



Reduction of sub-bituminous coal using carbon monoxide and carbon dioxide  
by Stephan Timothy Kujawa

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE  
in Chemical Engineering  
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**Abstract:**

The research presented in this thesis studied coal liquification by-means of the carbon monoxide - water shift reaction to hydrogen. Specifically, the conversion of coal to benzene soluble products when the feed gas consisted of both carbon monoxide and carbon dioxide was studied.

The purpose of this was to see if recycled reactor off-gas, consisting of both CO<sub>2</sub> and CO, could be used directly without stripping out all of the CO<sub>2</sub>. The test runs were made in a 500 ml rocking autoclave. The operating time was five minutes when the autoclave reached 450°C. Three initial pressures of 900, 1200, and 1500 psig, and a series of feed gas compositions were studied.

The higher initial pressures gave a high conversion when the feed gas was pure CO, but as the amount of CO<sub>g</sub> was increased to over 50% in the feed gas, the conversions for the three pressures approached the same value.

The amount of benzene soluble product boiling above 90°C increased as the pressure increased. At 900 psig initial pressure about 70% of the product boiled above 90°C while at 1500 psig about 80% of the product boiled over 90°C.

At 900 and 1200 psig, the off-gas CO<sub>2</sub> : CO ratio was found to stay about 1:1 up to 50% CO<sub>g</sub> in the feed gas. At 1500 psig the ratio was less than this, indicating excess CO in the feed stream.

The amount of water consumed in the reaction was found to be less than 50% of the water charged in all cases.

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Date August 7, 1974

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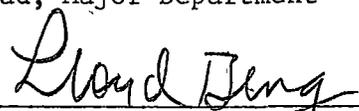
in

Chemical Engineering

Approved:



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## ABSTRACT

The research presented in this thesis studied coal liquification by means of the carbon monoxide - water shift reaction to hydrogen. Specifically, the conversion of coal to benzene soluble products when the feed gas consisted of both carbon monoxide and carbon dioxide was studied. The purpose of this was to see if recycled reactor off-gas, consisting of both CO<sub>2</sub> and CO, could be used directly without stripping out all of the CO<sub>2</sub>.

The test runs were made in a 500 ml rocking autoclave. The operating time was five minutes when the autoclave reached 450°C. Three initial pressures of 900, 1200, and 1500 psig, and a series of feed gas compositions were studied.

The higher initial pressures gave a high conversion when the feed gas was pure CO, but as the amount of CO<sub>2</sub> was increased to over 50% in the feed gas, the conversions for the three pressures approached the same value.

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The amount of water consumed in the reaction was found to be less than 50% of the water charged in all cases.

## INTRODUCTION AND BACKGROUND

### INTRODUCTION

The purpose of the research presented in this thesis was to provide engineering data on a process to convert sub-bituminous coal to liquids soluble in benzene. The liquids produced are intended to be used as an ash-free fuel for a magnetohydrodynamic generator now being developed by the AVCO Everett Research Laboratory of Everett, Massachusetts.

The original coal liquification process was devised originally by Berguis in the early 1900's, using hydrogen as a reducing agent. This process went into disuse when Fischer and Tropsch synthesized gasoline using carbon monoxide and hydrogen, but was brought to the forefront again as the Germans made fuel from brown coal in the second world war.

In the late 1960's, Appel and Wender of the U. S. Bureau of Mines (6) did some coal liquification work that showed at high temperatures and pressures, higher conversions could be obtained by using carbon monoxide and water to liquify coal via the shift reaction to carbon dioxide and hydrogen, than by using pure hydrogen in the first place. It was felt that the reason for this was that the shift reaction produced hydrogen in a more reactive form that would more easily combine with the free radicals formed in the coal matrix by high temperatures.

The Chemical Engineering Department at Montana State University began coal liquification research in 1968. The best scheme found so far has been to react powdered coal, slurried in phenanthrene in the presence of carbon monoxide and water.  $\text{Na}_2\text{CO}_3$  is used as a shift reaction catalyst, and the run conditions are 450°C to 475°C, and approximately 5500 psig.

As previously stated, the liquids formed are intended to be used as feed for an M.H.D. generator; they are too hydrogen deficient to be used as a synthetic crude oil. The liquids could possibly be used as feed to one of the new processes that use hydrogen to enrich and lighten residual fuel oils such as Chevron's or U. O. P's Isomax process.

