

4. Advanced Study of the Exxon Catalytic Coal Gasification Process (Reporting Category C04)

4.1 Kinetics of Gasification

The conversion of coal to gaseous products via Exxon's Catalytic Coal Gasification (CCG) process can be envisioned by a two-step mechanism. First, the coal undergoes rapid devolatilization to yield coal char and numerous volatile products. The resulting char is then gasified with steam and recycle gas to produce a mixture of methane, hydrogen, and carbon oxides. Additional amounts of these products are also produced from the devolatilization products as they pass through the bed of char. The purpose of this work was to better characterize the reaction rates and yield structures for the char gasification step. The results of this investigation were combined with appropriate mass transfer correlations to predict reaction rates and conversions in fluid bed gasifiers and help define optimum process conditions.

The kinetics of char gasification were previously investigated during the predevelopment phase of catalytic gasification research. The majority of the kinetic data was obtained using a fixed bed reactor at 1300°F and catalyst loadings of 10 and 20 wt % potassium carbonate on dry Illinois coal. The coal was devolatilized in a muffle furnace under an inert atmosphere before loading in the fixed bed reactor. Some data was also obtained at 1200°F. Additional kinetic data at various temperatures and at various partial pressures were necessary before a confident optimization of the gasifier conditions could be made.

In view of this need, a laboratory program was carried out to expand the kinetic data base for gasification of Illinois char. Feed for these studies was Illinois char produced at various levels of carbon conversion by the Fluid Bed Gasification Unit (FBG) and the Process Development Unit (PDU) under steady state conditions and the devolatilized coal used previously. The process variables studied were as follows:

- Effects of variations in potassium/carbon ratio in the char.
- Variations in temperature and pressure between 1100°F and 1400°F and between 0 and 500 psig, respectively.
- Variations in reactor feed gas including H₂O only, H₂O/H₂, and H₂O/H₂/CO mixtures.
- Variations in catalyst form, including KOH and K₂CO₃.

This laboratory program was carried out using a one atmosphere mini-fluid bed reactor and a fixed bed reactor capable of operating at high pressure. The atmospheric pressure unit was used to study variations in catalyst loading, temperature, catalyst form, and coal particle size. These studies were conducted using both H₂O only and H₂O/H₂ mixtures, using FBG and PDU steady state chars and muffle furnace chars, and using KOH, K₂CO₃,

and recycled catalyst. The fixed bed reactor was used primarily to study pressure effects. All runs in the fixed bed were made at 1300°F using muffle furnace char. Variations were made in feed gas composition and flow rate and in catalyst form. The various studies are presented in more detail below.

Experimental Apparatus

A schematic diagram of the mini-fluid bed reactor unit is shown in Figure 4.1-1. The reactor portion of the unit consists of a 1/4" I.D. quartz U-tube inside a hot steel block. Water is fed to the U-tube using a small syringe pump and is vaporized in the reactor. Argon or hydrogen gas is also fed to the unit. Ceramic beads are placed in the inlet leg of the U-tube to enhance the vaporization of water and to help disperse the gas flow. The exit gases from the reactor flow into an oxidizer where all carbon species are converted to carbon dioxide. After condensing any unreacted steam, the gas stream is bubbled through a sodium hydroxide solution where the amount of total carbon converted is automatically monitored by measuring the conductivity of the solution.

The argon or hydrogen gas fed to the mini-fluid bed serves to fluidize the char particles. The gas rate is typically about 40 cc/min STP which is equivalent to about 7 cm/sec linear superficial velocity in the reactor at 1300°F. The minimum fluidizing velocity of the char particles is 3-4 cm/sec. Char sample sizes varied from 0.25 grams to 1.00 gram in the minifluid bed. The water feed rate ranged from 0.2 to 2.5 ml/hour.

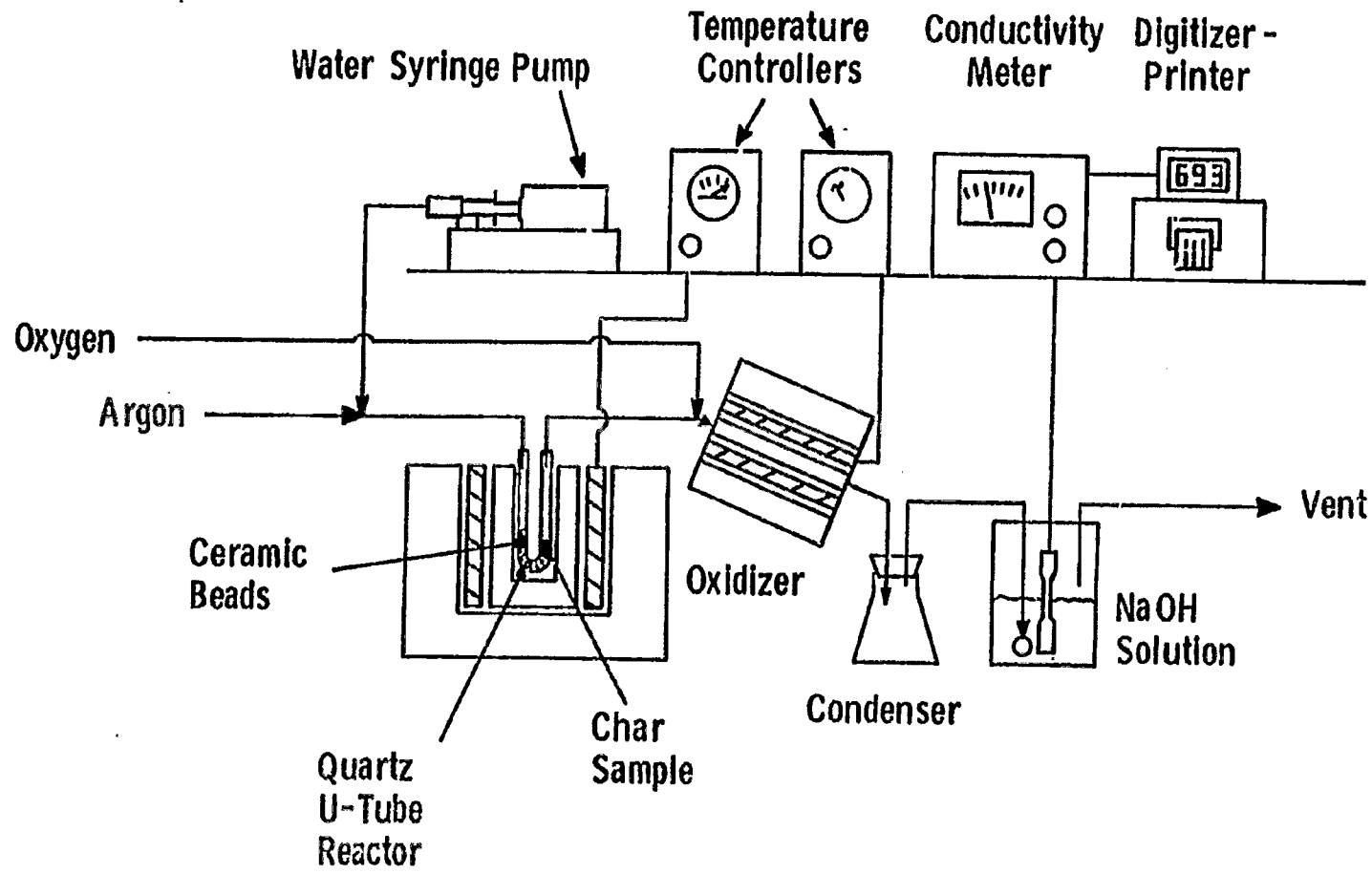
The fixed bed unit which had been used in predevelopment work was recommissioned for use in this program. A simplified flow diagram of this unit is shown in Figure 4.1-2. The unit consists of a high pressure water pump, steam generator, fixed bed reactor, condenser for unreacted steam, gas chromatographs, and dry gas flow measurement system.

The reactor itself is a one-inch Schedule.80 type 316 stainless steel pipe. The pipe holds a char sample inside a split tube furnace. Figure 4.1-3 shows data taken from the fixed bed unit where sample sizes between 5 grams and 50 grams were gasified at 1300°F and 250 psig. For sample sizes of 20 grams or more, the same gasification rate is found for the same amount of carbon remaining in the bed. For the smaller sample sizes, significant gas bypassing occurred resulting in lower observed gasification rates. As a result of these studies, a sample size of 20 grams was chosen for the fixed bed reactor.

Effect of Varying Potassium-to-Carbon Ratio

If the overall carbon conversion is altered in the CCG reactor, the ratio of potassium-to-carbon (K/C) in the reactor will change as well. Therefore, the effect of catalyst loading on kinetics must be known in order to be able to optimize initial catalyst loading as well as overall carbon conversion for the CCG process. Experiments were conducted in the atmospheric mini-fluid bed reactor to determine the effect of carbon conversion and catalyst loading on the gasification rate.

FIGURE 4.1-1
SCHEMATIC OF MINI-FLUID BED REACTOR UNIT



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FIGURE 4.1-2
SIMPLIFIED FLOW DIAGRAM OF BENCH
SCALE GASIFICATION UNIT

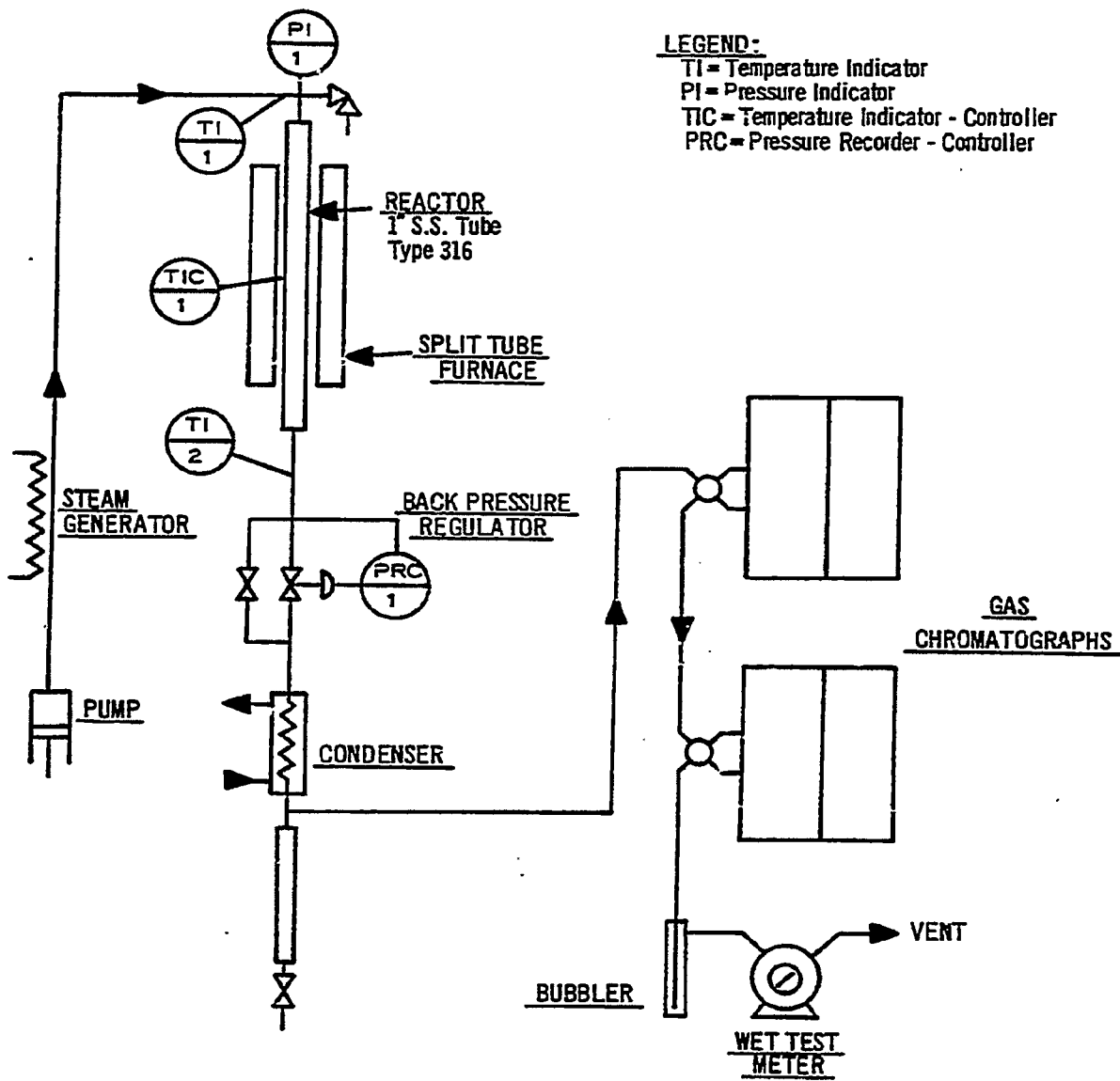
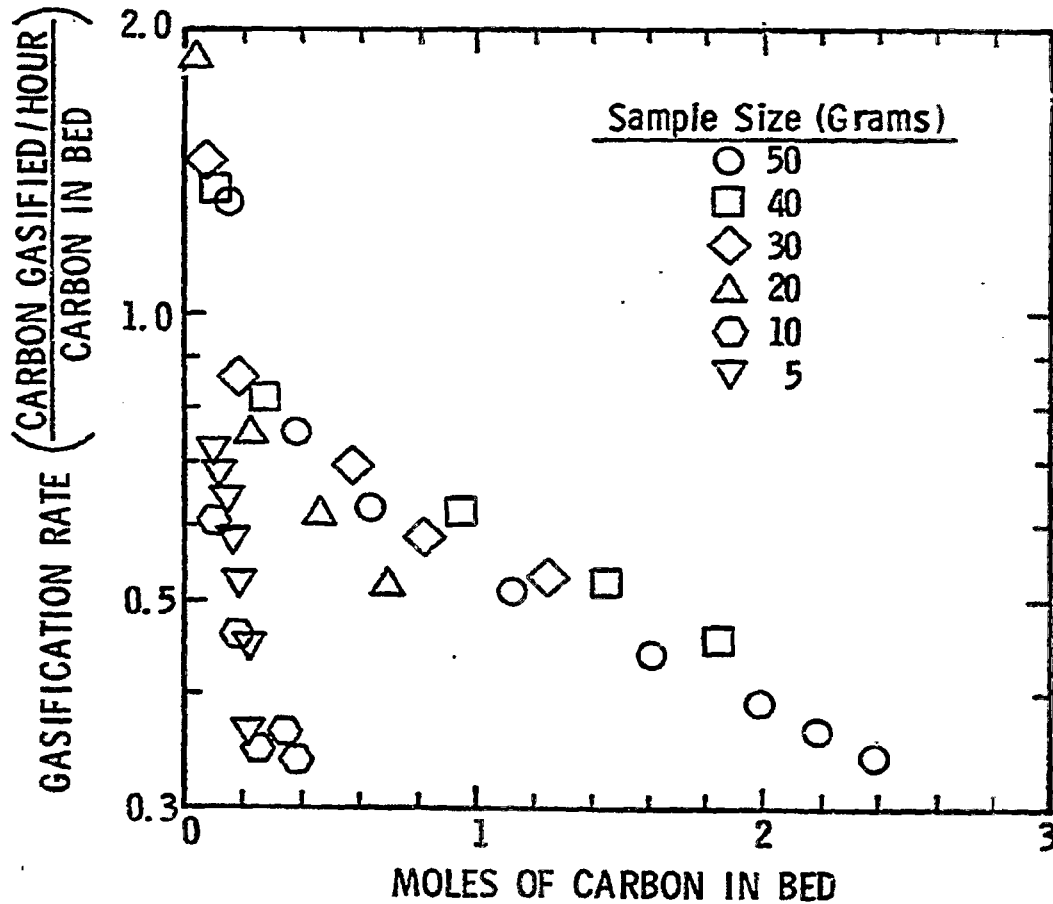


FIGURE 4.1-3
GAS BYPASSING EVIDENCED FOR SMALL SAMPLES

Fixed Bed Data
1300°F
250 psig
1.33 mph H₂O
0.46 mph H₂
0.15 mph CO



The chars used for this study were produced by the FBG and PDU and by devolatilization in the muffle furnace. For any given char sample, the potassium-to-carbon mole ratio (K/C) can be increased in either of two ways: (1) the carbon content of the char can be reduced by gasification of the char or (2) additional potassium catalyst can be added to the char. Studies have dealt with the effect of increased K/C ratio via each method on the observed overall gasification rate.

A series of runs was made in the mini-fluid bed gasifier at various steam flow rates using a char whose K/C ratio at the start of the run was 0.122. The results from these runs are presented in Figure 4.1-4. The data are plotted as percent of carbon in the bed gasified per hour versus the corresponding K/C ratio at the instant the rate was measured. The molar ratio of steam fed-to-carbon content of the char is used as a correlating parameter. The gasification rates plotted at K/C ratios of approximately 0.150 were determined at the 20% carbon conversion point of a run. Rates at higher K/C ratios correspond to higher carbon conversion levels. The data show that the carbon gasification rates of steady-state chars increase with the ratio of steam fed-to-carbon content of the char. The data in Figure 4.1-4 also indicate that the carbon gasification rate does not increase when the K/C ratio is increased by gasification of the char in the mini-fluid bed gasifier.

A series of runs was made in the mini-fluid bed gasifier using samples of FBG steady-state char to which additional K_2CO_3 catalyst was added. The base char sample for these runs had a potassium-to-carbon mole ratio of 0.122. The results from these runs are presented in Figure 4.1-5. The data are plotted as percent of carbon gasified per hour at the 20% carbon conversion point of a run versus the corresponding potassium-to-carbon mole ratio at the instant the rate was measured. The ratio of steam flow rate to carbon in bed at this same instant was 6.0 (moles/hr mole). These data clearly show that increasing the K/C mole ratio by adding additional potassium to a char sample increases the overall carbon gasification rate.

Figure 4.1-5 also includes data taken with other FBG steady-state chars. All chars corresponding to the open points were produced in the FBG from coal with identical initial catalyst loadings. The difference in K/C mole ratios of these chars is a result of the gasification of the coal in the FBG. The data in the vicinity of K/C equal to 0.3 is of particular interest. Note that the same increase in gasification rate can be obtained by adding additional catalyst to a char sample, as well as by reducing the carbon content of the char via gasification in the FBG. As the above results indicate, however, the gasification rate does not increase when the carbon content of the char is reduced via gasification in the mini-fluid bed unit. This may be due to the low pressure or short residence time in the mini-gasifier.

Furthermore, Figure 4.1-5 shows that as K/C mole ratio is increased beyond about 0.5 mole/mole, the gasification rate shows no further increase. Initially, it was believed that this result might be due to inadequate

FIGURE 4.1-4

EFFECT OF CARBON CONVERSION ON GASIFICATION RATE IN MINI-FLUID BED REACTOR

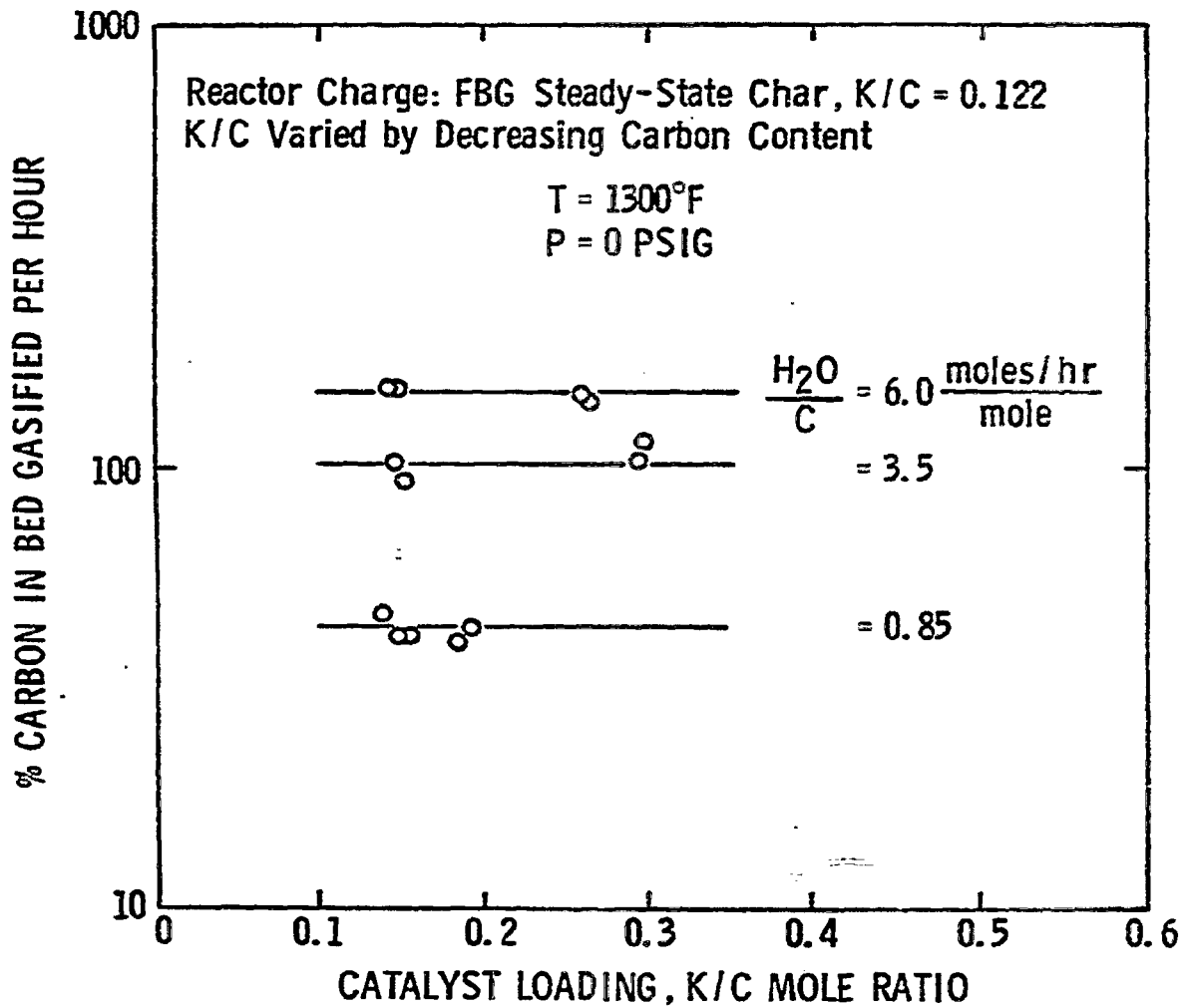
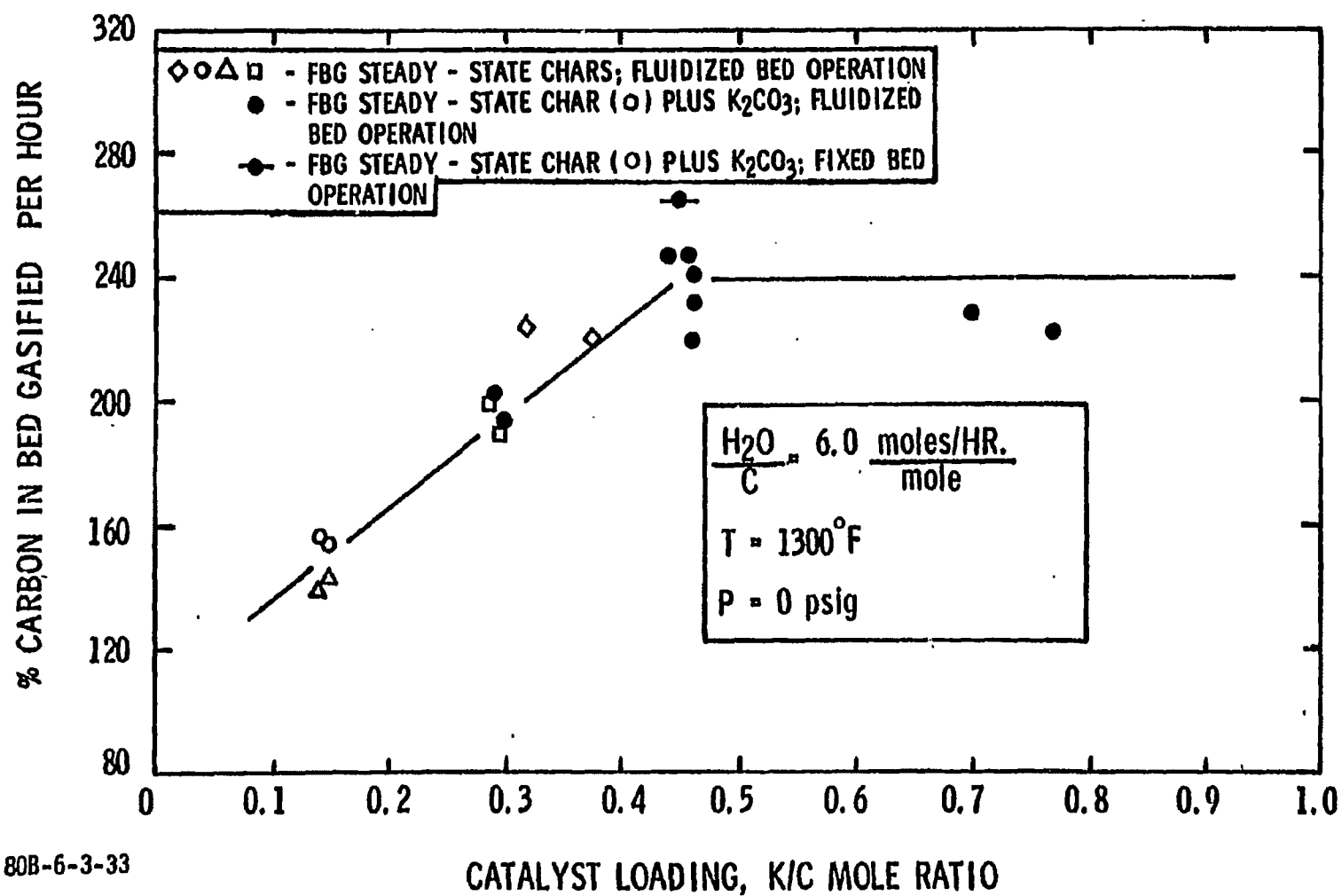


FIGURE 4.1-5

EFFECT OF CATALYST LOADING ON GASIFICATION RATE IN MINI - FLUID BED REACTOR



fluidization and gas bypassing of the char sample at the high catalyst loadings. Therefore, the configuration of the mini-reactor was changed to allow for operation as a down flow fixed bed. Figure 4.1-5 shows that similar results are obtained when the mini-reactor is operated in the fixed bed mode as when the char bed is fluidized.

