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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.

Ruether et al. (1985) using non-deuterated water studied the effects of water during direct hydroliquefaction on coal in uncatalyzed systems. They observed that at a substantial water partial pressure, coal conversion increases. Water was not considered to be a reactant (Ruether et al. 1986), however, the mechanism through which it aids conversion is unknown. Mikita and Fish (1986) suggested that water acts to open new ionic reaction pathways through its solvation effect. In a later study, Ruether et al. (1987) investigated hydroliquefaction coal conversion in the presence of catalysts and found that highest conversions are obtained without added water. They concluded that for reaction systems with the catalyst deposited from solution onto the coal particles, the resultant particles are highly reactive and that water retains a role as a solvent for the catalyst. In all studies, non-deuterated water was used, the percent coal conversion was measured by tetrahydrofuran (THF) solubles, and no product analyses were conducted. Thus, the role of water could not be ascertained.

One method of studying the chemical reactions occurring during the liquefaction of coal is to use deuterium-labeled compounds and to follow the incorporation of the deuterium into the coal-derived products. The coal liquefaction process can be divided into three distinct chemical reaction steps: (1) the reaction of pressurized H_2 gas with the coal, (2) the hydrogen exchange

reactions of the hydrogen donor solvents with the coal, and (3) the hydrogen exchange reactions of the water associated with the coal. In each of these steps the hydrogen can be replaced with deuterium to study the mechanism of the exchange reactions.

A number of deuterium exchange studies using deuterated hydrocarbon and D_2 gas under various experimental conditions have been conducted (Kuznetsov et al. 1991 and literature cited therein). In all of these studies, the alkyl group α to aromatic rings is shown to be important in coal liquefaction and that under coal liquefaction conditions deuterium is thoroughly scrambled.

Schweighardt et al. (1976) determined the distribution of deuterium incorporated among the various organic constituents of the liquid products resulting from coal liquefaction in a D_2 gas atmosphere, at 1600 psig, 450°C, for 15 minutes. The analysis of the product gases (H_2 , HD, and D_2) using mass spectrometry indicated that approximately 45% of the hydrogen originally present in the coal liquid had been replaced by deuterium. Deuterium nuclear magnetic resonance spectroscopy (NMR) was used to determine the hydrogen and deuterium distribution in the deuterated coal liquid and several fractions. Deuterium was found in all fractions at both aromatic and nonaromatic sites of the organic constituents. Schweighardt et al. (1976) found that a degree of specificity for the incorporation of deuterium at the α -alkyl and aromatic positions prevailed. Hydrogen bonded to carbons β or further removed from aromatic ring appeared to be least susceptible to deuterium labeling under the experimental conditions employed.

Hydrogen transfer reactions during coal liquefaction processes using deuterium-labeled tetralin was studied by Ratto et al. (1979, 1980). They measured the deuterium incorporated into the coal-derived products by 2H NMR and found that deuterium was preferentially incorporated into the α -alkyl position in the soluble products. Considerable isotopic exchange occurred between the deuterated tetralin at the α -position and the coal. Franz (1979) and Franz and

Camaioni (1981) conducted similar studies and found that at times longer than 10 minutes the deuterium was incorporated into the aromatic structure as well as at the α -alkyl position. The transfer of deuterium after 5 minutes at 427°C from deuterated tetralin to coal resulted in 80-85% of the deuterium appearing in the aliphatic structures (Franz and Camaioni 1981). The highest concentration occurred in benzylic and tertiary aliphatic sites.

The incorporation of deuterium into coal liquefaction products from D₂O has not been studied. The extent of deuterium scrambling from D₂O during coal liquefaction is unknown. However, Kuznetsov et al. (1991) studied the liquefaction of Kansk-Achinsk lignite in the presence of deuterated alcohols. From the analyses of the products obtained from the liquefaction process, they found that deuterium distribution in maltenes, asphaltenes, and solid residues increased in the order: solid residues > asphaltenes > maltenes. In all cases deuterium was detected mainly in the aliphatic structural groups and to a small extent in the aromatic rings. The deuterium distribution differs considerably from that observed by previous authors for coal liquefaction in deuterated tetralin or in the presence of gaseous deuterium. Kuznetsov et al. (1991) suggest that the apparent differences in deuterium distribution in tetralin and alcohol-derived coal products are connected with the initial exchange mechanism. For coal liquefaction in deuterated tetralin or gaseous deuterium, deuterium is transferred into the products through hydrogenation and exchange. For coal liquefaction in the presence of alcohol, the deuterium transfer is apparently made by alkylation.

Lewan (1992) used D₂O in hydrous pyrolysis of Woodford shale to better understand the role of water in petroleum formation. Deuterium NMR analyses of the pyrolyzate products showed that the expelled immiscible oil as well as the bitumen and kerogen retained in the rock contained significant quantities of deuterium. Deuterium substitution for hydrogen was found

to be approximately 40% for the expelled oil and 33% for the extracted bitumen. Quantification for the kerogen was not performed. Lewan interprets the high degree of deuterium substitution to be the result of free radical sites being terminated by deuterium atoms derived from the oxidation of carbonyl groups by D_2O . Thus, under hydrous conditions, the free radical sites formed on the bitumen molecule are terminated with water-derived hydrogen before β -scission of the molecule occurs. Under anhydrous condition, the lack of water-derived hydrogen for terminating free-radical sites that occur on the bitumen molecule results in frequent β -scissions.

