THE DUAL ROLE OF OXYGEN FUNCTIONS IN COAL PRETREATMENT AND LIQUEFACTION: CROSSLINKING AND CLEAVAGE REACTIONS

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SECOND QUARTERLY REPORT - CONTRACT NO. DE-AC22-91-PC91026

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ABSTRACT

All of the technical and legal issues with the subcontract have been resolved except for a clause on caps for indirect cost reimbursement. This is still being negotiated between DOE and SRI. However, permission has been granted for work to commence at SRI, so we do not expect any additional delays in the technical progress.

The coal sample modification apparatus was completed for the demineralization and ion-exchange procedures. This allows continuous rinsing of samples with the treatment solutions in an anaerobic environment. The test plan was completed and submitted to the project officer.

The literature work on coal demineralization methods was completed. It appears that to ensure complete demineralization for U.S. coals, which contain significant amounts of non-organically bound minerals, an HCl/ HF wash of the type used by Bishop and Ward (1958) is required. We are currently examining various techniques to monitor the degree of exchange of carboxyl groups, including an FT-IR spectroscopic technique developed by Painter and coworkers at Penn State.

One objective of this program is to prepare polymer models having phenolic, carboxylic, and/or aryl ether groups considered to be important in low rank coals. In order to study the chemistry of these functional groups in a polymeric matrix, it is necessary that the polymer backbone itself should not be subject to cleavage under the reaction conditions. It is expected that poly(phenylene) would fulfill this requirement as a backbone, while providing simple chemical routes for attaching other functional groups.

During this reporting period, the synthesis of oligomeric species such as sexi(phenylene) and octa(phenylene) was explored. The procedure of Bamfield and Quam was followed, which involves heating a paste of bromoarenes, water, sodium formate and Pd/C. The reaction products turned out to be very insoluble and difficult to purify. The insolubility of these products makes them difficult to work with, and it is doubtful that we will be able to prepare well-characterized polymers in the 10,000 Da range. We are presently considering other polymeric substrates that might serve as the backbone.

Pending the resolution of the polymeric substrate issue, the thermal behavior of the carboxyl and phenolic functions and the effect of ion-exchange will be studied using monomeric models. These studies will be needed to establish the baseline for considering the effect of the polymeric environment.
I. INTRODUCTION

The overall objective of this project is to elucidate and model the dual role of oxygen functions in thermal pretreatment and liquefaction of low rank coals through the application of analytical techniques and theoretical models. The project will be an integrated study of model polymers representative of coal structures, raw coals of primarily low rank, and selectively modified coals in order to provide specific information relevant to the reactions of real coals. The investigations will include liquefaction experiments in microautoclave reactors along with extensive analysis of intermediate solid, liquid and gaseous products. Attempts will be made to incorporate the results of experiments on the different systems into a liquefaction model.

II. TASK 1 - WORK PLAN

All of the technical and legal issues with the subcontract have been resolved except for a clause on caps for indirect cost reimbursement. This is still being negotiated between DOE and SRI. However, permission has been granted for work to commence at SRI, so we do not expect any additional delays in the technical progress.

The coal sample modification apparatus was completed for the demineralization and ion-exchange procedures. This allows continuous rinsing of samples with the treatment solutions in an anaerobic environment.

The test plan was completed and submitted to the project officer.

This task is complete except for finishing the subcontract.

III. TASK 2 - STUDIES WITH COALS AND MODIFIED COALS

The literature work on coal demineralization methods was completed. It appears that to ensure complete demineralization for U.S. coals, which contain significant amounts of non-organically bound minerals, an HCl/HF wash of the type used by Bishop and Ward (1958) is required. We are currently examining various techniques to monitor the degree of exchange of carboxyl groups. The classical technique is the barium titration technique developed by Schafer at CSIRO (Schafer, 1970). However, it appears that this technique tends to overestimate the amount of carboxyl
groups due to problems with steric hindrance. We are considering the use of lithium acetate instead of barium acetate in order to exchange metal cations. Lithium is a smaller molecule which should be less prone to problems of steric hindrance.

We are currently examining an FT-IR spectroscopic technique developed by Painter and coworkers (Starinsic et al, 1984) at Penn State to measure the carboxyl and phenolic group concentrations and the degree of exchange with alkali metals. These measurements require a controlled spectrometer environment to eliminate contamination from ambient moisture. A number of spectra from model compounds and modified coals are being examined in order to develop the technique.

Work also began on preparing demineralized coals.

IV. TASK 3 - STUDIES WITH POLYMERIC MODEL SYSTEMS

The first objective of this task is to prepare polymer models having phenolic, carboxylic, and/or aryl ether groups considered to be important in low rank coals. In order to study the chemistry of these functional groups in a polymeric matrix, it is necessary that the polymer backbone itself should not be subject to cleavage under the reaction conditions. We expected that poly(phenylene) would fulfill this requirement as a backbone, while providing simple chemical routes for attaching other functional groups.

During this reporting period, we explored synthesis of oligomeric species such as sexi(phenylene) and octa(phenylene). We followed the procedure of Bamfield and Quem (Synthesis 1978, 537), which involves heating a paste of bromoarenes, water, sodium formate and Pd/C. We used a 1:1 molar mixture of 4,4'-dibromobiphenyl and 4-bromobiphenyl to maximize the chances for octa(phenylene) \((n = 6)\).
The reaction products turned out to be very insoluble and difficult to purify. Tetra(phenylene) is reported to be soluble only in hot nitrobenzene, and we expect that higher oligomers will be even less soluble. Mass spectral analysis of the crude mixture using desorption chemical ionization showed a fair amount of hexa(phenylene) \((n = 4)\). Additional peaks at \(m/z\) 270 and 284 were also observed, but we are not sure of their source. The insolubility of these products makes them difficult to work with, and we doubt if we will be able to prepare well-characterized polymers in the 10,000 Da range. We are presently considering other polymeric substrates that might serve as the backbone.

Pending the resolution of the polymeric substrate, we will study the thermal behavior of the carboxyl and phenolic functions and the effect of ion-exchange using monomeric models. These studies will be needed to establish the baseline for considering the effect of the polymeric environment. Carboxyl functions have been implicated in the crosslinking of coals during heating at relatively low temperatures, and Solomon and coworkers have been able to model the pyrolytic loss of solvent swelling by including one additional crosslink in the network for every \(\text{CO}_2\) evolved. Moreover, pretreatments that have been found to be effective in promoting liquefaction, have also shown a corresponding decrease in the early \(\text{CO}_2\) evolution. These results strongly suggest that carboxyl functions are involved in the low-temperature crosslinking of coals. However, the chemical reactions linking decarboxylation with coupling have not been delineated. In a recent study, Siskin and coworkers showed that decarboxylation of naphthoic acid under hydrothermal conditions was attended by some binaphthyl, however, the coupling aspect was not elaborated in that study. We will conduct experiments with monomeric, albeit polycyclic, model compounds in organic media to see if crosslinking is associated with decarboxylation, and how a hydrothermal environment affects it.

V. TASK 4 - DATA INTEGRATION AND REPORTING

No work scheduled except routine report writing.

VI. PLANS FOR THIRD QUARTER

- Put subcontract into place.
- Complete preparation of modified coals.
- Complete preparation of modified polymers.
REFERENCES

END

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