EXXON CATALYTIC COAL GASIFICATION PROCESS: PREDEVELOPMENT PROGRAM. QUARTERLY TECHNICAL PROGRESS REPORT, JULY 1--SEPTEMBER 30, 1976

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EXXON CATALYTIC COAL GASIFICATION PROCESS - PREDEVELOPMENT PROGRAM

Quarterly Technical Progress Report
For the Period
July 1 - September 30, 1976

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ABSTRACT

This report covers the Predevelopment Program activities for the Exxon Catalytic Gasification Process during the period July, 1976 through September, 1976. This work is being performed by the Exxon Research and Engineering Company (ER&E) and is being supported by the United States Energy Research and Development Administration (ERDA) under Contract No. E(49-18)-2369.

The accomplishments during this quarter, summarized by reporting categories, are as follows:

1. Fluid Bed Gasifier Studies

- Recommissioning of the existing 20 lbs/hr Fluid Bed Gasifier (FBG) for operation in the Predevelopment Program was essentially completed.

- Modifications have been completed to the FBG data acquisition system including the on-line computer program for the calculation of unit material balances from process variable data.

2. Bench Scale Studies

- Start-up and initial operations of the 1-3 lbs/hr Continuous Gasification Unit (CGU) were completed.

- Computer programs were developed for CRT display of the CGU operating variables profile and for on-line material balance calculations

- Data were obtained in the CGU for the gasification of catalyzed Illinois coal during four continuous and two captive fluid-bed yield periods. Good agreement was obtained with previous fixed bed kinetic data.

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<u>INTRODUCTION</u>

This report covers the Predevelopment Program activities for the Exxon Catalytic Gasification Process during the period July, 1976 through September, 1976. This work is being performed by the Exxon Research and Engineering Company (ER&E) and is being supported by the United States Energy Research and Development Administration under Contract No. E(49-18)-2369. The Predevelopment Program covers the period July 1, 1976 through December 31, 1977.

Process Description

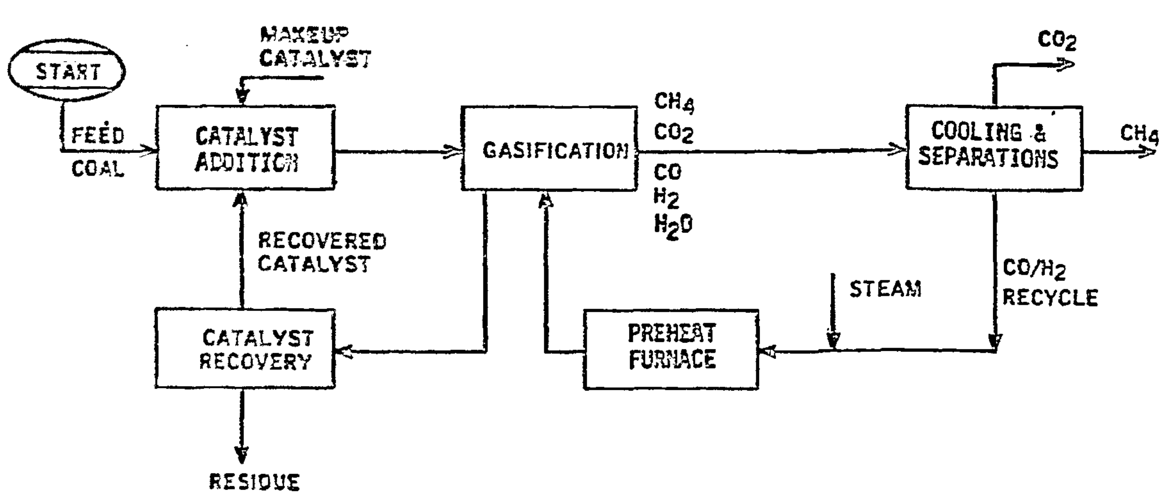
The Exxon Catalytic Gasification Process combines the use of alkali metal gasification catalysts with a novel processing sequence which maximizes the benefits which can be derived from use of the catalyst. The principal benefits for using alkali metal gasification catalysts are that they increase the rate of steam gasification, prevent agglomeration when gasifying caking coals, and promote the achievement of gas compositions closely approaching gas phase methanation equilibrium.

The process combines a relatively low gasifier temperature of about 1300°F with separation of synthesis gas ($CO + H_2$) from the product methane and recycle of the synthesis gas to the gasifier. Thus the only net products from gasification are CH_4, CO_2, and small quantities of H_2S and NH_3. The resulting overall gasification reaction can be represented as follows:

$$\text{Coal} + H_2O \longrightarrow CH_4 + CO_2$$

Since this reaction is essentially thermoneutral, major heat input to the gasifier is not required.

A simplified flow plan for the Exxon Catalytic Gasification Process is shown below.



Coal is impregnated with catalyst, dried and fed via a lockhopper system to a fluidized bed gasifier which operates at about 1300°F and 500 psia. The coal is gasified with a mixture of steam and recycled synthesis gas, and the major gasifier effluents are CH_4, CO_2, CO, H_2, and unconverted steam. No tars or oils are produced. Following heat recovery and water scrubbing, the product gas is treated in a series of separation steps including acid gas scrubbing to remove CO_2 and H_2S, and cryogenic fractionation to separate product methane from synthesis gas. The synthesis gas is combined with feed steam and recycled to the gasifier after preheating to approximately 150°F above the gasification temperature. Although there is no net heat required for the gasification reactions, some small amount of heat input is required to heat up the feed coal, vaporize residual water and provide for gasifier heat losses.

Ash/char residue from the gasification step is sent to a catalyst recovery unit in which a large fraction of the catalyst is leached from the residue using countercurrent water washing. The recovered catalyst, along with some makeup catalyst, is reimpregnated on the coal to complete the catalyst recovery loop.

Summary of Previous Research Results

Previous Exxon-sponsored research on catalytic gasification was performed in bench-scale units which have the capability of operating at pressures up to 1000 psig as well as in a small pilot-scale Fluid Bed Gasifier (FBG) unit with a coal feed capacity of up to 25 lbs/hr and a maximum operating pressure of 100 psig. This pressure limitation arises because the Fluid Bed Gasifier was originally built for thermal gasification work. During 1975, the Fluid Bed Gasifier Pilot Plant was operated with K_2CO_3 catalyzed Illinois coal for continuous periods of up to two weeks. Good quality data were obtained for yield periods covering a wide range of operating conditions. For many yield periods, the FBG operated with synthesis gas makeup (simulated recycle) such that inlet and outlet synthesis gas rates were in approximate balance.

Close approaches to gas phase methanation equilibrium were demonstrated with K_2CO_3 catalyst in both bench-scale units and the FBG pilot plant. Bench-scale rate data were obtained for Illinois coal with both K_2CO_3 and Na_2CO_3/K_2CO_3 catalysts. These data were combined with analytical descriptions of fluid bed contacting to develop a first-pass fluid bed gasifier model.

