

CO-STEAM COAL LIQUEFACTION IN A BATCH REACTOR

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ABSTRACT

The CO-steam process of coal liquefaction was studied at the Colorado School of Mines to determine the effects of temperature and pressure on the liquefaction and desulfurization of a high sulfur bituminous coal. The CO-steam process utilizes the shift reaction, which reacts water and carbon monoxide to form hydrogen and carbon dioxide, as the source of hydrogen for hydrogenation and desulfurization of the coal. The coal was dissolved with a creosote oil solvent before reaction.

Experimentation was done in batch autoclave reactors. Reaction temperatures were varied from 375°C to 475°C and reaction pressures were varied from 2500 psig to 3500 psig by varying the initial carbon monoxide pressure at room temperature from 400 psig to 600 psig. Fixed operating variables were: solvent-to-coal ratio, water-to-coal ratio, reaction time, and solvent type. The following analyses were performed on the liquid coal and solvent mixture: percent benzene insolubles, total sulfur analysis, kinematic viscosity, carbon hydrogen analysis, reaction gas analysis, and heating values. Sulfur balances and overall material balances were calculated.

The results indicate that conversion of coal to liquid increases with an increase in reaction temperature over the range studied. However, changes in carbon monoxide pressures did not appear to have any definite effect on coal conversion in the pressure range investigated. Coal conversions ranged from 57 to 99 percent on a moisture and ash-free basis.

Coal desulfurization increased with an increase in reaction temperature over the range studied. Desulfurization results found in this study were not as good as those potentially attainable using pure hydrogen. The maximum desulfurization attained in this study was 57 percent. The desulfurization obtained may not be the maximum attainable under the reaction conditions studied because of the equilibrium limitations of a batch reactor.

INTRODUCTION

Now, because of the energy shortage, pollution controls and dependence on foreign oil sources, there is a growing interest in coal liquefaction to produce a clean fuel oil from domestic resources. Many power plants burn fuel oil and natural gas instead of coal to meet environmental pollution regulations. If a coal-derived oil were used to replace the current feeds to power plants this would release the petroleum oils and gas consumed by power plants for use in home heating, industry, and motor fuel, thus relieving the shortage of petroleum-derived fuels. Conversion of coal to clean fuels can be accomplished both by liquefaction and gasification; however, the liquefaction conversion has a higher thermal efficiency. In addition, the liquid fuel produced in liquefaction has a higher energy density than gaseous fuels and therefore is cheaper to transport and store.

Converting coal to a liquid generally requires the addition of hydrogen. If the hydrogen content of the coal is increased by 2 to 3 percent, mild liquefaction results. The heavy oil produced under mild liquefaction conditions can be used as feed to electric power boiler generators. If the hydrogen content of the coal is increased by 6 percent or more, light oils and gasoline are produced. If the liquefied coal is to be used as a boiler feed a heavy oil is preferred because it is less costly to produce due to less hydrogen consumption (1) and it has a higher energy density (2). In addition the heavy oil product may be used as a low-sulfur utility fuel either directly or after further refinement by removal of the ash and unreacted coal. Its use would depend on the design of the furnace to be fired with the synthetic liquid fuel.

Hydrogen is a very expensive raw material; therefore, liquefaction of coal using hydrogen directly would be a costly process. A way around this problem is to produce the hydrogen needed for the liquefaction of coal from less expensive raw materials. This can be accomplished using the water-gas shift reaction. In this reaction water and carbon monoxide react to form hydrogen and carbon dioxide and both starting materials, water and carbon monoxide, are inexpensive and readily available.

The source of hydrogen used in liquefying the coal in the CO-steam process comes from the reaction of carbon monoxide and water to form hydrogen and carbon dioxide. The interaction of carbon monoxide and water with coal is not as simple as the interaction of pure hydrogen and coal (6). Carbon monoxide and water have been found to liquefy coal more completely than pure hydrogen as demonstrated by Appell, et al. (4). Not only does carbon monoxide and water liquefy the coal to a greater extent, but carbon monoxide is much cheaper and easier to obtain than hydrogen. In the future, one possible source of carbon monoxide would be from a synthesis gas.

The purpose of this study was to determine the effects of two operating variables, temperature and pressure, on the liquefaction of a bituminous coal using batch autoclave reactors. Reaction temperatures were varied from 375°C to 475°C and initial carbon monoxide pressures were varied from 400 psi to 600 psi. Fixed operating variables were: solvent-to-coal ratio, water-to-coal ratio, reaction time, and solvent type. The following analyses were performed on the liquid product: percent benzene insolubles, total sulfur analysis, kinematic viscosity, carbon hydrogen analysis, specific gravity, reaction gas analysis, and heating value. In addition, an overall material balance and sulfur balance was performed.

CARBON MONOXIDE-STEAM LIQUEFACTION - LITERATURE SURVEY

The following is a summary of all currently published work on the CO-steam process.

