

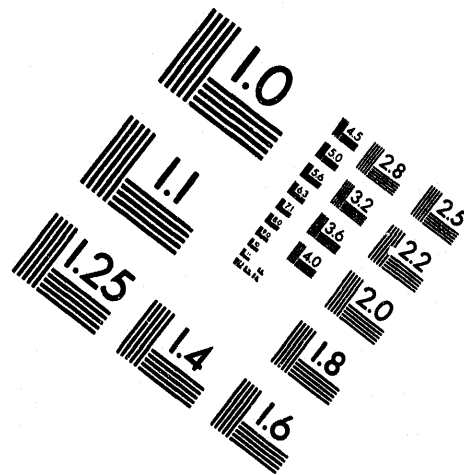
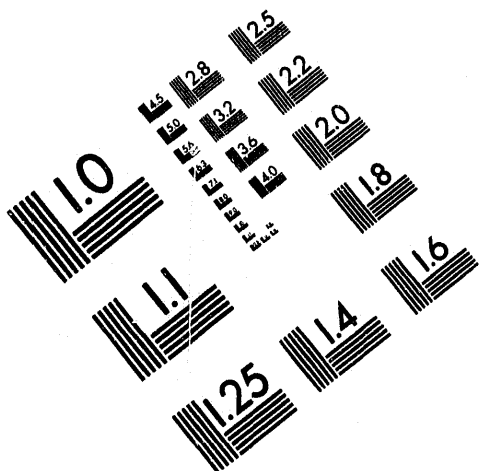


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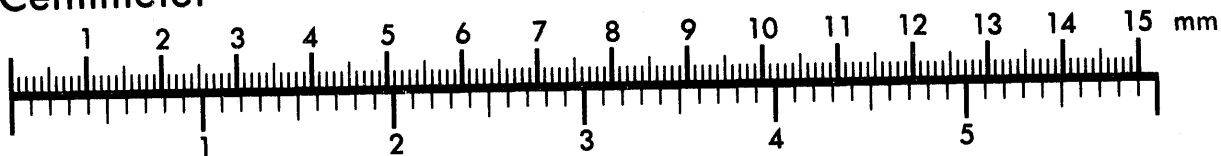
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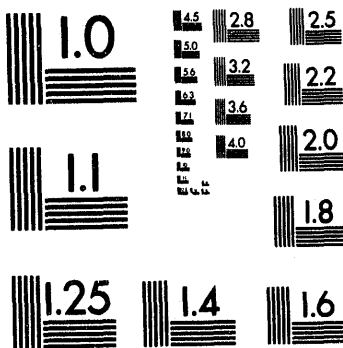
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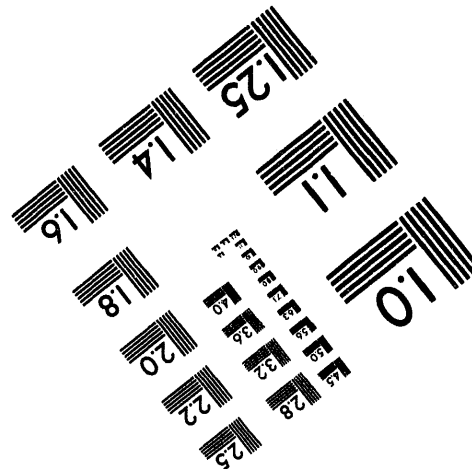
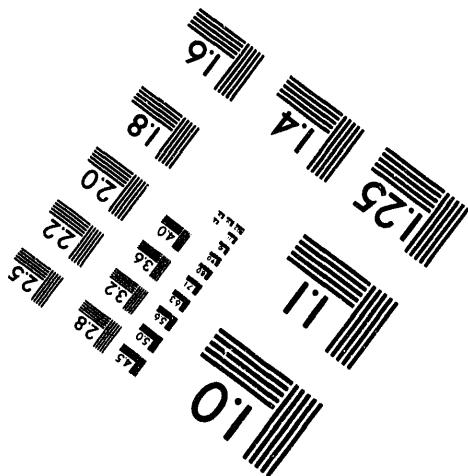
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**AN INVESTIGATION OF THE ROLE OF WATER ON RETROGRADE/  
CONDENSATION REACTIONS AND ENHANCED LIQUEFACTION YIELDS**

by  
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**April 1994**

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*for* **MASTER**

## TABLE OF CONTENTS

	<b><u>Page</u></b>
<b>LIST OF TABLES AND FIGURES .....</b>	<b>iii</b>
<b>INTRODUCTION .....</b>	<b>1</b>
<b>OBJECTIVES .....</b>	<b>1</b>
<b>EXPERIMENTAL .....</b>	<b>2</b>
<b>RESULTS AND DISCUSSION .....</b>	<b>5</b>
<b>FUTURE WORK .....</b>	<b>6</b>
<b>REFERENCES .....</b>	<b>6</b>

