



Effect of catalysts on the reduction of sub-bituminous coal by the co-steam process
by Stephen Scott Bodner

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

The research presented in this thesis is a scoping study of the effects of various catalytic materials on the reduction of Colstrip sub-bituminous coal using the carbon monoxide-water shift reaction.

The purpose was to identify catalysts which would increase conversion to a benzene soluble product and possibly decrease sulfur and nitrogen content. The test runs were made in a 500 ml rocking autoclave. The operating time was five minutes when the autoclave reached 475°C.

Red mud, sodium carbonate, and sodium hydroxide were found to effectively increase conversion. Sulfur and nitrogen contents were not reduced.

Without catalysis of the shift reaction, typical hydrogenation catalysts were not found effective.

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Date January 28, 1977

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COAL BY THE CO-STEAM PROCESS

by

STEPHEN SCOTT BODNER

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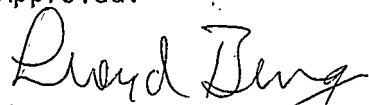
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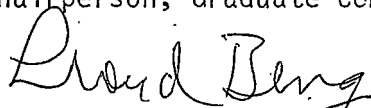
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TABLE OF CONTENTS

| | <u>Page</u> |
|--|-------------|
| VITA | ii |
| ACKNOWLEDGMENT | iii |
| LIST OF TABLES | vi |
| LIST OF FIGURES. | vii |
| ABSTRACT | viii |
| I. INTRODUCTION. | 1 |
| II. BACKGROUND. | 3 |
| III. RESEARCH OBJECTIVES | 6 |
| IV. EXPERIMENTAL PROCEDURE. | 7 |
| COAL PREPARATION AND ANALYSIS. | 7 |
| REACTOR CHARGING | 8 |
| REACTOR OPERATION. | 10 |
| EXTRACTION | 13 |
| CONVERSION CALCULATION | 13 |
| V. RESULTS AND DISCUSSION. | 16 |
| CATALYTIC EFFECTS ON CONVERSION. | 16 |
| QUALITATIVE PRODUCT PROPERTIES | 21 |
| GRINDING TECHNIQUE | 21 |
| SULFUR AND NITROGEN ANALYSES | 22 |
| CATALYST ECONOMICS | 23 |
| VI. CONCLUSIONS | 25 |

TABLE OF CONTENTS (Cont)

| | <u>Page</u> |
|--|-------------|
| VII. RECOMMENDATIONS FOR FUTURE STUDY. | 26 |
| VIII. APPENDIX. | 27 |
| IX. LITERATURE CITED. | 34 |

LIST OF TABLES

| <u>Table</u> | <u>Page</u> |
|--|-------------|
| I. Catalysts Previously Tested at MSU | 4 |
| II. Coal Particle Size Distribution | 7 |
| III. Analyses for Colstrip Sub-bituminous Coal | 10 |
| IV. Red Mud Composition | 16 |
| V. Catalysts and Conversions | 17 |
| VI. Sulfur and Nitrogen Analyses | 22 |
| VII. York's Product Analysis | 23 |
| VIII. Experimental Run Data | 28 |

LIST OF FIGURES

| <u>Figure</u> | | <u>Page</u> |
|---------------|---|-------------|
| 1 | APPARATUS USED TO DETERMINE WATER CONTENT OF THE COAL . . . | 9 |
| 2 | AUTOCLAVE AND HEATER DETAILS. | 12 |
| 3 | SOXHLET EXTRACTION APPARATUS USED TO DETERMINE COAL CONVERSION | 14 |
| 4 | EFFECT OF RED MUD CONCENTRATION ON CONVERSION | 20 |

ABSTRACT

The research presented in this thesis is a scoping study of the effects of various catalytic materials on the reduction of Colstrip sub-bituminous coal using the carbon monoxide-water shift reaction. The purpose was to identify catalysts which would increase conversion to a benzene soluble product and possibly decrease sulfur and nitrogen content.

The test runs were made in a 500 ml rocking autoclave. The operating time was five minutes when the autoclave reached 475°C.

Red mud, sodium carbonate, and sodium hydroxide were found to effectively increase conversion. Sulfur and nitrogen contents were not reduced.

Without catalysis of the shift reaction, typical hydrogenation catalysts were not found effective.

