



Hydrogenation of coal using a metal chloride-HCl catalyst
by David Lee Sire

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 studied the relative activity of different metal chloride catalysts in the hydrogenation of coal.

Since there is no way of analytically determining the optimum catalyst for a reaction, an experimental approach must be used.

In this study, 16—35 mesh prepared coal was impregnated with a metal chloride catalyst, mixed on a 1:3 weight basis with 40 mesh Ottawa sand and placed in a semibatch tube reactor. The coal was then reacted by continuously passing a 5% HCl-95% reactor gas through the reactor at 450°C and 1000 psi for 30 minutes. Conversion of the coal was calculated as the weight loss on the original amount of coal charged. In order to compare the relative activity of the different metal chloride catalysts, this conversion value was reported on a dry, ash-free basis.

Under these operating conditions, nickel chloride and stannic chloride exhibited the highest catalyst activity, converting an average of 67.3% and 67.5%, respectively, of the dry, ash-free coal to hydrogenated products. Stannous chloride was only slightly lower, converting 62.5% of the dry, ash-free coal.

This study also indicated that the alkali metal chlorides exhibited little or no activity or acted as a poison (potassium chloride) in the hydrogenation of coal.

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David Lee Sire

Date

March 28, 1975

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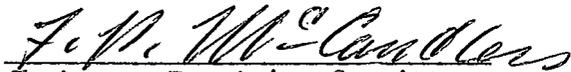
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TABLE OF CONTENTS

	<u>Page</u>
VITA	ii
ACKNOWLEDGMENT	iii
LIST OF TABLES	v
LIST OF FIGURES.	vi
ABSTRACT	vii
I. INTRODUCTION AND BACKGROUND	1
II. RESEARCH OBJECTIVES	4
III. EXPERIMENTAL APPARATUS.	5
IV. EXPERIMENTAL PROCEDURE.	9
A. Preliminary Work.	9
B. Coal Preparation and Analysis	15
C. Catalyst Preparation and Coal Impregnation.	16
D. Reactor Operation	17
V. RESULTS AND DISCUSSION.	21
VI. CONCLUSIONS	30
VII. APPENDIX.	34
A. Selected Preliminary Run Data	35
B. Run Data.	36
VIII. BIBLIOGRAPHY	39

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Average Conversion Rates (Preliminary Studies)	10
II	Nickel Catalyst Consumed During Reaction.	14
III	Grams of Metal Chloride Dissolved per 100 ml. Water	18
IV	Amount of Nickel Catalyst Consumed During Reaction.	22
V	Coal Conversion with Metal Chloride Catalyst.	24
VI	Comparison of Operating Conditions of Other Hydrogenation Catalysts with Other Coals.	28
VII	Selected Preliminary Run Data	35
VIII	Run Data.	36

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Schematic Flow Diagram of Reactor System	6
2.	Detailed Diagram of Reactor.	8
3	Nickel Absorbed on Coal as a Function of Nickel Chloride Concentration in Impregnating Solution.	12

ABSTRACT

The research presented in this thesis studied the relative activity of different metal chloride catalysts in the hydrogenation of coal. Since there is no way of analytically determining the optimum catalyst for a reaction, an experimental approach must be used.

In this study, 16-35 mesh prepared coal was impregnated with a metal chloride catalyst, mixed on a 1:3 weight basis with 40 mesh Ottawa sand and placed in a semibatch tube reactor. The coal was then reacted by continuously passing a 5% HCl-95% H₂ reactor gas through the reactor at 450°C and 1000 psi for 30 minutes. Conversion of the coal was calculated as the weight loss on the original amount of coal charged. In order to compare the relative activity of the different metal chloride catalysts, this conversion value was reported on a dry, ash-free basis.

Under these operating conditions, nickel chloride and stannic chloride exhibited the highest catalyst activity, converting an average of 67.3% and 67.5%, respectively, of the dry, ash-free coal to hydrogenated products. Stannous chloride was only slightly lower, converting 62.5% of the dry, ash-free coal.

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INTRODUCTION AND BACKGROUND

Coal is a solid combustible substance formed by the partial decomposition of vegetable matter without free access to air and under the influence of moisture and often increased pressure and temperature. Coal is also a highly unsaturated organic compound with a low BTU value. Coal is found in deposits throughout the world with vast amounts of it being found in the Western United States.

Coal, at one time, was a major source of energy in this country. Its use was pre-empted by the use of petroleum products and natural gas as energy sources. However, the world is now experiencing a shortage of natural gas and petroleum, and interest is again being focused on coal as an energy source. However, coal, in its natural form, is an inefficient source of energy. The purpose of this project was therefore to find a more active catalyst in the hydrogenating and hydrocracking of coal into a more desirable form of energy.