Cellulose Liquefaction

The Bureau of Mines (1) has experimentally converted cellulose, primary constituent of organic solid waste, to a low sulfur oil. Many types of cellulosic wastes have been converted to oil by reaction with carbon monoxide and water at temperatures of 350°C to 400°C and pressures near 4000 psig in the presence of various catalysts and solvents. Cellulose conversions of 90 percent and better were obtained.

Sucrose liquefaction was also studied using a continuous reactor with maximum reaction conditions of 500°C and 5000 psig. Oil yields of over 30 percent were obtained. This compares with oil yields of 40 to 50 percent for the cellulose liquefaction.

Work was also done by Yavorsky, et al. (2) using the CO-steam process to liquefy urban refuse. A continuous reactor with a flow capacity of 1 lb per hour was used. Sucrose was used to select the optimum conditions for the reaction of refuse. Results from the sucrose runs indicated that conversion to oil was weakly dependent on total pressure and strongly temperature sensitive up to the optimum at 350°C. Oil yields of 23 percent for garbage up to 38 percent for sucrose were obtained. The ultimate theoretical yield of oil is 50 percent because approximately half the carbohydrate material is oxygen which cannot be converted to oil. A preliminary cost analysis showed that a large scale refuse conversion plant could be economically operated.

Early CO-Steam Work

In 1921 Fisher (3) reported using carbon monoxide and water in dehydrogenating coal. He reported higher yields of ether-soluble material using carbon monoxide and water than with hydrogen at similar conditions. Low overall conversion along with several other problems caused the carbon monoxide plus water approach to coal hydrogenation to be ignored after 1925.

Lignite Liquefaction

Batch tests were conducted by Appell, et al. (4,5,6,7) using a 500 ml rocking autoclave filled with 2 moles of carbon monoxide, lignite coal, water, and solvent. The objective of the work was to convert lignite to low sulfur fuel oil. It was believed that hydrogenation of coal using carbon monoxide and water proceeded via nascent hydrogen formed by the water-gas shift reaction. It now appears that carbon monoxide and water react with lignite in a more complex manner and that a number of factors are involved. Carbon monoxide and steam had higher conversion levels and reaction rates than those obtained using hydrogen under similar conditions. Results also indicated that both carbon monoxide and water must be present if good conversions are to be obtained, and that increasing the carbon monoxide pressure has a greater effect than increasing the steam pressure. These effects are dependent on the ratio of carbon monoxide to water. Conversion of lignite increases with increasing amounts of carbon monoxide and steam; however, there was an optimum temperature. Decreased conversion resulted after the temperatures were increased past 400°C.

Appell, et al. (8) also did work using different solvent types and catalysts. Several lignite tars and pitches were used as solvents and all gave good results for lignite liquefaction. The type of solvent was found more important than the amount. In the presence of a good solvent, it is possible to reduce the operating pressure and maintain acceptable conversions (85-90%). Heterocyclic amines were found to have a catalytic effect when used with carbon monoxide and water. The effectiveness of the heterocyclic amines was related to the increased boiling point of the solvent.

EXPERIMENTAL DESIGN

The object of this study was to determine the effects of varying reaction temperature and the initial moles of carbon monoxide (pressure) on the liquefaction of coal. The coal used in this study was a bituminous coal from the Pittsburgh number 8 seam, Ireland Mine, in West Virginia. A proximate analysis, ultimate analysis, and a sulfur form distribution can be seen in Table 1. The bituminous coal was selected because of the relative difficulty in liquefying it. Also, the primary thrust of previous work was in liquefying a low rank coal such as a lignite.

Reaction temperatures were examined at five levels from 375-475°C. These temperatures are somewhat higher than those used in previous CO-steam work; however, it was thought that more severe conditions were needed to convert the high rank bituminous coal. Five temperature levels were used in order to obtain a definite trend in conversion as a function of temperature.

Two major cost factors in liquefying coal are the capital costs for high pressure equipment and the carbon monoxide cost. Therefore, if comparatively low operating pressures yield an acceptable

Table 1. Ultimate and Proximate Analyses of Coal Used.

Coal: IM
 Source: West Virginia
 Rank: Bituminous

<u>Proximate Analysis</u>	<u>As Received</u>	<u>Dry Basis</u>
% Moisture	0.75	-
% Ash	12.99	13.16
% Volatile	34.68	39.94
% Fixed Carbon	<u>51.58</u>	<u>51.90</u>
	100.00	100.00
 <u>Ultimate Analysis</u>		
% Moisture	0.75	-
% Carbon	61.09	61.55
% Hydrogen	4.54	4.57
% Nitrogen	0.95	0.96
% Chlorine	0.05	0.05
% Sulfur	4.14	4.18
% Ash	12.99	13.16
% Oxygen	<u>15.49</u>	<u>15.53</u>
	100.00	100.00
Heating Value (Btu)	11,143	11,227
% Total Sulfur	4.140	
% Organic Sulfur	3.157	
% Sulfate Sulfur	0.037	
% Pyritic Sulfur	0.946	

conversion of coal to oil, capital investment could be saved due to lower carbon monoxide consumption and utilization of lower pressure equipment. With this in mind, the low initial pressures of 400 to 600 psig of carbon monoxide were selected. Another factor in selecting the low initial pressures of carbon monoxide was the pressure limitations of the equipment used. The final pressures in some cases could exceed 3000 psig and the limit of the equipment is approximately 4000 psig at 400°C. It was decided not to exceed 600 psig initial pressure.