#### RESEARCH BACKGROUND

This is the fifth thesis on coal liquification by the carbon monoxide shift reaction that has resulted from research studies done by the Montana State University Chemical Engineering Department. In the year 1968, Wayne York began a project initiated by AVCO Research Corporation of Everett, Massachusetts with the purpose of determining whether a liquid fuel could be produced from coal using the water-gas shift reaction. The liquid was to be used as an ash-free fuel for an electrical generator operating on the magnetohydrodynamic principle. It was felt that a liquid fuel would solve erosion problems in the case of the generator because of its being essentially ash free, and also, a higher thermal efficiency would result if the coal was converted to a high btu liquid rather than a low heat content producer gas.

The following is a list, by the person who did the research of the most important conclusions made at Montana State University on this project and which led up to the area of investigation worked on in this present thesis.

Wayne York (1):

1. The ash in the coal catalyses the shift reaction producing nascent hydrogen that stabilizes the reactive fragments produced by thermal depolymerization of the coal.
2. Conversions were increased by about 10% when  $\text{Na}_2\text{CO}_3$  was added to the coal.
3. The liquid product has an ash content of less than 0.1% and a hydrogen to carbon ratio of about 1.14:1 with a molecular weight of about 400.
4. Increasing the reactor temperature increases conversion but the hydrocarbon gas production also increases.
5. Increasing the pressure increases the conversion of coal to benzene soluble material.

Dat Nguyen (2):

1. Less than 5% of the coal converted will go into the gas phase as methane and ethane. The remaining tarry product has an H/C ratio of 1.1:1, and an ash content of about 0.1%.
2. Conversion is zero at 300°C, and reaches a maximum over 70% at 475°C.
3. Initial reactor pressure has a very significant effect on conversion below 1000 psig, and becomes less so around 1500 psig where conversion begins to level out close to 80%.
4. Phenanthrene was found to be the best solvent, and the optimal

phenanthrene to coal ratio is around 2:1.

5.  $\text{Na}_2\text{CO}_3$  increases the conversion around 10% when present in a  $\text{Na}_2\text{CO}_3$  to coal ratio of 0.01:1.
6. With a five minute operating time at  $475^\circ\text{C}$ , a 70-80 percent conversion of Colstrip sub-bituminous coal could be obtained to benzene soluble products by reduction with carbon monoxide and water.

Thomas Fiske (3):

1. The optimal coal particle size for an initial operating pressure of 1210 to 1590 psig is -25 to -40 mesh.
2. The method of contacting the coal and phenanthrene makes no significant difference in conversion.
3. The exposure of ground coal to air decreases conversion.

Ronald Denney (4):

1. Aging of lump coal before use has no effect on conversion.
2. The rate controlling step in the hydrogenation reaction is not where the hydrogen attaches to the solvent surface.
3. The presence of  $\text{CO}_2$  as an impurity in the CO gas reactant apparently has no effect on the water gas shift reaction equilibrium at temperatures and pressures of  $450^\circ\text{C}$  and 5000 psig.
4. Conversion decrease in the CO feed stream occurs when the amount of CO present is not enough for the reaction.

## RESEARCH OBJECTIVES

### PURPOSE

The purpose of this thesis is to supply the engineering data necessary to design, ultimately, a large scale coal liquification plant. The data presented in and the results of this thesis are not sufficient to design large scale equipment. The data is here presented, therefore, to be used as a guide for the next step that should be taken in a research endeavor of this type, i.e., the design and operation of a continuous reactor capable of supplying kinetic and thermodynamic information sufficiently accurate and precise to be used as the design basis for an eventual large scale process plant. The results here can also be used to give economic guidelines in estimating the cost per unit of product for such a plant.

### OBJECTIVES

The primary research objective of this project was to extensively investigate what happens when carbon dioxide is fed to the reactor with the carbon monoxide reactant.

Preliminary CO<sub>2</sub> dilution work was done by R. Denny who reported no effect on conversion until insufficient CO was present to react with the water (4).

R. E. Gannon, principal research engineer from AVCO, the company sponsoring the project, suggested in a letter dated December 3, 1973, that Denny's work on CO<sub>2</sub> dilution should be thoroughly explored because if an acceptable conversion could be approached with a feed gas high

in  $\text{CO}_2$ , a more economical process could be designed by eliminating the equipment necessary to strip the  $\text{CO}_2$  from the reactor off gas before recycle to the process.

A second objective was to find out the approximate product distribution of the converted coal. It was decided to use a simple distillation to determine the amount of product that boiled above the temperature of the benzene used as an extraction solvent.

