1. FLUID BED GASIFIER (FBG) STUDIES (Reporting Category 1)

1.1 FBG RECOMMISSIONING

1.1.1 Mechanical Modifications

During the third quarter of 1976, the existing Fluid Bed Gasifier (FBG) was recommissioned for use in the Predevelopment Program, and some changes were made to improve overall data quality, unit operability, and safety. The unit can feed up to 25 lbs/hr of coal on a continuous basis and has the capability for continuous coal impregnation with catalyst, coal feeding, gasification, and catalyst recovery from ash/char residue. On-line computer facilities are available for continuous data acquisition and reduction. The maximum operating pressure is 100 psig because the FBG was originally built for thermal gasification.

A sketch of the gasification section of the FBG prior to recommissioning is presented in Figure 1.1-1. Coal is fed to the gasifier by means of lockhoppers. These lockhoppers are capable of being pressurized to 150 psia and are fitted with temperature controllers and electrical resistance heaters. The feed coal is conveyed from the feeder outlet to the gasifier with the steam/synthesis gas mixture to be used for gasification. The gas is preheated using electrical resistance heaters before it contacts the feed coal. The composition of the simulated syngas recycle stream can be adjusted by means of a gas blender. The coal-steam syngas mixture is introduced into the bottom of the 6 inch diameter gasifier which is constructed of Type 310 stainless steel. The gasifier is equipped with pressure taps, process thermocouples, and exterior wall temperature thermocouples. Wall temperature profiles are maintained by a series of temperature controllers connected to electrical resistance heaters along the length of the reactor. Although the FBG is equipped with a secondary gasifier, this was not used in the current program. Because high carbon conversions were later attained in the primary gasifier, it was determined that the secondary gasifier concept will not likely be justified economically. The raw product gas from the gasifier passes through two cyclones and a filter to remove residual solids. It is then cooled to condense the unreacted steam and the volumetric flow rate is measured with a dry test meter. The dry gas composition is measured using an on-line gas chromatograph.

One major change made to the FBG configuration to improve the data quality was to reactivate a second gas filtering and scrubbing system which had been used during the previous thermal gasification operating periods. The primary and secondary gas systems were then repiped so that if both gasifiers were operated, the gas rate and composition for each could be independently measured. Thus, the gasification rate in each vessel could be determined more precisely. A flow plan for the revised configuration is shown in Figure 1.1-2. Additional changes made to improve data quality included (1) instrumentation of the feed lockhopper to allow continuous, on-line weighing of feed coal, (2) centralization of the unit pressure transmitter system for ease of calibration and maintenance, (3) installation of a second dry test meter in series on both the primary and secondary product gas streams, and (4) addition of a second on-line gas chromatograph.

FIGURE 1.1-1

ORIGINAL FLUID BED GASIFIER (FBG) FLOW PLAN

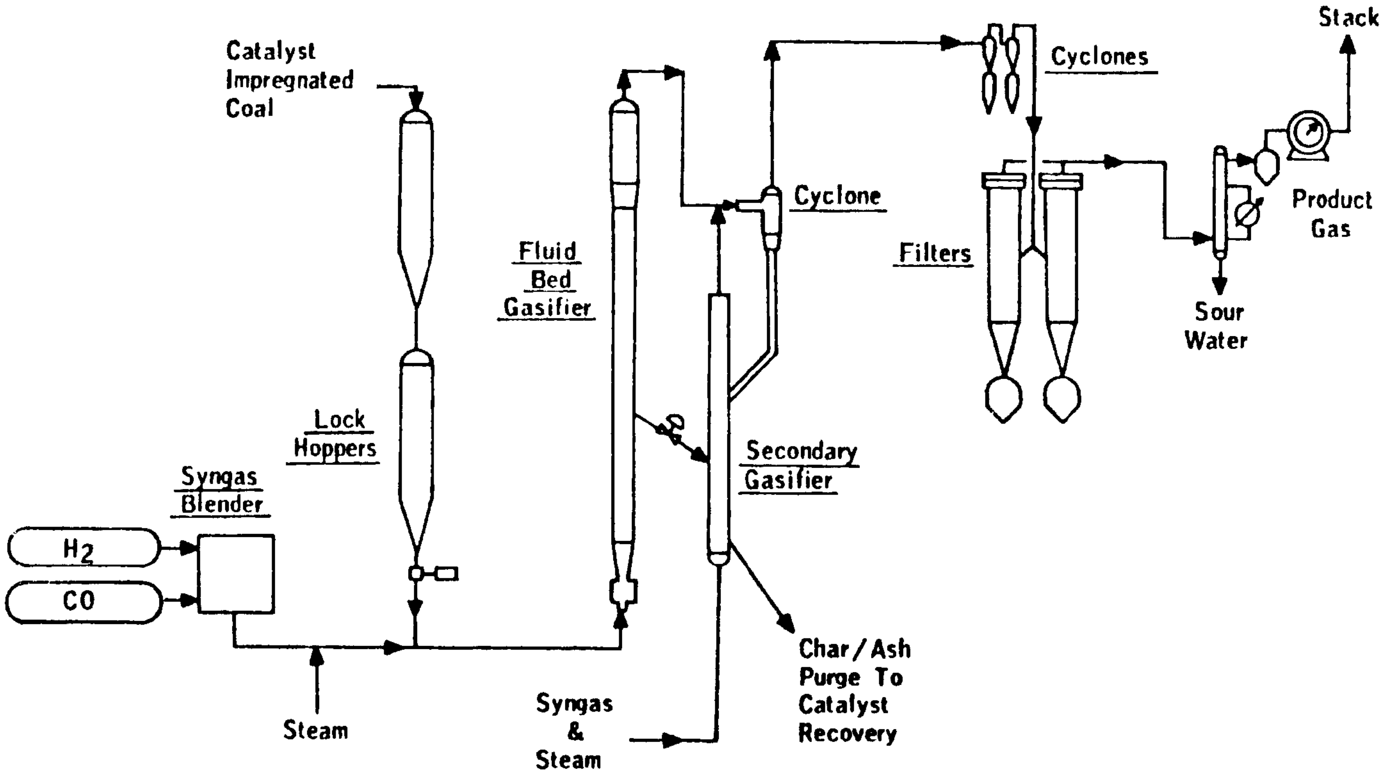
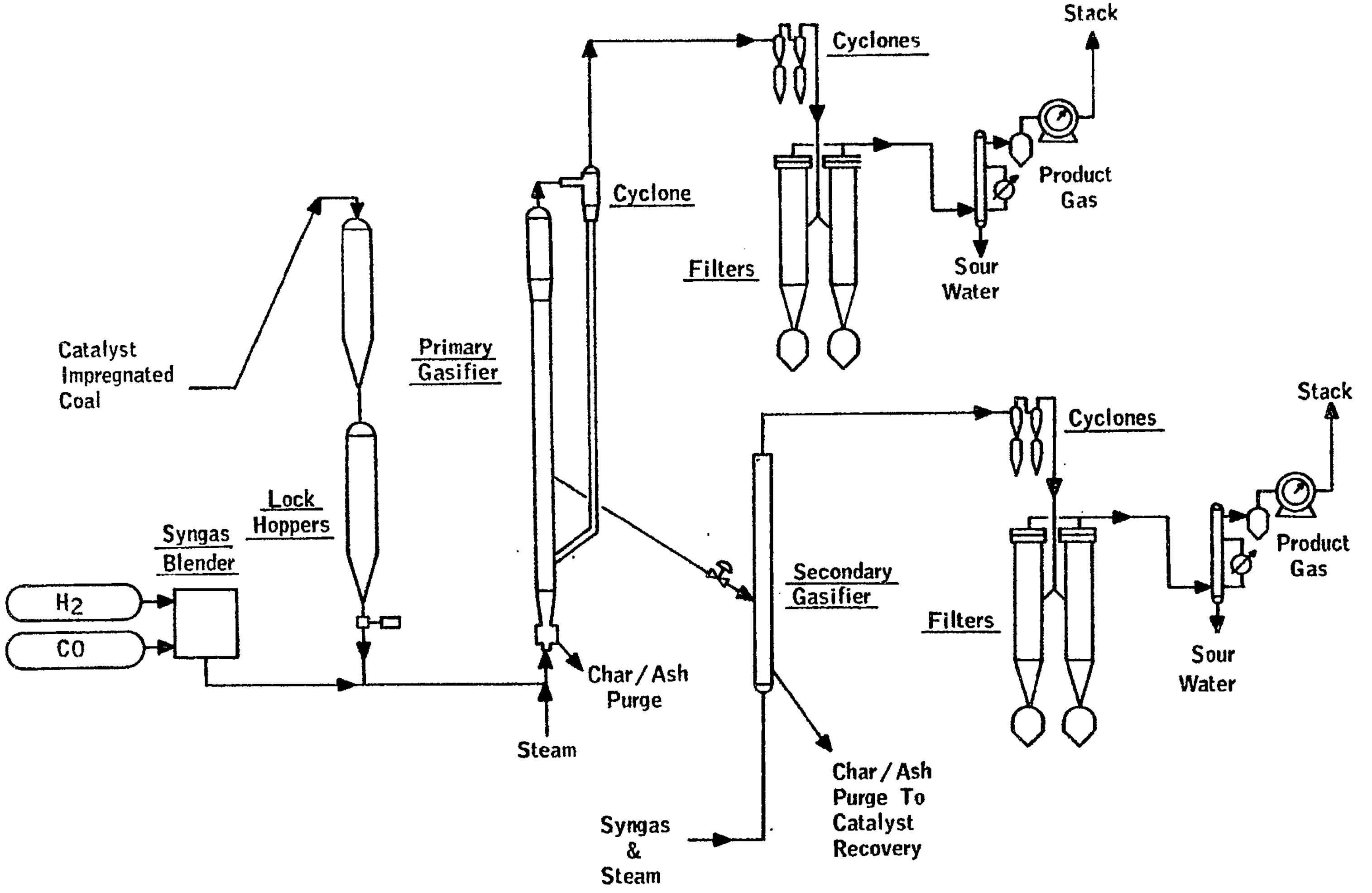


FIGURE 1.1-2

REVISED FLUID BED GASIFIER (FBG) FLOW PLAN



Changes made to improve unit operability included (1) reconstruction of the steam generating system to provide smoother and more reliable operation, (2) simplification of the piping around the backend gas scrubbing systems, and (3) centralization of the control systems for all tape heaters. Changes made to improve unit safety included (1) adding an automatic shutdown system to the synthesis gas blend system to protect against excess CO or H_2 gas flow and (2) expanding the CO alarm and combustible gas detector capacity.