In the area of catalyst recovery, the effectiveness of water wash for recovering about 75% of the catalyst was demonstrated, the forms of recovered catalyst were identified, and work was initiated on the recovery of water-insoluble catalyst. Also during this phase, engineering screening studies were carried out for commercial plants to establish preferred configurations for process flow and equipment sequencing and to determine investments and operating costs.

Predevelopment Program Objectives

The Predevelopment Program work is divided into three major tasks. The key research objectives for each task are listed on the following page.

Task I - FBG Operations with Illinois Coal

- Operate with mixed K_2CO_3/Na_2CO_3 catalyst
- Operate with recycled catalyst

Task II - Bench-Scale Studies

- Broaden data base to other coals
- Test reactivity of recovered catalyst
- Study critical factors in catalyst recovery
- Operate the small fluidized bed Continuous Gasification Unit (CGU) and fixed-bed units to obtain additional kinetic data

Task III - Engineering Research and Development

- Continue screening studies
- Prepare an updated commercial plant study design

1. FLUID BED GASIFIER STUDIES (Reporting Category 1)

1.1 Fluid Bed Gasifier Recommissioning

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 catalysts, 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. As previously mentioned, this limitation arises 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. Coal is fed to the gasifier via 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 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.

In the Exxon-sponsored program, operations of the FBG were carried out using only the primary gasifier or both the primary and secondary gasifier stages. The purpose of the secondary gasifier is to increase carbon utilization, thereby allowing higher overall process thermal efficiency. The secondary gasifier feed is a mixture of char withdrawn from the primary gasifier and char carried overhead from the primary and collected in the rough-cut cyclone. Synthesis gas and steam are fed to this bed usually at a substantially lower superficial velocity than in the primary. The raw product gas from the gasifier(s) 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 in use during the previous thermal gasification operating periods. The primary and secondary gas systems were then repiped so that when both gasifiers are operating, the gas rate and composition for each can be independently measured. Thus, the gasification rate in each vessel can be determined more precisely. A flow plan for the revised configuration is shown in Figure 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,

Figure 1

ORIGINAL FLUID BED GASIFIER (FBG) FLOW PLAN

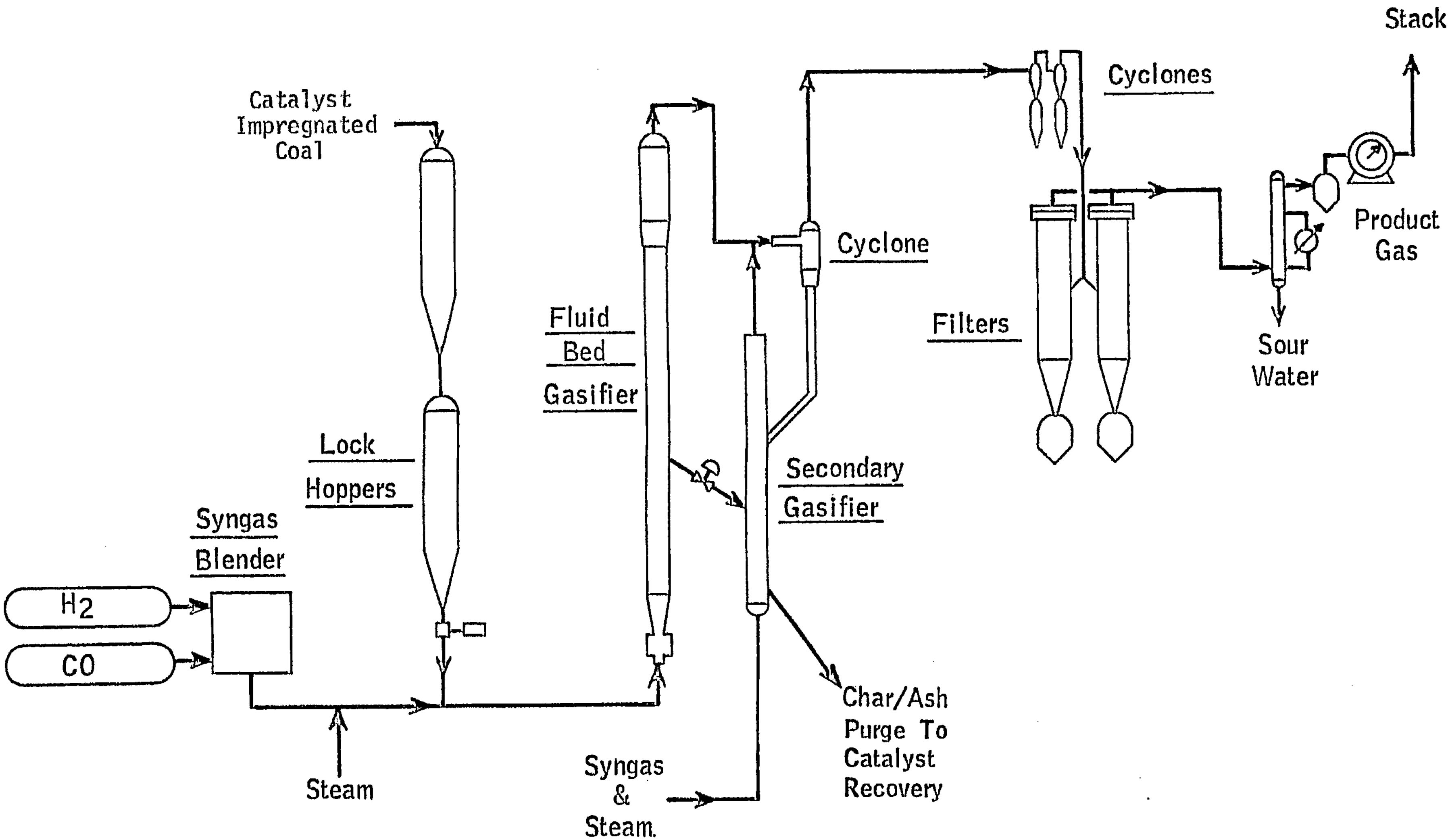
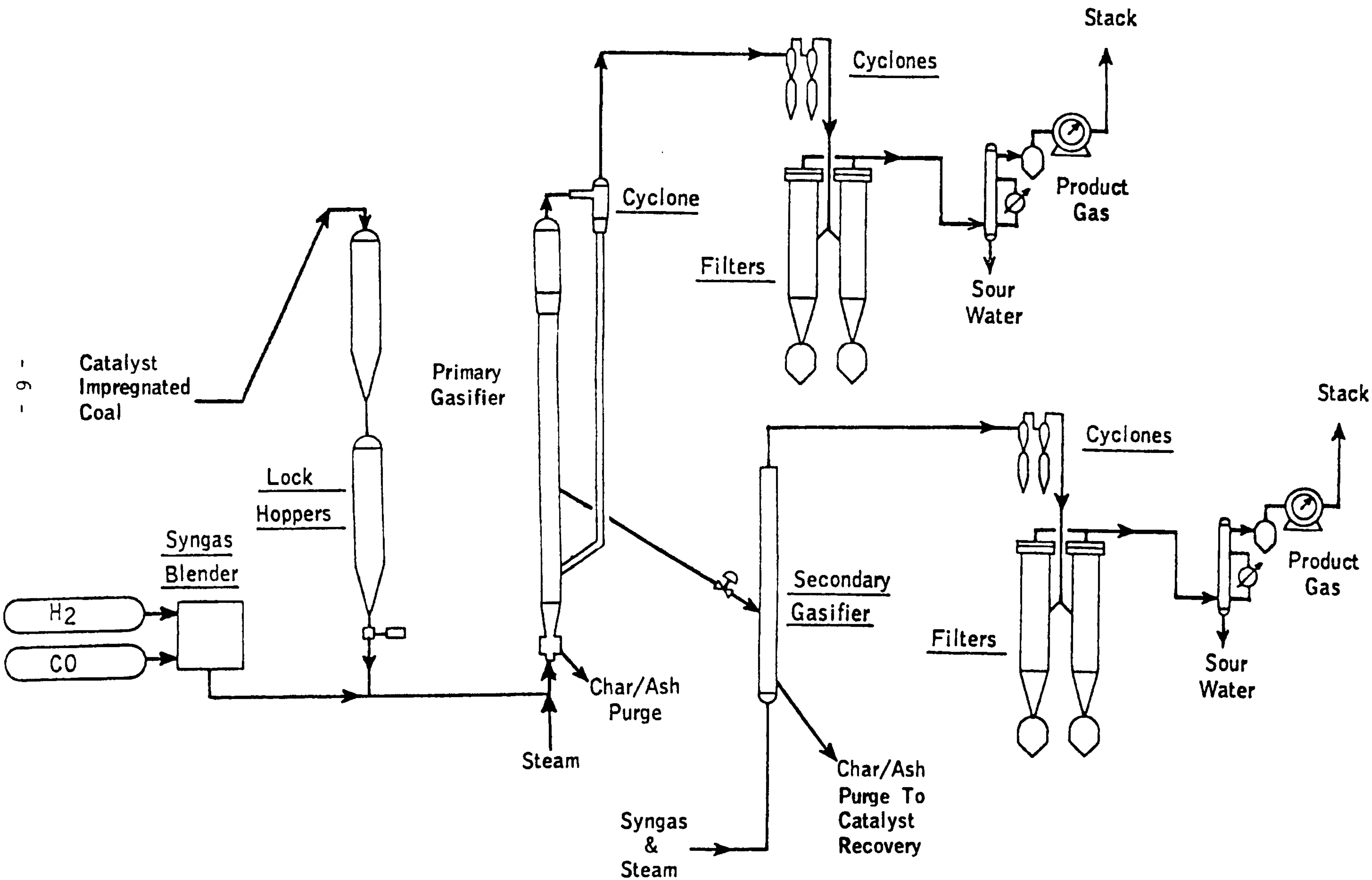


