



A study of parameters affecting hydrogenation of coal via the water-gas shift reaction
by Ronald Dayton Denney

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

The hydrogenation of sub-bituminous coal in a high pressure (5000 psi), high temperature (470° C) rocking autoclave via the water-gas shift reaction was studied.

The coal, which was converted into a benzene soluble oily product, will be used as a raw material for the low ash gases needed for production of electricity in a magnetohydrodynamic generator.

Experimental results show that aging of the coal does not affect the conversion to the desired product. Oxidation and water loss from coal were studied and seemed to have no negative effects on the desired properties of coal.

Carbon monoxide, which is used as a raw material for the water-gas shift reaction, has been shown that it need not be in pure form, but may contain a high percentage of carbon dioxide as an impurity. Thus, any CO recycle stream may not need a purification step. Agitation of the coal slurry in the reactor can be varied somewhat without affecting coal conversion.

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by

RONALD DAYTON DENNEY

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ABSTRACT

The hydrogenation of sub-bituminous coal in a high pressure (5000 psi), high temperature (470° C) rocking autoclave via the water-gas shift reaction was studied. The coal, which was converted into a benzene soluble oily product, will be used as a raw material for the low ash gases needed for production of electricity in a magneto-hydrodynamic generator.

Experimental results show that aging of the coal does not affect the conversion to the desired product. Oxidation and water loss from coal were studied and seemed to have no negative effects on the desired properties of coal. Carbon monoxide, which is used as a raw material for the water-gas shift reaction, has been shown that it need not be in pure form, but may contain a high percentage of carbon dioxide as an impurity. Thus, any CO recycle stream may not need a purification step. Agitation of the coal slurry in the reactor can be varied somewhat without affecting coal conversion.

INTRODUCTION AND BACKGROUND

Introduction

Today, the United States is facing an extraordinary and critical fuels supply situation. Energy demands are growing at a rapid rate and the levels of proved reserves are dropping. During the 30-year period ending in 1970, the energy demand grew at an average yearly rate of 3.4%. The Bureau of Mines predicts a 3.5% yearly increase for the next thirty years. The level of proved gas reserves have dropped from a 21/1 reserve/production ratio in 1960 to 12/1 in 1970. Although the Potential Gas Committee reported in 1969 that in addition to the 287 trillion scf proved reserves, that there are yet 1227 trillion scf of domestic gas, the rate of discovery is falling behind so that these gas reserves may not be recovered in time to avert a major energy shortage. Nuclear power is predicted to supply only 23% of the total energy demand in the year 2000. So far, oil from tar sands constitutes only a small fraction of the energy used today. A great development in this area is not foreseen. Imports cannot be depended upon to satisfy demands. Not only is the Middle East supply unstable, the Canadian National Energy Demand has forecast that, at most, Canada will be able to supply up to 2.3 trillion scf in 1980.

It is evident that the United States must go to another source of energy. Enormous reserves of coal have caused greater attention to possibilities of converting coal into an useable energy form. The spotlight was turned onto coal gasification in the President's June 4, 1971 energy message which said, "As we carry on our search for cleaner fuels, we think immediately of the cleanest fossil fuel-natural gas. But our reserves of natural gas are quite limited in comparison with our reserves of coal. Fortunately, however, it is technically feasible to convert coal into a clean gas which can be transported through pipelines. The Department of the Interior has been working with natural gas and coal industries on research to advance our coal gasification effort.... We are determined to bring greater focus and urgency to this effort." An eight year agreement has been signed between the American Gas Association and the Department of the Interior to finance research in coal gasification programs. Federal expenditures will be \$20 million per year and industry will provide \$10 million per year (1).

Most commercial research has been in the area of coal gasification to produce a gas of pipeline quality, i.e., 1000 BTU/scf.

There is one coal gasification process now in commercial use. This is the Lurgi Pressure Coal Gasification

method which has been under development since the 1930's. There are fourteen plants now using this process, the largest being in Sasolburg, South Africa with 13 gasifiers. Process economics are being studied on a 30 to 35 unit gasifier plant announced by Texas Eastern and Pacific Lighting. However, this process produces only 5000 BTU/scf gas so a methanation step is needed to produce the standard quality pipeline gas.

Four other processes have reached the pilot-plant stage. These are the 1) Bi-Gas process developed by Bituminous Coal Research, Inc., 2) Hygas Process by the Institute of Gas Technology, 3) CO₂ Acceptor Process by Consolidation Coal Co., and 4) Synthane Process by the U.S. Bureau of Mines. These processes are fairly similar in that all require a methanation step at the end to produce a pipeline quality product. Other gasification programs are under way by Garrett Research and Development Co., M. W. Kellogg, FMC, and Stone and Webster.

These coal gasification processes all have an energy conversion efficiency of only 65%. Coupled with this is the fact that all of these processes are faced with shortcomings. With some, high maintenance costs are a factor. Others face high cost economics of producing the electrical power, hydrogen and oxygen required. The amount of char

produced is also a factor. A factor faced by all is the temperature control of the methanator for prevention of catalyst deactivation and "runaway conditions." This is difficult because of the high heat of reaction (94,000 BTU/lb. mole) (2).

Another facet of the energy shortage is that of gasoline and electricity production. The reserves of petroleum are also running low. With the increased prices of gasoline, it may soon be economically feasible to produce gasoline from coal. Processes are available to produce gasoline from coal as evidenced by the large amounts of gasoline produced by Germany in World War II and the Fischer-Tropsch process being used in the Republic of South Africa at the present time. These processes, however, require enormous amounts of hydrogen of which production could amount to one third of the cost of the entire plant. Also the high pressures required call for great amounts of steel in the construction of the plant thus requiring a large initial capital investment (3).

Research is also being done on new processes to produce gasoline from coal. A molten-salts process is being investigated at Montana State University by Ph. D. student, Warren Scarrah. This process will give an ashless high grade crude oil, but it may not be ready for several years.

The COED liquefaction scheme by FMC has reached pilot plant stages.

Schemes are also being developed to produce electricity from coal. Steam generation plants are the order of the day; however, schemes must be found which will eliminate the fly ash and obnoxious gas emissions of the coal burners which produce the heat. These controls may cause shutdowns or higher priced electric power.

Magnetohydrodynamic (MHD) electric power generation may be the answer to these problems. Here, an ashless low contaminant gas is passed at high temperature and velocity through a magnetic field which produces an electric plasma in the gas which is collected by electrodes. The absence of moving parts keeps the maintenance costs low and recycle streams should enable achievement of a high energy conversion efficiency. The idea of MHD power generation is not entirely new. Reports dating from the late 1950's have foretold the forthcoming of commercial MHD. In the United States, this idea seems far from practice, but overseas, notably in Japan and the Soviet Union, evidence of large scale MHD research is seen. The Soviet Union has put a 25 MW MHD power unit into the Moscow power system in 1970 of which Soviet scientists are confident that it will rival the most modern turbine generators (4).

The Soviet Union is using natural gas as a source of the hot gases; whereas, the United States, with its shortage of natural gas will turn to coal for the production of the hot gases. With the high temperatures and the supersonic gas speeds, it is evident that the gases be completely ash free. Coal will have to be converted to a form from which the ash can be extracted.