Fixed operating variables were as follows:

- 1) Reaction time: 1 hr
- 2) Water-to-coal weight ratio: 1.5:1
- 3) Solvent-to-coal weight ratio: 3:1
- 4) Solvent type: Creosote oil

Determination of the percent conversion of coal to liquid product was done with benzene in a Soxhlet extractor. The percent conversion was 100% less the percent of insoluble residue remaining after benzene extraction. Calculations were done on an ash-free basis. Sulfur analysis on the liquid product was done to determine the percent desulfurization of the coal and also in conjunction with the off-gas analysis allowed calculation of a sulfur balance. Carbon hydrogen analysis was done to determine the carbon-hydrogen ratio of the liquefied coal product to determine the approximate hydrogenation and chemical alteration of the coal through processing.

Table 2 shows the run numbers and the corresponding reaction conditions. Each variable combination was triply replicated, resulting in an A, B, and C run at each reaction condition. All experimental runs were performed in a random order, not in the order listed in Table 2.

Table 2. Run conditions.

Run No.	Reaction Temperature (°C)	Initial CO Pressure (psig) *
1	375	400
2	375	500
3	375	600
4	400	400
5	400	500
6	400	600
7	425	400
8	425	500
9	425	600
10	450	400
11	450	500
12	450	600
13	475	400
14	475	500
15	475	600

*At room temperature

EXPERIMENTAL PROCEDURE

The following procedures are listed in the order in which they were performed on each individual run (see Figure 1).

All experimental runs were performed in a random order.

Coal Preparation

- 1) Raw coal from the mine was crushed and screened and all that which passed through a 28 mesh screen was retained.
- 2) One large sample of -28 mesh coal was then split into 16 equal size samples using a Jones sample splitter. This procedure was done three times in order to make enough samples for all the runs to be carried out.
- 3) Each sample was placed in a beaker with a watch glass cover and used when needed.

Processing

Reaction of the coal proceeded as follows:

- 1) The empty reaction vessel and head assembly were weighed.
- 2) One hundred fifty grams of anthracene oil solvent, 75 grams of distilled water, and 50 grams of coal were weighed and added to the bomb.
- 3) The reaction vessel assembly was reassembled and then reweighed to determine the amount of reactants added.
- 4) The assembled reaction assembly was then inserted into the heating jacket and shaking assembly. The connecting lines were then attached and the thermocouple was inserted into the thermowell.
- 5) The reaction vessel was then purged three times by pressuring to 500 psig with helium, then venting to atmospheric pressure. On the third pressurization the reaction assembly and connecting lines were leak tested using a water-soap solution. If there were no leaks the reaction vessel was pressurized with carbon monoxide once to 500 psig, then to the initial carbon monoxide pressure required for that run. The system temperature was also recorded in order to determine the weight of CO added to the reaction vessel.
- 6) The heating jacket and shaker assembly were both turned on and the temperature controller for the heating jacket set at reaction temperature.
- 7) When the system reached reaction temperature the total pressure was taken. (Three runs were done at the same conditions, only on the third run the pressure was not checked so no gas is lost. This was done so that an accurate overall material balance could be obtained.)

8) The system was allowed to react for one hour at which time both the shaker and the heater were switched off, the connecting line to the vessel was removed and the reaction vessel assembly was removed from the heating jacket. The reaction vessel was then placed in front of a fan and cooled to room temperature. This caused the temperature inside the bomb to decrease rapidly, thus quenching the reaction.

9) When the reaction vessel had cooled to room temperature the reaction vessel assembly was then weighed and carried to the gas analysis system.

10) After completion of the gas analysis, the reaction vessel was opened and the liquid product poured out into a beaker. In order to remove all the liquid product the inside of the reaction vessel was washed with acetone. The acetone wash was then poured in with the liquid product. This mixture was then placed in an oven at approximately 50°C until all the acetone was vaporized. The beaker was then weighed to determine the amount of liquid product recovered.

