Reduction of sub-bituminous coal using carbon monoxide and carbon dioxide
by Stephan Timothy Kujawa

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OE SCIENCE in Chemical Engineering
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Abstract:
The research presented in this thesis studied coal liquification by-means of the carbon monoxide - water shift reaction to hydrogen. Specifically, the conversion of coal to benzene soluble products when the feed gas consisted of both carbon monoxide and carbon dioxide was studied.

The purpose of this was to see if recycled reactor off-gas, consisting of both CO2 and CO, could be used directly without stripping out all of the CO2 The test runs were made in a 500 ml rocking autoclave. The operating time was five minutes when the autoclave reached 450°C. Three initial pressures of 900, 1200, and 1500 psig, and a series of feed gas compositions were studied.

The higher initial pressures gave a high conversion when the feed gas was pure CO, but as the amount of COg was increased to over 50% in the feed gas, the conversions for the three pressures approached the same value.

The amount of benzene soluble product boiling above 90°C increased as the pressure increased. At 900 psig initial pressure about 70% of the product boiled above 90°C while at 1500 psig about 80% of the product boiled over 90°C.

At 900 and 1200 psig, the off-gas CO2 : CO ratio was found to stay about 1:1 up to 50% COg in the feed gas. At 1500 psig the ratio was less than this, indicating excess CO in the feed stream.

The amount of water consumed in the reaction was found to be less than 50% of the water charged in all cases.

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Date August 7, 1974

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ABSTRACT

The research presented in this thesis studied coal liquification by means of the carbon monoxide - water shift reaction to hydrogen. Specifically, the conversion of coal to benzene soluble products when the feed gas consisted of both carbon monoxide and carbon dioxide was studied. The purpose of this was to see if recycled reactor off-gas, consisting of both CO_2 and CO, could be used directly without stripping out all of the CO_2.

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The amount of water consumed in the reaction was found to be less than 50% of the water charged in all cases.

INTRODUCTION AND BACKGROUND

INTRODUCTION

The purpose of the research presented in this thesis was to provide engineering data on a process to convert sub-bituminous coal to liquids soluble in benzene. The liquids produced are intended to be used as on ash-free fuel for a magnetohydrodynamic generator now being developed by the AVCO Everett Research Laboratory of Everett, Massachusetts.

The original coal liquification process was devised originally by Berguis in the early 1900's, using hydrogen as a reducing agent. This process went into disuse when Fischer and Tropsch synthesized gasoline using carbon monoxide and hydrogen, but was brought to the forefront again as the Germans made fuel from brown coal in the second world war.

In the late 1960's, Appel and Wender of the U. S. Bureau of Mines (6) did some coal liquification work that showed at high temperatures and pressures, higher conversions could be obtained by using carbon monoxide and water to liquify coal via the shift reaction to carbon dioxide and hydrogen, than by using pure hydrogen in the first place. It was felt that the reason for this was that the shift reaction produced hydrogen in a more reactive form that would more easily combine with the free radicals formed in the coal matrix by high temperatures.

The Chemical Engineering Department at Montana State University began coal liquification research in 1968. The best scheme found so far has been to react powdered coal, slurried in phenanthrane in the presence of carbon monoxide and water. Na_2CO_3 is used as a shift reaction catalyst, and the run conditions are 450°C to 475°C, and approximately 5500 psig.

As previously stated, the liquids formed are intended to be used as feed for an M.H.D. generator; they are too hydrogen deficient to be used as a synthetic crude oil. The liquids could possibly be used as feed to one of the new processes that use hydrogen to enrich and lighten residual fuel oils such as Chevron's or U. O. P's Isomax process.

RESEARCH BACKGROUND

This is the fifth thesis on coal liquification by the carbon monoxide shift reaction that has resulted from research studies done by the Montana State University Chemical Engineering Department. In the year 1968, Wayne York began a project initiated by AVCO Research Corporation of Everett, Massachusetts with the purpose of determining whether a liquid fuel could be produced from coal using the water-gas shift reaction. The liquid was to be used as an ash-free fuel for an electrical generator operating on the magnetohydrodynamic principle. It was felt that a liquid fuel would solve erosion problems in the case of the generator because of its being essentially ash free, and also, a higher thermal efficiency would result if the coal was converted to a high btu liquid rather than a low heat content producer gas.

The following is a list, by the person who did the research of the most important conclusions made at Montana State University on this project and which led up to the area of investigation worked on in this present thesis.

Wayne York (1):

1. The ash in the coal catalyses the shift reaction producing nascent hydrogen that stabilizes the reactive fragments produced by thermal depolymerization of the coal.
2. Conversions were increased by about 10% when Na_2CO_3 was added to the coal.
3. The liquid product has an ash content of less than 0.1% and a hydrogen to carbon ratio of about 1.14:1 with a molecular weight of about 400.
4. Increasing the reactor temperature increases conversion but the hydrocarbon gas production also increases.
5. Increasing the pressure increases the conversion of coal to benzene soluble material.

Dat Nguyen (2):

1. Less than 5% of the coal converted will go into the gas phase as methane and ethane. The remaining tarry product has an H/C ratio of 1.1:1, and an ash content of about 0.1%.
2. Conversion is zero at 300°C, and reaches a maximum over 70% at 475°C.
3. Initial reactor pressure has a very significant effect on conversion below 1000 psig, and becomes less so around 1500 psig where conversion begins to level out close to 80%.
4. Phenanthrene was found to be the best solvent, and the optimal

phenanthrene to coal ratio is around 2:1.

5. Na_2CO_3 increases the conversion around 10% when present in a Na_2CO_3 to coal ratio of 0.01:1.

6. With a five minute operating time at 475°C, a 70-80 percent conversion of Colstrip sub-bituminous coal could be obtained to benzene soluble products by reduction with carbon monoxide and water.

Thomas Fiske (3):

1. The optimal coal particle size for an initial operating pressure of 1210 to 1590 psig is -25 to -40 mesh.

2. The method of contacting the coal and phenanthrene makes no significant difference in conversion.

3. The exposure of ground coal to air decreases conversion.

Ronald Denney (4):

1. Aging of lump coal before use has no effect on conversion.

2. The rate controlling step in the hydrogenation reaction is not where the hydrogen attaches to the solvent surface.

3. 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 psig.

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

RESEARCH OBJECTIVES

PURPOSE

The purpose of this thesis is to supply the engineering data necessary to design, ultimately, a large scale coal liquification plant. The data presented in and the results of this thesis are not sufficient to design large scale equipment. The data is here presented, therefore, to be used as a guide for the next step that should be taken in a research endeavor of this type, i.e., the design and operation of a continuous reactor capable of supplying kinetic and thermodynamic information sufficiently accurate and precise to be used as the design basis for an eventual large scale process plant. The results here can also be used to give economic guidelines in estimating the cost per unit of product for such a plant.

OBJECTIVES

The primary research objective of this project was to extensively investigate what happens when carbon dioxide is fed to the reactor with the carbon monoxide reactant.

Preliminary CO_2 dilution work was done by R. Denny who reported no effect on conversion until insufficient CO was present to react with the water (4).

R. E. Gannon, principal research engineer from AVCO, the company sponsoring the project, suggested in a letter dated December 3, 1973, that Denny's work on CO_2 dilution should be thoroughly explored because if an acceptable conversion could be approached with a feed gas high

in CO_2, a more economical process could be designed by eliminating the equipment necessary to strip the CO_2 from the reactor off gas before recycle to the process.

A second objective was to find out the approximate product distribution of the converted coal. It was decided to use a simple distillation to determine the amount of product that boiled above the temperature of the benzene used as an extraction solvent.

In the previous theses, one common suggestion has been to obtain an accurate material balance. This objective was partially fulfilled here by finding out the relative amounts of carbon dioxide and carbon monoxide in the off gas (which will be used to determine how much CO_2 stripping equipment is necessary) and by finding out how much of the feed water was actually used in the reaction, which will determine the water requirements of a large process plant. Knowing the relative amounts of CO and CO_2 as feed and as off-gas would also give some insight into the stoichiometry of the shift reactions occurring.

EXPERIMENTAL PROCEDURE

COAL PREPARATION AND ANALYSIS

Approximately fifty grams of Colstrip sub-bituminous coal was ground to minus 38 mesh for each run by mortar and pestle.

Two samples of the coal of about one gram each were placed in porcelain crucibles and heated over bunsen burner flame, slowly at first to drive off the volatile matter, and then at a higher heat to burn off the fixed carbon. After about twenty-four hours, only a yellowish-grey ash was left.

The weight of the ash divided by the weight of the original coal was the fraction of ash in the coal. The arithmetic average of the two ash analyses was used as the fraction of ash in the coal charged to the reactor.

Another, ten gram sample of coal was weighed into a boiling flask and toluene was added. A water analysis tube with graduate sidearm and reflux condenser was then attached to the flask and the toluene was allowed to boil.

The toluene vapor carried the water in the coal to the reflux condenser where the two components condensed and dripped into the sidearm. The water in the sidearm separated from the toluene and sank to the bottom. After about twelve hours all the water had been extracted from the coal and the amount could be read on the graduated sidearm. The fraction of water was then calculated as the milliliters of water times its density divided by the weight of coal charged to the boiling flask.

A typical analysis of Colstrip coal is included in Table I which was taken from Wayne York's thesis (1).

