1 of 1

DOE/PC/91043-T7

S-2
3

SEP 11 1993

**An Investigation of the Role of Water on Retrograde/Condensation
Reactions and Enhanced Liquefaction Yields**

Francis P. Miknis

NOV 03 1993

0011

August 1993

Quarterly Progress Report for the Period April 1, 1993 - June 30, 1993

Work Performed Under DOE Contract, DE-AC22-91PC91043

By

**Western Research Institute
Laramie, Wyoming**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

yes

BD

no issue

SEP 14 1993

**An Investigation of the Role of Water on Retrograde/Condensation
Reactions and Enhanced Liquefaction Yields**

Francis P. Miknis

August 1993

Quarterly Progress Report for the Period April 1, 1993 - June 30, 1993

Work Performed Under DOE Contract, DE-AC22-91PC91043

By

**Western Research Institute
Laramie, Wyoming**

BACKGROUND

The overall objectives of this work are to conduct research that will provide the basis for an improved liquefaction process, and to facilitate our understanding of those processes that occur when coals are initially dissolved. Changes in coal structure that may occur during coal drying will be measured in order to determine the effects of coal drying on its reactivity toward liquefaction. Different methods for coal drying will be investigated to determine if drying can be accomplished without destroying coal reactivity toward liquefaction, thereby making coal drying a relatively economical and efficient method for coal pretreatment. Coal drying methods will include conventional thermal drying, microwave drying, and chemical drying at low temperature. State-of-the-art solid-state nuclear magnetic resonance (NMR) techniques using combined rotation and multiple pulse spectroscopy (CRAMPS) and cross polarization with magic-angle spinning (CP/MAS) will be employed: (1) to measure changes in coal structure brought about by the different methods of drying and by low temperature oxidation, and (2) to obtain direct measurements of changes in the aromatic hydrogen-to-carbon ratio of the solid/semisolid material formed or remaining during pretreatment and the initial stages of liquefaction. The aromatic hydrogen-to-carbon ratios are difficult, if not impossible, to measure without the use of solid-state NMR.

RESULTS

The objectives for this quarter were to begin coal liquefaction experiments on coals that had been dried to varying moisture levels using thermal, microwave, and chemical drying methods. However, during a project review at PETC on April 27, 1993, some concerns were raised and suggestions made to improve the experimental approach. Consequently, most of the work during the quarter focused on addressing those suggestions and concerns. Primarily, the suggestions and concerns dealt with whether the reactor was being well-stirred during the liquefaction experiments, the use of a 1:1 coal solvent ratio, and the use of THF as an extraction solvent especially when NMR measurements were planned for the liquid and residue products. In

addition to addressing these matters, some liquefaction experiments were conducted on partially dried coals, the kinetics of chemical dehydration of coals was investigated, and preliminary volumetric swelling ratio experiments were conducted.

Coal Preparation

Master batch samples (~500 g) of coals are prepared by grinding and screening to -20, +100 mesh particle size. The samples are placed in a wide mouth jar and placed in an oven with a beaker of water, and allowed to equilibrate at 40°C for 24 hr. The samples are then removed from the oven and placed in a humidifier until aliquots are taken for the different drying and liquefaction tests.

Thermal Drying

Solid-state ^{13}C NMR measurements made in the previous quarter indicated that overall, there were not any dramatic changes in the carbon structure as a result of ballistic heating to 250°C. These results were presented at the project review. Thermal drying experiments were not conducted during the quarter.

Microwave Drying

Microwave drying experiments were not conducted during the quarter. Results from the previous quarter were discussed at the project review meeting.

Chemical Drying Kinetics

The details of chemically drying coals using 2,2-dimethoxypropane (DMP) were described in the previous quarter. However, in order to be able to dry coals by this method to varying levels of remaining moisture, the kinetics of chemical drying were investigated. For the kinetic experiments, the amount of coal and volume of reagents were doubled. Aliquots of the reaction mixture were removed at 0.25, 0.50,

1.0, 2.0, 4.0, 6.0, 8.0, and 24.0 hr. The aliquots were diluted in CDCl_3 , and the ^1H NMR spectra were recorded. In some cases, the aliquots had to be refrigerated until the NMR spectrometer became available.