Research at Montana State University is being undertaken to produce a benzene-soluble product from which the ash is filtered out. This research is being financed by Avco. Corp. and was begun by Ph. D. student, Wayne York, in 1967. Further work has also been done by Ph. D. student, Dat Nyugen, and by Thomas Fiske. Operating conditions and catalysts are being studied to obtain optimum conversions from coal to product. Similar work was done by the German scientist, Bergius, in 1910 and later by the Office of Coal Research.

Background

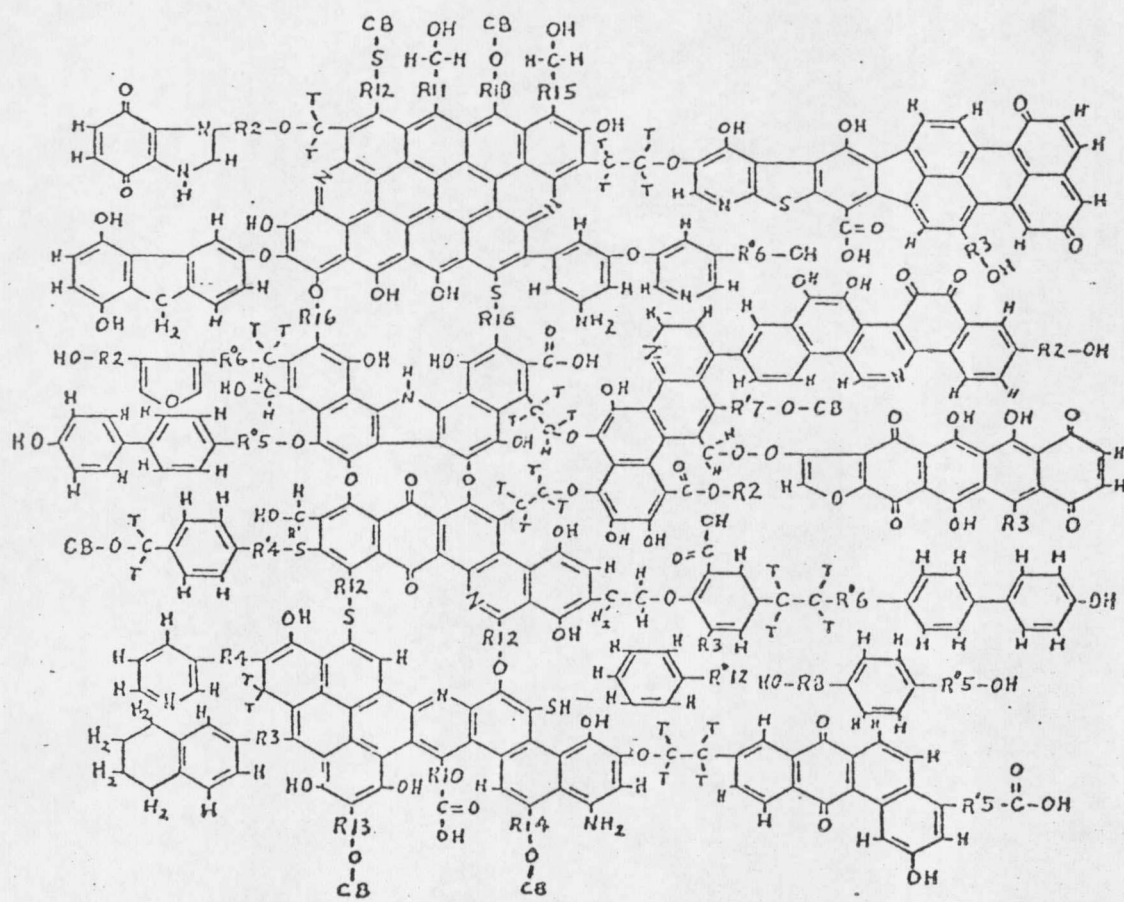
Bergius began his work at the request of the German government when they became concerned about shortages of high grade coal. During experiments to produce coal from peat, Bergius reacted some of his coal product in a hydrogen atmosphere at high pressures (2000 psi) and temperatures (450°C) to produce an oil. In 1913, he applied for a patent and eventually received a Nobel prize. After the first World War, the Bergius patent was further developed to a point where it was technically feasible. The Bergius process was basically two steps; the first step produced a middle fraction oil from the coal, which was then refined to high grade gasoline via the second step. The process eventually was phased out because of economics, but the technology used has been improved upon until today when economics have pointed again to processes of this type.

At approximately the same time that Bergius was developing his process, two other Germans, Fischer and Tropsch, had developed a process to make oil from coal using carbon monoxide and hydrogen. This was the first time that the water-gas shift reaction was used on coal. Rather than adding hydrogen, carbon monoxide and water were added to the reactor. The water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \xrightarrow{\text{heat}} \text{CO}_2 + \text{H}_2$) takes place during the reaction thus producing hydro-

gen. This hydrogen is in the nascent form, thus being more reactive than H_2 and giving a greater conversion in a shorter time (5).

An insight into the chemistry of the hydrogenation and coal breakdown reactions will help to understand why this process works. Figure 1. shows a typical structure of a high volatile coal. Note how the structure is composed of a series of aromatic ring structures ranging from one ring to several rings connected together, the average being three or four, which are in turn connected together by small aliphatic groups and various other linkages. When heated to over $400^\circ C$, these linkages begin to break, thus forming free radicals of the aromatic ring clusters. The free radicals are then available to react among themselves or with any other radicals present. The presence of hydrogen results in the stabilization of these free radicals by the completion of the free radical bonds. This results in a lower average molecular weight. The more reactive nascent hydrogen from the water-gas shift reaction would react more easily with the free radicals and thus give a greater conversion to a benzene soluble product.

Adding a solvent in which the coal is slurried and reacted and by which the hydrogen can be transferred from the gaseous atmosphere to the free radicals, will increase the



R^n Alicyclic Rings of n Carbons

R^n Alkyl Side Chains of n Carbons

R^n Unsaturated Alkyl Chains

CB Cross-bonding to Other Heterocyclic Groups

T Tetrahedral Bonds

Figure 1. Typical Cross-bonded Structure for High Volatile Coal. (7)

yields. Solvents such as phenanthrene, tetraline, and decaline which are similar to the product produced are used. Not only can separation from the unreacted coal and ash be accomplished in one step (benzene extraction), but the nascent hydrogen can be carried in on the double bonds of phenanthrene and those formed on tetraline and decaline when the hydrogens are robbed by the free radicals. The resulting mixture of solvent and coal product can then be distilled into lighter and heavier cuts of tar. The lighter cuts can be recycled for solvent and the heavier cuts sent on for MHD use.

The presence of hydrogenation catalysts such as alkaline carbonates will also increase the conversion of coal to oil (6).

It has been the objective of the work done at Montana State to coordinate all of these variables into an optimum process. Because the coal hydrogenation process does require great pressures and temperatures, most of the work being done has been to increase knowledge of the reactions and to repeatedly make economic feasibility studies to cut costs of a commercial plant wherever possible.

RESEARCH OBJECTIVES

The primary objective of this investigation was to develop a greater understanding of the coal hydrogenation process. In an effort to produce a more economical product, variables must be studied in test process to determine the effects of each.

More specifically, the variables covered by this thesis are the aging of the coal during the time it leaves the ground until it is sent to the reactor, and the purity of the carbon monoxide initially charged into the reactor. Both of these variables are concerned mainly with economics; the first dealing with purification schemes in the production of the carbon monoxide.