A similar set of experiments was conducted using chars from the PDU. Similar results were obtained. As shown in Figure 4.1-6, the gasification rate in the minibed reactor increased as the K/C mole ratio increased up to about 0.2 mole/mole on a water soluble K basis.

Nine batches of raw coal (Illinois No. 6) were impregnated with various concentrations of KOH solution. These were then dried and devolatilized under a nitrogen atmosphere. The resultant chars, containing varying levels of potassium catalyst, were gasified in the mini-gasifier. Two series of runs were made: one with steam only and the other with a mixture of steam and hydrogen at approximately one-to-one molar ratio.

Plotting the initial gasification rates against the water soluble K/C ratio reveals an approximately linear relationship between the two as shown in Figure 4.1-7. This is consistent with the earlier findings with FBG and PDU chars.

Unlike the FBG and PDU chars which contain 30-40% by weight carbon, the chars used in this set of experiments contain 50-80% carbon. While the FBG and PDU chars display first order gasification rates with respect to the carbon present, the initial rates in these experiments appeared to be zero order (i.e., independent of the amount of carbon present). This suggests that the rate of gasification is proportional to the concentration of a (C-K) species rather than carbon or potassium concentrations per se. At high carbon concentrations and low K/C ratios, the concentration of the (C-K) species is proportional to the concentration of (K) since there is an overabundance of (C). The gasification rate thus appears to be independent of carbon concentration (i.e., zero order kinetics). At low carbon concentrations and high K/C ratios, there is an overabundance of (K). The gasification rate will then appear to be first order with respect to carbon. From studies of FBG and PDU chars, the demarcation between high and low K/C ratios appears to be about 0.2 mole C/mole water soluble potassium.

Variation of Reaction Temperature

The rate of chemical reactions fall off as temperature is reduced. From prior research, it is known that the methanation activity of the potassium catalyst will fall off rapidly below about 1200°F. On the other hand, lower temperatures thermodynamically favor the conversion of CO and H₂ to CH₄. Very little methane can be formed above about 1400°F. The optimum reaction temperature for CCG is a trade-off of these two effects. Additional kinetic data at various temperatures were needed to allow confident optimization of gasifier temperature.

FIGURE 4.1-6
EFFECT OF CATALYST LOADING ON GASIFICATION

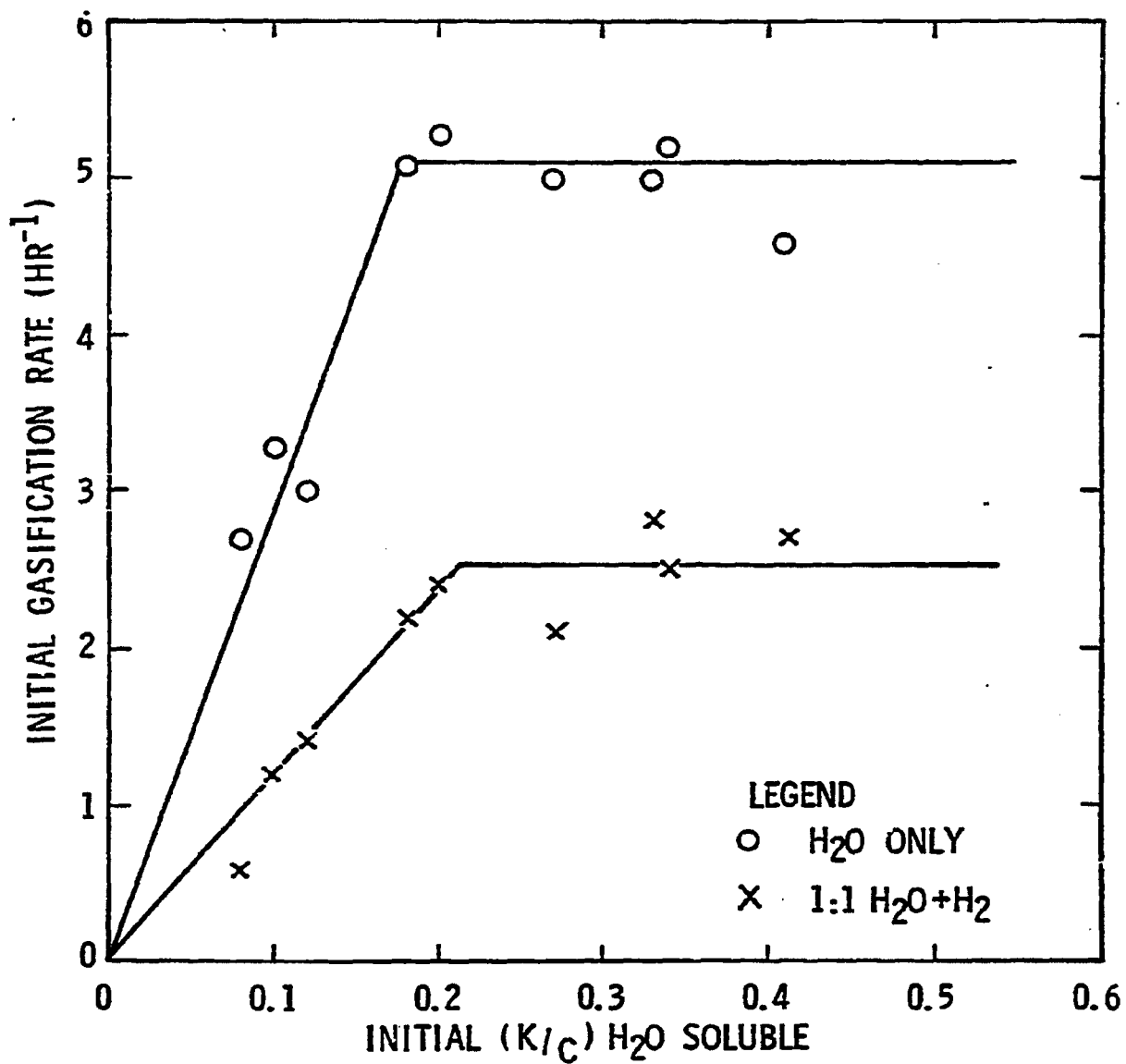
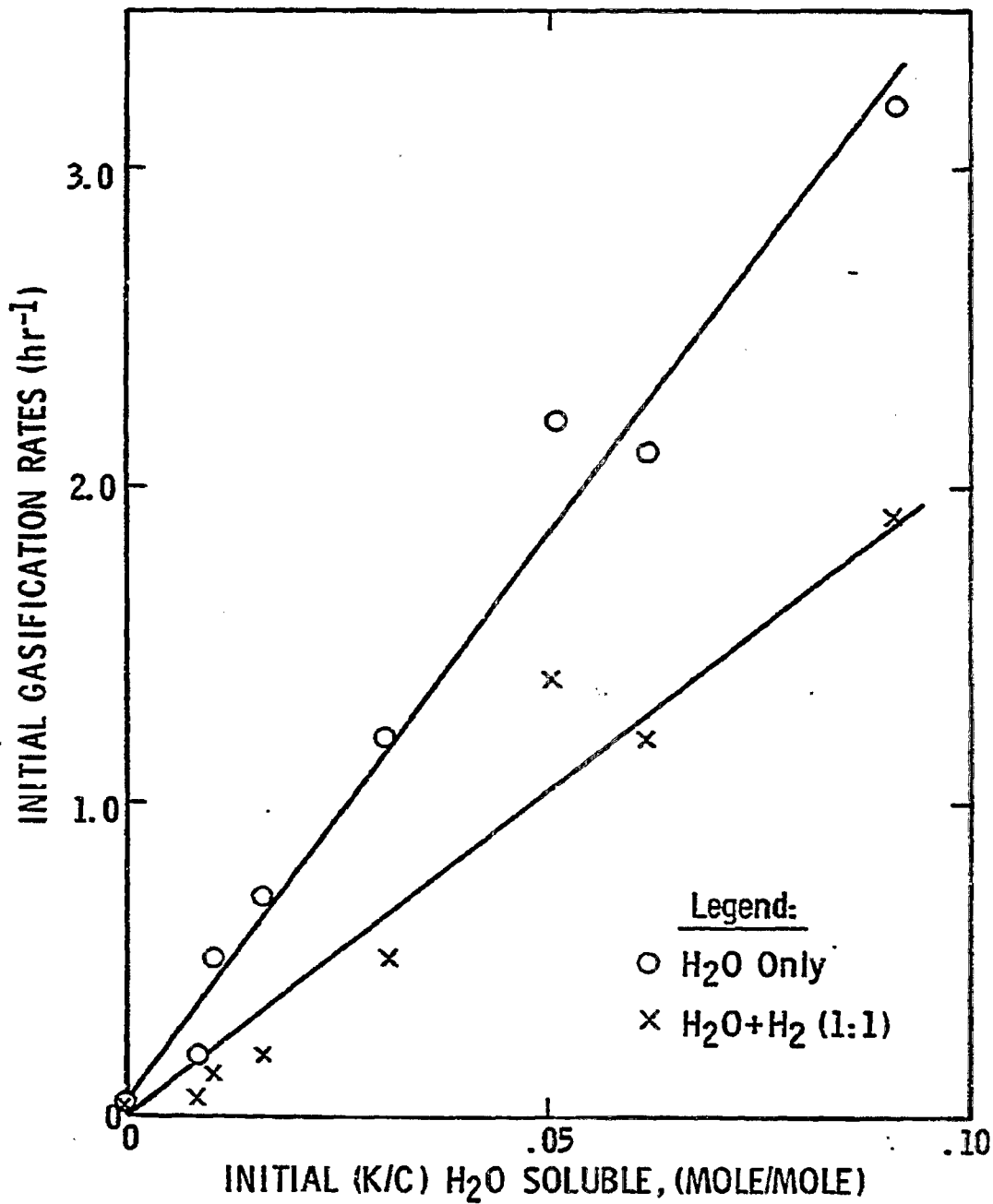


FIGURE 4.1-7GASIFICATION RATE INCREASES LINEARLY WITH (K/C) RATIO

The dependence of gasification rate on temperature was studied in the 1/4-inch diameter mini-gasifier, both with and without H₂ in the feed gas. The experimental conditions and the observed reaction rates for the series of experiments are summarized in Table 4.1-1.

Table 4.1-1

GASIFICATION RATE MEASUREMENTS

<u>Reactor Temperature (°F)</u>	<u>(H₂O/C) (mole/hr - mole)</u>	<u>(H₂/H₂O) (mole/mole)</u>	<u>Observed Reaction Rate (mole/hr-mole)</u>
1000	10	0	0.132
1094	10	0	0.564
1190	10	0	2.04
1286	10	0	4.74
1373	10	0	9.30
1100	10	0.93	0.084
1194	10	0.93	0.492
1290	10	0.93	2.22
1386	10	0.93	4.80

Steady Stage FBG Char (dated 2/3/79) containing approximately 30% carbon and K/C = 0.233

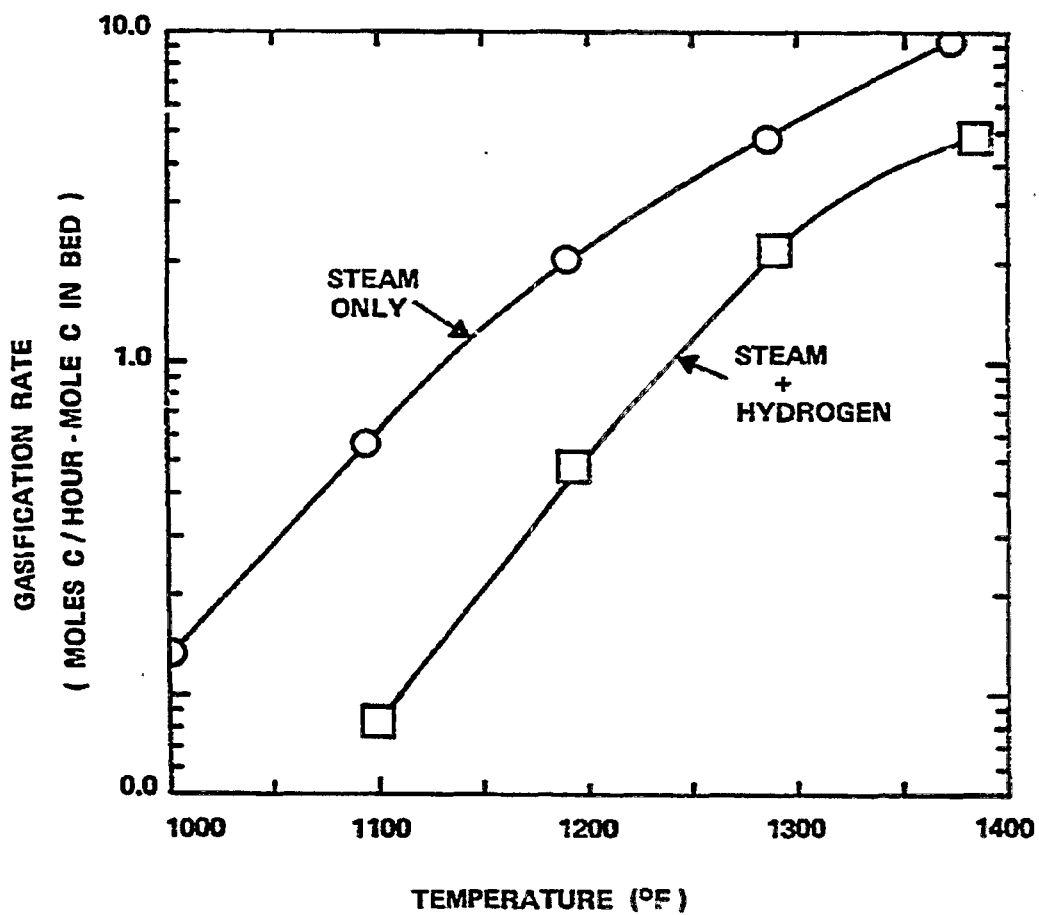
Sample size = 0.5 grams of char

Figure 4.1-8 shows the measured reaction rates as a function of temperature for experiments both with and without H₂ in the reactor. The apparent temperature dependence changes as the composition of the gas fed to the reactor changes. From Figure 4.1-8 it is seen that for H₂O + H₂ in the feed gas, gasification rate is very sensitive to temperature changes. Gasification rate approximately halves for each 50°F drop in reactor temperature below 1300°F.

There is an interaction between feed gas composition and apparent temperature dependence because the mini-reactor is an integral reactor. For example, when pure steam is introduced at the bottom of the bed of char, a mixture of H₂O + H₂ issues from the top of the bed. As the rate of reaction changes, the gas composition at various locations in the reactor changes even though the feed gas remains the same. Therefore, as temperature changes, some of the change in rate is due to activation energy, but some of the change is due to gas composition. The reactor model performs the integration required to account for both effects. The modeling work discussed in Section 3.1 of this report has identified the true activation energy as about 50 kcal/g mole.

FIGURE 4.1-8

REACTION RATE DEPENDS ON TEMPERATURE
AND GAS COMPOSITION



Effect of Pressure and Feed Composition on Gasification Kinetics

Higher total pressure and higher partial pressure of H_2 thermodynamically favor the formation of CH_4 . On the other hand, a high pressure gasifier will require thick vessel walls and will place severe demands on the coal feed lockhoppers. The optimum reaction pressure for CCG is a trade-off between these effects. Engineering sensitivity studies will find the best pressure based on considerations of operability and economics. These engineering studies require kinetic data at a variety of pressures and gas compositions.

A set of experiments was run in the one atmosphere mini-reactor to study the effect of H_2 concentration in the feed gas on gasification rates. Increasing the H_2 to H_2O molar ratio in the feed gas from 0.0 to 0.93 lowers the gasification rate to approximately half its initial value. Further increasing the H_2/H_2O ratio in feed gas to 2.3 only marginally lowers the gasification rate further. The experimentally measured gasification rates at various levels of H_2 in the feed gas are presented in Table 4.1-2. Gasification rate decreases with the mole fraction of H_2 in the total molar flow of H_2O and H_2 in the feed gas as shown in Figure 4.1-9.

Table 4.1-2

DEPENDENCE OF GASIFICATION RATE ON H_2 IN FEED GAS

(Reactor Temp.: 1300°F; Char: 0.5 g FBG char dated 2/3/79)

<u>H_2/H_2O Mole Ratio</u>	<u>H_2 Mole Fraction</u>	<u>Reaction Rate (mole/hr-mole)</u>
0.0	1.0	5.10
0.22	0.82	3.90
0.50	0.66	2.94
0.93	0.52	2.22
2.30	0.30	1.80

In order to further change the H_2O mole fraction in the reactor, a series of experiments was conducted in the mini-fluid bed over a four-fold change in reactor sample size (0.25g to 1.0g) and over a three-fold change in H_2O feed rate (0.72 to 2.25 ml per hour). The measured reaction rates in moles carbon gasified per hour per mole of carbon in the bed are shown in Table 4.1-3. Gasification rates were found to increase with the square root of the steam rate/carbon in bed ratio as shown in Figure 4.1-10.

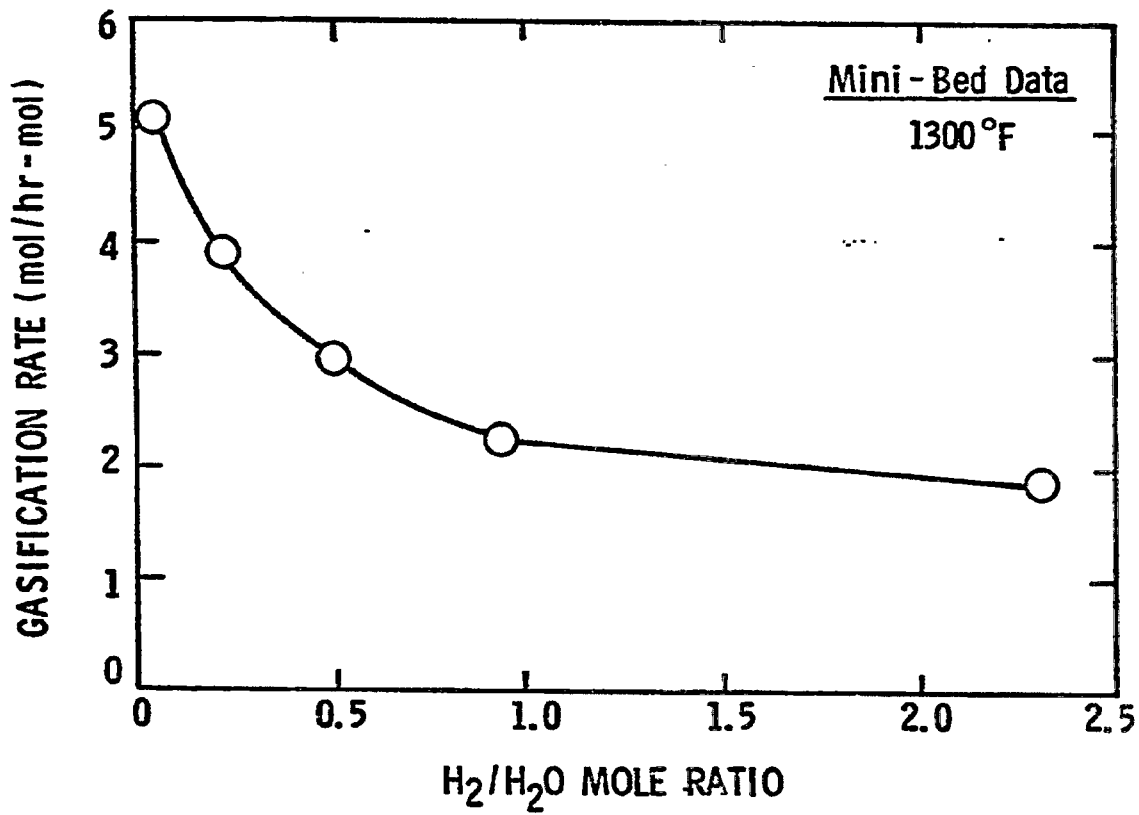
FIGURE 4.1-9HYDROGEN REDUCES GASIFICATION RATE

FIGURE 4.1-10

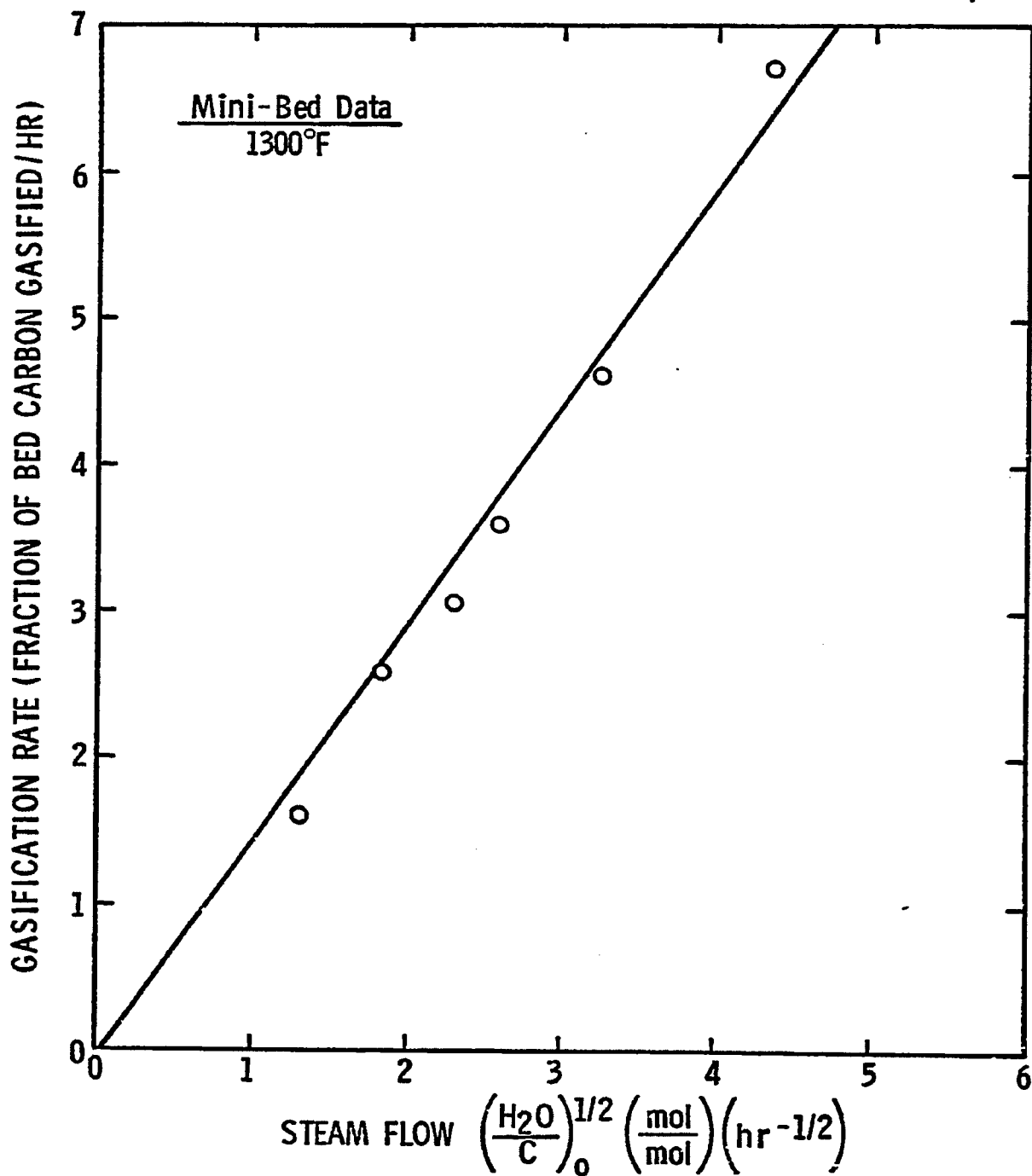
EFFECT OF H₂O FEED RATE ON THE GASIFICATION RATE

Table 4.1-3

DEPENDENCE OF GASIFICATION RATE ON H₂O RATE AND SAMPLE SIZE

(Reactor Temp.: 1300°F; Char: FBG dated 2/3/79)

<u>Sample Size (g)</u>	<u>H₂O Rate (ml/hr)</u>	<u>(H₂O/C) hr⁻¹</u>	<u>Reaction Rates moles/mole, hr</u>
1.0	2.25	5.0	3.06
1.0	1.40	3.1	2.57
1.0	0.72	1.6	1.62
0.5	2.25	10.0	4.62
0.5	1.40	6.2	3.60
0.25	2.25	20.0	6.72

Fixed bed runs were made at pressures between 0 and 500 psig with mixtures of H₂O/H₂, and H₂O/H₂/CO fed to the gasifier. All runs were made at 1300°F using a 15% K₂CO₃ impregnated Illinois #6 coal which was devolatilized in a muffle furnace prior to loading in the fixed bed reactor.

Eight runs were made with mixtures of H₂O and H₂ fed to the reactor. Four runs were made with the H₂/H₂O ratio fixed at about 1 mole/mole. Four other runs were made with a H₂/H₂O ratio of about 0.25 mole/mole. For each H₂/H₂O ratio, runs were made at 500, 250, 100, and 0 psig. The data from these eight runs match predictions made by the simple kinetic model shown below.

