Reduction of sub-bituminous coal and lignite using carbon monoxide
by Wayne Jason York

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

Abstract:
The reduction of a sub-bituminous coal and three lignites ,using C0 rather than H2 was investigated. The sub-bituminous coal was mined at Colstrip, Montana, and the three lignites were mined at Savage, Montana, and Stanton and Noonan, North Dakota. The equipment in this study consisted of a 500 ml,,rocking"autoclave which operated between 380°0.' and 4500O;, and a maximum operating pressure of 5000 psi. The analyses which were made included the conversion of the MAF coal to benzene soluble material, gas analyses of the reaction gases, and ultimate analyses and molecular weight determinations of the liquefied coal.

The results show that increasing pressure and temperature increase conversion, however, hydrocarbon gas production increases with temperature as well. The best solvent that was investigated for lignite was a mixture of alpha-naphthol and phenanthrene, and for sub-bituminous it was anthracene oil. Grinding the coal in a mortar and pestle produced better conversion results than pulverized coal because the coal was less oxidized in the former grinding method. Noonan lignite is more reactive than Stanton lignite, which in turn is more reactive than Savage lignite.

The reason for these differences has been attributed to the composition of the ash in the coal. Na2CO3 was studied as a catalyst for the liquefaction of coal using C0. with quite successful results.

The tar product obtained from the coal has a hydrogen-to-carbon ratio of about.1.1 and an ash content of less than 0.1% compared to coal's hydrogen-to-carbon ratio of 0.8 and 7% ash. This product would be an ideal fuel for magneto-hydrodynamics, and will overcome many of the obstacles that have prevented magnetohydr0dynamics from becoming a reality.

TSro processes utilizing the liquefaction of coal using CO were designed and studied economically. One process produces CO from char, H2O and 02, while the other produces the CO from CO2 and the char. The first process is competative with existing liquefaction, processes using; hydrogen, and the second process is more economically attractive than any liquefaction process that has been proposed for the production of tar products.

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ABSTRACT

The reduction of a sub-bituminous coal and three lignites using CO rather than H_2 was investigated. The sub-bituminous coal was mined at Colstrip, Montana, and the three lignites were mined at Savage, Montana, and Stanton and Noonan, North Dakota. The equipment in this study consisted of a 500 ml. rocking autoclave which operated between 380°C and 450°C, and a maximum operating pressure of 5000 psi. The analyses which were made included the conversion of the MAF coal to benzene soluble material, gas analyses of the reaction gases, and ultimate analyses and molecular weight determinations of the liquefied coal.

The results show that increasing pressure and temperature increase conversion, however, hydrocarbon gas production increases with temperature as well. The best solvent that was investigated for lignite was a mixture of alpha-naphthol and phenanthrene, and for sub-bituminous it was anthracene oil. Grinding the coal in a mortar and pestle produced better conversion results than pulverized coal because the coal was less oxidized in the former grinding method. Noonan lignite is more reactive than Stanton lignite, which in turn is more reactive than Savage lignite. The reason for these differences has been attributed to the composition of the ash in the coal. Na_2CO_3 was studied as a catalyst for the liquefaction of coal using CO with quite successful results.

The tar product obtained from the coal has a hydrogen-to-carbon ratio of about 1.1 and an ash content of less than 0.1% compared to coal's hydrogen-to-carbon ratio of 0.8 and 7% ash. This product would be an ideal fuel for magnetohydrodynamics, and will overcome many of the obstacles that have prevented magnetohydrodynamics from becoming a reality.

Two processes utilizing the liquefaction of coal using CO were designed and studied economically. One process produces CO from char, H_2O and O_2, while the other produces the CO from CO_2 and the char. The first process is competative with existing liquefaction processes using hydrogen, and the second process is more economically attractive than any liquefaction process that has been proposed for the production of tar products.

I. INTRODUCTION

A. United States Energy Requirements

Only until recently have we been able to keep pace with our country's insatiable appetite for energy. For the first time in our history in 1970, there was considerable discussion of power shortages. There are many reasons for the shortages, but the major factors are: the overselling of nuclear energy, mine safety laws which result in the closing of coal mines, coal exports, pollution control, and Middle East oil import curtailments (1).