EQUIPMENT

Two reactor systems of the batch autoclave generic type were used in this study. A gas delivery system, a reaction vessel, and a shaking assembly were the functional parts of the reactor systems. The reaction vessels were manufactured by the American Instrument Company (AMINCO) of Silver Spring, Maryland, and were from the 4 3/8-in. series. Both reaction vessels had inside depths of 10 in., inside diam. of 3 5/16 in., and approximate weights of 50 lbs. The vessels were fabricated from AISI 347 stainless steel. The vessels had a working pressure rating of 5,050 psi at 100°F and had an effective volume of 1410 ml. Two shaking assemblies were used in the reactor system. The shaking assemblies were standard Aminco 4 3/8-in. series and consisted of a 3,000-watt, 208-volt heating jacket mounted on a rocker assembly. The rockers for the shaking assemblies were actuated by 1/3-hp, 110-volt motors driving eccentric levers connected to the heating jackets. The heating jacket had the capacity to heat from room temperature to 400°C in approximately 1 1/2 hr. Aminco 30,000 psi valves and fittings were used to regulate the inlet and exit of the reaction gases from each reaction vessel. One reactor system was equipped with 0 to 3,000 pressure gauge. The other had a 0-5,000 psi pressure gauge. Tubing used on the shaking assemblies was 304 stainless steel, 1/4-in. o.d., and rated for operation at 100,000 psi at 100°F.

Leeds and Northrup Electromax III controllers, with Model 11906 SCR final control elements were used for temperature control. Temperatures were recorded on a Honeywell Electronik III two-channel continuous recorder. The temperature sensors were chromel-alumel thermocouples.

Both shaking assemblies were connected to purging-charging gas delivery systems. Each of these systems consisted of a helium cylinder, a carbon-monoxide gas cylinder, pressure regulators for each cylinder, and Aminco stainless steel tubing and fittings similar to those used on the shaking assemblies.

To analyze for the total sulfur content of the liquid coal, the Leco induction furnace technique was used. A gas purification train, an induction furnace and a semi-automatic titrator unit were the three components of the analysis system. The gas purifying train contained an acid tower, a dry reagent tower, and a rotameter, and was used to measure and scrub any residual sulfur from the entering oxygen. The induction furnace was a Leco model 521, equipped with the "L" modification on the combustion chamber. A special feature of the "L" modification was the inclusion of a high temperature igniter in the combustion chamber. The exhaust gases from the induction furnace combustion chamber were sent through an electrically heated glass delivery tube and into the Leco semi-automatic titrator model 518. The semi-automatic titrator used an idiometric reaction with a color change endpoint to analyze the combustion gases. The reported accuracy of the test is ± 0.01 weight percent sulfur. The Leco induction furnace technique used was ASTM D1552-64 (American Society for Testing and Materials, 1968, pp. 377-383).

Analysis of the reaction product gas was accomplished by gas chromatography. The gas chromatograph was fitted with an external valve oven, two eight-foot Porapak Q columns, and one six-foot molecular sieve column in a series by-pass arrangement. The columns were heated to 170°C . The chromatograph was supplied with a helium carrier gas. A heated thermal conductivity detector was used. The following components could be quantitatively determined:

- 1) CO
- 2) CO_2
- 3) CH_4
- 4) C_2H_6
- 5) C_3H_8
- 6) i- C_4H_{10}
- 7) n- C_4H_{10}
- 8) H_2S
- 9) COS

The hydrogen composition was determined indirectly using the average molecular weight and the hydrogen free gas composition of the reaction gases. The accuracy of the reported gas weight percents are ± 2.5 percent. Calibration of the gas chromatograph was accomplished by determining an average response factor for pure components relative to nitrogen, and an average retention time for each component was established.

RESULTS

Percent Conversion of Coal to Liquid

The results of the Soxhlet extractions are summarized in Figure 2. One definite trend shown by the data is that higher temperatures favor the liquefaction of coal. The carbon monoxide pressure effects are not as obvious. However, a trend can be seen if the highest and lowest pressure level are compared. At all but the lowest temperature investigated (375°C) the 600 psi conversion isobar was above the 400 psi conversion isobar. This suggests that higher initial pressures of carbon monoxide enhance the liquefaction of coal, which agrees with results from the Bureau of Mines research (5). Appell and Wender found that an increase of initial carbon monoxide pressure from 500 psi to 1100 psi results in an increase in conversion from approximately 40% to 70%, for a bituminous coal. Reaction temperatures and reaction times for the Bureau of Mines study were 425°C and 2 hours, respectively. A different solvent type, solvent-to-coal ratio, and water-to-coal ratio were used so the Bureau of Mines results cannot be directly compared with the results reported here. However, the conversions found in this study were higher than conversions of a bituminous coal reported by the Bureau of Mines. When all three isobars are plotted (Figure 2) no pressure trend seems apparent. The 500 psi isobar crosses both the 400 psi and the 600 psi isobars. This suggests that the pressure levels chosen were too close together for any trend to be observed.

Figure 3 shows the effect of hydrogen partial pressure on the conversion of the coal. The data was scattered, however the trend shows that increasing the hydrogen partial pressure increases the coal conversion. The reaction gas analysis was used to determine hydrogen partial pressures.