In the previous theses, one common suggestion has been to obtain an accurate material balance. This objective was partially fulfilled here by finding out the relative amounts of carbon dioxide and carbon monoxide in the off gas (which will be used to determine how much  $\text{CO}_2$  stripping equipment is necessary) and by finding out how much of the feed water was actually used in the reaction, which will determine the water requirements of a large process plant. Knowing the relative amounts of  $\text{CO}$  and  $\text{CO}_2$  as feed and as off-gas would also give some insight into the stoichiometry of the shift reactions occurring.

## EXPERIMENTAL PROCEDURE

### COAL PREPARATION AND ANALYSIS

Approximately fifty grams of Colstrip sub-bituminous coal was ground to minus 38 mesh for each run by mortar and pestle.

Two samples of the coal of about one gram each were placed in porcelain crucibles and heated over bunsen burner flame, slowly at first to drive off the volatile matter, and then at a higher heat to burn off the fixed carbon. After about twenty-four hours, only a yellowish-grey ash was left.

The weight of the ash divided by the weight of the original coal was the fraction of ash in the coal. The arithmetic average of the two ash analyses was used as the fraction of ash in the coal charged to the reactor.

Another, ten gram sample of coal was weighed into a boiling flask and toluene was added. A water analysis tube with graduate sidearm and reflux condenser was then attached to the flask and the toluene was allowed to boil.

The toluene vapor carried the water in the coal to the reflux condenser where the two components condensed and dripped into the sidearm. The water in the sidearm separated from the toluene and sank to the bottom. After about twelve hours all the water had been extracted from the coal and the amount could be read on the graduated sidearm. The fraction of water was then calculated as the milliliters of water times its density divided by the weight of coal charged to the boiling flask.

A typical analysis of Colstrip coal is included in Table I which was taken from Wayne York's thesis (1).

#### REACTOR CHARGING

The next step in the procedure was to place the fresh ground coal into the reactor, followed by the phenanthrene and the sodium carbonate. The reactants were then stirred dry and the water poured in. The head was then placed and bolted on. The specifications of the reactants other than coal were:

Phenanthrene : Aldrich, 90%, cat. no. P1142-5  
Na<sub>2</sub>CO<sub>3</sub> : Matheson, Anhydrous reagent, ACS grade,  
cat. no. SX 395  
Water : Chlorinated tap water

The charge quantities were,

coal : 30 gms  
H<sub>2</sub>O : 30 gms  
Phenanthrene : 60 gms  
Na<sub>2</sub>CO<sub>3</sub> : 0.3 gms

#### REACTOR OPERATION AND GAS CHARGING

The reactor was a 500 ml Parr Inconel Autoclave which is shown in Figure 1. This was the reactor part of a Parr series 4000 Hydrogenation Apparatus that consisted of the reactor and a rocking-heating apparatus for the autoclave. The autoclave was rated for 7000 psi at 500°C. The rocker operated at about 40 cycles per minute.

TABLE I. Proximate, Ultimate, and Ash Analyses for Colstrip  
Sub-Bituminous

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COLSTRIP SUB-BITUMINOUS

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PROXIMATE

Moisture	23.9%
Volatile Matter	30.9
Fixed Carbon	37.6
Ash	7.6

ULTIMATE

Moisture	23.9%
Carbon	50.3
Hydrogen	3.4
Nitrogen	0.7
Sulfur	0.4
Oxygen	13.7
Ash	7.6

ASH ANALYSIS OF MAJOR COMPONENTS

SiO <sub>2</sub>	36.4%
Al <sub>2</sub> O <sub>3</sub>	17.6
Fe <sub>2</sub> O <sub>3</sub>	4.6
TiO <sub>2</sub>	0.4
P <sub>2</sub> O <sub>5</sub>	0.8
CaO	22.7
MgO	9.4
Na <sub>2</sub> O	0.3
K <sub>2</sub> O	0.5
SO <sub>3</sub>	14.9