Unit construction was completed early in October, 1976, and the effort was then concentrated on pressure testing, instrument and computer tie-in, and instrument checkout. Following these activities, the unit heater systems and steam generation systems were started up. At the same time, operation of the coal addition system began, and a substantial inventory of catalyzed coal was produced.

In late November, 1976, just prior to the introduction of coal into the primary gasifier, a final pressure test of the system revealed a previously undetected leak in one of the two downstream fines filter vessels. Examination of the 304 SS vessels showed that cracking was present in the vicinity of the vessel welds. Metallurgical analysis of the vessels indicated that the cause of the leaks was chloride stress cracking. The FBG filter vessels were structurally sound at the time of the unit shutdown in December, 1975. Between that time and the start of recommissioning, the unit was kept under a nitrogen blanket. Since a liquid phase is necessary for chloride stress cracking to occur, condensation must have occurred during the recommissioning when the vessels were open to the atmosphere. Apparently there was sufficient residual chloride from previous operations with Illinois coal to cause this problem.

The damaged vessels were replaced with 304 SS filter vessels from the secondary gas handling system which was not scheduled to be operated during the initial period. New vessels made of carbon steel, which is not subject to chloride stress cracking, were subsequently constructed for the secondary system.

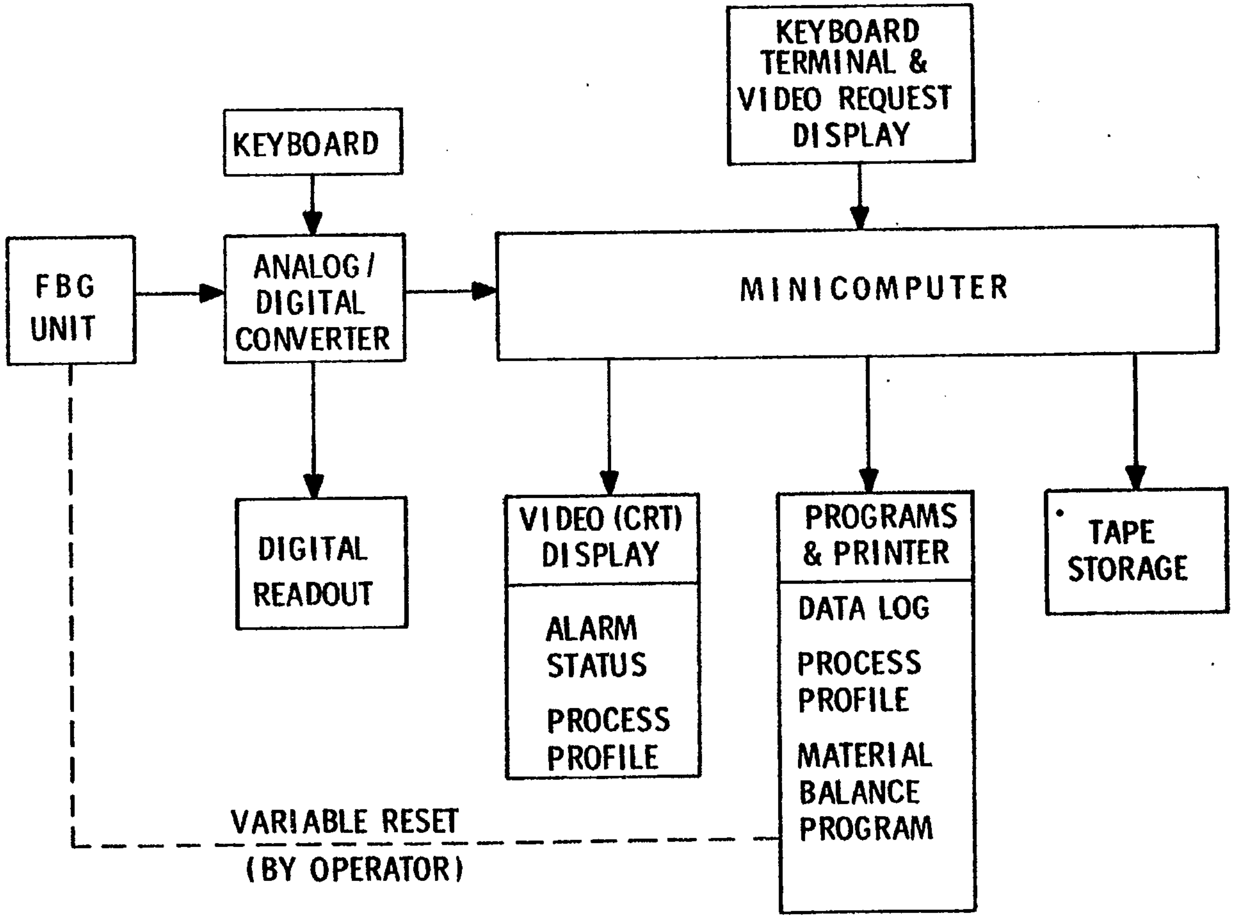
1.1.2 Updating of On-Line Data Acquisition System

Concurrent with the recommissioning of the Fluid Bed Gasifier (FBG), the real-time data acquisition system shown schematically in Figure 1.1-3 was also updated. Data acquisition is accomplished by a minicomputer interfaced with an analog/digital converter that continuously monitors process variables at frequencies ranging from once every 20 seconds to once every 20 minutes. Changes in the FBG process configuration required the addition of several new process variables bringing the total number of continuously monitored variables to more than 300. Installation of the process instrumentation hardware to measure these variables was completed during October, 1976.

During unit operations, the current values of all process variables are instantly available to the operators in the form of a digital readout accessed by a keyboard in the control room. The computer is also programmed to provide process data in many convenient forms that aid both unit operations and subsequent off-line data workup. First, on a real-time basis, video displays (cathode-ray tubes) are used to automatically keep the operator

FIGURE 1.1-3

FBG ON-LINE DATA ACQUISITION SYSTEM



informed of the alarm status of process variables, i.e., if a value exceeds a preset upper or lower limit, an alarm will sound. Another video display is used to provide a process profile which is a schematic representation of the FBG showing current values of the process variables such as the temperatures in the fluidized bed gasifier most critical to the operation of the unit. These video display programs for the recommissioned FBG were written, tested, and implemented as part of the system.

The computer is also programmed to compute and store hourly averages of all process variable values for up to 72 hours, any continuous time interval of which can be retrieved on demand. Current values, hourly averages, or an overall average for a specified interval can be requested. Printers provide a hard copy of these data which is used for further off-line analysis. Additionally, all hourly average values are stored on magnetic tape providing a permanent record of the unit operation. The computer is programmed to print out the stored data in several different forms. First, a "data log" provides a listing of the values for all process variables. Second, a more complete process profile similar to the video display is also accessible, and it can provide in graphic form the average unit operating conditions for a specified time interval. Third, an "instant replay" of selected critical variables allows the operator to monitor the last twenty minutes of unit operations. This is useful in locating operational difficulties during unit start-up. These on-line programs were all updated for the recommissioned FBG.

Central to the efficient operation of the FBG is the on-line program which automatically calculates material balances from the process variable data. This program provides a real-time evaluation of data quality and can aid in locating operational problems. The material balance program provides an instantaneous feedback loop for calculating variable settings required to achieve desired operating conditions. It also provides a preliminary evaluation of unit data during yield period operations. This program was written for the recommissioned FBG and implemented as part of FBG shakedown and base-line operations discussed below.

1.2 FBG OPERATIONS

FBG operations were divided into four general periods:

- Startup and Baseline Operations: December, 1976, and January, 1977, were devoted to startup of mechanical equipment: debugging of instrumentation and on-line computer interfacing and programming, establishing smooth, reliable operation; and obtaining lined-out data for the pre-selected base-case operating conditions.

- Process Variable Study: A program was carried out during February, March, and April, 1977, to investigate the effects of operating variables such as coal, steam, and synthesis gas feed rates; temperature; K_2CO_3 catalyst loading: and activity of mixed K_2CO_3/Na_2CO_3 catalyst.

- Catalyst Recycle Operations: During May, June, and July, 1977, the K_2CO_3 catalyst was recovered from the ash withdrawn from the FBG in the Catalyst Recovery Unit (CRU), reapplied to fresh coal along with makeup catalyst in the Catalyst Addition Unit (CAU), and recycled to the FBG. The purpose was to determine whether any unusual buildup of foreign material occurred in the recovered catalyst and to demonstrate continued high activity of the recovered catalyst in the FBG.

Char Production Operations: During the latter part of July and the first two weeks of August, 1977, the FBG was operated with fresh K_2CO_3 catalyst to make an inventory of char for studies of various catalyst recovery techniques. This provided the opportunity for further process variables studies to add to the data base.

A monthly summary of the operations and comments is shown in Table 1.2-1.

1.2.1 Startup and Baseline Operations

FBG operations were begun under baseline conditions in December, 1976. Initial operations were exceptionally smooth, even though major modifications had been made to the unit. The initial run lasted for six days during which coal was fed 70 percent of the time. The run was terminated to open the bottom of the gasifier when some symptoms of bridging were observed in the bottom section. No bridge was found. The gasifier was clean except for traces of gray ash-like material adhering loosely to the wall near the bottom.

In subsequent runs, it was determined that bridging symptoms correlated with the buildup of high ash, high density solids at the bottom of the fluidized bed. A bulk specific gravity of 0.75 was measured for the bottom drawoff material compared with a typical average gravity of 0.45 to 0.55 for the bed. This behavior was corrected by increasing the frequency of char draw-off from the bottom of the gasifier.

Continuous periods of coal feeding were limited to a maximum of about two days as a result of a number of minor problems. These consisted mostly of leaks in high temperature fittings and valves and plugging in the synthesis gas preheater due to carbon deposition. It now appears that the carbon was forming from CO via the Boudouard reaction ($2CO \rightarrow C + CO_2$) which apparently was being catalyzed by the metal walls of the heater. Initially, the preheater coil outlet temperature was set at 1000°F. Since carbon deposition had not been experienced during previous FBG operations with a syngas preheat temperature of 700°F, the outlet temperature was reduced to this level. No further plugging occurred. Subsequently, an H_2S addition system was installed in the synthesis gas line upstream of the preheater. H_2S is added to the syngas in ppm levels to poison the catalysis of the Boudouard reaction. The preheater has since been operated continuously at 1000°F with no further plugging.