INTRODUCTION

One of the missions of the newly formed Energy Research and Development Administration (ERDA) is to develop all energy sources to meet the energy needs of present and future generations while making the nation self-sufficient in energy. One means of decreasing the dependence of the United States on foreign energy sources is to upgrade coal into a clean burning solid, liquid, or gaseous fuel. The United States has vast coal reserves with about fifty-five percent of the nation's reserves in the West (1).

Processes for upgrading coal to synthetic liquid products, originally developed in the 1930's, are being improved so as to supply a more easily transportable, nonpolluting, liquid fuel. The liquified coal products also have potential for use as synthetic crude oils and chemical feedstocks. Several processes for upgrading coal are now being developed. These include the Char-Oil Energy Development (COED) pyrolysis process, the Solvent-Refined Coal (SRC) hydrogenation process, the Synthoil catalytic hydrogenation process, and the H-Coal ebullient-bed catalytic hydrogenation process (2).

Coal is a high molecular-weight solid consisting of many unsaturated ring compounds with alkyl side chains (3). At 400°C, single carbon-carbon bonds or bonds of equivalent energy are ruptured. Progressive hydrogenation serves to stabilize the lower molecular weight fragments produced during thermal cracking. Competing with the progressive reactions are regressive reactions, polymerization of

the reactive fragments, making the product more difficult to dissolve. Reactor environment controls which reaction will predominate. Dissolution and hydrogen donor properties of the coal liquefaction solvent are also important (4).

Low-rank coals found in the sparsely populated western United States have a higher moisture content, lower sulfur content, and are more reactive when compared to coals of higher rank (5). These qualities make sub-bituminous and lignite coals especially well suited for liquefaction using the CO-Steam process. Water and carbon monoxide undergo the shift reaction to produce the hydrogen needed to stabilize thermally cracked coal molecules.

The Grand Forks Energy Research Center (GFERC) in North Dakota and the Chemical Engineering Department at Montana State University (MSU) are investigating the CO-Steam process for liquefaction of lignite and sub-bituminous coals. At MSU powdered coal slurried in phenanthrene solvent is reacted with carbon monoxide and water at approximately 5500 psig and 475°C. The liquefied product, although too hydrogen deficient to be used as a synthetic crude oil, could be used as a low ash, low sulfur utility boiler fuel. It could also be utilized as a feedstock for other catalytic hydrogenation processes being developed to increase the H:C ratio and remove sulfur and nitrogen (6).

BACKGROUND

Declining conversions have been noted in the continuous fixed bed reactor of the Synthoil process due to catalyst aging. This aging is a result of coke formation, deposition of metal sulfides, and accumulation of mineral components of coal. These contaminants accumulated both on the exterior surface and in the pore mouths of the catalyst resulting in a 70% reduction in catalyst surface area and pore volume (7). Eventually pore mouth blocking and bed plugging could occur. For these reasons, research at MSU was directed toward investigating unsupported solid, liquid, or gaseous catalytic materials which would be mixed with the coal slurry flowing through the reactor. Better contacting of liquid or gaseous catalysts with the reactive mass were expected to enhance the reaction. Economics would require the separation and recovery of the catalytic material from the liquified product in most cases. However some materials are cheap enough that recovery would be uneconomical.

Catalytic materials previously tested at MSU are shown in Table I (8). York (9) states that ferric oxide and sodium carbonate contained in coal ash were effective in promoting the carbon monoxide-water shift reaction. Higher sodium contents increased conversion (9).

TABLE I. Catalysts Previously Tested at MSU

| <u>Catalyst</u> | <u>Conversion %</u> |
|--------------------|---------------------|
| Sodium carbonate | 72 |
| Sodium bicarbonate | 60 |
| Sodium formate | 45 |
| Stannous chloride | 60 |
| Calcium carbonate | 50 |
| Zinc chloride | 40 |

Conversions of 65 to 75 percent have been obtained at the University of Utah using zinc chloride catalyst. At operating conditions the catalyst vaporizes and diffuses into the coal to catalyze desulfurization. A 99% catalyst recovery was obtained using a nitric acid wash (10). Nickel nitrate and stannous chloride are also reported effective (10).

Rock Springs, Wyoming sub-bituminous coal was reacted with hydrogen in the presence of red mud, stannous chloride, and ammonium molybdate catalysts by the Bureau of Mines at Pittsburgh. Ammonium molybdate was found to have a higher catalytic activity than stannous chloride (11, 12).

Halogen acids have been reported effective as having a catalytic effect on the thermal splitting of the coal into reactive fragments.

