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EXXON CATALYTIC COAL GASIFICATION PROCESS: PREDEVELOPMENT PROGRAM. ANNUAL REPORT, JULY 1976--JUNE 1977

EXXON RESEARCH AND ENGINEERING CO.
BAYTOWN, TX

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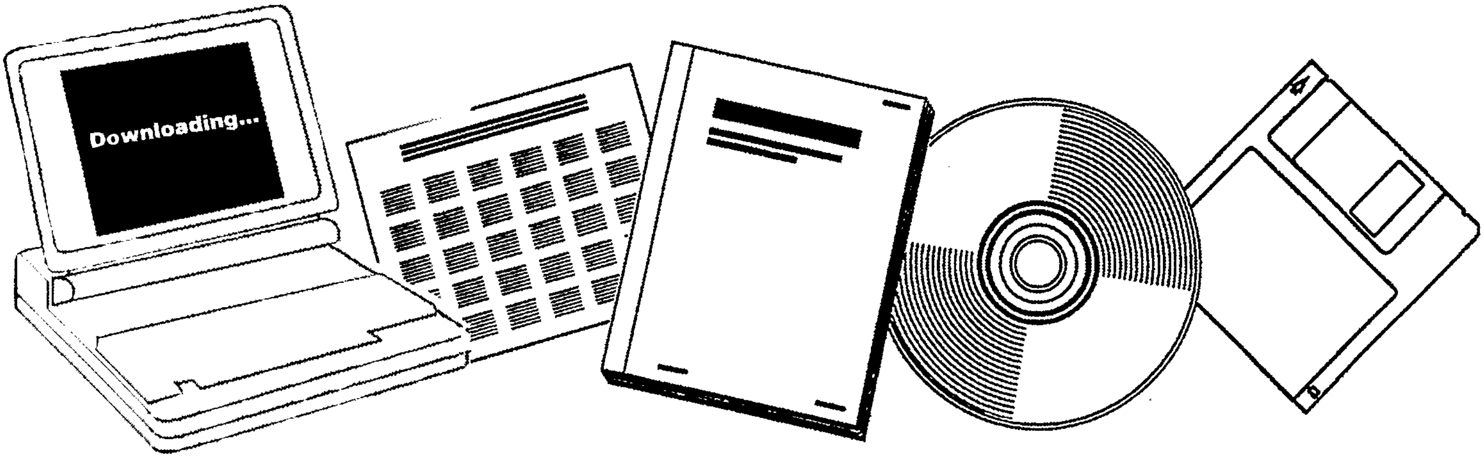

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EXXON CATALYTIC COAL GASIFICATION PROCESS - PREDEVELOPMENT PROGRAM

ANNUAL REPORT FOR THE PERIOD
July, 1976 - June, 1977

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EXXON RESEARCH AND ENGINEERING COMPANY
Baytown, Texas 77520

January 26, 1978

PREPARED FOR THE UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Contract No. E(49-18)-2369

ABSTRACT

This report covers the Predevelopment Program activities for the Exxon Catalytic Gasification Process during the period July, 1976 through June, 1977. 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 year summarized by reporting categories are as follows:

1. Fluid Bed Gasifier Studies

- The existing 20 lbs/hr Fluid Bed Gasifier (FBG) was recommissioned for operation in the Predevelopment Program. Modifications were made to the FBG data acquisition system including the on-line computer program for calculation of unit material balances from process variable data, and an off-line program for material balance data reduction.
- The FBG was started up and operated under baseline conditions. Material balance data obtained under these conditions showed steam conversions of about 40 percent and approaches to methane equilibrium of 15-35°F. These values are close to kinetic model predictions for the specified feed rate.
- A process variable study conducted with the FBG included runs with potassium carbonate and mixed potassium carbonate/sodium carbonate catalysts and covered a range of steam and coal flow rates, catalyst concentrations, and temperatures. Unit operations were excellent, and the longest continuous run lasted 336 hours.
- The Catalyst Recovery Unit (CRU) was recomissioned and started up, and catalyst recycle operations began. Recovery of water soluble catalyst was about 75 percent. FBG operations with recycle catalyst were excellent, with the longest continuous run lasting 587 hours and an overall unit service factor of 96%.

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 video 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 batch fluid-bed yield periods. Good agreement was obtained with previous fixed bed kinetic data.

- Carbon gasification rate data were obtained in fixed bed gasification units for sodium carbonate and mixed sodium carbonate/potassium carbonate catalysts. The activity for sodium carbonate was found to be significantly lower than that for potassium carbonate especially at high pressure. Also, analysis of the char streams from the mixed catalyst runs shows that potassium is selectively tied up by the coal minerals, reducing the incentive for using mixed catalysts. As a result of these findings, the FBG catalyst recovery and recycle operations were conducted with potassium carbonate.

- It was found that the levels of potassium sulfate and potassium thiosulfate are very low on fresh ash/char residue withdrawn from the FBG in a completely blanketed atmosphere and leached without exposure to air, and most of the sulfur in solution is in the form of potassium sulfide. As much as 15-20 percent of the catalyst can be in the form of potassium sulfide with the remainder being potassium carbonate, the original catalyst form, and potassium hydroxide. CO_2 stripping will convert essentially all the potassium sulfide in solution to potassium carbonate. Thus, if desired it will be relatively simple to minimize the level of potassium sulfide in recycle solutions.

- Work was initiated on the recovery of catalyst tied up in the ash/char gasification residue as water-insoluble catalytically inactive $KAlSiO_4$. The potassium from this compound can be recovered by aqueous digestion of the gasification residue with calcium hydroxide. Potassium recoveries in the range of 80-90 percent were achieved. Additionally, recoveries of insoluble potassium can be increased by the use of unwashed gasifier residue, due to the higher pH produced by water soluble compounds present on the char.

- Bench scale studies of catalyst recovery via water washing were initiated in order to investigate lower-than-expected recoveries of water soluble catalyst obtained in the CRU. The data suggest that the precautions previously taken to prevent exposure of the gasifier ash/char residue to air were inadequate, and that inadvertent exposure of the residue played a significant part in the difficulty experienced in recovering water soluble catalyst in the CRU.

3. Engineering Research and Development

- Work has been completed on engineering scoping studies to define and compare the cash flows for alternative processes for potassium catalyst manufacture. Based on current market proces, KOH solution produced by electrolysis of KCl would be the preferred form of makeup catalyst for catalytic gasification. Among the presently noncommercial manufacturing alternatives studied, the Engel-Precht process feeding KCl appears to be most attractive. A more definitive screening evaluation of this process is under way.

- Similar scoping studies to estimate cash flows for the processes to recover water-insoluble catalyst from spent gasifier solids have also been completed. Results show that catalyst recovery via hydrothermal treatment with $Ca(OH)_2$ offers the potential for substantial savings relative to purchased KOH. A screening study is in progress to firm up the economics for this catalyst recovery process based on current laboratory data.

- A screening study was completed which indicated that there is only a small economic incentive for adding a secondary gasification step to Catalytic Coal Gasification to raise carbon conversion over the base case level of 90 percent. However, this conclusion could change if it were not practical to obtain 90% carbon conversion in a single reaction step or if coal or catalyst costs increase significantly.

- Additional screening studies to evaluate the commercial impacts of alternative catalytic gasifier operating conditions have been completed. Compared with a base catalyst loading of 15 wt.% K_2CO_3 and with a base temperature of 1300°F, reducing the catalyst loading to 10 percent saved about 0.5 percent in gas cost, and decreasing the temperature to 1200°F saved about 2 percent in gas cost. It is too early to draw firm conclusions regarding preferred gasifier operating conditions from these screening studies because the bases do not necessarily reflect the extensive data currently being obtained in bench and FBG runs. However, these studies indicate that the potential exists for cost savings and, thus, after the laboratory data have been analyzed, the studies will be closely reviewed to see if change in the base conditions is warranted.

- Work began on the development of the process basis for a new Catalytic Coal Gasification Study Design. The Study Design will reflect the current conception of a commercial catalytic gasification plant producing approximately 250 MSCF/SD of SNG from Illinois coal. Estimates will be made of both investment and operating costs. Preparation of this Study Design will involve the major share of the engineering effort on the predevelopment program during the second half of 1977.

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INTRODUCTION

This report covers the Predevelopment Program activities for the Exxon Catalytic Gasification Process during the one-year period, July, 1976 through June, 1977. 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 catalyst with a novel processing sequence which maximizes the benefits which can be derived from use of the catalyst. The principal reasons for using alkali metal gasification catalysts are that they increase the rate of steam gasification, prevent agglomeration of 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 in Figure 0.1-1. Crushed 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 steam mixed with recycled synthesis gas, and the major gasifier effluents are CH_4, CO_2, recycled CO and H_2, and unconverted steam. No significant 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, preheated to approximately 150°F above the gasification temperature and recycled to the gasifier. Although there is no 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 step in which a large fraction of the catalyst is recovered from the residue using a calcium hydroxide digestion followed by countercurrent