Three material balance periods were obtained with overall material balance closures of about 90%. The baseline operating conditions include a gasifier bed temperature of 1300°F, a unit pressure of 100 psig, a coal feed rate of 10 pounds per hour, a steam feed rate of 12.5 pounds per hour, and a

TABLE 1.2-1

FBG OPERATING SUMMARY

Month	% of Time Onstream*	Longest Continuous Run - Hours	Material Balances, %	Comments
December, 1976	16	140	80-85	■ Start-up and debugging mechanical problems ■ Gasifier opened after six days - no bridging found - Traces of loose gray ash material found adhering to walls ■ High density ash found in bottom in subsequent operations - Increased bottom solids withdrawal frequency ■ Carbon plugging in syngas heater - Added 50 ppm H_2S to prevent carbon deposition: $2\,CO = C + CO_2$ - Now operate up to 1000°F
January, 1977	31	184	90	■ Improved operations ■ Product gas line burned out - Ground fault interrupts (GFI's) installed on all heater circuit - Flammable gas detection system installed ■ High char carry-over rate at times due to feeder blowby - Reduced carbon conversions to 56-86%
February, 1977	60	244	95	■ Generally good operation all month ■ Ten-day sustained operation - Terminated by backend upset resulting in partial loss of bed ■ Five-day sustained operation - Terminated by burned-out steam superheater - Redesigned part of steam system ■ Feeder blowby caused by broken auger on lockhopper agitator - Caused periods of excessive fines loss ■ Material balances approx. 95%
March, 1977	70	284	95-100	■ Excellent operation all month ■ Twelve-day sustained run - Terminated by backend upset ■ Broken U-joint on lockhopper agitator - Caused feeding problems and blowby for few days ■ High steam and carbon conversions ■ Material balances 95-100%
April, 1977	70	336	98-101	■ Catalyst Recovery Unit (CRU) operations started ■ 20% K_2CO_3 catalyst loading with varying coal and steam feed rates
May, 1977	64	407	97-102	■ Catalyst recycle operations started ■ 75% water-soluble catalyst recovery on CRU
June, 1977	96 (668 hours of material balance operation)	587	99-101	■ Excellent operations all month - Maintained at steady state for recycle catalyst study - CRU recovery 90% of water-soluble potassium
July, 1977	70	290	98-103	■ Excellent operation all month ■ Gasifier operating conditions held within narrow limits ■ High steam and carbon conversions ■ No deleterious effects observed as a result of catalyst recycle operations ■ Gasifier feed rates increased to produce char for various catalyst recovery studies
August, 1977	54	72	98-103	■ Excellent operation all month ■ Gasifier bed temperature and feed rates reduced to obtain data for reactor model development ■ Gasifier internal surface inspected - No deposits found - Only a minimal wall coating found at very bottom ■ Unit shutdown due to completion of all scheduled work

---

* All systems operating--excludes start-up and shutdown

catalyst loading of 10 wt.% potassium carbonate. Steam conversions calculated by oxygen balance varied between 38 and 41 percent.

FBG operations continued under baseline conditions during January, 1977. Data were obtained for four material balance periods. The overall material balance and oxygen balance closures were generally around 90 percent, while the hydrogen elemental balance was in the range of 80 percent. Steam conversions calculated by oxygen balance and water balance on the unit generally averaged around 40 percent.

The unit carbon conversion, expressed as the percent of feed carbon gasified, varied from 56 to 86 percent. Good agreement was obtained for conversions calculated by both gas analysis and by solids analysis of coal and char entering and leaving the unit. The lower carbon conversions resulted from lower steam rates coupled with higher synthesis gas feed rates, a combination which reduces the kinetic driving force for the gasification reaction.

Another factor contributing to the lower conversions of feed carbon was a high char carryover rate. The entrainment of carbon from the unit directly reduces the carbon conversion. The high carryover resulted from momentary upsets of the coal feed system during which pulses of nitrogen blew past the rotary feeder and produced very high velocities in the bed (3-4 ft/sec vs. a normal velocity of 0.6-1.0 ft/sec).

The major operating problem was the failure of a beaded wire electrical heater located on the overhead product gas line from the reactor. The heater wire failed and shorted to the pipe in several places. This burned small holes in the pipe causing the reactor contents to be depressured through the overhead line. The failure occurred so quickly that the circuit breakers did not shut off the power. To prevent a repeat of this problem in the event of a future heater failure, ground fault interrupters (GFI's) were placed on all the FBG electrical heater circuits. The GFI's will interrupt the flow of power within 25 milliseconds after a 5 milliamp power imbalance appears in the circuit. Initially there was concern that the GFI's would be too sensitive for the application involved, and would cause power interruptions as a result of minor stray currents. This has not proved to be the case.

Overall during January, the unit service factor was 31% with the longest continuous run lasting 184 hours. Material balances were generally around 90%.

1.2.2 Process Variable Studies

Process variable studies were initiated in February, 1977. Unit operations continued to improve both in terms of service factor and data quality. Approximately 450 hours of operations were logged (60% service factor) with all systems functioning. The longest continuous run extended for 224 hours. The run was terminated by an upset in the product gas handling system which resulted in partial carryover of the fluidized bed. Early in the month some problems with nitrogen feeder blowby, first observed during January, were traced to a broken lockhopper agitator. The agitator design was modified in an attempt to solve this problem. Modifications were also made to the steam system after control problems were encountered which caused overheating of the superheater. Further work was also done on the lockhopper online weighing system and on the gasifier valves which improved material balance closures to the range of approximately 95%. Five material balance periods were obtained during this period.

Unit carbon conversions expressed as the percent of feed carbon gasified varied from about 30 to 50 percent for the material balance periods. Fairly good agreement was obtained for conversions calculated by both gas analysis and by solids analysis of coal and char entering and leaving the unit. The lower conversions obtained in these material balance periods as compared with those obtained in January were the result of the higher throughput of coal coupled with a higher solids carryover rate. This carryover appears to be a result of both significantly higher gasifier superficial velocities (increased steam and syngas flow) and a continuation of past rotary feeder nitrogen blowby problems. Steps were taken to minimize this problem. These steps included reducing the feeder pressure differential and reducing the bed height to increase bed outage. Variable study operations were completed with a catalyst loading of 10 wt.% K_2CO_3.

The unit was operated with both K_2CO_3 and mixed Na_2CO_3/K_2CO_3 catalysts in March, 1977. Operations were again improved both in terms of service factor and data quality. The service factor was increased to 70% and the longest continuous run extended to 284 hours. Again, this run was terminated by an upset in the gas handling system which caused emergency depressuring of the unit. This resulted in the loss of a significant portion of the bed. As in February, feeding problems and nitrogen blowby were encountered. These were traced to a broken U-joint in the lockhopper agitator. Material balances were improved to the range of 95-100%. On-line data for seven material balance periods were obtained.

During April, 1977, FBG operations continued with potassium carbonate catalyst. Data were obtained for catalyst concentrations approaching 20 wt.% on feed coal at varying steam and coal feed rates to determine the sensitivity of these higher catalyst loadings. The gasifier temperature was maintained at 1300°F and the pressure at 100 psig. As in March, the overall unit service factor was about 70 percent. The longest continuous run extended for 336 hours. Overall material balance closures were generally between 98 and 101 percent. Seven material balance periods of 24 hours duration were run. Steam conversion averaged 43 to 47 percent. The effect on steam conversions of variations in catalyst loading within the range of 15-20 wt.% appeared to be relatively small.

1.2.3 Catalyst Recycle Operations

Catalyst recycle operations were initiated in May, 1977. The objective of this phase of work, which involved the Fluid Bed Gasifier (FBG), the Catalyst Recovery Unit (CRU), and the Catalyst Addition Unit (CAU), was to recover and recycle the water soluble catalyst remaining on the ash/char residue from gasification. The major effort was to coordinate the steps in the recycle operations since the CRU and CAU were not designed to run continuously in an integrated manner with the FBG. During an approximately 8 hour period each day, the CRU, a six-stage countercurrent water leaching unit using hydrocyclones for interstage liquid-solids separation, handled the char withdrawn from the FBG during the previous day. The resulting catalyst solution was collected and analyzed for potassium. Makeup catalyst was added to the solution, and the solution was then added to the feed coal. Catalyst addition is done in the CAU, a screw drier modified to permit simultaneous catalyst addition and coal drying.

Catalyst recovery operations were hampered by mechanical problems including excessive wear and leaking of the interstage pumps, and plugging of the interstage flow control valves. The valve problem was solved by replacing existing solenoid valves with air-operated ball valves.

After overcoming these initial mechanical problems, recycle of catalyst to the CAU began. Initial catalyst balances around the CRU indicated that the recovered catalyst was only in the range of 75 percent of the water-soluble catalyst on the feed char. This was below the recovery of 90 percent that should have been obtained, assuming no rate or equilibrium limitations to catalyst recovery other than physical holdup of the catalyst solution by the char. Subsequent bench and pilot scale studies revealed that the low recoveries were caused by inadequate blanketing of FBG char and by leaks in the CRU (cf. Section 1.4.1).

During May, the gasifier operating temperature was maintained at 1300°F and the steam rate held constant at 15 lbs/hr. The gasifier operated smoothly with an overall unit service factor of 64 percent and a long continuous run of 407 hours. The slight reduction in service factor below that obtained during April was caused by mechanical problems with the lockhopper agitator and the rotary feeder. These were probably related to a batch of feed coal of high moisture content. Overall material balance closures were between 97 and 102 percent for six material balance periods of 24 hours duration. Carbon and steam conversions continued to be maintained at a high level. However, it was still too early to tell whether catalyst recycle would result in the buildup of any inactive species with a resultant loss in activity.

FBG operations continued throughout June utilizing coal feed impregnated with recycled catalyst solution. The unit service factor was 96 percent. Approximately 668 hours of material balanced operations were logged during the month with closures averaging better than 99 percent. The longest continuous run lasted 587 hours.

Eight material balance periods were run. Operating conditions for the entire month were held within narrow limits. The coal feed rate was generally maintained at between 10 and 11 lb/hr, and the steam feed rate between 15.5 and 16.5 lb/hr. The reactor temperature and pressure were 1310 ± 10°F and 99 ± 1 psig respectively. The catalyst concentration on the feed coal was generally between 14 and 17 wt.%. Material balance closures were usually between 99 and 101 percent.

The carbon and steam conversions remained high during June operations with recycled catalyst. The carbon conversion was consistently greater than 80 percent, and the steam conversion varied between 50 and 55 percent. The approach to methanation equilibrium in the product gas averaged 70-90°F. This was not as close as in prior operations with once-through catalyst.