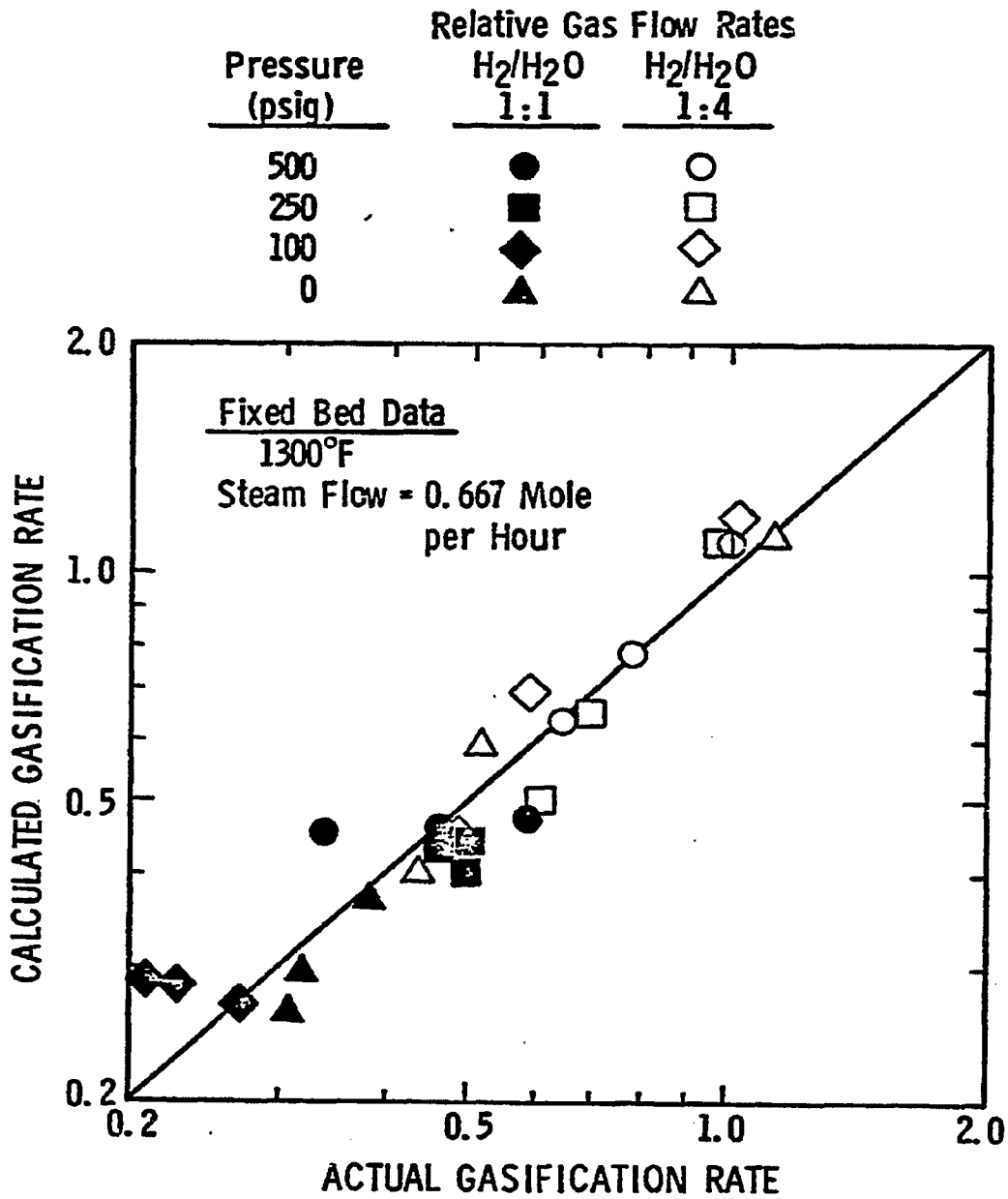
$$r_G = \frac{0.21[P_{H_2O} - P_{CO} P_{H_2/AC} K_G]}{P_{H_2}}$$

This model is consistent with predevelopment work encompassing a wide range of steam-only data. Figure 4.1-11 is a parity plot between the model predictions and the data for the eight H₂/H₂O runs. The standard deviation from parity is 0.078 hr⁻¹.

A similar set of experiments was made in the fixed bed reactor with a mixture of H₂O, H₂, and CO fed to the reactor. Two sets of four runs were completed one each at 500, 250, 100, and 0 psig. The H₂/CO ratio was fixed at 3 mole/mole for both sets of runs. The H₂O/syn gas ratio was about 1 mole/mole for the first set of runs. For the second set, the H₂O/syn gas ratio was about 4 mole/mole. The data from these eight runs also match the model predictions. Figure 4.1-12 is a parity plot between these data and the model predictions. The standard deviation from parity is 0.116 hr⁻¹.

FIGURE 4.1-11

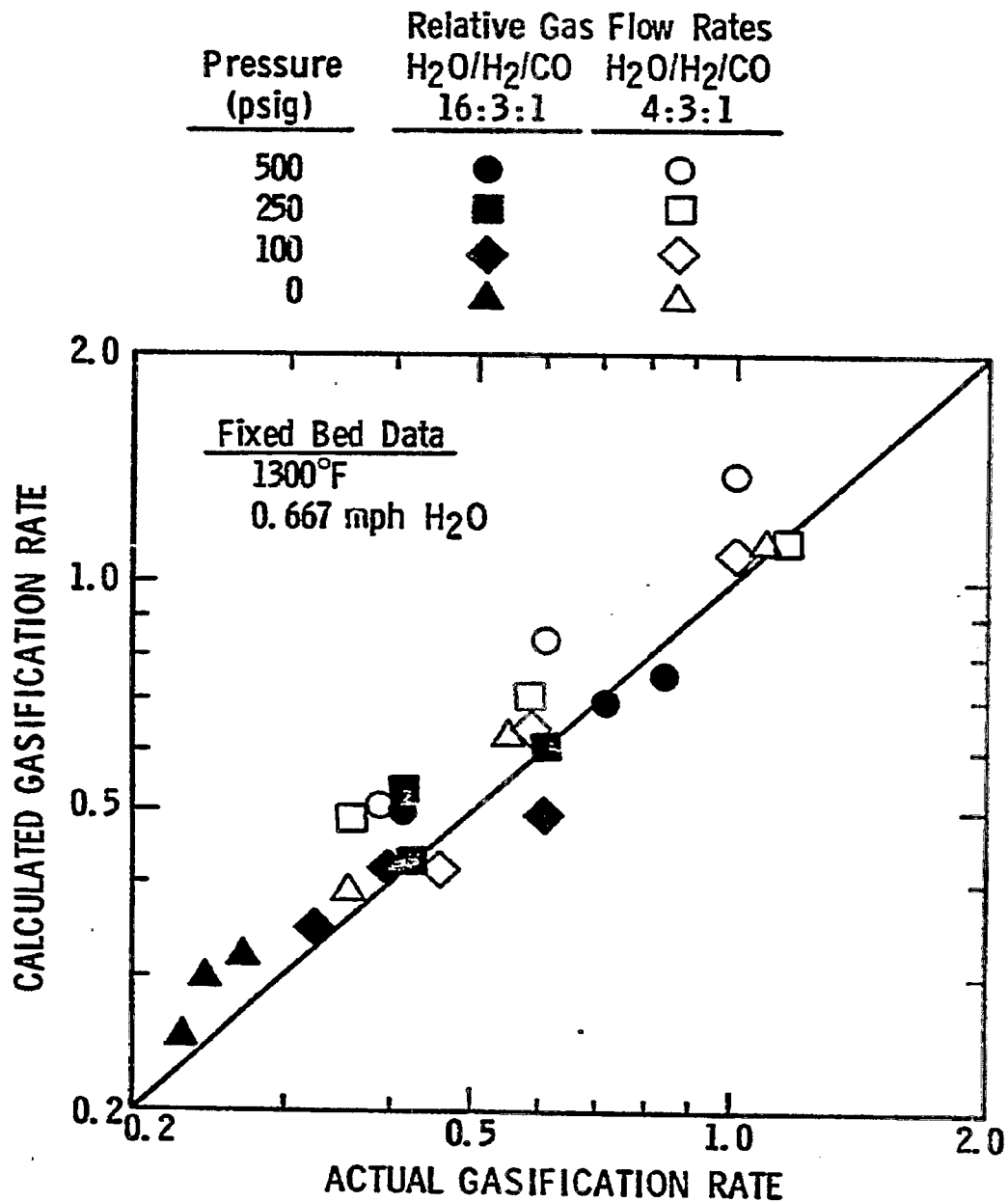
FIXED BED RUNS WITH STEAM AND HYDROGEN



Rate Expressed as Moles C Gasified / Hour - Mole C in Bed

$$\text{Model: } r_G = \frac{0.21 [P_{H_2O} - P_{CO} P_{H_2} / K_G]}{P_{H_2}}$$

FIGURE 4.1-12

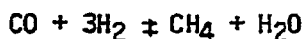
FIXED BED RUNS WITH H₂O, H₂, AND CO

Rate Expressed as Moles C Gasified/Hour - Mole C in Bed

$$\text{Model: } r_G = \frac{0.21 [P_{H_2O} - P_{H_2} P_{CO} / K_G]}{P_{H_2}}$$

4.2 Kinetics of Methanation

The desired product of the Catalytic Coal Gasification (CCG) Process is methane (CH₄). As described in section 4.1 of this report, some methane is formed directly from the coal during devolatilization at the reactor feed point. One of the important features of the CCG Process, however, is that additional methane is formed in the reactor from CO and H₂ gas in the presence of potassium catalyzed coal char. The purpose of the work described in this section was to investigate the effects of gasifier reactor conditions on the methanation reaction rate. The stoichiometry of this reaction is shown below:



Experimental Apparatus

The apparatus used for this work was a fixed bed reactor. The fixed bed reactor system is described in section 4.1 of this report. A schematic of the unit is shown in Figure 4.1-2.

Initial Shakedown of Apparatus

When the fixed bed reactor was first put to use to study methanation, it was found that significant amounts of CH₄ were formed from CO and H₂ in the hot reactor even when the reactor was void of catalyzed char. This "background" CH₄ would confound any experiments designed to test the catalytic ability of the catalyzed char. Several solutions were tried: injection of H₂S along with the CO and H₂ feed gas to passivate the metal surface; use of a quartz sleeve to mask the metal surface; and, use of a smaller reactor with less exposed metal surface.

A mixture of 25 mol % CO, 1 mol % H₂S, and 74 mol % H₂ was fed to the reactor at 1300°F and 500 psig. Table 4.2-1 shows data taken for an empty reactor and a reactor loaded with catalyzed char. The data show that the presence of the catalyzed char substantially increases the amount of CH₄ formed. The data also show that a significant amount of CH₄ is formed even in the empty reactor. This result was not expected since the hydrogen sulfide (H₂S) present should passivate the metal walls of the reactor.

It is now believed that the metal sulfides formed must be unstable at 1300°F and that enough active metal surface is exposed to the CO and H₂ to cause the production of the CH₄ observed in the runs with the empty reactor.

Efforts were then made to minimize this "background" CH₄ so that any CH₄ in the product gas would be a result of the catalyzed char and not a result of the experimental apparatus. Therefore, the reactor tube was fitted with a quartz sleeve. This sleeve masked as much metal surface as possible. It was believed that by masking the metal surface, the production of "background" CH₄ would be minimized.

Table 4.2-1

METHANATION OF SYNTHESIS GAS IN FIXED BED

<u>Sample</u>	<u>Feed Gas* Flow Rate (1/hr)</u>	<u>CH₄ In Dry Gas (%)</u>
Blank	13.10	15
PDU Bottom Char (8/1/80)	14.63	41
Char from Muffle Furnace	13.80	57

1300°F
500 psig
*74% H₂, 25% CO, 1% H₂S

Table 4.2-2 shows data taken for an empty quartz lined reactor and a quartz lined reactor loaded with catalyzed char. The data show that the quartz sleeve did significantly reduce the CH₄ produced in an empty reactor. The data also show that the addition of catalyzed char did not affect the CH₄ content as much as it did in previous runs without the quartz sleeve.

Table 4.2-2

METHANE FORMATION IN QUARTZ-LINED FIXED BED REACTOR

<u>Sample</u>	<u>Feed Gas Flow Rate (1/hr)</u>	<u>CH₄ In Dry Gas (%)</u>
Blank	14.60	3.2
PDU Bottom Char (8/1/80)	19.80 41.20	3.8 4.3
Char from Muffle Furnace	14.60	13.0

1300°F
500 psig

It is not possible to insure a tight fit between the quartz sleeve and the reactor metal wall due to differential thermal expansion. It is believed that reaction gas was bypassing the bed of char in the experiments with a quartz sleeve in the reactor. Therefore, use of the quartz sleeve was discontinued.

A new, all metal, smaller reactor was fabricated. Three blank runs were made in this reactor as shown in Table 4.2-3. Only minimal amounts of CH₄ were formed in these runs. These data indicated that the new reactor could be used to study the methanation reaction over potassium catalyzed char.

Table 4.2-3

NEW REACTOR DOES NOT CATALYZE METHANATION REACTION

<u>Feed Gas Flow Rate(*) (Liter/Hour)</u>	<u>CH₄ in Dry Gas (Mole %)</u>
19	1
27	1
35	1-2

1300°F
500 psig
(*)74% H₂, 25% CO, 1% H₂S

Effect of Carbon Conversion

The reaction of CO with H₂ to produce CH₄ also produces H₂O as a byproduct. In a reactor full of potassium catalyzed coal char, some of this byproduct steam may further react with C to produce additional CO and H₂. The loss of the C from the bed of char was thought to be an important parameter based on earlier work. In the earlier work, significant reaction of the C was avoided by operating at low temperature (1000-1200°F). Due to the importance of this variable in interpretation of experimental results, it was decided to study the effect of carbon conversion on methanation rate first.

The ability of PDU chars of various carbon conversions to form CH₄ from CO/H₂ mixtures was compared with the methanation ability of laboratory-prepared samples. The analyses of the samples are given in Table 4.2-4. All samples had an initial catalyst loading of 12.5 grams of KOH per 100 grams of dry coal. The PDU samples are from gasifier runs at 500 psia. The laboratory samples were prepared by devolatilizing KOH-catalyzed coal in a muffle furnace at 1200°F under an N₂ atmosphere for 30 minutes.

Table 4.2-4

ANALYSES OF PDU AND MUFFLE FURNACE CHARs

	<u>PDU</u> <u>9/29/80</u>	<u>PDU</u> <u>11/26/80</u>	<u>PDU</u> <u>1/27/81</u>	<u>Muffle</u> <u>Furnace</u>
Carbon Content (Wt %)	47	24	6	60
Carbon Conversion (% Fresh Coal)	70	90	97	25
Loose Bulk Density (g/cc)	0.62	0.30	0.80	0.66

Samples of these chars were loaded into the fixed bed reactor. The reactor was heated to 1300°F and a mixture of 74 mol % H₂, 25 mol % CO, and 1 mol % H₂S was passed over the sample at 500 psi.

The flow rate of the gas mixture was varied to give different residence times of the gas in contact with the char. The amount of CH₄ produced for each run is shown in Figure 4.2-1.

The data show that over the carbon conversion range of 25-90%, there is very little difference in the rate of CH₄ formation. Furthermore, over the range of 70-90% carbon conversion, there is no detectable difference in methanation rate. On the other hand, the CH₄ make drops rapidly at carbon conversions over 90%.

From these data it is apparent that the change in carbon inventory during a fixed bed run can be neglected in analysis of the experimental results. This conclusion is supported by the data from a sample run, presented in Table 4.2-5. In this run, the carbon inventory changed from about 0.35 moles to about 0.28 moles during the 5 hour experiment; however, the product gas composition was essentially constant.

FIGURE 4.2 - 1

HIGH DENSITY CHAR MAKES LESS METHANE

- 1300°F FIXED BED REACTOR
- 3/1 H₂/CO MOLE RATIO
- 500 PSIG

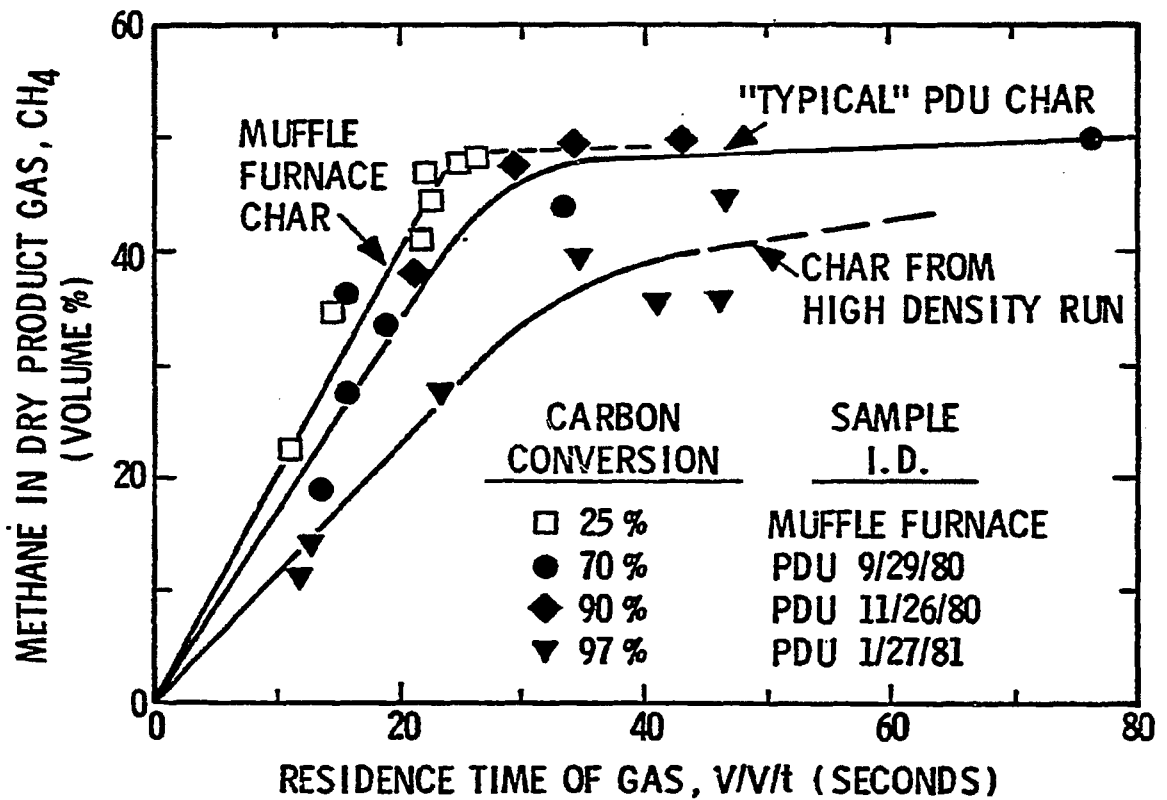


Table 4.2-5

FIXED BED RUN OF PDU GMC 11/26/81

Date: 2/23/81 Temperature: 1300°F Pressure: 500 psig

Time (Minutes)	Wet Gas Composition						Carbon In Bed (Moles)
	H ₂ S	H ₂	CO	CH ₄	CO ₂	H ₂ O	
15.	0.0	28.07	3.12	37.70	7.05	24.07	0.3426
30.	0.0	29.89	3.06	35.46	6.09	25.49	0.3361
45.	9.27	24.12	2.84	31.64	5.18	26.94	0.3315
60.	2.74	27.09	3.04	35.14	5.64	26.36	0.3281
75.	1.84	27.44	2.91	35.59	5.53	26.68	0.3252
90.	1.40	27.69	2.95	35.74	5.77	26.44	0.3223
105.	1.24	27.87	2.97	35.58	5.60	26.74	0.3191
120.	1.19	27.75	2.91	35.71	5.72	26.71	0.3155
135.	1.18	27.84	2.91	35.55	5.57	26.96	0.3116
150.	1.12	27.79	2.89	35.60	5.53	27.08	0.3075
165.	1.10	27.88	2.78	35.51	5.50	27.23	0.3032
180.	1.04	28.00	2.80	35.38	5.41	27.36	0.2990
195.	1.00	28.06	2.74	35.44	5.67	27.09	0.2951
210.	0.95	28.02	2.90	35.37	5.35	27.41	0.2915
225.	0.95	28.18	2.75	35.38	5.77	26.96	0.2884
240.	0.91	28.23	2.78	35.28	5.41	27.40	0.2856
255.	0.84	28.32	2.89	35.20	5.34	27.40	0.2831
270.	0.82	28.56	2.86	35.14	5.72	26.92	0.2805
285.	0.81	38.67	2.88	35.05	5.67	26.93	0.2772

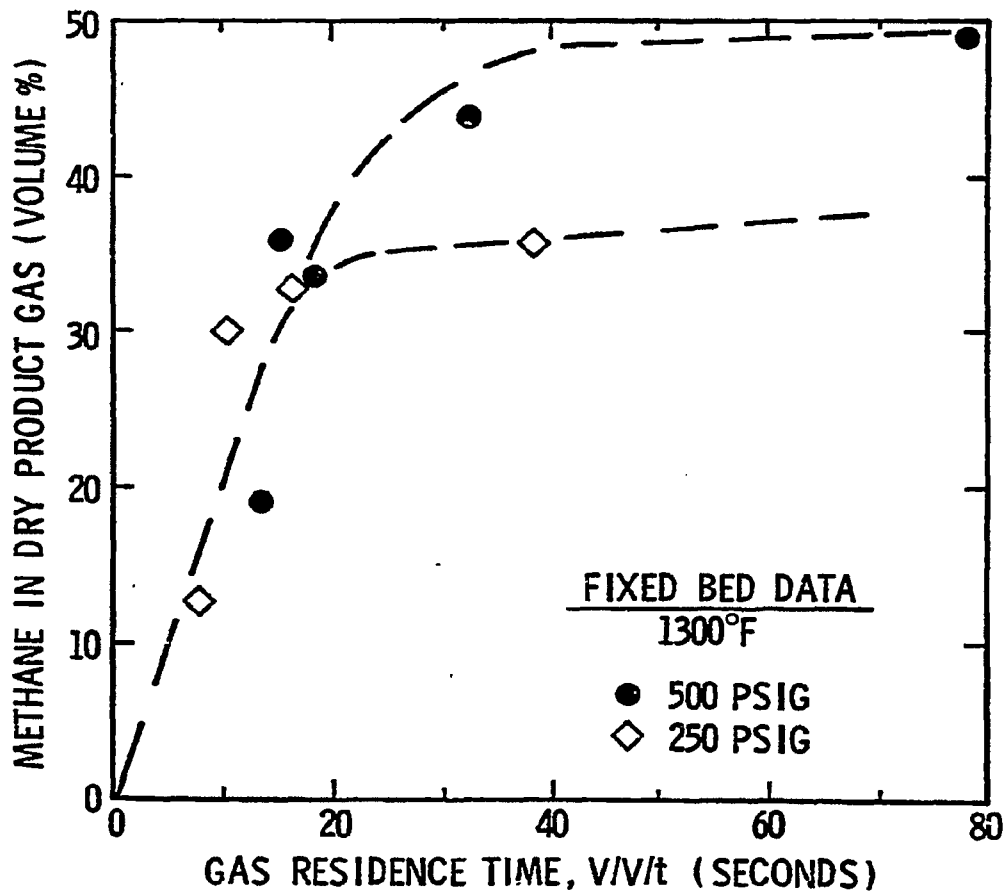
Effect of Pressure

The predevelopment work on methanation reaction rate modeling was conducted at 100 psig. The CCG process will most probably find commercial application within the range of 250-500 psig. In this study, the rate of formation of CH₄ at 250 psig was compared with the rate of formation of CH₄ at 500 psig.

Samples of PDU Gasifier Mid-Char (GMC) from 11/26/80 were loaded into the fixed bed reactor. The reactor was heated to 1300°F. Mixtures of 74 mol % H₂, 25 mol % CO, and 1 mol % H₂S were passed over the char at 500 psig. The experiment was repeated at 250 psig. The results are shown in Figure 4.2-2. At short gas residence times, the CH₄ yield is the same at either 250 psig or at 500 psig. At longer residence times, two different equilibrium values are obtained.

FIGURE 4.2-2
METHANE YIELD INDEPENDENT OF PRESSURE
AT SHORT RESIDENCE TIMES

- PDU 11/26/80 GMC
- 3/1 H₂/CO MOLE RATIO



This set of experiments was duplicated using a muffle furnace char. All of the data were taken at short residence times. As Figure 4.2-3 shows, there is no noticeable difference between the amount of CH_4 made at 250 psig and at 500 psig for a given gas residence time.

The experiments were run a third time, except this time the feed gas consisted of 89 mol % H_2 , 10 mol % CO , and 1 mol % H_2S . The results, shown in Figure 4.2-4 display the same pattern as seen in the earlier two sets of experiments. There is no noticeable difference between the results from 250 and 500 psig runs.

FIGURE 4.2 - 3

METHANE YIELD INDEPENDENT OF PRESSURE

- MUFFLE FURNACE CHAR
- 3/1 H₂/CO MOLAR RATIO

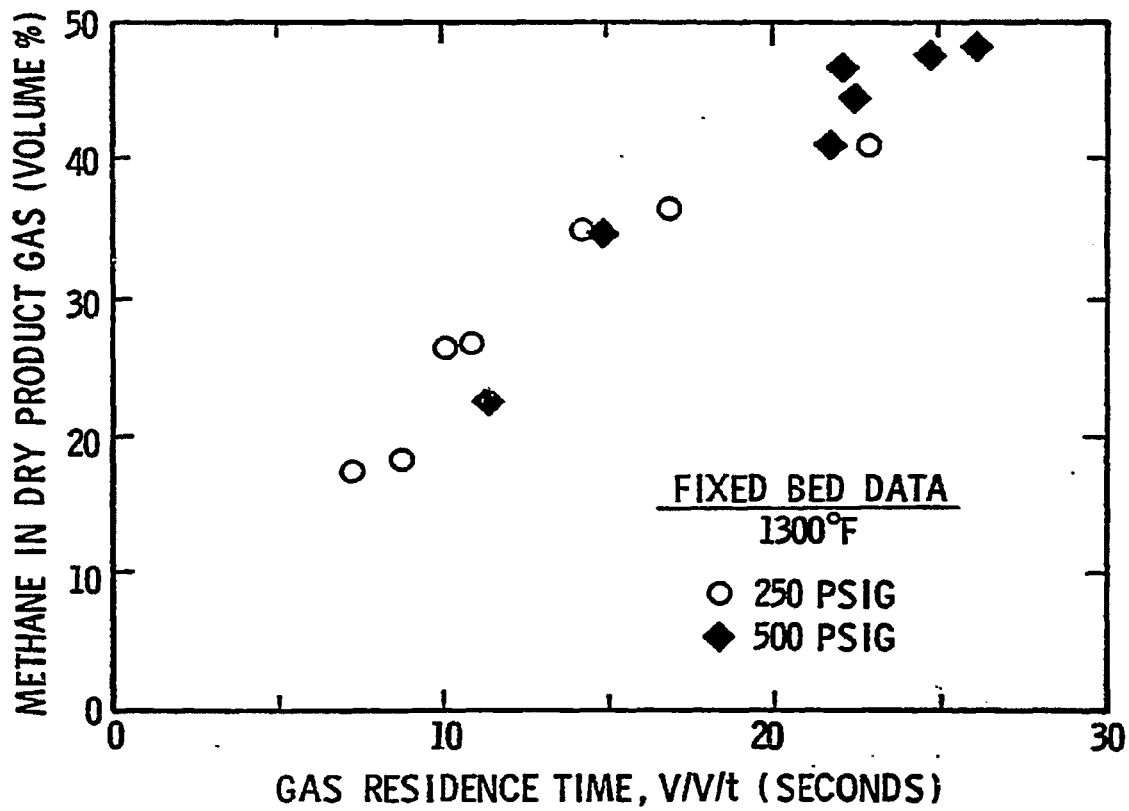
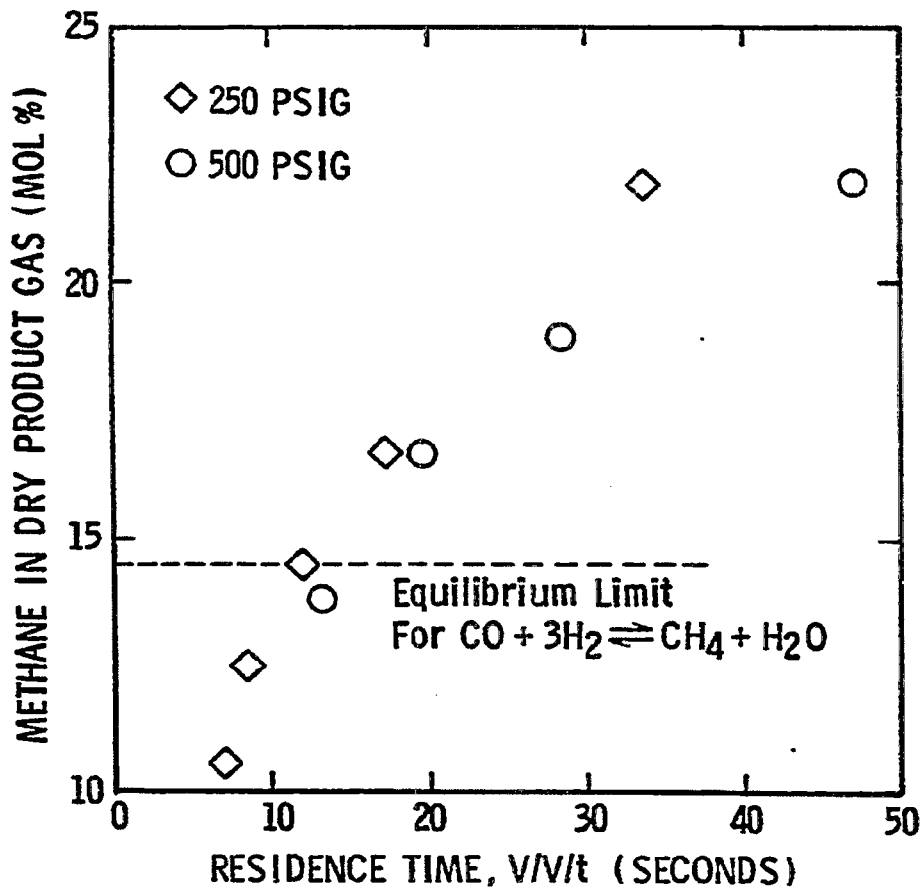


FIGURE 4.2 - 4

PRODUCTION OF CH₄ GREATER THAN DISAPPEARANCE OF CO.