One problem in the analysis of the liquefied coal was the inaccuracy in the Soxhlet extraction procedure. Repeatability tests were done and the error in the Soxhlet extractions ranged between 2 to 15 percent.

The temperature and pressure readings reported have an accuracy of $\pm 2.5^\circ\text{C}$ and ± 10 psi respectively.

Sulfur Balances

A tabular comparison of the sulfur balances for all the C runs is shown in Table 3.

Table 3. Sulfur Balance (all weights in grams).

Run No.	Sulfur In Total	Sulfur Out (Reaction Gas)	Sulfur Out (Liq. Coal)	Sulfur Out Total	Difference	% Error
1C	2.7	1.0	2.0	3.0	+0.3	11.1
2C	2.8	1.3	1.9	3.2	+0.4	14.2
3C	2.7	1.0	2.0	3.0	+0.3	11.1
4C	2.7	1.4	1.8	3.2	+0.5	18.5
5C	2.7	0.4	1.9	2.3	-0.4	14.8
6C	2.8	1.3	1.7	3.0	+0.2	7.1
7C	2.7	2.2	1.7	3.9	+1.2	44.4
8C	2.7	1.6	1.5	3.1	+0.4	14.8
9C	2.7	1.3	1.7	3.0	+0.3	11.1
10C	2.7	1.5	1.5	3.0	+0.3	11.1
11C	2.7	2.0	1.4	3.4	+0.7	10.3
12C	2.7	1.6	1.5	3.1	+0.4	14.8
13C	2.7	1.7	1.0	2.7	0.0	0.0
14C	2.7	1.6	1.1	2.7	0.0	0.0
15C	2.7	1.6	1.1	2.7	0.0	0.0

The largest source for error in the sulfur balance calculations was the determination of the percent sulfur in the reaction gas. The determination of the sulfur content in the reaction gas was done using a gas chromatograph. The sulfur percentages can have errors up to 4.5 percent.

The error in the sulfur balances range from 0.0 to 44 percent. The average error was approximately 10 to 15 percent with more apparent sulfur being accounted for in the products than in the combined feed. This suggests that the sulfur analysis on the raw coal or the creosote oil was low or the percent sulfur in either the reaction gas or liquid coal was consistently high. Despite the aforementioned problems the results from both the sulfur balance and the overall material balance are encouraging.

Sulfur Removal

Total sulfur analyses on the liquid coal and solvent mixture are shown in Figure 4. The points plotted in Figure 4 were found from the average of the three runs at the same temperature and pressure. Increases in reaction temperature and carbon monoxide pressure decrease the amount of sulfur in the liquid product. The only deviation from this general trend occurs at 375°C and 400°C at an initial carbon monoxide pressure of 400 psi. At both these temperatures the lowest carbon monoxide pressure had better desulfurization than the higher pressures.

Following is a possible explanation of the crossing of the desulfurization isobars in Figure 4. Several considerations are listed below:

- 1) Higher reaction pressures were obtained by charging more carbon monoxide to the reactor. Since the amount of water charged is fixed, a higher carbon monoxide-to-water ratio increases the yield of hydrogen produced from the shift reaction.
- 2) Higher temperature increases the reaction rates for both the hydrogen desulfurization reaction and the shift conversion reaction.
- 3) However, the thermodynamic yields of H_2S and H_2 from the desulfurization reaction and the shift conversion reaction are greater at lower temperatures.
- 4) Partial desulfurization of coal occurs by devolatilization of the coal. More devolatilization occurs at lower system pressures.

Items 1 and 2 indicate that greater desulfurization occurs at higher temperature and pressure. However, item 3 indicates low temperatures are more favorable to desulfurization, and item 4 indicates an advantage for low pressures. These considerations offer a partial explanation for the reversal of pressure effects at lower temperatures and the flat temperature response at the lower temperatures investigated.

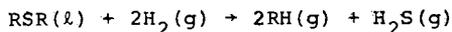
Figure 5 shows that the best desulfurization occurs at higher hydrogen partial pressures. This coincides with the higher temperatures investigated, and suggests that the shift reaction was going more to completion at higher temperatures as indicated in item 2.

The temperature effects on desulfurization are much more apparent. An increase in reaction temperature of $100^\circ C$ approximately doubles the desulfurization of the coal.

The error in the Leco procedure for determining the total sulfur in the coal product is ± 0.01 percent, which is not significant in comparison with the total sulfur percentages in the oil of 0.6 to 1.0 percent.

Actual desulfurization of the coal ranged from 23 to 57 percent. Desulfurization results on the same coal using hydrogen at similar reaction conditions were reported to be 77 percent desulfurization at $400^\circ C$ (9). Approximately 25 percent of the sulfur was removed using the CO-steam process at the same reaction temperatures. Apparently pure hydrogen gives much better desulfurization than carbon monoxide and water. Better desulfurization with hydrogen should be expected since there is more hydrogen in the gas phase present to react with the sulfur.