Figure 0.1-1

EXXON CATALYTIC GASIFICATION PROCESS

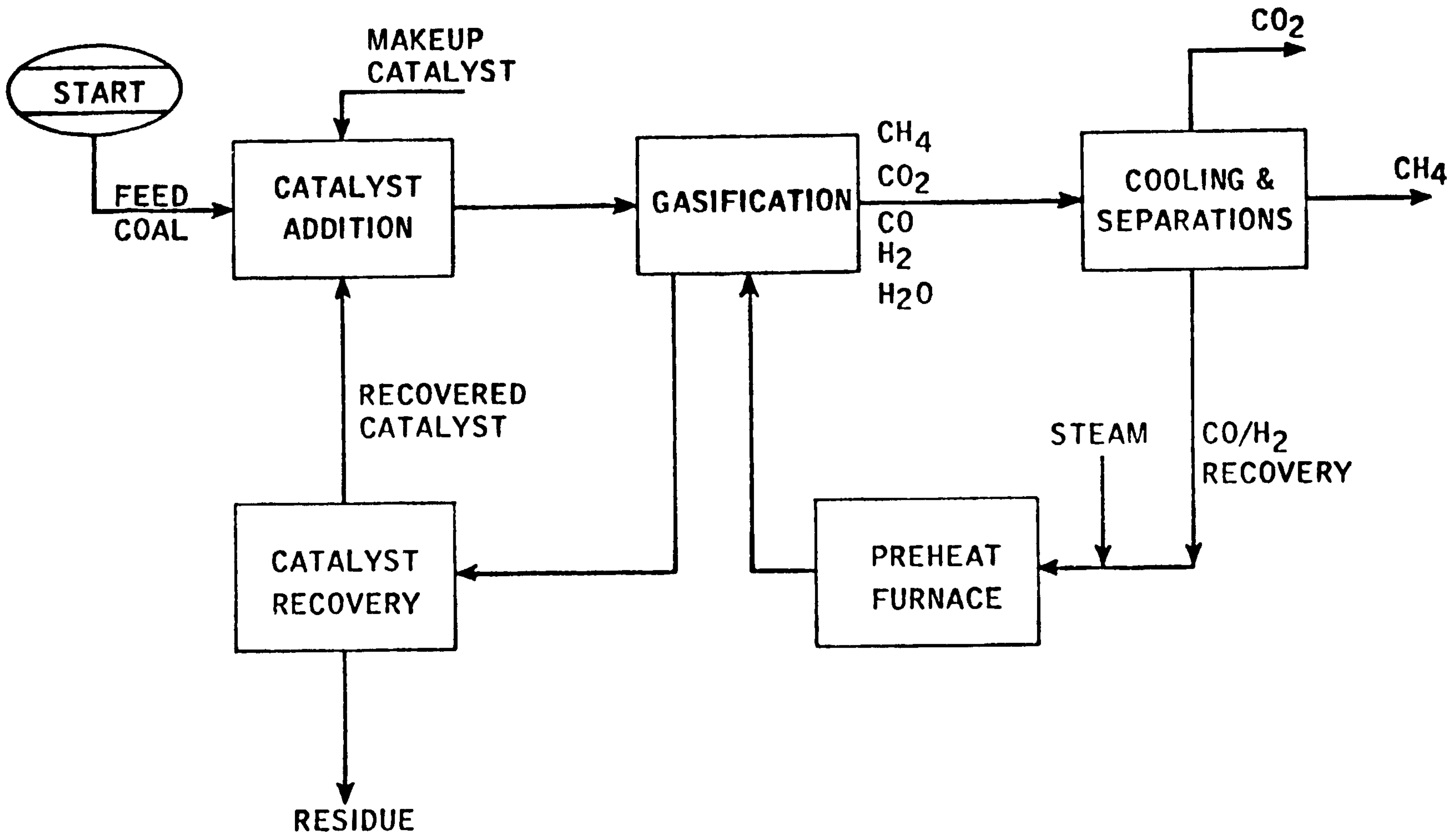
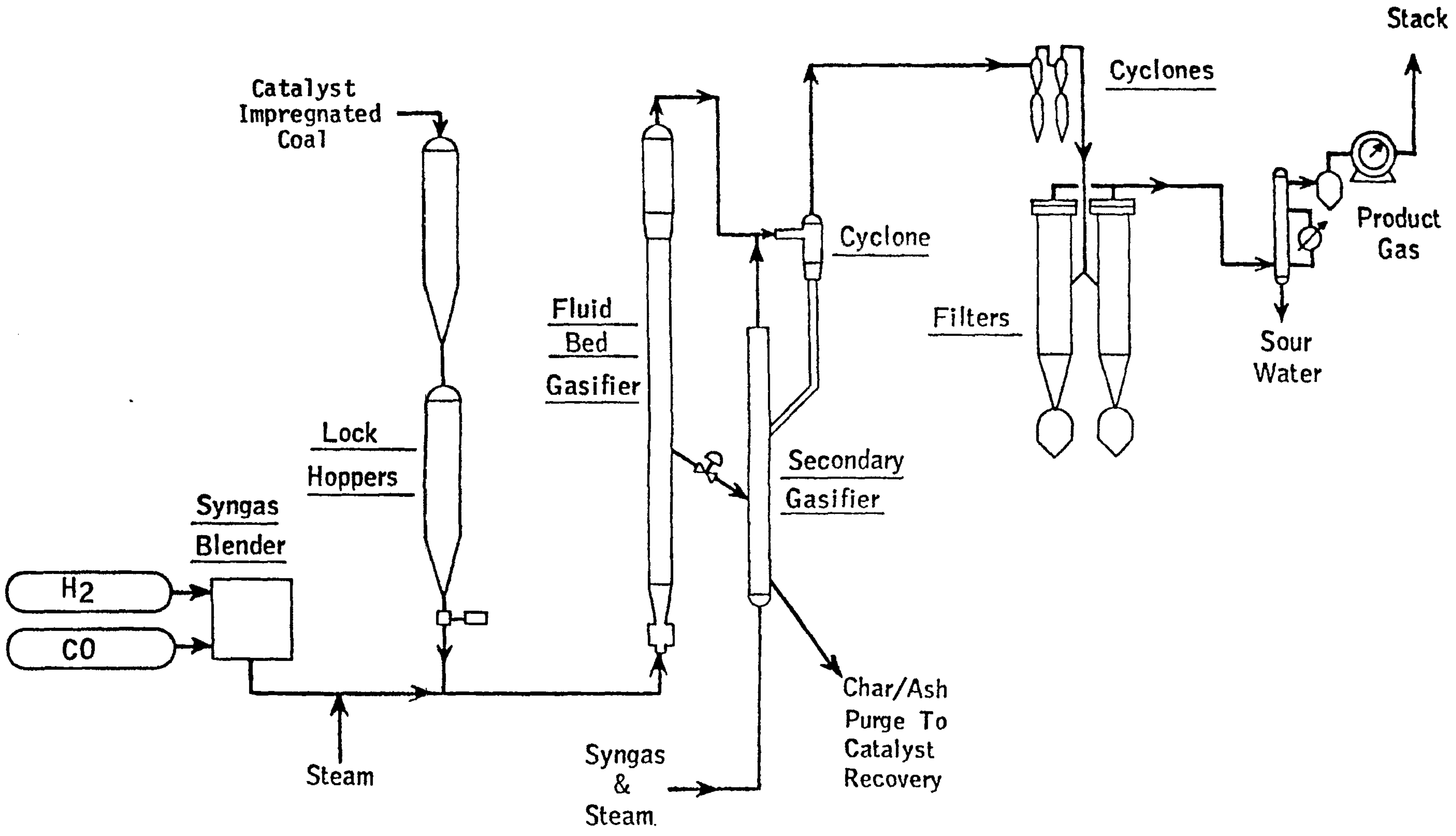


Figure 1.1-1

ORIGINAL FLUID BED GASIFIER (FBG) FLOW PLAN



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 1.1-1. 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 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 1.1-2. Additional changes made to improve data quality included: (1) instrumentation

Task III - Engineering Research and Development

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

water washing. The recovered catalyst, along with some makeup catalyst, is added to fresh 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 FBG was originally built for thermal gasification work. During 1975, the FBG 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 catalytic gasifier model.

In the area of catalyst recovery, the effectiveness of water wash for recovering about two-thirds 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 below.

Task I - FBG Operations with Illinois Coal

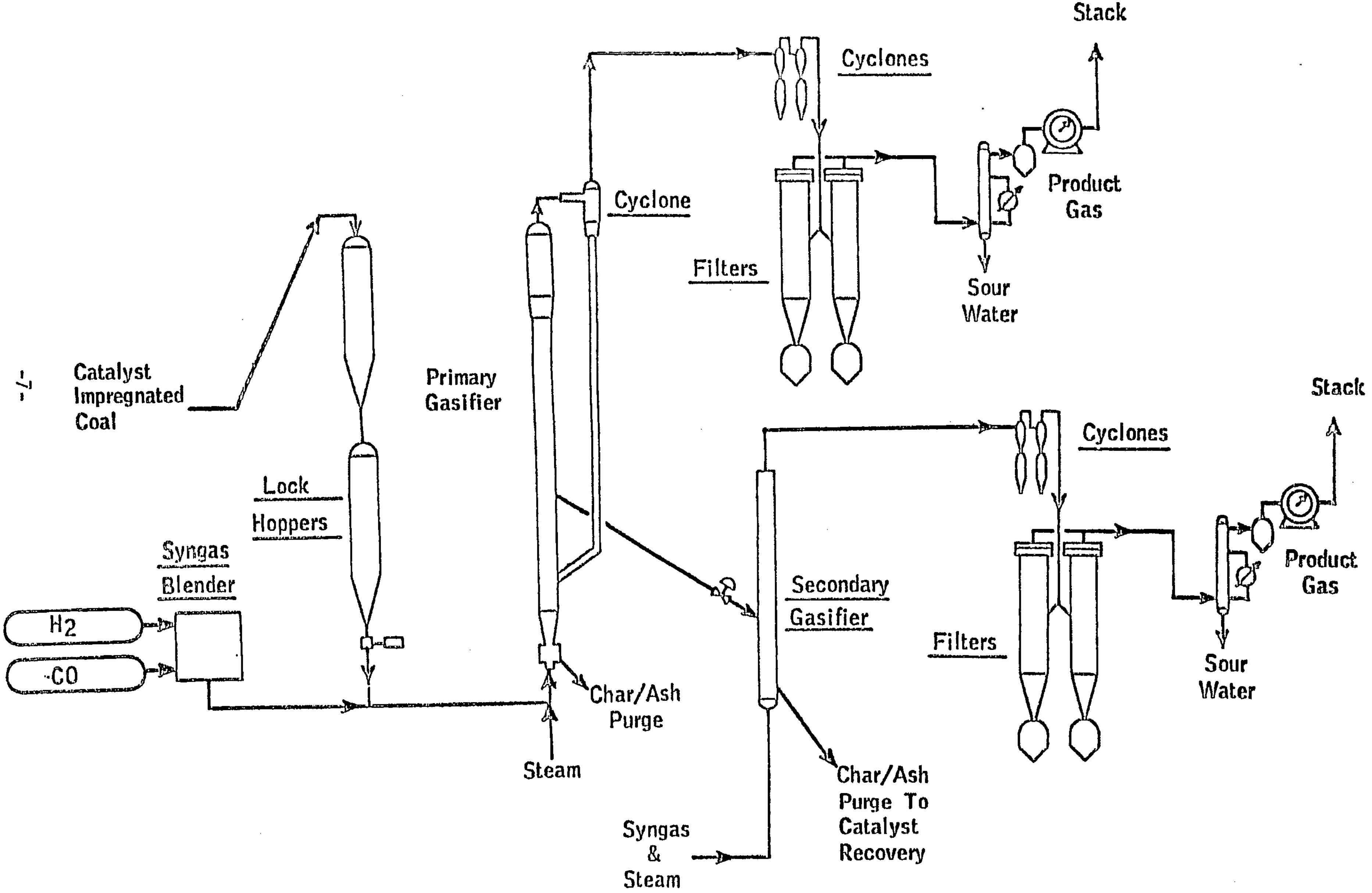
- Operate with mixed K_2CO_3/Na_2CO_3 catalyst
- Operate with recycled catalyst

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

Figure 1.1-2

REVISED FLUID BED GASIFIER (FBG) FLOW PLAN



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 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.

Unit construction was completed early in the month of October, and the effort thereafter was 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, operations of the coal impregnation system began, and a substantial inventory of catalyzed coal was produced.

In late November, 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.