Only through numerous small projects such as this will a fully commercial productive plant be designed and developed in an optimum manner.

Coal from Colstrip, Montana was used during the experiments to determine optimum run conditions. This was done with the objective in mind to develop Montana's vast coal resources into productive use for an increased Montana economy.

MATERIALS, EQUIPMENT, AND PROCEDURES

Materials

The coal used during this investigation was of the sub-bituminous type which is being mined at Colstrip, Montana. Two different batches of coal were used; the first being already available at Montana State University, which was used for the aging portion of the investigations, and the second obtained later for use in the tests for carbon monoxide purity. The laboratory analysis for the Colstrip coal is found in Table I.

Technical grade phenanthrene was used as the solvent in all of the runs made during this study. Comparative studies on solvents have been made by Dat Nyugen among various solvents, which showed phenanthrene to be among the better. Similar studies among catalysts were also completed by Dat in which a 1% by weight (of coal) of sodium carbonate was shown to be one of the most effective. Tap water was used as the source of water.

All other materials used, carbon monoxide, carbon dioxide, benzene, and toluene were of technical grade obtained from commercial suppliers.

Equipment

The reactor used consisted of a 500 ml Parr Inconel autoclave and a rocking-heating apparatus for the auto-

Table I. Proximate, Ultimate, and Ash Analyses for Colstrip Sub-Bituminous

Colstrip Sub-bituminous

Proximate

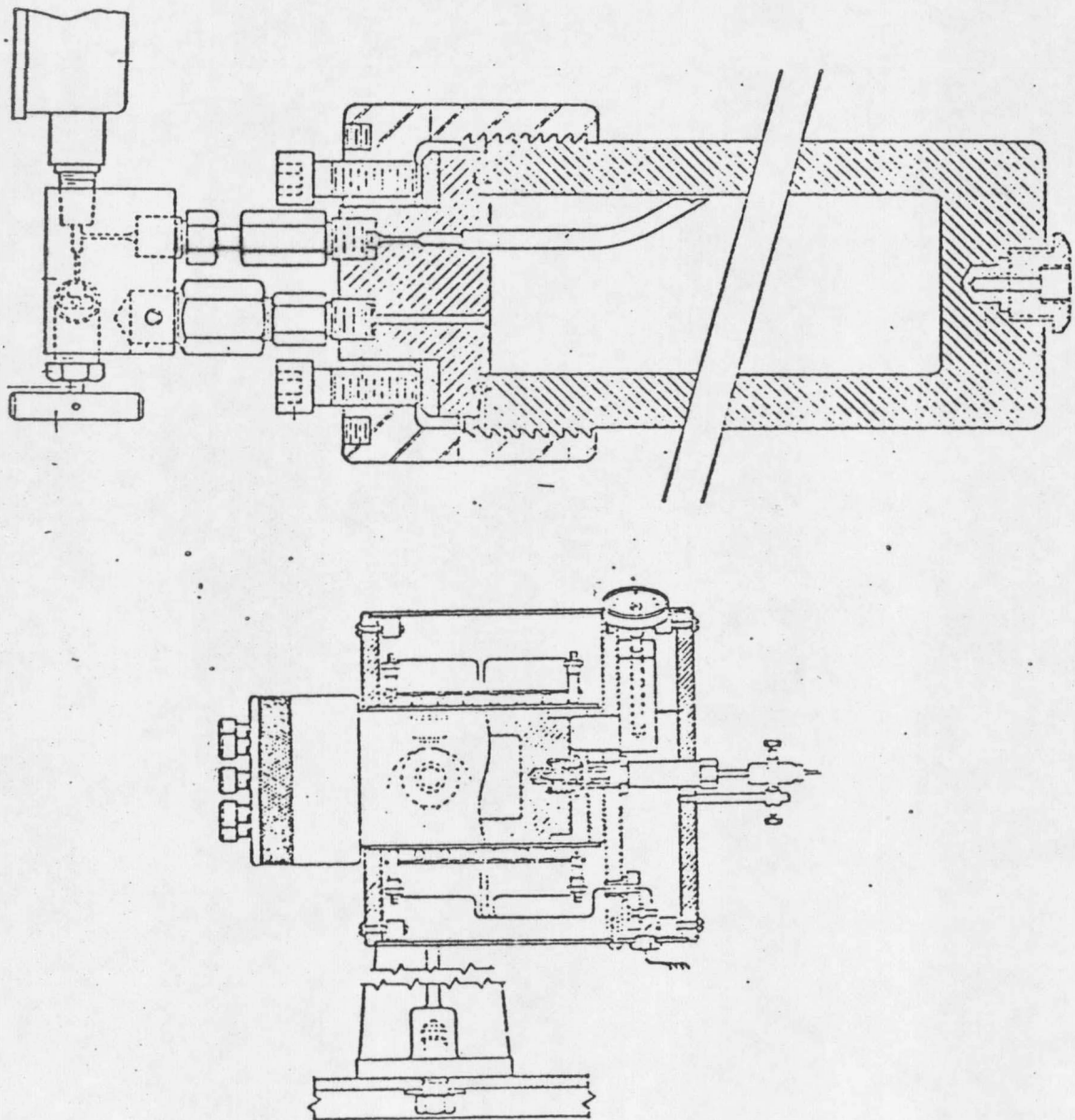
Moisture	23.9%
Volatile Matter	30.9
Fixed Carbon	37.6
Ash	7.6

Ultimate

Moisture	23.9%
Carbon	50.3
Hydrogen	3.4
Nitrogen	0.7
Sulfur	0.4
Oxygen	13.7
Ash	7.6

Ash Analysis of
Major Components

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



Bomb Heater Details

Figure 2. Rocking Autoclave Assembly Diagram.

clave (8). Both are shown in Figure 2. The autoclave was capable of containing 7000 psi at 500° C or 8800 psi at room temperature. The rocking assembly rocked at about 40 strokes per minute. The stroke was approximately 90° from top to bottom with the center of the stroke at the horizontal position. The angle of rock could be changed, however, to change the amount of agitation. The pressure was monitored by a gauge mounted on the block assembly of the autoclave and fed by a breather tube into the reactor. An iron-constantan thermocouple was inserted into a well at the bottom of the autoclave and was connected to a chart recorder to obtain a temperature history. For initial carbon monoxide pressures of 1500 psi, an oil-pressurizing system was used for compression. The CO was let into a high pressure cylinder into which oil was then pumped. This pressurizing system is shown in Figure 3.

A mortar and pestle was used to grind the coal to -38 mesh which was measured by a standard screen.

Extraction of the product from the ash and unreacted coal was done in a Soxhlet Extraction Unit as shown in Figure 4A. This was continued for 24 hours or until the benzene ran clear.

An electric forced-air dryer was used to dry the thimble from the extraction unit.

