



Reduction of sub-bituminous coal using carbon monoxide
by Thomas Angell Fiske

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemical Engineering
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Abstract:

The reduction of sub-bituminous coal mined at Costrip, Montana using CO + H₂O was investigated. The equipment used in this study was a 500 ml rocking autoclave which operated up to 500°C with a maximum operating pressure of 7000 psi. The analyses which were made included the conversion of the MAF coal to benzene soluble material, water and ash analyses of the coal, and proximate and ultimate analyses of the coal and the liquefied coal along with a molecular weight determination of the liquefied coal also being made.

The results show increasing the heating- time will increase-the conversion of the coal. An optimal particle size for the coal is -25 to -40 mesh for a pressure range of 1210-1590 psig. Exposure of the coal to air decreases conversion of the coal. The method of contacting the coal and solvent makes no significant difference in conversion. ZnCl₂ and CaCO₃ as catalysts are not as effective in increasing the conversion as another catalyst, Na₂CO₃. A. combined gas atmosphere of H₂-CO makes no appreciable increase in conversion over an atmosphere of pure CO.

The product obtained from the coal has a H:C ratio of about 1.1 and an ash content of 0.1% compared to coal's H:C ratio of 0.7 and 7*0\$ ash. This product seems to be ideally suited as a fuel for magneto hydrodynamics.

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USING CARBON MONOXIDE

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THOMAS ANGELL FISKE

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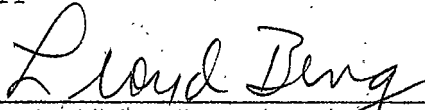
of


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Head, Major Department


Chairman, Examining Committee


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ABSTRACT

The reduction of sub-bituminous coal mined at Costrip, Montana using $\text{CO} + \text{H}_2\text{O}$ was investigated. The equipment used in this study was a 500 ml rocking autoclave which operated up to 500°C with a maximum operating pressure of 7000 psi. The analyses which were made included the conversion of the MAF coal to benzene soluble material, water and ash analyses of the coal, and proximate and ultimate analyses of the coal and the liquefied coal along with a molecular weight determination of the liquefied coal also being made.

The results show increasing the heating time will increase the conversion of the coal. An optimal particle size for the coal is -25 to -40 mesh for a pressure range of 1210-1590 psig. Exposure of the coal to air decreases conversion of the coal. The method of contacting the coal and solvent makes no significant difference in conversion. ZnCl_2 and CaCO_3 as catalysts are not as effective in increasing the conversion as another catalyst, Na_2CO_3 . A combined gas atmosphere of H_2 -CO makes no appreciable increase in conversion over an atmosphere of pure CO.

The product obtained from the coal has a H:C ratio of about 1.1 and an ash content of 0.1% compared to coal's H:C ratio of 0.7 and 7.0% ash. This product seems to be ideally suited as a fuel for magneto hydrodynamics.

INTRODUCTION AND BACKGROUND

Introduction

The demand for power in the United States is fast becoming a major problem, particularly as this demand doubles every fifteen years. With the United States using 1.9 billion tons of fossil fuels per year (30% of the world's consumption) and producing only 1.7 billion tons with the gap increasing, the problem is especially acute.

In 1970, the United States consumed 710 million tons of oil, or 15 million barrels per day. The barrels per day use is projected to be from 20 to 25 million by 1980. However, United States production is only 10 million barrels per day now and is only expected to rise to 11 million barrels per day with presently known sources. It should be noted that the newly discovered Alaskan oil fields and new off-shore deposits could increase this, but there are many problems to be met (mainly environmental). Even with these, the United States must import oil and this is becoming more expensive and more competitive.

In 1971, 22.1 trillion ft^3 of natural gas were consumed by users. Two hundred forty-seven trillion ft^3 remain in proven domestic reserves (high of 289 trillion in 1967). The possibility of more gas in United States and off-shore is good but cost of explor-

ation is high. Also, a two- or three-mile drill shaft is becoming common. Add to this the fact that United States gas companies say they can not meet current demands at officially regulated prices and are considering importing gas; then it seems natural gas is not our hope for future energy needs.

The United States consumed 530 million tons of coal, its most abundant fuel, in 1970. The known reserves of coal are two trillion tons. Though coal is plentiful, it also presents problems in pollution control and mining, for strip mining is prevalent and inexpensive.

With 25% of all United States fossil fuels going to produce 1.6 quadrillion kilowatt hours of electricity, this is one area for improvement in use of the natural resources. Magnetohydrodynamics (MHD) is a possible improvement. In MHD, a conductor is passed through a magnetic field to produce an electric current. An electrical conducting plasma, produced by burning a fuel with compressed, preheated oxygen, and a seed, usually potassium, added to increase conductivity, is passed through a channel at supersonic speeds. A large conducting magnet surrounds the channel; thus the movement of the conducting plasma through the magnetic field produces an electric current. MHD has a potential 60% efficiency, whereas steam generation systems yield an efficiency of 35-40%. The increase in

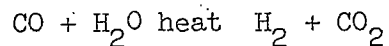
efficiency is partly due to the elimination of the steam turbine and a generator.

Coal is one of the proposed fuels for MHD due to its abundance. There is a drawback to using coal. The ash in the coal will be very erosive to the channel of high temperatures and it will interfere with the potassium seed recovery. It is in this area that this research may provide an answer.

By hydrogenating the coal with the objective of producing a suitable fuel (low in ash), an improvement in use of United States resources can be realized. There exists one extra attraction in hydrogenating coal. A material may be produced that in addition to being a possible fuel for MHD, the product may be suitable for hydrocracking. Thus a new feed stock may be found for the petroleum and petro-chemical industries.

Background

At Montana State University, the hydrogenation of coal is carried out by the water-gas shift reaction. The reaction of water and carbon monoxide is used to produce hydrogen.



The water-gas shift reaction was first used on coal by Franz Fischer, in Germany in 1921. For his experiments, he used Rhenish

brown coal. He found that the shift reaction produced better results than hydrogenation by hydrogen alone. He concluded that the liberation of nascent hydrogen was the reason for the improvement.

However, due to Fischer's poor results, his best run yielded only 35% conversion of the coal to an ether-soluble material, and the advent of the Fischer-Tropsch reaction caused the water-gas shift reaction to fall into relative obscurity after 1925. Interest was revived in the shift reaction in 1968 when the United States Bureau of Mines began to re-investigate the shift reaction with coal. G. Alex Mills also discusses the shift reaction in his paper on hydrogenated coal products in 1969 (2).

For the Bureau of Mines' study of the shift reaction, bituminous and lignite coals were used. It was found that the addition of carbon monoxide and water to coal produced more conversion to benzene-soluble material than did the addition of hydrogen to coal, as illustrated in Figure 1. The study also showed that the addition of a solvent and/or alkali or alkaline earth carbonates will increase the conversion of the coal. As can be noted from Figure 1, the Bureau of Mines was able to achieve conversions of 80 to 90 percent.

In further studies of the shift reaction on various materials, the Bureau was able to suggest reasons for the reaction's effectiveness. They concluded: 1) that the reaction is effective, due to