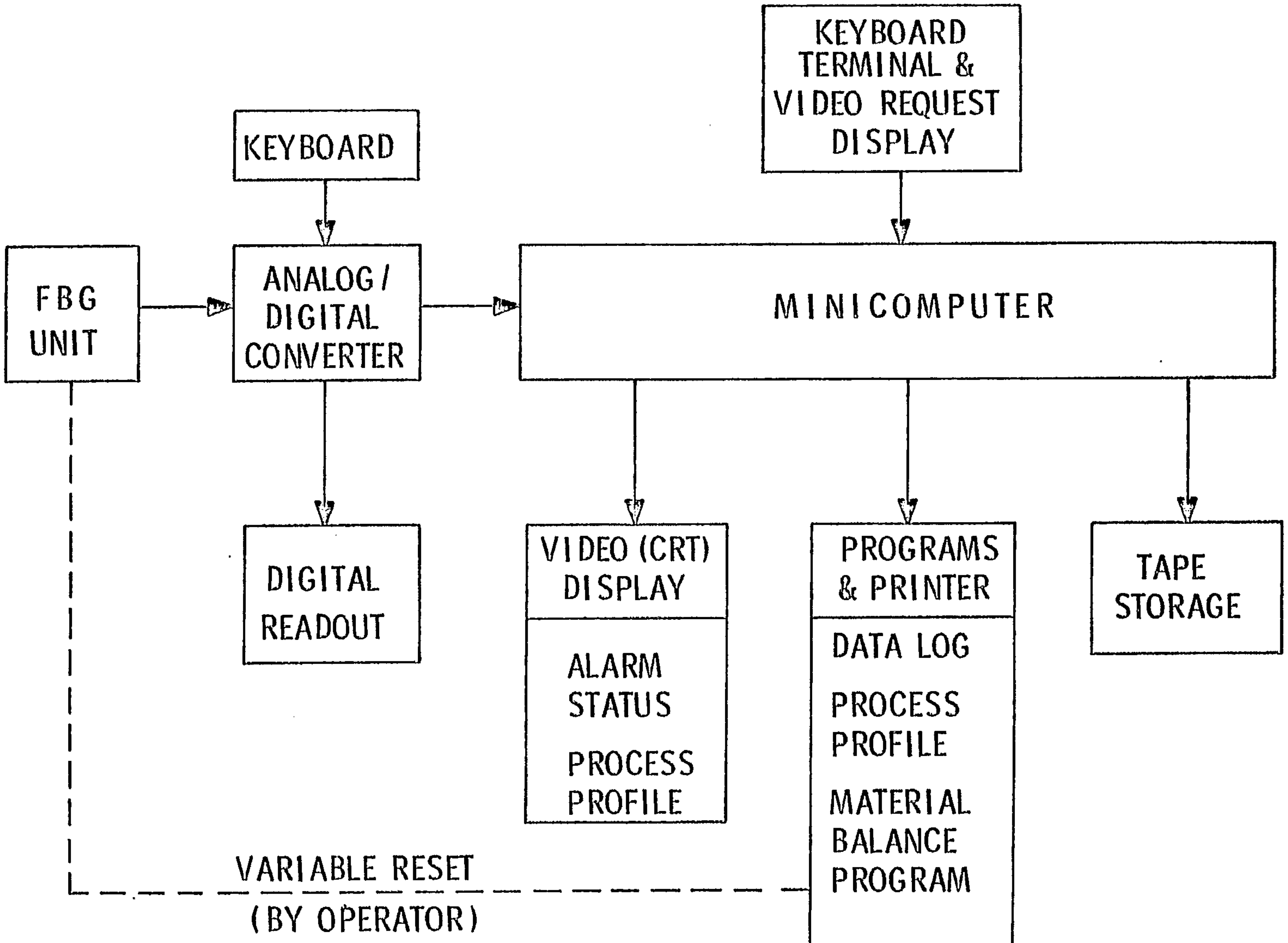
The damaged vessels were replaced with 304 SS Filter vessels from the secondary gas handling system which was not scheduled to be operated during the initial period. New vessels made of carbon steel, which is not subject to chloride stress cracking, were subsequently constructed for the secondary system.

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 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 more than 300. Installation of the process

Figure 1.1-3

FBG ON-LINE DATA ACQUISITION SYSTEM



instrumentation hardware that measures 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 was 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 informed of the 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 were written, tested and implemented as part of the system.

The computer was 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 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 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 baseline operations discussed below.

1.2 FBG OPERATIONS

The operations were divided into three general periods:

- Startup and Baseline Operations: December and January 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 to investigate the effects of operating variables such as coal, steam and synthesis gas feed rates; temperature; K_2CO_3 catalyst loading; and mixed K_2CO_3/Na_2CO_3 catalyst.
- Catalyst Recycle Operations: During May and June 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 build-up of foreign material occurred in the recovered catalyst and to demonstrate continued high activity of the recovered catalyst in the FBG.

A month-by-month summary of the operations and comments is shown in Table 1.2-I.

1.2.1 Startup and Baseline Operations

During December, FBG operations were begun under baseline conditions. Initial operations were exceptionally smooth, even though major modifications were 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 loosley to the wall near the bottom.

In subsequent runs, it was determined that the 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 drawoff from the bottom of the gasifier.

During December 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 Boudard 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 Boudard reaction. The preheater temperature has since been operated continuously at 1000°F with no further plugging.

TABLE 1.2-I

FBG OPERATING SUMMARY

Month	% of Time Onstream*	Longest Continuous Run--Hours	Material Balances, %	COMMENTS
December	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: $2\ CO \rightarrow C + CO_2$ - Now operate up to 1000°F
January	31	184	90	• Improved operations • Product gas line burned out - Ground fault interrupts (GFI's) installed on all heater circuits - Flammable gas detection system installed • High char carry-over rate at times due to feeder blowby - Reduced carbon conversions to 56 to 86%

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

TABLE 1.2-I

FBG OPERATING SUMMARY (Cont'd.)

Month	% of Time Onstream*	Longest Continuous Run--Hours	Material Balances, %	COMMENTS
February	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 ∿ 95%
March	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	70	336	98-101	• Catalyst Recovery Unit (CRU) operations started • 20% K_2CO_3 catalyst loading with varying coal and steam feed rates

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

TABLE 1.2-I

FBG OPERATING SUMMARY (Cont'd.)

Month	% of Time Onstream	Longest Continuous Run--Hours	Material Balances, %	COMMENTS
May	64	407	97-102	• Catalyst recycle operations started • 75% water-soluble catalyst recovery on CRU
June	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

Three material balance periods were obtained with overall material balance closures in the range of 90%. The base line 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 catalyst loading of 10 wt.% potassium carbonate. Steam conversions calculated by oxygen balance varied between 38 and 41 percent.

During January, FBG operations continued under baseline conditions. Data were obtained for four material balance periods. Overall material balance and the oxygen balance closures were generally around 90 percent, while the hydrogen elemental balance was in the range of 90 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 product gas line overhead from the reactor. The heater wire failed and shorted to the pipe in several places burning small holes in the pipe at which time the reactor contents were depressured through the overhead line. The failure occurred so quickly that the circuit breakers did not shut off the power. To prevent a recurrance 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 Variables Study

During February the process variables study was initiated. 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 lock hopper 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 runs were made.

Unit carbon conversions expressed as the percent of feed carbon gasified varied from about thirty to fifty 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 including 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.

During March the FBG was operated with both K_2CO_3 and mixed Na_2CO_3/K_2CO_3 catalysts. Unit 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 the emergency depressuring of the unit, resulting 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 the month of April, 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 to 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%. 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

During May, the catalyst recycle operations were initiated. The objective of this phase of work, involving 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 hydroclones for liquid-solids separation, handled the char withdrawn from the FBG during the previous day. The resulting catalyst solution was collected and analyzed for potassium. Sufficient makeup catalyst was added to the CAU to produce an amount of coal equivalent to one day of feed for the FBG.

CRU 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 initial mechanical problems, recycle of catalyst to the CAU began. However initial catalyst balances around the CRU indicated that the recovered catalyst was only in the range of 75% of the water soluble catalyst on the feed char. This was below the recovery of 90% that should be obtained in the CRU, with no rate or equilibrium limitations to catalyst recovery other than physical holdup of the catalyst solution by the char. Since such limitations were not observed in CRU operations prior to the start of the current program, additional study of catalyst recovery was planned in the CRU and in a bench scale program scheduled to begin in June.

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% and a long continuous run of 407 hours. The slight reduction in service factor compared with April was caused by mechanical problems with the lockhopper agitator and the rotary feeder. These were probably related to a batch of feed coal containing a high moisture level. 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.

During June, FBG operations continued utilizing coal feed impregnated with recycled catalyst solution. The unit service factor was 96%. 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 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. percent. Material balance closures were usually between 99 and 101 percent.

The carbon and steam conversions remained high during June operations utilizing 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 which was not as close as in prior non-catalyst recycle operations. 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. Preliminary indications were that recycled catalyst has the same activity as fresh catalyst.

1.3 RESULTS OF MIXED CATALYST OPERATIONS

Two essentially duplicate runs were made with a nominal mixed catalyst loading of 7.5 wt.% K_2CO_3/7.5 wt.% Na_2CO_3. These data showed substantially lower carbon and steam conversions and a greater departure from methanation equilibrium than K_2CO_3 runs 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.

Analyses of the char streams from the mixed catalyst runs confirmed the previous bench results that 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 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 and while 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.

	Water Insoluble K, % of Total K		Water Insoluble Na, % of Total Na	
Day	Bed Char	Bottom Withdrawal	Bed Char	Bottom Withdrawal
1	37	47	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

Based on the results from fixed-bed studies 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.

1.4 FLUID BED GASIFIER DATA

A total of 40 material balance periods were 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 1.4-I 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 real time data acquisition system.

Fifteen of these material balance periods which are of the greatest interest have been selected as yield periods. For these, a full spectrum of analyses are being performed on representative samples of feed coal, bottom char, and cyclone and filter fines collected during the period. Six of these off-line data workups have been completed and selected data from these are presented in Appendix A. An example of a complete data workup for one yield period is presented in Appendix B. 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. When solids analyses are complete these data will be combined with the previously collected on-line gas flow rate and composition data in the off-line material balance computer program. This program uses statistical methods to close all material balances while minimizing the total variance from measured values. The results from these yield periods will then be available for kinetic model development.