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 measure the volumetric swelling ratio for thermally- and microwave-dried coals and (2) to conduct preliminary experiments concerning the exchange of water in coal with deuterium oxide (D₂O).

EXPERIMENTAL

To conduct this study two coals, the North Dakota Beulah Zap lignite and the Utah Blind Canyon coals were chosen. These coals represent a low and high rank coal, respectively. In addition, the Beulah Zap lignite has a high moisture content whereas the Blind Canyon coal (hvA) bituminous has a very low moisture content.

Coal Swelling

The solvent swelling of the North Dakota Beulah Zap and the Utah Blind Canyon coals was conducted using the procedure described in the previous quarterly report. The coals were dried thermally and with microwave radiation. The methods of drying were described in the quarterly report dated December 1, 1992 - February 28, 1993.

D₂O Exchange

Two types of experiments were performed to study the D₂O exchange with the H₂O in coal. The first of these experiments involved taking aliquots of D₂O from coal-D₂O slurry (0.5 g coal, 5 mL D₂O). Every two hours an aliquot of D₂O was removed and put into an NMR tube, except for the last aliquot which was removed from the coal slurry after one week. The samples

were then run on the liquid state ^1H NMR. The second experiment involved repeated washings of the coal with D_2O . The samples were prepared by taking about 0.5 g of coal and covering it with about 2 mL of D_2O . After 20 minutes an aliquot of D_2O was drawn off and put in an NMR tube and the rest of the D_2O was discarded. This process was repeated twice more. For the last aliquot the D_2O was removed after one week in contact with the coal sample.

RESULTS AND DISCUSSION

Table 1 lists the swelling ratios in 1,4-dioxane for the raw coals and the thermally-, microwave-, and chemically-dried Utah Blind Canyon bituminous coal and the North Dakota Beulah Zap lignite.

Table 1. Swelling Ratios for Raw Coals and Thermally-, Microwave-, and Chemically-Dried Coals.

Drying Method	Swelling Ratio Using 1,4-Dioxane	
	Beulah Zap	Blind Canyon
Raw	1.40	1.23
Thermally Dried	1.15	1.15
Microwave Dried	1.13	1.12
Chemically Dried	1.44	1.37

The swelling ratios for the raw (1.40) and chemically-dried (1.44) Beulah Zap lignite are nearly the same indicating that no major structural changes in the lignite had occurred during the chemical dehydration process. However, relative to the raw lignite, a decrease in the swelling ratios were observed for both the thermally- (1.15) and microwave- (1.13) dried lignite samples.

These decreases in the swelling ratios indicate a greater degree of cross-linking had occurred in the lignite structure as the result of these drying methods. The decrease is greatest for the lignite presumably because of the greater decarboxylation that occurs during heating of these coals. The swelling ratios for the chemically-dried (1.37) Blind Canyon coal was observed to be greater than the raw (1.23) coal indicating a lesser degree of cross-linking of the structure and/or reduction in association such as hydrogen bonding of the chemical species of the chemically-dried coals. However, the swelling ratios for the coal when dried thermally (1.15) or with microwave radiation (1.12) decreased relative to the raw (1.23) coal. As observed for the lignite samples, these decreases in swelling ratios for the thermally- and microwave-dried Blind Canyon coal samples indicate an increase in the cross-linking or association in the chemical structure of this coal due to these drying methods.

Preliminary D_2O exchange experiments on coal samples have been performed. Repeated washing of lignite and bituminous coals with D_2O replaces essentially all H_2O in a short period of time as measured by 1H NMR of the HDO signal in D_2O . Figure 1 shows the decrease in the HDO NMR signal with four successive washings of the North Dakota Beulah Zap lignite with D_2O . Figures 2A and 2B show the kinetics of D_2O - H_2O exchange for the North Dakota Beulah Zap lignite and Utah Blind Canyon bituminous coal. The coals were treated with D_2O and aliquots removed over several hours. The replacement of surface H_2O , as measured by the HDO 1H NMR signal, is rapid followed by the replacement of the diffusion controlled pore H_2O . This is shown in Figures 2A and 2B as an increase in signal height with time. After a significant length of time a decrease in HDO signal is observed. Additional experiments are needed to confirm that the decrease in signal is real and to determine the exchange mechanism which can explain the observations.

The successive exchange of H_2O in coal with D_2O will provide D_2O -hydrated coal samples for coal liquefaction that have not been previously dried. Comparing the liquefaction data for H_2O -hydrated coals and D_2O -hydrated coals will provide the necessary information to evaluate the role of water in coal liquefaction.

FUTURE WORK

The North Dakota Lignite and the Utah Blind Canyon coal will be dried by the various methods and rehydrated with D_2O . These coal samples will then be subjected to coal liquefaction conditions, and the reactants and products analyzed for the incorporation of deuterium.

Figure 1. ^1H NMR Spectra of the HDO Resonance for Successive D_2O - H_2O Exchange for the North Dakota Beulah Zap Lignite

Figure 2. ^1H NMR Spectra of the HDO Resonance as a Function of Time: (A) North Dakota Beulah Zap Lignite and (B) Utah Blind Canyon Coal

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