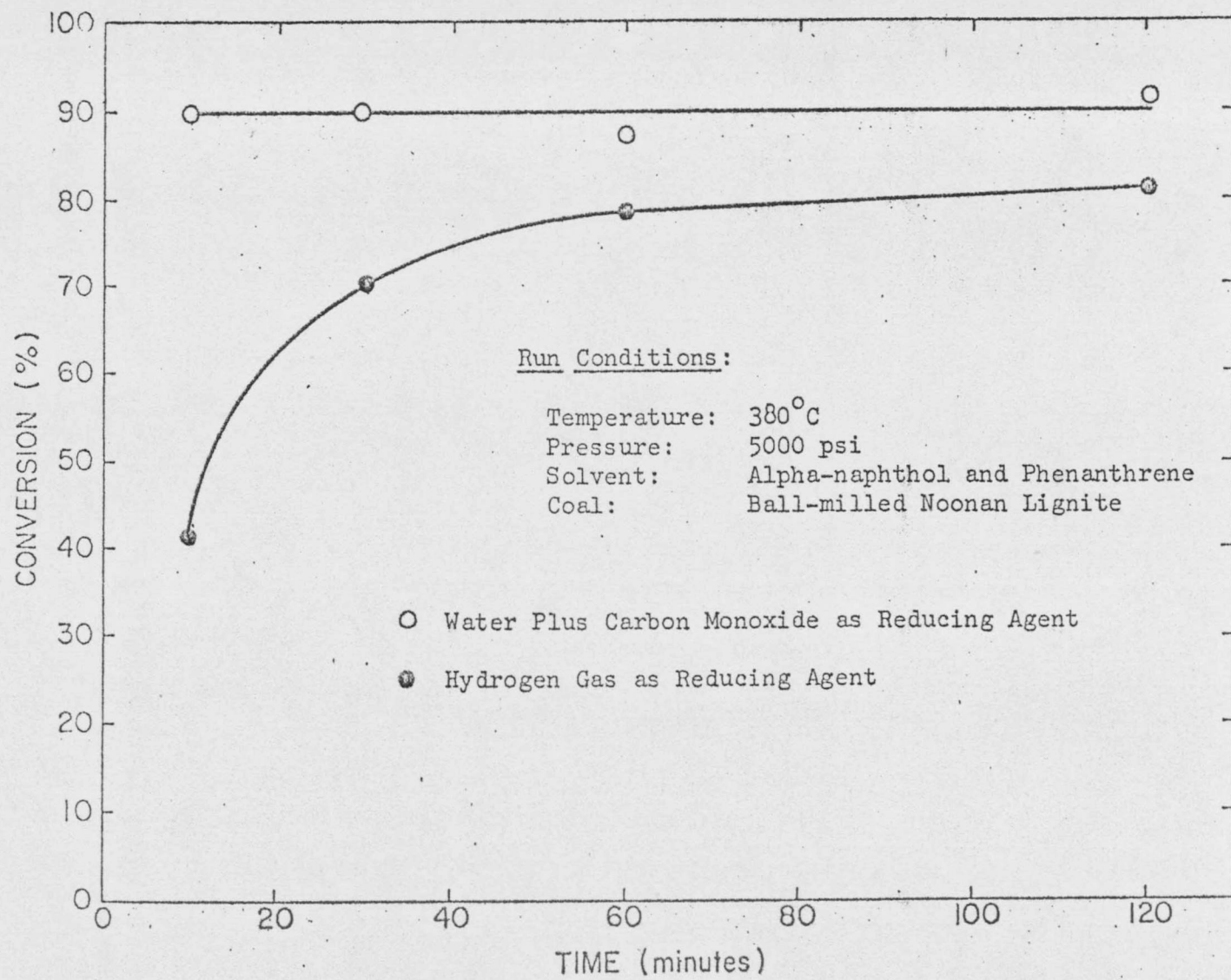


Figure 1. Coal Conversion Results Obtained by The United States Bureau of Mines.

hydrogenation with activated hydrogen produced by the shift reaction; 2) that the introduction of alkyl groups in the coal aids the reaction; and 3) that carbon monoxide has a unique ability to cleave certain types of bonds or to inhibit condensation reactions leading to benzene insoluble materials (3).

Spurred by the Bureau's publications, and investigation of coal hydrogenation via the water-gas shift reaction was launched at Montana State University. The main theme of this investigation was to reduce the cost of coal hydrogenation while still producing a suitable product. Wayne York, who has since graduated with a Ph.D., was the first graduate student to work on this project. He worked with one sub-bituminous and three lignite coals. He found that: 1) increasing the initial CO pressure will increase conversion to benzene-soluble material; 2) increased temperature increases conversion; 3) solvents vary in their effectiveness from coal to coal; 4) the more grinding done to the coal, the less the conversion; 5) under the same conditions, the coals would yield different results and he believed that this was due to the sodium content of the coals; 6) the amount of ash affects the conversion, and 7) Na_2CO_3 (sodium carbonate) added to the coal increases the conversion (7).

At present, there are two graduate students investigating the shift reaction on coal at Montana State University. Some work is

being done as a follow-up of Dr. York's work, but much of the work is proceeding along new lines in an effort to expand the present knowledge of coal hydrogenation by the water-gas shift reaction and to make the hydrogenation more economical.

RESEARCH OBJECTIVES

The primary objective of this investigation was to increase the knowledge of coal hydrogenation resulting from the water-gas shift reaction. This was done by reacting the coal under several different sets of conditions and by studying the results.

It was believed that this investigation would help relieve the energy problems of the United States. This was to be done by converting the coal to a product suitable as a fuel for MHD and/or suitable for hydrocracking.

If the shift reaction on coal were to prove attractive, both from the technical and the economical viewpoints, the possibility of utilization of Montana's coal resources exists. This is the reason that the investigation was conducted with Montana-mined sub-bituminous coal.

MATERIALS, EQUIPMENT, AND PROCEDURES

Materials

The coal used during this investigation was sub-bituminous coal that was strip-mined near Colstrip, Montana. It was obtained from the steam-generating plant of Montana Power Company at Billings, Montana in crushed form, which is minus one inch. After the coal has been received it is stored in plastic bags, three layers thick, with as much air forced out of the bags as possible. The three layers of bags and the air being forced out of the bags are steps taken to prevent drying of the coal (moisture loss) and aging of the coal (oxidation).

It should be noted that coal is not a chemical; rather it is a mixture that is complex and non-uniform. What the coal is composed of may be found by two methods: the proximate analysis and the ultimate analysis. The proximate analysis categorizes the coal as water, volatile matter, fixed carbon, and ash. Volatile matter is the part of the coal that vaporizes when heated to a temperature around 900°C, excluding water. The organic matter that remains after heating is called fixed carbon and the inorganic matter is ash. In an ultimate analysis, the coal is broken down as to the amount of carbon, hydrogen, sulfur, nitrogen, and oxygen present. The oxygen is determined by difference. For the proximate and ultimate analyses of Colstrip sub-bituminous coal, see Table I.

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

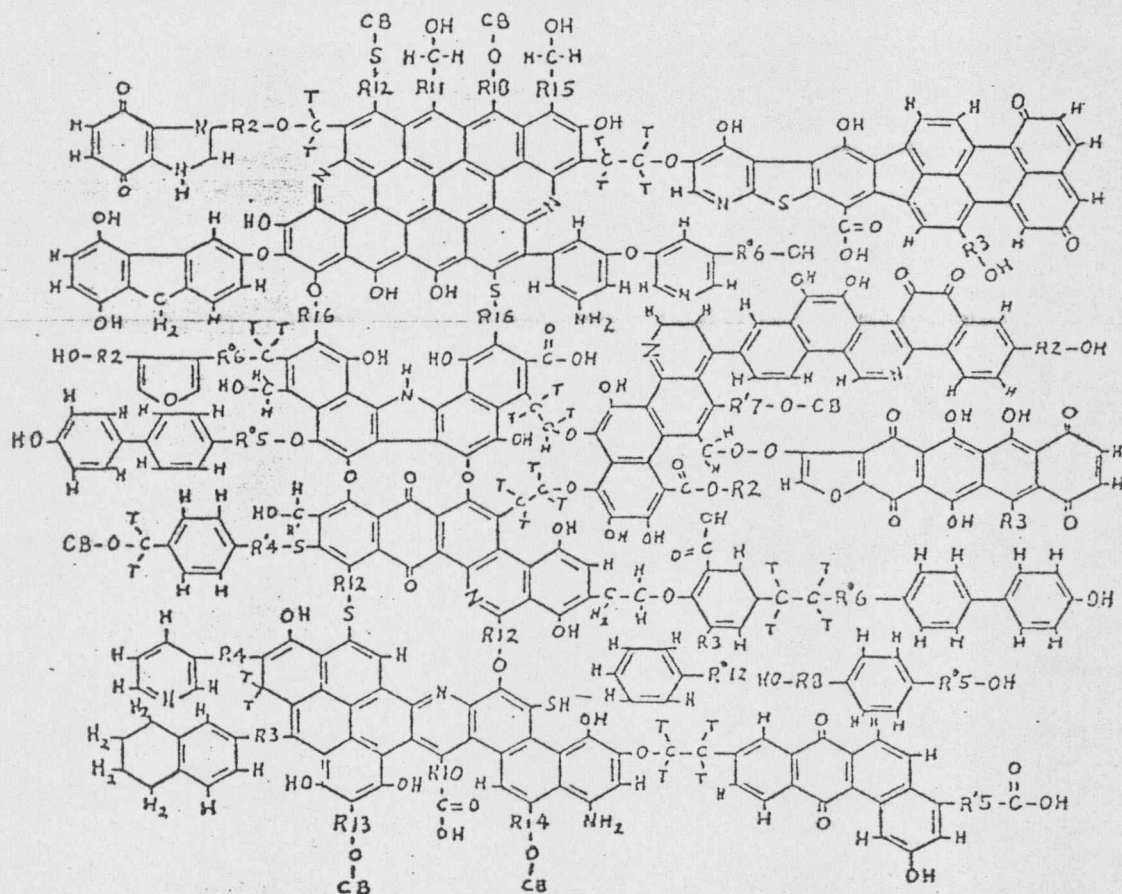
SiO ₂	36.4%
Al ₂ O ₃	17.6
Fe ₂ O ₃	4.6
TiO ₂	0.4
P ₂ O ₅	0.8
CaO	22.7
MgO	9.4
Na ₂ O	0.3
K ₂ O	0.5
SO ₃	14.9