Figure 2

REVISED FLUID BED GASIFIER (FBG) FLOW PLAN



(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.

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.

The work performed during the reporting period included design and materials procurement for the recommissioning,installation of vessels and piping and tie-in of electrical equipment and instrumentation systems. Construction was about 90% complete by the end of the third quarter of 1976. Start-up and base-line operations of the FBG are scheduled for the fourth quarter, 1976.

1.2 Updating of On-Line Data Acquisition System

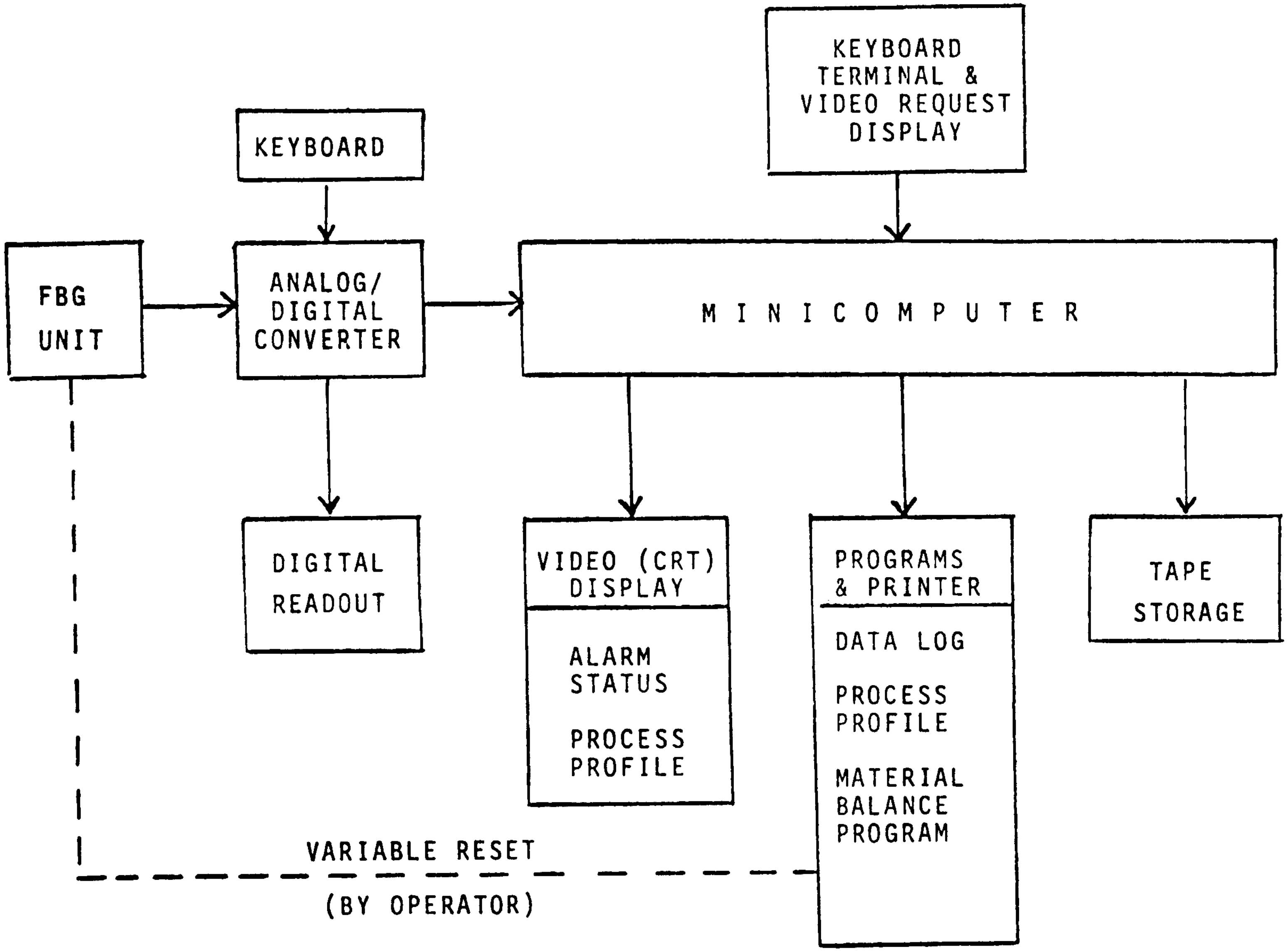
Concurrent with the recommissioning of the Fluid Bed Gasifier (FBG), the real-time data acquisition system shown schematically in Figure 3 has also been updated. Data acquisition is accomplished by a minicomputer interfaced with an analog/digital converter that continuously monitors process variables at frequencies ranging from once every 20 seconds to once every 20 minutes. Changes in the configuration of the unit described above have required the addition of several new process variables which brings the total number that are continuously monitored to over 300. Installation of the process instrumentation hardware that measures these variables is essentially complete.