However, it is believed that this was due to the combination of an unusually low level of carbon in the bed (about 20 wt.%) and a gasifier bed level which was maintained too low because of a faulty pressure tap reading.

Operations with coal feed impregnated with recycle catalyst solution were successfully terminated in July. Material balance periods 41-44 summarize the data obtained during the latter part of these operations. Gasifier operating conditions were held within narrow limits of target values 1300°F and 100 psia. Carbon and steam conversions remained high during catalyst recycle operations. Carbon conversion was consistently greater than 80 percent and steam conversion varied between 50 and 55 percent. No deleterious effects in FBG operations were observed during catalyst recycle operations. The recycle catalyst did not show buildup of any inactive species that could result in loss of catalyst activity.

1.2.4 Char Production Operations

During the remainder of July, 1977, the unit operated with coal impregnated with fresh catalyst. The synthesis gas flow rate to the unit was increased for material balance period 45. Beginning with material balance period 46, the coal and steam feed flow rates were increased to produce an inventory of gasified char for subsequent catalyst recovery studies.

Approximately 324 hours of material balanced operation were logged during July. The unit service factor was 70 percent. This was not as high as the previous month primarily because of several minor mechanical and computer problems. The longest continuous run was 290 hours.

During the first week of August, operations at high feed rates were continued as shown by material balance periods 47 and 48. During the second and final week of operation, the gasifier bed temperature and feed flow rates were reduced to obtain additional data for development of the reactor model (see Section 2.2). Balance periods 49 and 50 exemplify operation at these conditions.

Approximately 134 hours of material balanced operation were logged during the first two weeks of August. The unit service factor of 54 percent was lower than normal because of a feed line plug. The gasifier internal surface was inspected during the resulting downtime and found to be clean and free of deposits with the exception of a minimal wall coating at the very bottom. This coating was very friable and disintegrated when touched.

Because all FBG studies scheduled under the current contract had been completed, the FBG was shut down during the third week of August, 1977.

1.3 FBG DATA ANALYSIS

A total of 50 material balance periods was obtained for FBG operations at a variety of process conditions. For reporting purposes, these have been limited to 24 hours duration although steady, continuous material balanced operations have extended to 587 hours. Table 1.3-1 summarizes material balance data computed during these periods with the aid of an automatic on-line material balance program that is coupled to the FBG's real time data acquisition system.

TABLE 1.3-1

SUMMARY OF FBG MATERIAL BALANCE DATA FOR DECEMBER, 1976, THROUGH AUGUST, 1977

Material Balance Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Date	12/14	12/15	12/15	1/3	1/4	1/12	1/14	2/8	2/9	2/10	2/11	2/19	3/9	3/12	3/12	3/13	3/16
Duration, Hours	14	17	4	11	8	18	13	4	14	7	24	19	16	16	16	24	16
Yield Period Number	-	-	-	-	-	-	-	-	-	-	202	203	204	205	206	207	208
Reaction Conditions																	
Temperature, °F	1330	1330	1330	1285	1295	1300	1310	1300	1305	1305	1295	1292	1311	1315	1315	1305	1223
Pressure, psig	100	99	100	97	97	99	99	99	98	98	98	99	99	98	98	99	98
Nominal Catalyst Loading, % on dry coal																	
K_2CO_3	10	10	10	10	10	10	10	10	10	10	10	10	15	15	15	15	15
Na_2CO_3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Input, lbs/hr (ExN_2)																	
Coal + Catalyst	10.0	8.5	10.0	9.4	8.7	6.1	7.3	8.2	12.2	14.1	10.0	9.3	10.5	16.9	15.7	16.3	8.8
Steam	11.1	12.4	11.6	13.0	14.0	11.7	11.5	15.6	16.6	16.2	15.9	14.1	14.8	22.6	23.8	22.9	13.0
Syngas	9.1	7.4	6.3	7.7	6.1	9.4	9.6	17.0	16.8	16.6	14.4	13.7	14.2	12.2	16.6	15.9	9.6
Total	30.2	28.3	27.9	30.1	28.8	27.2	28.4	40.8	45.6	46.9	40.3	37.1	39.5	51.7	56.1	55.1	31.4
Output, lbs/hr (ExN_2)																	
Product gas	19.4	18.6	17.1	17.1	17.4	15.4	15.7	22.9	25.7	25.4	22.8	20.6	29.1	33.5	35.0	33.6	16.2
Water	5.5	5.4	6.3	7.1	5.6	7.2	5.8	10.8	10.6	10.3	10.2	8.7	6.2	10.6	12.7	12.9	9.4
Carryover	1.6	1.6	1.1	1.7	1.1	1.8	3.8	1.9	3.6	6.7	4.2	3.2	0.1	2.6	3.0	2.8	1.0
Withdrawn	0.0	0.0	0.0	0.7	0.2	0.4	1.3	1.9	1.6	2.0	1.9	1.4	2.0	2.0	2.1	2.1	3.5
Total	26.5	25.6	24.5	26.6	24.3	24.8	26.6	37.5	41.5	44.4	40.1	33.9	37.4	48.7	52.8	51.4	30.1
Accumulation, lbs/hr	2.1	0.0	4.4	0.6	0.6	0.0	(1.5)	0.7	1.8	0.6	(0.2)	0.4	0.3	(0.4)	0.0	0.1	(0.6)
Material Balance, %																	
Overall	94.7	90.4	103.6	90.4	86.4	91.2	88.4	93.6	94.9	95.9	99.0	92.4	95.4	93.4	94:1	93.5	93.9
Oxygen	92	85	95	91.6	87.0	91.7	83.3	93.1	92.3	91.8	94.2	89.9	97.1	97.1	95.2	95.5	95.9
Hydrogen	81	81	90	79.1	75.0	82.9	80.2	92.5	92.8	90.8	94.4	95.4	93.8	94.0	15.5	90.8	93.6
Syngas, SCFH																	
$CO + H_2$ in Unit	698	737	466	525	395	430	490	612	609	622	524	458	483	493	666	741	464
$CO + H_2$ in Product Gas	502	556	438	400	350	310	360	497	512	520	471	409	509	643	727	778	392
Syngas Balance, %	72	76	94	76	88	71	73	81	84	84	90	89	105	130	109	105	84
Steam Conversion, %																	
By Water Balance	52	57	47	47	61	40	51	32	38	38	37	37	59	54	48	45	29
By Oxygen Balance	40	38	41	36	45	28	26	21	26	25	24	29	55	51	41	39	24
Product Gas, Mol% (dry, ExN_2)																	
H_2	64.3	67.3	60.9	63.2	59.7	59.5	63.0	61.8	58.1	59.5	60.3	58.0	52.0	56.6	59.0	62.4	65.1
CO	10.7	10.0	13.3	11.0	12.1	12.1	11.1	14.0	12.1	13.9	13.9	15.4	20.0	17.0	15.9	13.7	10.2
CO_2	9.1	6.8	10.3	12.2	15.6	15.5	13.2	14.9	15.0	15.1	15.6	15.0	15.7	15.5	14.1	12.6	12.9
CH_4	15.6	15.6	15.1	13.2	12.2	12.5	12.3	9.3	12.1	11.5	10.1	11.6	11.8	10.9	10.0	11.3	11.4
H_2S	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.3
Approach to Methanation Equilibrium, °F	30	35	15	29	30	5	40	40	15	25	27	21	68	25	30	46	79
Carbon Conversion, %																	
By Solids Analysis	73	85	-	-	86	74	57	55	52	39	43	51	92	82	81	81	62
By Gas Analysis	-	-	80	73	-	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 1.3-1 (Continued)

SUMMARY OF FBG MATERIAL BALANCE DATA FOR DECEMBER, 1976, THROUGH AUGUST, 1977

Material Balance Period	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
Date	3/24	3/25	4/15	4/16	4/17	4/25	4/26	4/27	4/28	5/5	5/17	5/18	5/19	5/30	5/31	6/2	6/3
Duration, Hours	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24
Yield Period Number	209	210	-	-	211	212	-	-	-	-	-	-	-	-	-	-	213
Reaction Conditions																	
Temperature, °F	1311	1309	1307	1309	1313	1297	1298	1301	1297	1306	1297	1298	1302	1308	1312	1312	1324
Pressure, psig	98	99	98	99	99	99	99	99	99	98	100	99	99	99	99	99	98
Nominal Catalyst Loading, % on dry coal																	
K_2CO_3	7.5	7.5	20	20	20	20	20	20	20	15	15	15	15	15	15	15	15
Na_2CO_3	7.5	7.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Input, lbs/hr (ExN_2)																	
Coal + Catalyst	9.5	9.7	7.8	10.3	11.1	17.3	17.9	16.7	17.6	10.0	10.9	11.1	10.5	10.0	11.5	12.0	11.1
Steam	14.8	15.2	14.5	15.0	15.1	22.8	22.6	22.4	22.2	15.0	16.1	16.0	15.7	16.1	15.6	15.6	15.3
Syngas	11.5	11.7	11.8	12.9	13.2	14.5	15.0	13.8	14.6	11.3	13.5	14.4	13.7	12.1	16.2	15.1	15.5
Total	35.8	36.6	34.1	38.2	39.4	54.6	55.5	52.9	54.4	36.3	40.5	41.5	40.1	38.2	43.3	42.7	41.9
Output, lbs/hr (ExN_2)																	
Product Gas	22.0	22.3	23.9	26.7	33.9	34.0	34.0	33.7	33.4	26.0	28.3	28.7	29.3	26.8	31.4	31.7	31.6
Water	8.8	9.3	7.7	8.1	8.0	12.7	13.4	12.8	13.2	7.2	8.7	7.9	7.6	8.4	8.2	8.4	7.3
Carryover	0.8	0.9	1.2	1.9	1.7	3.6	2.5	1.9	2.2	1.2	1.1	1.2	0.9	1.1	1.5	1.1	1.2
Withdrawn	3.2	2.1	2.1	1.3	1.8	3.3	5.4	3.8	5.4	2.6	2.5	2.5	0.8	3.0	2.5	1.7	2.6
Total	34.8	34.6	34.9	38.0	38.6	53.5	55.8	52.2	54.2	37.0	40.6	40.3	38.6	39.3	43.6	42.9	42.7
Accumulation, lbs/hr	(0.1)	0.9	(0.4)	0.5	0.4	(0.2)	(1.2)	0.4	(0.2)	(0.1)	0.3	(0.4)	0.6	(0.3)	(0.3)	0.2	(0.1)
Material Balance, %																	
Overall	96.6	97.0	101.2	100.8	99.0	97.6	98.4	99.4	99.3	100.6	101.0	96.1	97.8	102.1	100.0	100.9	101.6
Oxygen	97.2	98.8	97.2	100.2	98.2	97.4	99.2	100.6	100.6	98.2	100.7	97.2	99.3	100.4	100.6	106.0	99.6
Hydrogen	96.2	95.5	99.2	100.7	98.4	96.7	99.8	100.4	99.6	90.8	97.2	95.0	96.4	89.8	99.1	95.6	99.9
Syngas, SCFH																	
CO + H_2 in Unit	512	521	511	552	569	619	632	592	602	485	501	542	545	594	639	649	644
CO + H_2 in Product Gas	538	546	532	578	567	666	699	705	681	496	488	552	573	564	626	639	654
Syngas Balance, %	105	105	104	105	100	108	111	119	113	102	97	102	105	95	98	98	102
Steam Conversion, %																	
By Water Balance	42	40	48	47	48	46	42	44	42	53	47	52	53	49	48	48	54
By Oxygen Balance	38	38	44	47	46	42	41	45	43	50	48	48	52	49	47	57	53
Product Gas, Mol% (dry, ExN_2)																	
H_2	65.7	65.6	60.8	59.9	58.6	57.4	58.7	59.8	58.8	56.1	54.3	57.1	53.4	59.9	57.6	58.1	58.6
CO	13.0	13.6	15.4	15.3	15.4	14.9	15.1	14.4	14.9	14.9	14.7	16.0	16.1	15.0	15.9	16.1	15.8
CO_2	13.1	13.1	12.7	13.0	13.1	14.5	13.8	14.2	14.5	14.6	17.3	15.5	14.9	13.8	14.2	14.3	13.4
CH_4	7.6	7.22	10.7	11.4	12.5	12.7	11.9	11.2	11.3	13.9	12.7	10.6	10.8	10.5	11.5	10.8	11.5
H_2S	0.6	0.5	0.3	0.3	0.4	0.5	0.4	0.4	0.4	0.4	0.9	0.8	0.8	0.8	0.8	0.7	0.8
Approach to Methanation Equilibrium, °F	85	92	68	64	53	34	42	48	44	20	35	72	75	62	61	76	73
Carbon Conversion, %																	
By Solids Analysis	58	64	82	87	77	76	73	75	74	80	78	81	89	79	81	86	83
By Gas Analysis	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 1.3-1 (Continued)