- MUFFLE FURNACE CHAR
- 1300°F FIXED BED
- 9/1 H₂/CO MOLE RATIO



4.3 Effect of Catalyst Addition and Coal Pretreatment on Char Properties

The FBG had been operated successfully during the predevelopment contract period on a feedstock of potassium carbonate (K_2CO_3) catalyzed Illinois No. 6 coal. During the last quarter of 1978, operation with a new carload of Illinois No. 6 coal and with potassium hydroxide (KOH) as the catalyst was accompanied by some initial operability problems as well as a lower fluidized bed density than was experienced in the predevelopment work. Operations were improved by removing the large (+16 mesh) particles from the feed coal. The fluidized bed density was increased by exposing the catalyzed coal to air prior to loading in the FBG. The density variations are summarized in Figure 4.3-1.

Analyses of FBG feed coals

Samples of coal from both the predevelopment (1977) and the 1978 operations were submitted for microscopic analysis. Petrographic and chemical analyses showed the two samples to have similar maceral compositions and mineral matter content. The major difference between the predevelopment and the current supply is that the 1977 coal had a higher reflectance. This may be due to either different types of vitrinite or a higher oxidation level of the 1977 coal. Since it is uncommon for samples from the same mine to have different types of vitrinite, the higher reflectance suggests that the older coal was more highly oxidized. This difference in oxidation level is confirmed by the elemental analysis shown in Table 4.3-1 which shows that the predevelopment coal had a higher oxygen content than the 1978 coal.

The difference in oxidation level agreed with pilot unit observations of an increase in bed density using catalyzed coal which was air exposed prior to loading in the FBG, but the result was inconclusive since the oxidation level of the older coal could have changed during storage. The effect of oxidation level on char density and agglomeration was therefore studied on samples whose history could be better defined.

FIGURE 4.3-1

CHAR DENSITY VARIED IN FBG

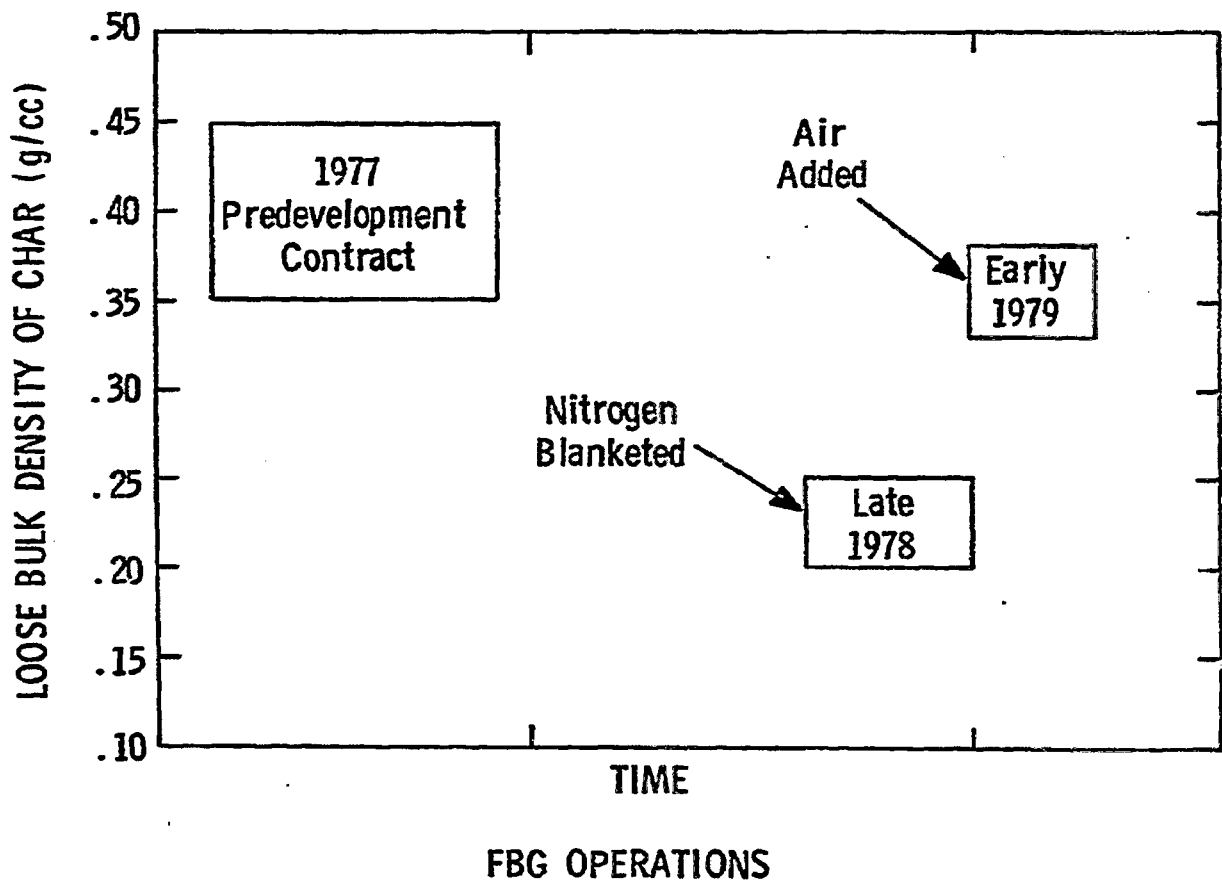


Table 4.3-1

ELEMENTAL ANALYSIS OF UNTREATED FBG FEED COALS

• Analyses on dry coal basis

	<u>Predevelopment Coal (1977)</u>	<u>1978 Coal</u>
Moisture	2.53	2.77
Ash	10.14	11.06
C-H Residue	10.55	9.40
Volatile Matter	40.70	43.47
Btu/lb	12117	12280
C	67.51	67.90
H	4.88	4.90
N	1.10	1.12
O	12.09	10.64
S	4.29	4.38
S _{pyritic}	1.05	1.59
S _{sulfate}	0.09	0.04
S _{organic}	3.15	2.74
SO ₃ Free Ash Elements		
P ₂ O ₅	0.37	0.22
SiO ₂	52.75	50.30
Fe ₂ O ₃	17.15	20.22
Al ₂ O ₃	19.79	18.60
TiO ₃	1.04	0.96
CaO	3.92	4.18
MgO	1.24	1.09
K ₂ O	2.48	2.43
Na ₂ O	1.25	1.31

Effect of Coal Particle Size

The particle size distributions of the coals used in the predevelopment work and in 1978 work are shown in Tables 4.3-2 and 4.3-3. K₂CO₃ catalyzed coal used in predevelopment operations did not contain as many large particles (+20 mesh) as that used in 1978. The +20 mesh particles account for 4.7% of the weight of the predevelopment feed coal and 28.1% of the recent feed coal. For both coals the catalyst loading of these large particles is low versus the smaller size fractions as shown by the potassium analyzes in Tables 4.3-2 and 4.3-3. Since the catalyst inhibits swelling and agglomeration during devolatilization, the low catalyst loading on the large +20 mesh particles was thought to be one factor which accounted for the poor operability of the FBG when feeding a coal with a relatively large fraction of such particles.

Samples of both the 1977 and 1978 feed coals and the large particles (+20 mesh) only from the 1978 feed were charred in the laboratory at 1300°F and atmospheric pressure in nitrogen. The 1977 feed did not agglomerate. The 1978 feed did form some agglomerates with the agglomerates containing most of the large particles initially present. The sample containing only +20 mesh particles agglomerated severely.

Table 4.3-2

SIEVE ANALYSIS OF PREDEVELOPMENT (1977) FBG FEED COAL

- Illinois No. 6 coal
- 15% K₂CO₃ treated
- Sampled 6/12/77

<u>Mesh Size</u>	<u>% (wt.) of Sample</u>	<u>% K₂O H₂O Soluble</u>	<u>% K₂O Acid Soluble</u>
+20	4.7	3.90	7.36
-20 + 60	59.3	5.41	7.96
-60 + 100	21.1	6.51	9.13
-100 + 200	11.4	7.08	9.86
-200 + 325	2.0	11.24	13.08
-325 + 400	0.5	11.83	15.48
-400	1.0	14.65	18.47

Table 4.3-3

SIEVE ANALYSIS OF 1978 FBG FEED COAL

- Illinois No. 6 Coal
- 15% KOH treated
- Sampled 11/29/78

<u>Mesh Size</u>	<u>% (wt.) of Sample</u>	<u>% K₂O H₂O Soluble</u>	<u>% K₂O Acid Soluble</u>
+20	28.1	5.58	9.98
-20 + 60	52.6	8.25	11.49
-60 + 100	14.8	8.83	12.91
-100 + 200	2.7	5.8	11.41
-200 + 325	1.3	10.40	13.75
-325 + 400	0.4	14.85	17.40
-400	0.1	--	--

The data in Tables 4.3-2 and 4.3-3 show that the large (+20 mesh) particles in the 1978 FBG feed coal had a lower catalyst loading than the remainder of the feed. Laboratory chars prepared from these larger particles showed a high degree of agglomeration. The study described below was performed to address the question of whether or not the low catalyst loading was the cause of agglomeration of the large particles during devolatilization.

A sample of uncatalyzed FBG feedstock was divided into sieve fractions. Portions of the individual fractions were then treated with either KOH or K_2CO_3 catalyst. The laboratory procedure for catalyst impregnation simulated that used in the Catalyst Addition Unit (CAU) of the FBG. In this procedure, the coal was mixed with a 30% (wt.) catalyst solution in the appropriate quantity to result in a final catalyst loading on the coal equivalent to 15% (wt) K_2CO_3 . Analysis of the sieve fractions treated in this manner showed that each fraction had the same catalyst loading.

The mixture was then dried under nitrogen and the treated coal samples were charred in a laboratory muffle furnace. The chars were examined for agglomeration and their loose bulk densities measured. The results are shown in Tables 4.3-4 and 4.3-5 below.

Table 4.3-4

KOH CATALYZED FBG FEEDSTOCK

- Illinois No. 6 Coal
- 12% KOH treated

<u>Sieve Cut</u>	<u>Loose Bulk Density of Muffle Furnace Char (g/cc)</u>	<u>Agglomeration</u>
+20	.51	No
-20 + 50	.52	No
-50 + 100	.56	No
-100	.52	No

Table 4.3-5

K_2CO_3 CATALYZED FBG FEEDSTOCK

- Illinois coal
- 15% K_2CO_3 catalyzed

<u>Sieve Cut</u>	<u>Loose Bulk Density of Muffle Furnace Char (g/cc)</u>	<u>Agglomeration</u>
+20	.58	No
-20 + 50	.53	No
-50 + 100	.55	No
-100	.55	No

The lack of agglomeration, particularly for the +20 mesh particles, suggests that uniform catalyst impregnation would allow this sieve size to be included in the reactor feed. In addition, the observed loose bulk densities have virtually the same value for chars from coal of all particle sizes and for equivalent loadings of both KOH and K₂CO₃ catalysts. Therefore, it should be possible to include larger size particles in the gasifier feed if a method of uniform catalyst impregnation is obtained.

Effect of Soak Time on Catalyst Distribution

A study was designed to test the effect of increasing the length of time the catalyst solution is in contact with the coal before drying on the uniformity of catalyst distribution.

The data in Table 4.3-6 were obtained using dried Illinois No. 6 coal and a 33% KOH solution. Samples of coal were treated with catalyst solution, allowed to stand under nitrogen for the specified contact time, and then dried in a vacuum oven at 100°C. The data indicate that for a laboratory prepared sample, increasing the contact time to 16 hours results in some improvement in uniformity of catalyst distribution on particles of all sizes. However, all of the laboratory samples have a more uniform catalyst loading than the samples prepared by the FBG Catalyst Addition Unit. This suggests that adjusting the contact time would be of little benefit for catalyst impregnation of Illinois coal and effective mixing in the catalyst addition unit should be more important. Therefore, no further work was carried out in the area of contact time and catalyst impregnation in the bench scale program.

Table 4.3-6

EFFECT OF INCREASED CONTACT TIME
ON KOH IMPREGNATION OF COAL

Contact Time (hr)	Wt % Acid Soluble K ₂ O			
	<u>-100 Mesh</u>	<u>-60 + 100 Mesh</u>	<u>-20 + 60 Mesh</u>	<u>-8 + 20 Mesh</u>
1	12.72	14.66	15.50	12.12
8	14.20	15.32	15.27	10.97
16	13.64	13.40	14.50	13.70
24	14.19	14.31	14.80	13.53

Coal Pretreatment

When Illinois coal is heated, it undergoes a plastic transformation whereby micelles of lamellae in the vitrinite become mobile and realign. Thus, the coal softens and becomes deformable. While in this "plastic" state, evolution of gases within the coal particle lead to the development of vacuoles. The overall result of this transformation is a light, friable particle. In the CCG process, these particles could be quickly broken down into an extremely light and fine powder. This powder may lead to processing problems for two reasons: (1) the fine particles result in a very low fluid bed density (a high density char is desirable in order to maximize the amount of material handled by any given size gasifier), (2) the fine particles may make catalyst recovery and solid-liquid separations difficult. Therefore, research was aimed at eliminating the swelling tendency of Illinois coal.

Previous work by coal scientists has identified three necessary and sufficient conditions for the development of plasticity in coal: (1) the presence in the coal of lamellae-bridging structures that can be thermally ruptured, (2) a supply of hydroaromatic hydrogen, and (3) an initial, intrinsic potential for micellar and lamellar mobility (not related to the rupture of chemical bonds) which provides opportunity for free-radicals formed by bond rupture to contact potentially transferable hydrogen.

In the PDU operations, the approach is to eliminate the swelling tendency of Illinois coal by oxidation of the catalyzed coal. Oxidation is believed to increase the cross-linking in the coal, thereby reducing the micellar and lamellar mobility. Furthermore, oxidation is a process which can be integrated into unit operations easily. Bench scale data and unit operability data were obtained simultaneously.

A second approach to eliminating swelling behavior is dissolution of humates into hot KOH. Both of these approaches are discussed in more detail below.

Atmospheric Pressure Devolatilization Studies

Initial devolatilization studies at the bench scale were performed by pyrolyzing the coal in a muffle furnace under an inert atmosphere. The observed value of the bulk density of the devolatilized coal (0.51-0.58 g/cc) is higher than densities of char from the fluidized bed pilot plant reactor (0.2-0.4 g/cc) which suggests that muffle furnace char may not be directly comparable to reactor char. Scanning electron microscope analysis confirmed this hypothesis. Microscopic analysis showed that all of the muffle furnace chars consisted of particles which remained angular and irregular in shape, indicating that they did not go through a plastic state during devolatilization. FBG and PDU bottom chars consist of rounded, enlarged particles that have melted and resolidified.

A procedure which closely simulates pilot unit devolatilization was desired. Therefore, a bench scale devolatilization process which reproduces the characteristics of the FBG char was developed.

A small fluidized bed reactor was designed for this study. The unit simulates coal addition to a hot, fluidized bed gasifier in all respects except pressure conditions. Figure 4.3-2 illustrates the unit. The reactor system is constructed of quartz. The bed is supported by a porous screen and is fluidized by gas which is preheated in the outer section of the vessel. A movable thermocouple is used to measure bed temperature at any desired position.

A narrow cut of prepared coal (20-60 mesh) is fed to the reactor. A 100-200 mesh sand has been chosen for the initial bed material for the reactor because of its fluidizing properties and because a fine cut of bed material is required in order to separate the bed from the product char.

Feeding coal directly into the top of the reactor appears to simulate pilot unit production of char at 100 psig. Uncatalyzed Illinois coal agglomerated as expected, and coal catalyzed with 15% K_2CO_3 and exposed to air at ambient temperature for 64 hours did not agglomerate. The loose bulk density of the latter char was 0.38 g/cc. This value is comparable to the high density char produced in the FBG at low carbon conversions during the predevelopment contract.

In order to quantify the effect of air exposure, data were obtained using Illinois No. 6 coal catalyzed with KOH and oxidized to varying degrees. Thus, samples of -20 + 60 mesh Illinois coal were catalyzed with KOH, dried, and exposed to air by blowing air through a packed bed of coal. Each sample was rehomogenized after air exposure to prevent anomalous results due to sampling errors. A 10 g aliquot was then devolatilized in the fluidized bed pyrolyzer. The results, shown in Figure 4.3-3, indicate that exposure to air increases the density of chars produced from KOH catalyzed Illinois coal. This result agrees with FBG pilot unit experience.

Since KOH is known to react with CO_2 to form K_2CO_3 and water, it was not clear from these data alone whether it was O_2 or CO_2 which caused the high density char. Therefore, K_2CO_3 catalyzed coal was studied to learn if CO_2 pretreatment rather than oxidation would be sufficient to produce a high density char from KOH catalyzed coal. It is desirable to avoid oxidation if possible since oxidation may adversely affect the sulfur forms present in recycled catalyst. The results of this study are shown in Figure 4.3-4.

The data indicate that oxidation is required to produce a high density char from K_2CO_3 catalyzed coal. This also demonstrates that oxidation of KOH catalyzed coal, not reaction of KOH with CO_2 to form K_2CO_3 , is responsible for the increase in densities shown in Figure 4.3-3.

Figure 4.3-5 presents data obtained from air exposures at 350°F. Previous data obtained at ambient temperature are included for comparison. Effective air exposure is seen to be obtained in a shorter time at the higher temperature. After only six hours of exposure at 350°F in the laboratory unit, the coal produced a char with a density comparable to that seen only after much longer exposure times at ambient temperature.