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 has also been programmed to provide process data in many convenient forms that aids 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 operators 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 CRT 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 have been written and tested and are now 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

Figure 3

FBG ON-LINE DATA ACQUISITION SYSTEM



record of the unit operation. The computer is programmed to print out the stored data described above 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 CRT 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 very valuable in locating operational difficulties during unit start-up. These on-line programs have all been 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 has been written for the recommissioned FBG and will be implemented as part of FBG shakedown and base-line operations in the upcoming quarter.

2. BENCH-SCALE STUDIES (Reporting Category 2)

2.1 Description of the Continuous Gasification Unit

The Continuous Gasification Unit (CGU) is a very small fluidized bed unit designed for continuous coal feeding and withdrawal of ash/char residue. It was built so that kinetic data could be obtained in a fluidized mode at a lower cost and with less manpower than required for the FBG. Construction of the CGU was completed with Exxon funding prior to the start of the Predevelopment Program.

Although the CGU is smaller than the FBG, it has the additional capability of operating at high pressure, with 1000 psig being the design maximum. In addition, although the primary source of synthesis gas was intended to be cylinder gas, the capability does exist for synthesis gas recycle. A flow plan of the unit is shown in Figure 4. The feed is conveyed into the bottom of the unit using the synthesis gas/steam gasification mixture. The gas rates are very low and the design gasifier superficial velocity is near minimum fluidization. The overhead gas is filtered for solids removal, water scrubbed to condense unreacted steam, and the flow rate and composition are measured. For the option in which synthesis gas recycle is employed, the gasifier product is treated to remove acid gases and then cryogenically separated into product methane and recycle gas.

Operation of the CGU is expedited by the use of a programmable controller for logic control of Start-up, alarm, and emergency sequences, and a 50-channel digital process controller. In addition all instrumentation, including a continuous process gas chromatograph, is interfaced with an on-line computer for data logging and monitoring, flow calculations, and material balance and equilibrium calculations with operating condition set point feedback to the operator.

2.2 CGU Operating Experience

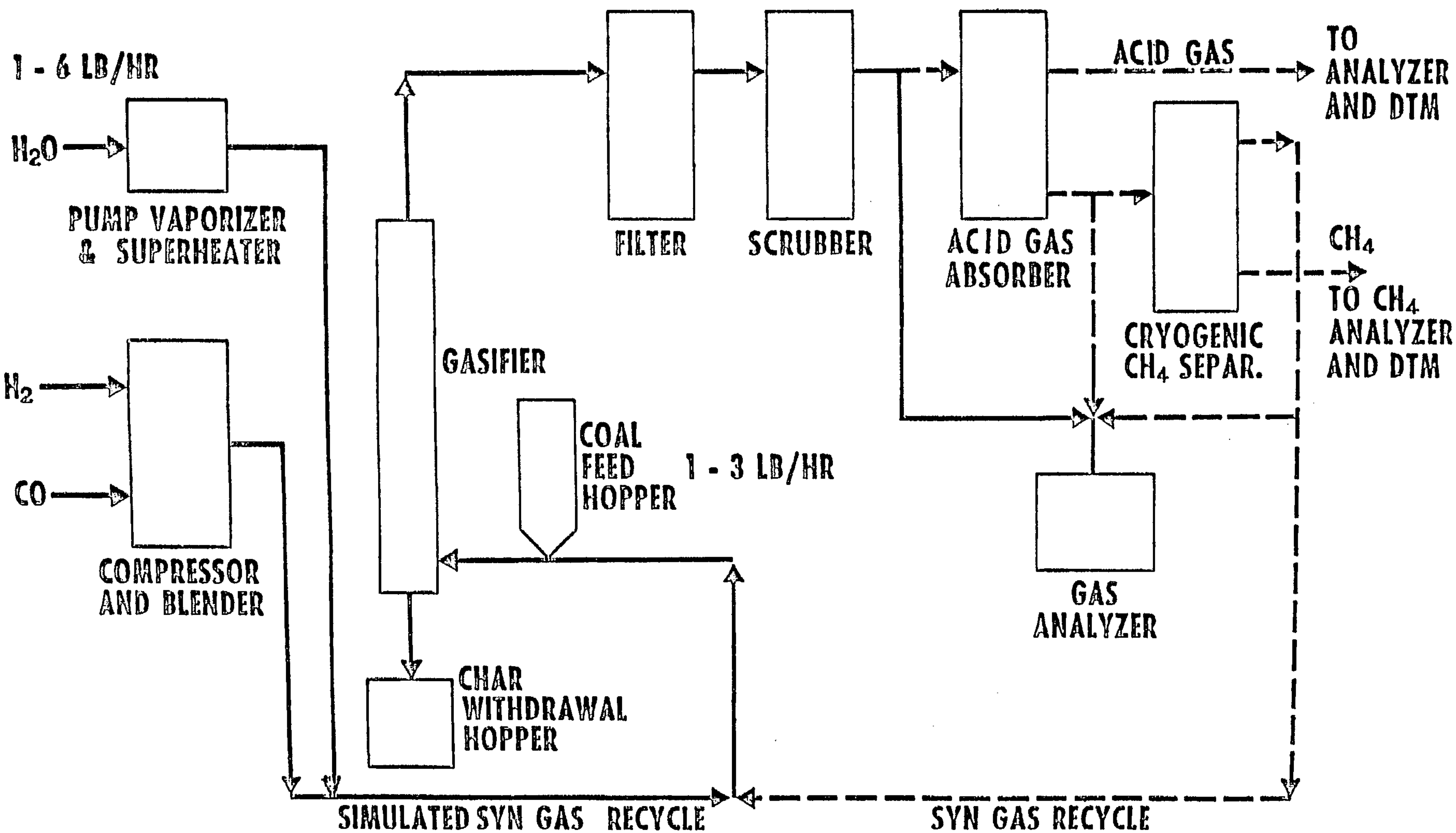
Start-up and initial operations of the CGU were completed during the third quarter of 1976. Because of operating difficulties, the periods of continuous unit operation were limited to a maximum of 26 hours. As a result, true steady-state conditions were not reached. Data were obtained for four continuous yield periods of up to six hours length. In addition, two batch-type yield periods with a captive fluid bed were conducted for comparison with previous fixed-bed experiments.

This work completed the initial phase of CGU operations. Additional CGU runs are scheduled for the third quarter of 1977, after completion of FBG operations. Operating difficulties which were experienced during the start-up phase are discussed below. An analysis of the data obtained is presented in Section 2.3.

