



Reduction of subbituminous coal with carbon monoxide and water
by Dat Nguyen

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
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Abstract:

This research studied the effects of temperature, pressure and the type and concentration of a selected number of solvents and catalysts on the reduction of Colstrip (Montana) subbituminous coal through the use of carbon monoxide and water. The reactor was a 500-cc rocking autoclave. Conversion was calculated based on the amount of moisture-and ash-free coal that was converted into benzene-soluble products in a run.

The operating time--during which the autoclave was maintained at the final temperature--was fixed at 5 minutes. Temperatures under investigation ranged from 300 to 475 °C and the initial pressure, from 1000 to 1500 psi.

The conversion, varying with the individual coal batch as well as with the time of storage, was close to zero at 300 °C but increased steeply as long as the temperature was raised. Increasing the initial carbon monoxide pressure also resulted in drastic increases in conversion, but the pressure effect became less significant as the 1500 psi region was approached.

Of the six solvents studied (decalin, tetralin, naphthalene, anthracene, phenanthrene and FMC coal tar), phenanthrene was found to perform best. When present at a 2:1 weight ratio with respect to coal, phenanthrene resulted in conversions twice as high as those of runs without any solvent. Among the five catalysts investigated (sodium formate, sodium bicarbonate, sodium carbonate, ferric oxide and stannous chloride), the bicarbonate appeared most promising, raising the conversion by about 10 percentage points when present at a ratio of 1:100 with respect to coal.

Less than 5 per cent of the converted coal went into the gas phase as methane and ethane. The remainder was a tar having a H/C ratio of about 1.1, a sulfur content close to 0.3 per cent and an ash content of about 0.1 per cent. Preliminary estimates for a plant to produce the tar yielded production costs ranging from 50 to 90 cents per million Btu's worth of tar, depending upon the plant capacity and the total direct cost employed.

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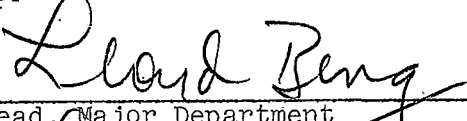
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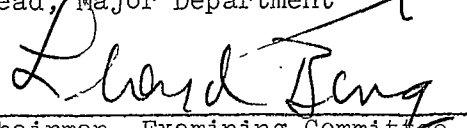
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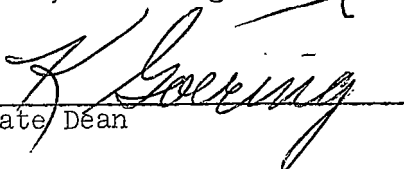
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ABSTRACT

This research studied the effects of temperature, pressure and the type and concentration of a selected number of solvents and catalysts on the reduction of Colstrip (Montana) subbituminous coal through the use of carbon monoxide and water. The reactor was a 500-cc rocking autoclave. Conversion was calculated based on the amount of moisture- and ash-free coal that was converted into benzene-soluble products in a run.

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I. INTRODUCTION

That we are today facing an increasingly grave shortage of energy has been reiterated often enough by authoritative voices (4,12). To meet this upcoming crisis, a great deal of effort has been devoted to the development of latent and yet more abundant energy from the sun, the atom and the traditional family of fossil fuels, of which coal is the most voluminous member (4,13).

The great abundance of coal, together with the ever-increasing cost of fuel, have of late caused much attention to be turned again to coal conversion technology, and more specifically to the gasification and liquefaction of coal (12,15). The present research on the batchwise reduction of Colstrip (Montana) subbituminous coal using carbon monoxide and water is a small part of this general effort to develop cleaner and affordable fuels from low-rank coals.

It is hoped that the information gained on the behavior of this particular--and yet to be popular--process will encourage additional studies on a larger scale, leading to more detailed knowledge which can some day be successfully applied to the conversion of our vast low-rank coal reserves.

II. TECHNICAL BACKGROUND

A great deal of research and development work on coal hydrogenation has been carried out in various countries in the past fifty years, resulting in a large volume of literature on the subject. These many research projects and their results have been ably summarized by various authors (5,27).