REACTOR CHARGING

The next step in the procedure was to place the fresh ground coal into the reactor, followed by the phenanthrene and the sodium carbonate. The reactants were then stirred dry and the water poured in. The head was then placed and bolted on. The specifications of the reactants other than coal were:

Phenanthrene	:	Aldrich, 90%, cat. no. P1142-5
Na_2CO_3	:	Matheson, Anhydrous reagent, ACS grade, cat. no. SX 395
Water	:	Chlorinated tap water

The charge quantities were,

coal	:	30 gms
H_2O	:	30 gms
Phenanthrene	:	60 gms
Na_2CO_3	:	0.3 gms

REACTOR OPERATION AND GAS CHARGING

The reactor was a 500 ml Parr Inconel Autoclave which is shown in Figure 1. This was the reactor part of a Parr series 4000 Hydrogenation Apparatus that consisted of the reactor and a rocking-heating apparatus for the autoclave. The autoclave was rated for 7000 psi at 500°C. The rocker operated at about 40 cycles per minute.

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_2O_3	17.6
Fe_2O_3	4.6
TiO_2	0.4
P_2O_5	0.8
CaO	22.7
MgO	9.4
Na_2O	0.3
K_2O	0.5
SO_3	14.9

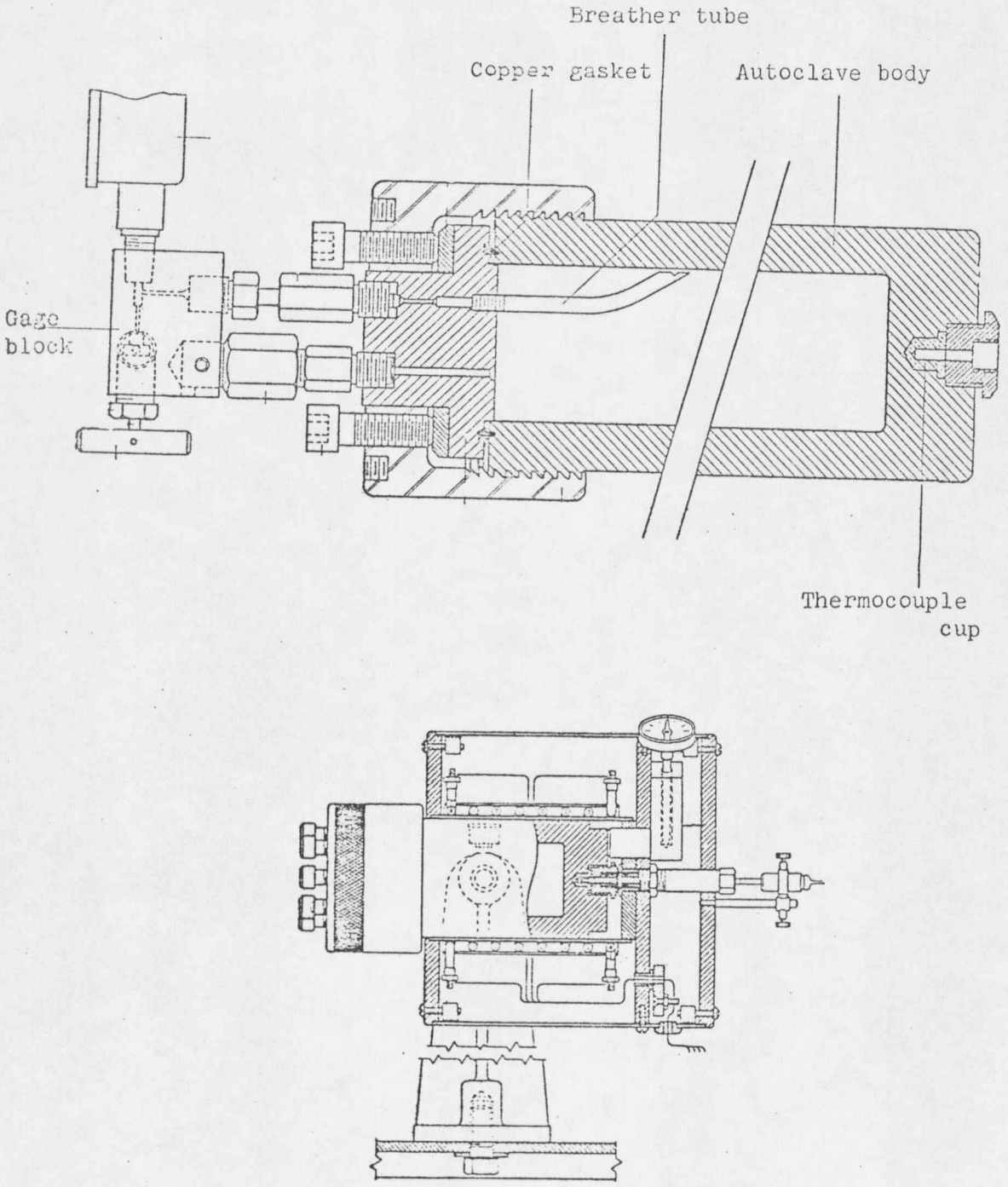

FIGURE 1. Rocking Autoclave Assembly Details

After the head of the reactor was tightened, the bomb was pressurized depending on the run specifications, with up to 800 psig of CO_2 from a standard cylinder. Then an oil pressurizing system was used to bring the bomb up to the initial run pressure with CO. The pressurizing system is shown in Figure 2.

The bomb, after charging, was placed in the heater-rocker and an iron-constantan thermocouple was placed in a thermowell in the base of the bomb. The heaters and rocker were turned on and the bomb heated to 450°C, which usually took about 70 minutes. The bomb was held at 450°C for a run time of five minutes, then the rockers and heaters shut off and the bomb pulled from the heater with threaded pullrods, and allowed to cool in the air.

After the bomb had cooled, the off-gas was bled slowly into an evacuated twenty gallon drum. The drum had a sample port where a .1 ml sample was taken and injected into a chromatograph. The chromatograph was packed with Porapak Q-S which detects CO_2, CO, N_2, CH_4, and C_2H_6, and operated with helium as a carrier gas at a temperature of 70°F.

The chromatograph was standardized with two mixtures containing different amounts of CO_2, CO, CH_4 and H_2 which approximated expected off-gas compositions. The peak heights of the recorder output were used to obtain the relative amounts of CO_2 and CO in the off-gas.

The bomb was then taken apart and the liquid and solid mass removed. This usually consisted of a small amount of black liquid, a greater amount of brown or black tarry substance, and a much greater

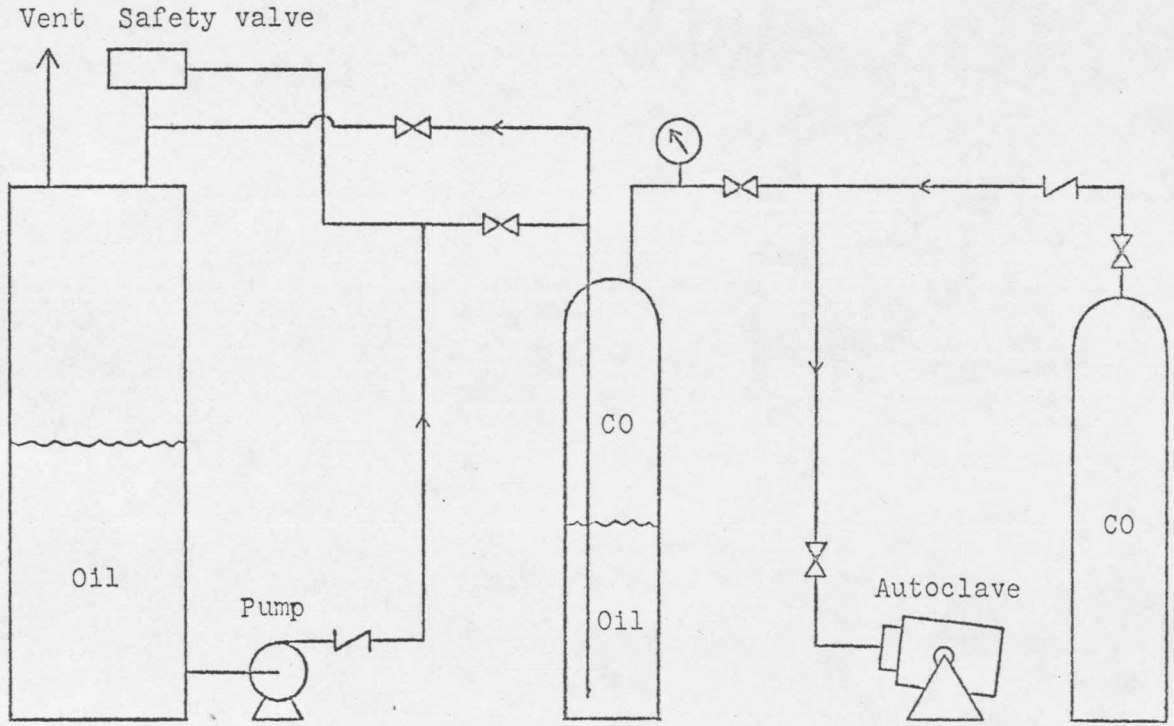

FIGURE 2. Pressurization System.

amount of phenanthrene solvent which had settled to the bottom of the mass.