SUMMARY OF FBG MATERIAL BALANCE DATA FOR DECEMBER, 1976, THROUGH AUGUST, 1977

Material Balance Period	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
Date	6/13	6/14	6/19	6/20	6/27	6/30	7/1	7/3	7/4	7/11	7/22	7/31	8/1	8/5	8/12	8/13
Duration, Hours	24	24	24	24	24	24	24	24	24	24	25	25	24	24	24	24
Yield Period Number	-	214	-	215	-	216	-	-	217	218	-	-	-	219	-	-
Reaction Conditions																
Temperature, °F	1318	1317	1315	1318	1311	1313	1314	1316	1315	1317	1330	1309	1310	1305	1287	1289
Pressure, psig	100	99	99	99	99	99	99	99	99	100	100	99	97	100	99	99
Nominal Catalyst Loading, % on dry coal																
K_2CO_3	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Na_2CO_3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Input, lbs/hr (ExN_2)																
Coal + Catalyst	11.5	10.7	11.1	10.6	9.3	9.1	8.5	9.3	8.6	8.5	7.8	19.7	16.3	15.2	8.9	6.9
Steam	16.2	16.2	16.7	16.4	16.5	15.8	16.0	16.1	15.7	15.6	13.7	24.3	24.3	24.0	14.4	15.0
Syngas	13.3	14.0	13.7	13.3	11.8	12.5	12.3	12.1	12.2	12.8	16.3	13.1	11.8	13.8	14.0	12.7
Total	41.0	40.9	41.5	40.3	37.6	37.4	36.8	37.5	36.5	36.9	37.8	57.1	52.4	53.0	37.3	34.6
Output, lbs/hr (ExN_2)																
Product gas	30.1	30.5	29.3	29.7	25.7	26.0	26.0	26.6	26.1	25.5	27.0	36.2	35.2	35.1	22.7	22.8
Water	7.3	7.4	8.0	7.5	8.3	8.4	8.3	8.0	8.0	8.3	8.3	12.8	12.3	12.3	10.2	9.4
Carryover	1.0	1.1	0.9	0.9	1.1	1.0	1.1	1.0	1.0	1.2	1.3	3.3	1.4	2.5	1.3	0.7
Withdrawn	2.1	2.2	2.8	2.5	2.2	2.3	2.0	2.3	2.5	2.1	2.2	3.9	3.5	3.6	3.0	1.1
Total	40.5	41.2	41.0	40.6	37.3	37.7	37.4	37.9	37.6	37.1	38.8	56.2	52.4	53.5	37.2	34.0
Accumulation, lbs/hr	(0.0)	(0.3)	0.1	0.1	0.0	(0.1)	(.60)	.60	(.24)	(.20)	(.45)	(.48)	(.26)	(.60)	(1.05)	.03
Material Balance, %.																
Overall	98.9	100.0	99.0	100.6	99.2	100.5	100.0	102.7	102.4	100.0	101.4	97.6	99.6	99.8	96.9	98.4
Oxygen	99.5	99.4	98.1	99.6	98.1	100.1	100.3	100.0	100.5	97.9	100.2	100.2	102.0	97.3	99.8	100.6
Hydrogen	98.2	99.6	98.1	97.7	96.1	95.4	94.6	95.1	97.0	93.8	98.0	95.2	96.9	98.3	97.2	98.9
Syngas, SCFH																
CO + H_2 in Unit	512	545	552	554	507	527	523	520	514	569	609	488	434	457	508	452
CO + H_2 in Product Gas	587	620	625	634	585	573	561	573	568	553	521	635	646	657	439	462
Syngas Balance, %	115	114	113	115	116	109	107	110	111	97	86	130	149	141	86	102
Steam Conversion, %																
By Water Balance	56	56	53	55	50	48	48.8	51.2	49.9	48.0	40.6	48.6	50.4	50.0	30.8	31.8
By Oxygen Balance	55	55	50	55	48	48	49.3	51.1	50.7	44.9	40.9	48.9	53.0	49.0	30.5	39.0
Product Gas, Mol% (dry, ExN_2)																
H_2	57.3	58.7	60.8	60.3	63.2	61.9	61.4	61.6	62.0	61.7	56.9	54.2	56.1	56.7	58.4	59.4
CO	16.5	16.2	15.2	15.9	14.8	15.4	15.3	14.8	14.5	13.7	15.8	16.9	17.4	17.5	15.4	16.0
CO_2	15.0	14.5	14.3	14.0	13.9	14.1	14.6	14.7	14.7	14.3	14.8	16.8	16.9	16.6	15.3	15.6
CH_4	10.3	9.8	8.8	9.0	7.3	7.8	8.0	8.1	7.9	9.5	11.7	10.9	8.6	8.2	11.0	8.2
H_2S	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.8	0.8	0.8	0.8	1.1	1.0	1.0	0.9	0.8
Approach to Methanation Equilibrium, °F	70	82	85	88	88	79	79	81	80	67	31	30	54	70	38	74
Carbon Conversion, %																
By Solids Analysis	85	-	-	-	-	-	84.5	82.6	83.4	77.3	66.9	71.5	-	76.5	-	-
By Gas Analysis	-	86	82	82	80	76	87.7	85.3	86.3	84.2	78.5	66.8	79.2	74.4	52.6	73.5

Eighteen of these material balance periods were selected as yield periods. These yield periods covered operating conditions of greatest interest. For these, a full spectrum of analyses were obtained on representative samples of feed coal, bottom char, and cyclone and filter fines collected during the period. The complete off-line data workup is presented in Appendix A. These data include critical process temperatures, carbon and steam conversions, relative gasification rates, methane yields, solids composition, catalyst distribution, fluid bed properties, cyclone performance, and particle size distribution.

To develop Appendix A, all of the raw data were entered in a second computer program which reconciled the raw values to force overall and individual component material balance closures. This program, known as the "reconciliation program," uses statistical methods to close all material balances while minimizing the total variance from measured values. This procedure smooths the data in a consistent manner for use in kinetic model development. There are 124 operating variables measured in the raw data. They are subjected to 31 material balance constraints.

For each of the 18 yield periods, Appendix A lists the 124 operating variables in the data workup program which were adjusted by the reconciliation program. Also shown are lists of the raw data and the reconciled data. The reconciliation program produced very minor changes in the data to force the material balance closures. This was true of all the yield periods since the raw data gave good material balance closures. Appendix A also lists the 31 constraints which must be satisfied in the reconciliation program.

1.3.1 Initial Operations

Material balance periods 1-3 (see Table 1.3-1) represent initial operating data that were obtained under target baseline conditions. These conditions include a gasifier temperature of 1300°F, a unit pressure of 100 psig, a coal feed rate of 10 pounds per hour, a steam feed rate of 12.5 pounds per hour, and a catalyst loading of 10 wt. % potassium carbonate on feed coal. The overall material balances close within ± 5 percent, but the oxygen and hydrogen elemental balances do not agree as well. It was subsequently found that synthesis gas was leaking into the vent system through a faulty valve causing material balance error. Steam conversions calculated by oxygen balance vary between 38 and 41 percent. Although higher steam conversions are calculated from measurements of the collected condensate from the product gas, these numbers are more likely to be in error because of the possibility of water loss through pumps and through entrainment from the gas scrubbing system.

Initial baseline operating conditions were also maintained during material balance periods 4-12. These periods are marked by a steady improvement in unit operations in terms of data quality and continuity of operation. Product gas compositions measured by the on-line gas chromatograph for these material balance periods show close approach to gas phase methanation equilibrium. The methane equilibrium temperature is obtained by calculating the ratio $K = (P_{CH_4})(P_{H_2O})/(P_{CO})(P_{H_2})^3$. Published data for the equilibrium constant of the methanation reaction as a function of temperature are used to determine the temperature corresponding to the calculated ratio. The difference between this methane equilibrium temperature and the actual temperature is a measure of the approach to equilibrium. For the first 12 material balance periods the approach to equilibrium varied between 5 and 40°F.

For these early balance periods, syngas feed rate was above that required to balance the gasifier. The CO + H_2 in the feed and the CO + H_2 in the product gas were brought to within 90 percent closure for material balance periods 11 and 12, however, and these two have been designated as yield periods.

