



The hydrogenation of a Montana sub-bituminous coal using a catalyst-acid system  
by David Paul Alzheimer

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 catalytic hydrogenation of a Colstrip, Montana sub-bituminous coal was studied. Three catalysts were investigated - nickel chloride, stannic chloride, and stannous chloride. Hydrogen and a mixture of 5% HCl-95% H<sub>2</sub> were the two feed gases examined.

The semi—continuous reactor in this study was a two foot length of one inch schedule 80 Inconel Alloy 600 pipe, which was operated between 300°C and 600°C, and a maximum operating pressure of 1500 psi.

The catalysts were impregnated on 16—35 mesh coal in the following concentrations (measured as weight % metal on the coal): 1.9% Nickel, 2.9% Tin (Stannic), 13.2% Tin (Stannous). The analyses which were made included a proximate coal analysis and the conversion of the MAF coal to benzene-soluble material.

The results showed that increasing pressure or temperature increased conversion. At all temperatures and pressures studied, conversions of catalytic coal were better than conversions using non-impregnated coal. Conversions using stannous chloride as a catalyst were superior to both nickel chloride and stannic chloride. The highest conversion reached was 76.2% (MAF) at 600°C, 1000 psi and with the HCl-H<sub>2</sub> feed gas.

At lower temperatures, the addition of HCl to the feed gas showed improvements in conversions but had little effect at higher temperatures.

In general, the addition of a vehicle decreased the conversions of catalyst impregnated coal.

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Date 8/25/75

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by

DAVID PAUL ALZHEIMER

A thesis submitted in partial fulfillment  
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Approved:

J. P. McCandless  
Chairman, Examining Committee

Lloyd Berg  
Head, Major Department

Henry S. Parsons  
Graduate Dean

MONTANA STATE UNIVERSITY  
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## ABSTRACT

The catalytic hydrogenation of a Colstrip, Montana sub-bituminous coal was studied. Three catalysts were investigated - nickel chloride, stannic chloride, and stannous chloride. Hydrogen and a mixture of 5% HCl-95% H<sub>2</sub> were the two feed gases examined.

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In general, the addition of a vehicle decreased the conversions of catalyst impregnated coal.

## INTRODUCTION

### A. CURRENT PETROLEUM RESERVES OF THE UNITED STATES


With the depletion of natural oil reserves, finding a dependable source of liquid fuel becomes a problem of national interest. Research directed towards the conversion of coal to liquid products has received increasing interest in recent years. This has been initiated by a sharp decline in known reserves of petroleum and natural gas in the United States, as measured in terms of the number of years supply which these reserves represent. (5,7)

Increasing difficulty in locating sufficient petroleum reserves has resulted in an appreciable increase in exploration costs. The location of these reserves at greater depths or offshore on the continental shelf will result in high production costs as the reserves are exploited.

The current unease in foreign relations and an unfavorable balance of trade make it undesirable to depend on increased importation of oil. Therefore, it appears necessary to satisfy a significant portion of the growing market for petroleum derived fuels with products derived from coal. (14)

The search for new liquid fuels invariably leads to coal because immense coal reserves are available. Published estimates indicate that the coal reserves of the United States are sufficient to supply all the nation's fuel needs for almost 3000 years. (16)

B. COAL STRUCTURE AND CONVERSION TO USEFUL PRODUCTS

Coal is a high molecular-weight solid with a high ash content. Its structure is very complex and consists of many unsaturated ring compounds with alkyl side chains. (Unsaturated rings are those which contain double bonds, example:  ). Petroleum contains three to four times more chemically bound hydrogen (less unsaturation) than coal. Consequently, to convert coal to oil, it is necessary to increase the hydrogen content of coal by a process known as "hydrogenation". Hydrogenation is the addition of hydrogen to unsaturated molecules ( $\text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3-\text{CH}_3$ ). This eliminates the double bond, increasing saturation, which is a step closer to the chemical structure of petroleum.

C. GENERAL HYDROGENATION MECHANISM

A lack of information on the chemical constitution and structure of coal handicaps the study of reactions occurring in its hydrogenation. It is currently believed that the hydrogenation process is accompanied by the decomposition (cracking) of high molecular-weight compounds to smaller fragments. (15) Without hydrogen or a catalyst, these fragments will polymerize, forming a solid residue. In the presence of high hydrogen pressure and a catalyst, these fragments are hydrogenated forming benzene soluble components. Of the benzene soluble components, there exist two types of substances:

- (1) OILS - the liquid product soluble in benzene and also in hexane or pentane.

(2) ASPHALTENES - the liquid product soluble in benzene but insoluble in hexane or pentane. These compounds are generally of polynuclear aromatic structure. The production of asphaltenes is undesirable, since further hydrogenation of these aromatics is necessary to reach a desired product. Hydrogenation of asphaltenes is an extremely difficult step, requiring both high temperature and pressure. Any hydrogenation method preventing the production of asphaltenes would be very helpful.

D. EARLY DEVELOPED COAL HYDROGENATION PROCESS

The hydrogenation of coal has been studied for many years. From early studies made by Bergius, and modified by I. G. Farben (a German dye trust), a process was developed to make oil from coal. (1) It is called the Bergius Process and involves two basic steps; the first step is liquid-phase hydrogenation and the second step is vapor-phase hydrogenation.