PRODUCT EXTRACTION

The product was removed manually, broken into small lumps, and placed in a weighted, cellulose, 43 x 123 extraction thimble. The remaining product in the bomb was washed out with benzene and poured into the thimble. All the benzene that flowed through the thimble was saved to be used in the liquid distribution distillation.

A Soxhlet continuous extraction apparatus was used to extract the benzene soluble product and the phenanthrene from the unreacted coal. The extraction lasted for about 24 hours, at which time the benzene ran clear. The thimble was then removed, the benzene ran through a #2 Whatman filter paper, and the thimble and filter paper put in an oven at 110°C to dry.

After the thimble had dried the conversion was calculated using the formula:

$$x = \frac{MAF(in) - MAF(out)}{MAF\ (in)}$$

x is the fractional converson, MAF(in) is the weight of moisture and ash free coal charged, and MAF(out) is the weight of moisutre and ash free coal out obtained from the weight of the dried filter paper and thimble.

PRODUCTION DISTRIBUTION

All the liquid from the extraction and cleaning of the reactor was placed in a weighed boiling flask and the benzene, boiling at 74°C in Bozeman, was driven off. That all the benzene had been driven off was determined by a sudden rise in vapor temperature occurring near the end of the distillation. The heat was taken away from the distillation flask as the temperature rise occurred, and the vapor temperature never got above 90°C. The data on liquid distribution therefore is reported here as the fraction of the converted product that boils over 90°C.

To calculate the weight of liquid boiling over 90°C, the weight of the bottoms and distilling flask was subtracted from the weight of the phenanthrene charged to the reactor (here assuming none was lost) and the weight of the dry flask. This weight of liquid boiling over 90°C was then divided by the grams of coal converted which gave the fraction of the product which boiled over 90°C.

INTERPRETATION OF EXPERIMENTAL RESULTS

CHOICE OF OPERATING CONDITIONS

The first thing necessary to find was the initial pressures at which to make tests. This was done by making a series of runs at different initial pressures, but all at a feed gas composition of 50% CO_2 and 50% CO. The results of these tests are plotted versus initial total pressure.

It was felt that a 50% conversion was about as low as would be economically feasible. From Figure 3, it is obvious that this conversion occurs at an initial pressure of about 900 psig.

Three initial reactor pressures were then chosen: 900, 1200, and 1500 psig. The purpose of the different pressures was to determine the effect of the total amount of reactant gas.

To show the effect of CO_2 in the CO gas feed, reactant gas compositions were chosen to give four to five test compositions at each initial pressure, and three runs were made at each composition. The maximum feed gas composition of CO_2 was 100% at 900 psig, 67% at 1200 psig, and 59% at 1500 psig initial pressure, these due to CO_2 being available at a pressure of 850-900 psig only at the charging temperature. To make a statistically sound experiment, at least three runs were made at each combination of initial pressure and composition.

CONVERSION AS A FUNCTION OF INITIAL PRESSURE AND GAS COMPOSITION

In Figure 5, the conversion of moisture and ash free coal to benzene solubles is plotted against the percent of CO_2 in the feed gas with the initial total pressure as the curve parameter.

The top curve, labeled 1500 psig, is essentially a duplication of

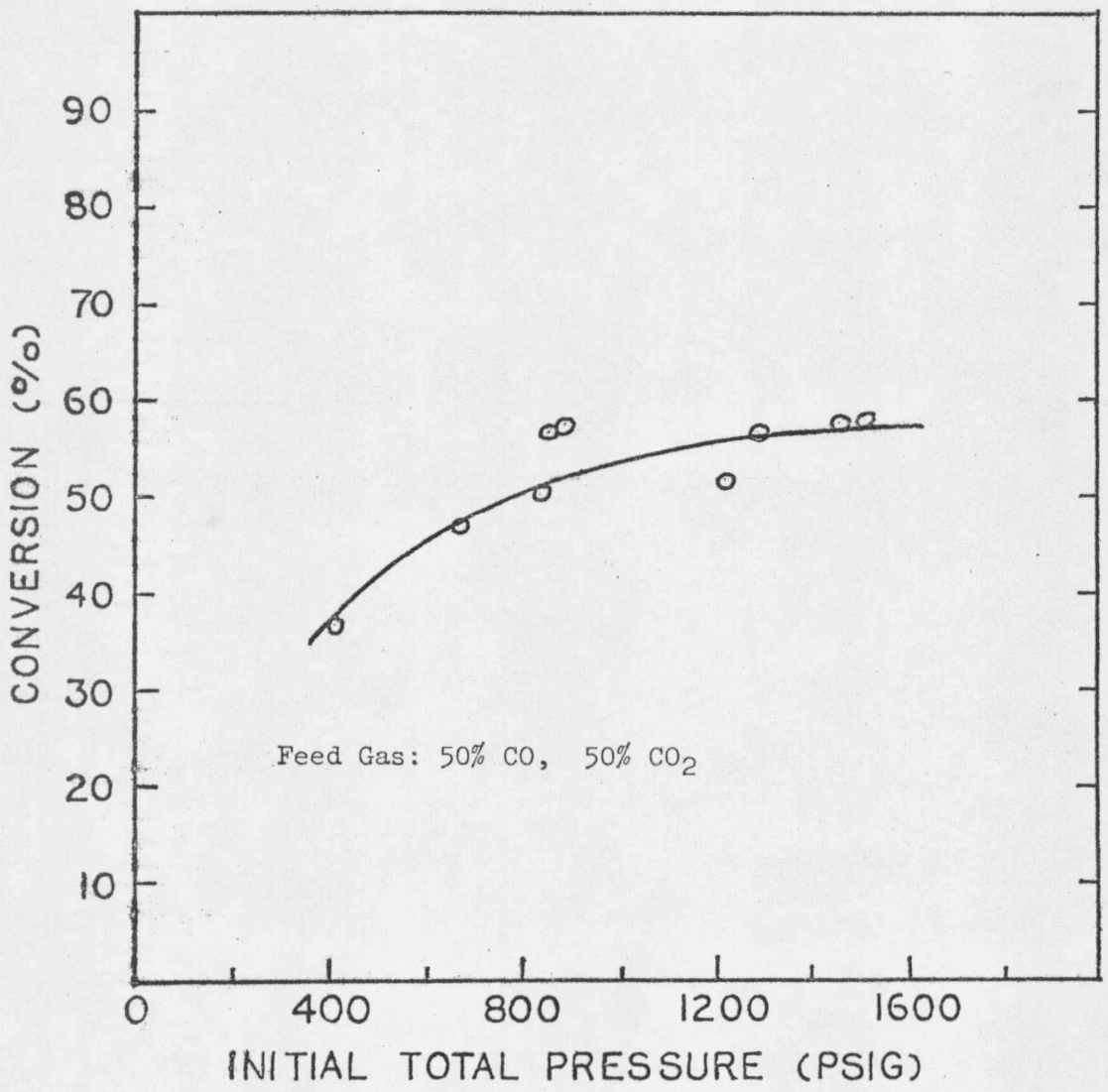

Figure 3. Effect of Total Pressure on Conversion at 50% CO_2 in Feed Gas

the work done by Ron Denney (4). The sharp drop off at 55% CO_2 presented in his work is repeated here also.

The three curves show the following things:

(1) With a feed of pure CO, the highest conversion will take place at the highest pressure.

(2) At all pressures, conversion does not begin to drop until the composition of CO_2 reaches about 25%.

(3) As CO_2 compositions go above 25%, the lower the initial pressure, the slower the rate of drop in conversion.

(4) As CO_2 compositions go above 50%, conversion at 1200 initial pressure are higher than at 1500 initial pressure and the pattern seems to happen again as compositions go above 65%; 900 psig runs seem to give higher conversions than 1200 psig runs.

THEORETICAL EXPLANATION OF FIGURE 4

To give a probable explanation of the phenomenon presented in Figure 4, the thermodynamic investigation of the shift reaction done by York was expanded to include the effects of having CO_2 present initially (1). Using York's equilibrium constants and activity coefficients, a plot of the equilibrium yield of hydrogen in the shift reaction was prepared. Figure 5 gives the yield as a function of pressure and composition of the feed gas at about the run temperatures.