1.4.1 Initial Operations

Material balance periods 1-3 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 closed within ± 5 percent, but the oxygen and hydrogen elemental balances did 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 were marked by a steady

Table 1.4-I

SUMMARY OF FBG MATERIAL BALANCE DATA FOR DECEMBER 1976 THROUGH JUNE 1977

Material Balance Period (Duration, Hours)	1 14	2 17	3 4	4 11	5 8	6 18	7 13	8 4	9 14	10 7	11[1] 24	12[1] 19	13[1] 16	14[1] 16
Reaction Conditions														
Temperature, °F	1330	1330	1330	1285	1295	1300	1310	1300	1305	1305	1295	1292	1311	1315
Pressure, psi	100	99	100	97	97	99	99	99	98	98	98	99	99	98
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
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
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
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
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
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
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
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
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
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)
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
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
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
Syngas, SCFH														
$CO + H_2$ in Unit	698	737	466	525	395	430	490	612	609	622	524	458	483	493
$CO + H_2$ in Product Gas	502	556	438	400	350	310	360	497	512	520	471	409	509	643
Syngas Balance, %	72	76	94	76	88	71	73	81	84	84	90	89	105	130
Steam conversion, %														
By Water Balance	52	57	47	47	61	40	51	32	38	38	37	37	59	54
By Oxygen Balance	40	38	41	36	45	28	26	21	26	25	24	29	55	51
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
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
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
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
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
Approach to Methanation Equilibrium, °F	30	35	15	29	30	5	40	40	15	25	27	21	68	25
Carbon Conversion % (by Solids Analysis)	73	85	80[2]	73[2]	86	74	57	55	52	39	43	51	92	82

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1. Yield Periods
2. Carbon conversions by Product Gas Analysis

Table 1.4-I (continued)

SUMMARY OF FBG MATERIAL BALANCE DATA FOR DECEMBER 1976 THROUGH JUNE 1977

Material Balance Period	15[1]	16[1]	17[1]	18[1]	19[1]	20	21	22[1]	23[1]	24	25	26	27
(Duration, Hours)	16	24	16	24	24	24	24	24	24	24	24	24	24
Reaction Conditions													
Temperature, °F	1315	1305	1223	1311	1309	1307	1309	1313	1297	1298	1301	1297	1306
Pressure, psi	98	99	98	98	99	98	99	99	99	99	99	99	98
Input, lbs/hr (ExN_2)													
Coal + Catalyst	15.7	16.3	8.8	9.5	9.7	7.8	10.3	11.1	17.3	17.9	16.7	17.6	10.0
Steam	23.8	22.9	13.0	14.8	15.2	14.5	15.0	15.1	22.8	22.6	22.4	22.2	15.0
Syngas	16.6	15.9	9.6	11.5	11.7	11.8	12.9	13.2	14.5	15.0	13.8	14.6	11.3
Total	56.1	55.1	31.4	35.8	36.6	34.1	38.2	39.4	54.6	55.5	52.9	54.4	36.3
Output, lbs/hr (ExN_2)													
Product gas	35.0	33.6	16.2	22.0	22.3	23.9	26.7	33.9	34.0	34.0	33.7	33.4	26.0
Water	12.7	12.9	9.4	8.8	9.3	7.7	8.1	8.0	12.7	13.4	12.8	13.2	7.2
Carryover	3.0	2.8	1.0	0.8	0.9	1.2	1.9	1.7	3.6	2.5	1.9	2.2	1.2
Withdrawn	2.1	2.1	3.5	3.2	2.1	2.1	1.3	1.8	3.3	5.4	3.8	5.4	2.6
Total	52.8	51.4	30.1	34.8	34.6	34.9	38.0	38.6	53.5	55.8	52.2	54.2	37.0
Accumulation, lbs/hr.	0.0	0.1	(0.6)	(0.1)	0.9	(0.4)	0.5	0.4	(0.2)	(1.2)	0.4	(0.2)	(0.1)
Material Balance, %													
Overall	94.1	93.5	93.9	96.6	97.0	101.2	100.8	99.0	97.6	98.4	99.4	99.3	100.6
Oxygen	95.2	95.5	95.9	97.2	98.8	97.2	100.2	98.2	97.4	99.2	100.6	100.6	98.2
Hydrogen	15.5	90.8	93.6	96.2	95.5	99.2	100.7	98.4	96.7	99.8	101.4	99.6	98.8
Syngas, SCFH													
CO + H_2 in Unit	666	741	464	512	521	511	552	569	619	632	592	602	485
CO + H_2 in Product Gas	727	778	392	538	546	532	578	567	666	699	705	681	496
Syngas Balance, %	109	105	84	105	105	104	105	100	108	111	119	113	102
Steam Conversion, %													
By Water Balance	48	45	29	42	40	48	47	48	46	42	44	42	53
By Oxygen Balance	41	39	24	38	38	44	47	46	42	41	45	43	50
Product Gas, Mol % (dry, ExN_2)													
H_2	59.0	62.4	65.1	65.7	65.6	60.8	59.9	58.6	57.4	58.7	59.8	58.8	56.1
CO	15.9	13.7	10.2	13.0	13.6	15.4	15.3	15.4	14.9	15.1	14.4	14.9	14.9
CO_2	14.1	12.6	12.9	13.1	13.1	12.7	13.0	13.1	14.5	13.8	14.2	14.5	14.6
CH_4	10.0	11.3	11.4	7.6	7.2	10.7	11.4	12.5	12.7	11.9	11.2	11.3	13.9
H_2S	0.0	0.0	0.3	0.6	0.5	0.3	0.3	0.4	0.5	0.4	0.4	0.4	0.4
Approach to Methanation Equilibrium, °F	30	46	79	85	92	68	64	53	34	42	48	44	20
Carbon Conversion % (by Solids Analysis)	81	81	62	58	64	82	77	77	76	73	75	74	80

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1. Yield Periods
2. Carbon conversions by Product Gas Analysis

Table 1.4-1 (continued)

SUMMARY OF FBG MATERIAL BALANCE DATA FOR DECEMBER 1976 THROUGH JUNE 1977

Material Balance Period (Duration, Hours)	28 24	29 24	30 24	31 24	32 24	33 24	34[1] 24	35 24	36[1] 24	37 24	38[1] 24	39 24	40[1] 24
Reaction Conditions													
Temperature, °F	1297	1298	1302	1308	1312	1312	1324	1318	1317	1315	1318	1311	1313
Pressure, psi	100	99	99	99	99	99	99	99	99	99	99	99	99
Input, lbs/hr (ExN_2)													
Coal + Catalyst	10.9	11.1	10.5	10.0	11.5	12.0	11.1	11.5	10.7	11.1	10.6	9.3	9.1
Steam	16.1	16.0	15.7	16.1	15.6	15.6	15.3	16.2	16.2	16.7	16.4	16.5	15.8
Syngas	13.5	14.4	13.7	12.1	16.2	15.1	15.5	13.3	14.0	13.7	13.3	11.8	12.5
Total	40.5	41.5	40.1	38.2	43.3	42.7	41.9	41.0	40.9	41.5	40.3	37.6	37.4
Output, lbs/hr (ExN_2)													
Product gas	28.3	28.7	29.3	26.8	31.4	31.7	31.6	30.1	30.5	29.3	29.7	25.7	26.0
Water	8.7	7.9	7.6	8.4	8.2	8.4	7.3	7.3	7.4	8.0	7.5	8.3	8.4
Carryover	1.1	1.2	0.9	1.1	1.5	1.1	1.2	1.0	1.1	0.9	0.9	1.1	1.0
Withdrawn	2.5	2.5	0.8	3.0	2.5	1.7	2.6	2.1	2.2	2.8	2.5	2.2	2.3
Total	40.6	40.3	38.6	39.3	43.6	42.9	42.7	40.5	41.2	41.0	40.6	37.3	37.7
Accumulation, lbs/hr.	0.3	(0.4)	0.6	(0.3)	(0.3)	0.2	(0.1)	0.0	(0.3)	0.1	0.1	0.0	(0.1)
Material Balance, %													
Overall	101.0	96.1	97.8	102.1	100.0	100.9	101.6	98.9	100.0	99.0	100.6	99.2	100.5
Oxygen	100.7	97.2	99.3	100.4	100.6	106.0	99.6	99.5	99.4	98.1	99.6	98.1	100.1
Hydrogen	97.2	95.0	96.4	89.8	99.1	95.6	99.9	98.2	99.6	98.1	97.7	96.1	95.4
Syngas, SCFH													
CO + H_2 in Unit	501	542	545	594	639	649	644	512	545	552	554	507	527
CO + H_2 in Product Gas	488	552	573	564	626	639	654	587	620	625	634	585	573
Syngas Balance, %	97	102	105	95	98	98	102	115	114	113	115	116	109
Steam conversion, %													
By Water Balance	47	52	53	49	48	48	54	56	56	53	55	50	48
By Oxygen Balance	48	48	52	49	47	57	53	55	55	50	55	48	48
Product Gas, Mol % (dry, ExN_2)													
H_2	54.3	57.1	53.4	59.9	57.6	58.1	58.6	57.3	58.7	60.8	60.3	63.2	61.9
CO	14.7	16.0	16.1	15.0	15.9	16.1	15.8	16.5	16.2	15.2	15.9	14.3	15.4
CO_2	17.3	15.5	14.9	13.8	14.2	14.3	13.4	15.0	14.5	14.3	14.0	13.9	14.1
CH_4	12.7	10.6	10.8	10.5	11.5	10.8	11.5	10.1	9.8	8.8	9.0	7.3	7.8
H_2S	0.9	0.8	0.8	0.8	0.8	0.7	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Approach to Methanation Equilibrium, °F	35	72	75	62	61	76	73	70	82	35	88	88	79
Carbon Conversion % (by Solids Analysis)	78	81	89	79	81	86	83	85	86	82	87	80	80

1. Yield Periods
2. Carbon conversions by Product Gas Analysis

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 $K = (P_{H_2O})(P_{CH_4})/(P_{CO})(P_{H_2})^3$. Published data for the equilibrium constant of the methanation reaction as a function of temperature were 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% closure for material balance periods 11 and 12 however, and these two have been designated as yield periods. Off-line solids analysis data for periods 11 and 12 appear in Appendix A.

Carbon conversions for the first 12 material balance periods varied widely from a low of 40% to a high of about 85%. 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 agreed quite well. For most of the low conversion runs the major factor contributing to the observed conversion was the high char carryover rate. The entrainment of carbon from the unit directly reduces the carbon conversion. The high entrainment appeared to result from the quantity of fines in the feed coal, lockhopper feeding problems, and nitrogen blowby across the feeder due to excessive pressure differential across the feeder. These problems were minimized for the latter material balance periods. Also during subsequent periods leaks in flow lines and the scrubber water system were corrected as evidenced by excellent material balance closures and close agreement of steam conversion calculated by both oxygen and condensate water balance.

1.4.2 Process Variable Study with K_2CO_3 Catalyst

Process variables that have been studied include level and type of catalyst, 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 was in the range of 105-130 percent. For material balance period 13 the steam conversion was about 55 percent. The char carryover during balance period 13 was only 1 to 2 percent of the feed. A very low level (0.4 weight percent) 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 coal feed also contributed to the increase. The observed increase in entrainment indicated that the FBG cyclone dipleg may not have been operating properly possibly because sufficient height is not available to pressure balance the gasifier. The higher feed rates and carbon carryover in balance periods 14-16 reduced the steam conversion to about 45% and the carbon conversion to about 80%. A slightly further deviation from methanation equilibrium was also noted for these high conversion balance periods Material balance periods 13-16 were all designated as yield periods. Solids data for periods 13 and 16 appear in Appendix A. In addition a complete data workup for period 13 in the form of output from the off-line material balance computer program is presented in Appendix B.