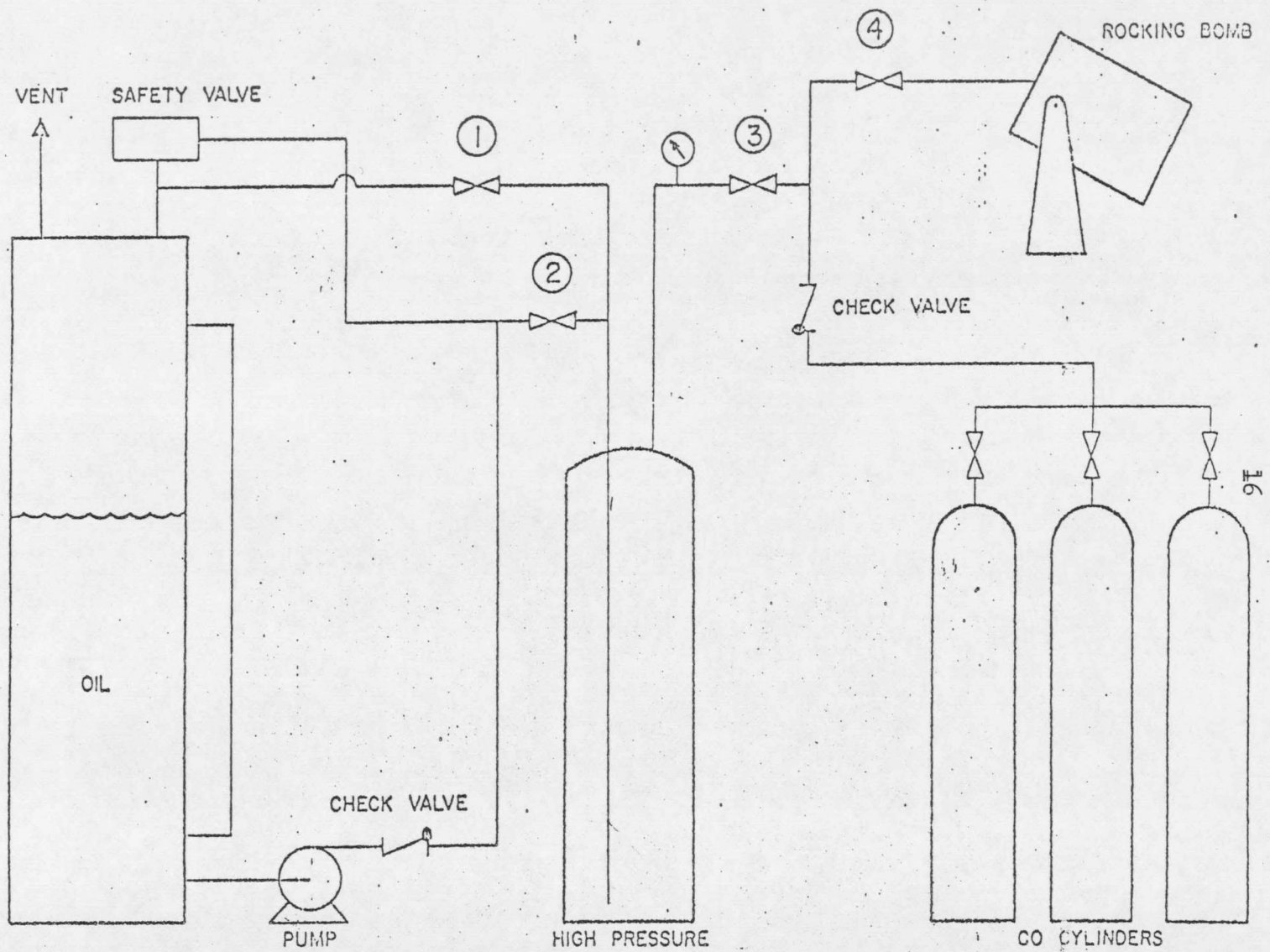
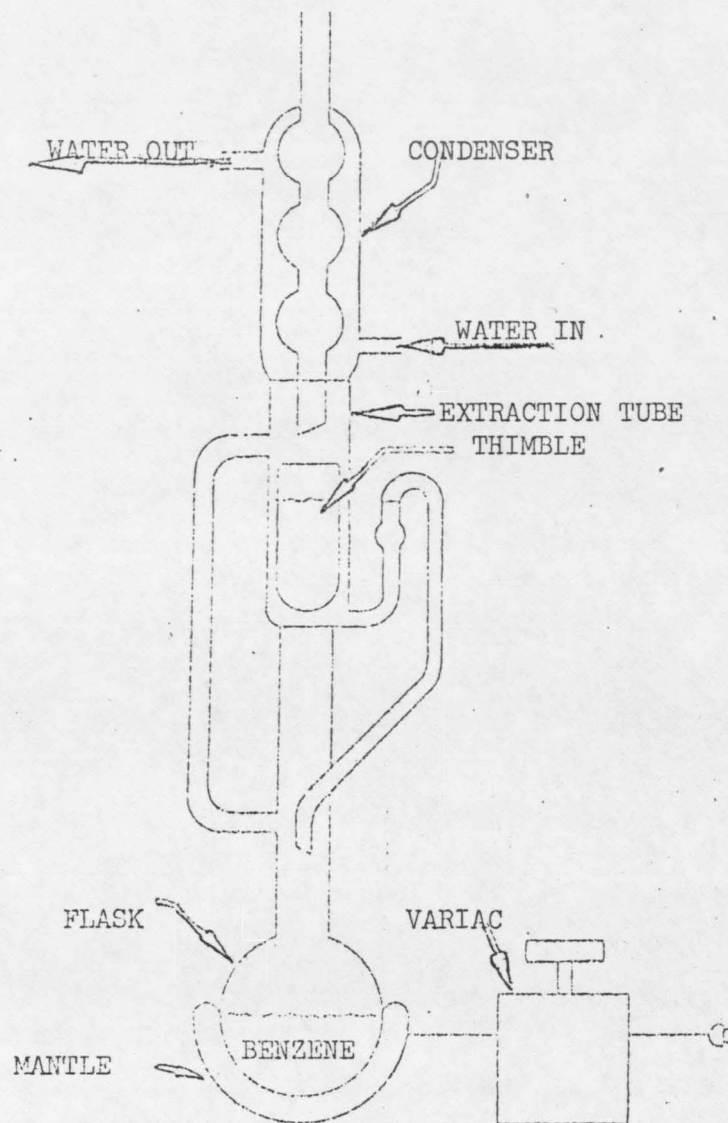
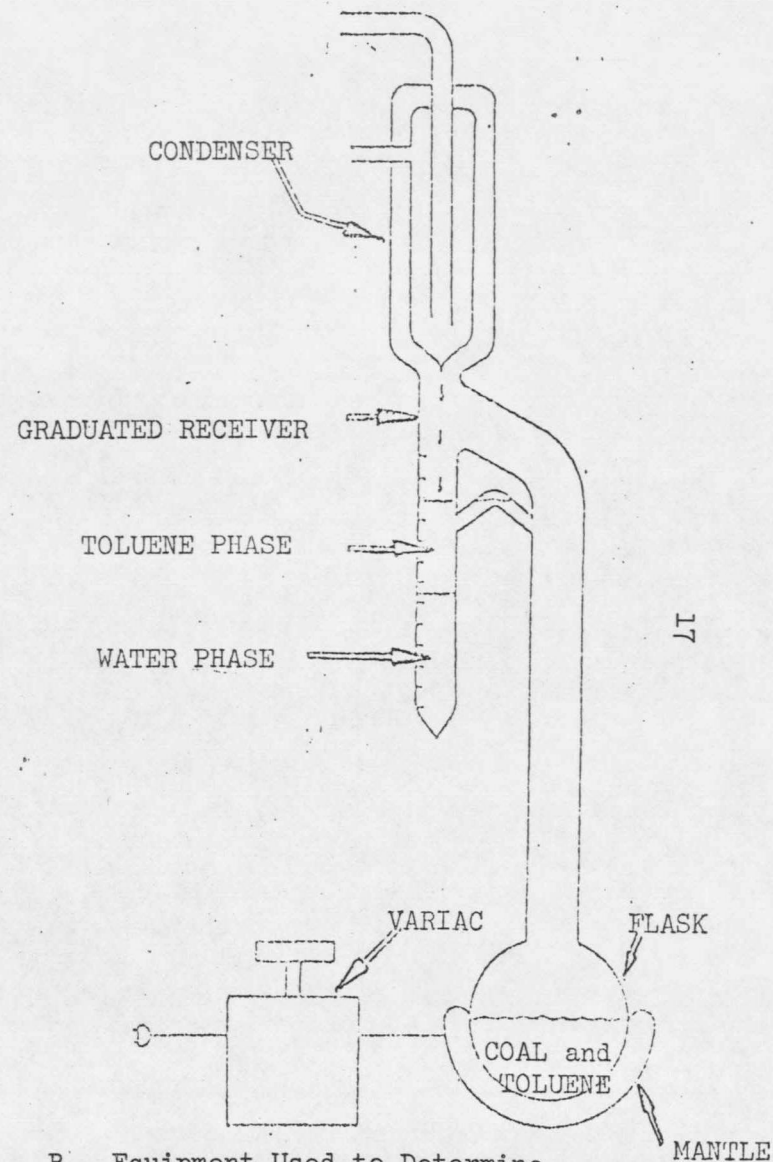