The question one may ask at this point is then: Why further studies on coal hydrogenation? In order to answer this, it is necessary to look at some of the more technical aspects of coal hydrogenation in the past and see how these aspects affect the present state-of-the-art.

From the patented process by Bergius, conceived in 1913, to its eventual modification and adaptation to large scale production during World War II by Germany, the principle behind coal hydrogenation had been merely to break up the coal "molecules" into reactive fragments and subject the latter to the presence of hydrogen, supplied from outside sources, for hydrogenation through a number of steps.

Only four of the eighteen coal hydrogenation plants in Germany still operated after World War II because the process was extremely expensive, largely from the high cost of generating hydrogen (27).

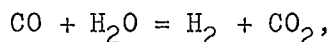
Besides these large scale operations in Germany, a must at the time because of the country's war-time fuel shortage, much additional

research had been carried out at research institutions in France, Japan, Germany, Great Britain, the Soviet Union and the United States. These works involved studies on the effects of pressure, temperature, various catalysts and solvents, and have been well summarized by Donath (5).

Despite all these efforts, no major breakthrough has been made, and the use of hydrogen from an outside source remains to this day a main feature. Hence the continued high cost of coal hydrogenation.

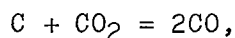
From these observations, it is only too clear that drastic changes in major concepts regarding coal hydrogenation must be made if the latter is to be more economically attractive. This is explained clearly by the Chief of the Division of Coal, Energy Research, U.S. Bureau of Mines, Dr. G. A. Mills (11), who in the same article enumerates a number of new ideas on coal hydrogenation, presently considered to be of great significance by Bureau of Mines scientists. Among these ideas is the use of water and carbon monoxide in coal reduction.

The main difference between the carbon monoxide-water approach and the ordinary approach to coal hydrogenation is that in the former case, the hydrogen does not come from an outside source. Instead, it is supplied by the water-gas "shift" reaction



to take place directly in the hydrogenation reactor. With the elimination of the expensive hydrogen generation step, this simpler scheme should result in large cost reductions. It is worth noting that for

this particular approach, the carbon monoxide would come, say, from a synthesis gas generator using the unconverted char, or from the reaction between the latter and the CO_2 from the shift reaction



thereby making the process CO self-sufficient.

Although the idea of using carbon monoxide and water in coal reduction was conceived as early as in the 1920's (7), published works on the approach have been scarce. Interest in it was renewed only after some sketchy but encouraging results were reported by Bureau of Mines scientists in 1968, showing a remarkable increase in conversion with the CO-water approach over that with the hydrogen approach on the hydrogenation of North Dakota and Texas lignites (1). In particular, these authors reported a striking 89 per cent conversion in the hydrogenation of North Dakota lignite for only 10 minutes at 380 °C.

Additional research has since been carried out by the Bureau, which reported further findings on the CO-water approach in the 1971 North Dakota Lignite Symposium (2). Their results showed a significantly faster conversion rate when CO was used. Regardless of the solvent and the operating time, highest conversions always resulted from runs made at 380-400 °C final temperature. Conversion up to 95 per cent was obtained during a 2-hour operating time at 380 °C. In the same paper, the authors hypothesized the formation and decomposition of alkaline metal formates as possible intermediate steps in coal reduction reactions.

At Montana State University, research to adapt the CO-water approach to Montana coals began in 1969. The effects of temperature, pressure, mode of coal grinding and various solvents on the conversion of a number of North Dakota lignites and Montana subbituminous coals were briefly investigated to yield support data for a number of designs of coal hydrogenation plants (28).

Although the economics of these proposed designs appear promising, it was felt that by additional, systematic studies of the various process variables involved, significant improvements in conversion could still be made, giving a more accurate and more realistic process picture, helpful not only to future economic analyses but also to the operation of future larger, pilot-plant types of equipments should commercialization be eventually visualized.