Two things can be explained by Figure 5:

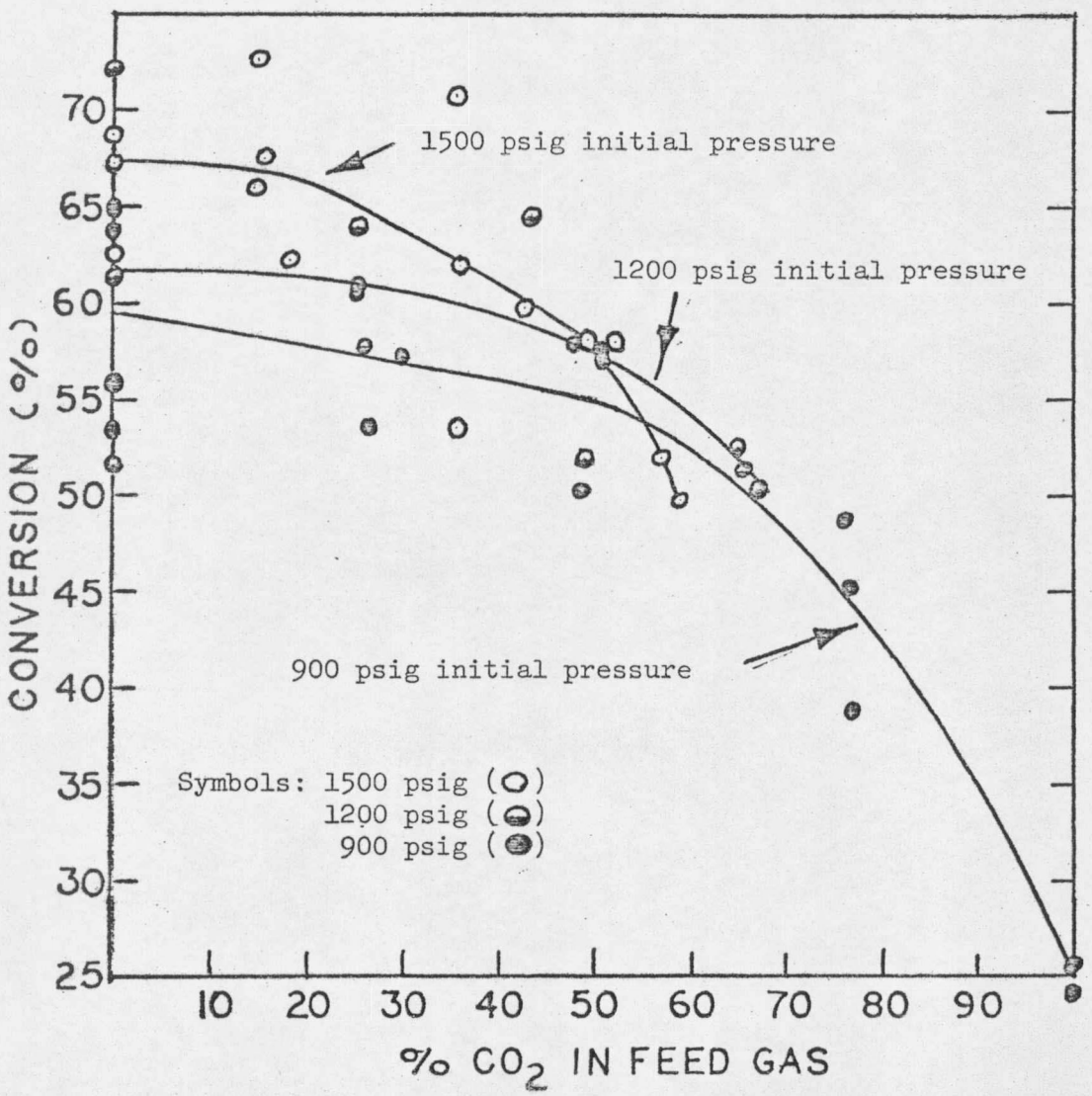

Figure 4. Effect of Amount and Composition of Feed Gas on Conversion

(1) At any initial pressure, as the amount of CO_2 increases in the feed gas, less hydrogen is produced, therefore there is less available hydrogen for the coal to react with, causing lower conversions.

(2) Figure 5 shows that the lower the pressure at 427°C, the more complete the shift reaction. This can perhaps explain the tendency of the high pressure curves in Figure 4 to approach or go below the lower pressure curves as the CO_2 feed increases.

There is a possibility that the low pressure runs produce more hydrogen at high CO_2 contents. This higher quantity of hydrogen would then tend to give comparable conversions for all pressures studied at high feed gas CO_2 compositions.

To explain why higher pressures give higher conversions of coal to benzene soluble liquids, Le Chatelier's principle can be applied. The higher a pressure put on a gaseous system that has a tendency to react to form fewer moles of gas, the more that system will react to relieve the pressure. Therefore, a high initial pressure of CO will cause a greater coal reaction because as the hydrogen is used to convert coal, fewer moles of hydrogen will be present, which will induce the shift reaction to proceed further, and the higher the initial pressure of CO, the higher the tendency there is for this to occur.

It seems that up to about 50% CO_2 in the feed gas, Le Chatetier's principle and the equilibirum conversion of the available feed gas

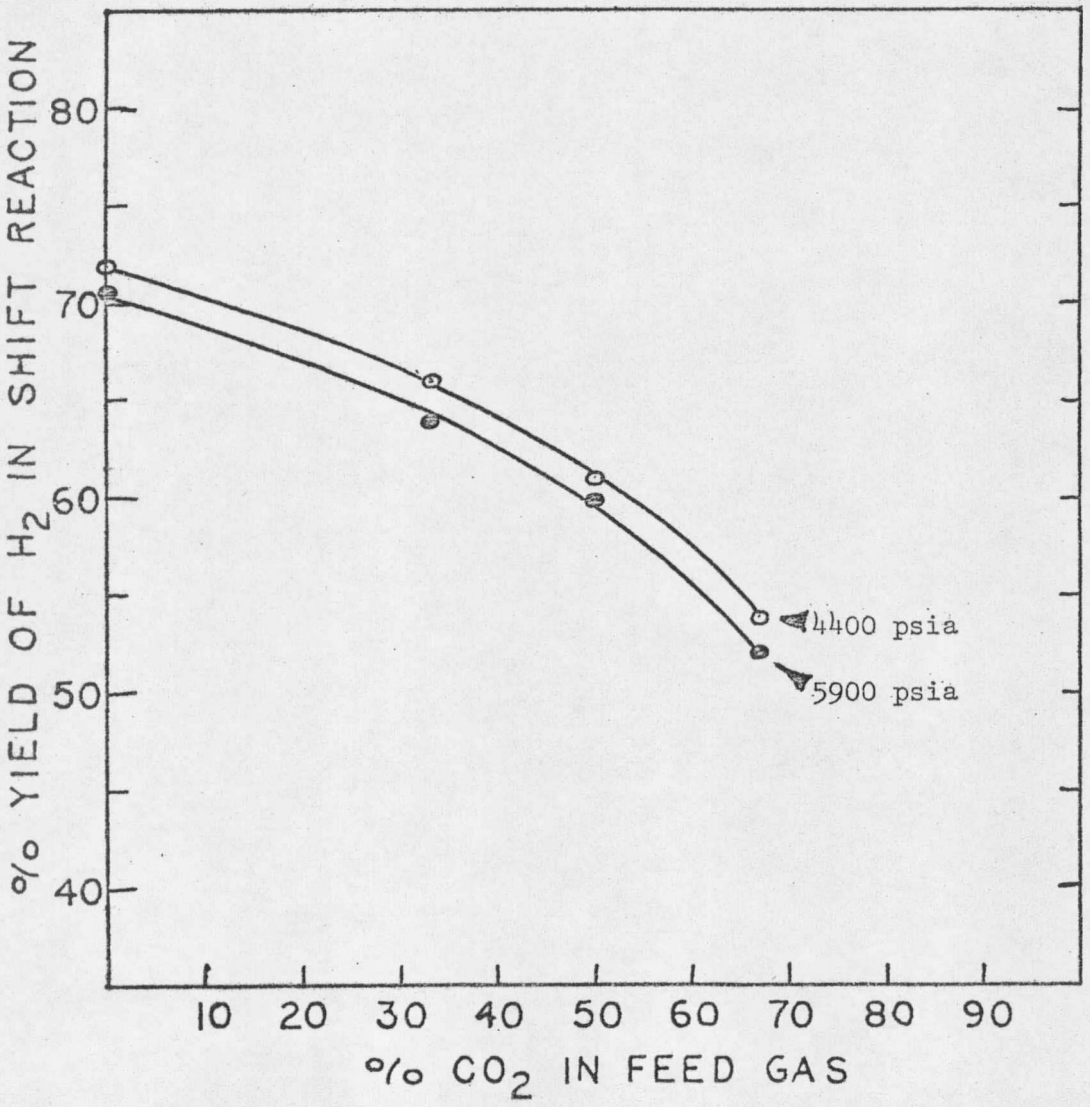

Figure 5. Equilibrium Yield of H_2 in Shift Reaction

control the coal conversion.

Above about 50% CO_2 in the feed gas, the curves for conversions tend to run together, which could possibly mean that the cause for the faster rate of drop of the high pressure conversion lines is that there is a lower equilibrium yield of hydrogen at higher pressure.

If the reader will refer to Figure 11 of this thesis, at an initial pressure of 1500 psig, the run pressure is about 6300 psig at a 60% CO_2 feed; the run pressure for a 900 psig initial pressure run is about 3500 psig. Since the run pressures are so vastly different, the hydrogen production is probably greatly different also, causing the sharp drop in conversion for the 1500 psig runs at 60% CO_2 while in the 900 psig runs the conversion drops at a much slower rate. Therefore, it is theoretically possible that the lower pressure runs will give higher coal conversions at high CO_2 feed gas compositions.

SIGNIFICANCE OF EXPERIMENTAL CONVERSIONS

What is significant about Figures 4 and 5 is that there is a possibility that a low pressure 50% CO_2 gas feed can give almost as high a conversion as a higher pressure pure CO feed. It might be more economical to operate at the lower pressure when equipment costs are considered.

The greatest use of Figure 4 in the near future is probably that is shows the highest conversions that can be expected in a continuous reactor. Theoretically, a continuous reactor with good phase contact should give higher conversions, but, with the inherent pumping and

heating problems of the process, the conversions given by Figure 4 are probably the highest expectable.