Figure 3. Pressurizing Unit Flow Diagram



A. Soxhlet Extraction Equipment Used to Determine Coal Conversion



B. Equipment Used to Determine Water Content in the Coal

Figure 4. Glassware and Equipment for Coal Determinations

Other equipment used was the apparatus shown in Figure 4B to determine coal water content and a porcelain crucible and flame to measure ash content of the coal. The water content analysis required a measured amount of coal and some toluene to be placed in the bottom flask to be vaporized. Condensation overhead and separation in the collection tube gave the water content of the coal.

Procedure

The method of charging the autoclave could be varied somewhat to get the same results, but to eliminate any excess variables, the charging was done the same way for all the runs undertaken. First, approximately fifty grams of coal was ground by mortar and pestle. Thirty grams of water was measured out of which around half was poured into the autoclave. Then, 0.3 grams of sodium carbonate was dissolved in the water in the autoclave. Thirty grams of coal was added next, and then sixty grams of phenanthrene was added. The contents were then stirred well and the remaining water was used to wash the stirrer off. The autoclave was then sealed and assembled.

The autoclave was then pressurized to approximately 1500 psi, placed in the heating rocker, and the thermocouple attached. The heating element was then started

and a record of temperature and pressure was taken. The time taken to heat the autoclave to its final temperature ranged from 50 to 60 minutes and a five minute run time was taken at this final temperature. Immediately after, the autoclave was pulled from the heater with pull rods and allowed to cool. Because of variations in heating time, the heating cycle was varied to allow similar runs to be made.

After cooling, the reaction gases were bled from the autoclave slowly to prevent foaming. Sample ports were available for gas sample to be taken for analysis.

When the autoclave was opened, usually around 20 ml of water could be poured off and measured. The remaining material was dug out of the autoclave and slurried with benzene in a container. Special care was taken not to lose any of this material because of the method of calculating conversion. The slurry was transferred to a weighed cellulose thimble where the solid product, ash and unconverted coal were collected. This thimble was then placed in the Soxhlet Extraction Unit where the rest of the benzene soluble product was extracted out over a 24 hour period. The thimble and contents were then removed and dried.

During the last forty runs made, after it became apparent that the ash and water contents of the coal were

not constant, ash and water content analyses were made for each run. For the ash analysis, two grams of the initial fifty grams ground were placed in the porcelain crucible and heated. Heating was done very slowly at first until most of the water was driven off, then a cover was put on the crucible and the heating rate increased. The coal was heated for approximately 24 hours. The water content analysis required putting 10 grams of coal into the water content analysis apparatus described earlier. Toluene was added and the mixture heated. The amount of water in the coal was then read from the graduations on the collector and the content calculated.

From the ash and water content calculations and the weights of the charged coal, the empty thimble, and the dried thimble and its residue, the percent conversion could be calculated. The conversion was calculated by difference using the following equation

$$C = \frac{MAF_i - MAF_f}{MAF_i} \times 100\%$$

where

C = percent of organic matter in the coal that was converted to benzene soluble product,

MAF_i = weight of ash and moisture free coal charged to the autoclave,

MAF_f = weight of ash and moisture free residue remaining in the dried thimble.

RESULTS AND DISCUSSION

A. Experimental Work and Results

Over 70 runs were made during the course of investigation. This work was carried out to further the knowledge required to design and develop a MHD power generation plant. Variables that were studied are the aging of the coal between the time it was mined and the time it was used in the hydrogenation reaction; the purity of the initially charged carbon monoxide which was used in the water-gas shift reaction to produce nascent hydrogen; and as a supporting experiment, the agitation of the solvent and coal in the rocking autoclave.

Most of the runs were repeated for verification of results, although this was not always done in the interests of time or lack of the proper material to work with.

1. Accuracy of Experimental Results

Several unrecorded preliminary runs were made in order to become familiar with the equipment and experimental techniques. These were made under the direction of Dat Nyugen. Identical runs with his were run until closely correlated data was being obtained.

2. Effects of Coal Aging

Before this series of runs was begun, several theories were put forth by fellow researchers as to why the aging

and conversion drops should take place. Water loss to the coal and oxidation were two of these theories. Therefore, in this experiment, several sets of coal were kept under different conditions to see what factors did lead to loss of conversion during a long period of time. To check water loss, some lump coal was placed into a dessicator in which water was put. A vacuum was then pulled on this dessicator to give an atmosphere of almost complete water vapor. This turned out to be a fairly effective method, as water content analyses on this coal showed only a 4% moisture content drop (from 22% to 18%) over a nine month period. To check the theory of oxidation, some lump coal was placed in a dessicator filled with nitrogen gas. A vacuum was first pulled on the dessicator and then the nitrogen was pumped in to slightly above atmospheric pressure. The water content of this coal dropped almost 10% over the 9 month period. Finally, some lump coal and some coal milled to -38 mesh were placed outdoors to check on actual aging conditions. The powdered coal was to obtain an accelerated conditions test to get exaggerated results from which a better picture of the results could be taken.

Two runs were made for each condition every other month. The results of these tests are shown in Table II. and Figure 5. The data appears to prove the fact that the

Table II. Conversion of Coal for Different Aging Conditions

Month	Water Vapor	Conversions		Powder in Atm.
		Nitrogen	Lumps in Atm.	
August	Initial Runs for All Conditions—82.6, 71.7, 67.2			
October	48.8 48.6	30.0 —	43.4 —	38.8 —
December	81.0 75.0	69.4 66.0	75.0 58.0	70.0 65.0
February	65.0 74.0	77.0 85.0	69.3 60.0	75.0 63.0
April	64.0 69.4	75.0 —	60.7 63.4	80.0 63.6

conversion of the coal does not drop with the aging of the coal. All of the different conditions tested gave approximately the same results. For some reason, the runs made in October gave smaller conversions than those during the rest of the runs. Evidently, the run conditions were not set properly. A new set of heaters were installed immediately after, evidently bringing experimental results up to where they resembled the results obtained at the first of the experiment.