Carbon conversions for the first 12 material balance periods vary widely from a low of 40 percent to a high of about 85 percent. The carbon conversion was usually calculated by both gas analysis and by a preliminary analysis of carbon in feed coal and char streams entering and leaving the unit. Generally, the solids analysis method is more accurate, although in most cases the two values agree quite well. For most of the low conversion runs the major factor contributing to the observed conversion is a high char carryover rate. The entrainment of carbon from the unit directly reduces the carbon conversion. The high entrainment apparently results from the quantity of fines in the feed coal, lockhopper feeding problems, and nitrogen blowby across the feeder due to excessive pressure differential. These problems were minimized for the latter material balance periods. Also, leaks in flow lines and the scrubber water system were corrected during subsequent periods as evidenced by excellent material balance closures and close agreement of steam conversion calculated by both oxygen and condensate water balance.

1.3.2 Process Variable Studies with K_2CO_3 Catalyst

Process variables that have been studied include catalyst loading, temperature, coal rate, steam rate, and synthesis gas rate. Material balance periods 13-16 employed potassium carbonate catalyst with a nominal concentration of 15 wt.% on feed coal and a gasifier temperature of 1300°F. The synthesis gas balance for these periods is in the range of 105-130 percent. For material balance period 13, the steam conversion is about 55 percent. The char carryover during this balance period was only 1 to 2 percent of the feed. A very low level (0.4 wt.%) of -325 mesh fines in the feed coal contributed to the low carryover. The low carryover in turn helped achieve a high carbon conversion of 92 percent by solids analysis.

For periods 14-16, steam and coal rates were increased by about 50 percent. The higher gas rates appeared to be the major factor in causing a sharp increase in the fines entrained overhead, although higher fines levels in the feed coal also contributed to the increase. The observed increase in entrainment indicated that the FBG cyclone dipleg may not have been operating properly. This could possibly be due to lack of sufficient height to pressure balance the gasifier. The higher feed rates and carbon carryover in balance periods 14-16 reduced the steam conversion to about 45 percent and the carbon conversion to about 80 percent. A slightly increased deviation from methanation equilibrium was also noted for these high conversion balance periods. Material balance periods 13-16 were designated as yield periods.

During balance period 17, the gasifier temperature was reduced to 1225°F. As expected, even with relatively low steam and coal feed rates, the carbon conversion dropped to about 60 percent. Since entrainment was reduced by the decreased gas rates and the carbon conversion was low, it was necessary to substantially increase char withdrawal rate to maintain a steady-state bed height in the gasifier. Operation at 1225°F also reduced the rate of methane formation evidenced by the 80°F approach to methanation equilibrium. At 1300°F the approach to equilibrium averaged 35°F.

Material balance periods 20-26 completed the phase of work concerned with process variable studies. For these balance periods, data were obtained for potassium carbonate catalyst concentrations approaching 20 wt.% on feed coal at both high and low feed rates. The effect of variations in catalyst loading on steam and carbon conversion within the 15-20 wt.% range appeared to be relatively small.

1.3.3 Mixed Catalyst Operations

Material balance periods 18 and 19 are two essentially duplicate runs with a nominal mixed catalyst loading of 7.5 wt.% K_2CO_3/7.5 wt.% Na_2CO_3 on coal. These data show substantially lower carbon and steam conversions and a greater departure from methanation equilibrium than material balance period 13 although the temperature, coal, steam, and synthesis gas rates were essentially the same. This confirmed the low reactivity for Na_2CO_3 and mixed Na_2CO_3/K_2CO_3 catalysts observed in the fixed bed unit gasification tests. (cf. Section 2.2).

Analyses of the char streams from the mixed catalyst runs confirmed previous bench results, i.e., potassium is selectively tied up by the coal minerals. The data were obtained by analyzing for water soluble and total potassium and sodium on the char. The difference between the water soluble and total values represents the water insoluble fraction which previously has been shown to be comprised primarily of the inactive aluminosilicates. Summarized below are data on the levels of water insoluble potassium and sodium on gasifier bed char and bottom char withdrawn during the mixed catalyst runs. The results are shown on a daily basis.

	Water Insoluble K, % of Total K		Water Insoluble Na, % of Total Na	
Day	Bed Char	Bottom Withdrawal	Bed Char	Bottom Withdrawal
1	37	4	5	0
2	47	40	11	11
3	53	75	9	9
4	39	37	6	0
5	62	58	12	16
6	29	37	2	11
7	48	58	2	13
8	55	43	11	12
Avg.	46	47	7	9

Although there is some scatter, the data show that about 50 percent of the potassium and less than 10 percent of the sodium are tied up with the coal mineral matter. Based on the results from fixed-bed and FBG operations with mixed catalyst, the FBG catalyst recycle operations were done with K_2CO_3 catalyst, and emphasis in other program areas was shifted to secondary recovery of water insoluble potassium.

1.3.4 Catalyst Recycle Operations

Material balance periods 27-44 represent FBG operations utilizing coal feed impregnated with recycle catalyst solution. Spent bottom char and fines were washed in the Catalyst Recovery Unit (CRU), and the water soluble portion of the catalyst was used to impregnate the fresh coal about to enter the gasifier. The necessary amount of fresh makeup catalyst was added to the feed coal to bring the concentration up to 15 wt.% on coal. During these recycle operations, gasifier operating conditions were held to within narrow limits of the target conditions of 1300°F and 100 psig. Material balance closures were between 98 and 102 percent. Carbon and steam conversions remained high during catalyst recycle operations. Carbon conversion was consistently greater than 80 percent and steam conversion varied between 50 and 55 percent. The approach to methanation equilibrium in the product gas averaged 70-90°F. This approach is not as close as that obtained in the earlier non-catalyst recycle operations. However, it is believed that a lower than normal bed level in the gasifier due to a faulty pressure tap reading is partially responsible for this. No deleterious effects of FBG operations were observed during catalyst recycle operations. Recycle catalyst did not show the buildup of any inactive species with a resultant loss in activity.

1.3.5 Char Production Operations

Material balance periods 45-50 were made with fresh K_2CO_3 catalyst for the primary purpose of producing char for subsequent catalyst recovery studies.

The synthesis gas rate was increased in material balance period 45. In periods 46-48, the coal and steam rates were increased while the syngas rate was decreased. Material balance periods 49-50 were made at reduced temperatures and feed rates.

1.3.6 Comparison of FBG Data with Reactor Model Predictions

A proprietary mathematical model for the fluid bed gasification reactor was developed prior to the Predevelopment Research Program reported here. The objective of this work was to have a unified model which would simulate the slugging mode of pilot scale fluid beds as well as the bubbling mode of projected commercial reactors. Such a model was developed based upon the two-phase theory of fluidization. According to this theory, a gas-fluidized solids bed consists of a dense "emulsion phase", through which gases pass slowly upward at the minimum fluidization velocity, and a "bubble phase" of relatively solids-free gas pockets or bubbles rising rapidly up through the emulsion phase. The fluid bed is divided into a series of compartments along the axial distance of the bed. The gas flows in the bubble and emulsion phases are adjusted at each compartment entrance. All physical properties and fluidization characteristics are established based upon the temperature, pressure, and overall gas composition at the beginning of each compartment. Ordinary differential equations describing the flow of each component in the bubble and emulsion phases are numerically integrated through each such compartment over the length of the reactor. The ordinary differential equation which describes the flow of component i in the emulsion phase is:

$$\frac{1}{A}\frac{dN_{iE}}{dx} = -\frac{Q_i}{RT}(P_{iE} - P_{iB}) + (1 - \delta)(\alpha_{iG}r_G + \alpha_{iS}r_{SE} + \alpha_{iM}r_M)$$

where N_i is the molar flow rate of component i (subscript E = emulsion, B = bubble), A is the cross-sectional area of the bed, x is the distance up the reactor from the distributor, Q_i is the bubble-emulsion transfer coefficient (volume gas per unit time per unit volume of bed), R is the universal gas constant, T is the temperature, P_i is the partial pressure of component i, δ is the fraction of bed in the bubble phase, α_{iG} is the stoichiometric coefficient of component i in the gasification reaction (subscript S = shift, M = methanation), and r_G is the molar rate of the gasification reaction per unit volume (subscript S = shift, M = methanation). The ordinary differential equation which describes the flow of component i in the bubble phase is:

$$\frac{1}{A}\frac{dN_{iB}}{dx} = \frac{Q_i}{RT}(P_{iE} - P_{iB}) + \delta\alpha_{iS}r_{SB}$$

where terms are as previously defined.

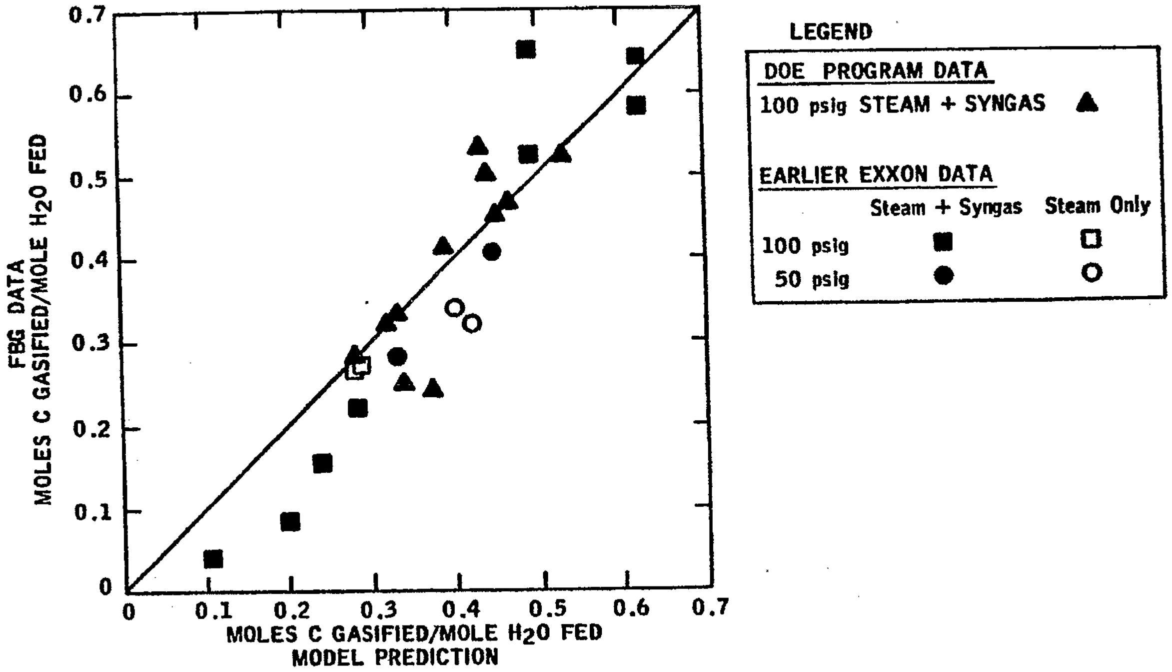
Expressions based on earlier, proprietary, small scale pyrolysis experiments were used to predict devolatilization yields from the coal at the feed point. Devolatilization was assumed to be instantaneous. A new rate expression derived from a kinetic analysis of bench-scale, fixed bed data was used to update the model based on results from this predevelopment program. This analysis is presented in Section 2.2. Shift and methanation reactions are assumed to be at equilibrium.