FIGURE 4.3-2
BENCH SCALE FLUIDIZED BED UNIT

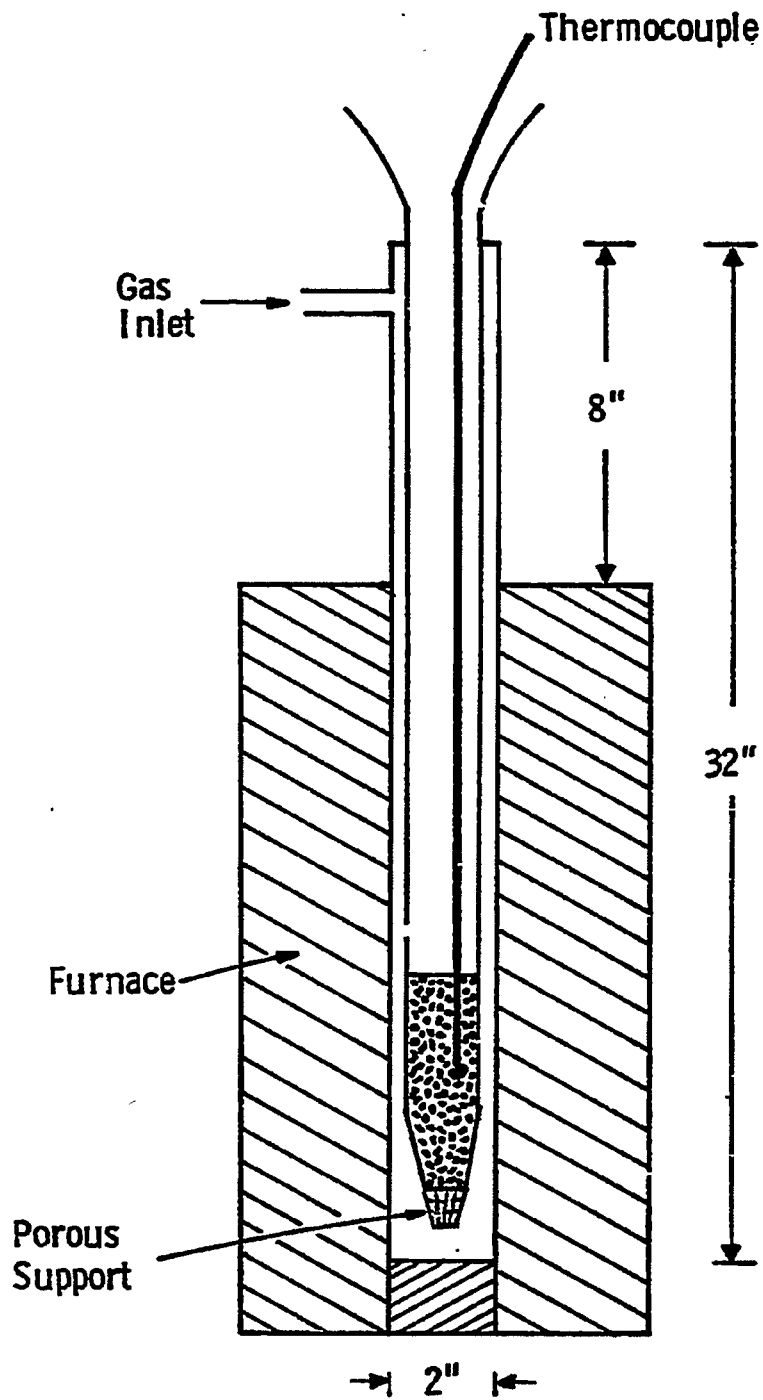


FIGURE 4.3-3

CHAR DENSITY INCREASES WITH AIR EXPOSURE
FOR KOH CATALYZED COAL

- ILLINOIS #6 COAL
- 12% KOH CATALYZED
- -20 + 60 MESH
- AIR EXPOSED AT AMBIENT TEMPERATURE

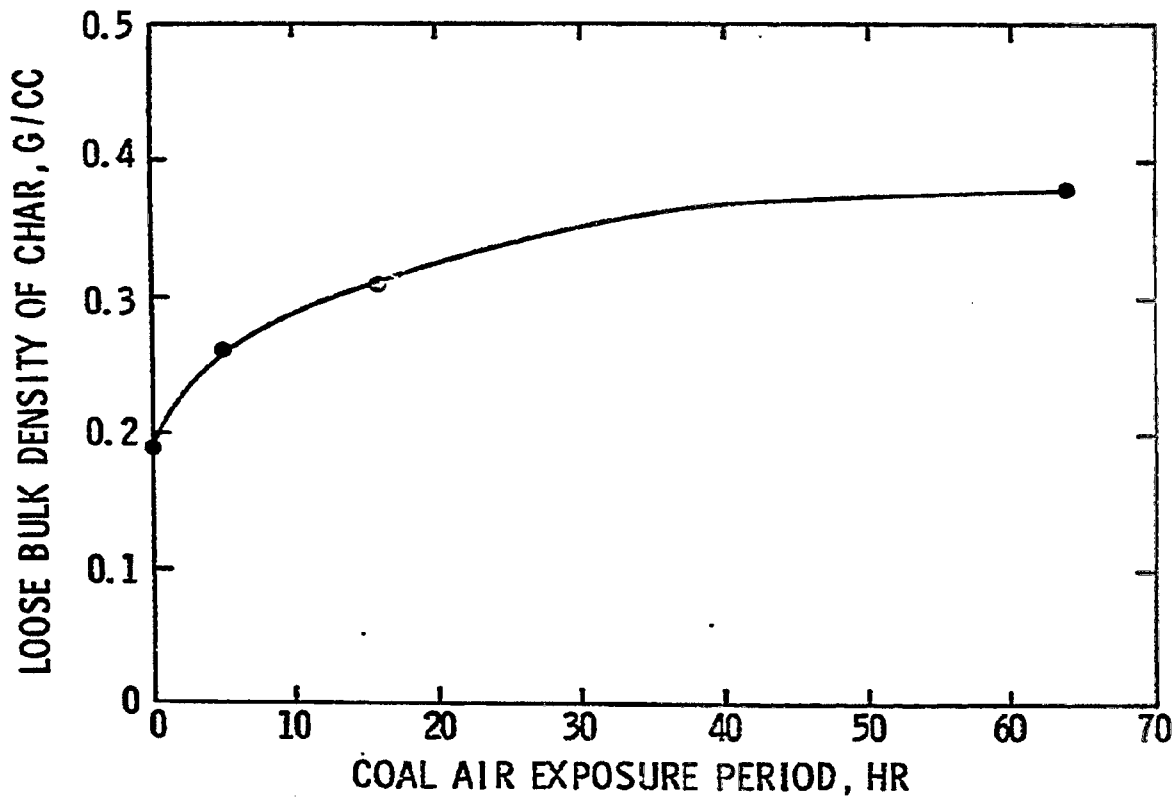


FIGURE 4.3-4CHAR DENSITY INCREASES WITH AIR EXPOSURE
FOR K_2CO_3 CATALYZED COAL

- ILLINOIS #6 COAL
- 15% K_2CO_3 CATALYZED
- -20 + 60 MESH

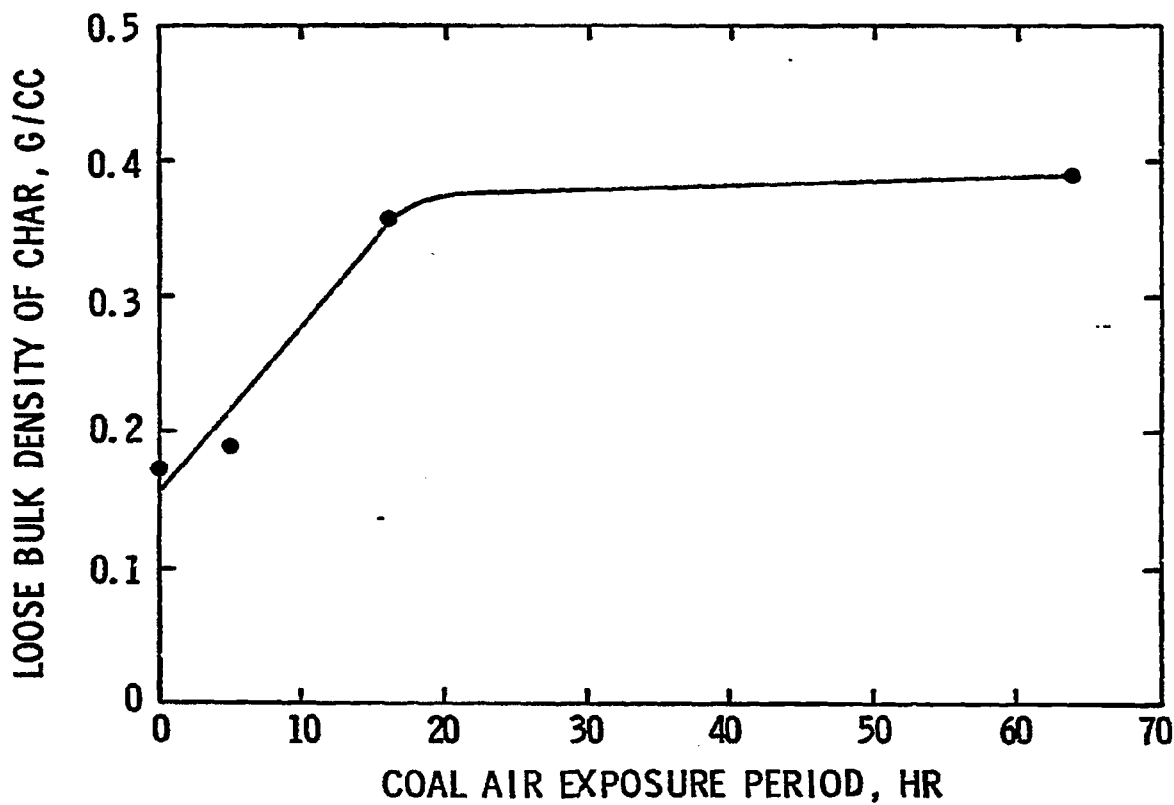
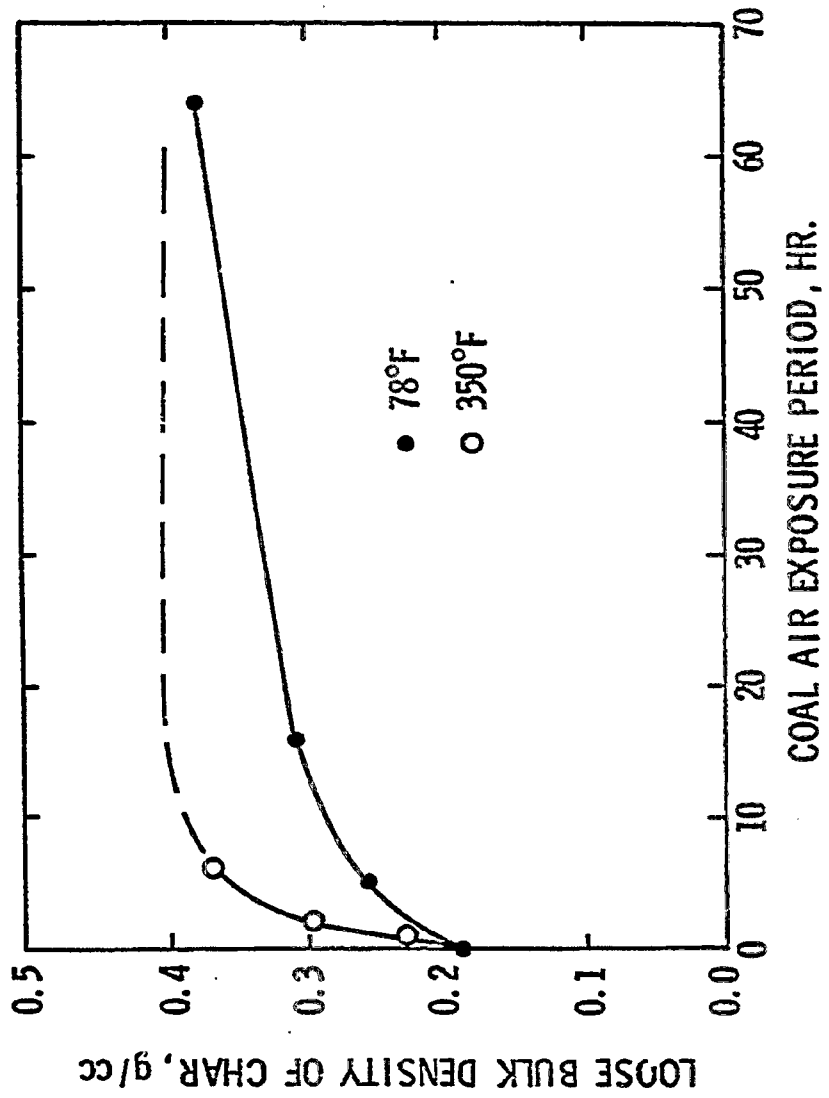


FIGURE 4.3-5

AIR EXPOSED COAL PRODUCES HIGH DENSITY CHAR

- ILLINOIS COAL
- 12% KOH CATALYZED
- 0.6 SCF/HR AIR FLOW



Pressurized Free Fall Unit Studies

The fluidized bed devolatilization unit, described above, can operate only at atmospheric pressure. A pressurized Free Fall Unit (FFU) was used to study the effect of pressure during devolatilization on char properties.

The FFU is shown in Figure 4.3-6. A 10 gram sample of -80 + 100 mesh coal is loaded into the feeder and the reactor is brought to the desired pressure and temperature. The coal is allowed to trickle into the reactor, which is a 3/4-inch O.D. by 8 foot long tube. The coal is heated rapidly, producing a char sample which is collected in a cold receiver beneath the reactor and liquids which are condensed in a cell immersed in liquid nitrogen. The solids produced are retained for analysis.

The experiments performed are summarized in Table 4.3-7. Illinois No.6 coal catalyzed with K_2CO_3 with a minimum of air exposure during handling produced high density chars when devolatilized at atmospheric pressure or 100 psia (the pressure at which the FBG was operated). Changing the gaseous atmosphere to 80% N_2 , 20% H_2 at 100 psia total pressure did not affect the density. However, all attempts to feed unoxidized or mildly oxidized Illinois coal catalyzed with K_2CO_3 failed due to plug formation in the reactor at 500 psia. The plugs formed are similar to feed line plugs experienced in early PDU operations. Plug formation is an indication of swelling and agglomeration during the pyrolysis. These data suggest that swelling and agglomeration problems increase with increasing pressure.

Unoxidized Illinois coal plugged the reactor at 500 psia regardless of catalyst form (KOH or K_2CO_3); however, Wyodak coal catalyzed with K_2CO_3 did not plug the reactor and formed a high density char (0.44 g/cc). Further oxidation of Illinois coal samples were tried. Two samples were air exposed for 16 hours at 100°C. The first sample was catalyzed and then air exposed; however, the second sample was air exposed before catalyst impregnation. The first sample did not plug the reactor, but it produced a low density char of only 0.25 g/cc. The second sample plugged the reactor.

The char samples obtained from operations which did not plug the reactor were analyzed for particle size distribution. The results are plotted in Figure 4.3-7. These data show that higher pressure devolatilization tends to produce a greater number of fine particles.

This work and Process Development Unit (PDU) operations have indicated that pressure is an important variable in coal devolatilization. Therefore, emphasis shifted from atmospheric pressure studies to pyrolysis at high pressures.

Tubing Bomb Devolatilizations Studies

The above discussion describes studies conducted using the Free Fall Pyrolysis Unit. The service factor for this unit is low due to plugging problems. The most easily operable system for pyrolyzing coal under pressure

FIGURE 4.3-6

**FREE FALL PYROLYSIS UNIT
(FFU)**

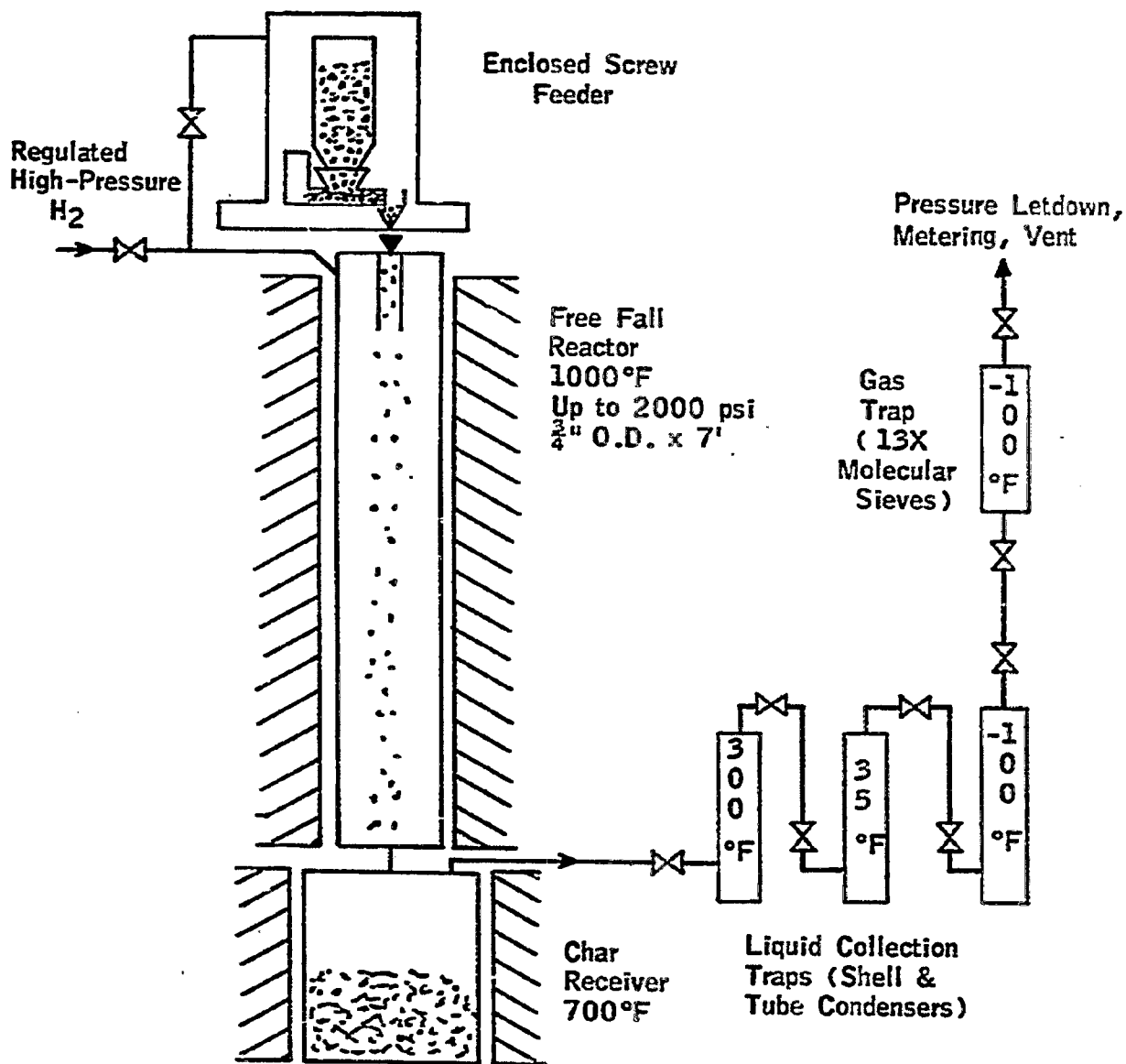


Table 4.3-7

FREE FALL UNIT CHAR DENSITIES

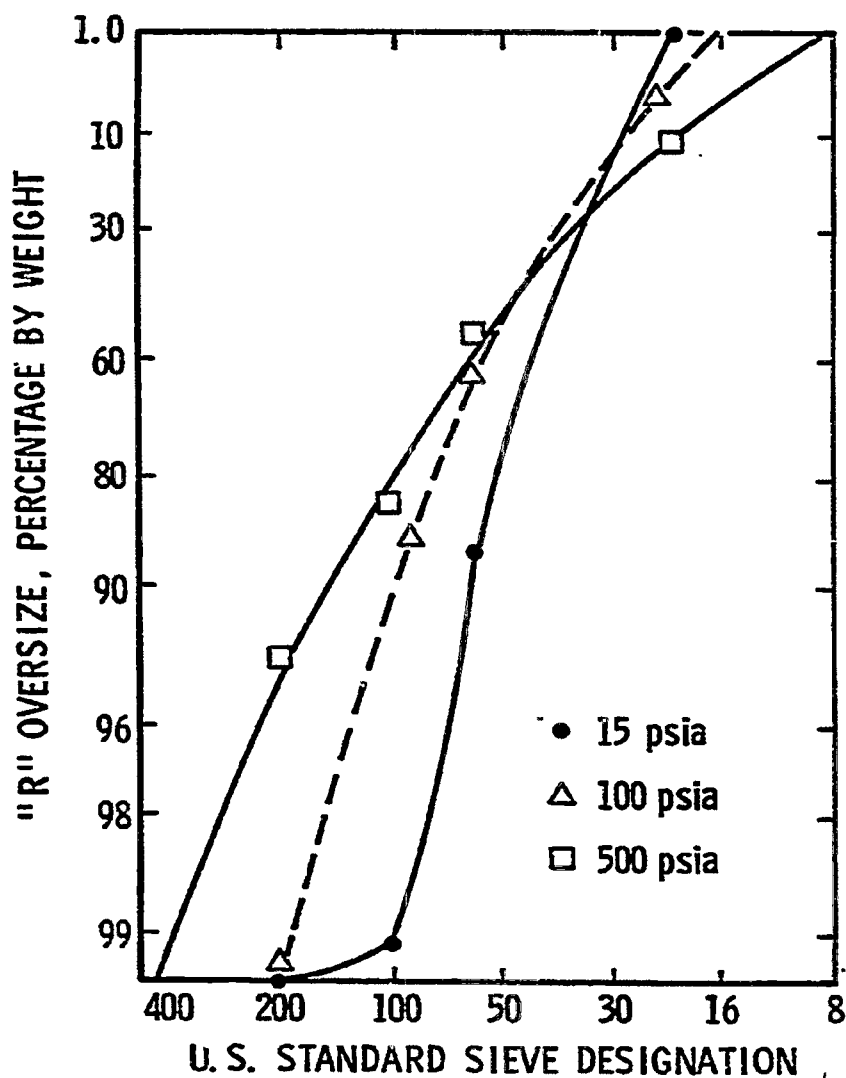
<u>Sample</u>	<u>Atmosphere</u>	<u>Loose Bulk Density, g/cc</u>
15% K ₂ CO ₃ on Illinois No.6	1 atm ₂ N	0.39
15% K ₂ CO ₃ on Illinois No. 6	100 psia N ₂	0.46
15% K ₂ CO ₃ on Illinois No. 6	80 psia N ₂ * 20 psia H ₂	0.44
15% K ₂ CO ₃ on Illinois No. 6	500 psia N ₂ *	Reactor plugged
15% K ₂ CO ₃ on Illinois No. 6	400 psia N ₂ 100 psia H ₂	Reactor plugged
12% KOH on Illinois No. 6	400 psia N ₂ 100 psia H ₂	Reactor plugged
15% K ₂ CO ₃ on Wyodak	400 psia N ₂ 100 psia H ₂	0.44
15% K ₂ CO ₃ on Illinois, catalyzed and then dried in air for 16 hr. @ 100°C	400 psia N ₂ 100 psia H ₂	0.25
15% K ₂ CO ₃ on Illinois, dried in air for 16 hr. @ 100°C, then catalyzed	400 psia N ₂ 100 psia H ₂	Reactor plugged

*Duplicate runs performed on each of these samples

FIGURE 4.3-7

INCREASED DEVOLATILIZATION PRESSURE PRODUCES
SMALLER CHAR PARTICLES

- FREE FALL PYROLYSIS UNIT
- ILLINOIS #6 COAL
- 15% K_2CO_3 CATALYZED



is a tubing bomb reactor. Figure 4.3-8 illustrates a typical reactor. For these studies, the coal is weighed into ceramic "boats" which are placed in the reactor. The reactor is heated by immersion into a large, fluidized sand bath. The bath temperature used for these studies was about 920°F, the maximum allowed on the available equipment. A gauge is used to measure the pressure. A series of screening runs was made in tubing bomb reactors. Table 4.3-8 summarizes the results of these runs.

As found in studies with the Free Fall Unit, and in PDU operations, pressure was important in determining the extent of agglomeration for the tubing bomb samples. For those samples which did agglomerate, agglomeration increased with increasing pressure. Air exposed samples showed less agglomeration than fresh coal. One sample which had been air exposed for six hours at 350°F showed no agglomeration.

Another series of experiments was performed at 1300°F. The tubing bomb was modified so that it could be inserted vertically into a small fluidized sand bath. The results of these tests are shown in Table 4.3-9. The first four samples listed are the same as the correspondingly lettered samples in Table 4.3-8. The results indicate that higher temperature causes somewhat more severe agglomeration.

High Pressure Pyrolyzer

It has been shown that pressure is an important variable in determining char density and agglomeration properties. Also, fixed bed reactors do not produce chars with densities comparable to fluid bed reactors. Therefore, a High Pressure Fluidized Bed Pyrolyzer (HPP) was designed and constructed. A diagram of this unit is shown in Figure 4.3-9. It is similar in operation to the atmospheric pressure fluid bed reactor in that the feed coal is fed into the top of the reactor and falls into a fluidized bed of hot sand. The reactor is continually swept with inert fluidizing gas. The system pressure is maintained by an automated control valve.

During initial 500 psig operation of the high pressure unit with PDU feed coal, large chunks were formed inside the reactor. These chunks resemble low conversion chunks found in early PDU operations. The chunks are much larger than the feed line diameter. Operations with Wyodak coal at high pressure did not form chunks. Chunks were also not formed when a fluidized sand bed pyrolyzer was run at atmospheric pressure. These observations lend support to the theory that the low fluid bed density in the PDU is related to a plastic phase which the feed coal experiences during devolatilization and that high pressure favors the formation of a plastic state.

Chunk formation is avoided in the PDU by entraining the feed coal in a high velocity nitrogen stream. The nitrogen dilutes the feed with inert material and avoids agglomeration. In order to avoid chunks in the HPP, the feed coal was diluted with sand of the same size and composition as present in the bed.

FIGURE 4.3-8
TUBING BOMB REACTOR

NOTE:
ALL TUBING
SS 316 SEAMLESS

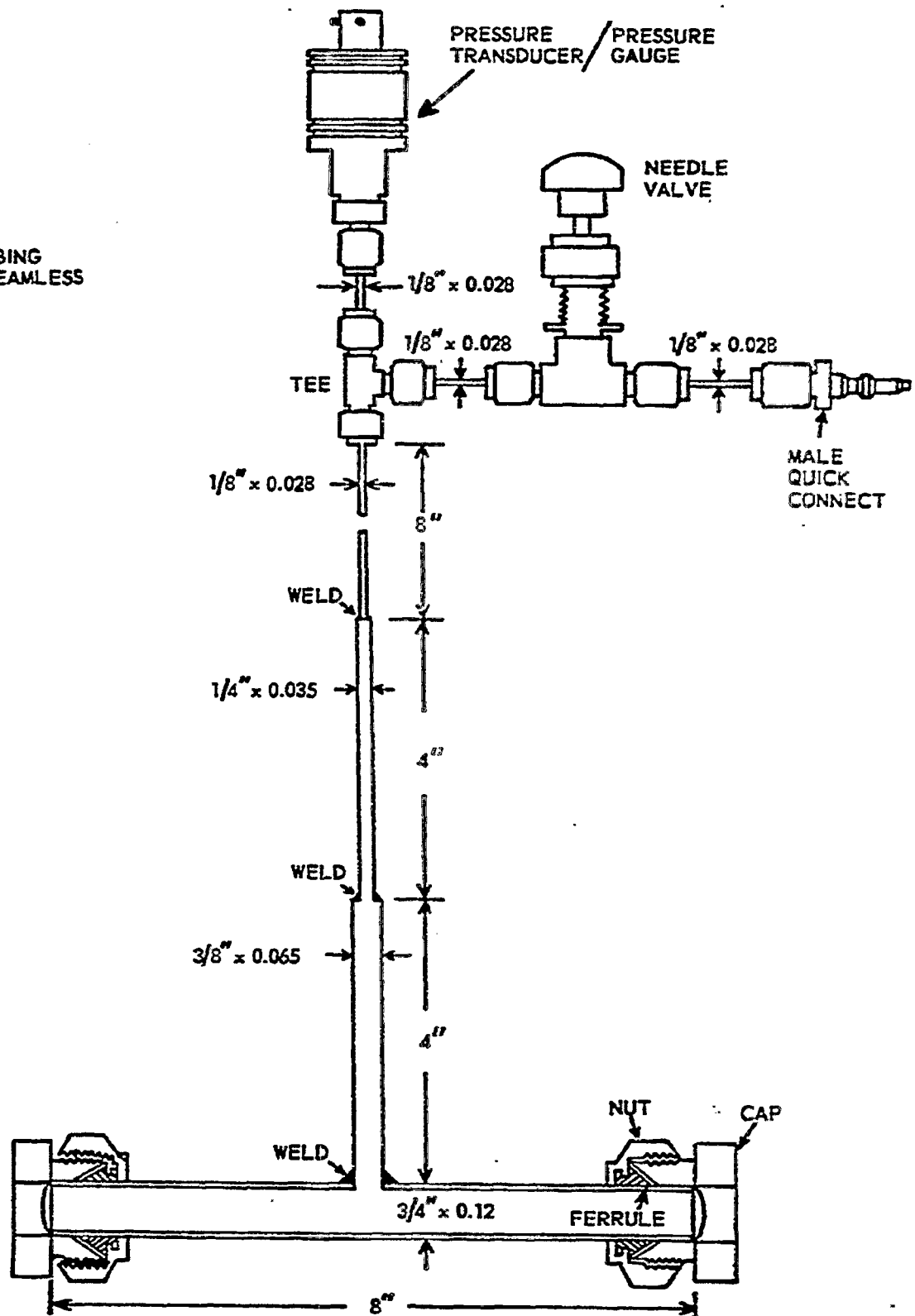


Table 4.3-8

TUBING BOMB DEVOLATILIZATION STUDIES

- 920°F
- Fixed bed
- PDU feed (partially oxidized Illinois #6 with 12% KOH)

Treatment	Result at Final Pressure	
	265 psia	465 psia
A. None (62.1% C, 4.36% H)*	Weakly Agglomerated	Agglomerated
B. 15% Ca(HCO ₂) ₂ added	Agglomerated	Agglomerated
C. Air exposed 41 hr. @ 75°F (61.7% C, 4.32% H)	Very Weakly Agglomerated	Agglomerated
D. Air exposed, 16 hr. @ 200°F (60.4% C, 4.32% H)	Very Weakly Agglomerated	Agglomerated
E. Air exposed, 48 hr. @ 200°F	--	Weakly Agglomerated
F. Air exposed, 24 hr. @ 275°F		Weakly Agglomerated
G. Air exposed, 4 hr. @ 350°F	--	Agglomerated
H. Air exposed, 6 hr. @ 350°F (59.4% C, 3.87% H)	Bulk Density = 0.59 g/cc	Bulk Density = 0.53 g/cc
I. Sample D with 10 % FBG bottom char added	--	Bulk Density = 0.38 g/cc
J. 10% FBG Bottom Char added	--	Bulk Density = 0.31 g/cc
K. 1% FBG Bottom Char added	--	Very Weakly Agglomerated
L. Wyodak (56% C, 4.34% H)	Bulk Density = 0.48 g/cc	Very Weakly Agglomerated
M. PDU Fluid Bed Dryer Batch I	--	Very Weakly Agglomerated

*Analyses on dry coal basis

Table 4.3-9

1300°F TUBING BOMB DEVOLATILIZATIONS

- 1300°F
- Fixed bed
- Illinois #6 coal
- 500 psia final pressure

<u>Sample</u>	<u>Result</u>
A. PDU Feed (CAU)	Agglomerated
D. PDU Feed (CAU), Air Exposed 16 hr @ 200°F	Agglomerated
H. PDU Feed (CAU), Air Exposed 6 hr @ 350°F	Very Weakly Agglomerated
M. Fluid Bed Dryer Batch 1 with Catalyst Redistributed	Agglomerated
N. Fluid Bed Dryer Batch 2	Agglomerated
O. Fluid Bed Dryer Batch 3	Weakly Agglomerated
P. Fluid Bed Dryer Batch 3, N ₂ Exposed 2 hr @ 350°F	Very Weakly Agglomerated

Table 4.3-10 contains the densities of chars produced in this manner from a series of PDU feed samples. The pretreatment of these samples and PDU experience with them is also summarized in Table 4.3-10.

In all cases, the density is inversely correlated with pressure. The char density at the lower pressures is high, relative to the density of the catalyzed coal before devolatilization.