Not only must we supplement present shortages of fuel, but we must supply the expected increase of fuel requirements in the years to come. Since 1880, the United States' energy consumption has doubled every 30 years and it is expected to do so again in the next 20 to 25 years. Even more important, the United States' power consumption has been doubling every eight to ten years. Based on these predictions, we will require well over 125 quadrillion BTUs of energy in the year 2000 (2). This increase is due to the population increase and the per capita increase in energy consumption.

In addition to the growth problem, we are now facing the possibility of shortages in presently used fuels. For example, the natural gas and petroleum reserves-to-consumption ratios have been decreasing for the last several years, and even the Alaskan oil find will not replace the expected shortages (3,4). Known recoverable United States reserves of oil, gas, and uranium each could supply about 300 quadrillion BTUs of energy or a total of 900 quadrillion BTUs. About ten percent of the fossil fuel consumption is also used as a feed stock for the organic chemical industry. Because of the increase in future energy requirements and the potential shortages of presently used fuels, we must obviously find new and more effecient ways of producing energy and organic chemicals.

The most desirable solution to this problem would be atomic fusion, and at this time the Atomic Energy Commission is convinced that fusion-power reactors are not blocked by laws of nature. "Depending on one's underlying assumptions, or the level of the effort and the difficulties ahead, the time it would take to produce a large prototype could range from as much as 50 years to as little as ten years (5)." This would indicate that commercial hydrogen-powered reactors <u>may</u> be developed by the turn of the century, which is much too long to wait for a suitable solution to the energy problems for the near future. Breeder reactors, which will make more efficient use of nuclear fuels, are more promising and may be used on a commercial scale by 1984 (6).

B. Fossil Fuel Potential

Fossil fuels will continue to play a very important role in satisfying our energy demands, particularly in the transportation sector. More efficient methods of generating electricity from fossil fuels, and new processes to utilize or convert heretofore unused fossil fuels into usable fuels will have to be investigated. The three major sources of these fuels are coal, tar sands, and oil shale, but each offers advantages and disadvantages.

The advantage of tar sands is that the oil is easy to extract from the sand. The oil after extraction requires only small amounts of hydrogen to obtain a synthetic crude oil. Tar sands are undesirable in that they are located in northern Canada, which is a considerable distance from markets in the United States. The ore contains only 15 percent carbon, but nonetheless Sun Oil Corporation has a 45,000 bbl/day plant processing tar sands.

Oil shale technology is fairly well developed and the reserves are fairly large (they contain about 80 billion barrels of oil). Unfortunately, the crude oil is of rather poor quality and the shale oil reserves are not close to processing water sources.

When compared to other fossil fuels, we note that there are huge reserves of coal in the United States, or about 4,600 quadrillion BTUs. Coal reserves are a short distance from market; are cheap to obtain in many areas, and provide a great versatility of uses. However, the big disadvantage is that technology has not been fully developed in order to make use of many of coal's potentials. Thus, with future improvements in coal technology, and with utilization of its vast reserves and versatility, coal will play a major role in supplying energy for the future. Factors, other than technological factors, which will dictate when coal will be used for the production of hydrogenated coal products include: cost of money, taxes on mineral extraction, assigning of royalties for coal leases, and guidelines for oil import quotas (7).

One of the largest reserves of coal in the world is the Fort Union formation (Figure 1). It contains about 700 billion tons of sub-bituminous coal and lignite, or about seven percent of the world's known reserves (25