The fragments can be stabilized to form benzene soluble products by the addition of hydrogen or can polymerize to form benzene insoluble products (12, 13). The hydrogenation stabilization is catalyzed by tin (13).

Several metal chloride catalysts were tested by Sire and Alzheimer in a hydrogen plus hydrochloric acid atmosphere (14,15). Stannic chloride, nickel chloride, and stannous chloride were found to be the most active metal chlorides for coal hydrogenation using this technique.

RESEARCH OBJECTIVES

The objective of this research was to determine the catalytic effects of various materials on the CO-Steam process for the liquefaction of Montana sub-bituminous coal. The purpose of this research was to find a "good" catalyst which would reduce the operating costs of a full scale liquefaction plant.

A "good" catalyst is defined as a material enhancing conversion to a benzene soluble product with a possible side benefit of reducing sulfur and nitrogen content of the product. The catalyst should be either inexpensive so as to be throw-away, or easily recovered, regenerated, and recycled.

The catalytic effects of materials are unpredictable and therefore empirical data is needed for catalyst comparison.

EXPERIMENTAL PROCEDURE

COAL PREPARATION AND ANALYSIS

Large variations in Colstrip sub-bituminous coal composition were realized when small samples were taken from different lumps of a coal sample. In an attempt to minimize these variations, approximately ten pounds of coal were ground to minus 38 mesh in a porcelain ball mill. The batches of ground coal were then thoroughly mixed and stored in glass containers to prevent further water loss and oxidation. Water and ash analyses were performed on samples from each reactor charge. The ground coal size distribution is shown in Table II.

TABLE II. Coal Particle Size Distribution

Size: Tyler Standard

| <u>mesh/inch</u> <u>Through</u> | <u>On</u> | <u>Wt. %</u> |
|------------------------------------|-----------|--------------|
| - | 50 | 30 |
| 50 | 100 | 37 |
| 100 | 200 | 18 |
| on pan | | 15 |

Ash analyses were performed on two samples, each approximately one gram, from each reactor charge. The samples were heated in covered porcelain crucibles over Bunsen burners until all of the volatile matter was driven off. Then the lids were removed and the

flame was increased to burn off the remaining fixed carbon. The weight of the remaining ash divided by weight of the coal sample determined the weight fraction of the ash. The average of the two samples was used in the conversion calculations.

A water analysis was performed on a ten gram sample of coal from each reactor charge. A diagram of the apparatus is shown in Figure 1. Coal, toluene, and boiling chips were placed in a boiling flask attached to a 5 ml distilling receiver with a reflux condenser. The mixture was allowed to boil for 10-12 hours as condensed water and toluene collected in the graduated receiver. The volume of water collected times the density of water divided by the weight of the coal sample determined the weight fraction of the water.

York's thesis contained a typical analysis of Colstrip coal which is shown in Table III (16).

REACTOR CHARGING

First 30 ml of distilled water was poured into the reactor. Next 60 g of phenanthrene (Aldrich, 90%) and 30 g of coal were carefully added. The layers of phenanthrene and coal served to isolate the catalyst charge, which was then added, from the water. In some cases the catalyst would have reacted violently with the water had this precaution not been taken.