The primary desulfurization reaction that is favored by chemical equilibrium is reaction of sulfide sulfur in the coal with hydrogen gas. The reaction is:



A plot of coal desulfurization versus hydrogen partial pressure and reaction temperature was made to determine the effects of each on desulfurization. The plots are shown in Figures 5 and 6. Two conclusions can be made from these plots. One, desulfurization increases with an increase in hydrogen partial pressure, and desulfurization increases with an increase in reaction temperature. The hydrogen partial pressure has to be increased by 3 times to double the desulfurization, however, and increase of 25 percent in the reaction temperature doubles the desulfurization. It therefore appears that reaction temperature has a stronger effect on desulfurization than does hydrogen partial pressure.

It must be noted that the experimental runs were done in batch reactors. As a result the desulfurization is limited by equilibrium and therefore, the desulfurization obtained may not be the maximum attainable under the reaction conditions studied.

Carbon-Hydrogen Ratio of Coal Liquid

Tabular values of the C/H weight ratio are shown in Table 4. There appears to be no discernible trend in these results. The C/H ratios ranged from 14.5 to 15.8 with a standard deviation of 0.32.

The carbon hydrogen ratio of the raw coal and the raw solvent is 13.45 and 15.31 respectively. The carbon hydrogen ratio of the raw coal plus solvent slurry is 14.85. The average carbon hydrogen ratio of the mixture after treating was 14.97. Therefore, it appears that little hydrogenation of the coal and solvent occurred.

Table 4. Carbon-Hydrogen Ratios of Liquid Coal Product.

<u>Run No.</u>	<u>C/H</u>	<u>Run No.</u>	<u>C/H</u>
1	14.7	9	14.6
1	14.8	9	15.0
1	14.6	9	14.7
2	14.9	10	15.2
2	14.8	10	15.5
2	14.8	10	15.0
3	15.0	11	15.0
3	14.5	11	15.5
3	14.9	11	15.0
4	14.9	12	14.5
4	14.7	12	14.7
4	15.3	12	14.7
5	14.9	13	15.8
5	14.7	13	15.4
5	14.9	13	15.6
6	14.7	14	15.6
6	14.6	14	15.3
6	14.8	14	15.3
7	15.1	15	15.4
7	15.1	15	15.3
7	14.9	15	15.3
8	14.9		
8	14.8		
8	14.8		

Final Reaction Pressures

Reaction pressures were not taken on the C runs so that an accurate material balance could be calculated. A plot of reaction pressures is shown in Fig. 7.

Reaction pressures increased with increased reaction temperature and with increased initial carbon monoxide pressure. The increase was not linear but slightly exponential. The highest reaction pressure encountered was 3540 psig at 475°C and an initial carbon monoxide pressure of 600 psig.

Viscosity of the Liquid Coal

Viscosities ranged from 39 SSU to 77 SSU. Liquid viscosities are shown in Table 5. Product viscosity decreased with an increase in both temperature and pressure with reaction temperature having a greater effect on the product viscosity than reaction pressure. At the lowest reaction temperature the pressure effect was reversed. The higher reaction pressures and temperatures cracked the coal molecules to a greater extent making the liquid product less viscous.

It must be noted that the viscosities were taken of the mixture of both treated coal and solvent with the unreacted coal being separated before analysis. Several samples were analyzed twice to check the results. A maximum variation of 2 Saybolt seconds, or approximately 3 percent error, was found.

Run No.	SSU (sec)		Kinematic Viscosity (cst.)	
	1	2	1	2
1	68	67	12.7	
2	71		13.4	
3	74	76	14.2	14.7
4	77		14.9	
5	72	73	13.7	13.9
6	61		10.9	
7	63	62	11.4	11.2
8	60		10.6	
9	50		7.9	
10	55	55	9.3	9.3
11	47		7.1	
12	44	44	6.2	6.2
13	45		6.5	
14	45		6.5	
15	39	40	4.7	5.0

Heating Values of Liquid Coal

Heating values were determined on the mixture of liquid coal and solvent after treating. The heating values are shown in Table 6. The untreated mixture of coal and solvent had a heating value of 15,388 BTU/lb. After treating the heating values of the mixture ranged from 16,873 BTU/lb to 17,818 BTU/lb. Therefore, the heating values were increased approximately 10 percent through treating.

Table 6. Liquid Coal and Solvent Mixture Heating Values.

<u>Run No.</u>	<u>Heating Values BTU/lb</u>
1A	16,922
2A	17,045
3A	16,889
4A	16,902
5A	17,157
6A	17,090
7A	17,178
8A	17,320
9A	16,873
10A	17,818
11A	16,994
12A	17,269
13A	17,278
14A	17,294
15A	17,407
Creosote Oil	16,775
Coal (Dry)	11,227

CONCLUSIONS

The following conclusions can be made from this study.