The ash of coal is also a mixture. Its arrangement in coal is complex (not fully understood), but the elements of the ash are known. They are silicon, aluminum, iron, titanium, phosphorous, calcium, magnesium, sodium, potassium, sulfur, and many trace elements. The ash analysis of Colstrip sub-bituminous coal can be seen in Table I.

While the exact structure of coal is a subject of debate and largely a matter of conjecture, a typical structure of a high volatile coal is shown in Figure 2. To make something out of coal, it is necessary to remove the ash, oxygen, sulfur, and nitrogen from the coal, and it is necessary to break the structure of the coal into smaller fragments and to hydrogenate these fragments.

For each run a solvent for the coal was used. Phenanthrene was the solvent and was of a technical grade. A catalyst was also used in every run and the catalyst was sodium carbonate, Na_2CO_3 . The water used in each run was tap water.

All other materials, carbon monoxide, hydrogen, calcium carbonate, zinc chloride, benzene, and toluene, in this investigation were obtained from commercial suppliers. They all were technical grade.



- R^N Alicyclic Rings of N Carbons
 RN Alkyl Side Chains of N Carbons
 $R'N$ Unsaturated Alkyl Chains
 CB Cross-bonding to Other Heterocyclic Groups
 T Tetrahedral Bonds

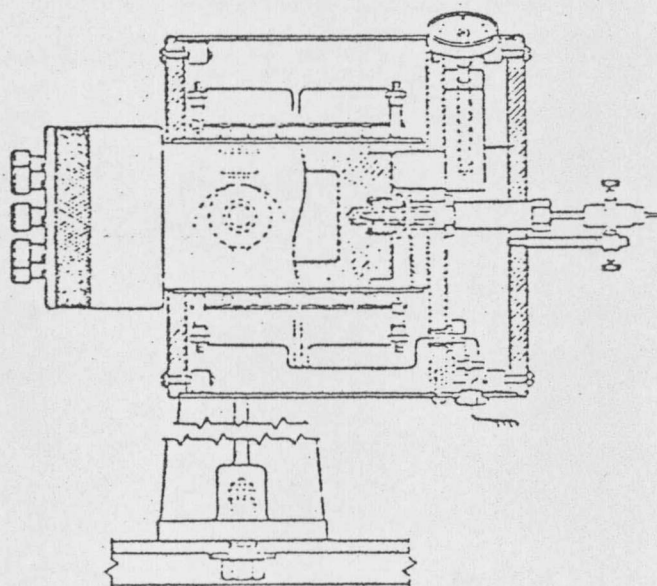
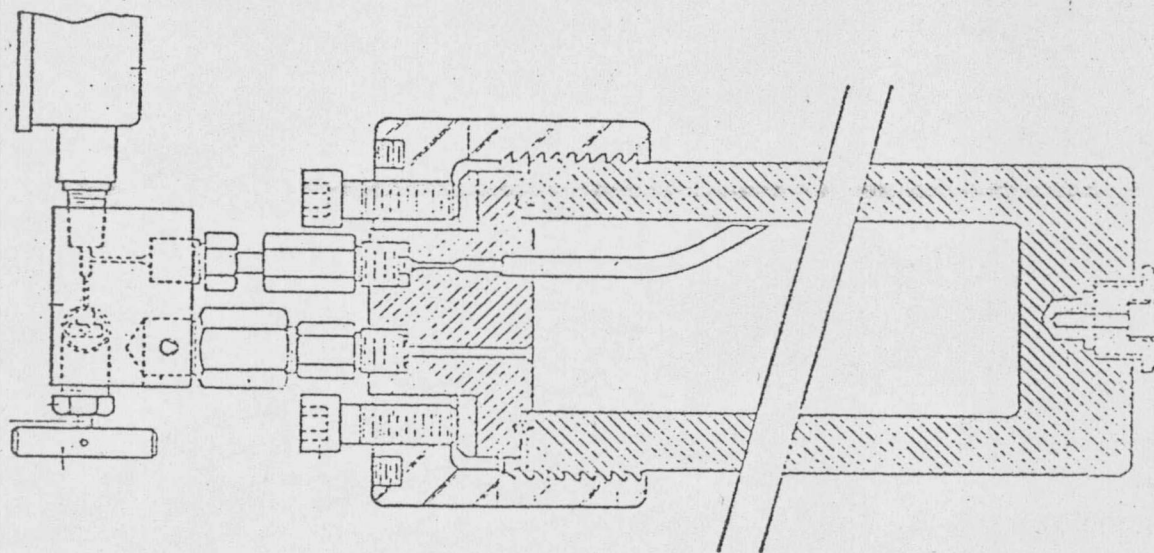
Figure 2. Typical Cross-bonded Structure for High Volatile Coal.

Equipment and Procedure

The main pieces of equipment used in this investigation were a 500 ml Parr Inconel autoclave and a rocking-heating apparatus for the autoclave. Both are shown in Figure 3. The autoclave was used as the reactor and was rated at 7000 psi at 500°C or 8800 psi at room temperature. The rocking-heating apparatus rocked at about 40 strokes per minute.