The CGU operating problems generally were related to the small size of the unit although normal pilot plant mechanical problems (e.g., compressor

Figure 4

CONTINUOUS GASIFICATION UNIT (CGU)



failures) were also encountered. One major CGU constraint is the low feed gas rate which requires a small feed line diameter (0.25 inches) to provide sufficient velocity to convey the feed char to the gasifier. The gas velocity in the feed line is very close to the theoretical saltation velocity. Thus, momentary upsets, caused for example by fluctuations in synthesis gas supply pressure, occasionally resulted in a solids plug in the feed line. This problem was corrected by modifying the syngas supply pressure regulation system to assure very steady flow and by operating at higher than design syngas rates. However, the higher rates did result in gas residence times lower than those projected for commercial operations and consequently in lower steam conversions. To correct this, it is planned that for future operations, the gasifier diameter be increased to give a 1.8 fold increase in gasifier volume and a corresponding increase in gas residence time. This would be within the capability of the present heater system.

Occasional plugging problems also were experienced in the gasifier pressure taps which are used to indicate the level of the fluidized char bed. Since synthesis gas is used for the pressure tap bleed gas, the greater the volume of bleed gas the less the volume available to the feed line. To maximize the feed line gas, small diameter pressure taps (0.055 inches I.D.) were used with low gas velocities in the taps. Again, upsets in the syngas supply pressure, or in the gasifier, occasionally resulted in solids backing into the taps and plugging them. For future operations, it is proposed to modify the bleed gas supply system to simplify blowing out the taps in the event of solids plugging.

Another major problem encountered in the CGU, but one easily correctable, was steam condensation at some locations. This was caused by inadequate electrical trace heating and resulted in two types of operating difficulties - formation of soft plugs and metal failure. The soft plugs in the unit formed in the char sample and char withdrawal lines. At 500 psig, the steam saturation temperature is 471°F. Char impregnated with K_2CO_3 catalyst may stick at temperatures higher than the saturation temperature due to the hygroscopic character of K_2CO_3. The prevention of wet spots in very small lines and especially around valves and thermocouples where heat losses are concentrated is particularly difficult with a unit as small as the CGU. However, additional heaters and insulation were used and the plugging problems were apparently solved.

Two instances of metal failure were encountered. The first was in the product gas filter vessel in the weld region between a 316 SS pipe and a 316 SS butt welded hub. Figure 5 is a sketch of the vessel showing the position of the affected area. While in service, tape heaters and insulation were wrapped around the pipe up the the weld area. The hub and clamps were not heated. Analysis of a piece of scale from the weld area showed 5,000 ppm chloride. Radial cracks initiating at the inner metal wall were found in a ring containing the weld area cut from the vessel. These are shown in Figure 6. Characteristic branching transgranular chloride-stress cracks are seen. The ring sprung open when cut, indicating that a high tensile stress state existed in the crack region due to the residual weld stresses. Since chloride stress cracking could not occur without a liquid phase, it is clear that steam was condensing. After the vessel was rebuilt, heaters were added to the weld and flange area to prevent steam

Figure 5

CGU FILTER VESSEL FLANGE END

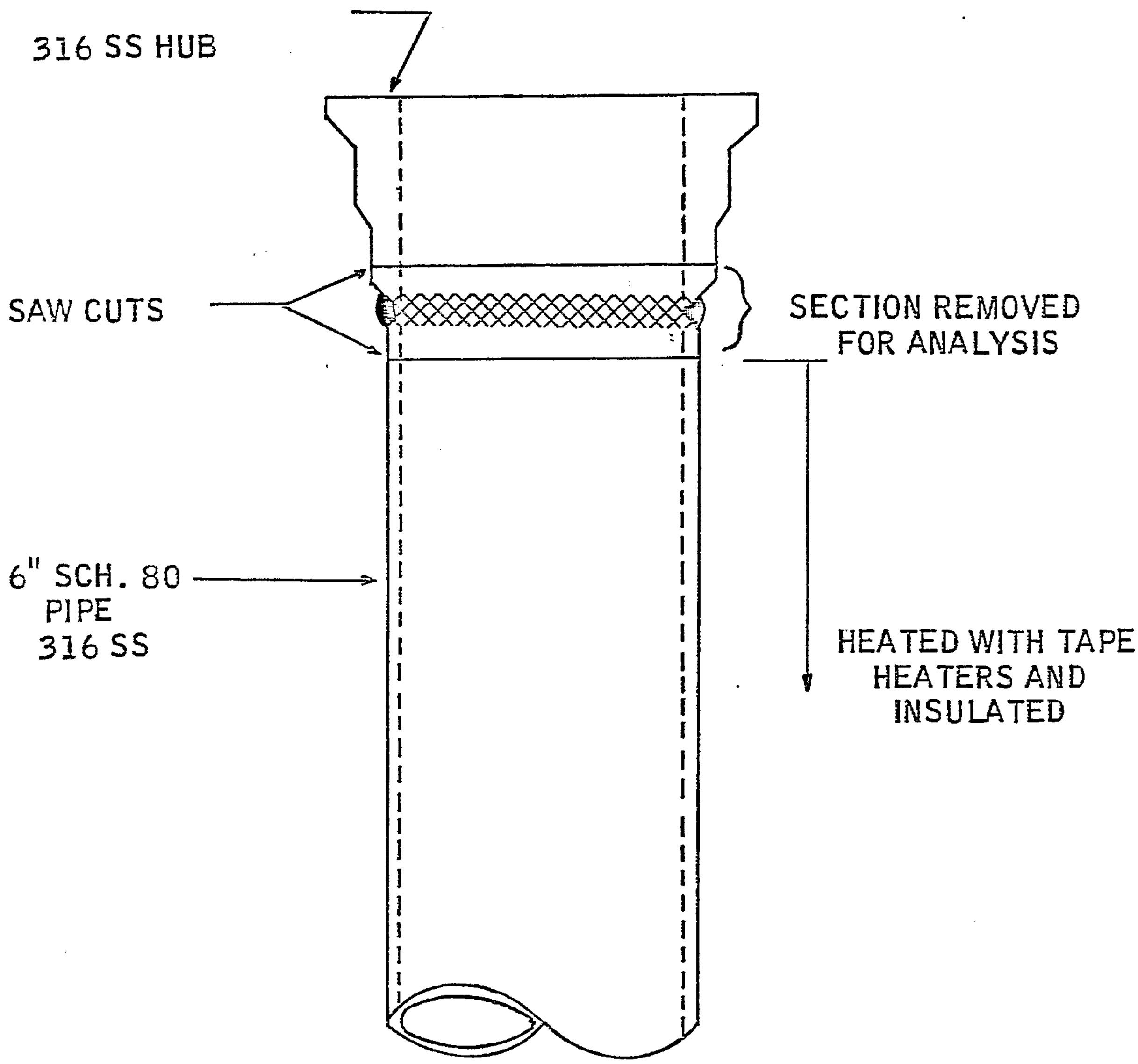
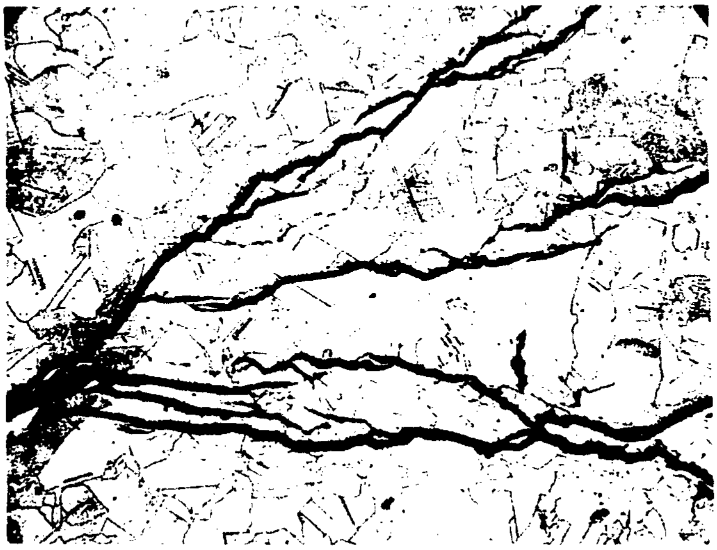
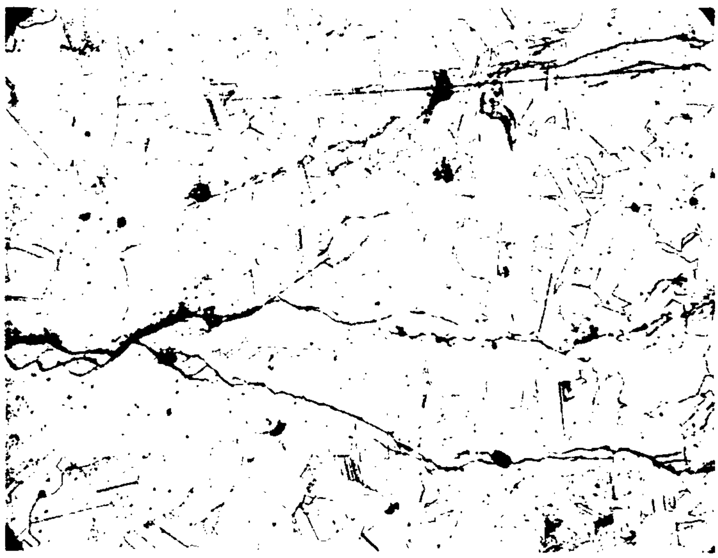