In most cases 0.5 g of catalyst were charged. Catalysts were

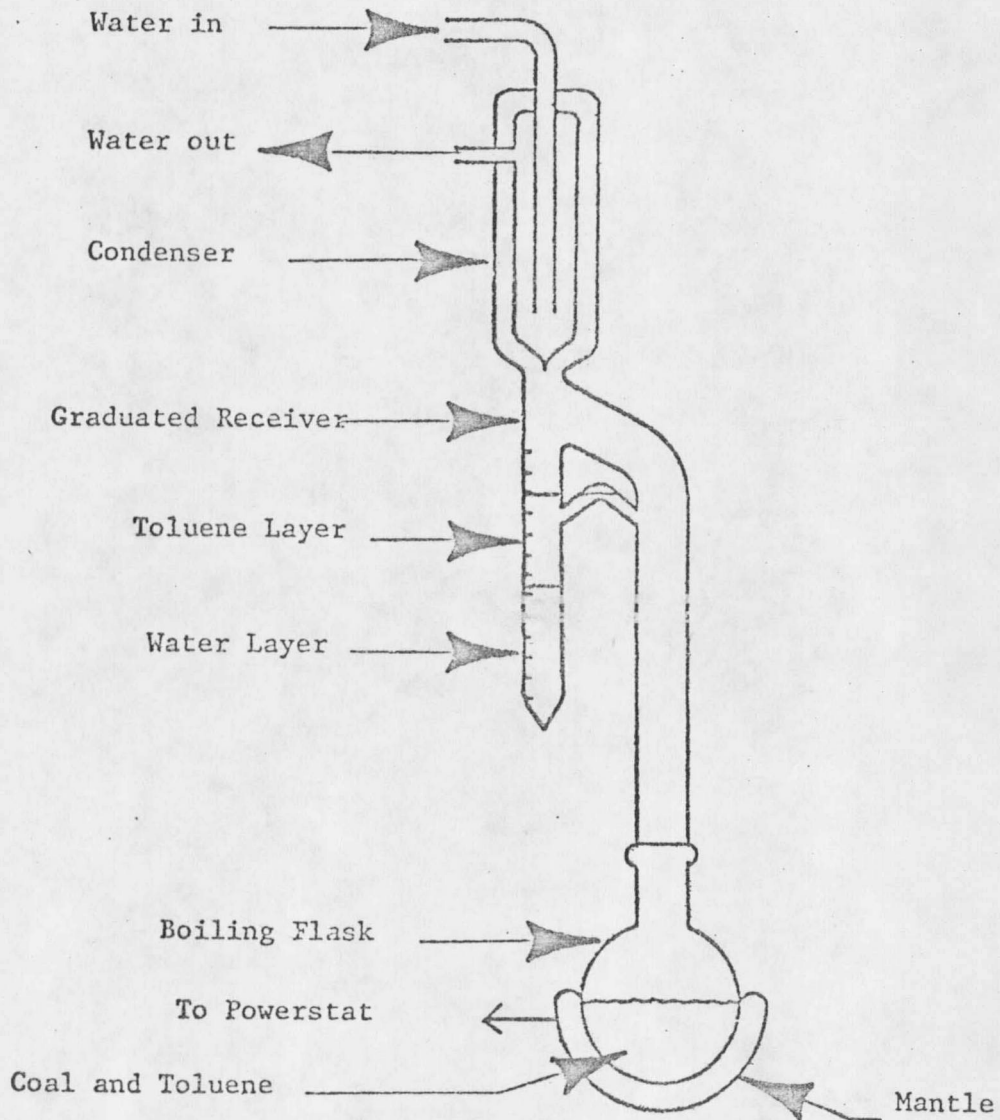


FIGURE 1. APPARATUS USED TO DETERMINE WATER CONTENT OF THE COAL

TABLE III. Analyses for Colstrip Sub-bituminous Coal

Proximate Analysis

| | |
|------------------|-------|
| Moisture | 23.9% |
| Volatile matters | 30.9 |
| Fixed carbon | 37.6 |
| Ash | 7.6 |

Ultimate Analysis

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

Ash Analysis

| | |
|--------------------------------|------|
| SiO ₂ | 36.4 |
| Al ₂ O ₃ | 17.6 |
| Fe ₂ O ₃ | 4.6 |
| TiO ₂ | 0.4 |
| P ₂ O ₅ | 0.8 |
| CaO | 22.7 |
| MgO | 9.4 |
| Na ₂ O | 0.3 |
| K ₂ O | 0.5 |
| SO ₃ | 14.9 |

compared on a weight basis rather than on a molecular or atomic basis since the "active" ion or ions in the catalyst molecule were unknown.

Next the head of the reactor was secured and the gauge block was installed. The reactor was then pressurized to 1500 psig \pm 50 psi with carbon monoxide.

REACTOR OPERATION

The reactor used for this study was a 500 ml Parr T316 stainless steel rocking autoclave. The Parr Series 4000 pressure reaction apparatus is shown in Figure 2. The reactor head was equipped with an 8000 psig rupture disk. The reactor will withstand working pressures up to 7000 psig at 400°C.

The reactor was placed into the heater-rocker apparatus and heated to 475°C \pm 4°. The temperature was recorded on a chart recorder using an iron-constantan thermocouple installed in the thermowell in the base of the reactor. As the reactor temperature neared 465°C, power input to the heaters was reduced to allow the temperature to line out at 475°C. After the reaction time of five minutes at 475°C, the heater-rocker apparatus was turned off and the reactor was removed.

After cooling, the reactor gases were bled off slowly under a vented hood. Then the reactor was disassembled and the unused water was poured off. The remaining sticky, solid material was removed and placed into a dried, weighted, cellulose, 43 x 123 extraction