## LIST OF TABLES

<b><u>Table</u></b>	<b><u>Page</u></b>
1. 1,4-Dioxane Swelling Ratios of Coals Dried Thermally, Chemically, and with Microwave Radiation .....	5

## LIST OF FIGURES

<b><u>Figure</u></b>	<b><u>Page</u></b>
1. Schematic of VaSTeC Autoclave System .....	3

## INTRODUCTION

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) technique of 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 measure the changes in the aromatic hydrogen-to-carbon ratio of the solid/semisolid material formed or remaining during pretreatment and the initial stages of liquefaction.

## OBJECTIVES

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.

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 measure the swelling ratios of the coal dried thermally, chemically, and with microwave radiation.

## EXPERIMENTAL

### Coal Liquefaction

Discussions with DOE personnel at a project review 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 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.

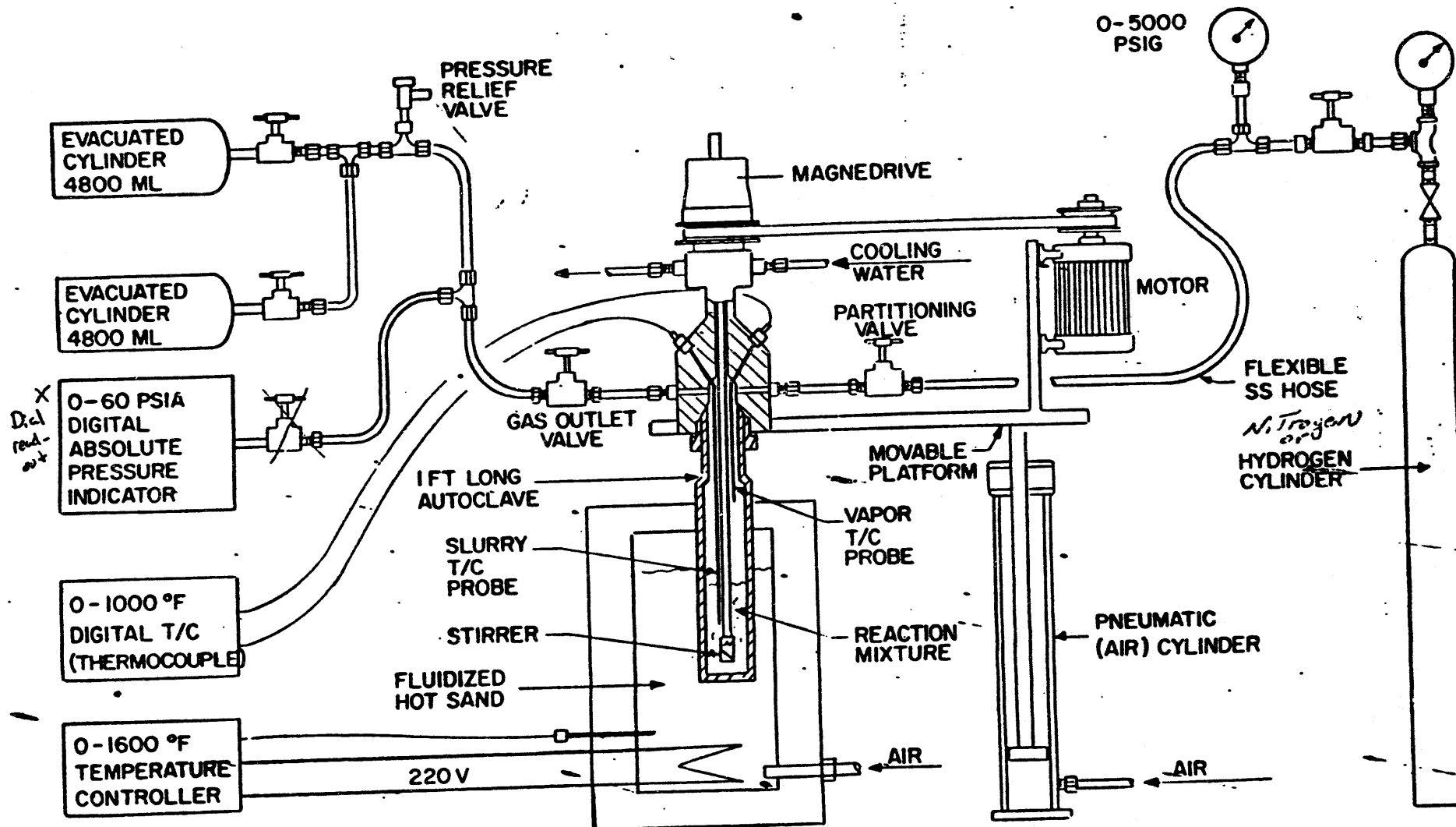


FIGURE 1. SCHEMATIC OF VASTEC AUTOCLAVE SYSTEM



Instead of using THF solubles as a measure of coal conversion, conversion will be based on  $\text{CH}_2\text{Cl}_2$  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  $160^\circ\text{C}$  and a flow rate of 16 cc/min. The analyses are performed with an oven temperature ranging from  $-45$  to  $160^\circ\text{C}$ . 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  $\text{CH}_2\text{Cl}_2$ , and the stirring assembly reattached. The reactor and stirring assembly are then allowed to set for 1 week. The  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_2\text{Cl}_2$ . Nitrogen gas is bubbled through the  $\text{CH}_2\text{Cl}_2$ . A rotary evaporator at  $40^\circ\text{C}$  and at the atmospheric pressure in Laramie is used to remove the  $\text{CH}_2\text{Cl}_2$ . The remaining liquid is the  $\text{CH}_2\text{Cl}_2$  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 ~ 100°C for 20 hrs to remove solvent. The coal residues are analyzed using solid-state carbon-13 NMR.