Figure 6

TRANSGRANULAR STRESS-CHLORIDE CRACKS IN 316 SS FILTER VESSEL NEAR HUB WELD. 55X. ELECTROLYTIC OXALIC ACID ETCH





condensation. The second stress-chloride cracking failure was in the char-sampling line in a weld area between a 316 SS male connector and a 316 SS half coupling. This line had been fully wrapped with tape heaters and insulation and held at 600-650°F. Steam evidently condensed at some time, however, probably during a shutdown as a result of inadequate purging.

2.3 CGU Data Analysis

Material balances for the four CGU continuous yield periods (101-104) are presented in Table I. For all four yield periods, the fluid bed temperature was in the range of 1300°F. In three cases, the pressure was 500 psig and in one case, 350 psig. The feedstock was Illinois coal char catalyzed with 20% K_2CO_3. The gasification medium was steam/H_2 or Steam/H_2/CO. Because of the operating problems discussed above, it was not possible to obtain a representative sample of the ash-char residue. Thus, the unconverted carbon in the residue was estimated by carbon balance assuming no accumulation or depletion of carbon in the bed. The inlet and outlet gas compositions and the measured steam condensate collected in the scrubber were used to check the overall hydrogen and oxygen balances. These balances closed to within five percent in over half of the cases and to within ten percent in all cases.

The calculated carbon conversions for Yield Periods 102-104 vary from 60 to 90 percent. The calculated carbon conversion of 99 percent for Yield Period 101 is almost certainly in error as a result of carbon depletion in the bed. The percent carbon in the residue is an important parameter because assuming a well mixed bed, it sets the carbon holdup in the bed. This in turn fixes the steam residence time (steam feed rate/carbon holdup) a parameter used in correlating the data. The percent carbon on residue and residence time for Yield Period 101 appear to be low by an order of magnitude.

Material balances for the two captive fluid-bed yield periods (105 and 106) are summarized in Table II. One run was made with pure steam as the gasification medium. In the other run, a mixture of steam and synthesis gas was used. The feed was devolatilized Illinois coal catalyzed with 20% K_2CO_3. The pressure was 500 psig and the temperature, 1250°F. With the captive fluid-bed operation, which is analagous to the fixed-bed operation, the steam or steam/synthesis gas mixture flow rate is kept constant throughout the run. As the run proceeds, and the carbon is gasified, the carbon content of the bed decreases, and the relative residence time decreases. Since in runs of this type the gas composition is changing, it is not possible to make an accurate measurement of the water content of the outlet gas by collecting the condensate produced. Thus, the product H_2O is calculated from the inlet and outlet dry gas analyses using an oxygen balance. Since no carbon is withdrawn, the carbon gasification rate is calculated by carbon balance. A check of the hydrogen balance is possible for each time period and this is shown in the table. The hydrogen balances close within $\pm$ 5% in essentially all cases.

The gasification rates for the three good continuous yield periods (102-104) and both captive bed yield periods (105 and 106) are compared with fixed-bed gasification data obtained during the previous Exxon-sponsored research phase in Figure 7. The fixed-bed data were obtained in multiple runs at

Table I

MATERIAL BALANCES FOR CGU CONTINUOUS YIELD PERIODS

	Yield Period 101					Yield Period 102				
Temperature, °F	1280					1310				
Pressure, psig	350					500				
	Total	C	H	O	N	Total	C	H	O	N
Input (lbs/hr)										
Char	2.500	1.213	0.015			2.500	1.213	0.015		
H_2O	5.300		0.593	4.707		4.907		0.549	4.358	
H_2	0.502		0.502			0.738		0.738		
CO										
N_2(5)						0.174				0.174
Total	8.302	1.213	1.110	4.707		8.320	1.213	1.302	4.358	0.174
Output (lbs/hr)										
Char	1.285[1]	0.012[2]				1.740[1]	0.469[2]			
H_2O	4.200		0.470	3.730		4.430		0.496	3.934	
H_2	0.548		0.548			0.621		0.621		
CO	0.532	0.228		0.304		0.191	0.082		0.109	
N_2						0.174				0.174
CH_4	0.738	0.553	0.186			0.654	0.489	0.164		
CO_2	1.540	0.420		1.120		0.636	0.173		0.463	
Total	8.843	1.213	1.204	5.154		8.446	1.213	1.281	4.506	0.174
Material Balance, %	107		108	110		102		98	103	