Hydrogenation itself refers to the saturation (with hydrogen) of unsaturated organic compounds in the presence of a metal catalyst. The hydrogen attacks π bonds and forms new C-H σ bonds. Hydrogenation saturates C=C and C=N (also C \equiv C and C \equiv N) groups but generally leaves C=O groups unaffected. (1)

As previously mentioned, coal is a highly unsaturated solid. As a solid, it is bulky and expensive to transport. Being highly unsaturated, it has a low BTU value. When coal is hydrogenated, gaseous and liquid products are formed. This serves two purposes. The coal

is converted into a more efficient, higher BTU source of energy and the coal becomes easier and less expensive to transport.

In converting coal to a liquid or gaseous product, an effective hydrogenation catalyst must accomplish several functions. These include an integral means of separating the catalyst from the ash and product streams, high catalytic ability at relatively low pressure, a high activity-high selectivity ability, and a high hydrocracking activity. Molten metal chloride catalysts have been tried (2), but were abandoned because of the relative high pressures necessary for the operation and the difficulty encountered in regeneration and in the recovery of the catalyst from the product stream.

The basis for this thesis comes from a study done by Dr. F. P. McCandless and Dr. Lloyd Berg of the Department of Chemical Engineering at Montana State University in Bozeman, Montana on hydrodenitrogenation of petroleum. (3). In this study, the hydrodenitrogenation of a heavy California gas oil was investigated using a supported NiCl_2 catalyst. Methylene chloride was used to maintain a high HCl partial pressure in the reactor and to keep the metal in the chloride form. Results from this study indicated that under the proper operating conditions, 90+% of the nitrogen present could be removed from the oil as ammonium chloride (NH_4Cl). The removal of nitrogen in this manner is a single-bond cleavage of hydrogenation known as hydrogenolysis where C-N or C-S groups are hydrogenated to C-H groups. (1)

This system not only exhibited a high hydrogenation ability, but, more important, also showed a high hydrocracking ability. Based on these results, it was proposed to use metal chloride catalysts in the hydrogenation and hydrocracking of coal. The main purpose of this hydrogenation would be to form saturated liquid or gaseous compounds to be used as an energy source. However, it is also possible that the two major pollutants found in coal, nitrogen and sulfur, could also be hydrogenolysized into compounds that could be removed from the product streams.

RESEARCH OBJECTIVES

The purpose of this research was to find a highly active metal chloride catalyst for use in the hydrogenation of coal. This catalyst will have to exhibit a high activity at a relatively low pressure. The process will be carried out in a partial HCl atmosphere. It is felt that this partial HCl atmosphere will help keep the metal in the chloride form and help form active sites for the hydrogenation mechanism.

A second objective of this research was to briefly investigate the amount of metal catalyst consumed during the hydrogenation process.

This research, then, is intended as the initial step in the development of a catalyst that will make hydrogenation of coal economically feasible. It is also intended as a guide for future research in this area.

EXPERIMENTAL APPARATUS

WARNING: When operating this equipment, be careful to wrap all screw thread fittings with Teflon tape. Failure to do so can allow hydrogen to escape into the furnace, causing fire and small explosions to occur.

The reactor design used for this research is shown in Figure 1. The reactor tubing was a 24-inch length of schedule 80 1-inch Inconel Alloy 600 pipe fitted with appropriate inlet and outlet sections. The top 9-3/4 inches was bored out slightly to accommodate a 1 inch outside diameter, 2 inch long porous alumina thimble. Since the inside diameter of the pipe is 0.957 inches, this kept the bottom of the thimble at 9-3/4 inches from the top of the pipe. A 110 volt, 5 ampere electric furnace was used to heat the Inconel pipe reactor.

The feed gas entered through the inlet section at the top of the pipe. The inlet section also had a bleed valve to relieve the internal pressure of the system upon completion of a run. The exit gases passed through a back pressure regulator, into a water trap and then vented through a hood to the atmosphere. A sampling port was located between the back pressure regulator and water trap for sampling of exit gases. A 1/4" tube ran up through the outlet section to the base of the thimble to accommodate an alumel-chromel thermocouple. The temperature inside the reactor tube at the thimble site could then be recorded on a temperature recorder.

