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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**

by
Daniel A. Netzel

Quarterly Report: March 1, 1994 - May 31, 1994

**Work Performed Under Grant Agreement
DE-FG22-91PC91310**

**For
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236-0940**

**By
University of Wyoming Research Corporation
a.k.a. Western Research Institute
Laramie, Wyoming**

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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 D_2O exchange studies to ascertain the role of water in coal liquefaction.

The objectives for this quarterly report period were (1) to conduct coal liquefaction experiments on the North Dakota Beulah Zap and Utah Blind Canyon coals that were premoisturized, dried thermally, dried with microwave radiation, and dried using the chemical dehydration method; (2) to determine the carbon aromaticity values for the coal residues using solid state NMR; (3) to analyze the gases produced during liquefaction using gas chromatography; and (4) to measure the ratio of light and heavy oils in the coal liquids using gas chromatography.

EXPERIMENTAL

The experimental procedures used in the analysis of the coal residues, gases, and liquids were described in previous reports.

RESULTS AND DISCUSSION

Tables 1 and 2 give the results of the coal liquefaction of North Dakota Beulah Zap and Utah Blind Canyon coals dried using various methods. These tables contain data on the percent gas, liquid, and residue produced, and the percent conversion for different drying techniques. Table 3 shows the ^{13}C NMR aromaticity values for the coal liquefaction residues from the two coals dried by various methods. Also included in the table are the aromaticity values for the dried coals before liquefaction. Gas chromatographic analyses of the coal liquids are reported in Table 4. The analysis is reported as the percent of oil below and above a retention time (RT) of 14 min. The amount of oil below an RT of 14 minutes is defined as a light oil and above an RT of 14 minutes as a heavy oil. The type and amount of gases from the coal liquefaction experiments for the two coals are given in Table 5.

Table 1. Coal Liquefaction Data of North Dakota Beulah Zap Lignite Dried by Various Methods

Drying Method	% H ₂ O	Coal Liquefaction			
		% Gas	% Liq	% Residue	% Conversion
Premoisturized Coal	33.5	35.6	38.8	25.6	74.4
Thermal	0	1.3	51.0	47.7	52.3
Microwave	0	14.4	38.6	47.0	53.0
Chemical	0	14.1	46.9	39.0	61.0

Table 2. Coal Liquefaction Data of Utah Blind Canyon Bituminous Coal Dried by Various Methods

Drying Method	% H ₂ O	Coal Liquefaction			
		% Gas	% Liq	% Residue	% Conversion
Premoisturized Coal	5.2	9.1	61.0	30.0	70.0
Thermal	0	1.9	67.9	30.2	69.8
Microwave	0	1.7	72.6	25.6	74.4
Chemical	0	4.0	65.0	31.0	69.0

Table 3. ¹³C NMR Aromaticity Values for Coal Liquefaction Residue from Coals Dried by Various Methods

	North Dakota Beulah Zap		Utah Blind Canyon	
	Dried Coal	Coal Residue	Dried Coal	Coal Residue
Premoisturized Coal	0.745	0.892	0.618	0.809
Thermal	0.751	0.886	0.610	0.809
Microwave	0.728	0.894	0.638	0.775
Chemical	0.684	0.880	0.637	0.700

Table 4. GC Analysis of Coal Liquids from Coal Liquefaction of Coals Dried by Various Methods

	<u>North Dakota Beulah Zap</u>		<u>Utah Blind Canyon</u>	
	<u>Percent of Oil</u>		<u>Percent of Oil</u>	
	Below 14 min RT	Above 14 min RT	Below 14 min RT	Above 14 min RT
Premoisturized				
Coal	78.5	21.5	71.6	28.4
Thermal	87.4	12.6	67.3	32.7
Microwave	82.1	17.9	66.0	34.0
Chemical	84.1	15.9	69.9	30.1

Table 5. GC Analysis of the Gas from Coal Liquefaction of Coals Dried by Various Methods

Component Mole %	<u>North Dakota Beulah Zap</u>				<u>Utah Blind Canyon</u>			
	Raw	Thermal	Micro-wave	Chem-ical	Raw	Thermal	Micro-wave	Chem-ical
Hydrogen	0	0	0	0	0	0	0	0
Nitrogen	83.9	98.3	89.9	89.4	93.0	97.8	98.0	95.4
Oxygen	0	0	0	0	0	0	0	0
Argon	0	0	0	0	0	0	0	0
CO	1.09	0	.638	.693	.584	0	0	.128
CO ₂	10.1	.067	5.91	5.43	2.57	.390	.368	.996
Methane	2.14	1.521	2.51	3.53	2.50	1.46	1.31	2.86
Ethene	.087	0	0	0	.043	0	0	0
Ethane	.569	.062	.686	.633	.692	.199	.188	.364
Propane	.325	.046	.262	.287	.407	.145	.139	.247
Isobutane	.019	.004	.015	.016	.046	.010	.010	.014
n-butane	.075	.011	.039	.042	.102	.025	.023	.029
H ₂ O	.103	0	0	0	0	0	0	0
H ₂ S	.007	0	0	0	0	0	0	0
COS	1.56	0	0	0	.071	0	0	0

North Dakota Beulah Zap Lignite: The data in Table 1 show that the percent conversion decreases for all drying methods relative to the premoisturized coal. The percent of coal residue increased for the different drying methods. However, the ^{13}C NMR aromaticity values for all residues are the same within experimental error (Table 2). The percent of gas formed during liquefaction decreased for the dried coals. All of the components of the gas mixture decreased (Table 5) except for methane which increased when the coal was chemically dried. This increase may be due to methanol at the site previously occupied by the water molecules. The most noticeable decrease was the suppression of CO_2 produced during coal liquefaction. The percent of coal liquid increased for the thermally and chemically dried coals and remained the same for the microwave dried coal relative to the premoisturized coal. Relative to the premoisturized coal, the percent of light oil increased (Table 4) was independent of the drying method.

Utah Blind Canyon Bituminous Coal: In contrast to the Beulah Zap lignite, little change in the percent conversion (Table 3) was observed for the Utah coal for the three different drying methods used. The percent of coal residue formed for each drying method was about the same. The ^{13}C NMR aromaticity value decreased slightly for the coal samples dried by microwave heating and chemical dehydration (Table 3). The percent of gas formed upon coal liquefaction decreased for all methods of drying. The most noticeable component decrease occurred for CO_2 (Table 5). The percent of coal liquid increased for all drying methods. The percent of light oil decreased slightly relative to the premoisturized coal and appears to be independent of the drying method.

FUTURE WORK

The coal liquefaction experiments will be conducted on the North Dakota and Utah coals in which the water in these coals have been replaced by D_2O . An effort will be made to determine the extent of D_2O incorporated into the coal liquids and gases during the liquefaction process.

Work will begin on assembling the data for the final report and papers for publication.

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