III. RESEARCH OBJECTIVE

The objective of this research was to study the effects of

1. Temperature,
 2. Pressure,
 3. The type and concentration of a selected number of solvents,
 4. The type and concentration of a selected number of catalysts
- on the batchwise, short operating time reduction of Colstrip (Montana) subbituminous coal via the water-gas "shift" reaction between carbon monoxide and water.

The ultimate aim of these studies was to arrive at the most suitable operating conditions based on which

1. More realistic and detailed economic analyses of the process could be made in the future,

2. Provisions for the construction and operation of pilot-plant scale equipment for the process could be obtained.

IV. MATERIALS, EQUIPMENT, AND PROCEDURE

A. Materials The materials to be used in each run were subbituminous coal, the solvent, the catalyst, water and carbon monoxide.

1. Coal and Analyses of Coal The subbituminous coal was obtained specifically from the Colstrip mine in Eastern Montana, a part of the Fort Union coal formation. The proximate, ultimate and ash analyses of the coal are given in table 1. It is worth noting that the values shown in this table are average values and often tend to be misleading. For example, it was found that 30-gram samples from any one, say, 20-pound chunk of coal could differ considerably in ash contents, as typified in the following table:

<u>Sample number</u>	<u>Per cent ash</u>
163	9.4
165	7.3
167	6.0
169	7.9
171	8.1

These variations presented great difficulties in the interpretation of moisture- and ash-free (m.a.f.) conversion data, especially when, in order to avoid the considerable loss of water and severe oxidation in the coal due to prolonged periods of exposure to air, it was not possible to obtain completely uniform samples by grinding up at any one time an amount of coal large enough for a series of runs. To remedy this in the later experiments, an ash analysis had to be made with each run.

TABLE 1. Analyses for Colstrip
Subbituminous Coal (28).

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

The merit of this additional step will be discussed in Part V. The ash content determination was done by heating up a ground coal sample in a covered porcelain crucible. The heating was slow at first to prevent other materials from being carried away along with the volatile matter, then was accelerated until the crucible became red hot. Combustion of the sample was complete when the weight of the crucible became constant. The per cent of ash was defined as 100 times the ratio of the weight of the non-combustible materials to that of the original coal sample.

As the coal lost approximately 1.5 per cent of its water per month of storage, this water was determined monthly to ensure accuracy in the calculation of the m.a.f. conversion. In a water test, the ground coal sample was distilled with toluene, the water volume in the condensed two-phased distillate being read off on a graduated distillate trap.

2. Solvent The purpose of the solvent is to dissolve the organic matter in coal, making it more susceptible to attack by the available hydrogen. In order to be effective, therefore, a solvent should have a molecular structure similar to those of the organic compounds constituting coal. From the basic conjecture that coal contains organic clusters of compounds having two, three or four aromatic rings (5), the following chemicals were selected for testing: decalin, tetralin, naphthalene, anthracene, phenanthrene and FMC coal tar. The structural formulae for the first five chemicals are shown in figure 1. The structure of FMC coal tar, a product of FMC Corporation's COED (Char-Oil-