FIGURE 4.3-9

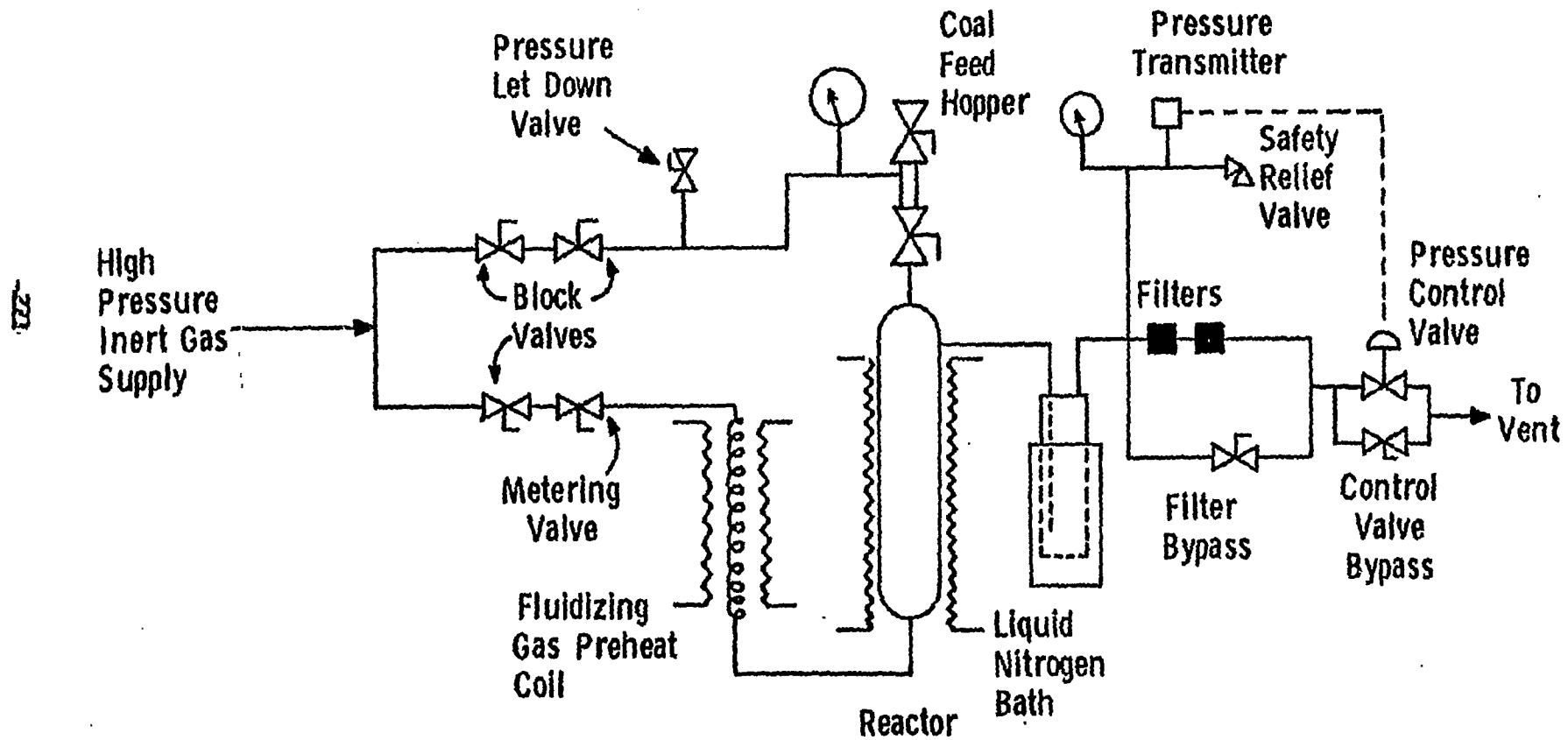
HIGH PRESSURE FLUIDIZED BED DEVOLATILIZER

Table 4.3-10 contains the densities of chars produced in this manner from a series of PDU feed samples. The pretreatment of these samples are PDU experience with them is also summarized in Table 4.3-10. In all cases, the density at the lower pressures is high, relative to the density of the catalyzed coal before devolatilization.

Devolatilization of Extracted Coals

Another approach to elimination of swelling ability is the removal of the vehicle "solvent". Extraction of a small amount of low molecular weight material (called bitumen) from the coal eliminates swelling. On the other hand, process pressure aggravates the swelling tendency by not allowing the hydrogen-donating bitumen to escape. Removal of the bitumen from the coal prior to processing will allow coal to be processed at any pressure.

When KOH catalyzed coal is washed with hot water, organic material is extracted from the coal. The observation of organic material in the basic aqueous extracts of catalyzed Illinois coal suggests a method of removing "bitumens" from coal. The water solubility of these salts suggests that they have a low molecular weight and that they contain hetero-atom functionality, such as carboxylic acid functions and phenolic groups. Low molecular weight materials and reactive functionalities which may produce low molecular weight materials upon pyrolysis are the expected sources of volatiles in coal. Removing these moieties by KOH extraction may improve the swelling properties of the coal.

Table 4.3-11 shows the effect of an aqueous extraction of Illinois No. 6 coal which had been previously catalyzed with 8.5 wt % K^+ . All of these samples were subjected to an aqueous Soxhlet extraction until the fresh extract became colorless. The coal was then dried and analyzed. Attempts to analyze the extract failed due to the small sample size.

The potassium carbonate treated coal produced an extract solution that was only moderately colored by extracted organic compounds. The coal analysis shows that only small amounts of carbon and hydrogen have been removed as compared to the blank run on raw Illinois coal without catalyst. The potassium concentration is relatively low, indicating that most of the catalyst has been washed off the coal, apparently as K_2CO_3 . The coal has a high swelling index, well above the range that indicates PDU operability.

The potassium hydroxide catalyzed coal produced a dark brown extract solution from which traces of solid could be precipitated by addition of hydrochloric acid. The analysis of the coal shows a decrease in carbon and hydrogen. The potassium content of this coal is relatively high. Potassium hydroxide is easier to impregnate onto coal. Its higher basicity allows it to react with larger, less acidic molecules in the coal which are not soluble in water even as potassium salts.

Table 4.3-10

LOOSE BULK DENSITIES OF CHARs
FROM HIGH PRESSURE PYROLYZER

Pressure (psig)	Density (g/ml) Batch Number			
	<u>0</u>	<u>6</u>	<u>7</u>	<u>8</u>
500	0.42	0.44	0.41	-
350	0.51	0.56	-	-
250	0.61	0.60	0.43	0.41
100	0.85	0.73	0.45	0.44
Catalyzed Coal Starting Material		0.74		
Sand		1.56		

<u>Batch</u>	<u>Pretreatment</u>	<u>PDU Fluid Bed Density</u>
0	None	6-8 lbs/ft ³ @ 500 psig
6	Mild oxidation only	6-8 lbs/ft ³ @ 500 psig
7	Very mild oxidation followed by oxygenless heat treatment	8-9 lbs/ft ³ @ 250 psig
8	Mild oxidation followed by oxygenless heat treatment	8-9 lbs/ft ³ @ 500 psig

Table 4.3-11

SOXHLET EXTRACTION OF ILLINOIS COALS

Sample	Wt. Loss	Extracted Coal					
		%K	%C*	%H*	%S*	C/H	SI***
Raw Illinois No. 6	--	0.18	71.45	5.09	--	14.0	2.5-3.4
12% KOH Catalyzed PDU Prep.	5.7%	3.5	67.25	4.57	4.17	14.7	0.92-0.95
12% KOH Catalyzed PDU Oxidized	8.3%	3.52	67.13	4.58	4.10	14.7	--
15% K ₂ CO ₃ Catalyzed Lab Prep.	2.6%	1.06	68.44**	4.98	--	13.7	1.40
Uncatalyzed, Mildly Oxidized PDU Prep.	2.0%	0.18	69.56	4.91	4.16	13.8	--

*Dry, potassium-free basis

**Dry, potassium carbonate-free basis

***Swelling Index

A sample which was mildly oxidized but uncatalyzed was also seen to release a small amount of organic material to the aqueous solution.

A sample which was both catalyzed and oxidized was seen to release an amount of organic material roughly equal to the sum of the catalyzed only and the oxidized only samples.

Removal of potassium catalyst is undesirable in a pretreatment process because a second catalyst impregnation would be required in order to re-establish the desired catalyst loading for gasification. Removal of organic material is also undesirable because it decreases the amount of carbon available for conversion to product gas.

Further studies were aimed at modifications of this process which would not actually remove the extracted material. A procedure was chosen which includes separating the coal and the aqueous extract, concentrating the extract to remove the bulk of the water, and then recombining the two components. The data in Tables 4.3-12 and 4.3-13 were obtained in this manner.

The data in Table 4.3-12 were obtained using 0.75N (3 wt % K^+) solutions. The amounts of solution and coal were chosen to provide a catalyst loading of 8.5 wt % K^+ , equivalent to 15 wt % K_2CO_3 on coal. Solutions containing only KOH and only K_2CO_3 were used, along with a mixture of K_2CO_3 and KOH in a 1:2 ratio which was chosen to simulate recycle catalyst solution from water-wash plus make-up catalyst in the form of KOH.

The data in Table 4.3-12 show that the pH of the catalyst solution affects the swelling properties of the treated coal. As the basicity of the initial solution is decreased, the swelling index of the treated coal increases, indicating that the coal will swell more in the PDU. This agrees with the earlier observation that less material is extracted from K_2CO_3 catalyzed coal than from KOH catalyzed coal.

A swelling index of less than 1.0 has been shown to indicate high density in the PDU. Thus, the coals treated with KOH and with the simulated recycle catalyst plus make-up are both predicted to run smoothly in the unit. The coal treated with K_2CO_3 may have only marginal performance in the PDU.

Table 4.3-13 includes data designed to test the hypothesis that oxidation during the reflux step of the pretreatment should improve the swelling index of the treated coal. It is known that oxidation of coal in basic solutions produces small molecules of aromatic carboxylic acid. This oxidation is more efficiently carried out under pressure.

Table 4.3-12

pH OF SOLUTION IS IMPORTANT FOR REFLUX-EXTRACTION TECHNIQUE

- Illinois No. 6 Coal
- 6 Hour Reflux
- 8.5 wt % K⁺ Loading
- Extract Decanted, Concentrated, and Recombined with Coal

<u>KOH</u>	<u>K₂CO₃</u>	<u>Coal</u>	<u>Swelling Index</u>
0.75 N	--	35 g/100 ml	0.86
0.25 N	0.50 N	35 g/100 ml	0.93
--	0.75 N	35 g/100 ml	1.02

The data indicate that oxidation under these conditions causes little, if any, improvement in the coal swelling properties.

Analytical work was undertaken to determine the nature of the extracted material for both oxidized and unoxidized coals. Elemental analyses and infrared spectra indicated that substantial amounts of colloidal inorganic material, primarily silicates, are present when the solutions are not carefully filtered. Nuclear magnetic resonance spectra were unobtainable even on filtered extracts, indicating that the organic material present is probably also colloidal.

Table 4.3-13

ATMOSPHERIC PRESSURE OXIDATION DURING EXTRACTION
DOES NOT AFFECT SWELLING BEHAVIOR

- Illinois No. 6 Coal
- Four Hour Reflux
- 12.9% K⁺ Loading
- Extract Decanted,
Concentrated, and
- Recombined with Coal

<u>Catalyst Solution</u>	<u>Gas Atmosphere</u>	<u>Swelling Index</u>
1 N KOH	N ₂	0.90, 0.95
1 N KOH	Air*	0.88, 0.90
0.67 N K ₂ CO ₃ + 0.33 N KOH	N ₂	0.90, 0.90
0.67 N K ₂ CO ₃ + 0.33 N KOH	Air*	0.88, 0.88

*Air Bubbled Through Slurry

Crosslink Additives

While extraction attacks the swelling problem by removal of the bitumens or conversion to inactive forms, additives may serve to react with the bitumens during pyrolysis in the gasifier. The ability of the coal molecules to crosslink, forming larger molecules, is believed to be important in determining the swelling behavior of a coal. Tables 4.3-14 and 4.3-15 contain the results of attempts to crosslink the coal during pyrolysis.

The first additives tested were elemental sulfur and tetramethylthiuramdisulfide (TTD), a common vulcanizing agent rubbers. For both additives, a solution in an organic solvent (CH_2Cl_2) was prepared and used to impregnate catalyzed coal. Blank samples treated with solvent only were also prepared.

The data in Table 4.3-14 show that impregnation with 2% sulfur has no effect. The blank sample showed no solvent effect. The data in Table 4.3-15 show that a 2% TTD loading has no effect and possibly promotes swelling. A 10% TTD loading resulted in a small improvement.

Further data was then obtained using carboxylic acid and phenolic compounds.

Catalyzed coal was treated with 2 weight % of each organic acid shown in Figure 4.3-10. The additives are all aromatic carboxylic acids or phenolic compounds. The acid forms of these compounds are insoluble in water, so that the attempt to wet impregnate the coal failed. In these cases, the mixture before drying was a slurry of catalyzed coal and additive in water. Dissolution in KOH solution allowed a true wet impregnation of the additive in the form of its potassium salt. The swelling indices for both types of application are shown in Figure 4.3-10.

In both the acid and salt form, the carboxylic acids tested, 2-naphthoic acid and benzoic acid showed little or no improvement in swelling. Coal treated with neutral benzoic acid was actually worse than the untreated, catalyzed blank.

The phenolic compounds do show promise as additives, particularly in the salt form. Addition of 2% 2-Naphthol decreased the swelling index to 1.04. A higher loading would probably bring the swelling index under 1.0, the limiting value used to predict PDU operability.

The coal treated with 2% phenol as a potassium salt, had a swelling index of 0.91, well within the desirable range. This promising result was followed by tests of two dihydroxy aromatic compounds, 2, 3-dihydroxynaphthalene and 1, 3-dihydroxybenzene (resorcinol). The difunctional compounds were tested on the basis of improving crosslinking by incorporating two cross-linking sites in one molecule.

As seen in Figure 4.3-10, both of the dihydroxy compounds tested reduced the swelling index to within the range used to predict smooth PDU operations. Although it contains more hydroxyl groups per gram of additive phenol, 2, 3-dihydroxynaphthalene reduced the swelling less than phenol. 1, 3-dihydroxybenzene showed some extra improvement over phenol, but not in proportion to the extra functionality per gram of additive. Apparently difunctionality in molecules used as additives to inhibit swelling is not important.

Table 4.3-14

SWELLING INDICES OF SULFUR
IMPREGNATED ILLINOIS COAL

<u>SAMPLE</u>	<u>SWELLING INDEX</u>
12.5 KOH Catalyzed Coal	1.29 ₊ .03
Catalyzed Blank Slurried with CH ₂ Cl ₂ and dried	1.28 ₊ .03
Slurried with CH ₂ Cl ₂ solution of sulfur to give 2 wt % impregnated on coal	1.30 ₊ .011

Table 4.3-15

SWELLING INDICES OF TTD* IMPREGNATED COAL

<u>SAMPLE</u>	<u>SWELLING INDEX</u>
12.5% KOH Catalyzed Coal	1.12 ₊ .04
Catalyzed blank slurried with CH ₂ Cl ₂ solvent and dried	1.06 ₊ .05
2% TTD impregnated using CH ₂ Cl ₂ solution and catalyzed coal	1.20 ₊ .02
10% TTD impregnated using CH ₂ Cl ₂ solution and catalyzed coal	1.04 ₊ .02

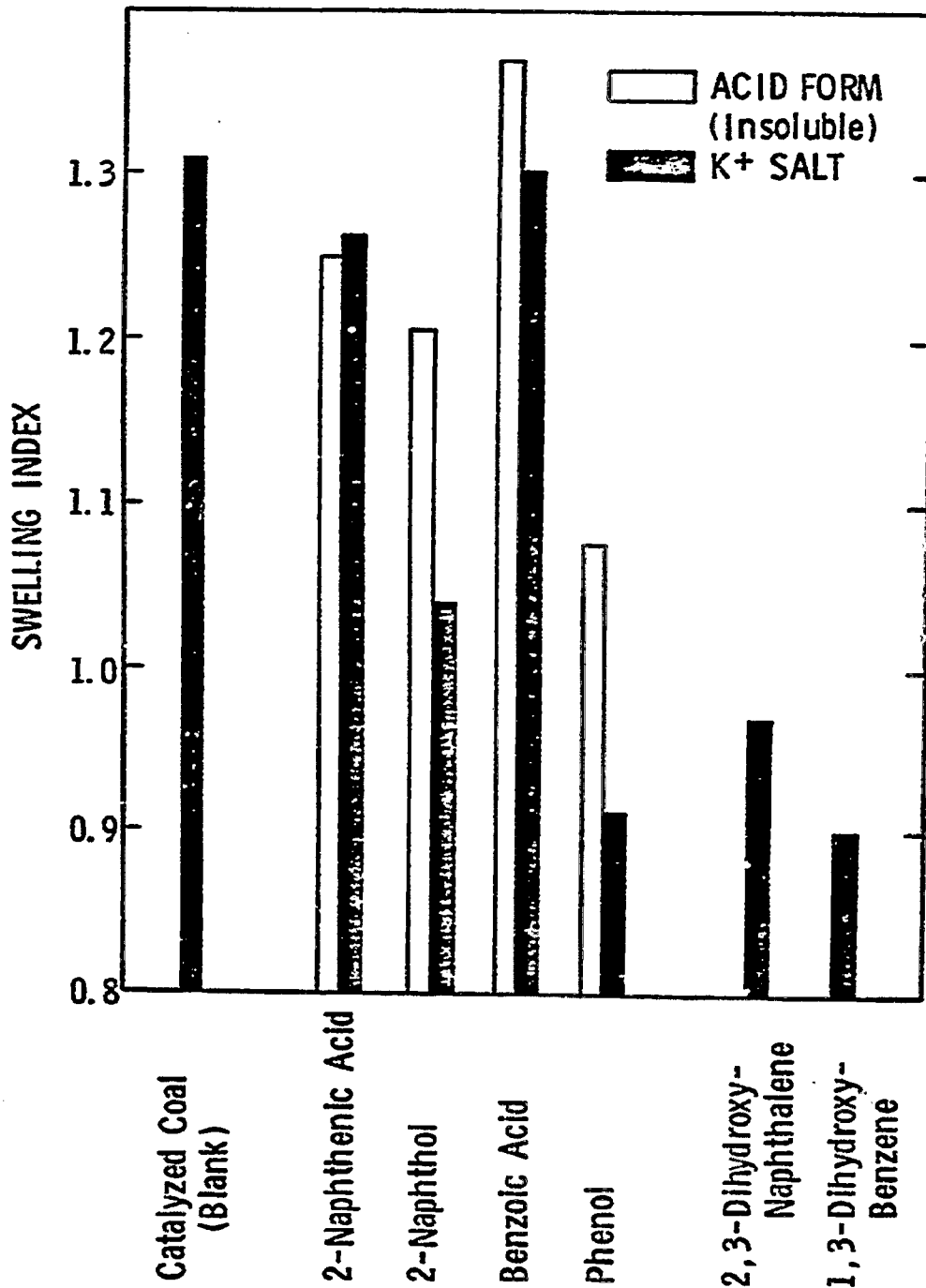
*TTD = Tetramethylthiuram disulfide - A common vulcanizing agent for rubbers

FIGURE 4.3 - 10

81B-1-38

ORGANIC ADDITIVES INHIBIT SWELLING

- KOH CATALYZED ILLINOIS COAL
- 2% ORGANIC COMPOUND ADDED BY WET IMPREGNATION



Char Dilution Studies

Experience with coking operations indicated that dilution of a caking coal with gasifier char might improve its agglomeration properties. Data for fresh, catalyzed coal is shown in Table 4.3-16.

Table 4.3-16

CHAR DILUTION IS NOT EFFECTIVE
ON FRESH, CATALYZED COAL

- Illinois coal
- 12.5% KOH catalyzed
- PDU char sampled 8/3/80

<u>Wt % Char Added</u>	<u>Swelling Index</u>
0	1.31 + .01
1	1.30 + .02
2	1.30 + .06
5	1.16 + .00
10	1.17 + .04
25	1.05 + .01
100	1.00

The data in Table 4.3-16 indicate that with as much as 25% by weight of char added to the catalyzed coal, the swelling tendency of the coal is not sufficiently reduced. Therefore, no further data was obtained for these samples.

4.4 Catalyst/Char Equilibrium Studies

Bench scale studies were undertaken to determine the effects of variable pH and potassium ion concentration on the amount of catalyst remaining on the char. This information is needed for the design of a multiple stage char washing process to recover potassium from the char. The equilibrium concentrations of potassium on digested FBG char, undigested FBG char, and PDU char were determined as a function of potassium concentration in solutions of constant pH and as a function of the pH of solutions of constant potassium concentration. Data have been obtained at room temperature. Studies were conducted to test the sensitivity of the results to temperature. This fundamental information will be used both in the PDU and in the commercial CCG catalyst recovery system process definition.

Preliminary experiments on the effect of agitation on equilibration and on particle breakdown were carried out. Methods of agitation considered were: (1) magnetic stirrer, (2) rotating flask, (3) wrist-action shaker, and (4) no agitation.

Particle breakdown was seen in both the magnetic stirrer and in the wrist-action shaker. Particle integrity was maintained with the rotating flask and without agitation, but solid-liquid contact was ineffective as judged by potassium concentrations remaining on the chars after removal of the solution by filtration.

As a result, all ambient temperature equilibrations were performed using the wrist-action shaker since K^+ absorption rather than particle breakdown was considered to be of primary importance in these experiments. This method was chosen over the magnetic stirrer because the shaker can handle a larger number of samples simultaneously.

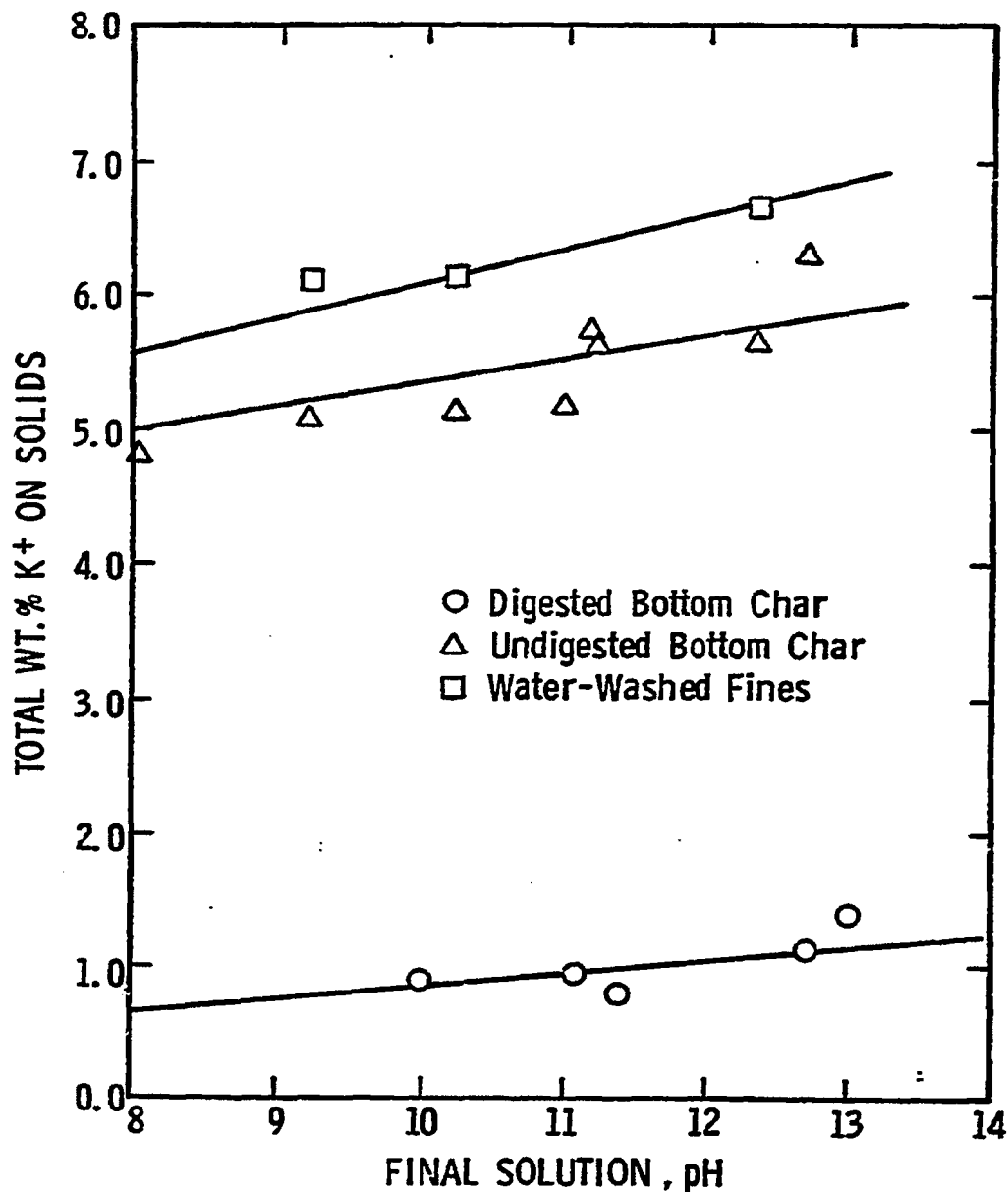
Three types of solids were studied: gasifier fines, digested bottom char, and undigested bottom char. The data for 0.4 wt % K^+ solutions in contact with each of the above are presented in Figure 4.4-1. The results indicate that for all three types of solids, the K^+ absorbed increases with increasing pH. The total K^+ concentration is lowest for the digested solids due to the absence of K^+ tied up with mineral matter in the char. The small difference between the fines and the undigested char is due to a difference in carbon conversion. The fines have a lower carbon conversion than the bottom char; therefore, the same quantity of K^+ tied up with the mineral matter will appear as a lower weight percentage in the fines.

Since less K^+ is absorbed by the char at lower pH values, leaching or other water wash operations may be performed more efficiently in solutions whose pH has been lowered. This might be accomplished by contacting the solutions with the acid gas separated from the gasification product gas.

FIGURE 4.4-1

EQUILIBRIUM K^+ ABSORBED ON THREE TYPES OF SOLIDS INCREASES AT HIGH pH

- 24°C
- 0.1 M K^+ (0.4 WT.%)
- KOH + KCl
- FBG Chars



The results shown above were obtained by changing the relative amounts of potassium chloride and potassium hydroxide in solution as a method of pH variation. Since chloride ion will not be the major component of a recovered catalyst solution, studies were performed to determine if the counter ion present affects the potassium absorption. These data are presented in Table 4.4-1.

The counter ions chosen include hydroxide, carbonate and sulfate. These ions are expected to be present in an air-exposed catalyst recovery solution. The data show that the counter ion present does not significantly affect the amount of potassium absorbed, except to the extent that the solution pH is affected.

Table 4.4-1

COUNTER ION DOES NOT AFFECT K⁺ ABSORPTION

- 1.0 M K⁺ solutions (4 wt %)
- FBG Char, water washed

<u>K⁺ Salt</u>	<u>Total wt % K⁺ on Char</u>	<u>Original pH</u>
KOH	6.81	14.0
K ₂ CO ₃	6.89	11.2
K ₂ SO ₄	6.49	7.0
KCl	6.35	7.0

Further data were then obtained using mixtures of potassium carbonate and potassium hydroxide to vary the pH. These ions are expected to predominate in recovered catalyst solutions.