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 also carbon conversion, it was necessary to substantially increase char withdrawal rate to maintain a steady-state bed height in the gasifier. Operating at 1225°F also reduced the rate of methane formation evidenced by the 90°F approach to methanation equilibrium. At 1300°F the approach to equilibrium averaged 35°F.

1.4.3 Process Variable Study with Mixed Na_2CO_3/K_2CO_3 Catalyst

Material balance periods 18 and 19 are essentially duplicate runs with a nominal mixed catalyst loading of 7.5 wt.% K_2CO_3/7.5 wt.% Na_2CO_3. These data also 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 are essentially the same. This confirms the low reactivity for Na_2CO_3 and mixed Na_2CO_3/K_2CO_3 catalysts observed in the fixed bed unit gasification tests.

Analyses of the char streams from the mixed catalyst runs have corroborated bench results showing that potassium is selectively tied up by the coal minerals. Data were obtained by analyzing for water soluble and total (acid soluble) potassium and sodium on the char. The difference represents the water insoluble fraction which previously has been shown to be comprised primarily of inactive alkali metal aluminosilicates. Item 2 in Appendix A for periods 18 and 19 shows that water-to-acid soluble ratios for gasifier bed char correspond to about 50 percent tieup of potassium with coal mineral matter while this value is only 10 percent for sodium.

1.4.4 Catalyst Recycle - FBG Data

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.

The remainder of the material balance periods (27-40) represent continuing 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.%. During these recycle operations, gasifier operating conditions were held to within narrow limits of the target conditions of 1300°F and 100 psia. 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 which is not as close as 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 in 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.

1.5 SCRUBBER-WATER ANALYSIS

The Fluid Bed Gasifier (FBG) product gas which is 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 Fluid Bed Gasifier (FBG) sour water from the product gas scrubber was intermittently 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 1.5-I.

Though the FBG was operating well, one problem did develop for a short period with the wet gas scrubber. Early in June, the wrappings on the bag filters were changed, and it was subsequently learned that spaces in the wrappings had 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 recycled catalyst phase for the FBG also started in June, it would be 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.

Carbon 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 seem to comprise the majority of the organic compounds present in the scrubber water, are more easily adsorbed than straight chain compounds. The

Table 1.5-I

FLUID BED GASIFIER SCRUBBER WATER ANALYSES

		Concentration (ppm)*										
Material Balance Period	pH	Ammonia	Alkalinity as Na_2CO_3	Carbon Dioxide	Chlorides	Free Cyanide	Thio-cyanate	Phenols	Sulfides	Thio-sulfate	Total Organic Carbon	Chemical Oxygen Demand
13	8.2	13,200	N.A.	39,500	240	2	4	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.

phenol levels were very low during June (material balance periods 33, 35, 37), and the total organic carbon levels apparently decreased. The chemical oxygen demand levels did not decrease, however. This result is consistent 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 the result of a slow buildup over the period of 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 under the operating conditions in effect at the times the samples were collected. Numerous factors, such as temperature, pressure, bed height, and product gas residence time, can affect the quantities of sour water contaiminants produced by a particular coal. Further analyses of sour water from gasifier operations under different process conditions will be needed to provide a more complete data base for the catalytic gasification process.

2. BENCH-SCALE STUDIES (REPORTING CATEGORY 2)

2.1 CONTINUOUS GASIFICATION UNIT (CGU) OPERATIONS

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 expanded 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 2.1-1. The solid 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 superficial velocity in the gasifier is near minimum fluidization. The overhead gas is filtered for solids removal, water scrubbed to condense unreacted steam, and its flow 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.

2.1.1 CGU Operating Experience

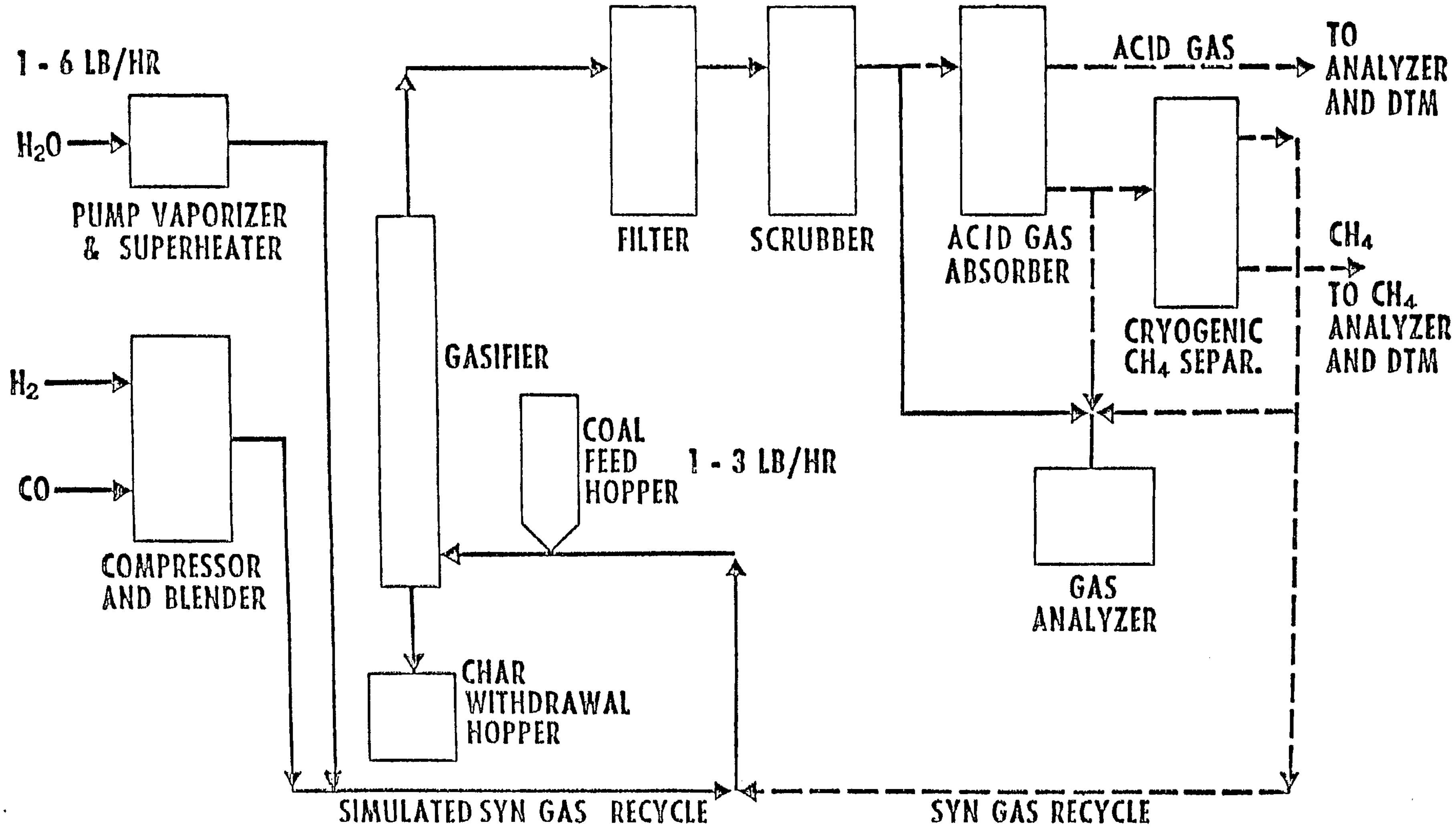
Start-up and initial operations of the CGU were completed during the third quarter of 1976. Because of operating difficulties, the periods of continuous unit operation were limited to a maximum of 26 hours. As a result, true steady-state conditions were not reached. Data were obtained for four continuous 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. Operating difficulties which were experienced during the start-up phase are discussed below. An analysis of the data obtained is presented in Section 2.1.2.

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

Figure 2.1-1

CONTINUOUS GASIFICATION UNIT (CGU)
FLOW PLAN



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 will be increased to give a 1.8 fold increase in gasifier volume and a corresponding increase in gas residence time. This is within the capability of the present heater system.

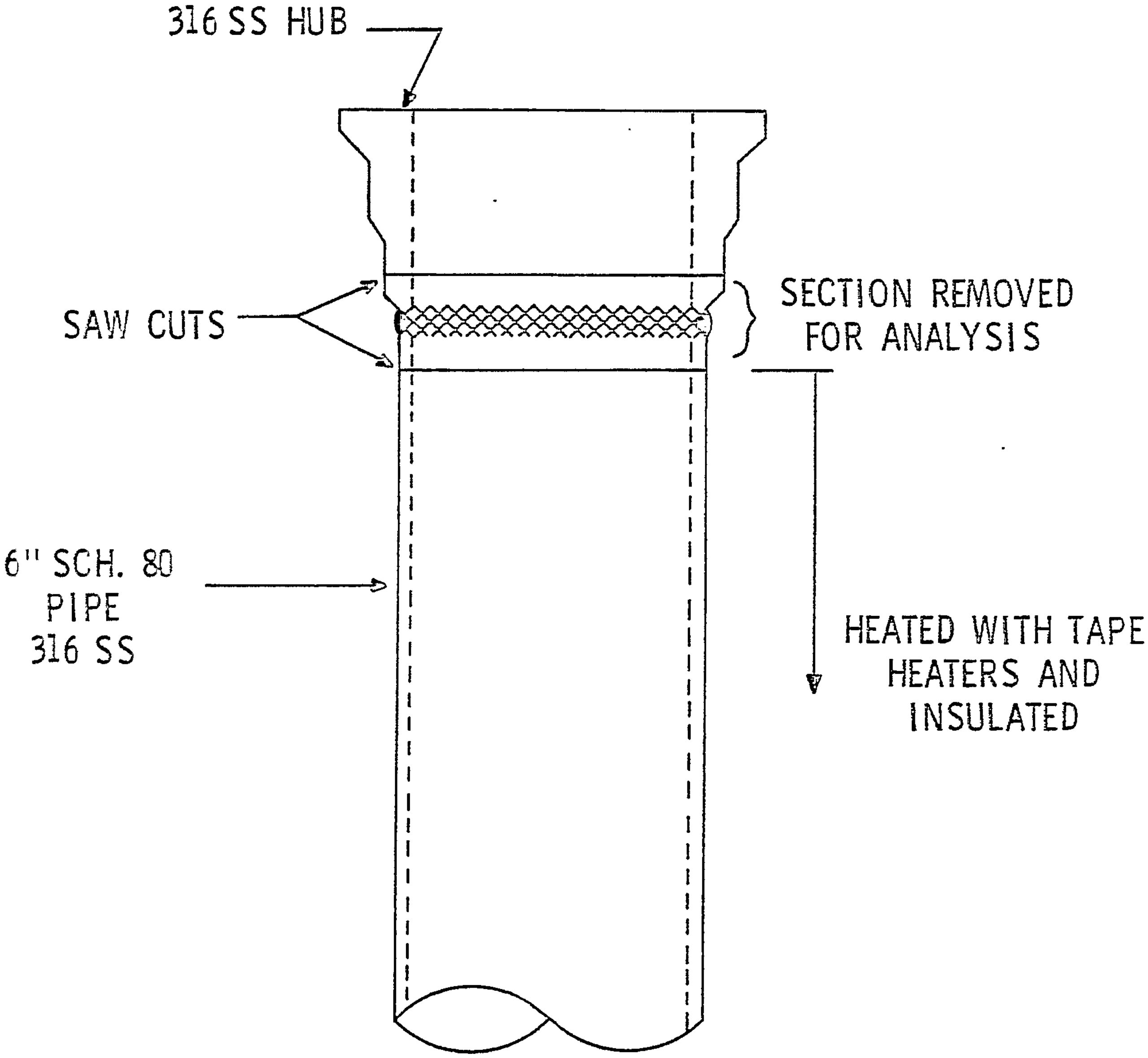
Occasional plugging problems also were experienced in the gasifier pressure taps which are used to indicate the level of the fluidized char bed. Since synthesis gas is used for the pressure tap bleed gas, the greater the volume of bleed gas the less the volume available to the feed line. To maximize 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 SSpipe and a 316 SS butt welded hub. Figure 2.1-2 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 in 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. Characteristic branching transgranular chloride-stress cracks were 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 condensation. The second stress-chloride cracking