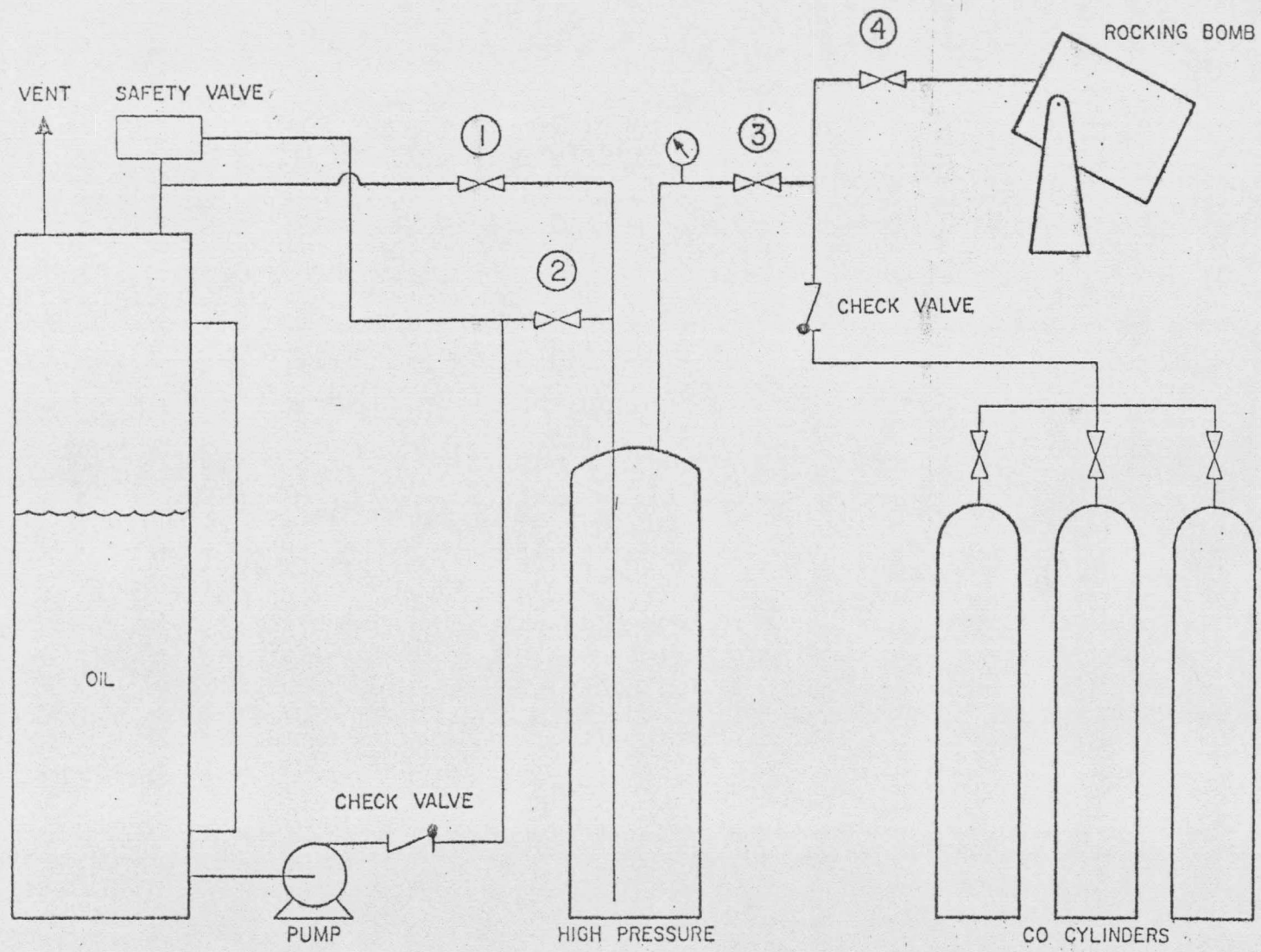
As can be seen from Figure 3, the pressure was monitored by a gauge in the block assembly of the autoclave and was fed by a breather tube. This gauge was checked against a gauge in the pressurizing system and was occasionally checked by a gauge testing system. The temperature of the autoclave was detected by an iron-constantan thermocouple that was placed in a thermocouple well at the bottom of the autoclave. This thermocouple was connected to a chart recorder to keep a temperature history for a run.

A pressurizing system, Figure 4, was used, for FCC regulations only allow carbon monoxide to be shipped in 1500 psi cylinders. A pressurizing system allowed the maximum use of a cylinder of carbon monoxide and allowed the initial pressure of the reactor during a run to be maintained around 1400 psi for a greater number of runs than would be possible without such a system.



Bomb Heater Details

Figure 3. Rocking Autoclave Assembly Diagram.



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Figure 4. Pressurization Unit Flow Diagram

In the pressurizing system, the CO cylinder was connected to the system and some CO was transferred to a high pressure cylinder. To achieve a desired pressure, oil was then pumped into the high pressure cylinder and the pressure was achieved simply by displacement. When the high pressure system was out of CO, the oil was drained and more CO was added. The cycle was then repeated.

In charging the autoclave to make a run, all the materials were weighed to hundredths of a gram for accuracy. The catalyst, usually 0.3 grams of Na_2CO_3 , was added to the autoclave. Then 30.0 grams of tap water was added. Next, 30.0 grams of coal, which was ground with a mortar and pestle to reduce exposure to the air and thus reduce loss of water and oxidation, was added to the autoclave. The solvent, 60.0 grams of phenanthrene, was added last.

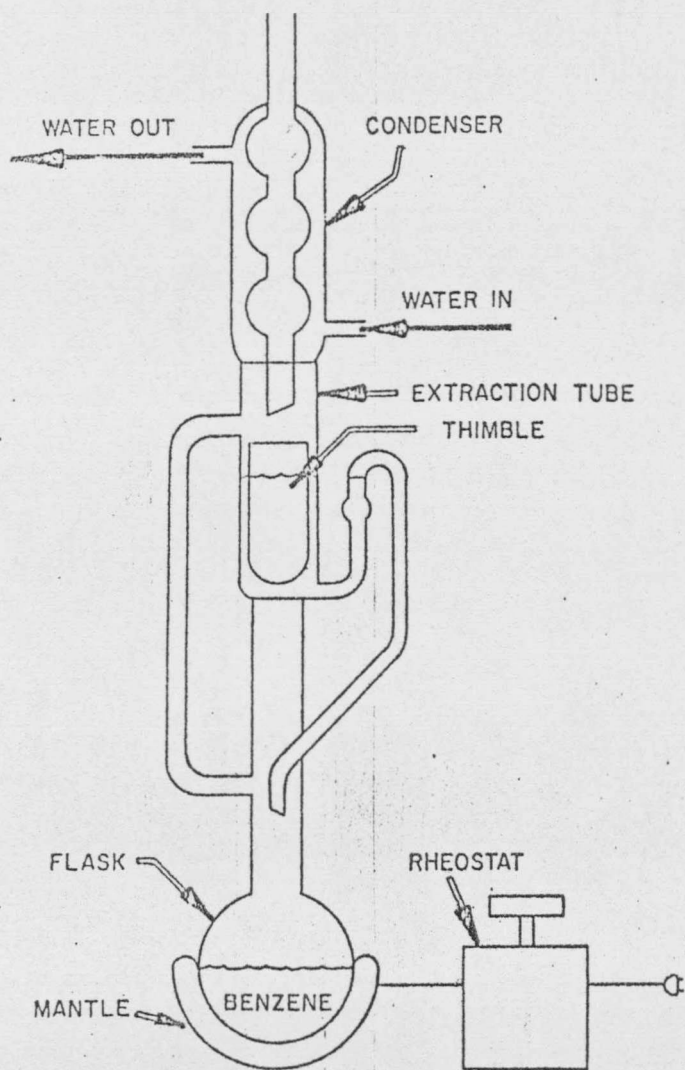
The autoclave was then sealed and assembled. (See Figure 3.) The next step was to pressurize the autoclave with CO, usually to 1400 psi, from the high-pressure cylinder. After this was done, the autoclave was placed in the rocking-heating assembly and allowed to remain motionless for five minutes to check for leaks. If no leaks developed, the rocking and heating elements were turned on. In a typical run the autoclave would reach the desired temperature, around 475°C, in 50 to 65 minutes. Once the desired temperature was reached, the reaction time started at zero and the reaction

proceeded for five minutes at the final temperature. The final pressure was usually around 5100 psi. After five minutes of reaction time, the autoclave was pulled from the rocking-heating assembly by means of threaded pull rods and was allowed to cool overnight.

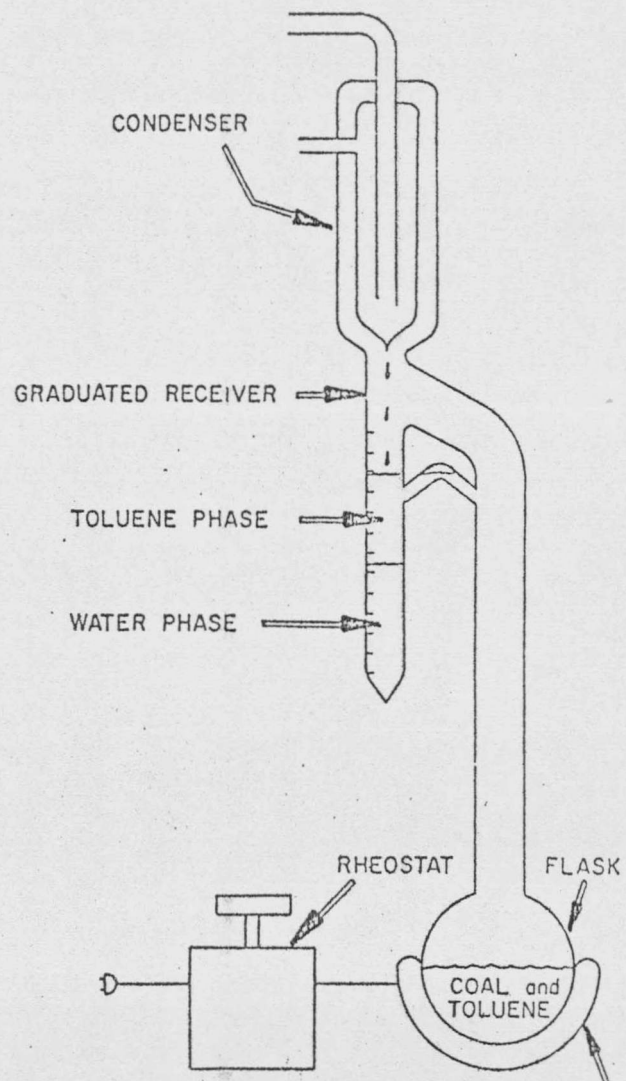
A twenty-gallon drum was equipped so that it could be evacuated to twenty-four inches of Hg. Thus, after the autoclave was cooled to room temperature, the reaction gases were bled to the drum. This bleeding was done slowly to prevent foaming. The drum was equipped with a sampling port so samples of the gas could be taken with a syringe.

