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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. In part, this may have been the result of not having the techniques that are now available, such as solid-state nuclear magnetic resonance (NMR) spectroscopy.

OBJECTIVES

The overall objectives of this study are to develop an 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, and to determine the mechanism by which water may enhance coal reactivity toward liquefaction. Different methods of drying will be investigated to determine if drying can be accomplished without destroying coal reactivity toward liquefaction, thereby making coal drying an attractive and economical method for coal pretreatment.

The objectives for this quarterly report period were (1) to determine the cause of the decrease in percent recovery of water with

increasing water concentrations, (2) to improve the accuracy of the water determinations using NMR, and (3) to determine the moisture content by ^1H NMR of eight Argonne Premium coals for which the moisture content is known.

Difficulties encountered in improving the accuracy and precision of the ^1H NMR method for measuring the moisture content in coals prevented us from achieving objective 3 during this time period.

EXPERIMENTAL

Instrument

Because of the number of University of Wyoming students using the JEOL GSX-270 NMR spectrometer and some instrumental difficulties, hydrogen-1 NMR spectra were obtained on a JEOL GS-400 NMR spectrometer. The experimental conditions for recording a ^1H spectrum were eight scans, a pulse width of 9.9 μs , an acquisition time of 1.0 s, a pulse delay of 20 s, and 16K time-domain data points. A line broadening factor of 2 Hz was used to obtain the transformed spectra. Resonance areas for acetone and cycloheptane were performed on a Gateway 2000 PC using Lab Cal^{TM} curve-fitting routine. Line width at half-height of 0.010 ppm was used for curve-fitting. Twenty iterations of a Lorentzian line shape give quite acceptable agreement between the experimental and fitted resonance.

Procedure

Since the last quarterly report, several changes have been made in the methodology for determining water using 2,2-dimethoxypropane. To catalyze the reaction, 2 mL of 0.2N methanesulfonic acid in methanol was used. Various amounts of water (0.0, 0.05, 0.10, 0.20, and 0.30 g) were added to separate solutions of acid in methanol. To insure complete reaction, the solutions were allowed to stand for about 1.5 hours before analysis.

RESULTS AND DISCUSSION

Three separate experimental runs using solutions of a known amount of water were made to determine the precision and accuracy of the method (Table 1). The amount of water in the blank solutions was found to be an average of 0.0107 ± 0.0004 g. The average relative error was found to be $< \pm 3\%$ and the absolute error was found to be better than ± 0.005 g for all solutions with a known amount of water. The percent recovery was determined to be $100 \pm 3\%$ over the concentration range of 0.0 to 0.3 g of water. Figure 1 shows the hydrogen spectrum of acetone, cycloheptane and the methyl hydrogen resonance of 2,2-dimethoxypropane. Also shown are the Lorentzian curve-fits of the resonance lines. The curve-fitting routine for determining the area under the peaks increased the precision and accuracy of the method by eliminating instrumental and other artifacts which contributed to the peak shape.

Figure 2 shows a plot of the known amount of water in solution versus the amount of water as determined by ^1H NMR.

CONCLUSIONS AND FUTURE WORK

Using a curve-fitting routine for measuring the area of the resonance lines, as well as increasing the acid concentration and reaction time, improved the precision and accuracy of technique for measuring water content by ^1H NMR. It is anticipated that the water content in Argonne coal samples, Eagle Butte coal, and an Alaskan coal will be determined during the next quarterly report period. In addition, cyclohexane will be tried as a hydrogen reference material because of its availability and purity relative to cycloheptane.

Table 1. Precision and Accuracy for Solutions of a Known Amount of Water by ^1H NMR

Sample	Water, grams		Recovery, %	Relative Error, %	Absolute Error, grams
	Added	Found			
Run #1					
H651011	-	0.0103			
12	0.0509	0.0495	97	-2.75	-0.0014
13	0.1023	0.1065	104	4.11	0.0042
14	0.2029	0.2026	100	-0.15	-0.0003
15	0.3036	0.2995	99	-1.35	-0.0041
Run #2					
H651011A	-	0.0106			
12A	0.0668	0.0662	99	-0.90	-0.0006
13A	0.1323	0.1316	100	-0.53	-0.0007
14A	0.2027	0.2008	99	-0.91	-0.0019
15A	0.3079	0.2973	97	-3.40	-0.0106
Run #3					
H651001	-	0.0111			
2	0.0578	0.0588	102	1.73	0.0010
3	0.1070	0.1080	101	0.93	0.0010
4	0.2040	0.1988	97	-2.55	-0.0052
5	0.3098	0.3063	99	-1.13	-0.0035

Res= .98

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DNAME,COALDRY.009,FNAME,H651013A,NB678P75,.1ML_H2O

Figure 1. ^1H Spectrum with Lorentzian Line-Fit of a Standard Solution

Figure 2. Known Water Content versus Water Content Determined by ^1H NMR

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