FIGURE 2.1-2

CGU FILTER VESSEL FLANGE END



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, probably during a shutdown as a result of inadequate purging.

2.1.2 CGU Data Analysis

Material balances for the four CGU continuous yield periods (101-104) are presented in Table 2.1-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, 250 psig. The feedstock was Illinois coal char catalyzed with 20% K_2CO_3. The gasification medium was 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 60-90 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 2.1-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 analogous 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 compositon 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

Table 2.1-I

MATERIAL BALANCES FOR CGU CONTINUOUS YIELD PERIODS

	Yield Period 101					Yield Period 102					Yield Period 103					Yield Period 104				
Temperature, °F	1230					1310					1310					1304				
Pressure, psig	350					500					500					500				
	Total	C	H	O	N	Total	C	H	O	N	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			2.500	1.213	0.015			2.000	0.970	0.012		
H_2O	5.300		0.593	4.707		4.907		0.549	4.358		5.000		0.560	4.440		5.060		0.566	4.494	
H_2	0.502		0.502			0.738		0.738			0.865		0.865			1.197		1.197		
CO																0.287	0.123		0.164	
N_2[5]						0.174				0.174	0.207				0.207	0.281				0.281
Total	8.302	1.213	1.110	4.707		8.320	1.213	1.302	4.358	0.174	8.572	1.213	1.440	4.440	0.207	8.825	1.093	1.775	4.658	0.281
Output (lbs/hr)																				
Char	1.285[1]	0.012[2]				1.740[1]	0.469[2]				1.387[1]	0.114[2]				1.135[1]	0.118[2]			
H_2O	4.200		0.470	3.730		4.430		0.496	3.934		4.620		0.517	4.102		4.819		0.539	4.280	
H_2	0.548		0.548			0.621		0.621			0.625		0.625			0.878		0.878		
CO	0.532	0.228		0.304		0.191	0.082		0.109		0.157	0.067		0.090		0.180	0.077		0.103	
N_2						0.174				0.174	0.207				0.207	0.281				0.281
CH_4	0.738	0.553	0.186			0.654	0.489	0.164			1.109	0.830	0.279			1.087	0.814	0.273		
CO_2	1.540	0.420		1.120		0.636	0.173		0.463		0.739	0.202		0.538		0.308	0.084		0.224	
Total	8.843	1.213	1.204	5.154		8.446	1.213	1.281	4.506	0.174	8.844	1.213	1.421	4.730	0.207	8.688	1.093	1.690	4.607	0.281
Material Balance, %	107		108	110		102		98	103		103		99	107		98		95	99	
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 %)	Measured	Calc. Gas Phase Equil.	Measured	Calc. Gas Phase Equil.	Measured	Calc. Gas Phase Equil.	Measured	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

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[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 2.1-II

MATERIAL BALANCES FOR CGU CAPTIVE BED YIELD PERIODS

Temperature, °F			1250(1)				1250		
Pressure, psig			500				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

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(1) Bleed N reduced effective pressure to 420 psig
(2) H_2O by O 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

research phase in Figure 2.1-3. The fixed-bed data were obtained in multiple runs at 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 abcissa, 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 2.1-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 2.1-4, 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.

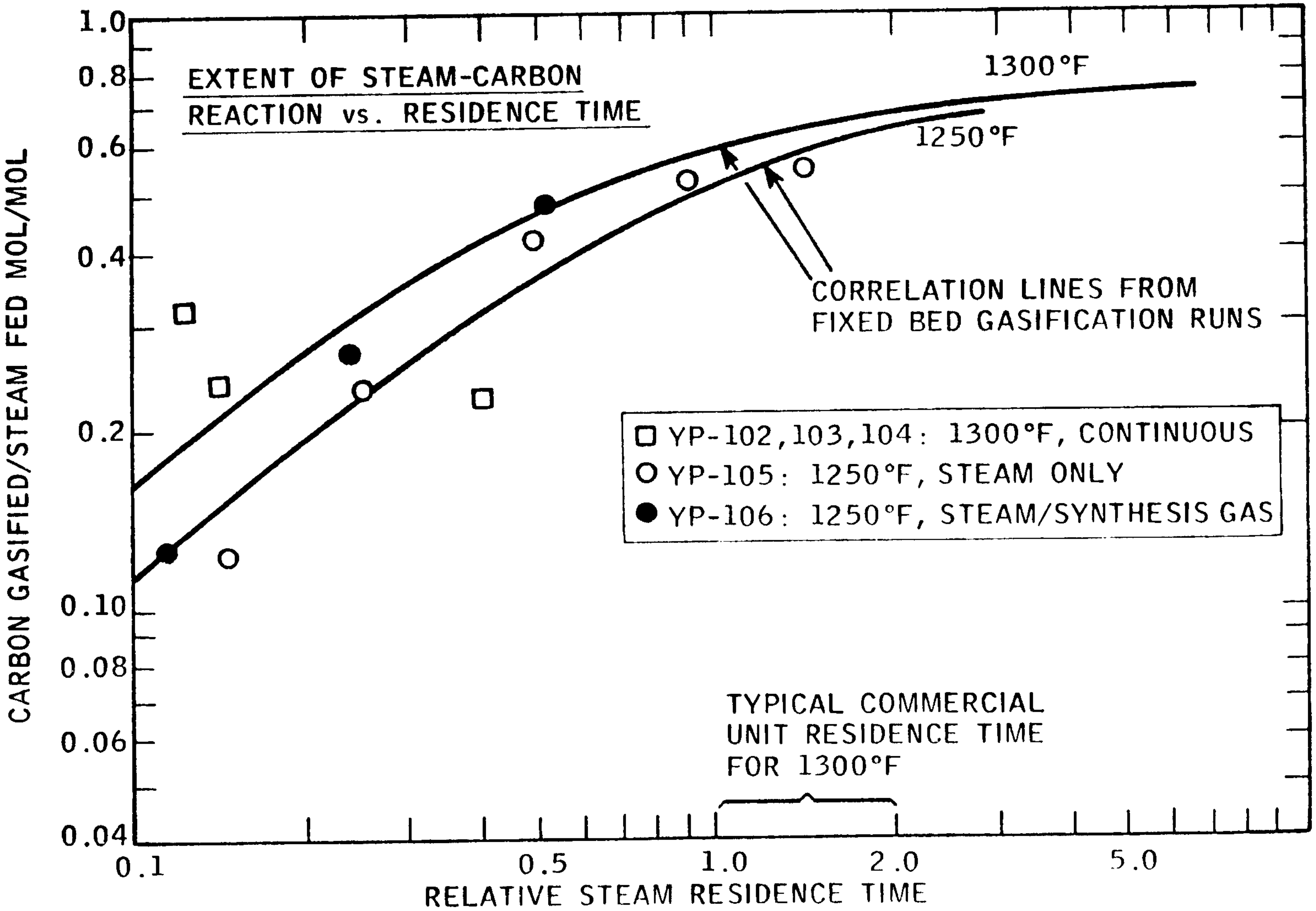
At low residence times, the methane production exceeds that observed in the fixed-bed runs. The reason for this is not clear. It is possible that a small amount of methanation is occurring downstream of the gasification bed in cooler zones, tending to increase methane yields. At the low residence times 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.

2.2 FIXED BED GASIFICATION REACTION STUDIES

Fixed bed gasification experiments performed during the past year focused on the use of Na_2CO_3 and mixed Na_2CO_3/K_2CO_3 catalysts. The incentive for using Na_2CO_3 is that its cost is only 20-30% of the cost of K_2CO_3. The activity of sodium carbonate was found to be significantly lower than that of potassium carbonate especially at high pressure. Also, analysis of the char streams from the mixed catalyst runs showed that potassium is selectively tied up by the coal minerals, reducing the incentive for using mixed catalysts. As a result of these findings, potassium carbonate was selected for catalyst recovery and recycle operations.