After the gas had been removed the autoclave was opened and a liquid--water--was poured off and measured. The reacted material was then removed and placed in a container. Benzene was added to the material to form a slurry and if large chunks of material were present an effort was made to reduce these chunks as much as possible.

The slurry was poured into a weighed 43 x 123 double thickness cellulose thimble. The thimble was then placed in a Soxhlet extraction unit. (See Figure 5A.) The liquid used in the extraction was benzene. Benzene was used because the organic matter in coal (as well as the rest of the coal) is not soluble in benzene



A. Soxhlet Extraction Equipment Used to Determine Coal Conversion



B. Equipment Used to Determine Water Content in the Coal.

Figure 5. Glassware and Equipment for Coal Determinations

but a tar or oil produced from the organic matter is. Thus a benzene extraction indicates the conversion to a benzene-soluble material, hopefully a tar or an oil. The thimble was left in the extraction unit for at least twenty-four hours. The thimble and the residue it contained were removed from the unit, the benzene-soluble material now being in the boiling flask, and placed in an electric forced air cabinet dryer for at least twenty-four hours. The dried thimble and residue were then weighed.

To calculate the conversion of the coal to benzene-soluble material, it was necessary to know the ash and water content of the coal. By knowing these, it was possible to know the amount of moisture- and ash-free (MAF) coal put in the autoclave and it was possible to calculate the amount of ash-free coal in the thimble residue (the water was lost in the reaction and in drying). By using this knowledge in the equation

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

where

C = percent of organic matter in coal that is benzene soluble (the conversion),

MAF_i = weight of moisture and ash-free coal added to autoclave,

MAF_f = weight of moisture and ash-free material remaining in thimble residue, the conversion could be calculated.

This analytical procedure was found to be the best one from past work.

Special Procedures

It occasionally was necessary to make ash and water analyses during this investigation. The water analysis was done with the apparatus shown in Figure 5B. Toluene and a small amount of water were first added to the flask and allowed to boil for twenty-four hours. This was done to saturate the toluene with water. A known weight of coal was then added to the boiling flask and the mixture was again allowed to boil for twenty-four hours. At the end of this time the amount of water collected in the graduated receiver was measured (the toluene and water formed layers with the excess toluene being returned to the flask). A simple ratio calculation was then done to determine the percent water in the coal.

For the ash analysis, a weighed amount of coal was added to a porcelain crucible. The crucible was placed over a flame until a white residue remained (coal stirred carefully occasionally), then a direct flame was applied to the residue until the sparkling ceased. The residue was then weighed and a simple calculation was done to determine the amount of ash in the coal.

RESULTS AND DISCUSSION

A. Experimental Work and Results

The run time is defined as time at the final temperature and was always five minutes.

Over sixty runs were made during the course of this investigation. The main purpose of these runs was to increase the knowledge of the hydrogenation of coal due to the water-gas shift reaction. Variables that were studied are: particle size, aging, catalyst, contacting method, time, and gas atmosphere.

In all cases, conversions are based upon the amount of benzene-soluble material produced from the coal reacted. It is to be assumed, unless otherwise stated, that all of the following materials were added to the autoclave for each run:

0.30 g of Na_2CO_3 (catalyst)

30.0 g of H_2O

60.0 g of phenanthrene (solvent)

30.0 g of coal

CO until initial pressure was 1410 psig.

An attempt was made to repeat all runs for verification of results. However, this was not always done due to the nature of the particular experiment or in the interest of time.

1. Preliminary Runs

In a training period under Dat Nyugen, technique and procedure were learned. Some runs to duplicate previous work were made for practice and learning, though no records were kept of these runs. Near the end of this period a decision was made to purchase an Inconel autoclave. This was done to allow more runs to be made, but primarily the autoclave was purchased because it allowed operation at higher pressures and pressures more than safely possible with the present stainless steel autoclaves.

Once the new autoclave was received, runs were made to determine the heating characteristics of the Inconel and to develop a method of controlling the final temperature. The initial results are shown below. After these runs had been made, a technique was developed that reduced the heating time to around 65 minutes at a final temperature of $475^{\circ}\text{C} \pm 8^{\circ}$. However, the conversions never again went above 70%. It should be noted that the shorter heating time is desirable to reduce the initial cost (steel) and the running costs (pumping) of a continuous plant.

From Table II below it can be seen that time is a very important factor in the hydrogenation of coal by the water-gas shift reaction. Even at relatively low temperatures the conversion can be increased by allowing the heat-up time to increase.

Table II. Results of First Three Runs

Mesh Size	Time in Heater	T _f	Conversion
-40	85 minutes	451°C	81.4%
-40	85 minutes	469°C	85.1%
-140	95 minutes	465°C	73.9%

2. Particle Size

In a commercial operation it would be desirable to know the optimal grinding policy for the coal so that maximum conversion might be obtained at a minimal cost. In the study of the effect of particle size upon conversion, mesh sizes of -12, -25, -40, -100, and -140 U. S. Standard Size Series were investigated. For each mesh size, runs were made in three pressure ranges: 1210-1290 psig, 1390-1430 psig, and 1540-1590 psig. The results are tabulated in Table III and graphed in Figures 6, 7, 8, and 9.

For the 1210-1290 psig range, the optimal mesh size occurred between -25 and -40 meshes. It could be noticed that the variation from one mesh to another is not very large, for the largest variation is only 8%. However, the -100 and -140 meshes are the least desirable grinding sizes.

Table III. Effect of Particle Size on Conversion

Screen	P_i	T_f	Conversion	Average Conversion
12	1230	469	56.51	56.51
25	1290	470	56.04	57.20
25	1210	465	58.36	
40	1220	467	57.69	58.045
40	1220	470	58.40	
100	1270	475	46.22	50.415
100	1270	467	54.61	
140	1240	469	54.35	50.04
140	1200	471	45.73	
12	1430	473	55.02	55.81
12	1400	472	56.60	
25	1420	471	49.23	54.05
25	1430	475	58.87	
40	1430	475	69.55	64.36
40	1430	471	59.17	
100	1410	469	59.79	54.88
100	1390	472	49.97	
140	1410	469	59.08	45.30
140	1410	475	30.73	
140	1400	470	46.09	

Table III. Effect of Particle Size on Conversion (continued)

Screen	P_i	T_f	Conversion	Average Conversion
12	1580	478	61.03	61.03
25	1570	472	66.49	62.89
25	1580	475	59.29	
40	1570	473	61.39	59.38
40	1590	470	57.37	
100	1590	466	47.00	51.67
100	1580	475	56.34	
140	1560	475	40.29	42.115
140	1540	465	43.94	

In the 1390-1430 psig range, the mesh size yielding the best conversion was -40. In this range a peak occurred at -40 mesh with the conversion falling off on either side of -40, especially for -100 and -140 meshes. If the initial pressure is to be 1390-1430 psig, it is indicated that a -40 mesh be used to obtain the best conversions.