RUNS WITH INERT GAS AND NO CARBON MONOXIDE

H_2 and CO_2

Four runs were made with no carbon monoxide in the feed gas. The upper curve in Figure 6 shows the effect of mixing hydrogen with CO_2. The graph shows that pure hydrogen gives a conversion of only 40%, and when mixed 50-50 with CO_2, the conversion drops.

That pure hydrogen didn't give as high a conversion as CO and water has been reported before by the Bureau of Mines and was the basis of the start of this research program in 1968.

When the off-gas from the 50-50 run was analyzed, it was found that some carbon monoxide had been formed. This suggests that maybe some of the reverse reaction of hydrogen plus carbon dioxide to water and carbon monoxide had occurred.

What is significant about the reaction with hydrogen is that the low conversion shows that the CO-water shift reaction is a much more effective scheme.

$N_2 + CO_2$

The lower line in Figure 6 shows the conversion for N_2, and N_2 plus CO_2 used as a feed gas. The conversion this line shows is about what should be expected if the volatile matter alone in the coal is driven off. Probably no reaction occurred here other than driving off the

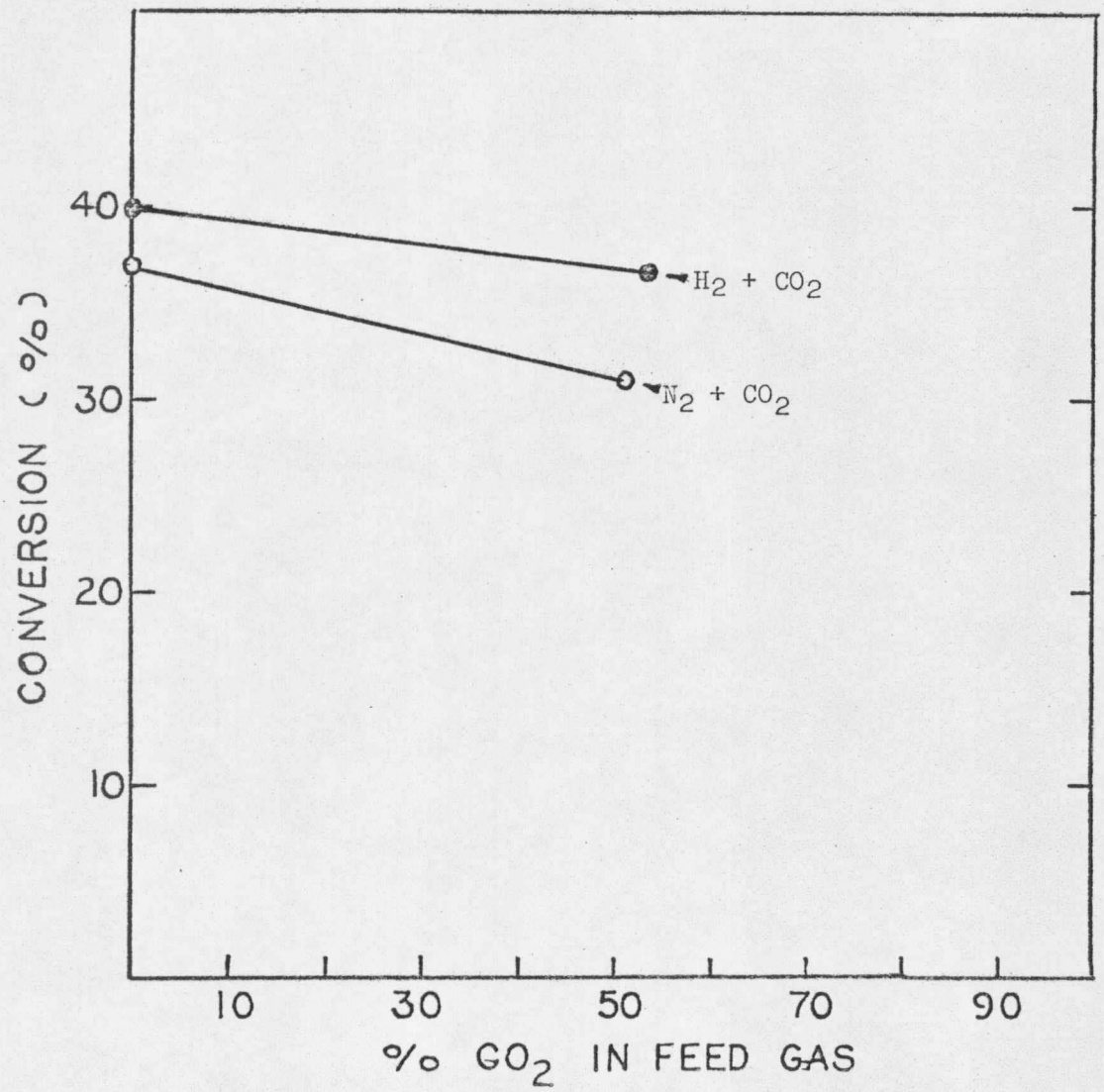

Figure 6. Effect of Other Feed Gases on Conversion

volatile matter. The line shown here essentially indicates that the CO-water shift reaction increases the conversion from about 35% to around double that.

DISTRIBUTION OF LIQUID PRODUCTS

In Figure 7, as a function of the percent CO_2 in the feed gas, is plotted the fraction of the total moisture and ash free coal converted that gives a liquid boiling over 90°C. The upper line is for 1200 and 1500 psig runs, and the lower line is for runs made at 900 psig initial pressure. These lines imply two things:

1. 70 to 80 percent of the product boils at a temperature higher than the boiling point of benzene.
2. If the hypothesis proposed by Nguyen that only about 5% of the coal is converted to gaseous hydrocarbons, then 15 to 20 percent of the converted coal is liquid that boils around the benzene range.

Figure 7 says that in the products separation step in a process plant producing these liquids, three liquid products would be obtained. For a one hundred pound charge of product liquid to a column (not including extraction solvent) about 74 pounds would be phenanthrene, 18.5 pounds would be in the range of MHD fuel (solid at ambient temperature) and about 7.5 pounds would be similar to benzene and could be used either as MHD fuel or extraction solvent.

Figure 7 also shows that the higher pressure produces more of the

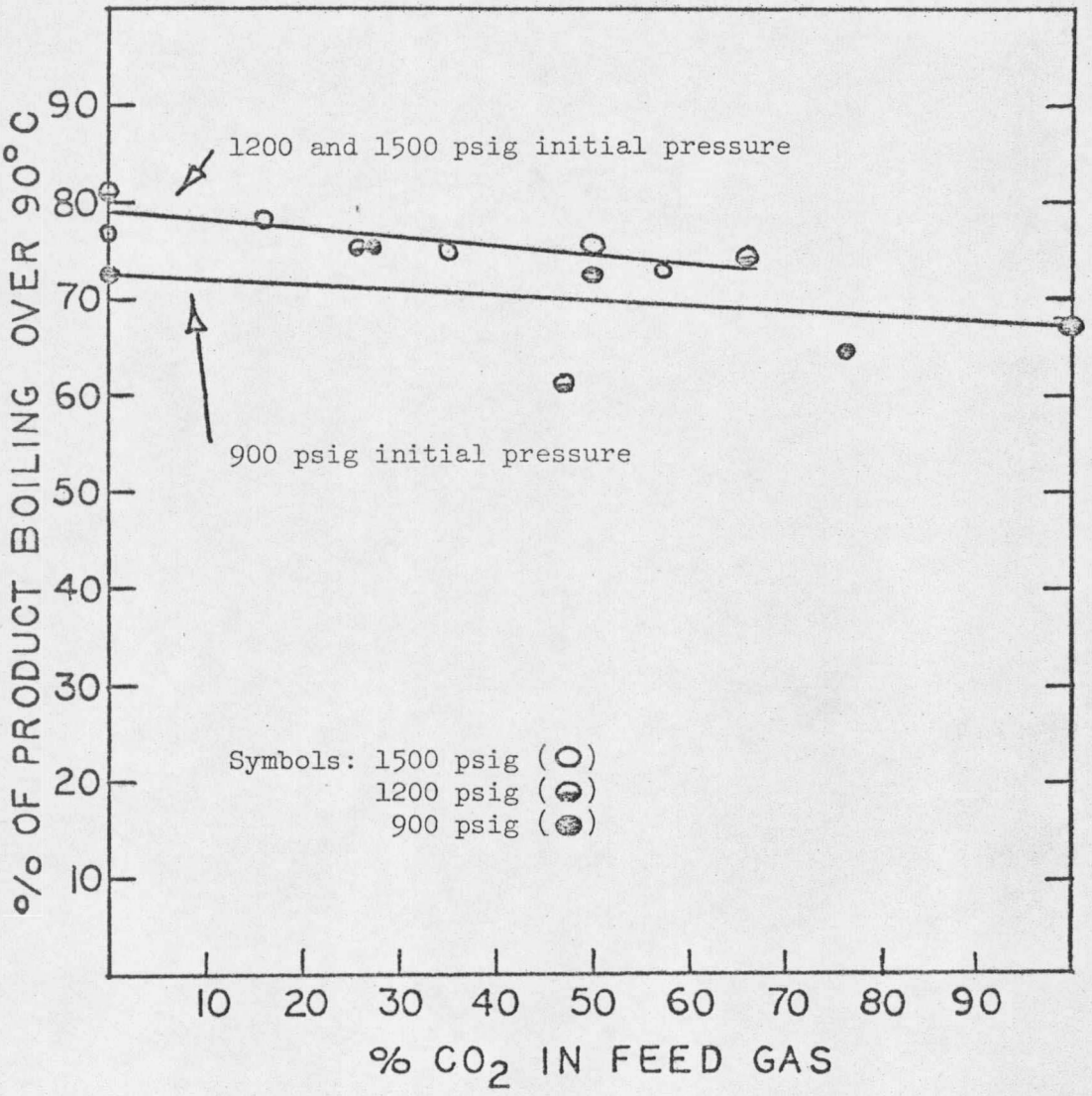

Figure 7. Amount of Product Boiling Over 90°C.

high boiling product. This too can be explained by Le Chatelier's rule. More pressure stress will be relieved on the system if a few larger high boiling molecules are formed than if many smaller low boiling molecules are formed.

