



Production of liquids and gases from Savage, Montana lignite by hydrogenation with a nickel tungsten catalyst
by Jack Dean Olson

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:

Eastern Montana and the adjacent states are a vast source of untapped hydrocarbon fuel reserves in the form of coal. The area contains nearly 700 million tons of coal reserves that could provide 300 years of liquid fuels to the United States if converted.

Present conversion methods being investigated by the Office of Coal Research are tending to aim at only moderate conversions, around 60 percent, and would not be suitable in the Montana economic environment unless a use for the char was found other than as a boiler fuel for electrical production. The process described in this paper leads to a conversion from 75 to 95 percent of the coal and would not require use of the char as a boiler fuel for electrical production.

The equipment used in this study is based around a high pressure autoclave operated in batch fashion. Supporting equipment allows the autoclave to be charged while it is at operating temperature and also discharged at operating conditions. The gas stream is sampled to determine hydrocarbon gas percentages, the liquid stream is vacuum distilled into a fraction boiling below 325°C and a heavy liquid that is reused as a recycle oil, and the sludge is separated by benzene extraction to determine the amount of coal unconverted.

Data obtained from 94 runs were used to obtain correlations of the various yields with operating conditions. A suitable correlation using the main effects, the second order interactions, and the third order interaction of reaction time, temperature, and catalyst concentration was found. Second order terms were not considered due to the limited scope of the data. An overall yield term based on a linear combination of the products was defined and an equation determined. The units of dollars per hundred pounds of moisture and ash free (MAF) lignite were set for the overall yield and the approximate values of each of the products used as linear multipliers. While all yields were found to vary considerably for various recycle numbers, a discussion of recycle three appears to have the best merits.

For operation of a commercial plant, the oil boiling below 325°C would be the main product and could not be withdrawn from the process at a rate greater than the rate of total oil formation from the coal. Using these criteria, a set of conditions were obtained at which the process could be operated continuously. For recycle three, operation at 468.9°C for one hour at 4 percent catalyst concentration would allow 95.8 lbs. of lignite (MAF) and 4.16 lbs. of hydrogen to be processed into: 6.2 lbs. unconverted char, 13.2 lbs. hydrocarbon gas, 12.2 lbs. of reaction water, and 68.4 lbs. of oil boiling below 325°C.

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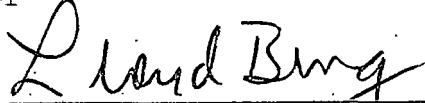
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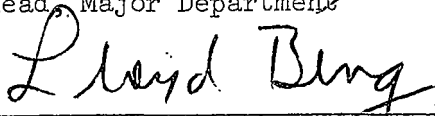
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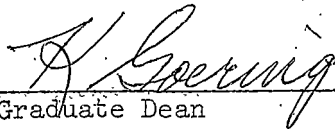
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ABSTRACT

Eastern Montana and the adjacent states are a vast source of untapped hydrocarbon fuel reserves in the form of coal. The area contains nearly 700 million tons of coal reserves that could provide 300 years of liquid fuels to the United States if converted.

Present conversion methods being investigated by the Office of Coal Research are tending to aim at only moderate conversions, around 60 percent, and would not be suitable in the Montana economic environment unless a use for the char was found other than as a boiler fuel for electrical production. The process described in this paper leads to a conversion from 75 to 95 percent of the coal and would not require use of the char as a boiler fuel for electrical production.

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FORWARD

This doctoral thesis is written a little differently than most in style and format. The first major portion is designed to present the problem, a possible solution, and important conclusions from the experimental data. This first major portion is kept as brief as possible and is fairly well self-contained to allow a wide readership without bogging down in the details of the data. But, the second portion presumes that the first has been read.

The second major portion is contained in the appendix. Here the reader should be able to find as much detail about the experimental run data as he desires. Background literature is pointed out that would allow a reader to become fairly expert in the field of coal hydrogenation. Some of the experimental procedures have been expanded to show what weaknesses in technique could be improved upon. Two computer programs are described and their output is listed. The output from these programs details in tabular form all the data collected in this research program. The second program is one in which the data are correlated and the output is yield equations based on the experimental data. A results section discusses the equations and graphs drawn from them in a detail that is not available in the first portion.