The pipe to the inlet section was branched and fitted with appro-

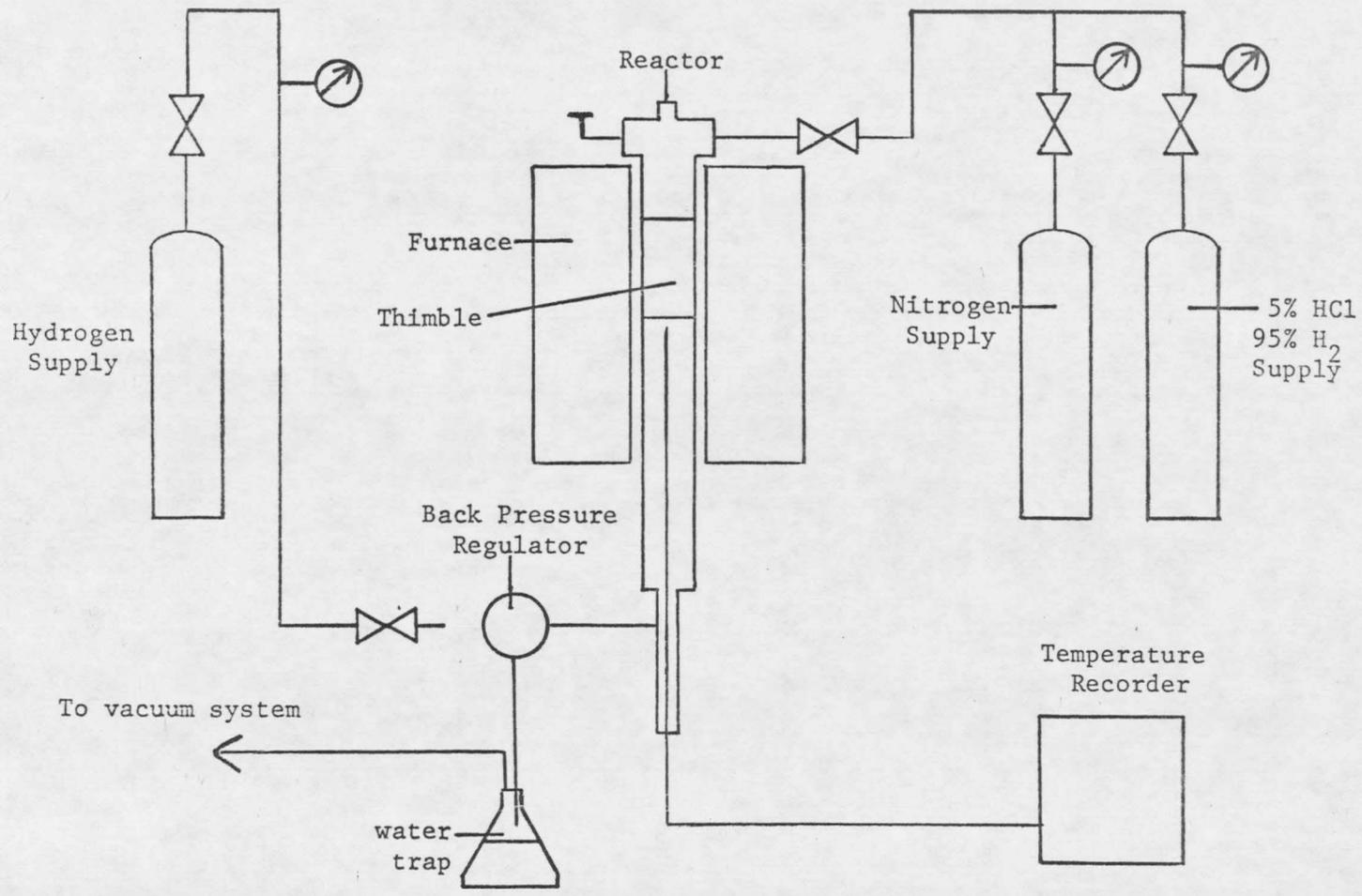


FIGURE 1. Schematic Flow Diagram of Reactor System

appropriate valves to allow the feed gas to enter the reactor and to allow nitrogen to purge and cool the reactor after the completion of a run.

Figure 2 shows a detailed sketch of the reactor and the proximate equipment.