## RESULTS AND DISCUSSION

Table 1 gives the results of coal swelling measurements using 1,4-dioxane as the swelling reagent for premoisturized coals (raw) and coals dried thermally, chemically, and with microwave radiation. An increase in the swelling ratio relative to raw coal indicates a decrease in the amount of cross-linking in the coal. Conversely, a decrease in the ratio indicates an increase in cross-linking. The extent of cross-linking (as measured by 1,4-Dioxane) for Texas, Black Thunder, and Eagle Butte Coals are about the same. Illinois #6 coal appears to have less cross-linking relative to the other three coals. These results are expected on the basis of coal rank.

Table 1. 1,4-Dioxane Swelling Ratios of Coals Dried Thermally, Chemically, and with Microwave Radiation.

Drying Method	Coals			
	Texas	Black Thunder	Eagle Butte	Illinois #6
Raw	1.49	1.45	1.46	1.62
Thermally	1.28	1.34	1.26	1.54
Microwave	1.33	1.33	1.31	1.45
Chemically	1.41	1.68	1.55	1.59

The increase in cross linking is most pronounced for coals dried thermally and with microwave radiation. A decrease in the swelling ratios for all four coals suggests that cross-linking had occurred possibly due to partial devolatilization process. However, low temperature,

chemical dehydration of the coals causes only a small or no change in the internal structure for Texas and Illinois #6 coals whereas a significant decrease in the cross-linking structure for the Black Thunder and Eagle Butte coals is observed. It is possible that the solvent ( $\text{CH}_3\text{OH}$ ) and products resulting from the chemical dehydrating (acetone and methanol) occupy the surface sites that water had before the reaction and thus preventing cross-linking to occur. These reagents can also promote swelling of coals and may account for some of the decrease in the cross-linking of the coal structure observed for the chemically dried coals.

Personnel problems that had plagued the project since July 1993 have been resolved by the hiring of two chemical engineering students.

### **FUTURE WORK**

Liquefaction experiments on dried and partially dried Texas, Black Thunder, Eagle Butte, and Illinois #6 coals will begin next quarter. 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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