- 1) Conversion of coal to liquid increases with an increase in reaction temperature over the range of 375°C to 475°C. However, the total system pressure, over the range of 2300 psig to 3500 psig, does not appear to have any definite effect on coal conversion.
- 2) Conversion of bituminous coal to liquid was better than conversions reported in previous studies at the same reaction conditions.
- 3) Desulfurization increases with an increase in reaction temperature over the range of 375°C to 475°C. Again, the pressure effects on coal desulfurization were not apparent from this study.
- 4) Desulfurization results found in this study using the CO-steam process were not as good as the desulfurization potentially attainable using pure hydrogen.
- 5) Desulfurization increases with an increase in hydrogen partial pressure from 100 psia to 800 psia.

- 6) Maximum desulfurization attained with the CO-steam process in the temperature and pressure range studied was 57 percent.
- 7) Reaction pressures increase exponentially with increases in reaction temperature over the range studied.
- 8) The carbon-hydrogen ratio of the coal and solvent mixture did not change appreciably through processing in the temperature and pressure ranges studied.
- 9) Liquid coal and solvent viscosities decrease with increases in both reaction temperature and reaction pressures over the range studied.

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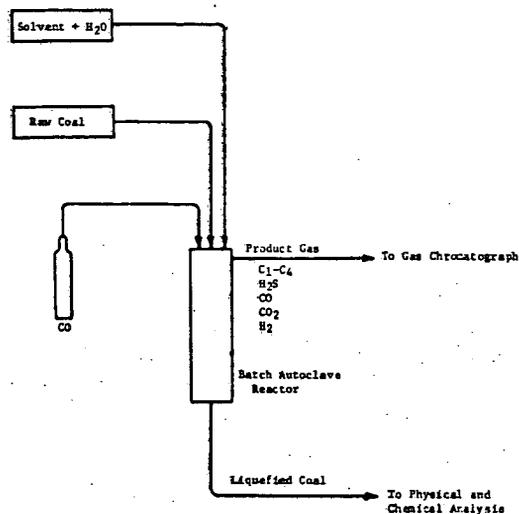


Figure 1. Simplified Process Flow Diagram, CO-Steam Liquefaction of Coal.

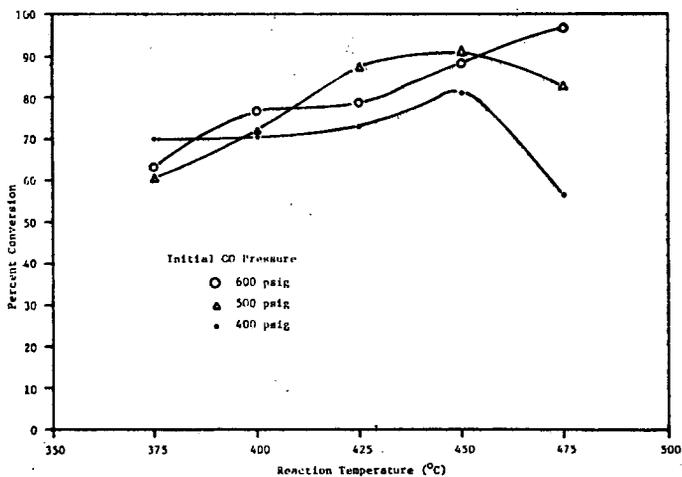


Figure 2. Weight Percent Conversion of Solid Coal to Liquid Coal.

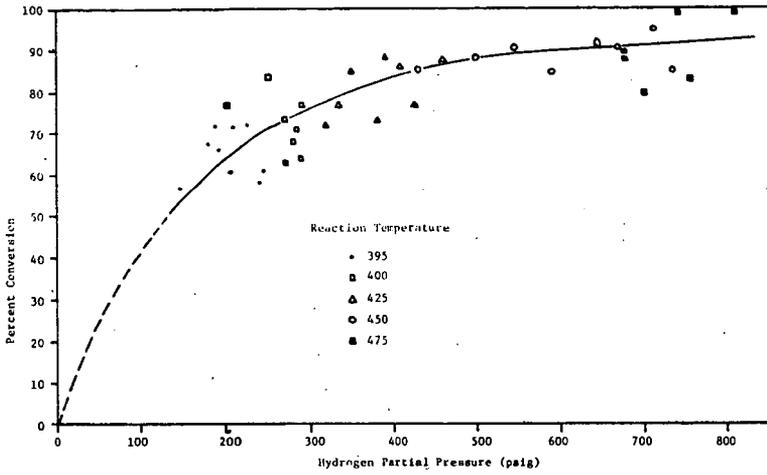


Figure 3. Coal Conversion as a Function of Hydrogen Partial Pressure.