The 1540-1590 psig range yielded results that showed the -25 mesh to be the optimal grinding policy. However, it should be mentioned that -12 and -40 meshes do not differ from -25 mesh by much

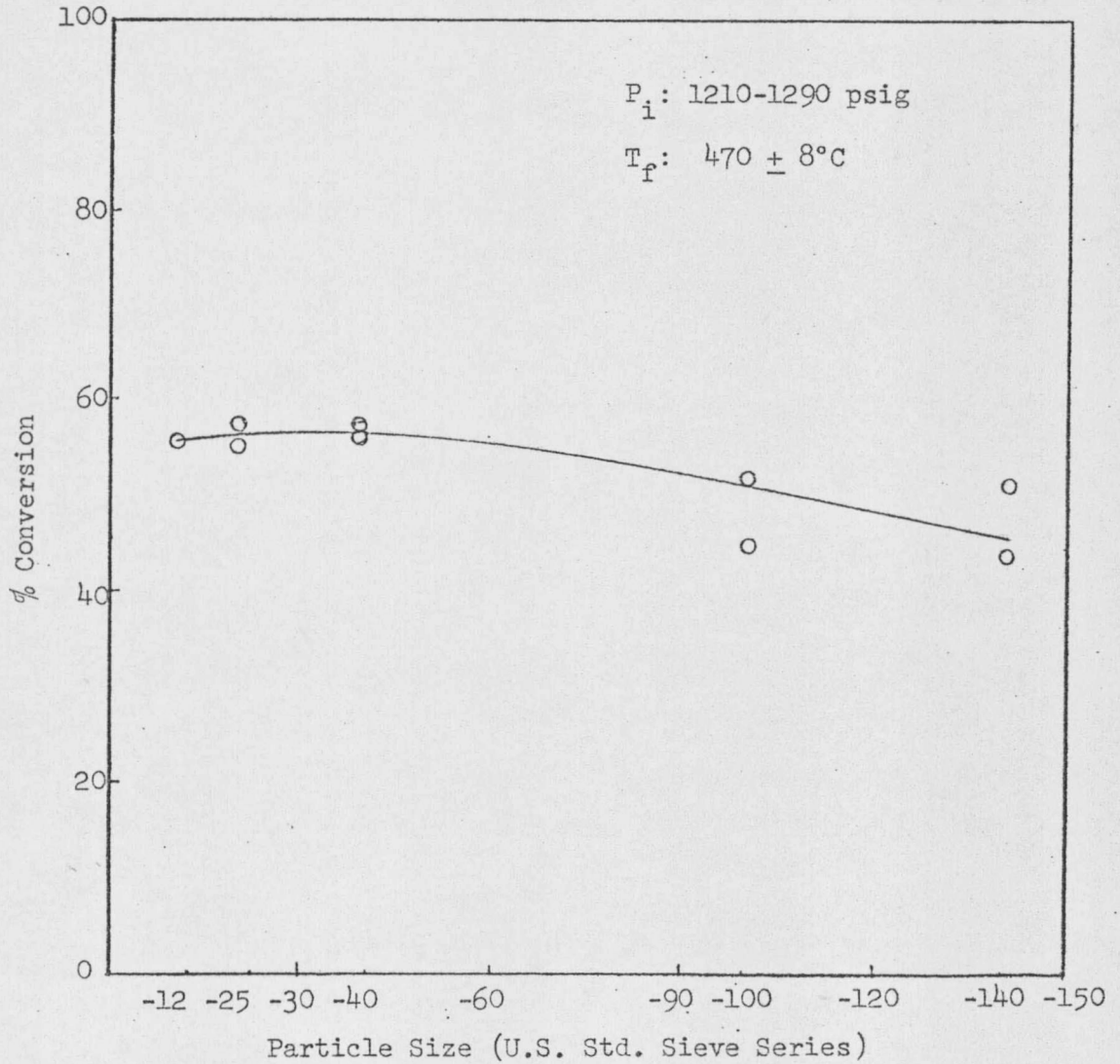


Figure 6. Effect of Particle Size on Conversion for 1210-1290 psig Range.

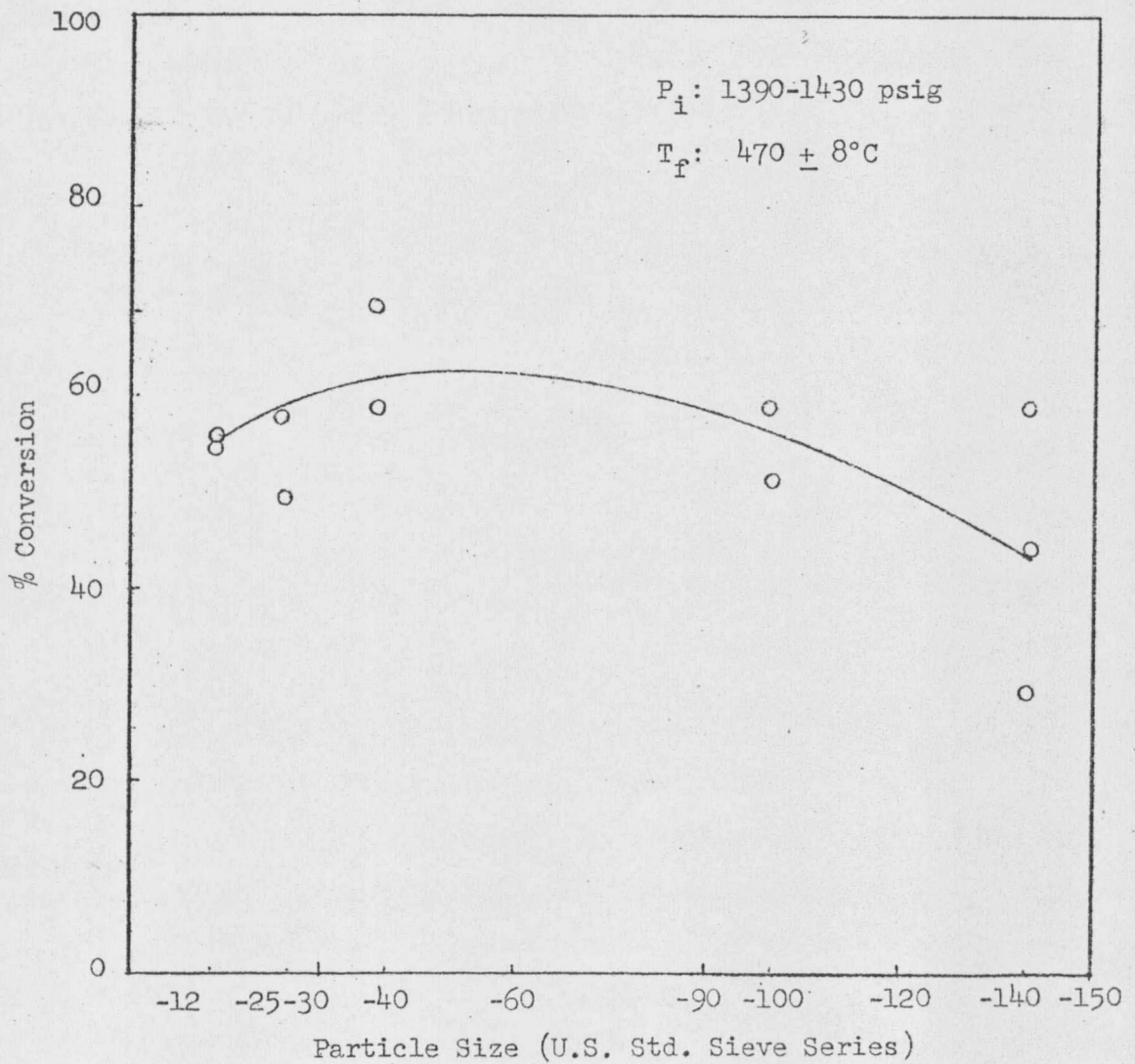


Figure 7. Effect of Particle Size on Conversion for 1390-1430 psig Range.