The percentages of moisture removed as a function of reaction time are shown in Figures 1 through 4. In all cases, a significant amount of moisture is removed in the first 15 min of reaction with 2,2-dimethoxypropane (DMP), particularly in the Black Thunder coal. Presumably, the initial reaction is with free and surface water. Removal of the remaining moisture requires longer times and may be due to diffusion limitations of DMP contacting water in smaller pores.

The chemical drying data were fit to 1st- and nth-order kinetic equations. The kinetic parameters are listed in Table 1. For the Eagle Butte and Illinois No.6 coal, there is little difference between the 1st- and nth-order treatment of the data. However, the nth-order model gave a more representative initial moisture value. The main concern of this exercise was to obtain an estimation of how fast moisture is removed by chemical drying, so that coals dried to different moisture levels by chemical drying could be generated for liquefaction experiments.

For $n = 1$

$$M = C_i + M_o (1 - e^{-kt})$$

For $n \neq 1$

$$M = C_i + M_o - [1 / ((n - 1) kt + 1/M_o^{n-1})]^{1/(n-1)}$$

where: M = total percent moisture removed

C_i = percent moisture removed during the initial reaction

M_o = percent moisture in coal at $\tau = 0$ (not including the water removed during the initial reaction)

k = rate constant

τ = time

n = order of reaction

Coal Swelling Experiments

Solvent swelling measurements were made on the coals using the procedure described by Green et al. (1984). Experiments were conducted on the initial coals, and coals dried using microwaves. The particle size was -20 + 100 mesh. One-half gram of coal was weighed in a centrifuge tube, centrifuged for 5 min at 1700 rev/min. and the height of the coal was measured in millimeters. Four mL of cyclohexane was added, the mixture stirred, and then centrifuged for 5 min. The procedure was repeated until a constant height was obtained. The experiments were repeated using 1,4 dioxane as a swelling solvent.

The volumetric swelling ratio, $Q_{v,dry}$, was calculated from the ratio of the measured heights of the coal in the solvent (h_2) and the height of the initial coal (h_1),

$$Q_{v,dry} = h_2/h_1$$

Results are given in Table 2.

The purpose of the swelling experiments is to study the effects of drying on the physical structure of the coals and the extent of crosslinking that might result from the different drying methods. These changes can have an effect on the liquefaction yields. In all cases, microwave drying affected the swelling ratios of the low rank coals (Texas, Eagle Butte, and Black Thunder). These coals also have greater amounts of oxygen functionalities in the form of carboxylates, that are known to be precursors to crosslinking during heating of coal. Additional drying experiments are planned for next quarter on coals dried by different methods.

Coal Liquefaction Experiments

Coal liquefaction experiments were conducted to determine the effect of stirring speed, solvent ratio, and solvent type on liquefaction yields of Eagle Butte coal.

Once these parameters are optimized, they will be used in subsequent investigations of different drying processes on liquefaction yields of different coals. Table 3 summarizes all the liquefaction experiments carried out to date. For the initial experiments to determine the effects of drying methods on liquefaction yields, a 1:1 weight ratio of coal to tetralin was used. The initial coal sample had a weight of 20 grams and was screened to a -20 +100 mesh particle size. The autoclave was pressurized with hydrogen at 900 psig. The volume of this reactor was ~200 cc. Liquefaction experiments were conducted at 425 °C for a period of 30 min. The spinning rate was 435 rpm, which corresponds to about 60% of maximum rate.

The coal liquefaction experiments conducted on Eagle Butte coal are summarized in Figure 5. The original coal, containing ~20% moisture, had a conversion of ~80%, based on extracting the coal residue with THF. The liquefaction conversions of Eagle Butte samples that were "completely" dried by ballistic heating (thermal), microwaves, or chemical drying are substantially lower. These results agree with other results that have reported reduced liquefaction conversions for "completely" dried coals. Although only a few liquefaction experiments were carried out on partially dried coals, there does appear to be a trend of relatively constant conversions with moisture removal, until about 80% of the coal moisture is removed. Removal of the remaining 20% of the moisture appears to have an adverse effect on coal conversion.