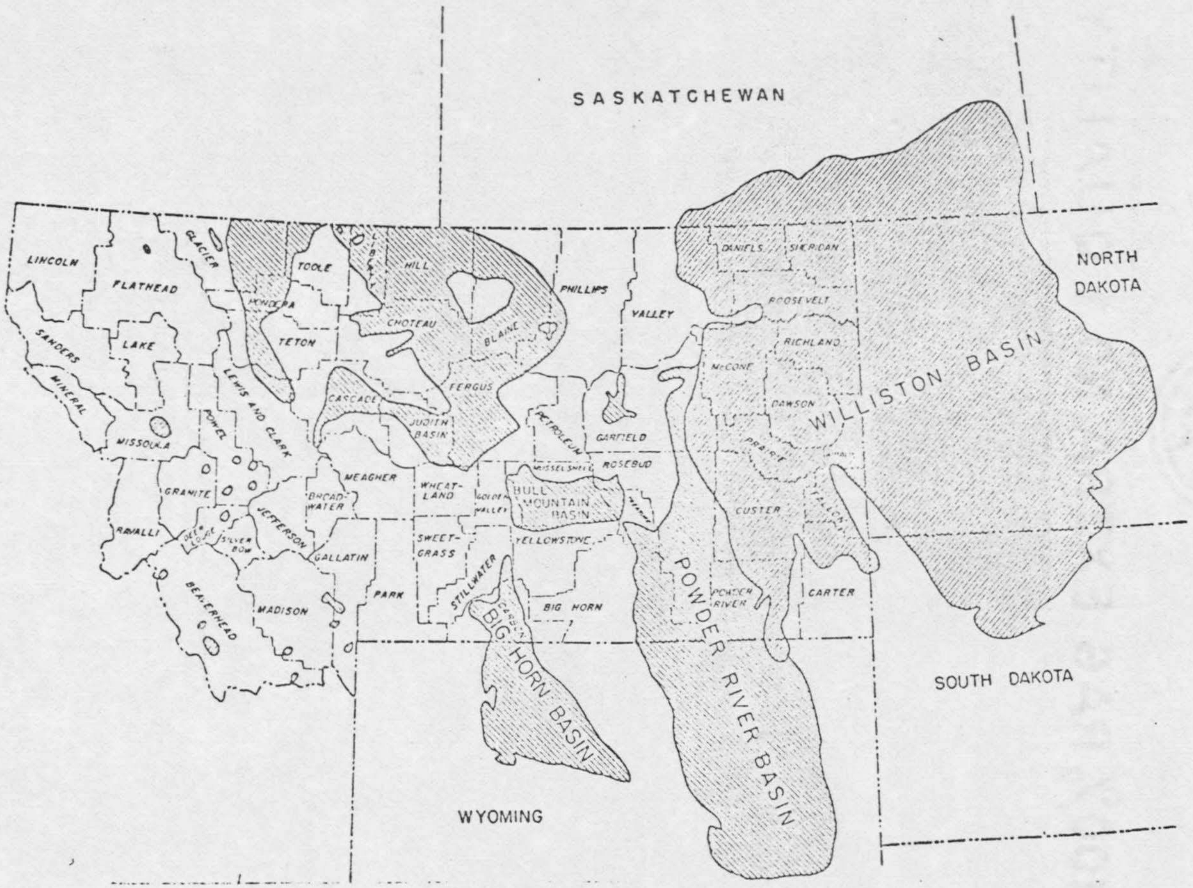

Figure 1. The Fort Union Coal Region in Montana and Adjacent States. Also shows other coal areas in Montana. (8)

percent of the United States' reserves). Montana shares about 220 billion tons of this coal, of which about 20 billion tons can be strip mined economically today.

The Fort Union coal will probably have four major uses before the turn of the century. It will be liquefied, gasified, used to obtain chemicals, and burned for electric power generation. In fact many elaborate systems utilizing these processes have been proposed (9,10).

Liquefaction to gasoline, aviation fuel, and synthetic crude oil has been studied for many years. Because of its importance to the direction that this project took, the historical developments of liquefaction will be discussed in the next chapter. Chemicals and carbon products are produced from coal by essentially the same methods as liquefaction. During the early 1950's, Union Carbide had a large pilot plant in West Virginia to obtain chemical feeds, but the Bergius process that they used proved to be uneconomical (11). New concepts of obtaining chemicals from coal via hydrogenation have since been proposed (12).

Gasification is becoming increasingly important and a great deal of research is being conducted in the United States (13,14,15). The processes are designed to replace natural gas with a high BTU gas containing mostly methane.