	Yield Period 103					Yield Period 104				
Temperature, °F	1310					1304				
Pressure, psig	500					500				
	Total	C	H	O	N	Total	C	H	O	N
Input (lbs/hr)										
Char	2.500	1.213	0.015			2.000	0.970	0.012		
H_2O	5.000		0.560	4.440		5.060		0.566	4.494	
H_2	0.865		0.865			1.197		1.197		
CO						0.287	0.123		0.164	
N_2(5)	0.207				0.207	0.281				0.281
Total	8.572	1.213	1.440	4.440	0.207	8.825	1.093	1.775	4.658	0.281
Output (lbs/hr)										
Char	1.387[1]	0.114[2]				1.135[1]	0.118[2]			
H_2O	4.620		0.517	4.102		4.819		0.539	4.280	
H_2	0.625		0.625			0.878		0.878		
CO	0.157	0.067		0.090		0.180	0.077		0.103	
N_2	0.207				0.207	0.281				0.281
CH_4	1.109	0.830	0.279			1.087	0.814	0.273		
CO_2	0.739	0.202		0.538		0.308	0.084		0.224	
Total	8.844	1.213	1.421	4.730	0.207	8.688	1.093	1.690	4.607	0.281
Material Balance, %	103		99	107		98		95	99	

	Yield Period 101	Yield Period 102	Yield Period 103	Yield Period 104
Carbon Conversion, %[3]	99[4]	61	91	88
Relative Steam Residence Time	0.13	0.41	0.12	0.14
Mol Carbon Gasified/ Mol Steam Fed	0.34	0.23	0.33	0.26

Product Gas Comp. (Mole %)	101 Measured	101 Calc. Gas Phase Equil.	102 Measured	102 Calc. Gas Phase Equil.	103 Measured	103 Calc. Gas Phase Equil.	104 Measured	104 Calc. Gas Phase Equil.
H_2O	38.52	45.37	39.53	42.94	38.54	39.77	33.67	34.83
H_2	44.96	35.41	49.50	45.82	46.60	45.09	54.85	53.87
CO	3.14	2.19	1.10	0.53	0.84	.75	0.81	0.27
N_2	-	-	1.00	1.02	1.11	1.13	1.26	1.22
CH_4	7.60	12.53	6.55	8.95	10.38	12.27	8.53	9.54
CO_2	5.78	4.50	2.32	0.74	2.53	0.99	0.88	0.27
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

(1) Ash and catalyst balance estimated assuming no accumulation or depletion in bed

(2) Estimated by carbon balance assuming no carbon accumulation or depletion in bed

(3) From carbon balance. See note 2

(4) Appears to be in error because of carbon depletion during yield period

(5) N_2 from feeder blow-by calculated by N balance

Table II

MATERIAL BALANCES FOR CGU CAPTIVE-BED YIELD PERIODS

Temperature, °F	1250					1250			
Pressure, psig	500(1)					500			
Gasification Medium	H_2O					$H_2O/H_2/CO$			
	Yield Period 105					Yield Period 106			
Time, Hours	1	2	3	4	5	1	2	3	4
Input, Moles/Hr									
H_2O	0.295	0.295	0.295	0.295	0.295	0.229	0.229	0.229	0.229
H_2	0	0	0	0	0	0.092	0.092	0.092	0.092
CO	0	0	0	0	0	0.028	0.028	0.028	0.028
Output, Moles/Hr									
H_2O(2)	0.122	0.122	0.145	0.201	0.232		0.115	0.156	0.191
N_2	0.098	0.083	0.081	0.071	0.051		-	-	-
H_2	0.073	0.081	0.086	0.072	0.055		0.092	0.086	0.074
CO	0.038	0.033	0.024	0.011	0.004	Note	0.032	0.015	0.007
CH_4	0.054	0.050	0.036	0.012	0.004		0.051	0.035	0.020
CO_2	0.068	0.070	0.063	0.042	0.029	(5)	0.055	0.043	0.030
Carbon Gasified, Mole/Hr(3)	0.160	0.153	0.123	0.065	0.037		0.110	0.065	0.029
Steam Conversion, %(2)	58.6	58.6	51.0	32.0	21.3	-	49.7	31.8	16.7
Hydrogen Balance, %(4)	96	97	98	98	99	-	93	95	94
Relative Steam Residence Time	1.43	0.91	0.49	0.27	0.15		0.52	0.24	0.11

(1) Bleed N_2 reduced effective pressure to 420 psig

(2) H_2O by O_2 balance

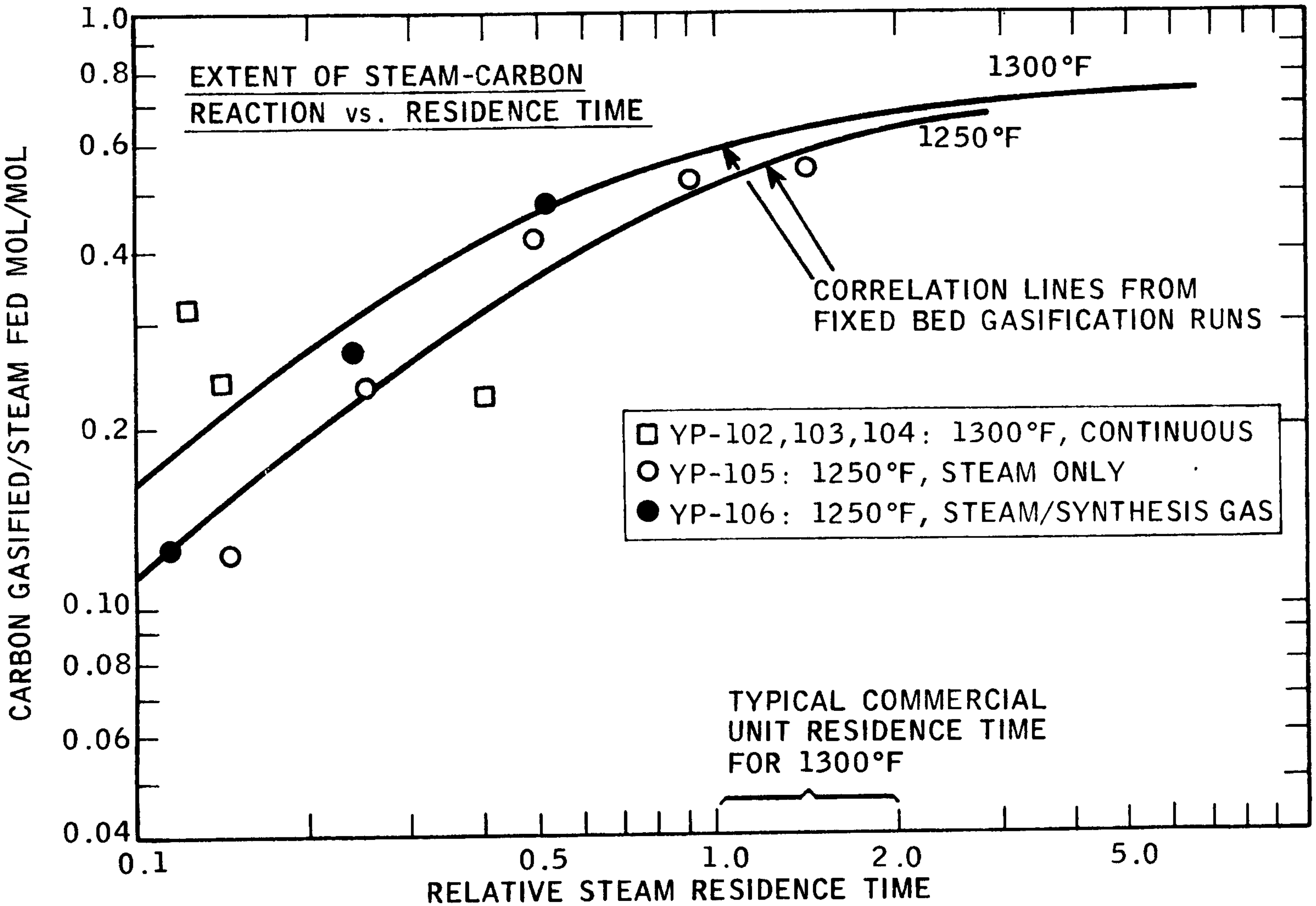
(3) By carbon balance

(4) Based upon feed char with .02 H/C weight ratio

(5) Gas chromatograph problems were encountered during this first hour of operation