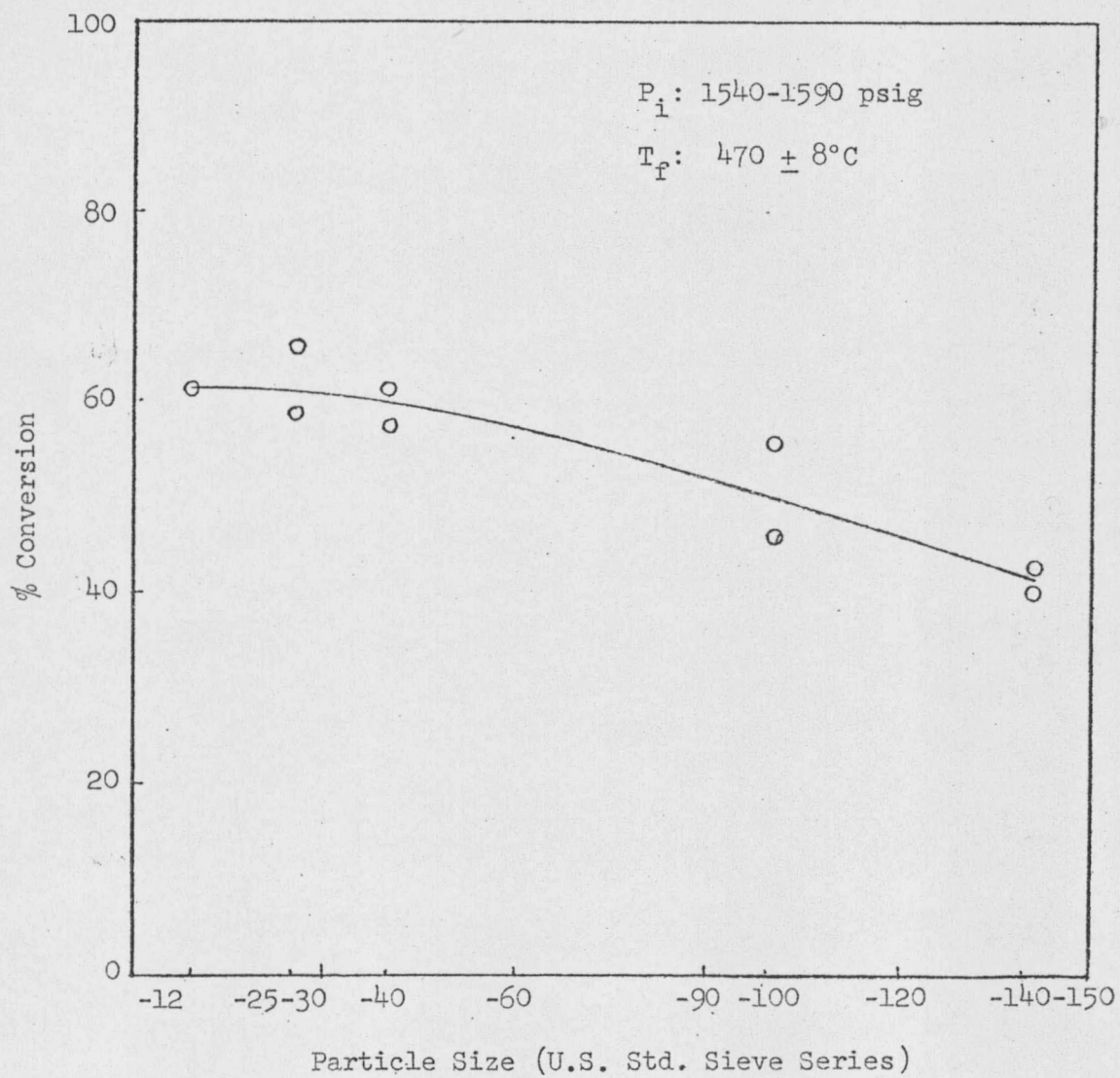


Figure 8. Effect of Particle Size on Conversion for 1540-1590 psig Range.

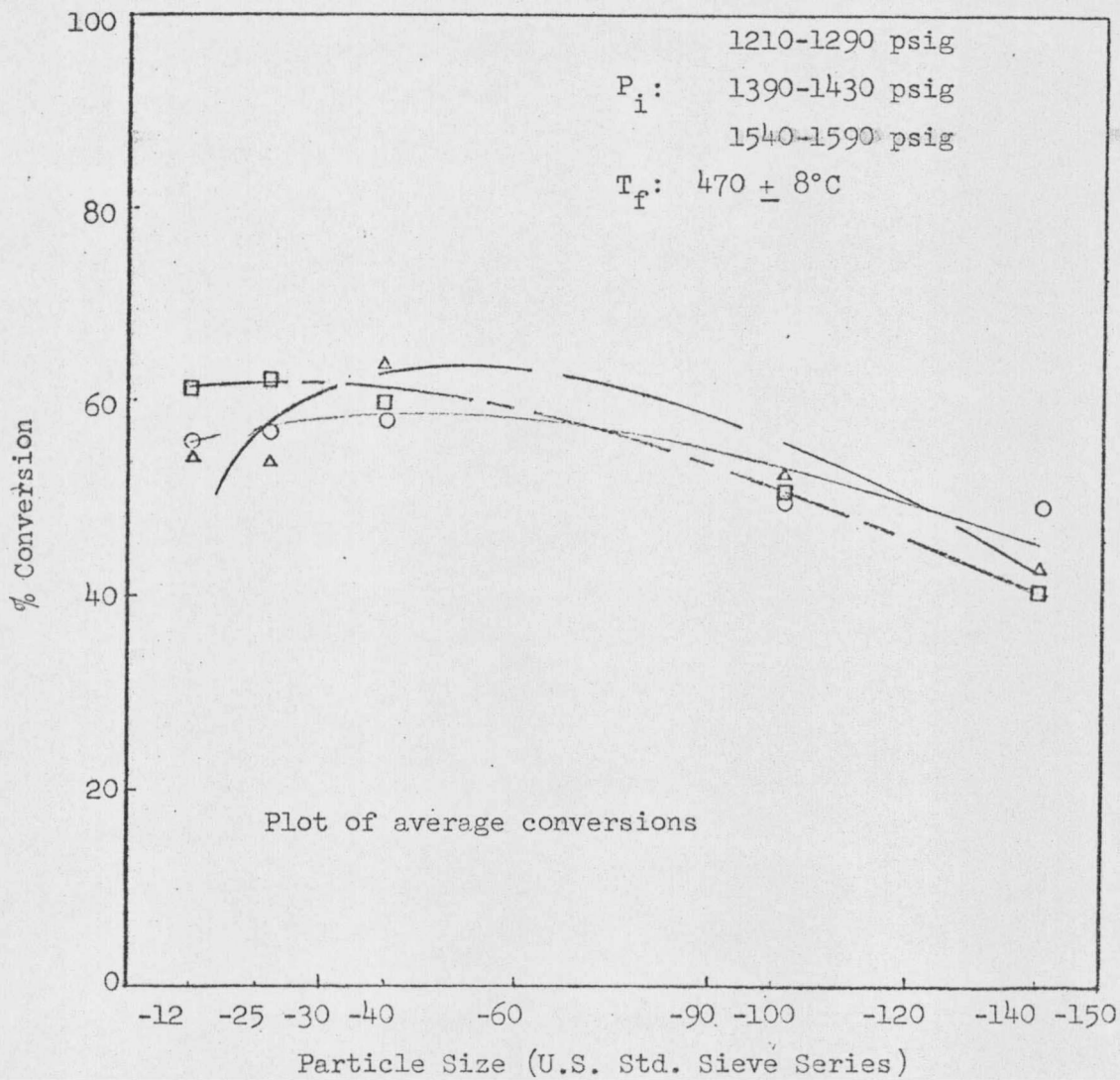


Figure 9. Effect of Particle Size on Conversion.

(maximum deviation = 3.51%). Again there is a large decrease in conversion when -100 and -140 meshes are used.

The results for this part of the investigation indicated that an optimal grinding policy would be to use a mesh size between -25 and -40, inclusive, for any initial pressure from 1210 psig to 1590 psig.

3. Aging

Two questions that may arise in operating a commercial hydrogenation plant are:

- a) Should the coal be stockpiled as lumps or after it has been ground?
- b) Can the coal be stockpiled after grinding as a precautionary measure against equipment failures and delivery delays?

In seeking the answer to these and other questions, the effect of aging upon coal conversion was studied.

For this phase of the investigation, two 160-gram samples of coal were ground to -25 and -100 meshes. Then 30 grams of each particle size were reacted immediately while the other 30-gram samples of each size were set out in the air for two weeks. After the two weeks had elapsed, these 30-gram samples were reacted.