Figure 2.1-3

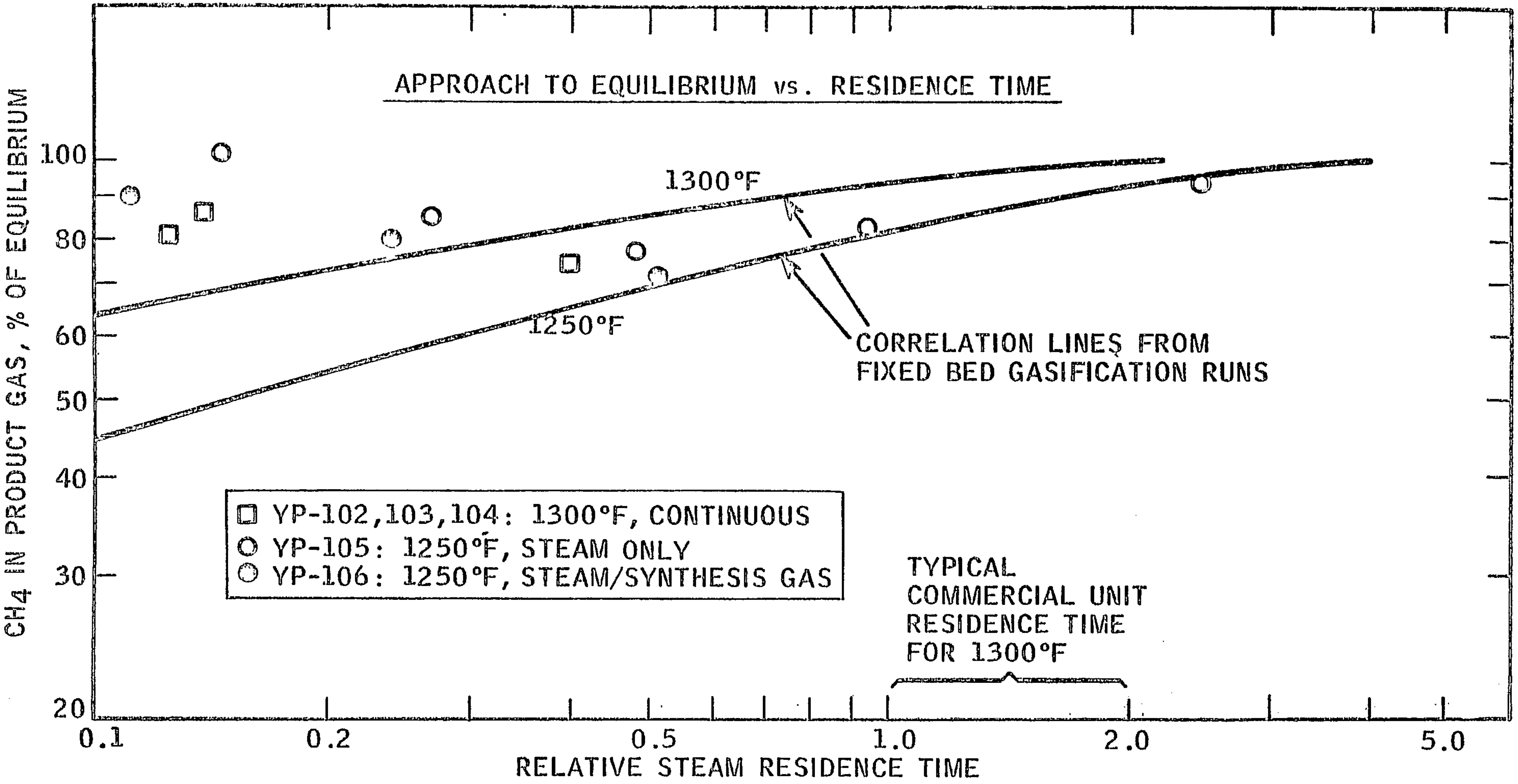
COMPARISON OF CGU AND PREVIOUS FIXED BED DATA



76B-12-4

Figure 2.1-4

COMPARISON OF CGU AND PREVIOUS FIXED BED DATA



76B-12-5

Initially, carbon gasification rate data were obtained for catalyst loadings of 15 wt.% Na_2CO_3 and 5 wt.% Na_2CO_3/5 wt.% K_2CO_3. These data are compared in Figure 2.2-1 with correlation lines for K_2CO_3 catalyst from multiple runs made prior to the start of the ERDA program. Some check runs were also made with 10 wt.% K_2CO_3. The moles of carbon gasified per mole of steam fed is plotted on the ordinate and the relative steam residence time on the abscissa. For all runs the temperature was 1300°F and the pressure, 500 psig. Steam rates were varied over an eight-fold range.

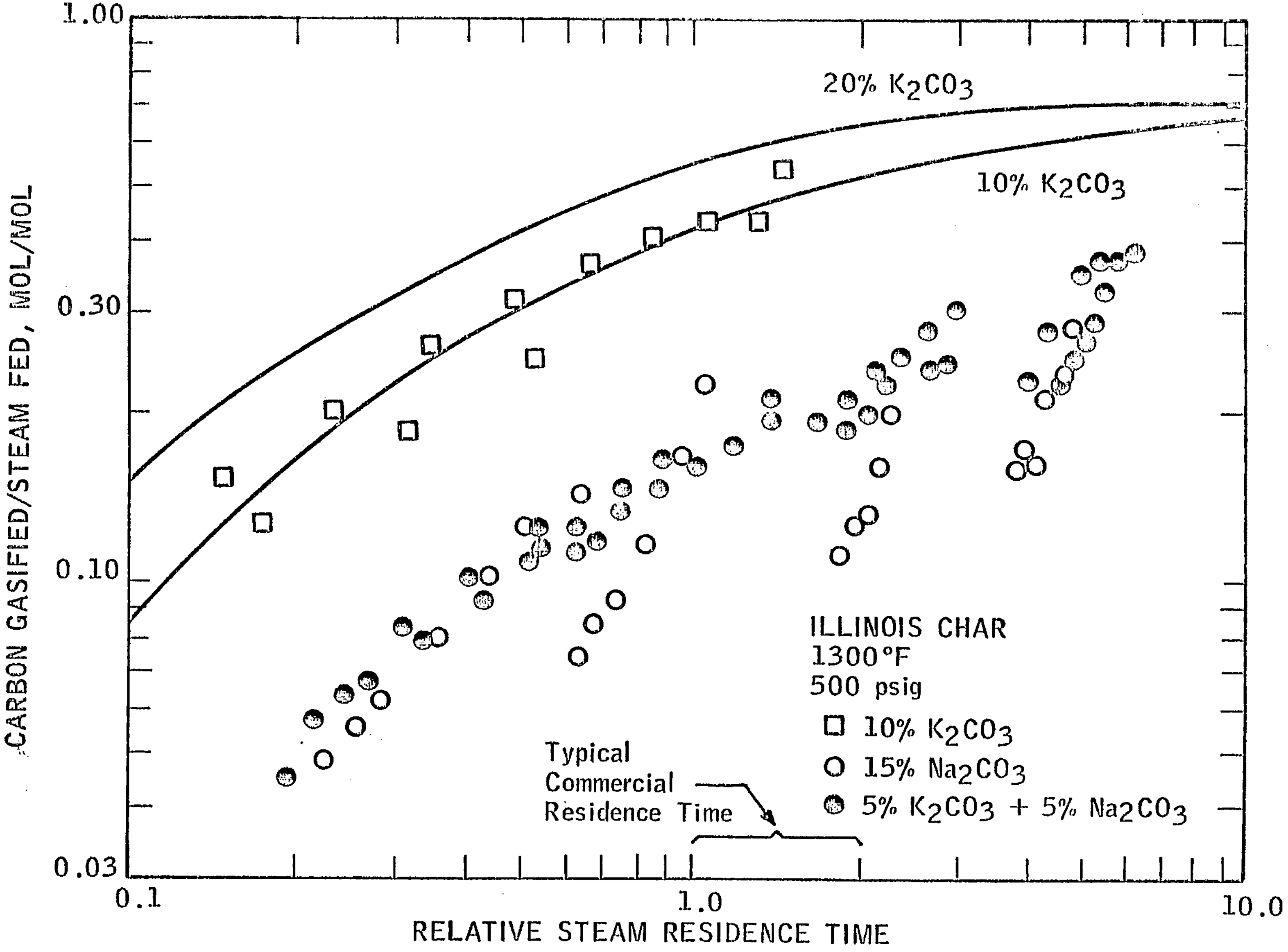
The data from individual runs on the 5% K_2CO_3/5% Na_2CO_3 mixed catalyst form a continuous curve relating carbon converted/steam fed to steam residence time, over a wide range of initial steam rates. This is similar to the data for K_2CO_3 catalyst except that the curve has been displaced along the abscissa. This displacement is a measure of the reduced activity for the mixed catalyst. The data for the pure Na_2CO_3 catalyst on the other hand form discrete curves for each steam rate. Thus, these runs suggest that the Na_2CO_3 catalyst does not maintain activity as the run proceeds as well as K_2CO_3.

Gasification rate data for 50/50 weight mixtures of Na_2CO_3 and K_2CO_3 at levels of 10, 15, and 20 wt.% on coal are compared with the correlation line for multiple runs with 10% K_2CO_3 in Figure 2.2-2. Based upon the data obtained, the 5% Na/5% K mixed catalyst has about 20-25 percent of the activity of the 10% K_2CO_3. A fundamental measure of the relative activity of two catalysts is the ratio of residence times required to achieve a given level of the ordinate--moles carbon gasified/mole steam fed ("effective " steam conversion). As expected, reactivity increases as catalyst loading increases; with the 10% Na_2CO_3/10% K_2CO_3 catalyst only about one-fourth the residence time is required to reach the same value of the ordinate (carbon gasified/steam fed) as with 5% Na_2CO_3/5% K_2CO_3 catalyst. More importantly, however, although the data for the 10% Na_2CO_3/10% K_2CO_3 catalyst show some scatter, it is clear that the mixed catalyst has essentially the same activity (within experimental accuracy) as 10% K_2CO_3 alone. Thus, at the reaction conditions of interest, Na_2CO_3 has little catalytic activity when used in combination with K_2CO_3.

One of the original incentives for using the mixed catalyst rather then K_2CO_3 alone was a belief that sodium would act as a scavenger for aluminum compounds in the coal, which have been found to tie-up a portion of the potassium catalyst as catalytically inactive aluminosilicates. Analyses of the char residues from the mixed catalyst runs revealed that while some sodium is initially tied up, the sodium is displaced by the more active potassium as carbon conversion increases. Figure 2.2-3 shows this progressive tie-up for the 20 wt.% mixed catalyst. Similar results obtained for the 15 wt.% and 10 wt.% mixed catalyst are shown in Figures 2.2-4 and 2.2-5. Thus at high carbon conversions only small amounts of sodium are present as aluminosilicates. Since with a mixed Na_2CO_3/K_2CO_3 catalyst the makeup required to compensate for catalyst tied up with the ash would still be essentially all K_2CO_3, there is little incentive for using Na_2CO_3 in admixture with K_2CO_3.