FIGURE 7

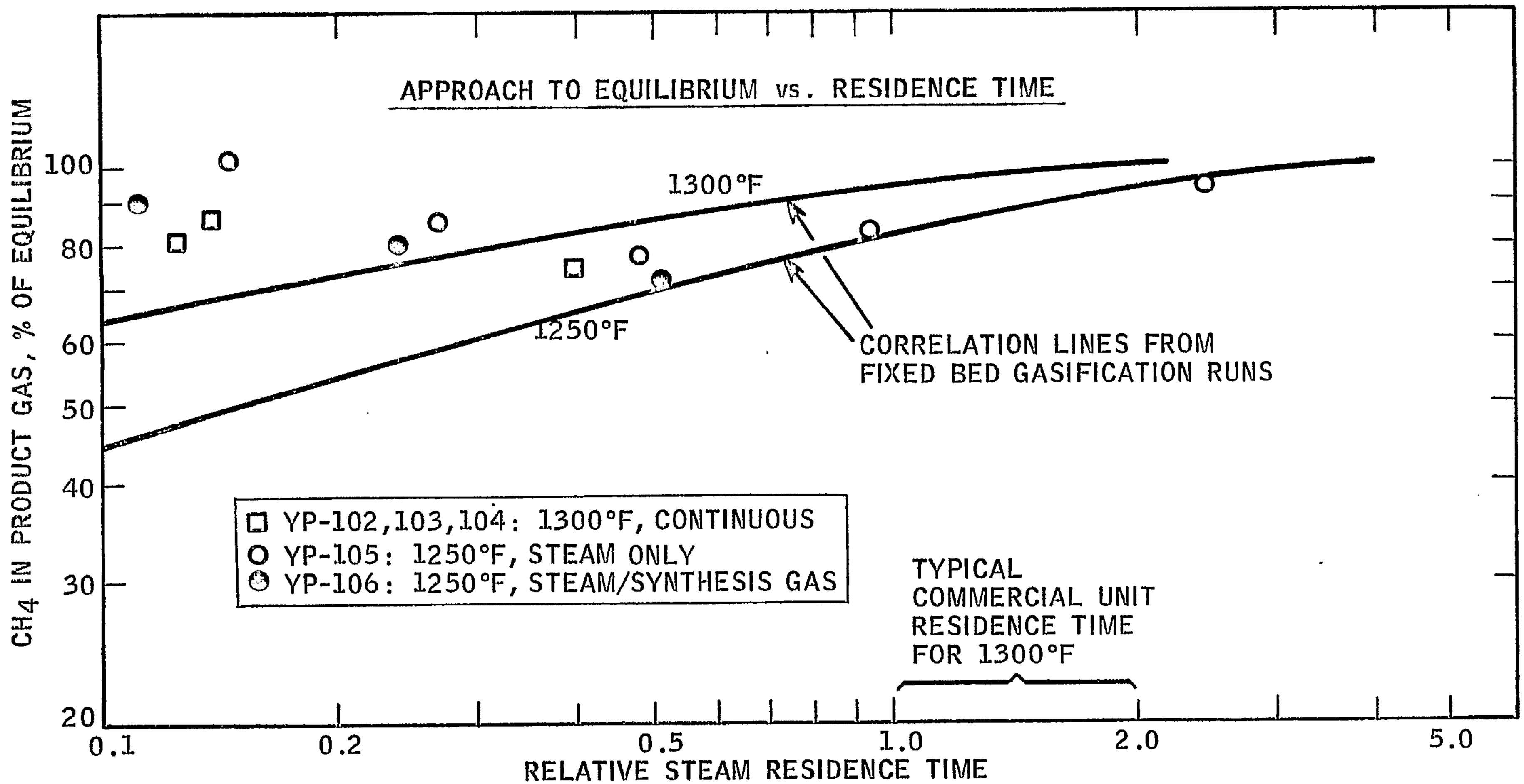
COMPARISON OF CGU AND PREVIOUS FIXED BED DATA



76B-12-4

FIGURE 8

COMPARISON OF CGU AND PREVIOUS FIXED BED DATA



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1200-1300°F and 100-500 psig with catalyzed devolatilized coal containing 20% K_2CO_3. The fixed-bed correlation lines are shown for 1250°F and 1300°F. The moles of carbon gasified per mole of steam fed is plotted on the ordinate. Since the moles of carbon gasified are related to the moles of steam consumed, the ordinate can also be thought of as the fraction of steam converted by reaction with carbon. When operating in synthesis gas balance, this quantity becomes identical to the overall steam conversion. On the abscissa, the relative steam residence time is plotted. At low residence times, the extent of gasification is a strong function of residence time. At higher residence times, there is a leveling out as carbon-steam equilibrium is reached.

In general the CGU data fall very close to the fixed-bed correlation lines indicating that contacting is excellent in the CGU. This is not surprising in view of the fact that the CGU is operating at very low superficial velocity. As might be expected because the continuous runs were not at steady state, they show considerably more scatter than the captive bed yield periods.

Also shown in Table I are the measured gas compositions for the continuous CGU yield periods and the gas compositions which would be obtained if the product gas were at gas phase methanation equilibrium. In Figure 8, the continuous and captive-bed data are compared with the correlation line for previous fixed-bed data on the approach to methane equilibrium. Methane in the product expressed as a percent of equilibrium is plotted against relative steam residence time. The data were obtained at 500 psig and 1200-1300°F. At the higher residence times, the CGU data are in fairly good agreement with the fixed-bed correlation line. The correlation line for 1300°F and relative residence times between 1 and 2, conditions typical of projected commercial unit operations, shows that gas phase methane equilibrium is very closely approached.

At low residence times, the methane production exceeds that observed in the fixed-bed runs. The reason for this is not clear. It is possible that a small amount of methanation is occurring downstream of the gasification bed in cooler zones, tending to increase methane yields. At the low residence times where the steam conversions are relatively low, the absolute level of methane produced even at equilibrium is low and thus the effect could be more pronounced. This hypothesis will be checked in future CGU operations by sampling the product gas directly from the outlet of the gasifier bed.

3. ENGINEERING RESEARCH AND DEVELOPMENT (Reporting Category 3)

No work on this task was scheduled in the period July-September, 1976.

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