These results answer the questions of 1) will stockpiling of the coal for prolonged periods of time reduce

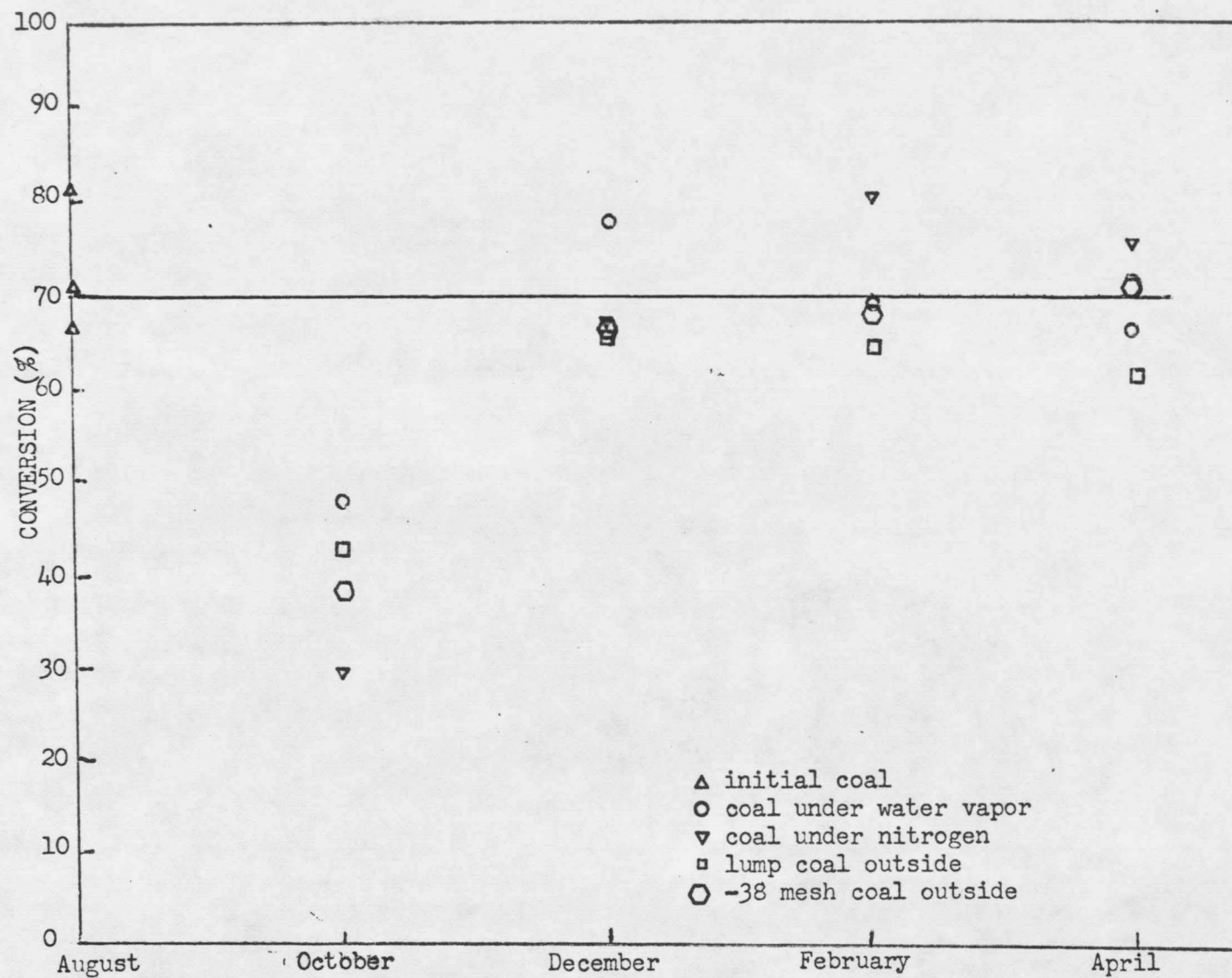


Figure 5. Conversion Versus Time For Aging Studies

conversions, and 2) regarding equipment failures, how can the coal be stored? These results show that stockpiling can be done so now a reserve pile can be placed between mine and reactor, thus elimination of a close correlation between the reactor and mine. Also, these results show that the coal can be stored in the atmosphere in both lump and powdered form, which knowledge can be used for storing between the grinders and reactors.

3. Effects of CO_2 in the CO Reactor Gas Feed

Proposed schematics of the MHD power cycle show production of the CO that is used in the water-gas shift reaction to come from either a recycle of the exhaust gases of the MHD generator or from a char- CO_2 reaction. In any case, if pure CO were needed, costly separation and purification schemes would be required. This part of the project was done to see how impurities in the gas charge would decrease conversion. Partial pressures of CO_2 , the primary impurity that would be present from the two processes mentioned above, from 0 psi to 1000 psi were mixed with the CO to a total initial pressure of 1500 psi. As seen from Table III. and Figure 6., the conversion wasn't affected until approximately 40% of the initial gas charge was CO_2 . This shows that the mixture with the lower concentrations of CO does not affect the mechanism of hydrogenation until

Table III. Effects of CO_2 in the CO Feed

Partial Pressure of CO_2 Total Initial Pressure Was 1500 psi	Conversion
0	72.0 75.0 77.0
200	66.0 74.0
400	74.0 67.0
600	74.0 73.0
800	68.0 69.0
1000	58.0 63.0

evidently not enough CO is present for efficient hydrogenation to take place. The controlling mechanism for this reaction is probably not the water-gas shift reaction or the surface attachment to the solvent by the hydrogen until decreased concentrations force it to be so. Also, it can be concluded that the presence of moderate amounts of CO_2 will not affect the equilibrium of the water-gas shift reaction until concentrations get much higher. A