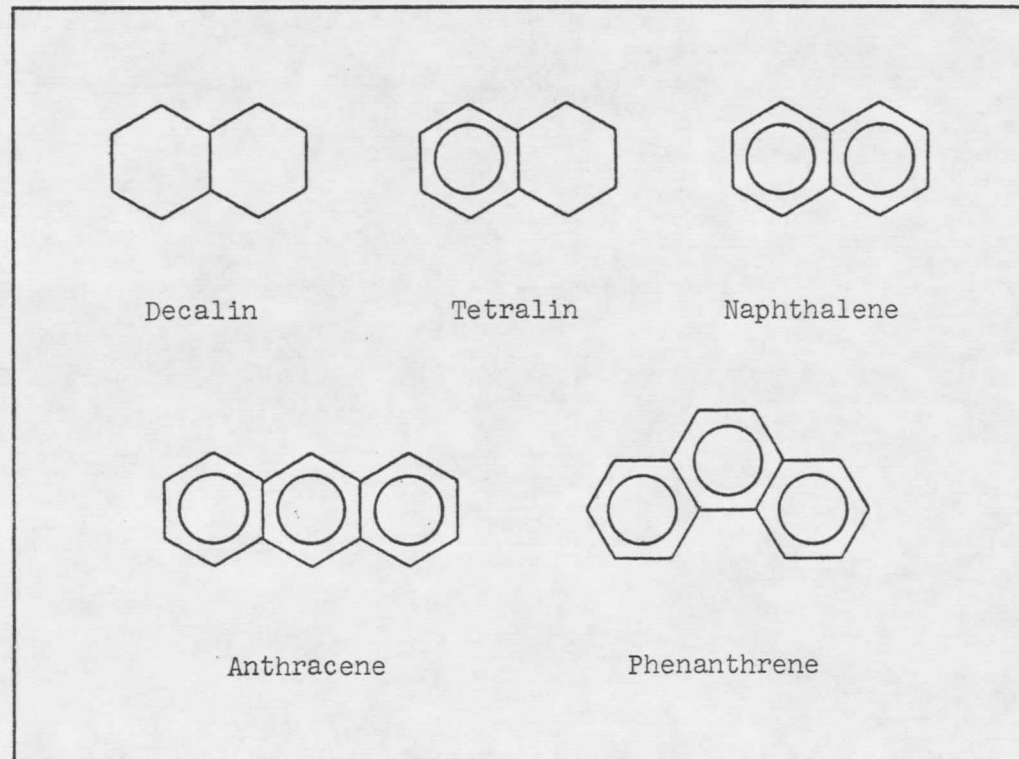


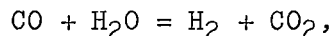
FIGURE 1. Structural Formulae of Tested Solvents.

Energy-Development) process (8), is not known.

Figure 1 does not show any four- or five-ring compounds, which were not tested because of their high melting points. Nitrogen-based compounds such as isoquinoline, which have been shown to be quite effective (2), were not included due to environmental problems that are conceivable in the large scale application of the process.

Except for the naphthalene, available in reagent grade, and for the FMC coal tar, all the other chemicals were technical grade.

3. Catalyst For this particular process, two types of catalysts had to be tested. The first type would catalyze the hydrogen-forming reaction



and the second type would catalyze the reduction and stabilization reactions between the newly-formed hydrogen and the thermally cracked coal, the reactive fragments of which now dispersed in the solvent. The following compounds were tested for catalytic effects: sodium formate, sodium bicarbonate, sodium carbonate, ferric oxide and stannous chloride.

The sodium compounds were selected because of (a) their catalytic effects on the water-gas shift reaction (28), (b) their relatively low price, which would be a must if they were to be used commercially on an once-through basis, and (c) their solubility in water, which ensured their even distribution among the reaction mass.

Ferric oxide was included also because of the well known catalytic

action of iron compounds on the shift reaction (20).

The selection of stannous chloride was based on observations elsewhere (24) that tin compounds were moderately effective as catalysts for the stabilization of the reactive coal fragments through hydrogenation reactions. Stannous chloride was also water-soluble, a desirable property not found in most tin compounds. Used at very low concentrations, the tin salt was comparable in cost to the sodium salts. And finally, the corrosiveness of SnCl_2 to the reactor could be expected to be negligible at these levels of concentrations.

Tin metal and other tin compounds were not used either because they were not soluble in water, which at low concentrations would have made them even more difficult to be dispersed among the reactants, or because they would conceivably cause environmental problems in large scale operations. This was also the reason for the exclusion of ammonium chloride in spite of the fact that the latter has been reported to be particularly effective when used in conjunction with tin compounds (24).

4. Carbon Monoxide Technical grade carbon monoxide was used. In order for the gas to be continually available at 1500 psi, a pressurization system was used in which CO was let flow to a high pressure cylinder where it was subjected to a decrease in volume by hydraulic oil being pumped in from an oil reservoir. From the high pressure cylinder, the CO flowed directly into the reaction autoclave (figure 2).