Figure 4.4-2 illustrates the effect of pH on the K⁺ absorption. Solutions of different pH and different potassium concentrations were prepared by adjusting the relative amounts of potassium carbonate and potassium hydroxide. For a given concentration of potassium in solution, a higher pH results in a larger amount of potassium on the char.

FIGURE 4.4-2

K⁺ LEFT ON CHAR VARIES WITH SOLUTION pH

- FBG Char, Water Washed
- K₂CO₃ + KOH Solutions
- Ambient Temperature

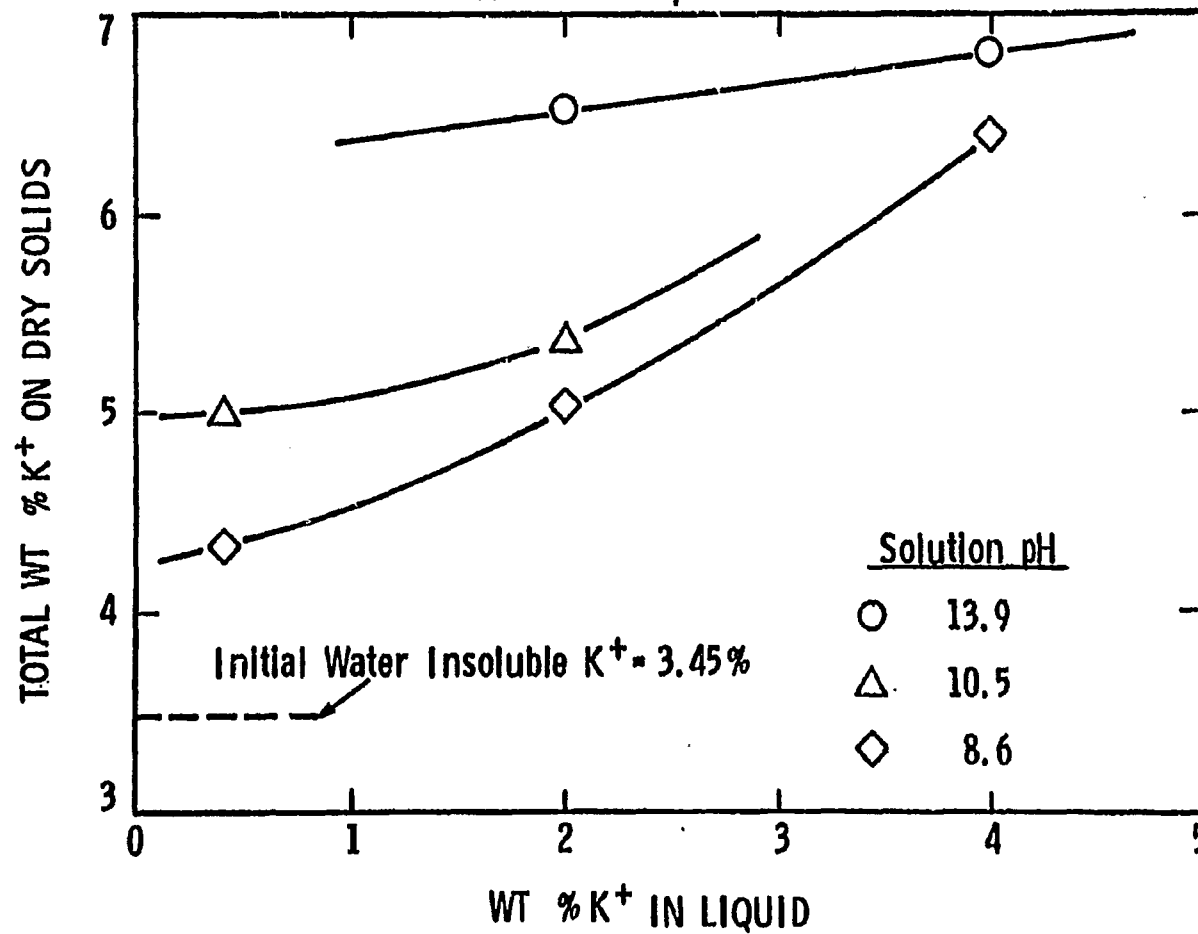


Figure 4.4-3 shows the effect of potassium concentration in solution. At any given pH, the amount of potassium absorbed is lower for lower aqueous potassium concentration. A range of concentrations from 0.05 M K^+ to 1.0M K^+ (0.2 to 4.0% by weight) was studied.

Figure 4.4-4 compares earlier data obtained using a prototype digester with bench scale results from this study. The bench scale data were obtained using digested char and potassium hydroxide solutions, because digested catalyst solutions have been shown to contain primarily the hydroxide form of the potassium catalyst. The data are seen to be in close agreement.

FIGURE 4.4-3

POTASSIUM ABSORPTION DECREASES WITH DECREASING pH
AND DECREASING POTASSIUM IN SOLUTION

- FBG CHAR, WATER-WASHED
- $K_2CO_3 + KOH$ SOLUTIONS
- AMBIENT TEMPERATURE ($24^\circ C$)
- 7% SOLIDS CONCENTRATION

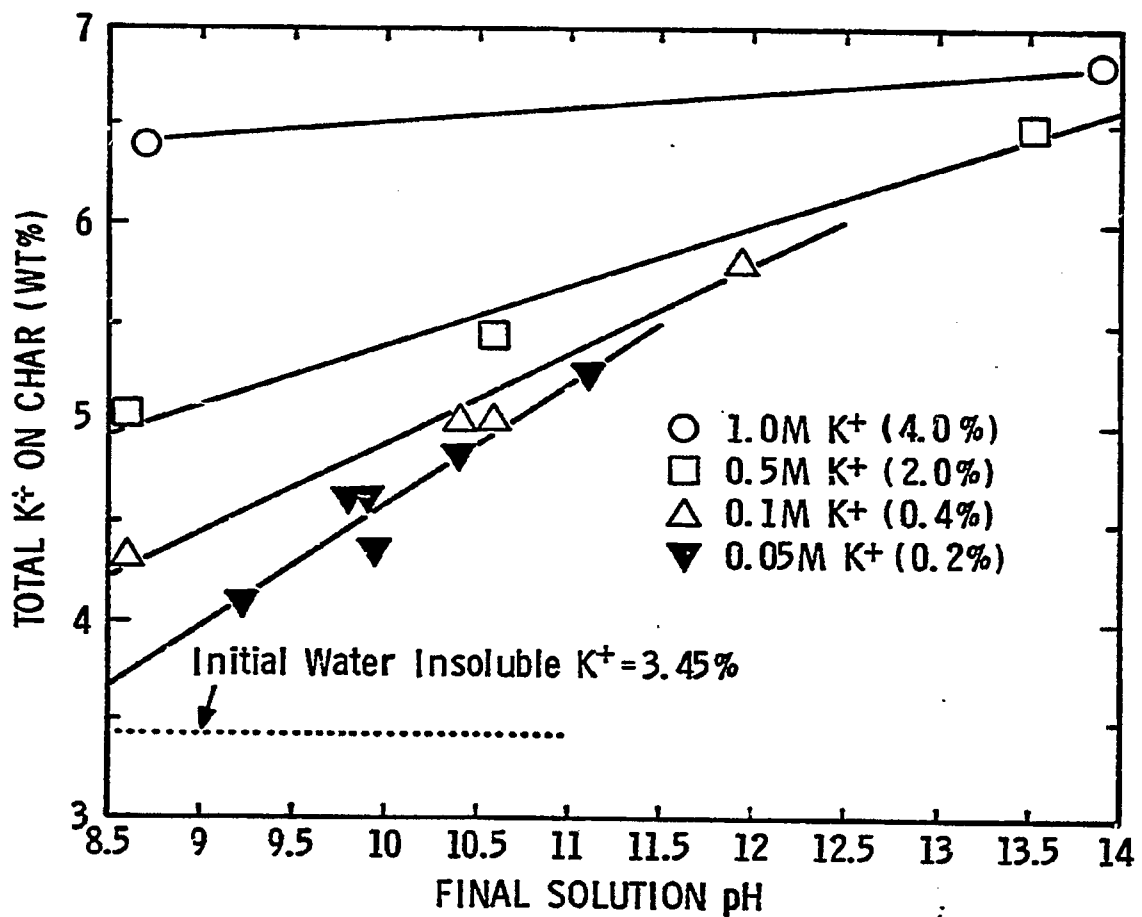
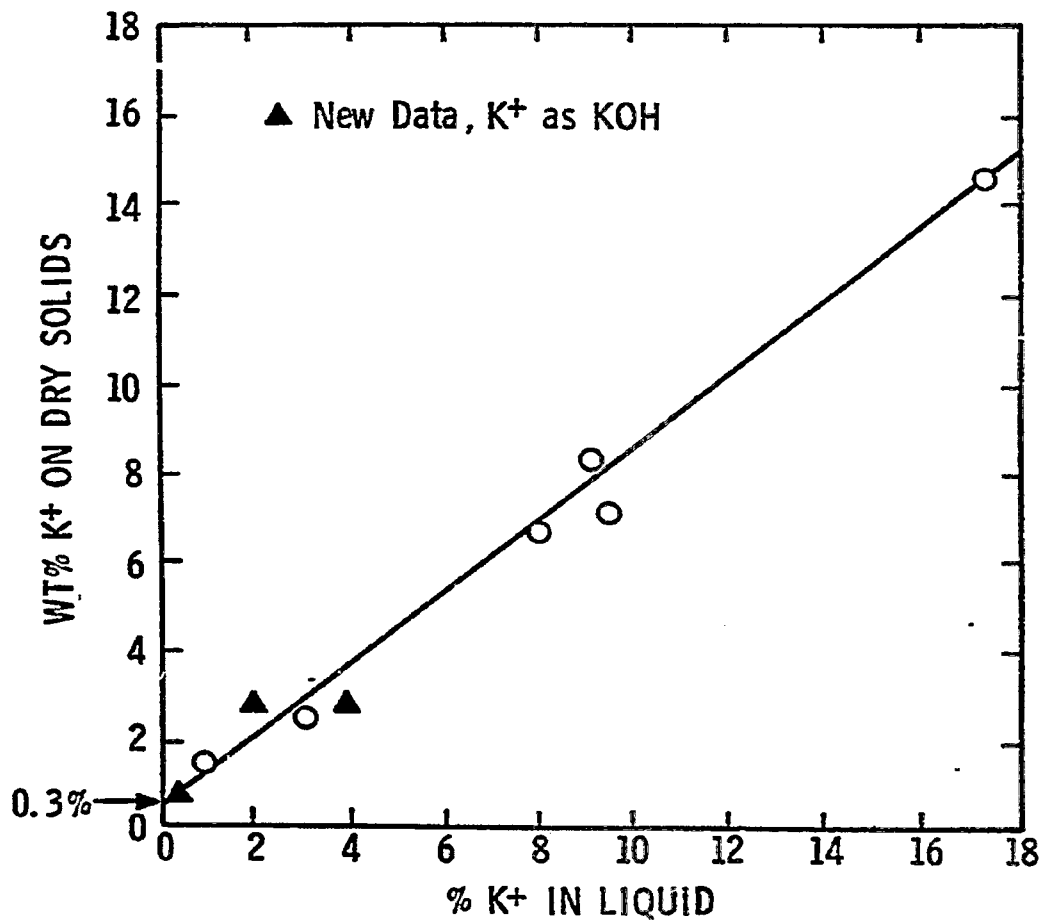


FIGURE 4.4-4
POTASSIUM EQUILIBRIUM ON DIGESTED
SOLIDS AND IN LIQUID



4.5 Mineral Matter/Catalyst Reactions

The goal of this work was to determine the reactions of the mineral matter and catalyst as the coal proceeds from raw feed to catalyst recovery residue. The main effort was to characterize the mineral matter (for these purposes, added catalyst is regarded as a mineral matter constituent) at each stage during its progression through the PDU. From this information, it may be possible to develop stoichiometric reaction equations which account for the compounds identified.

Samples were collected from the PDU at the points shown in Figure 4.5-1 and listed on Table 4.5-1. Every effort was made to obtain representative material during a period of smooth operation. Precautions were taken to prevent sample exposure to oxygen or water vapor. The analytical procedure for each sample is depicted on Figure 4.5-2.

In general, it was possible to obtain excellent quantitative information about the elements present in the coal, coal char, and coal ash (both high temperature and low temperature ashing methods were used). Unfortunately, since compounds rather than elements are the reactants and products of the mineral matter reactions, elemental information alone is not sufficient. Certain analytical techniques, such as Fourier Transform Infrared Spectroscopy (FTIR) are capable of identifying chemical compounds in a qualitative (or, at best, semi-quantitative) manner. It was possible to combine these two pieces of information--quantitative elemental analysis and qualitative compound analysis--to give quantitative compound analyses. The sample analytical procedure shown in Figure 4.5-2 was designed to provide the necessary information to execute such an analysis for each sample. Some redundancy was provided in order to minimize the opportunity for error in extracting the desired quantitative compound information.

Table 4.5-1

PDU SAMPLING POINTS AS SHOWN ON FIGURE 4.5-1

- 1) Raw coal from Coal Preparation Unit (CPU)
- 2) Raw coal from PDU (LH-3)
- 3) Wet catalyzed coal
- 4) Dry catalyzed coal
- 5) Gasifier feed coal (LH-2A)
- 6) Gasifier bottom char (GBC)
- 7) Gasifier mid-char (GMC)
- 8) Gasifier fines (A-4)
- 9) Washed char from CRU

FIGURE 4.5-1

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SAMPLING POINTS FOR INVESTIGATION OF MINERAL MATTER

○ INDICATES SAMPLING POINT

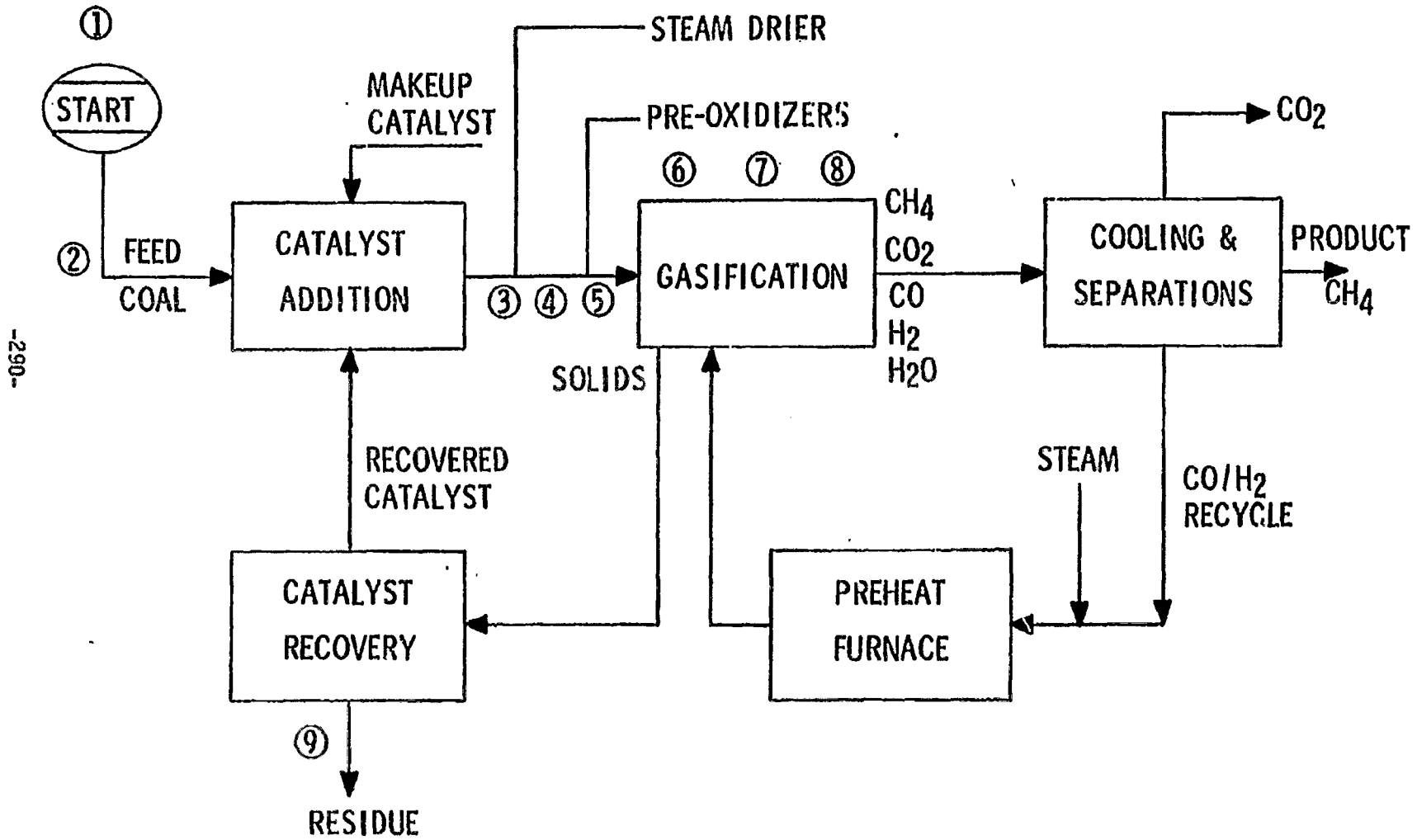
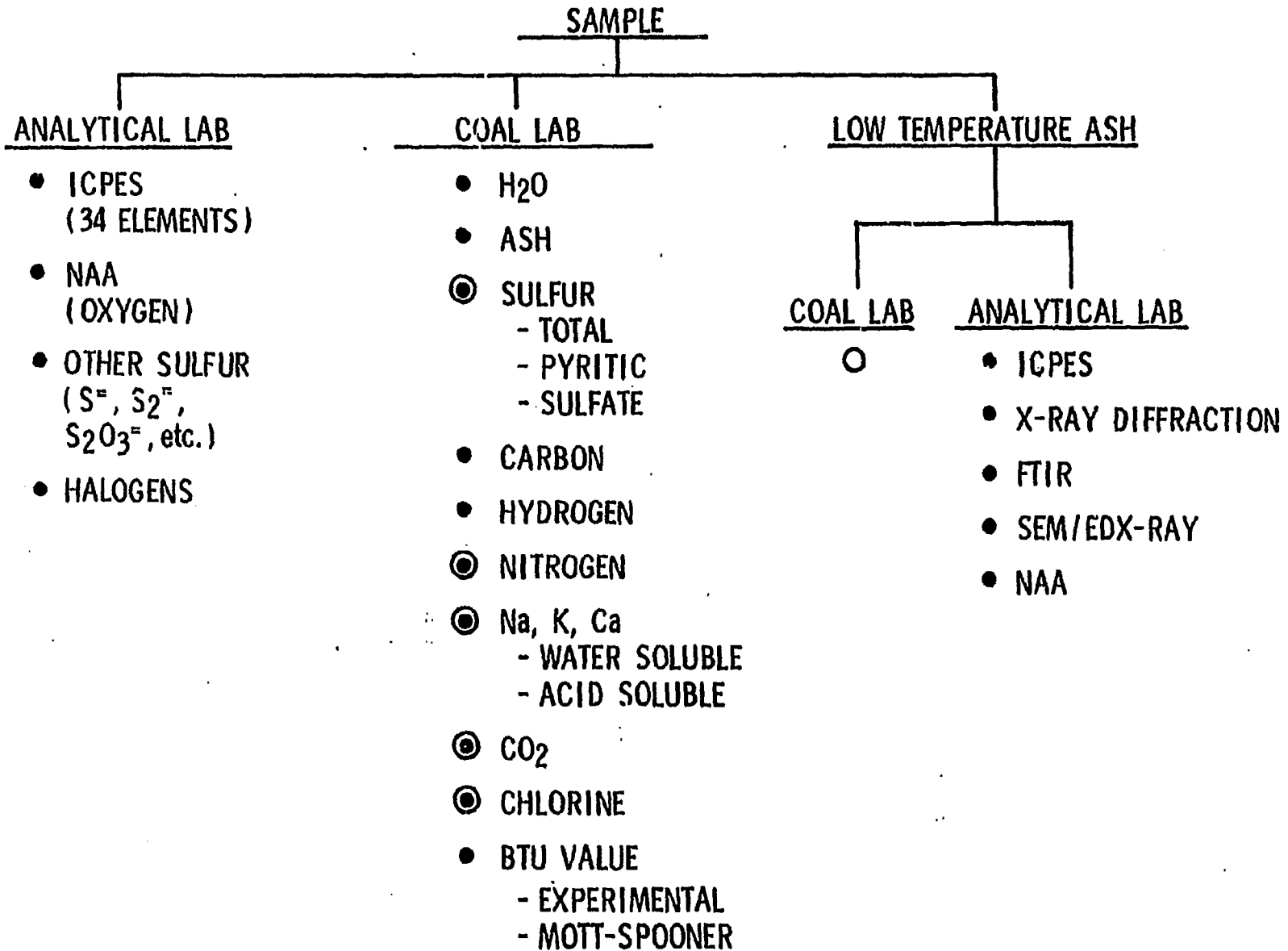


FIGURE 4.5-2

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SAMPLE ANALYTICAL PROCEDURE



For each of the PDU sample points, two ash materials were prepared. One ash is the common combustion material obtained by reaction of the coal at high temperature and atmospheric pressure in the presence of excess oxygen. It is well known that mineral matter undergoes reactions under these conditions--so the material in the high temperature ash (HTA) is not representative of that in the original sample. The second type of ash, low temperature ash, is obtained at reduced temperature and pressure. The idea of low temperature ash (LTA) is to liberate the mineral matter from the organic matrix without altering its form.

Each LTA sample and the corresponding whole sample was analyzed by inductively coupled plasma emission spectroscopy (ICPES) for the concentrations of 32 elements. Note that the data are reported on a whole dry sample basis. In particular, the LTA values have been "backed out" to the appropriate whole sample concentration. Generally, there is excellent agreement between the LTA and raw sample analyses. There are, however, two exceptions:

- The char samples have very high potassium concentrations due to the catalyst. Some potassium is lost from these samples during the LTA experiment.
- These samples are prepared for ICPES analysis by a procedure that uses hydrofluoric acid to solubilize silicon. The reaction produces SiF_4 . Since SiF_4 is a gas, and the sample preparation system is open, there is an opportunity for an indeterminate amount of silicon to escape during sample preparation.

The HTA sample was analyzed by ICPES using a closed sample preparation technique. The values have been backed out to a whole dry sample basis. Presumably, the analytical accuracy, especially for silicon, is improved by use of a closed system. However, sample loss is not the sole (and possibly not the major) determinant of ICPES analytical accuracy.

Complete sets of samples were collected and analyzed when the gasifier was operating at 265 psia and at 500 psia. The 265 psia samples were collected during material balance periods 26-33. The 500 psia samples were collected during material balance periods 37-38. All samples were collected, dried and prepared without exposure to air. The analytical data is presented in Table 4.5-2 for the 265 psia case whole samples. For the 500 psia whole samples, the analytical data is presented in Table 4.5-3. The data in these tables is explained below:

- Moisture

Sample moisture, as collected, ranged from a low of 0.01% in gasifier mid-char to a high of about 60% in the catalyst recovery residue. All of the remaining data is on a dry sample basis.

- Inorganics

The high temperature ash values are given on an SO_3 -free basis. Mineral matter is calculated from ash and elemental analyses. The low temperature ash values include nitrogen and sulfur fixed during this experiment.