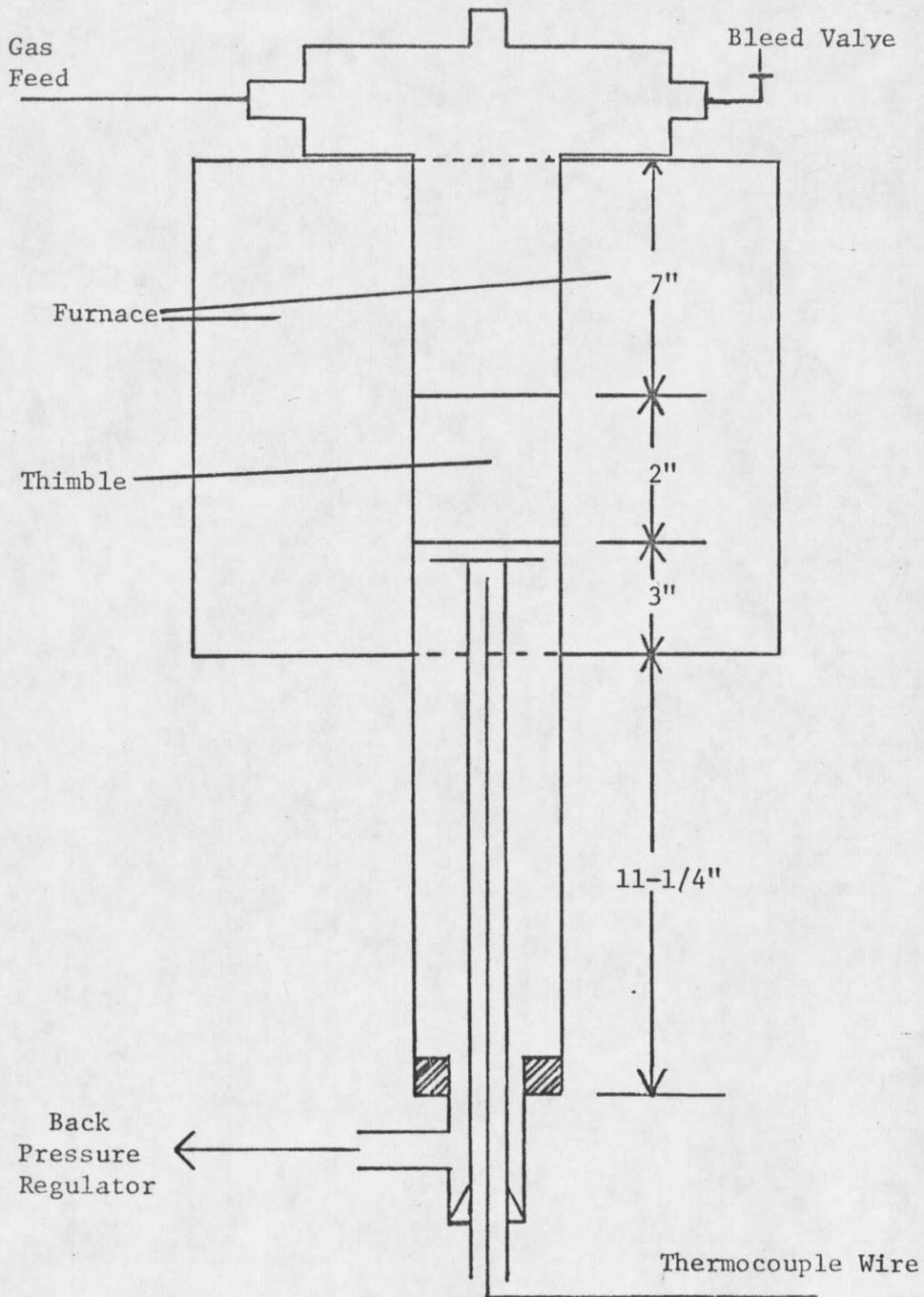


FIGURE 2. Detailed Diagram of Reactor

EXPERIMENTAL PROCEDURE

PRELIMINARY WORK

Initial reaction runs were made with a nickel chloride catalyst and coal ground to minus 100 mesh. A ten gram sample was placed in the thimble for each run and a feed gas of 5% HCl and 95% H₂ was used. Reactor temperature was 450°C and reactor pressure was 1000 psi. In the first runs, methylene chloride was also pumped into the system to help maintain the HCl partial atmosphere. (The equilibrium constant for the reaction $\text{CH}_2\text{Cl}_2 + 2\text{H}_2 \rightarrow 2\text{HCl} + \text{CH}_4$ is approximately 1.4×10^{14} at 425°C). However, the use of methylene chloride had to be discontinued. During these early runs, it was found that some of the methylene chloride was converted to carbon and was laid down in the thimble. Since conversion was based on weight loss, this made the calculation of the conversion impossible.

The next series of runs indicated the need for separating the coal particles. After reacting for a short period of time, the coal in the thimble formed a shell leaving the interior coal unreacted. This indicated that the diffusion rates were both slow and the controlling mechanism. This is briefly illustrated in Table I. Conversion is accomplished quickly until the shell is formed. The extent of conversion is relatively low after this point has been reached. Specifically, approximately 47.5% of the dry, ash-free coal is converted in the first 15 minutes of reaction when the shell is forming. Only an additional 5+% is converted in the next 45 minutes.