GAS ANALYSES

900 and 1200 psig runs

The off-gas was analyzed for the ratio of CO_2:CO. This data was then presented as a function of the CO_2:CO ratio in the feed gas. No conclusions were made from this data concerning the gas reaction taking place because the off-gas was not analyzed for all things present, and the results for similar runs scattered widely. Figure 8 presents the results for 900 psig runs, and Figure 9 presents results for 1200 and 1500 psig runs. Because of equipment malfunctions, not as much data was available for these graphs as for the conversion graphs.

To explain Figures 8 and 9, first of all, if no reaction had taken place, the curves should have been strainght lines through the origin with a slope of positive one. For 900 and 1200 psig runs, the graphs show that, for runs with up to 50% CO_2 in the feed gas, the output gas CO_2:CO ratio is approximately 1:1. This means that the off-gas contains approximately equal amounts of CO_2 and CO. If there is more CO present than CO_2 initially, the reaction will proceed to the point where enough CO_2 is produced to give equal amounts of the two gases. Thus, another reason for lower conversions as CO_2 feed increases is that less reaction

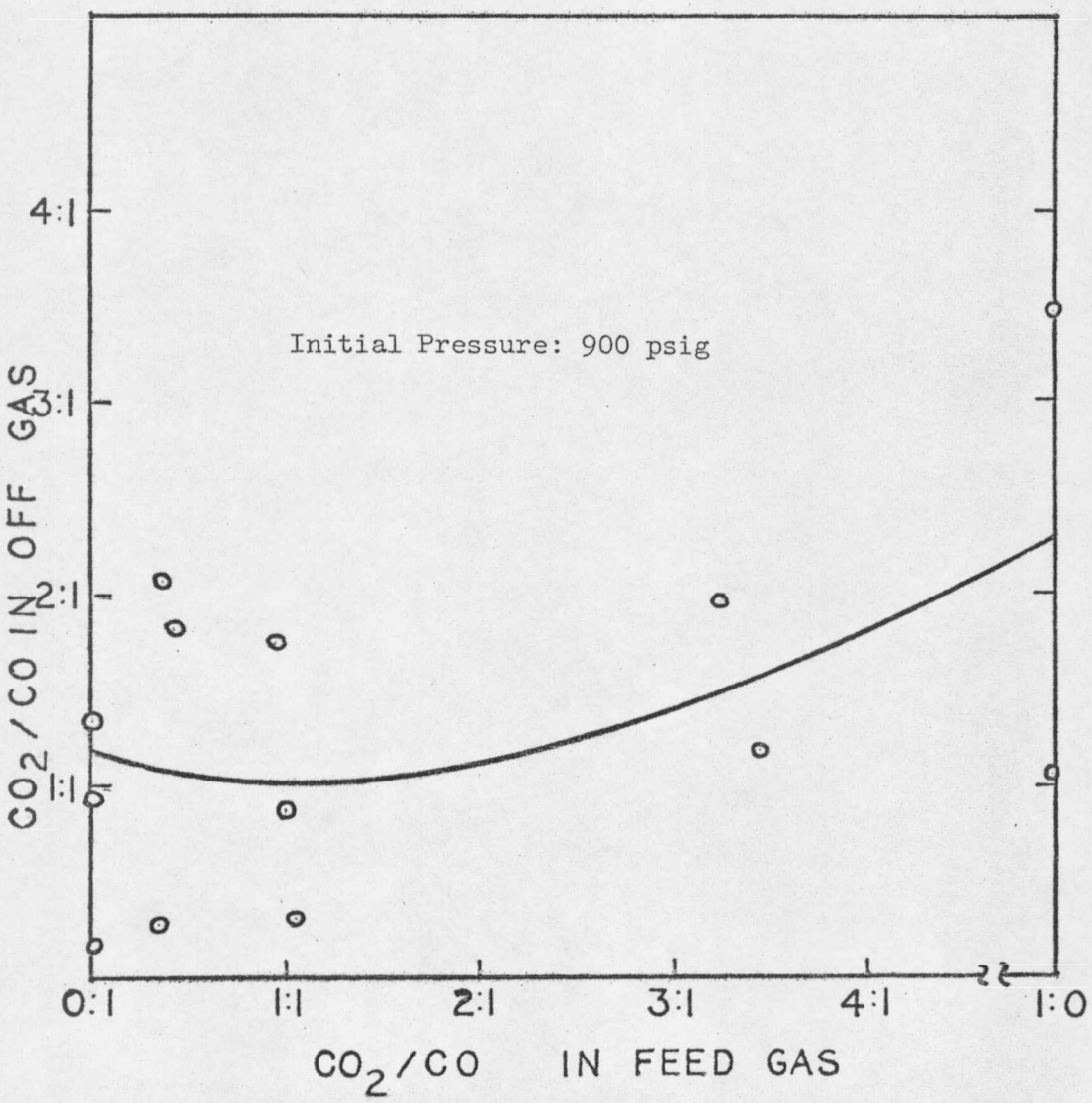

Figure 8. 900 psig Initial Pressure Gas Analysis

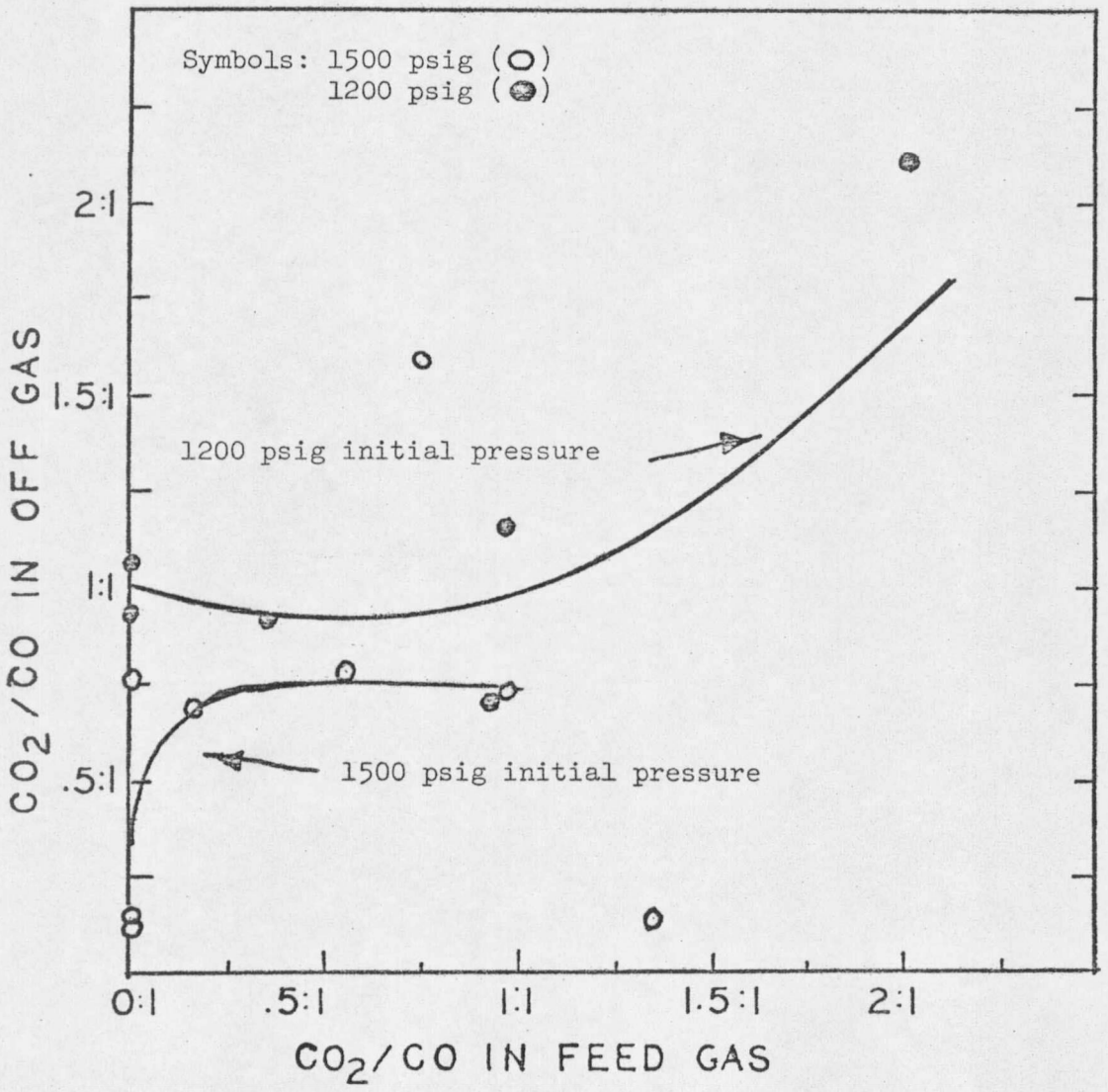

Figure 9. 1200 and 1500 psig Initial Pressure Gas Analyses

has to take place to balance the CO and CO_2 present.