Liquefaction experiments were also carried out in a small (~70 cc) reactor in which solvent ratio, stirring speed, and solvent type were varied. These are summarized in Table 3. For convenience and ease of operation, the conditions of: a 1:1 ratio of methylene chloride, and a stirring speed of 60% of maximum speed have been chosen for future experiments on coal liquefaction.

Future Work

Toward the end of the quarter, WRI underwent an organizational right sizing. As a result, key personnel who had been working on the project were either laid off,

or reassigned to other divisions. Consequently, future work will be delayed until the personnel problem can be resolved.

Reference

Green T.K., J. Kovac, and J.W. Larsen, 1984, A rapid and convenient method for measuring the swelling of coals by solvents, Fuel, 63, 935-938.

Table 1. Kinetic Parameters for Chemical Dehydration of Coals

Parameter	<u>Eagle Butte</u>		<u>Texas</u>		<u>Illinois No. 6</u>		<u>Black Thunder</u>	
	1st Order	nth Order	1st Order	nth Order	1st order	nth Order	1st Order	nth Order
n	1	3.62	1	5.61	1	1.07	1	0.943
k	2.17×10^{-3}	0.157	8.39×10^{-3}	12.8	1.93×10^{-2}	2.49×10^{-2}	1.85×10^{-3}	1.62×10^{-2}
C_i	12.5%	11.2%	18.4%	13.0%	4.6%	4.5%	19.9%	15.3%
M_o	11.5%	18.8%	11.3%	23.6%	6.5%	6.6%	2.2%	7.1%
r^2	0.997	0.998	0.997	0.993	0.999	0.999	0.999	0.993

Table 2. Volumetric Swelling Ratios

Solvent	<u>Eagle Butte</u>		<u>Texas</u>		<u>Illinois No. 6</u>		<u>Black Thunder</u>	
	Raw	Microwave	Raw	Microwave	Raw	Microwave	Raw	Microwave
1,4-Dioxane	1.50	1.15	1.28	1.18	1.10	1.18	1.39	1.24
Cyclohexane	1.10	1.06	1.12	1.22	1.10	1.18	1.16	1.18

Table 3. Summary of Coal Liquefaction Experiments on Partially Dried Coals

Coal	Test No.	Drying Method	Moisture, wt %	Conversion, wt %	Coal:Tetralin Ratio	Stirring Rate	Extraction Solvent
Eagle Butte	9	None	20.0	75.2	1:1	60	THF
	11	Thermal	0.0	56.2	1:1	60	THF
	12	Thermal	2.8	75.0	1:1	60	THF
	13	Microwave	0.0	61.1	1:1	60	THF
	15	Microwave	5.0	70.9	1:1	60	THF
	17	None	18.7	74.8	1:1	60	THF
	20	Thermal	10.6	78.1	1:1	60	THF
	21	Microwave	7.0	75.3	1:1	60	THF
	10	None	18.7	79.9	1:1	60	THF
	14	Chemical	0.0	65.3	1:1	60	THF
Black Thunder	22	None	24.9	75.1	1:1	60	THF
Texas	23	None	28.1	83.5	1:1	60	THF
Illinois No. 6	24	None	9.9	86.7	1:1	60	THF
	28	Chemical	12.2	78.2	1:1	60	THF
<u>Small Reactor, 70 cc</u>							
Eagle Butte	30	None	21.1	78.3	1:1	60	CH ₂ Cl ₂
	34	None	18.8	59.2	1:4	30	CH ₂ Cl ₂
	31	None	20.8	70.6	1:4	60	CH ₂ Cl ₂
	33	None	19.1	70.1	1:4	90	CH ₂ Cl ₂
	35	None	19.7	82.0	1:4	60	THF

Figure 3. Weight Percent of Water Removed by DMP in Texas Coal as a Function of Time

Figure 4. Weight Percent of Water Removed by DMP in Illinois No.6 Coal as a Function of Time

Figure 1. Weight Percent of Water Removed by DMP in Eagle Butte Coal as a Function of Time

Figure 2. Weight Percent of Water Removed by DMP in Black Thunder Coal as a Function of Time

Figure 5. The Effect of Moisture Removal on the Coal Liquefaction Conversion of Eagle Butte Coal

**DATE
FILMED**

1 / 3 / 94

END