Proprietary correlations and selected literature correlations were used to calculate the physical properties and fluidization characteristics necessary to evaluate the fraction of the bed in the bubble phase δ, and the transfer coefficients Q_i, for gas interchange between the emulsion and bubble phase in the slugging and bubbling regimes.

The predictions from this model were compared to reconciled FBG yield period operations data (tabulated in Appendix A). A parity plot is provided in Figure 1.3-1 which shows a comparison between predicted and observed pilot plant conversions for yield periods conducted during this program as well as during earlier proprietary work. The variable plotted, moles carbon gasified per mole steam fed, is equivalent to steam conversion for syngas-balanced operation. Considering the broad range of steam conversions, the agreement appears quite good. However, fluid bed data are needed at 500 psig to confirm predicted conversions at the commercial conditions assumed in the Catalytic Coal Gasification Study Design (see Section 4). This is a key objective of the next development phase.

FIGURE 1.3-1

COMPARISON OF FBG DATA WITH REACTOR MODEL PREDICTIONS



1.4 CATALYST RECYCLE OPERATIONS

1.4.1 Operations of The Catalyst Recovery Unit (CRU)

Operation of the Catalyst Recovery Unit (CRU) was initiated in May, 1977. The objective of this work was to recover and recycle the water soluble portion of the catalyst remaining on the ash/char residue from the FBG gasifier. The CRU is a six-stage countercurrent water leaching unit with discrete staged mixing of the char and leaching solution. Hydrocyclones are used for liquid-solids separation between stages.

During an approximately eight hour period each day, the CRU processed the char withdrawn from the FBG the previous day. The resulting catalyst solution was collected and analyzed for potassium. Sufficient makeup catalyst was then added to allow the Catalyst Addition Unit (CAU) to produce an amount of coal equivalent to one day of feed for the FBG.

After overcoming initial mechanical problems in the CRU, recycle of catalyst to the CAU began. Initial catalyst balances around the CRU indicated that the recovered catalyst was only about 75 percent of the water soluble catalyst on the feed char. This was below the recovery of 90 percent that should have been obtained, assuming no rate or equilibrium limitations to catalyst recovery other than physical holdup of the catalyst solution by the char. Bench and pilot scale studies revealed that the low recoveries were due to inadequate nitrogen-blanketing of FBG char and leaks in the CRU.

These studies led to several changes in the CRU during June which increased the recovery of the water-soluble portion of the catalyst from about 75 percent to about 90 percent. The first change was to place a drip pan under the pumps to prevent leakage losses, since even small leaks could significantly reduce catalyst recovery. The second change was to increase the water flow rate so that the solution withdrawal/char feed ratio increased to 5:1 from 3:1. This reduced the effect of backmixing due to solution leaving the hydrocyclones with the char. Two further changes resulted from the bench scale studies. One change was to add $Ca(OH)_2$ to the wash water. This was to enhance removal of potassium ions from ion-exchanged sites on the char. The other change was to improve the nitrogen-blanketing procedures in char removal from the FBG in order to minimize the formation of ion-exchange sites on the char by oxidation during air exposure.

Figures 1.4-1, 1.4-2, and 1.4-3 give detailed summaries for three periods of operation. It can be seen that the best recovery of water soluble K^+ was obtained during period 2. Lower recoveries were obtained during periods 1 and 3 when the char was not blanketed and no $Ca(OH)_2$ was used, respectively. These results are consistent with the hypothesis that potassium is tied to the char by ion exchange, and that prevention of formation of ion-exchange sites or displacement by calcium ions enhances the potassium recovery.

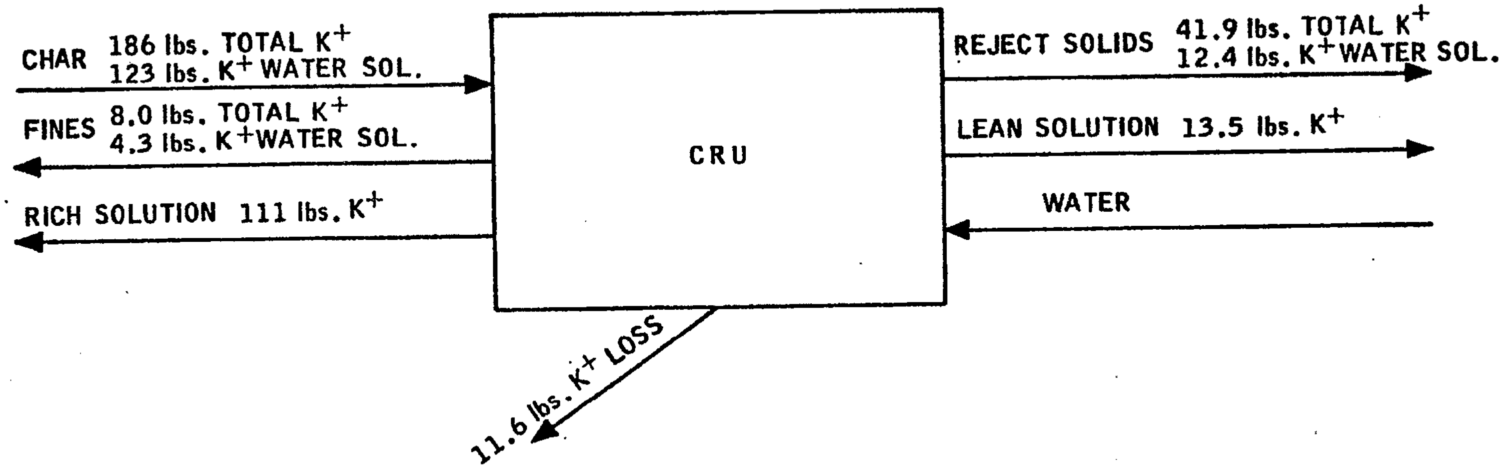
1.4.2 Overall Catalyst Recycle Loop Operations

The catalyst solution recovered each day from the CRU was weighed and analyzed for potassium, and makeup K_2CO_3 was added to provide a one day inventory for the CAU. The concentration of potassium in the blended

FIGURE 1.4-1

CATALYST RECOVERY OPERATIONS

PERIOD 1 - OPERATION WITH LIME AND UNBLANKETED CHAR



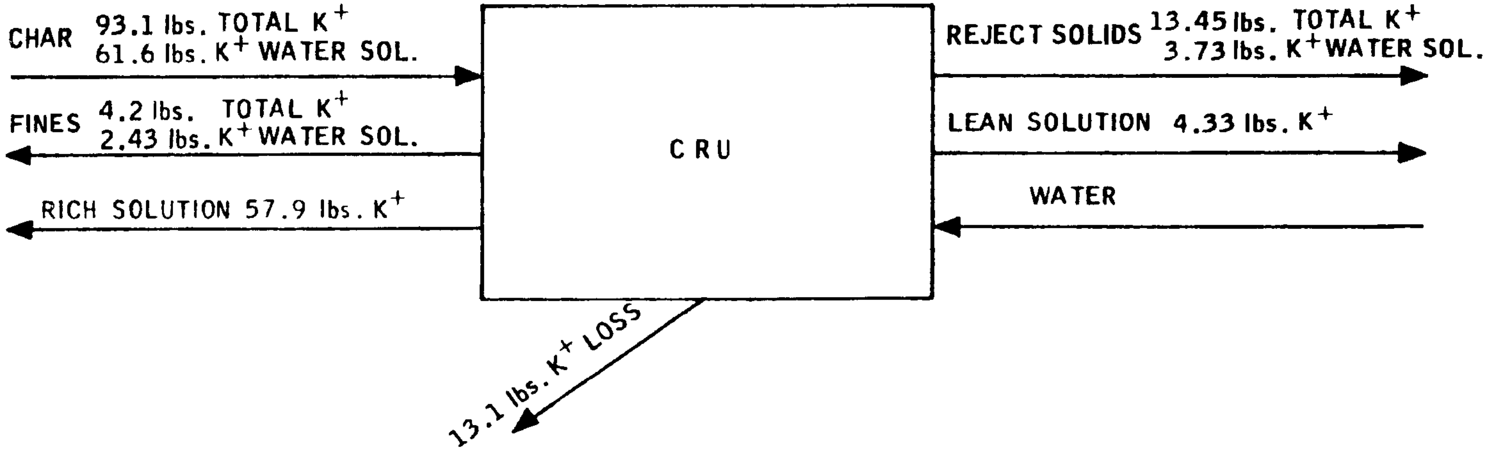
RECOVERY WATER SOLUBLE $K^+ = 111/123 \times 100\% = 90.2\%$