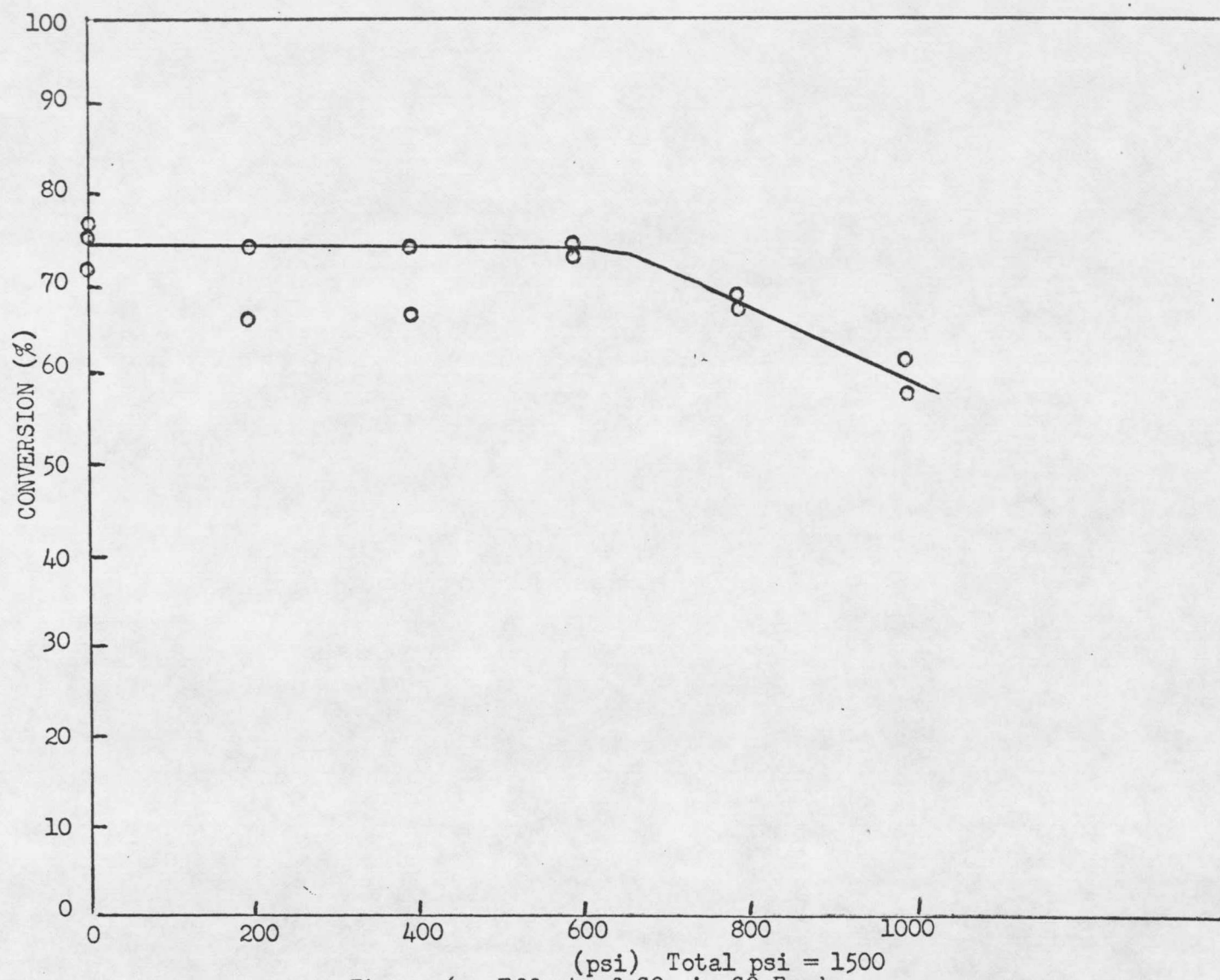


Figure 6. Effect of CO_2 in CO Feed.

continuous hydrogenation process probably could take even higher concentrations of CO_2 in the feed gas because the buildup of the CO_2 from the water-gas shift reaction would not be as great. A material balance and a kinetic study would determine how much CO gas will have to flow through the reactor for a certain amount of coal. If batch reactors are used a study of purity versus volume of gas needed for a certain amount of coal will be needed to get the correct charge of gas to the reactor.

4. Agitation

During the tryout period in October of the new heaters, in which the proper rheostat settings were found to obtain the proper temperature control, it was noticed that the rocker was no longer rocking at the same angle. During March, in an attempt to correlate the low conversions in October, tests were made to see if the degree of agitation had changed noticeably which could have an affect on the conversions. Runs were made with the rocker back in the position it held before the new heaters were installed, as well as runs made at the new position. Figure 7. shows the positions used in the study. Position B was the old position, while Position A was the new position which all of the remaining runs were made at. It was expected that Position A would give a higher degree of agitation because

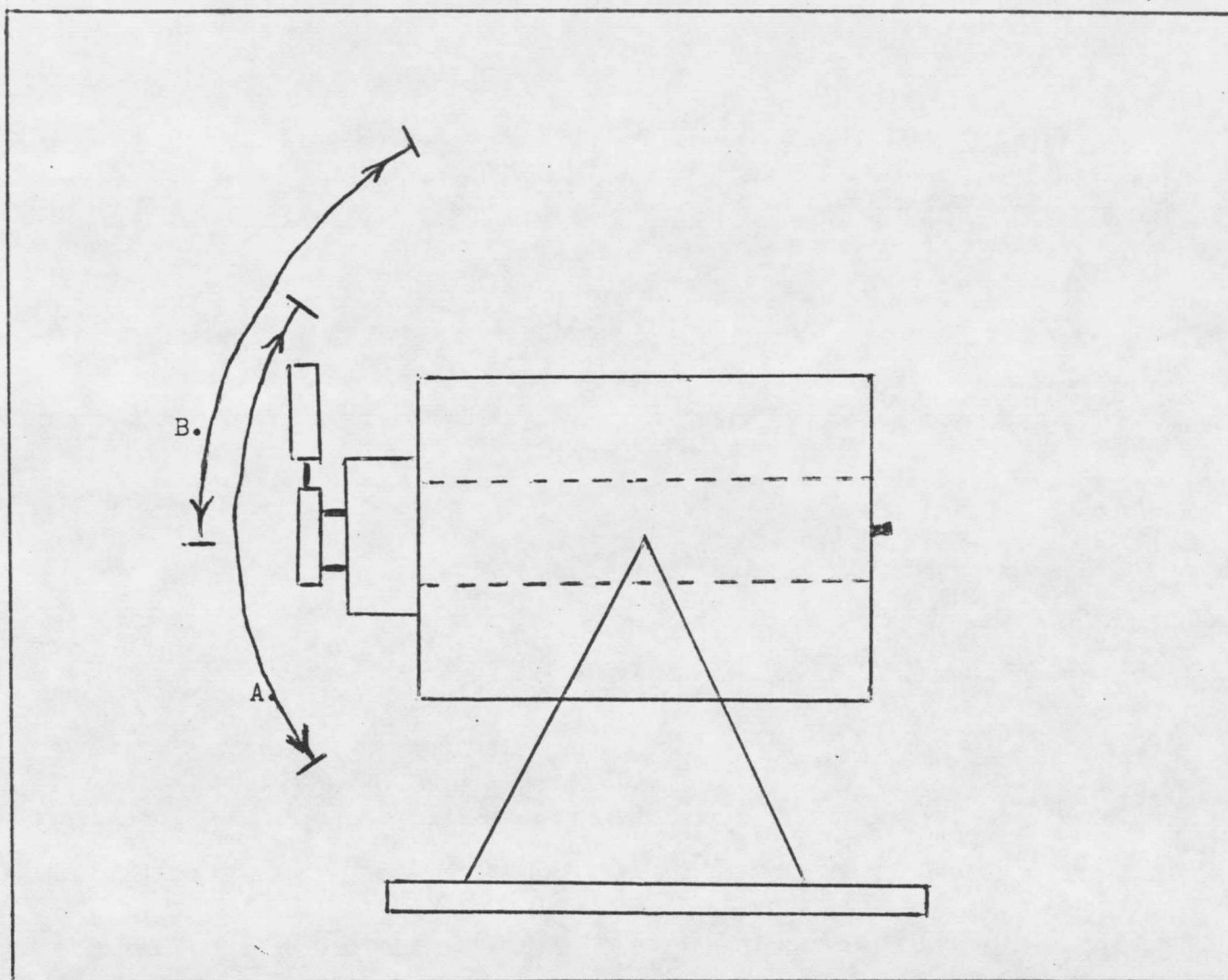


Figure 7. Levels of Agitation Used.

