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**THE USE OF SOLID-STATE NMR TECHNIQUES FOR THE ANALYSIS OF
WATER IN COAL AND THE EFFECT OF DIFFERENT COAL DRYING
TECHNIQUES ON THE STRUCTURE AND REACTIVITY OF COAL**

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INTRODUCTION

One area for improvement in the economics of coal liquefaction is coal drying, particularly for the lower rank coals. However, there is considerable evidence to show that drying has a detrimental effect on the liquefaction behavior of coals. Regarding the liquefaction of coal, there does not appear to have been any systematic study of the methods of coal drying on coal structure and the role water plays in enhancing or lessening coal reactivity toward liquefaction.

For the research program reported here, different methods of drying are being investigated to determine if drying can be accomplished without destroying coal reactivity toward liquefaction. In an effort to understand the mechanism of water for enhancing coal liquefaction yield, the reactions of D_2O with the molecular constituents of coal during coal liquefaction are being investigated. This study involves the use of solution-state deuterium NMR, as well as, conventional solution-state 1H and ^{13}C NMR analyses of the coal, and the coal liquids and residue from a coal liquefaction process. These D_2O transfer reactions will be conducted on coals which have been dried by various methods and rehydrated using D_2O and by successive exchange of H_2O associated with the coals with D_2O . The drying methods include thermal, microwave, and chemical dehydration of the coal.

OBJECTIVES

The overall objectives of this study are to develop a nuclear magnetic resonance (NMR) method for measuring the water in coal, to measure the changes in coal structure that occur during coal drying, to determine what effect water has on retrograde/condensation reactions, to

determine the mechanism by which water may impact coal reactivity toward liquefaction, and to conduct D₂O exchange studies to ascertain the role of water in coal liquefaction.

The objectives for this quarterly report period were (1) to train students in the operation of the coal liquefaction reactor, gas analysis, extraction of the coal residue and coal liquids, and to calculate the percent conversion from the coal liquefaction data; and (2) to implement the changes in the coal liquefaction experimental procedure.

EXPERIMENTAL

Coal Liquefaction

Discussions with DOE personnel in April 1993 resulted in changing the coal liquefaction experimental procedure.

Coal liquefaction experiments are conducted in a magnetically-stirred microautoclave reactor using a fluidized sandbath as a heating medium. The autoclave has a capacity of 200 cc with an inside diameter of 1.75 cm. This system was modified at the Wilsonville Advanced Coal Liquefaction Research and Development Facility to increase the volume and, as a result, improve material balances. The improved system, called VaSTeC for Variable Submergence Temperature Control, was developed by Catalytic Inc. (1986) and has been used extensively and reliably to predict and augment test results from the thermal liquefaction unit at the Wilsonville Direct Liquefaction facility. The VaSTeC system is large enough to provide adequate materials for post experiment analyses, yet is small enough to provide the rapid heating and cooling required for kinetic experiments. A schematic of the VaSTeC autoclave system is shown in Figure 1.

Liquefaction experiments are carried out using a 2:1 weight ratio of tetralin to coal instead of a 1:1 weight ratio. The greater fluid mass should insure better reproducibility and more

FIGURE I. SCHEMATIC OF VASTEC AUTOCLAVE SYSTEM

efficient liquefaction. The autoclave is pressurized to 900 psig with nitrogen gas instead of hydrogen gas. This change was necessary for future studies on the liquefaction of coal samples that will have water replaced by D_2O . It is anticipated that by using nitrogen gas, the role of water can be studied without the complication of the exchange of deuterium from D_2O with H_2 at the operating condition used for liquefaction. Thus scrambling of deuterium in the products should be limited to only those reactions in which water is involved.

Instead of using THF solubles as a measure of coal conversion, conversion will be based on CH_2Cl_2 solubles. Methylene chloride was chosen because it can be easily removed from the coal residue and coal liquid products. Because our objective is to determine the effects of different drying methods on coal structure, coal liquefaction experiments conducted under the same experimental conditions are considered acceptable to meet the objectives of the project.

Gas Analysis

The gases produced during the coal liquefaction process are collected in a gas bomb and analyzed using an HP 5890 Series II GC fitted with both an FID and TCD detectors. A 6 ft, porapak N, packed column is used to separate the gases. Helium is used as the carrier gas at a pressure of 20 psig at $160^\circ C$ and a flow rate of 16 cc/min. The analyses are performed with an oven temperature ranging from -45 to $160^\circ C$. The instrument is calibrated using a standard gas mixture of known volume percent.

Liquid and Solid Extraction

Upon completion of the coal liquefaction experiment, the reactor is opened, filled with CH_2Cl_2 , and the stirring assembly reattached. The reactor and stirring assembly are then allowed to set for 1 week. The CH_2Cl_2 containing the soluble coal products and coal residue is removed from the reactor and poured into a Soxhlet thimble.

The Soxhlet extraction is carried out for 30 hr at the refluxing temperature of CH_2Cl_2 . Nitrogen gas is bubbled through the CH_2Cl_2 . A rotary evaporator at 40°C and at the atmospheric pressure in Laramie is used to remove the CH_2Cl_2 . The remaining liquid is the CH_2Cl_2 soluble coal product and tetralin. The coal extract is analyzed for the soluble coal products above and below the tetralin gas chromatographic peak using an HP5890 gas chromatograph with flame ionization detector.

The solid residue in the Soxhlet thimble and thimble are placed into a furnace set at $\sim 100^\circ\text{C}$ for 20 hrs to remove solvent. The coal residues are analyzed using solid-state carbon-13 NMR.

RESULTS AND DISCUSSION

Since July of 1993, WRI has been downsizing for more cost effective operation. However, the effects of downsizing seriously impacted the coal liquefaction program in which two persons familiar coal liquefaction procedures were terminated. It became necessary to hire and to train chemical engineer students from the University of Wyoming in the coal liquefaction process procedures. The training has been completed and once again we are able to conduct coal liquefaction on coal samples. However, no data is available for discussion during this report period.

FUTURE WORK

The coal liquefaction of the dried North Dakota lignite and the Utah Blind Canyon coal will begin. These coals will be dried thermally, chemically, and with microwave radiation. The percent conversion of the coals will be calculated. The liquid products will be analyzed using

gas chromatography and the solid residue will be characterized using solid-state carbon-13 NMR spectroscopy.

REFERENCES

Catalytic Inc., 1986, Development of VaSTeC Autoclave Technique and Applications to Pilot Plant Guidance, Catalytic Inc. Wilsonville, AL, April Topical Report prepared for USDOE (Contract No. DE-AC22-82PC50041 and EPRI (Contract No. RP12324-1-2).

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