Water analyses were also made on each particle size immediately after grinding and after the two weeks' exposure. The results are shown in Table IV.

Table IV. Effect of Aging

Mesh Size	Length of Exposure	Water Content	Conversion
-25	0	23.67%	58.84
-25	2 weeks	4.65%	44.99
-100	0	23.67%	66.15
-100	2 weeks	3.49%	55.58

The results showed that exposure to the air for two weeks resulted in a decrease in conversion for each particle size. The -25 mesh conversion dropped about 14% while the -100 mesh conversion decreased by about 11%. The water content was lowered upon exposure. It went down about 19% for -25 mesh and down about 20% for -100 mesh.

The loss in conversion due to aging of the coal can be due to the loss of water from the coal and/or the oxidation of the coal. The large water loss of the two samples upon aging would seem to indicate that the water loss is a factor in the drop in conversion. How much of a factor is hard to say. This is one area that is open to future study.

There is one oddity about this data that should be noted. In each case, immediate reaction or two weeks' exposure and then reaction, the -100 mesh coal yielded higher conversions than the -25 mesh coal. According to the previous findings of this investigation, the opposite should be true. To explain this reversal is beyond the capability of this investigator.

4. Contacting Method

The next phase of the investigation was to study the contacting method of the coal and phenanthrene. Since the reactor was an autoclave, it was decided that three contacting methods could be used. The methods were pouring the coal into the reactor first, then pouring in the phenanthrene, layering the coal and phenanthrene by first pouring one and then the other, and mixing the coal and phenanthrene before pouring them into the autoclave.

The results of this series of runs is shown in Table V.

Table V. Effect of Contacting Method

Initial Pressure	Contacting Method	Conversion
1390	pouring	57.80%
1400	layering	56.28%
1390	layering	58.79%
1400	mixing	56.14%
1410	mixing	64.26%

From these results it was concluded that the contacting method used for coal and phenanthrene made no difference in the conversion of the coal to benzene-soluble material. This was the expected result. It was felt that the rocking motion of the heater would provide enough agitation to thoroughly mix the reacting materials, regardless of the contacting method employed as the higher temperatures and pressures were reached.

5. Catalysts

In the early Bureau of Mines' work and in York's thesis (7), it was stated that alkali or alkaline earth carbonates, in particular Na_2CO_3 , would increase the conversion of the coal if added to the reactor. It is for this reason that a search was made during this investigation for a catalyst to improve the coal's conversion, thus enhancing the water-gas shift reaction as a coal hydrogenator. The term 'catalyst' was used even though it was not certain if the chemicals remained after the hydrogenation or if they were incorporated in the hydrogenation product.

Two catalysts were studied. One of them was CaCO_3 , an alkaline earth carbonate. It was selected due to the Bureau's recommendation of alkali or alkaline earth carbonates, and since Na_2CO_3 , an alkali earth carbonate, had already been proven effective, it remained to be seen if an alkaline earth carbonate could

be as effective. CaCO_3 is also the cheapest alkaline earth carbonate. The results are shown in Table VI.

Table VI. CaCO_3 as a Catalyst

Amount of CaCO_3	Initial Pressure	Conversion
0.3 grams	1390	50.26%
0.6 grams	1410	39.30%
0.6 grams	1410	51.40%
0.9 grams	1410	47.66%
0.9 grams	1400	42.61%

The other catalyst studied was ZnCl_2 . It was chosen because it is a hydrocracking catalyst and could possibly aid in breaking down the coal, thus aiding the hydrogenation, and it had been recommended as a catalyst by others in this field. The results are shown in Table VII.

Table VII. ZnCl_2 as a Catalyst

Amount of ZnCl_2	Initial Pressure	Conversion
0.3 grams	1410	41.76%
0.6 grams	1400	30.85%
0.6 grams	1410	39.52%
0.9 grams	1410	39.43%
0.9 grams	1400	29.72%

Neither CaCO_3 nor ZnCl_2 proved to be an effective hydrogenation catalyst for the water-gas shift reaction. Results were not as high as those obtained with Na_2CO_3 . This indicated that Na_2CO_3 should remain as the catalyst until a better one is found.

6. Gas Atmosphere

The remaining factor studied in the experimental work was the effect of the autoclave's initial gas atmosphere upon conversion. The autoclave was not always charged with only CO as done previously. An initial pressure of H_2 was added for the runs and then the initial pressure was brought up to about 1400 psig by adding CO.

There were two reasons that the gas atmosphere was studied. The first was to see if an atmosphere of CO-H_2 would surpass the conversion achieved by adding only CO to the autoclave. The other reason is that in many processes a CO-H_2 product gas is common and this results in CO-H_2 gas being cheaper than pure CO or H_2 .

Some previous work has been done in this area. Fischer, in the initial investigation of the $\text{CO-H}_2\text{O}$ reaction on coal, reported that CO was more satisfactory than H_2 under the same conditions. In the Bureau of Mines' work it was found that the conversion of low rank coals with $\text{CO-H}_2\text{O}$ is greater than that obtained with H_2

even when the H_2 initial pressure was significantly higher than the $CO-H_2O$ initial pressure. It was also found that for short contact times, the formation of benzene-soluble material proceeds more rapidly for $CO-H_2O$ than for H_2 . The use of synthesis gas ($CO-H_2$) was also studied. The results are shown in Table VIII. As can be seen, the synthesis gas yields almost the same conversion as CO .

Table VIII. Effect of Gas Composition

Gas	Initial psi	Operating psi	Time, min.	Temp. °C	Conversion ¹
2:1 syn ²	800	3,070	15	380	77%
1:1 syn	800	3,000	15	380	82%
1:1 syn	800	3,010	120	380	87%
CO	800	2,970	15	380	86%

¹ weight percent on a dry, ash-free basis

² two parts H_2 to one part CO

The results of the investigation are shown in Table IX and graphed in Figure 10. In Figure 10, there are two lines drawn. One line is a least squares line (see Appendix) that assumes a straight line will represent the tendency of the data. It should be stated that this line is based on all eleven data points. The equation for the line is

$$y = 0.554 - 0.00001916x$$

where y is the conversion while x is the initial H_2 partial pressure. The other line in Figure 10 is a line that assumes the data fits a curve. The curve, as are all curves in this thesis, is an estimate of the best fitting curve.

The conclusions one reaches on the effect of gas atmosphere depend upon which line one selects, but in either case the conclusions are essentially the same. If the straight line relationship is chosen, one is forced to say that any combined atmosphere of $CO-H_2$ will help in achieving the highest conversion possible under any conditions. If the curve is chosen, one is led to believe that except for pure CO and nearly pure H_2 , the combination of $CO-H_2$ used in charging the autoclave makes no difference in the final conversion. Also, the use of pure CO or of nearly pure H_2 only slightly decreases the conversion.

B. Product Description and Analysis

The product received from the hydrogenation of coal by the water-gas shift reaction often varied in appearance. It ranged from a flaky, fluffy material to a hard, caked mass at the bottom of the autoclave. Often, varying amounts of each type of product were found.

The fluffy product always yielded good conversions. The caked product would at times yield good conversion, but mostly the

Table IX. Effect of Gas Composition

Partial H ₂ Pressure	Initial Pressure	Initial H ₂ %	Temp., °C	Conversion %
0	1410	0.0	475	51.86
290	1410	20.5	472	57.23
520	1410	36.9	476	55.65
520	1400	37.1	486	63.23
610	1410	43.3	479	59.43
610	1410	43.3	480	58.92
800	1420	56.3	480	55.10
800	1400	57.1	483	41.71
1000	1430	69.9	483	58.78
1210	1410	85.8	482	49.10
1400	1400	100.0	473	43.14

yields were low. The caked material would also at times yield a cakes substance that was unreacted coal or carbon. The caked material would vary in color. At times, it was black, brown, or black streaked with brown. The fluffy product was always a black.

The only analysis that was ever made of the product was made by the Huffman Laboratories, for our labs were not equipped to make analyses through micro techniques. This analysis was made for York (7). The results for the analysis of Colstrip sub-bituminous hydrogenated product and the residue are shown in Table X.

