painter, P.C., Snyder, R.W., Starsinic, M., Coleman, M.M., Kuehn, D.W. and Davis, A. (1981). Concerning the Application of FT-IR to the Study of Coal: A Critical assessment of Band Assignments and the Application of Spectral Analysis Programs. Applied Spectroscopy. v. 35, pp. 475-485.