K^+ CLOSURE OUT/IN x 100% = 93.8%

FIGURE 1.4-2

CATALYST RECOVERY OPERATIONS

PERIOD 2 - OPERATION WITH LIME AND BLANKETED CHAR



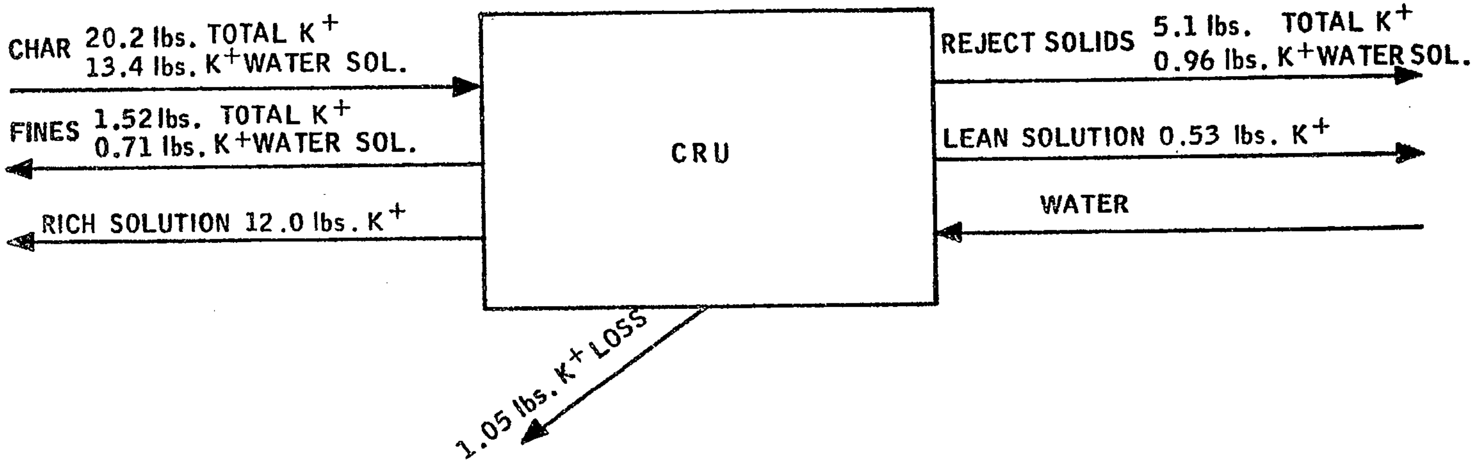
RECOVERY WATER SOLUBLE $K^+ = 57.9/61.6 \times 100\% = 94.0\%$

K^+ CLOSURE OUT/IN $\times$ 100% = 85.9%

FIGURE 1.4-3

CATALYST RECOVERY OPERATIONS

PERIOD 3 - OPERATION WITHOUT LIME AND BLANKETED CHAR



RECOVERY WATER SOLUBLE $K^+ = 12/13.4 \times 100\% = 89.6\%$

K^+ CLOSURE OUT/IN = 94.8%

solution was adjusted to 20 percent K_2CO_3 equivalent by either evaporation or addition of water before the solution was sent to the CAU. Samples were analyzed daily, and rates were determined for every stream entering and leaving each step in the catalyst recycle loop. Total time for catalyst to make an entire loop through the gasifier, the CRU, and the CAU, was 5-7 days.

Material balances were made for each of the steps involved in the catalyst recycle loop operation. The period June 1 to June 27 produced an average of 25 percent recycled catalyst. This relatively low recycle rate resulted from not processing all of the FBG fines and from the 70-75% recovery of water soluble potassium in the CRU. During the period June 28 to July 25, the overall recycle of potassium was increased to 47 percent by improved CRU operations as previously described and by processing all of the FBG fines in the CRU. Approximately 25 percent of the potassium was lost as water insoluble $KAlSiO_4$ which was rejected along with the spent char/ash from the CRU.

1.5 PILOT SCALE SECONDARY CATALYST RECOVERY

A pilot scale secondary catalyst recovery unit (SCRU) was built in order to test on a larger scale the calcium digestion process developed from bench scale studies (cf. Section 2.4). This unit was designed to solubilize the insoluble compound $KAlSiO_4$, which amounts to about 30 percent of the total potassium on gasified char. Recoveries of total potassium catalyst in excess of 90 percent were subsequently obtained in operations of the SCRU.

In the SCRU, char, $Ca(OH)_2$, and process liquid (KOH solution) are mixed and heated in a digester. This digester is a pressure vessel with a capacity of approximately 100 gallons. After digestion, a drum filter is used to separate solids from liquids in the slurry.

During a run, process solution - either water or KOH solution - is pumped into the digester, where it is mixed with calcium hydroxide. Then FBG char is added, the unit is sealed, and the slurry is heated to 300-400°F and agitated for 1-4 hours. The slurry is then pumped from the digester and filtered, separating solids from liquids. The solids are washed up to six times by reslurrying with an amount of water equal to two or three times their weight. In each wash, the slurry is boiled for 15 minutes and refiltered. All liquid and solid streams are weighed and analyzed for potassium to determine potassium recovery and material balances.

Process variables which have been investigated in this study are: $Ca(OH)_2$ loading, digestion temperature, residence time in digester, and number of water washes. The results, presented in Table 1.5-1, confirm trends observed in bench scale studies of catalyst recovery. Recoveries in excess of 90 percent can be achieved after five cross-current water washes at temperatures as low as 300°F, a calcium loading as low as 1.1 moles Ca/mole K, and a residence time of 1 hour. As observed in bench scale work, there are tradeoffs between temperature, calcium loading, and residence time.

TABLE 1.5-1

RECOVERY OF POTASSIUM CATALYST BY DIGESTION WITH $Ca(OH)_2$

Conditions					Cumulative Percent Potassium Recovered						
Run No.	Reaction Time (hrs)	Temperature (°F)	$\frac{\text{Moles Ca}}{\text{Moles K}}$(1)	Solution Weight per lb. Char	Digestion Step	First Wash	Second Wash	Third Wash	Fourth Wash	Fifth Wash	Sixth Wash
2	4	400	0.61	3 lb. H_2O	30.2	-	-	-	-	-	-
4	4	400	0.60	4 lb. H_2O	36.5	77.2	84.9	88.2	-	-	-
5	4	400	0.39	4 lb. 8.8% K	-84.4(2)	47.4	71.9	76.7	81.2	83.4	-
6	4	400	0.37	4 lb. 9.3% K	-21.9	62.9	77.9	82.5	84.7	-	-
7	4	400	0.57	4 lb. 4.6% K	-0.7	50.1	75.3	81.2	84.1	85.1	-
8	4	400	0.89	3 lb. H_2O	46.4	71.7	82.1	87.5	90.7	93.0	-
9	2	300	0.81	4.6 lb. 8.9% K	-60.1	51.4	71.2	83.2	89.0	93.5	96.0
10	2	300	1.2	3.1 lb. 10.2% K	-61.8	45.3	77.9	89.4	94.7	97.0	97.9
11	1	300	0.86	3 lb. 10.4% K	-97.0	26.8	61.6	71.2	79.9	86.4	88.3
12	1	300	1.1	4 lb. 7.7% K	-69.0	38.9	73.0	88.6	94.7	97.1	97.9

Notes:

(1) Ca/K ratio based on potassium in char.

(2) Negative recoveries indicate holdup of KOH solution on char.

1.6 FBG SCRUBBER WATER ANALYSIS

The FBG product gas, maintained at temperatures above the dew point, flows from the reactor to a cyclone and then to bag filters for removal of particulates. The unreacted steam present in the product gas is then condensed in the product gas scrubber. The condensate picks up contaminants from the product gas and becomes "sour water".

During operation of the FBG, sour water from the product gas scrubber was periodically collected and analyzed for several contaminants including ammonia, carbon dioxide, chlorides, cyanides, phenols, sulfides, and total organic carbon. The results of those analyses which can be associated with designated material balance periods are shown in Table 1.6-1.

Though the FBG was operating well when samples were collected, one problem did develop for a short period with the wet gas scrubber. Early in June, 1977, the wrappings on the bag filters were changed, and spaces were left in the wrappings which allowed gasifier fines to enter the scrubber and mix with the sour water. The scrubber was opened and some attempt was made to remove the buildup of fines. However, fines present in the transfer lines June, 1977, the wrappings on the bag filters were changed, and spaces were left in the wrappings which allowed gasifier fines to enter the scrubber and mix with the sour water. The scrubber was opened and some attempt was made to remove the buildup of fines. However, fines present in the transfer lines from the bag filters to the scrubber continued to enter the scrubber all through June. Since the catalyst recycle operations also started in June, it is difficult to distinguish changes in the sour water which might be due to the recycle operation from those which might be due to the presence of fines in the scrubber.

arbon fines from other gasification processes have been shown to act as activated carbon by adsorbing organic contaminants from waste water. It is possible that the fines in the scrubber may have reduced the levels of some contaminants in the scrubber water. Aromatic hydrocarbons, which comprised the majority of the organic compounds present in the scrubber water, are more easily adsorbed than straight chain compounds. The phenols levels were very low during June (material balance periods 33, 35, 37), and the total organic carbon levels decreased. The chemical oxygen demand levels did not decrease. This result, however, is consistent with the others since aromatic hydrocarbons are not oxidized by this test.

Some of the total organic carbon levels were surprisingly high in view of the low phenol levels. Mass spectroscopy was used to analyze chloroform extracts of several unfiltered sour water samples. Analysis of the residue left after evaporation of the chloroform indicated the presence of a variety of aromatic ring compounds, the majority containing two or three rings. This organic matter is apparently suspended rather than dissolved and the majority can probably be removed by filtration.

Small amounts of a tar-like substance were sometimes present in the sour water. When the scrubber was opened for cleaning, an accumulation of this tar-like substance was found in the bottom of the scrubber. This accumulation may have been either the result of a slow buildup over the period of

TABLE 1.6-1

FLUID BED GASIFIER SCRUBBER WATER ANALYSES

		Concentration (ppm)*										
Material Balance Period	pH	Ammonia	Alkalinity as Na_2CO_3	Carbon Dioxide	Chlorides	Free Cyanide	Thiocyanate	Phenols	Sulfides	Thiosulfate	Total Organic Carbon	Chemical Oxygen Demand
13	8.2	13,200	N.A.	39,500	240	2	3	9	370	44	2800	2768
16	8.2	14,200	27,900	37,300	30	3	6	92	700	28	N.A.	N.A.
18	8.4	9,900	41,500	27,000	30	1	1	7	330	0	2100	1124
23	8.1	13,700	12,700	42,800	179	1	0	49	536	36	3780	1118
27	8.6	16,300	42,200	46,600	14	9	28	13	57	0	3400	5443
28	8.4	12,600	83,600	28,800	0	1	2	1	27	0	580	1290
33	8.2	14,900	24,800	40,900	17	2	4	0.4	271	3	6780	950
35	8.4	16,900	43,100	47,200	<1	1	1	0.2	54	38	40	1130
37	8.7	16,800	37,600	17,700	96	1	3	0.6	61	31	194	1665

* Analyses run on filtered samples.

operation of the FBG or the result of the recent influx of solids due to the holes in the bag filter wrappings. A sample of this tar was analyzed by mass spectroscopy, and it was found to contain organic compounds similar to those found in the sour water samples.

The scrubber water analyses shown for the FBG can be considered only as preliminary for Illinois coal at the operating conditions in effect when the samples were collected. Numerous factors, such as temperature, pressure, bed height, and product gas residence time, can affect the quantities of contaminants produced by a particular coal in the sour water from a particular process.