I. INTRODUCTION

Montana is a land of vast coal reserves that stretch from the Wyoming border to the Canadian border almost everywhere east of Forsyth. The Fort Union coal formation in Montana and adjacent states contains an estimated 700 billion tons of coal,¹ or putting it in terms of liquid fuels, enough liquid fuel could be produced to supply the United States for 320 years at the present rate of 12 million barrels per day consumption. Considering the diminishing rate of oil discovery compared to the consumption rate, there is a possibility of the domestic supply becoming shorter than the demand sometime in the 1980's.² Such an occurrence would demand that fuel be produced either from increased oil imports or from one of the synthetic fuel sources, e.g., coal, tar sands, or shale.

Oil companies realize that they may have to move into the synthetic fuel market sometime in the future and are aligning themselves through mergers with existing coal companies or acquiring coal leases of their own. Thus, Continental Oil Company merged with Consolidation Coal, Gulf Oil Company with Pittsburg and Midway, and Sohio acquired Ben Ben Coal. In addition to these, Standard of New Jersey has spent nearly 25 million dollars leasing lands in Illinois, Montana, and Wyoming.³ All the aforementioned companies also are engaged in research to improve the technology of coal refining. Project Coed, Project Gasoline, and H-Coal are well known joint ventures of private companies with the Office of Coal Research. Other companies are engaged in private research and results from their work are not generally available.

The Department of Chemical Engineering at Montana State University has always been interested in development of the natural resources of the state. A series of theses and articles has been published in the past decade on low temperature carbonization of coal to produce a low volatile char, possibly usable as a coke substitute in some of the local phosphorus and mining industries. Because of the potential rewards that a synthetic fuel coal refinery would involve for the state, a decision to begin exploratory research in coal refining was made in October 1964. General goals of such research were to find, (1) if coal could be refined into low molecular weight fuels at moderate hydrogenation pressures, (2) if a catalyst could be found that would give high yields of oil with low amounts of gas production, (3) if products from such hydrogenation would have desirable properties, and (4) if such products could compete with fuels from petroleum crudes. This article is directed at answering these questions.

Presumably, our goals are similar to those of Project Gasoline, Project Coed, and H-Coal. Because of basic differences in technique we shall briefly describe these processes.

Project Gasoline is a two-step process wherein coal is dissolved at low pressure in a solvent which is then filtered to remove ash and solid coal and then hydrogenated in a catalyst bed at pressures around 3000-5000 psig. Conversion is expected to be about 60% based on the MAF (moisture and ash free) coal. The solid residue would be used as a boiler feed for electric power production.⁴

Project Coed uses a low pressure carbonization of the coal in a multi-stage bed to remove all volatile matter. The remaining char is then

used as a boiler feed and the volatile matter is processed by hydrogenation at moderate pressures into liquid fuels.⁵ Conversion is slightly lower than that of Project Gasoline and probably is highly dependent on the type of coal used.

H-Coal is a project using a single-stage ebullated bed with coal slurry passed upwards through the bed. Reaction takes place on the catalyst surface to a conversion of about 90% with bituminous coal. Total liquid yield is 70% for bituminous coal. The process produces a wide range of distillates that would have to be further processed into usable fuels.⁶

Economics for the first two of the above projects require a ready sale of the residual char as a boiler feed. Consideration of ash in the char as well as the potential of a greater supply of char from one large coal refinery than could be used by the presently existing 180 megawatt power plant in Billings, Montana, forces a re-evaluation in terms of conversion. The process described in this article attains conversions between 75 and 97% and hence would not require being operated in conjunction with a power plant. Use of a single step process would lower the cost of building a plant and simplify its maintenance. Such a savings appears to be offset by other advantages of the two-step process, as will be shown later, and so may not be realistic.

The cost of hydrogen is a very large factor in the economics of coal hydrogenation. While the development of pressure coal gasification by Texaco Development Corporation will lower the costs well below that for natural gas reforming, further research work will need to lower the cost even more.¹⁰

II. EQUIPMENT AND PROCEDURE

The availability of equipment, specified to a large degree, the procedures. Since only limited funds were available, the process uses salvage equipment donated by Monsanto Chemical Company and Dow Chemical Company. Shown below is a simplified flow diagram of the system which is basically a batch autoclave with auxillary equipment necessary to allow efficient operation. The entire project is placed in an enclosure eight by ten feet with an L shaped, six foot high, concrete wall built for fire protection. Instrumentation and remote controls allow complete operation from outside the enclosure during the time the equipment is pressurized.