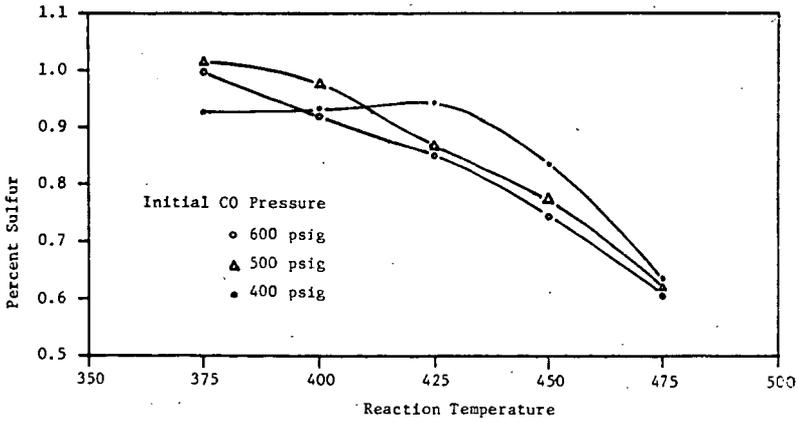


Figure 4. Weight Percent Sulfur in Liquid Coal Product.

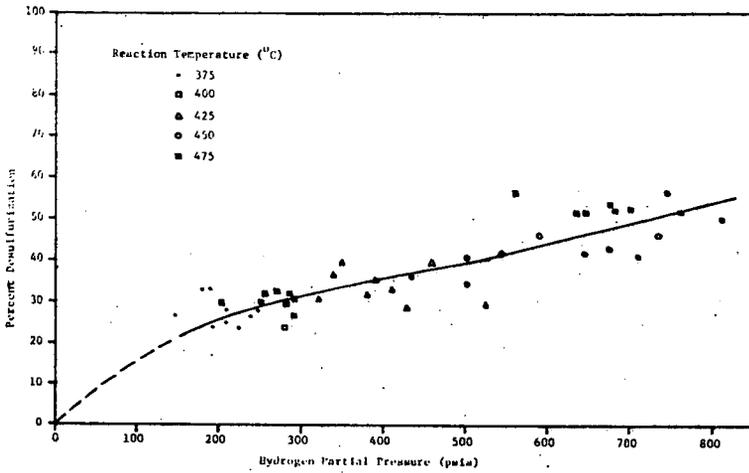


Figure 5. Coal Desulfurization as a Function of Hydrogen Partial Pressure.

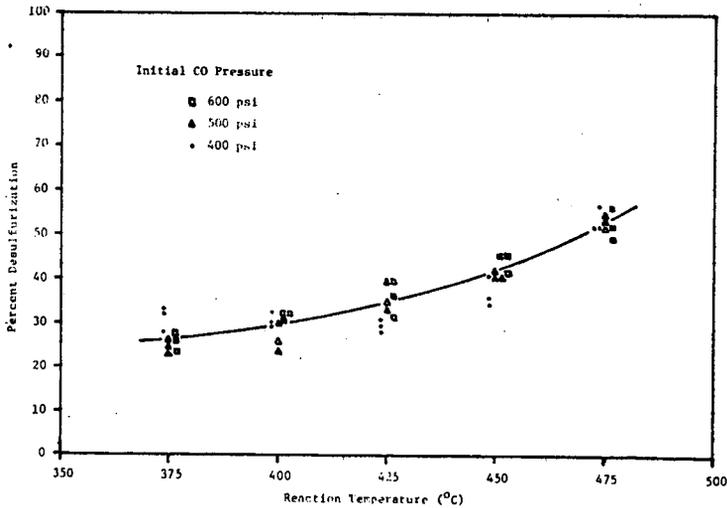


Figure 6. Coal Desulfurization as a Function of Reaction Temperature.

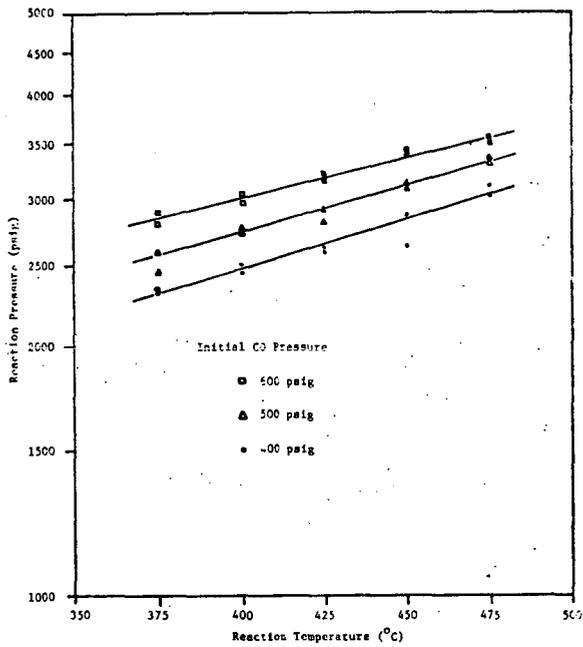


Figure 7. Final Reaction Pressures.