In liquid-phase hydrogenation, coal and a catalyst are added to a pasting oil, forming a slurry. The slurry passes into a converter where it is contacted with hydrogen for one hour at 450°C and 10,000 psi. The coal is converted mainly to a middle fraction oil, which boils below 325°C. The heavy oil and residue are separated and the heavy oil is recycled as pasting oil. The middle oil is sent to the vapor-phase hydrogenation reactor. It is passed over a fixed catalyst bed (nickel, tungsten) yielding products of gasoline and aviation fuel quality.

During World War II, Germany had twelve similar coal hydrogenation plants in operation. However, after 1953, there was not a single Bergius plant being used. The main reason being that oil and natural gas were meeting all necessary demands at less cost. The high pressure of 10,000 psi and long residence time required were probably the biggest obstacles preventing its use. The extreme conditions demand expensive equipment and material costs, decreasing its economical attractiveness.

In order to compete with the price of petroleum products, the manufacturing costs of producing gasoline from coal must be reduced. Generally, hydrogenation at lower temperatures reduces the formation of gaseous hydrocarbons, but increases asphaltene production. At lower pressures, the cost of power and installation is reduced. If a hydrogenation catalyst active at low temperature and pressure were developed, the cost of gasoline production could be decreased substantially.

An ideal process to produce gasoline from coal would be direct degradation of the high molecular weight components to desired products without producing intermediate asphaltenes. Thus the raw material would be fully utilized, and the waste would be minimal. To approach this ideal degradation, active selective catalysts for cracking functional groups should be developed, and the degradation should be carried out at low pressure. (2) High hydrogen pressure in the primary hydrogenation of coal is not required thermodynamically but is important

because of the kinetics of reaction.

E. RECENT CATALYTIC DEVELOPMENTS

Any new effective coal conversion process will probably involve the use of a highly active catalyst. The following significant developments in the field of catalysis look very encouraging for hydrogenation processes (5):

1. Complexes of transition metals have shown activity at relatively low temperature (200°C). For example, both cobalt carbonyl and a mixture of cobalt, molybdenum, and aluminum oxides (Co-Mo-Al<sub>2</sub>O<sub>3</sub>) have shown to be very active in the hydrogenation of specific aromatic compounds.
2. Alkali metals such as sodium, lithium, and rubidium, can act as direct hydrogenation catalysts with hydrogen or amines and appear to be active in catalytic electrochemical reduction processes.
3. The solution of coal by extraction using organic "hydrogen donor" solvents, has been studied for years. A mixture of tetralin, phenol, and naphthalene seems to be the most satisfactory solvent for bituminous coal. Tetralin is a hydroaromatic "donor", capable of transferring hydrogen to the coal. The function of the phenol is apparently to assist in pulling the hydrogenated coal into solution. This area of study needs more investigation to find a mechanism where the coal molecules,

hydrogen donor, and catalyst can all interact together.

4. Finally, the use of halide catalysts, show promise in the production of oil from coal in only one step. Using high concentrations of metal chloride catalysts, almost all of the coal can be converted to benzene solubles, with asphaltene conversion (the most difficult step) nearly complete.

The basis of this investigation utilizes the high activity of metal chloride catalysts in the hydrogenation of coal to obtain products of low asphaltene content. In this study, metal chloride catalysts and gaseous hydrochloric acid are used. The principle catalytic activity for the cracking of high molecular-weight compounds is that of the "acid", which is maintained by the hydrochloric acid. The metal acts as a hydrogenation catalyst, to stabilize the "cracked" components, which were fragmented through catalysis by the acid. It is hypothesized that this type of system will result in high conversion of coal to liquid and gaseous products.

## RESEARCH OBJECTIVES

The primary objective of the investigation was to examine the effects of temperature, pressure, types of catalysts and types of vehicles on the conversion of a Montana sub-bituminous coal. Because coal has such a complex structure, there is no one reaction mechanism describing the parameters of conversion to products. The effects of catalysis are also unpredictable and therefore empirical tests are required to determine effective reaction conditions.



## MATERIALS, EQUIPMENT & PROCEDURE

### A. PREPARATION AND ANALYSIS OF COAL

The coal used in this study was a Rosebud bed sub-bituminous mined near Colstrip, Montana. It was supplied by Western Energy and was shipped in metal drums. To prevent water loss, the inside of the drum was lined with plastic. Upon its receipt, a large sample was drawn randomly from the drums. The sample was crushed to 16-35 mesh using a mortar and pestle. Preliminary research indicated that catalytic conversions showed promise with coal of this size. (8) The coal was then placed into bottles and sealed to prevent any further loss of water or alteration in composition.

Conversions were determined on a moisture-ash-free (MAF) basis, requiring an analysis of the moisture and ash content of the coal. The water analysis was performed using the apparatus shown in Figure 1. Toluene and a weighed amount of coal were added to the boiling flask. The rising toluene and water vapor were condensed and collected into a graduated receiving arm. Since water has a higher density than toluene, it settled to the bottom of the arm. From the volume of water present in the arm, the amount of water per gram of coal was easily determined.

The ash content was determined by heating a weighed sample of coal in a covered porcelain crucible with a bunsen burner. After the volatile components were driven off, the lid was removed and the fixed carbon burned off. The ash remaining was weighed and a simple calculation was made.













































































