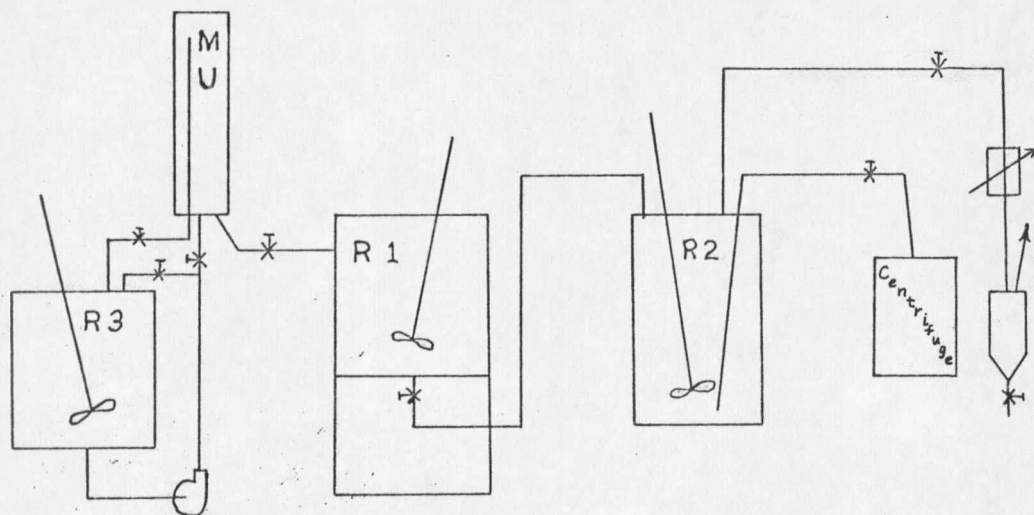


Figure 1. Experimental Equipment Layout

Lignite coal used in this study was obtained ground and partially dried from the Lewis & Clark generating station of Montana-Dakota Utilities. The coal was fed slowly into 130°C recycle oil in the slurry tank labeled R 3, until a 20% by weight of raw coal slurry had been reached. The

mixture was then kept stirred and mixed by a stirrer and recirculating pump. A portion of the mixture would then be introduced into the measuring unit (MU in figure) which allowed approximately 1475 ml. to be pressured into the hot main reactor (R 1). Within six minutes of the time the slurry was introduced to the main reactor, hydrogen and catalyst dust were injected until the pressure reached 2500 psig. At the end of the reaction time (one, two, or four hours) the slurry was released through the bottom dump valve into another prewarmed pressure reactor (R 2). A vent valve released the unused hydrogen and hydrocarbon gases through a condenser and out the roof. While the gas was being released, a sample was taken from the vent line beyond the condenser to determine the composition of the hydrocarbon gases. When the slurry in R 2 dropped to approximately 240°C, it was pressured by nitrogen into a spinning centrifuge bowl where it remained for about ten minutes. The measured quantities of solids, recycle liquids, oils boiling below 325°C, reaction water, and hydrocarbon gases were used to determine mass balance, conversion, and various yields.

III. DISCUSSION AND RESULTS.

A. Preliminary Research

A year of research was spent using a small rocking bomb autoclave experimenting with various slurry oils and catalysts. Conversion of the coal to a benzene soluble material was found to be very dependent on the slurry oil media and catalyst type. Low boiling slurry media showed almost no conversion. Also, dry coal with impregnated molybdenum or tungsten catalyst showed little conversion. Tetralin worked well as a solvent with tungsten catalysts, but tetralin tends to revert to naphthalene in the presence of molybdenum. The best slurry media found was Dowtherm A., but later experiments proved that the Dowtherm was unstable at the hydrogenation conditions and broke down into a two layer liquid. Since the size of charge in the rocking bomb and lack of a good stirring mechanism prevented any product identification, we decided to build the present process system.

B. Reaction Model

Considering the problem of coal hydrogenation from a commercial viewpoint, we can define certain parameters that may affect yields and hence should be well known before a plant is designed. Thus, yield would be: $Y = F$ (temperature, pressure, catalyst type, catalyst amount, recycle number, coal particle size, slurry oil type, slurry concentration, reaction time, and other variables needed to specify equipment design): This article will not specify all the required data, but some of the parameters have been thoroughly studied.

The coal particle size was found in preliminary research to have a definite inverse affect on conversion. It was found that by grinding