By the equilibrium conversions, more CO_2 should be present than 50% at equilibrium for feeds less than 50% CO_2 gas input; a 50% conversion of the shift reaction when the feed is pure CO giving a 1:1 CO_2 to CO ratio in the off-gas. The experimental data does show this for 900 and 1200 psig runs, but the error in the data could be pretty large, so to conclude that the shift reaction proceeds to 50% conversion is very risky.

Above the 1:1 input gas mixture for the 900 and 1200 psig runs, the system no longer becomes balanced, mainly because the reverse shift reaction would have to take place for this to happen or CO_2 would have to react with fixed carbon to form CO, a reaction which does not take place appreciably at 450°C. Also, at input gas ratios above 1:1, conversions of coal are so low as to be of no commercial interest.

1500 psig runs:

At 1500 psig initial pressure runs, Figure 9 shows that less CO_2 is produced; the off-gas CO_2:CO ratio never reaches 1:1. This shows that the actual shift gas conversion is lower at this higher pressure, and the CO present initially is in great excess. It is apparent that the CO will react to produce enough hydrogen to liquify the coal that is to be liquified, probably as much or more than in a 1200 psig run, but the CO_2 produced is still much less than the CO present. The curve shows also that probably no back shift reaction occurs to give

an off-gas CO_2:CO ratio of 1:1, probably because all available hydrogen reacted with the coal and none was left to react to form CO and water.

The data available for the 1500 psig runs were much less than for the other pressures, so not too much weight should be placed on any conclusions drawn from this curve.

DESIGN USEFULNESS OF GAS ANALYSES

Probably the most useful facts that can be gleaned from Figures 8 and 9 are that they show what CO_2:CO ratios can be expected in the off-gas. The off-gas will, in all cases, have to be scrubbed of H_2S and other impurities, but, more than likely, these graphs show that by operating at a pressure and CO_2 composition that will give a relatively high conversion, much absorption equipment can be cut from the plant designs, perhaps enough to justify the lower conversions.

It is to be stressed that the ordinates of Figures 8 and 9 give only the relative ratio of CO_2 to CO in the off-gas. They say nothing of the total composition or amount of the off-gas.

AMOUNT OF WATER REACTED

Figure 10 shows the average amount of water used in a reaction as a function of CO_2 composition and total pressure. The purpose of this graph is its use in determining the amount of make up water necessary to be supplied to a continuous recycle reactor.

The ordinate of Figure 10 presents the data as the fraction of total water charged (30 gms in all cases) that was actually used in

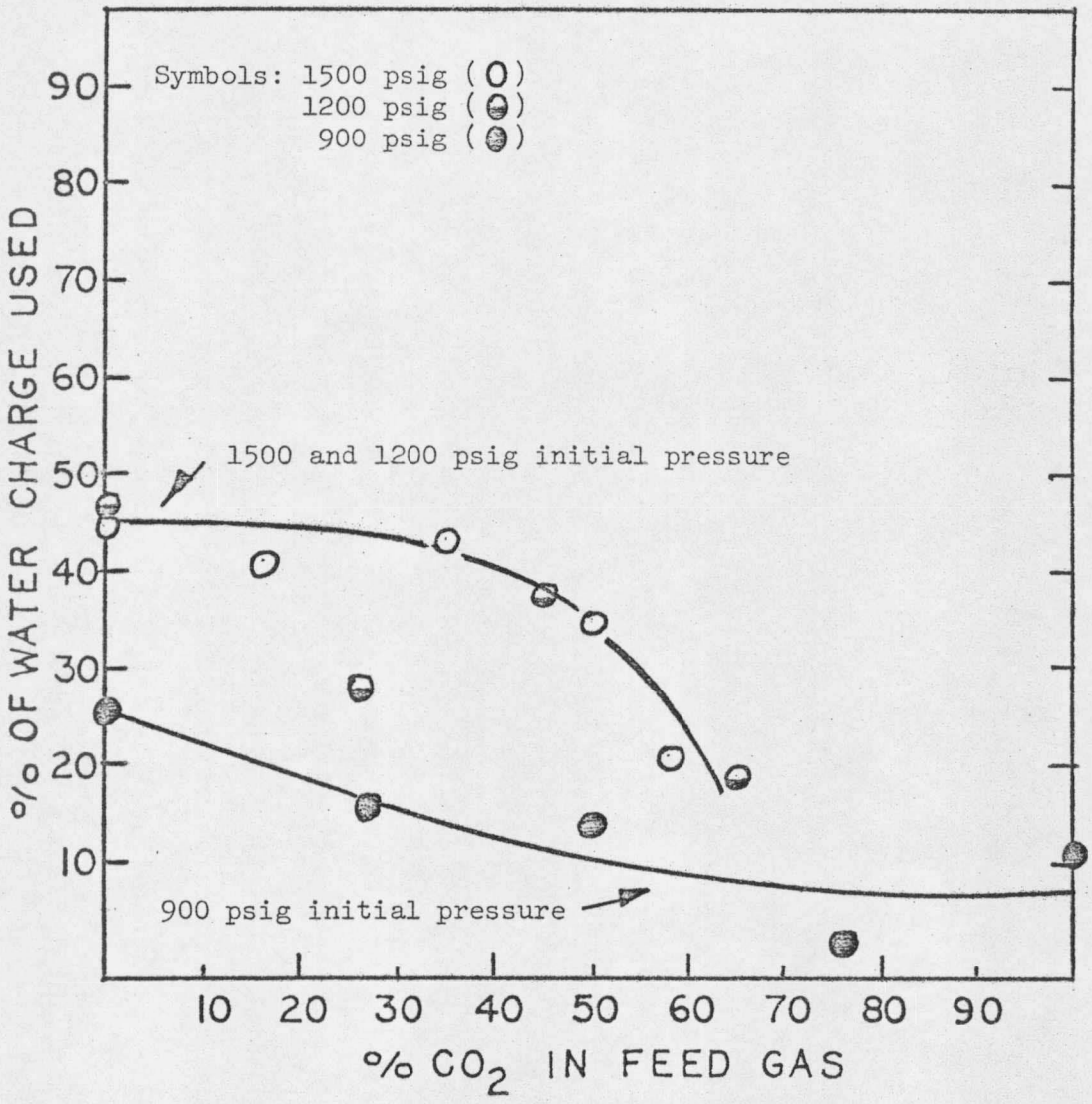

Figure 10. Weight Fraction of Water Charged that was used in the Reaction (30 gms. charged)