Table 4.5-2

ANALYSIS OF WHOLE SAMPLE (DRY BASIS) - 265 PSI CASE

Item	Method/Comment	Sample Point								
		1	2	3	4	5	6	7	8	9
Material Balance Period	Samples Not Air Exposed	27	26	27	27	26	33	33	33	27
Moisture (%)	As Sampled		0.60	43.30	14.67	3.20	0.90	0.00	2.80	69.70
Inorganics (%)										
Ash (SO ₃ Free)	High Temperature	10.87	10.42	18.65	19.22	17.88	45.39	41.76	38.53	47.25
Mineral Matter	Coal Lab Calculation	15.40	13.21	22.02	24.72	26.04	54.83	50.29	50.34	53.05
Low Temperature Ash	Organic N and S Are Fixed		14.92	30.63	37.05	31.00	75.05	69.36	63.14	66.50
Halogens (ppm)										
Fluorine	Ion Specific Electrode	188	139	177	111	108	260	216	371	50
Chlorine -	Ion Specific Electrode	1001	813	674	742	874	1658	1872	3620	23
-	Titration	1000	500	1100	900	1100	1500	1500	1300	100
Bromine	Ion Specific Electrode	123	13	20	14	15	22	25	129	4
Iodine	Ion Specific Electrode	<2	<2	<2	<2	<2	<2	<2	15	<2
Elemental Analysis (%)										
Nitrogen	Leco Analyzer	1.24	1.27	1.31	1.08	1.56	0.03	0.18	0.09	0.01
Sulfur - Total	Leco Analyzer	3.96	4.01	3.09	4.27	3.49	3.70	3.12	1.60	3.48
- Pyritic	From HNO ₃ Soluble Iron	1.44	1.39	1.02	0.95	1.36	0.23	0.09	0.10	0.20
- Sulfate	From Total (HCl Soluble) Iron	0.11	0.04	0.04	0.18	0.23	0.18	0.15	0.16	0.06
- Organic	By Difference	2.41	2.58	2.03	3.14	1.90	3.30	2.89	1.33	3.22
Oxygen -	Neutron Activation Analysis	14.80	18.50	20.30	18.40	19.70	20.40	19.80	28.40	23.30
-	Difference Calculation	10.92	11.96	13.55	12.74	11.79	4.03	5.01	12.39	2.86
Hydrogen	Combustion Followed By	4.79	4.96	4.38	3.81	4.10	1.13	0.92	1.56	1.03
Carbon	Analysis For H ₂ O and CO ₂	68.22	67.38	59.02	58.88	51.18	45.72	49.01	45.83	45.37
Heating Value (BTU/lb)										
Experimental - Dry	Combustion	12169	12354	10287	10329	10961	6480	6971	7503	7111
- DMF		14341	14164	13139	13708	14839	14487	14155	16381	15152
Calculated	Mott-Spooner	14423	13936	14523	13536	14508	15939	15016	13921	15112
Carbon Dioxide	Acid Evolution	2.46	0.96	0.89	2.48	5.12	4.40	4.02	8.06	0.76
Water Soluble (%)										
Na as Na ₂ O	16 Hour Reflux	0.24	0.12	0.37	0.34	0.45	0.40	1.00	0.76	0.05
K as K ₂ O		0.68	0.38	7.12	8.30	4.12	11.94	11.69	15.10	4.46
Ca as CaO		0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01
Acid Soluble (%)										
Na as Na ₂ O	16 Hour Reflux in 0.1 N HCl	0.22	0.16	0.04	0.19	0.19	0.36	0.36	0.41	0.09
K as K ₂ O		0.20	0.21	10.86	11.05	8.62	18.85	19.43	20.02	13.11
Ca as CaO		0.01	0.01	0.01	0.03	0.01	0.07	0.01	0.01	0.35

Table 4.5-3

ANALYSIS OF WHOLE SAMPLE (DRY BASIS) - 500 PSI CASE

Item	Method/Comment	Sample Point								
		1	2	3	4	5	6	7	8	9
Material Balance Period	Samples Not Air Exposed	37-38	37-38	37-38	37-38	37-38	37-38	37-38	37-38	37-38
Moisture (%)	As Sampled	NA	1.54	33.83	5.71	0.46	0.00	0.00	3.82	67-72
Inorganics (%)										
Ash (SO ₃ Free)	High Temperature	10.58	9.65	15.96	14.23	17.89	46.40	49.88	47.72	25.97
Mineral Matter	Coal Lab Calculation	13.53	12.06	19.44	17.67	22.89	56.40	60.62	61.27	29.90
Low Temperature Ash	Organic N and S Are Fixed	11.72	12.85	15.45	21.95	26.90	71.62	82.32	69.64	31.05
Halogens (ppm)										
Fluorine	Ion Specific Electrode	225	154	153	147	176	220	241	482	90
Chlorine -	Ion Specific Electrode	1002	750	693	538	844	1894	1993	3873	70
-	Titration	400	600	400	1100	800	1600	1400	2200	700
Bromine	Ion Specific Electrode	20	16	9	12	10	24	25	231	1
Iodine	Ion Specific Electrode	<2	<2	<2	<2	<2	<2	<2	48	<2
Elemental Analysis (%)										
Nitrogen	Leco Analyzer	1.30	1.30	1.33	1.34	1.43	0.16	0.16	0.10	0.13
Sulfur - Total	Leco Analyzer	4.80	4.20	3.86	3.94	3.60	3.33	3.85	2.22	2.27
- Pyritic	From HNO ₃ Soluble Iron	1.75	1.23	1.32	1.13	1.13	0.05	0.05	0.05	0.06
- Sulfate	From Total (HCl Soluble) Iron	0.08	0.08	0.06	0.11	0.28	0.19	0.20	0.21	0.15
- Organic	By Difference	2.97	2.89	2.48	2.70	2.39	3.09	3.61	1.96	2.05
Oxygen	Neutron Activation Analysis	15.38	15.95	17.93	16.55	18.55	21.50	18.75	23.48	12.58
-	Difference Calculation	11.02	10.51	17.05	13.05	13.44	6.92	5.74	9.91	1.63
Hydrogen	Combustion Followed By	4.71	4.96	4.00	4.43	3.95	0.75	0.59	0.53	0.82
Carbon	Analysis For H ₂ O and CO ₂	67.59	69.38	57.80	63.01	69.49	42.44	39.78	39.52	69.18
Heating Value (BTU/lb)										
Experimental -	Combustion	12549	12629	11725	11786	10995	6431	6848	6737	10220
- DWF		14413	14291	14487	14261	14206	14940	15083	15200	14589
Calculated	Mott-Spooner	13936	14217	12174	13400	13364	14484	15042	14348	14970
Carbon Dioxide	Acid Evolution	0.66	0.45	1.06	1.02	1.30	4.93	5.37	8.77	0.56
Water Soluble (%)										
Na		0.12	0.08	0.21	0.26	0.30	0.25	0.28	0.44	0.06
K	16 Hour Reflux	0.02	0.02	2.61	1.86	4.86	18.44	12.60	14.82	2.23
Ca		0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Acid Soluble (%)										
Na		0.12	0.09	0.10	0.09	0.11	0.28	0.30	0.36	0.05
K	16 Hour Reflux in 0.1 N HCl	0.15	0.15	4.88	3.85	7.07	17.19	18.85	19.57	6.29
Ca		0.06	0.04	0.07	0.04	0.01	0.12	0.11	0.05	0.03

For raw coal, fixation is not important, thus the mineral matter and LTA values are in good agreement for sample point 2. For catalyzed coal and char, fixation results in high LTA values.

- Halogens

The concentration of halogens in these samples decreases in the following order: Cl>F>Br>I. CRU residue has a low halogen content, highlighting the concern about build-up of halogens in the catalyst recycle loop. There is an obvious enhancement of halogen concentration in the A-4 fines.

- Elemental Analysis

Elemental analyses are given for nitrogen sulfur (total, pyritic, sulfate, and organic) oxygen, hydrogen, and carbon. Oxygen is generally calculated "by difference" (100% - %N - %S - %H - %C - % SO₃-free ash). Neutron activation analysis is presumed to give an accurate direct measure of total oxygen content. Both numbers are given in the tables.

- Heating Value

Experimental heating values are backed out to a dry mineral matter free (DMF) basis. These numbers may be compared to the Mott-Spooner calculation of heating value. In general, agreement is within 300 BTU/pound except for the char samples. In the char cases, as much as 1400 BTU/pound may separate the calculated and experimental BTU values.

- Carbon Dioxide

- Water Soluble Na, K, Ca

The sample is refluxed in water for about 16 hours. The Na, K, and Ca extracted are reported as the corresponding oxide. Calcium concentration is uniformly very low. Sodium as well as potassium is extracted from the char.

- Acid Soluble Na, K, Ca

This experiment is analogous to the water case, but uses 0.1 N HCl for the extraction. The acid is able to extract considerably more potassium from the CRU residue, as one would anticipate.

Table 4.5-4 is a summary of the data for the LTA material from the 265 psia operation case. The significance of the analyses other than for minerals was discussed in connection with whole sample work-up. The interesting addition here is the mineralogical analysis discussed below:

- Quartz

Quartz is easily identified by X-ray diffraction (XRD). Moreover, the analysis of a good standard sample allows excellent quantification by fourier transform infrared spectroscopy (FTIR).

- Kaolinite

The same comments apply here as in the quartz case. However, the standard sample is more difficult to develop, leading to less accurate quantification.

- Illite

While illite can be identified by XRD, the lack of a standard sample prevents quantification by FTIR. Fortunately, the existence of certain characteristic clay peaks in FTIR allows the estimation of total clay. In this case, all clay not taken as kaolinite was assumed to be illite. This over-simplification does not consider expandables as a separate category.

- Pyrite

Pyrite can be identified by XRD, but is transparent in FTIR. Hence, it is quantified using iron analysis.

- K_2SO_4

K_2SO_4 is an artifact of the LTA procedure. It is determined and quantified by FTIR.

- Calcite

The same comments apply here as in the quartz case. However, the generally low level of calcite in coal samples means quantification is more difficult.

- KNO_3

KNO_3 is like K_2SO_4 , an artifact of the LTA procedure. It is determined and quantified by FTIR.

- $KAlSiO_4$

The same comments apply here as for kaolinite.

- $KFeS_2$

The same comments apply here as for pyrite.

Table 4.5-4

ANALYSIS OF LOW TEMPERATURE ASH SAMPLE (DRY BASIS) - 265 PSI CASE

Item	Method/Comment	Sample Point								
		1	2	3	4	5	6	7	8	9
Material Balance Period	Samples Not Air Exposed	27	26	27	27	26	33	33	33	27
Inorganics (%)										
Ash (SO ₃ Free)	High Temperature	10.87	10.42	18.65	19.22	17.88	45.39	41.76	38.53	47.25
Mineral Matter	Coal - Calculation	15.40	13.21	22.02	24.72	26.04	54.83	50.29	60.34	53.05
Low Temperature Ash	Organic and S Are Fixed		14.92	30.63	37.05	31.00	75.05	69.36	63.14	66.50
Elemental Analysis (%)										
Nitrogen	Leco Analyzer		0.10	0.80	0.72	0.44	2.43	2.66	3.29	0.01
Sulfur - Total	Leco Analyzer		14.23	8.91	9.62	11.72	5.19	4.16	2.99	4.42
- Pyritic	From HNO ₃ Soluble Iron		9.84	2.33	1.89	1.93	0.33	0.69	0.31	0.54
- Sulfate	From Total (HCl) Soluble Iron		1.97	5.45	6.79	5.30	2.52	0.00	0.00	0.13
- Organic	By Difference		2.42	1.13	1.94	4.49	2.34	3.93	2.68	3.75
Oxygen	Neutron Activation Analysis		48.30	36.80	36.70	33.70	36.11	48.20	64.90	40.10
Chlorine	Titration		0.52	0.19	0.16	0.23	0.10	0.07	0.05	0.22
Water Soluble (%)										
Na as Na ₂ O			0.62	0.49	0.50	0.70	0.00	1.35	1.72	0.19
K as K ₂ O	16 Hour Reflux		0.70	22.21	22.92	27.02	38.98	44.47	51.14	6.70
Ca as CaO			0.17	0.01	0.01	0.01	0.02	0.01	0.01	0.07
Acid Soluble (%)										
Na as Na ₂ O			0.74	0.36	0.40	0.77	1.30	1.35	1.60	0.13
K as K ₂ O	16 Hour Reflux in 0.1 N HCl		1.29	25.09	26.23	27.90	65.70	61.33	65.72	21.28
Ca as CaO			0.09	0.01	0.01	0.01	0.01	0.01	0.01	0.24
Carbon Dioxide	Acid Evolution		2.62	2.15	2.02	0.79	2.82	1.54	5.00	1.17
Minerals (%)										
Quartz	XRD and FTIR		15	7	6	4				
Clay - Kaolinite	XRD and FTIR		11	5			1			
- Other (Illite)	Estimate using FTIR		35	37	32	18	3	3	6	8
Pyrite	XRD and Iron Analysis		21	6	7	7				
K ₂ SO ₄	LTA Artifact - FTIR			37	47	62	13	23	14	16
Calcite	XRD and FTIR		2	2	2	2				
KNO ₃	LTA Artifact - FTIR			4	6	7	16	17	22	
KAlSiO ₄	XRD and FTIR						14	17	16	38
KFeS ₂	XRD and Iron Analysis						13	10	8	18
Undetermined			16	3			40	30	35	14

Table 4.5-5 presents elemental data for both the whole sample and the corresponding LTA (corrected to a whole sample basis for direct comparison) for the 265 psia case. Table 4.5-6 presents the same data for the 500 psia case.

Tables 4.5-7 through 4.5-14 compare the elemental and mineralogical balances for the 265 psia case. The LTA experiment is of questionable value on the three char samples due to high potassium loading. The entries in these tables are discussed below:

- Aluminum and Silicon

The aluminum and silicon values are affected by their assumed ratio in clays. Here, only two clays were considered. Hence some error in the mineralogical values is expected.

- Calcium

The only assumed source for calcium is calcite. Since calcium is a common trace component of clays, the mineralogical values for calcium should be somewhat low.

- Iron

Iron balances exactly since it is used to quantify pyrite.

- Potassium

Potassium is overestimated in the assumed formula for illite. Moreover, illite is overestimated since it is the only identified clay other than kaolinite. For both of these reasons, mineralogical potassium values are slightly high.

- Nitrogen

On an LTA basis, no nitrogen bias is anticipated or seen. Of course, on a whole sample basis, the existence of organic nitrogen becomes obvious.

- Oxygen

Oxygen values are quite large in an absolute sense. For this reason, total element values are also given with oxygen excluded. Relative oxygen values are, of course, affected by assumed formulas for clays. Again, as for nitrogen, the existence of organic oxygen is obvious from the data.

- Sulfate sulfur

In the case of sulfate sulfur (from K_2SO_4), the FTIR analysis is likely to be very accurate. Hence, it now seems possible that the elemental analysis is low.

Table 4.5-5
 ELEMENTAL ANALYSIS - MOLE DRY SAMPLE BASIS (PPM), 240 PSI CASE

Element	- Analyzed From	Sample Point								
		1	2	3	4	5	6	7	8	9
Aluminum	- Raw		10885	8670	8889	9380	22613	21300	11272	10600
	- LTA		11399	7157	9040	7998	21194	20731	12541	4630
Antimony	- Raw		0.5	0.3	0.1	0.1	0.1	0.1	0.1	0.1
	- LTA		(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
Arsenic	- Raw		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	- LTA		0.1	(0)	(0)	(0)	(0)	(0)	(0)	(0)
Barium	- Raw		56.2	34	40	43	142	115	113	147
	- LTA		56.2	34	40	43	142	115	113	147
Beryllium	- Raw		6	5	5	5	5	5	5	5
	- LTA		6	(5)	(5)	(5)	(5)	(5)	(5)	(5)
Bron	- Raw		130	177	191	140	380	415	309	151
	- LTA		130	177	191	140	380	415	309	151
Cadmium	- Raw		0.4	0.6	0.4	0.4	0.4	0.4	0.4	0.4
	- LTA		(0)	(17)	(9)	(0)	(0)	(22)	(15)	(10)
Calcium	- Raw		2103	2480	3152	2124	8802	9170	3021	910
	- LTA		3034	2956	3632	2624	8802	9170	3021	1185
Chromium	- Raw		24	11	21	16	21	21	27	26
	- LTA		24	11	21	16	21	21	27	26
Cobalt	- Raw		17	12	12	9	0.0	0.0	0.0	0.0
	- LTA		6	(12)	(12)	(9)	0.0	0.0	(0)	(0)
Copper	- Raw		11	6.1	4.2	13	4.0	0.5	15.19	38
	- LTA		18	6.1	4.2	13	4.0	0.5	15.19	38
Iron	- Raw		9125	885	1789	313	1275	2460	1654	136
	- LTA		1439	885	1789	313	1275	2460	1654	136
Lead	- Raw		0	0	0	0	0	0	0	0
	- LTA		(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
Lithium	- Raw		5	4	4	4	12	11	9	11
	- LTA		5	4	4	4	12	11	9	11
Magnesium	- Raw		804	399	1570	571	1746	1466	212	250
	- LTA		804	399	1570	571	1746	1466	212	250
Manganese	- Raw		44	23	33	22	106	71	54	106
	- LTA		44	23	33	22	106	71	54	106
Molybdenum	- Raw		0	0	0	0	0	0	0	0
	- LTA		(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
Nickel	- Raw		30.4	12	12	15	24	12	4.3	10
	- LTA		30.4	12	12	15	24	12	4.3	10
Phosphorus	- Raw		117	63	124	108	214	159	128	12
	- LTA		117	63	124	108	214	159	128	12
Platinum	- Raw		0	0	0	0	0	0	0	0
	- LTA		(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
Potassium	- Raw		223	8810	9004	8817	18166	17600	17068	10000
	- LTA		223	8810	7491	7703	8537	8538	7179	11416
Selenium	- Raw		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	- LTA		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Silicon	- Raw		2647	21100	3854	2221	5751	5150	4370	8200
	- LTA		2647	51765	2119	1909	6977	56112	10024	91530
Silver	- Raw		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	- LTA		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium	- Raw		1076	136	1301	1446	1291	240	105	92
	- LTA		1107	136	1193	1194	1206	1045	105	92
Strontium	- Raw		0	0	0	0	0	0	0	0
	- LTA		0	0	0	0	0	0	0	0
Thallium	- Raw		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	- LTA		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Tin	- Raw		0.2	0.4	0.16	0.0	0.4	0.4	0.4	0.4
	- LTA		(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
Titanium	- Raw		111	1124	121	112	1121	1115	115	115
	- LTA		111	1124	121	112	1121	1115	115	115
Tungsten	- Raw		0.51	0.72	0.77	0.66	0.6	0.6	0.6	0.6
	- LTA		(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
Uranium	- Raw		1.9	1.2	2.3	0.0	0.0	0.0	0.0	0.0
	- LTA		1.9	1.2	2.3	0.0	0.0	0.0	0.0	0.0
Vanadium	- Raw		26	0.2	0.4	0.4	0.4	0.4	0.4	0.4
	- LTA		26	0.2	0.4	0.4	0.4	0.4	0.4	0.4
Zinc	- Raw		112	0	124	24	109	104	107	112
	- LTA		112	0	124	24	109	104	107	112

Notes: < Means not detected. Detection limit is given.
 () Means value may not be significant.

TABLE 4.5-6
ELEMENTAL ANALYSIS - MOIST DRY SAMPLE BASTS (PPM), 500 PSI CAST

Element	Analyzed From	Sample Point								
		1	2	3	4	5	6	7	8	9
Aluminum	- Raw	820	830	810	800	850	2710	2760	2810	2850
	- LTA	780	750	560	800	860	2754	2818	2820	2821
Antimony	- Raw									
	- LTA	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Arsenic	- Raw									
	- LTA	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Barium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Beryllium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Boron	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Calcium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Calcium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chromium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cobalt	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Copper	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Iron	- Raw	13000	9560	9650	10000	9710	29000	29000	29000	29000
	- LTA	11837	10319	5382	8736	8689	28075	28342	28956	28182
Lead	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Lithium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Magnesium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Manganese	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Molybdenum	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nickel	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Phosphorus	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Platinum	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Potassium	- Raw	1660	1660	0.000	0.000	0.000	16600	20500	20700	16600
	- LTA	1368	1722	2011	3401	0.000	21725	21329	23700	0.000
Selenium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Silicon	- Raw	22100	20200	20600	19500	19500	59100	57500	62300	0.000
	- LTA	17111	21311	1742	18435	19906	64673	64374	57582	38502
Silver	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Strontium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Thallium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Tin	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Titanium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Tungsten	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Vanadium	- Raw									
	- LTA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Zinc	- Raw	157	89	88	108	118	211	228	163	244
	- LTA	72	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Notes: < Means not detected. Detection limit is given.
() Means value may not be significant.

Table 4.5-7

SAMPLE NUMBER 2 - MATERIAL BALANCE (%)

ELEMENT	LTA BASIS		WHOLE SAMPLE BASIS		
	Experimental Elemental	Mineralogical	Experimental Elemental	Calculated From LTA Basis Elemental Mineralogical	
Aluminum	7.6	9.4	1.1	1.1	1.4
Calcium	2.6	0.8	0.2	0.4	0.1
Iron	9.6	(9.8)	0.9	1.4	(1.5)
Potassium	1.6	3.4	0.2	0.2	0.5
Nitrogen	0.1	ND	1.3	0.0	-
Oxygen	48.3	32.0	18.5	7.2	4.8
Sulfur - Pyritic	9.8	11.2	1.4	1.5	1.7
- Sulfate	2.0	ND	0.0	0.3	-
Silicon	17.7	16.8	2.4	2.6	2.5
TOTAL - with Oxygen	99.3	83.4	26.0	14.7	12.5
- w/o Oxygen	51.0	51.4	7.5	7.5	7.7

Table 4.5-8

SAMPLE NUMBER 3 - MATERIAL BALANCE (%)

ELEMENT	LTA BASIS		WHOLE SAMPLE BASIS		
	Experimental Elemental	Mineralogical	Experimental Elemental	Calculated From LTA Basis Elemental	Mineralogical
Aluminum	2.3	8.6	0.9	0.7	2.6
Calcium	1.0	0.8	0.3	0.3	0.2
Iron	2.2	(2.3)	0.9	0.7	(0.7)
Potassium	22.8	21.8	8.8	7.0	6.7
Nitrogen	0.8	0.6	1.3	0.3	0.2
Oxygen	36.8	40.8	20.3	11.3	12.5
Sulfur - Pyritic	2.3	2.7	1.0	0.7	0.8
- Sulfate	5.5	6.8	0.0	1.7	2.1
Silicon	16.9	12.2	2.1	5.2	3.7
TOTAL - with Oxygen	90.6	96.6	35.6	27.9	29.5
- w/o Oxygen	53.8	55.8	15.3	16.6	17.0

Table 4.5-9

SAMPLE NUMBER 4 - MATERIAL BALANCE (%)

ELEMENT	LTA BASIS		WHOLE SAMPLE BASIS		
	Experimental Elemental	Mineralogical	Experimental Elemental	Calculated From LTA Basis Elemental Mineralogical	
Aluminum	2.4	6.5	0.9	0.9	2.4
Calcium	1.0	0.8	0.3	0.4	0.3
Iron	3.2	(3.3)	0.9	1.2	(1.2)
Potassium	20.2	26.6	9.0	5.5	9.8
Nitrogen	0.7	0.8	1.1	0.3	0.3
Oxygen	36.7	39.7	18.4	13.6	14.7
Sulfur - Pyritic	1.9	3.7	1.0	0.7	1.4
- Sulfate	5.8	8.6	0.2	2.1	3.2
Silicon	5.7	9.6	3.7	2.1	3.6
TOTAL - with Oxygen	77.6	99.6	35.5	28.8	36.9
- w/o Oxygen	40.9	59.9	17.1	15.2	22.2

Table 4.5-10

SAMPLE NUMBER 5 - MATERIAL BALANCE (%)

ELEMENT	LTA BASIS		WHOLE SAMPLE BASIS		
	Experimental Elemental	Mineralogical	Experimental Elemental	Calculated From LTA Basis Elemental	Mineralogical
Aluminum	2.6	3.7	0.9	0.8	1.1
Calcium	0.8	0.8	0.2	0.3	0.2
Iron	3.1	(3.3)	0.8	1.0	(1.0)
Potassium	25.1	32.3	8.8	7.8	10.0
Nitrogen	0.4	1.0	1.6	0.1	0.3
Oxygen	33.7	37.8	19.7	10.4	11.7
Sulfur - Pyritic	1.9	3.7	1.4	0.6	1.2
- Sulfate	5.3	11.4	0.2	1.6	3.5
Silicon	6.4	5.7	2.2	2.0	1.8
TOTAL - with Oxygen	79.3	99.7	35.8	24.6	30.8
- w/o Oxygen	45.6	61.9	16.1	14.2	19.1

Table 4.5-11

SAMPLE NUMBER 6 - MATERIAL BALANCE (%)

ELEMENT	LTA BASIS		WHOLE SAMPLE BASIS		
	Experimental Elemental	Mineralogical	Experimental Elemental	Calculated From LTA Basis Elemental Mineralogical	
Aluminum	3.9	3.2	2.4	2.9	2.4
Calcium	1.1	0.0	0.8	0.8	0.0
Iron	4.6	(4.6)	3.3	3.4	(3.4)
Potassium	11.4	19.0	18.2	8.6	14.2
Nitrogen	2.4	2.2	0.0	1.8	1.7
Oxygen	36.3	20.0	20.4	27.2	15.0
Sulfur - Pyritic	0.3	0.0	0.2	0.2	0.0
- Sulfate	2.5	2.4	0.2	1.9	1.8
Silicon	9.3	3.3	5.8	7.0	2.5
TOTAL - with Oxygen	71.8	54.7	51.3	53.8	41.0
- w/o Oxygen	35.5	34.7	30.9	26.6	26.0

Table 4.5-12

SAMPLE NUMBER 7 - MATERIAL BALANCE (%)

ELEMENT	LTA BASIS		WHOLE SAMPLE BASIS		
	Experimental Elemental	Mineralogical	Experimental Elemental	Calculated From LTA Basis Elemental Mineralogical	
Aluminum	3.7	3.5	2.1	2.6	2.4
Calcium	0.8	0.0	0.5	0.6	0.0
Iron	3.7	(3.5)	2.4	2.6	(2.4)
Potassium	11.9	23.9	17.6	8.3	16.5
Nitrogen	2.7	2.3	0.2	1.8	1.6
Oxygen	48.2	24.8	19.8	33.4	17.2
Sulfur - Pyritic	0.7	0.0	0.1	0.5	0.0
-- Sulfate	0.0	4.2	0.2	0.0	2.9
Silicon	8.1	3.6	5.2	5.6	2.5
TOTAL - with Oxygen	79.8	65.8	48.1	55.4	45.5
- w/o Oxygen	31.6	41.0	28.3	22.0	28.3

Table 4.5-13

SAMPLE NUMBER 8 - MATERIAL BALANCE (%)

ELEMENT	LTA BASIS		WHOLE SAMPLE BASIS		
	Experimental Elemental	Mineralogical	Experimental Elemental	Calculated From LTA Basis Elemental Mineralogical	
Aluminum	2.4	3.8	1.3	1.3	2.0
Calcium	0.7	0.0	0.4	0.4	0.0
Iron	2.7	(2.8)	1.7	1.4	(1.5)
Potassium	13.5	21.0	17.4	7.2	11.1
Nitrogen	3.3	3.0	0.1	1.7	1.6
Oxygen	54.9	24.6	28.4	29.2	13.1
Sulfur - Pyritic	0.3	0.0	0.1	0.2	0.0
- Sulfate	0.0	2.6	0.2	0.0	1.4
Silicon	5.6	3.9	4.5	3.0	2.1
TOTAL - with Oxygen	83.4	61.7	54.1	44.4	32.8
- w/o Oxygen	28.5	37.1	25.7	15.2	19.7

Table 4.5-14

SAMPLE NUMBER 9 - MATERIAL BALANCE (%)

ELEMENT	LTA BASIS		Experimental Elemental	WHOLE SAMPLE BASIS	
	Experimental Elemental	Mineralogical		Calculated From LTA Basis Elemental	Mineralogical
Aluminum	8.2	8.1	4.0	4.6	4.6
Calcium	2.1	0.0	1.0	1.2	0.0
Iron	6.5	(6.3)	3.3	3.6	(3.6)
Potassium	20.2	21.8	10.3	11.4	12.3
Nitrogen	0.0	0.0	0.0	0.0	0.0
Oxygen	40.1	28.3	23.3	22.7	16.0
Sulfur - Pyritic	0.5	0.0	0.2	0.3	0.0
- Sulfate	0.1	2.9	0.1	0.1	1.7
Silicon	16.2	11.2	8.3	9.2	6.3
TOTAL - with Oxygen	93.9	78.6	50.5	53.1	44.5
- w/o Oxygen	53.8	50.3	27.2	30.4	28.5

Table 4.5-15

MINERALOGICAL COMPOSITION OF ILLINOIS NO. 6 COAL

MINERAL	FORMULA	WEIGHT % IN MINERAL MATTER			
		RANGE ⁽¹⁾	HERRIN ⁽²⁾	STUDY DESIGN	THIS STUDY
QUARTZ	SiO ₂	6-25	17	11	15
KAOLINITE	Al ₂ Si ₂ O ₅ (OH) ₄	8-12	10	17	11
ILLITE	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	13-19	16	25	35
EXPANDABLES	--	20-30	24	25	21
PYRITE	FeS ₂	7-30	21	7	2
CALCITE	CaCO ₃	0-21	9	15	16
OTHER	--	--	3		

(1) Illinois State Geological Survey Circular 476 (1973)

(2) Average value for Herrin County Samples from Circular 476.