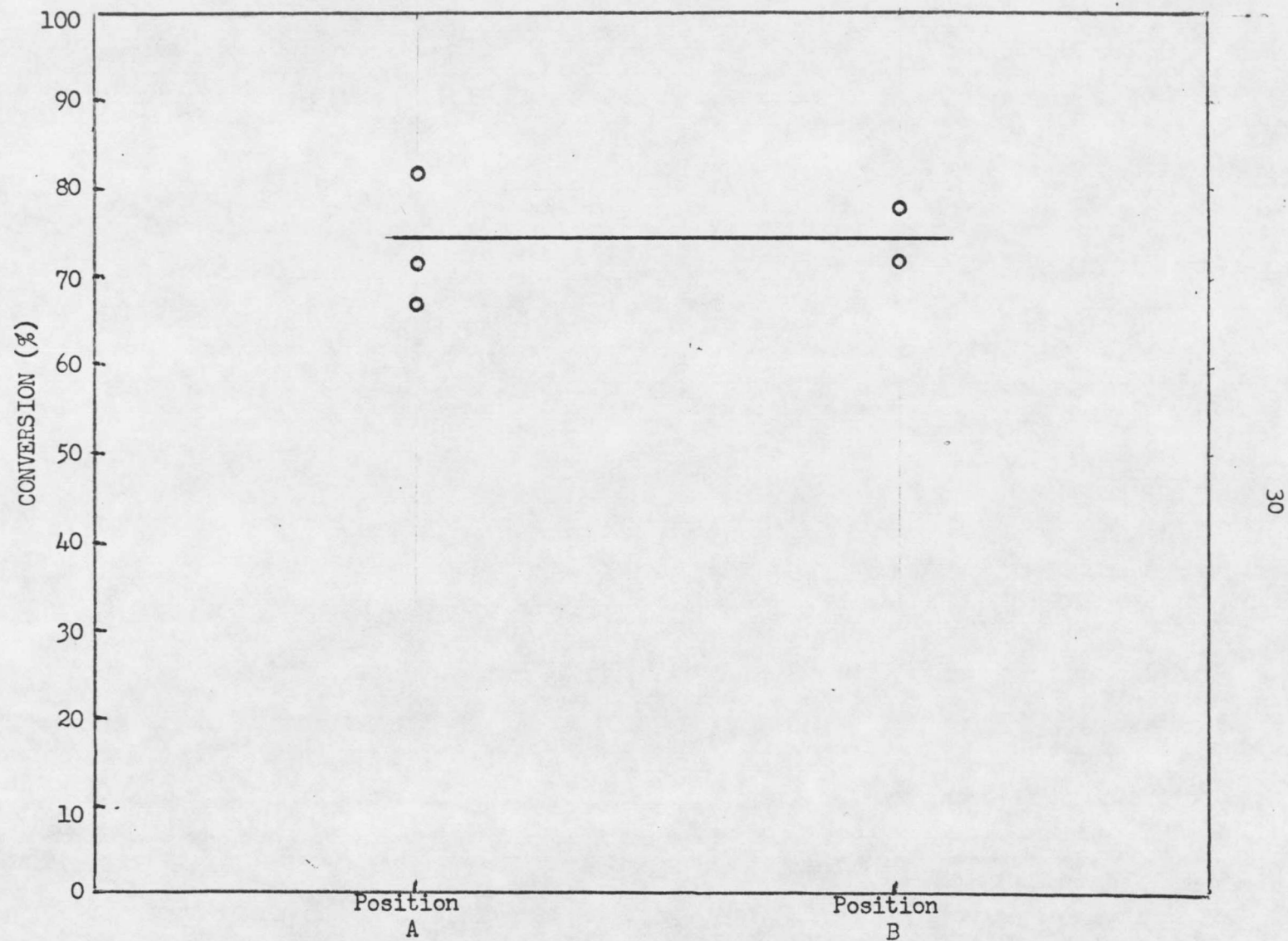


Figure 8. Effects of Agitation.

Table IV. Rocker Agitation

Position	Conversion
A	67.2
	71.7
	82.6
B	71.8
	77.2

the liquid solvent would splash against the ends more. This would give a greater chance to the hydrogen to become entrapped on the surface of the solvent. However, it was found that the conversions at the two positions did not differ. Evidently, the difference in agitation was not enough to cause a noticeable change in the conversions which resulted. Table IV. and Figure 8. show the results of this study. Perhaps a study with a more drastic change in the rocking angle might produce a noticeable difference in the conversions which can be applied during plant design.

B. Product description

The product obtained from these runs before it was extracted with benzene resembled a light tar in weight and color. It was a fairly sticky substance and took some ef-

fort to dig out of the autoclave. The product did not stick to the walls of the autoclave, but only to itself. After the extraction had taken place, and the product was collected in a container, the product was a very sticky black heavy oil, resembling used oil from an automobile engine. An interesting property of the product was the ability to climb up in a capillary action on crystals of phenanthrene which had collected on the sides of the container. The laboratory analysis done for Wayne York and presented in his thesis showed a 0.02% ash content in the product which does make it very good for MHD use.

CONCLUSIONS ,

The following conclusions can be made from this investigation of the process of hydrogenation of coal.

1. Aging of the coal before use in a hydrogenation reactor appears to have no effect on the conversion.

2. The presence of CO_2 as an impurity in the CO gas reactant apparently has no effect on the water-gas shift reaction equilibrium at temperatures and pressures of 450°C and 5000 psi.

3. The rate controlling step in the hydrogenation step is not the hydrogen attaching to the solvent surface step.

4. Conversion decrease with impurities in the CO feed stream occurs when the amount of CO present is not enough for the reaction.

RECOMMENDATIONS FOR FUTURE STUDY

1. A detailed energy balance around the hydrogenation reactor is essential.
2. A more advance study of the agitation required for good conversion yields will aid in plant design.
3. Solvent and product separation techniques should be developed.
4. Recycle solvent reactivity should be known.
5. Optimum CO feed stream to initial charged coal ratios should be determined.

BIBLIOGRAPHY

1. Mills, G. Alex. "Gas From Coal: Fuel of the Future," Environmental Science and Technology, Vol. 5 No. 12, (1971) pp. 1178-83.
2. Klingman, G. E., and R. P. Schaaf. "Make SNG From Coal?" Hydrocarbon Processing, Vol. 51 No. 4, (1972) pp. 97-101.
3. Mills, G. Alex. "Conversion of Coal to Gasoline," Industrial and Engineering Chemistry, Vol. 61 No. 7, (1969) pp. 6-17.
4. Evans, R. K. "75-MW Power Plant Nears Completion," Power, 113: 66-7, January, 1969.
5. York, Wayne. "Reduction of Sub-Bituminous Coal and Lignite Using Carbon Monoxide," Ph. D. Thesis, Montana State University, 1971.
6. Wiser, W. H., L. L. Anderson, S. A. Qader, and G. R. Hill. "Kinetic Relationship of Coal Hydrogenation, Pyrolysis and Dissolution," Journal of Applied Chemistry and Biotechnology, Vol. 21, March 1971, pp. 82-86.
7. Hill, G. R. and L. Lyon. "A New Chemical Structure for Coal," Industrial and Engineering Chemistry, Vol. 54 No. 6, (1962).
8. Parr Instrument Company, Instructions for the Series 4000 Hydrogenation Apparatus, Parr Manual 125.

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