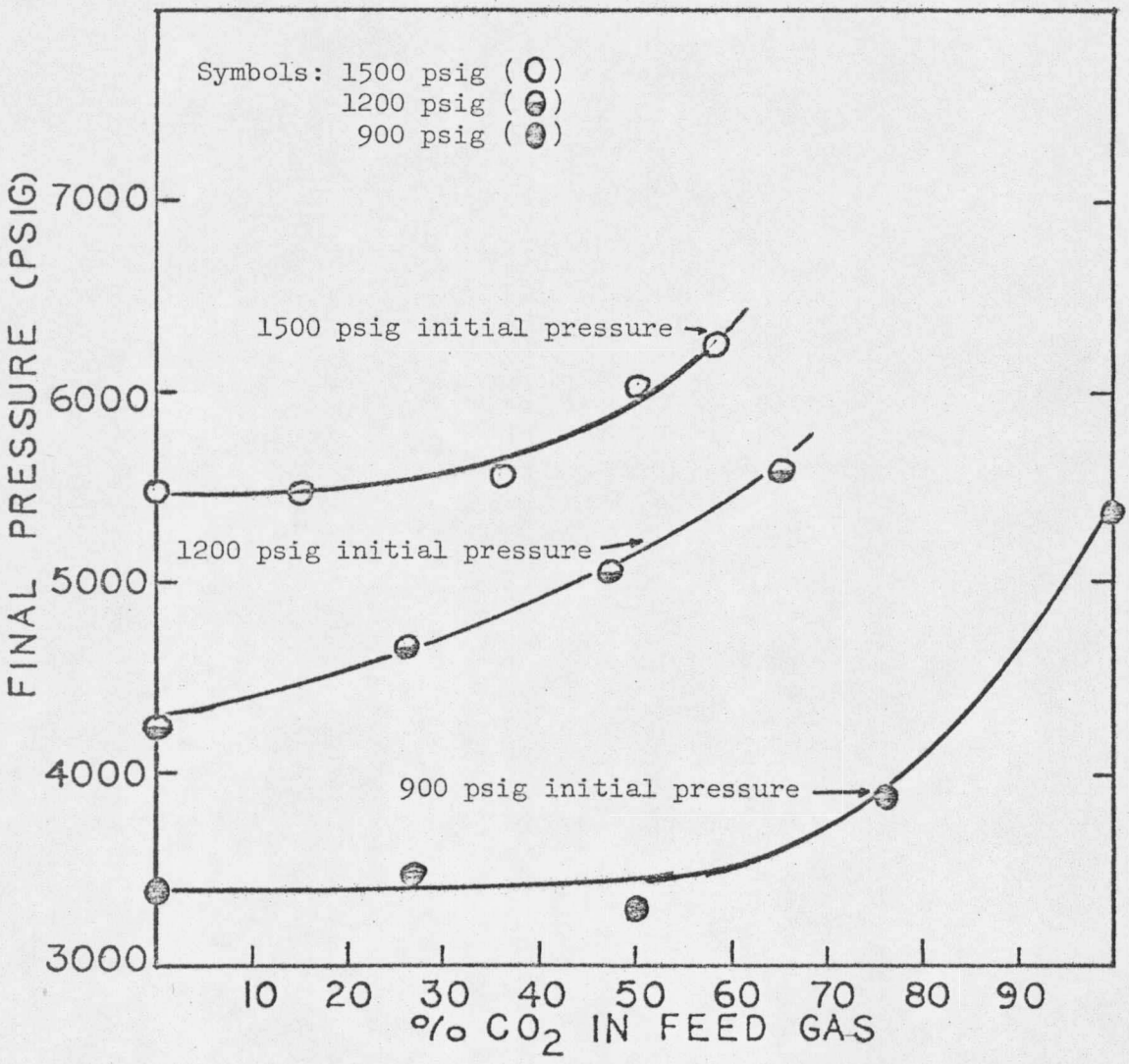

Figure 11. Average Final Reactor Pressure at 450°C.

the reaction.

REACTOR OPERATING PRESSURE

The final graph, Figure 11, shows the pressure of the batch reactor at 450°C as a function of total initial pressure and CO_2 feed composition. This final pressure is the operating pressure continuous reactors would have to be designed for. Also, as had already been stated, the operating pressure has a great effect on the equilibrium conversion of the shift reaction, and is possibly the reason that the coal conversion drops more sharply for high initial reactor pressures than for low initial pressures as the feed gas CO_2 composition increases.

PRODUCT ANALYSIS

No product analysis was made for the runs presented in this thesis. York had Huffman Laboratories analyse the product and char that resulted from liquification of Colstrip sub-bituminuous coal, the results of which are presented in Table II.

TABLE II. Proximate and Ultimate Analyses and Molecular Weight Determinations of Hydrogenated Product and Char

ANALYSIS	CHAR	HYDROGENATED PRODUCT
Proximate		
Water	1.2%	
Volatile	19.5%	
Fixed Carbon	49.7%	
Ash	29.6%	
Ultimate		
Ash	29.7%	0.02%
Hydrogen	3.3%	7.71%
Carbon	56.6%	84.10%
Sulfur	0.3%	0.24%
Nitrogen	1.0%	1.86%
Oxygen	9.1%	6.07%
Molecular Weight		365

CONCLUSIONS

1. The drop in the conversion of coal to benzene soluble products that happens when the amount of CO_2 increases in the gaseous feed is caused by the decrease in the conversion to hydrogen in the CO-water shift reaction.
2. At feed gas compositions over 50% CO_2, the coal conversions at the three pressures studied approach the same value because the conversion to hydrogen in the shift reaction decreases as the pressure increases.
3. Mixtures of CO_2 and H_2, and pure hydrogen as feed gas give much lower conversions than pure CO or mixtures of CO and CO_2.
4. From 70 to 80 percent of the product is liquid boiling over 90°; the higher pressures giving the higher percentages.
5. Off-gas analyses of 900 and 1200 psig initial pressure runs gave a 1:1 ratio in the relative amount of CO_2 to CO present.
6. Off-gas analyses of 1500 psig initial pressure runs showed that at this pressure the shift reaction was not as complete as at 1200 and 900 psig. At 1500 psig, the CO present was probably in excess of that necessary to convert the coal.
7. The amount of water used in the reaction was in all cases less than 50% of the water charged.
8. The difference in operating pressure between a 1500 psig and a 900 psig initial pressure run at high CO_2 compositions in the feed gas was probably great enough to cause a great difference in the shift reaction conversion to hydrogen, the lower pressure having

higher equilibrium conversion.

RECOMMENDATIONS FOR FUTURE STUDY

1. The most important quantity to determine right now is whether a five minute residence time in a continuous reactor is a reasonable figure. Therefore, a continuous reactor should be built, no matter what the obstacles, to determine if the system can be run continuously and then to obtain global rate data on the reaction occurring.
2. For distillation purposes, a large quantity of product should be made to obtain product distribution data.
3. Data must be obtained on the extraction of product and phenanthrene from the unreacted coal. The amount of benzene to do a complete extraction must be found, and the residence times in continuous extractors must be found.
4. Data must be obtained on separation of the unreacted coal from the extractor effluent. Whether filters or centrifuges can be used must be determined.
5. The heat of combustion of the product must be determined.
6. The viscosity of the coal-phenanthrene slurry must be found before pump designs can be made. Also, the viscosity of the liquid product stream has to be found for the same reason.

APPENDIX

TABLE III: Run Data

Run No.	Total Initial Pressure	Initial PCO_2	Compos-ition %	Conv. x frac.	L:C frac.	CO_2/CO in	CO_2/CO out	Final Pressure	gms H_2O Used
1	1430	0	0	.628	.675	0	.103	5120	13.6
2	1510	0	0	.043	None didn't react 450°C	0	.133	2700 190°	15.9
3	1490	530	35.6	53.6	None	.552	.782	5400	5.91
4	Blew Rupture Disk								
5	1460	840	57.5	.281	.702	1.35	.144	6510	3.33
6	1470	630	42.8	.597	1	.75	1.59	5900	9.78
7	1440	710	49.3	.581	.77	.972	.731	6100	10.13
8	1290	620	48.1	.579	.70	.925	.709	4890	6.78
9	900	900	100	.61	.1132	∞	1.087	5590	4.65
10	890	890	100	.254	.423	∞	17.16	5320	4.28
11	850	850	100	.241	1.36	∞	3.47	5270	.6
12	890	450	50.6	.576	None	1.02	.898	3300	4.13
13	900	0	0	.57	.73	0	.182	3610	6.11
14	670	340	50.7	.4735	None	1.03	None	2700	None
15	910	PN_2=460	.505	.31	.389	-	-	4350	.02
16	Pure N_2 P_t = 850		-	.37	.32	-	-	3590	.94 made
17	P=840 H_2+CO_2	PH_2=450	.535	.368	.39	∞	.035	3200	.19
18	Pure H_2	P=860		.40	.62	÷	.319		0
19	860	440	.512	.57	.748	1.05	.309	3520	3.08

TABLE III: Run Data (Cont).

Run No.	Initial Pressure	Initial PCO_2	Composition %	Conv. x frac.	L:C frac.	CO_2/CO in	CO_2/CO out	Final Pressure	gms H_2O Use
20	890	690	77	.399	.848	3.45	1.191	4390	1.4
21	880	220	25	.607	.739	.333	.293	3590	5.09
22	890	680	76	.487	.521	3.24	None	3890	1.51
23	910	240	26.4	.536	.85	.358	2.057	3680	4.99
24	900	0	90	.65	.717	0	1.338	3380	7.1
25	850	650	76.5	.45	.573	3.25	1.964	3490	1.02
26	870	260	30	.572	.622	.426	1.805	3200	4.96
27	900	0	0	.638	.734	0	.973	3290	7.01
28	840	410	48.8	.502	.70	.953	1.76	3090	4.99
29	410	210	51	.368	.64	1.05		1880	4.00
30	1100	0	0	.515	.91	0	.941	3620	8.99
31	860	0	0	.534	.713	0	1.363	3000	11.02
32	1500	540	36	.62	.793	None	None	5700	9.98
33	1490	0	0	.687	.82	-	-	5660	9.99
34	1520	280	18.4	.621	.76	-	-	4490	9.2
35	1500	230	15.33	.673	.76	-	-	5300	8.98
36	1560	230	41.7	.66	.82	-	-	5500	10.99
37	1500	530	35.3	.708	.701	-	-	5180	26.02
38	1500	225	15	.726	.78	.176	1.199	5780	19.49
39	1550	0	0	.762	.81	0	.758	5720	17.01
40	1210	810	66.9	.503	.82	2.02	2.11	5800	8.02
41	1500	880	Blew Up						

TABLE III: Run Data (Cont.)

42	1220	600	49.2	.52	.57	.968	1.162	2810	22
43	1500	890	59	.498	.75	-	-	5170	9.91
44	1550	890	57	.52	.73	-	-	7050	6.01
45	1460	760	52.1	.58	.75	-	-	6200	10.99
46	1240	810	65.3	.512	.752	-	-	5920	10.2
47	1250	0	0	.63	.705	-	-	4520	15.04
48	1190	770	64.7	.527	.657	-	-	5180	7.97
49	1210	310	25.6	.61	.76	-	-	5000	10.99
50	1210	310	25.6	.64	.735	-	-	4320	8.02
51	1190	520	43.7	.645	.57	-	-	2600	5.02
52	1240	0	0	.721	.81	0	1.071	4610	18.6
53	1220	320	26.2	.579	.745	.356	.929	4750	6.05

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