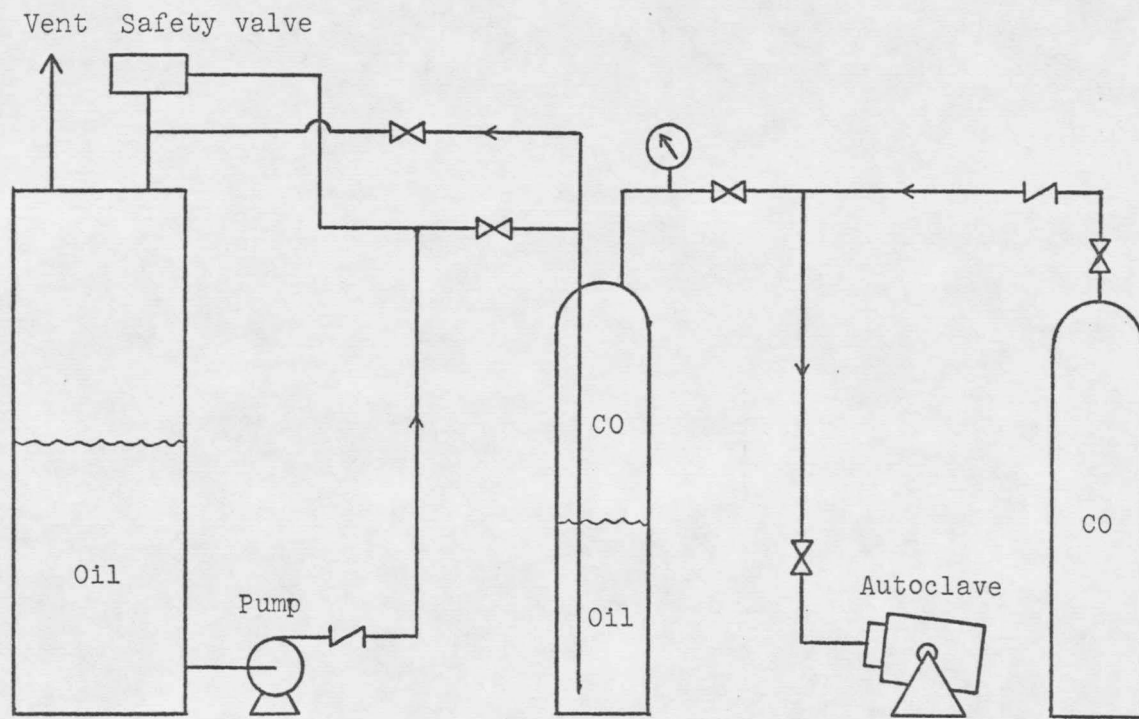


FIGURE 2. Pressurization System.

B. Experimental Procedure and Equipment Figure 3 shows the major steps taken in each run. More specifically:

1. Coal Preparation The Colstrip subbituminous coal, under storage in three-layer plastic bags or bottles as lumps approximately two inches in diameter, was hand-ground with a mortar and pestle to -40 mesh. Ball-milling enough coal for more than one run was avoided because of the adverse effects such prolonged exposure to air would cause, through oxidation and loss of water, on conversion.

It was felt that at -40 mesh, the coal would still be fine enough to be easily disintegrated further in the presence of the solvent at the high final temperature. This was in fact the case because the unconverted coal from each run was always found to be in an extremely fine powder form.

2. Charging Thirty grams of the ground coal, 30 grams of water and the appropriate amounts of solvent and catalyst were charged to the reaction autoclave. To ensure even catalyst distribution, the catalyst was first completely dissolved in the water, and the fine coal then added and allowed to soak up the solution. Where a catalyst was not water-soluble, as in the case of ferric oxide, it was manually mixed with the coal and the solvent before the addition of water. Ball-milling the catalyst with coal would have created better mixing, but was not done because of the negative effects of this type of operation on conversion, as has been previously discussed.