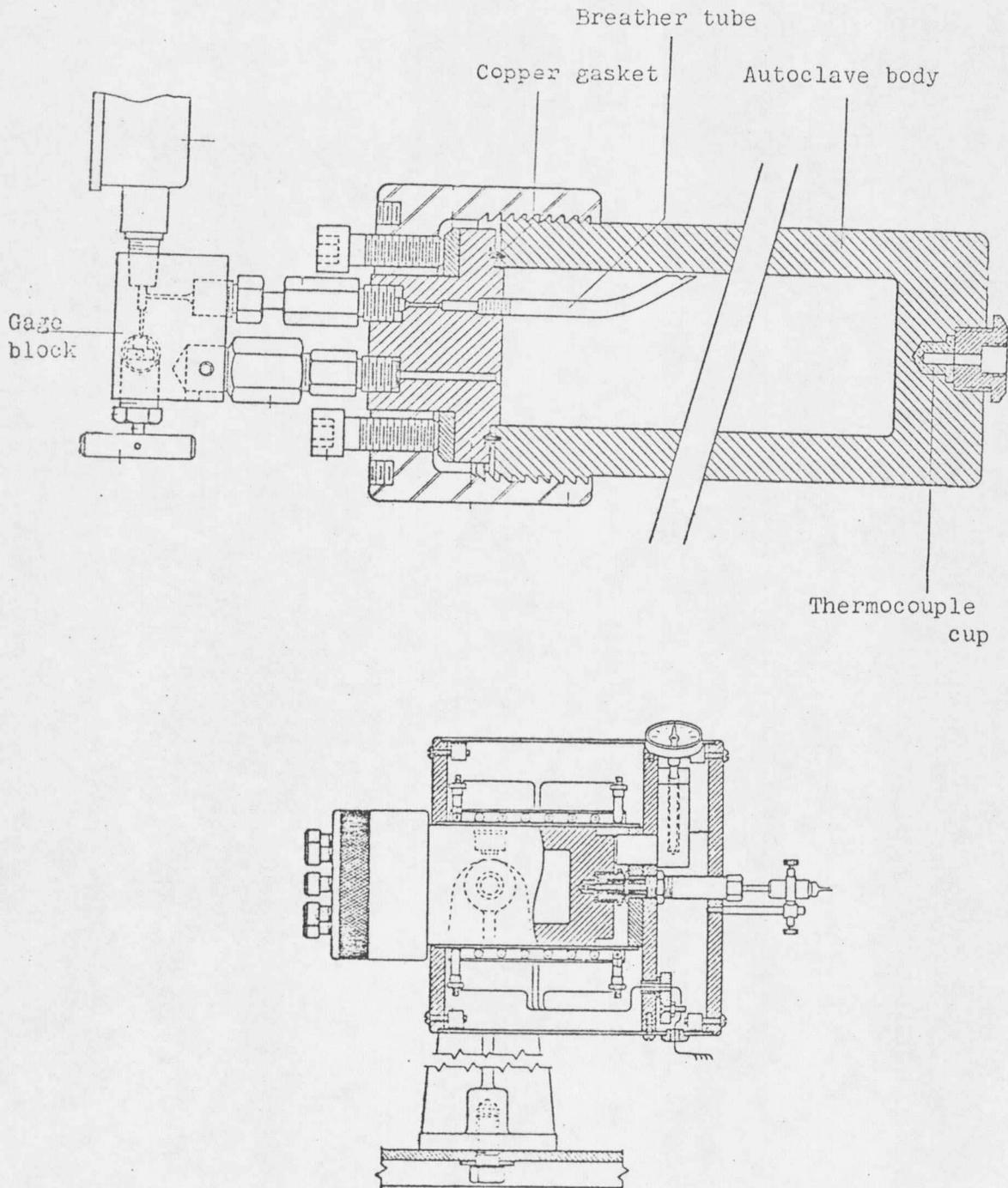


FIGURE 1. Rocking Autoclave Assembly Details

After the head of the reactor was tightened, the bomb was pressurized depending on the run specifications, with up to 800 psig of CO<sub>2</sub> from a standard cylinder. Then an oil pressurizing system was used to bring the bomb up to the initial run pressure with CO. The pressurizing system is shown in Figure 2.

The bomb, after charging, was placed in the heater-rocker and an iron-constantan thermocouple was placed in a thermowell in the base of the bomb. The heaters and rocker were turned on and the bomb heated to 450°C, which usually took about 70 minutes. The bomb was held at 450°C for a run time of five minutes, then the rockers and heaters shut off and the bomb pulled from the heater with threaded pullrods, and allowed to cool in the air.

After the bomb had cooled, the off-gas was bled slowly into an evacuated twenty gallon drum. The drum had a sample port where a .1 ml sample was taken and injected into a chromatograph. The chromatograph was packed with Porapak Q-S which detects CO<sub>2</sub>, CO, N<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, and operated with helium as a carrier gas at a temperature of 70°F.

The chromatograph was standardized with two mixtures containing different amounts of CO<sub>2</sub>, CO, CH<sub>4</sub> and H<sub>2</sub> which approximated expected off-gas compositions. The peak heights of the recorder output were used to obtain the relative amounts of CO<sub>2</sub> and CO in the off-gas.

The bomb was then taken apart and the liquid and solid mass removed. This usually consisted of a small amount of black liquid, a greater amount of brown or black tarry substance, and a much greater































