FIGURE 2.2-1

GASIFICATION RATES IN FIXED BED TESTS



77B-2-11

Figure 2.2-2

FIXED BED GASIFICATION RUNS

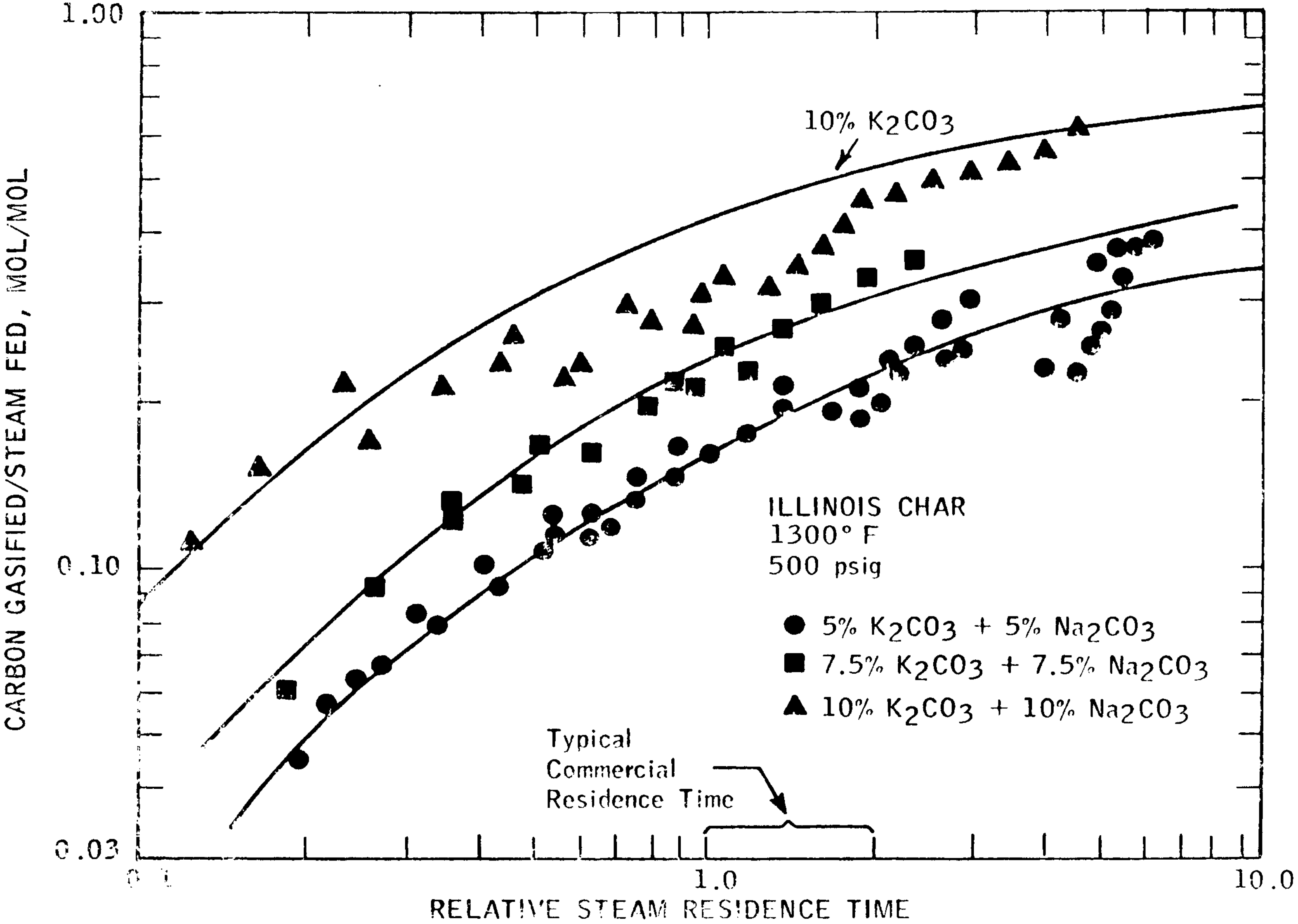


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Figure 2.2-3

CATALYST RECOVERY IN MIXED CATALYST SYSTEM

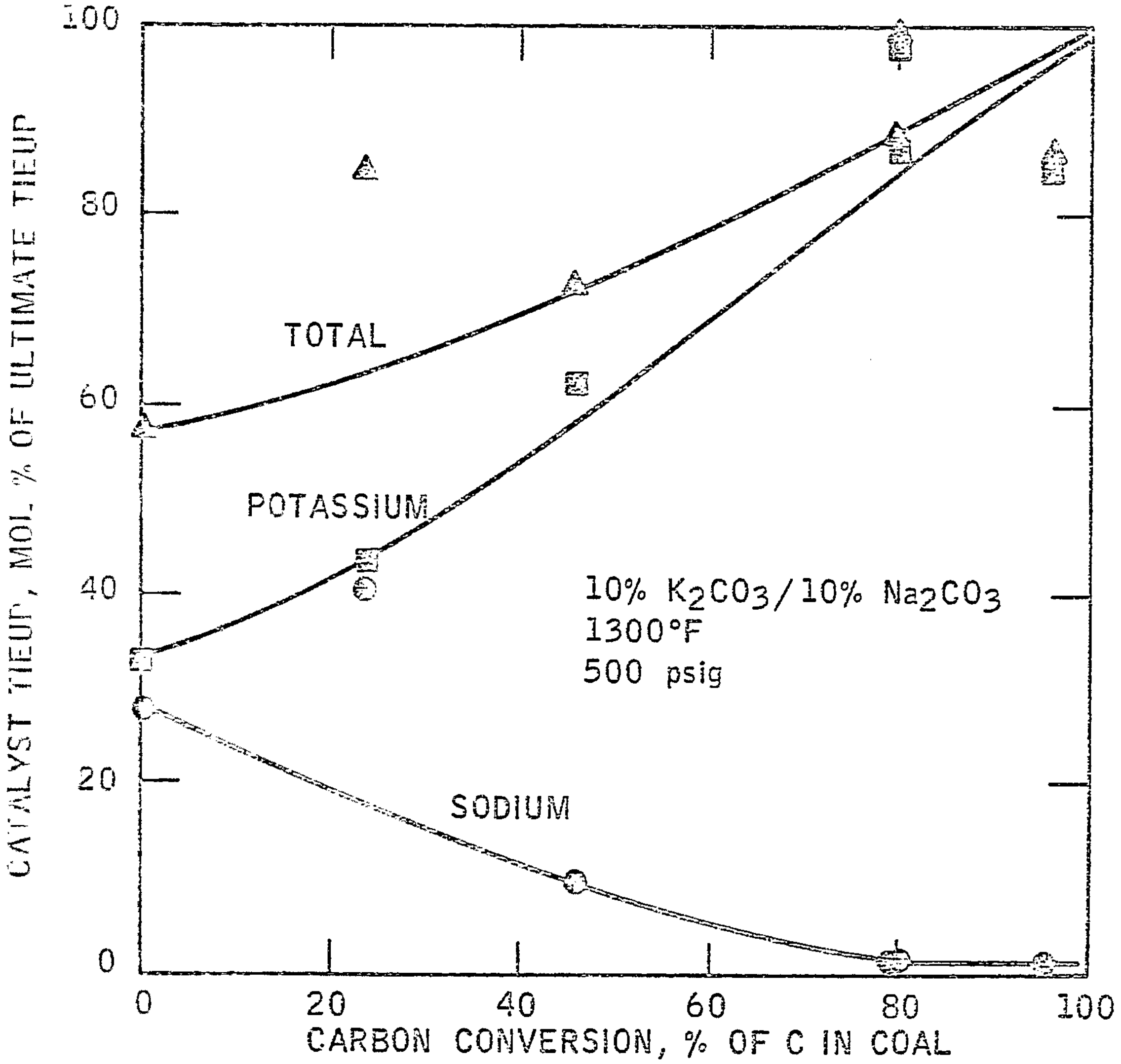

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Figure 2.2-4

CATALYST RECOVERY IN MIXED CATALYST SYSTEM

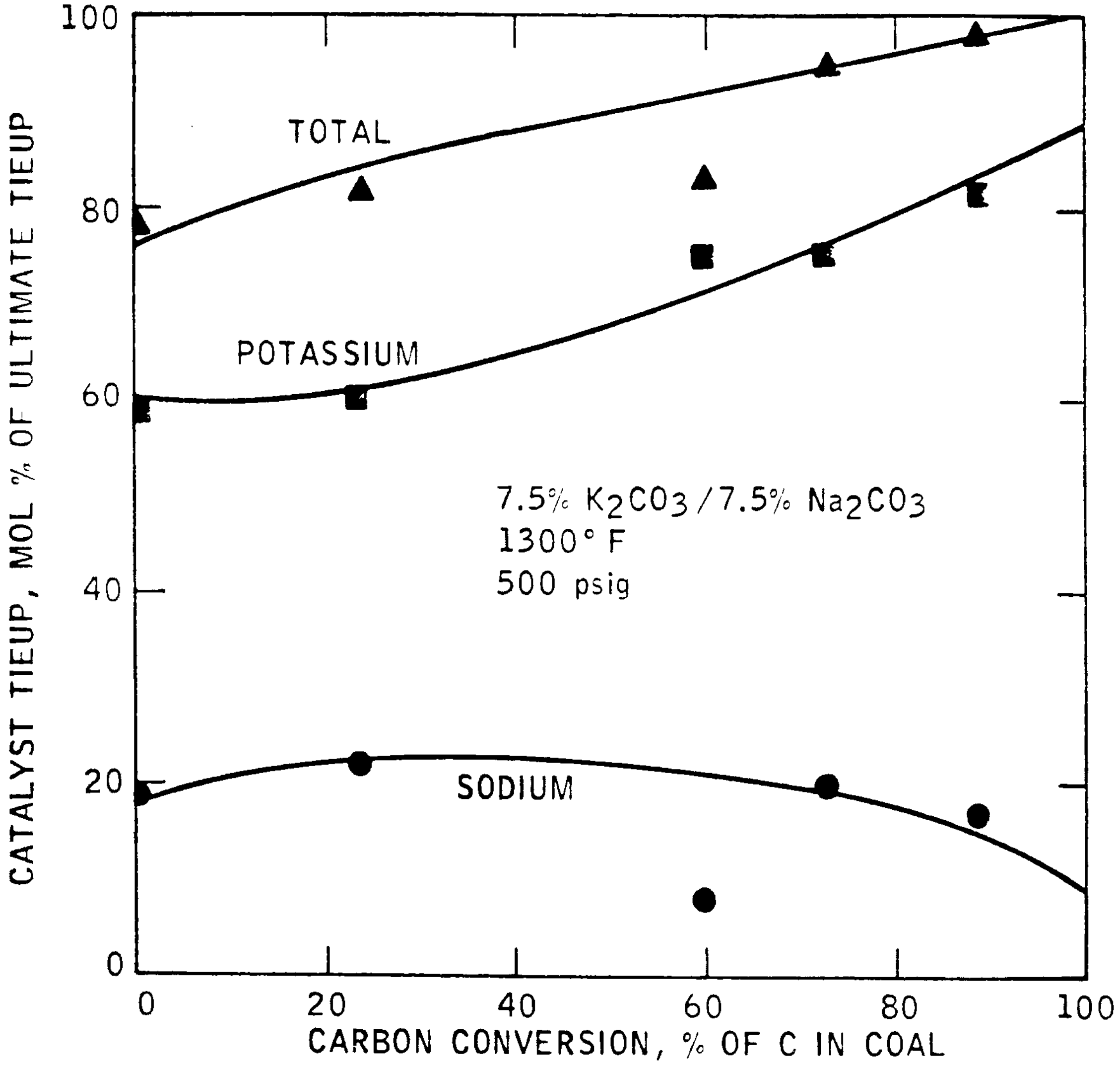

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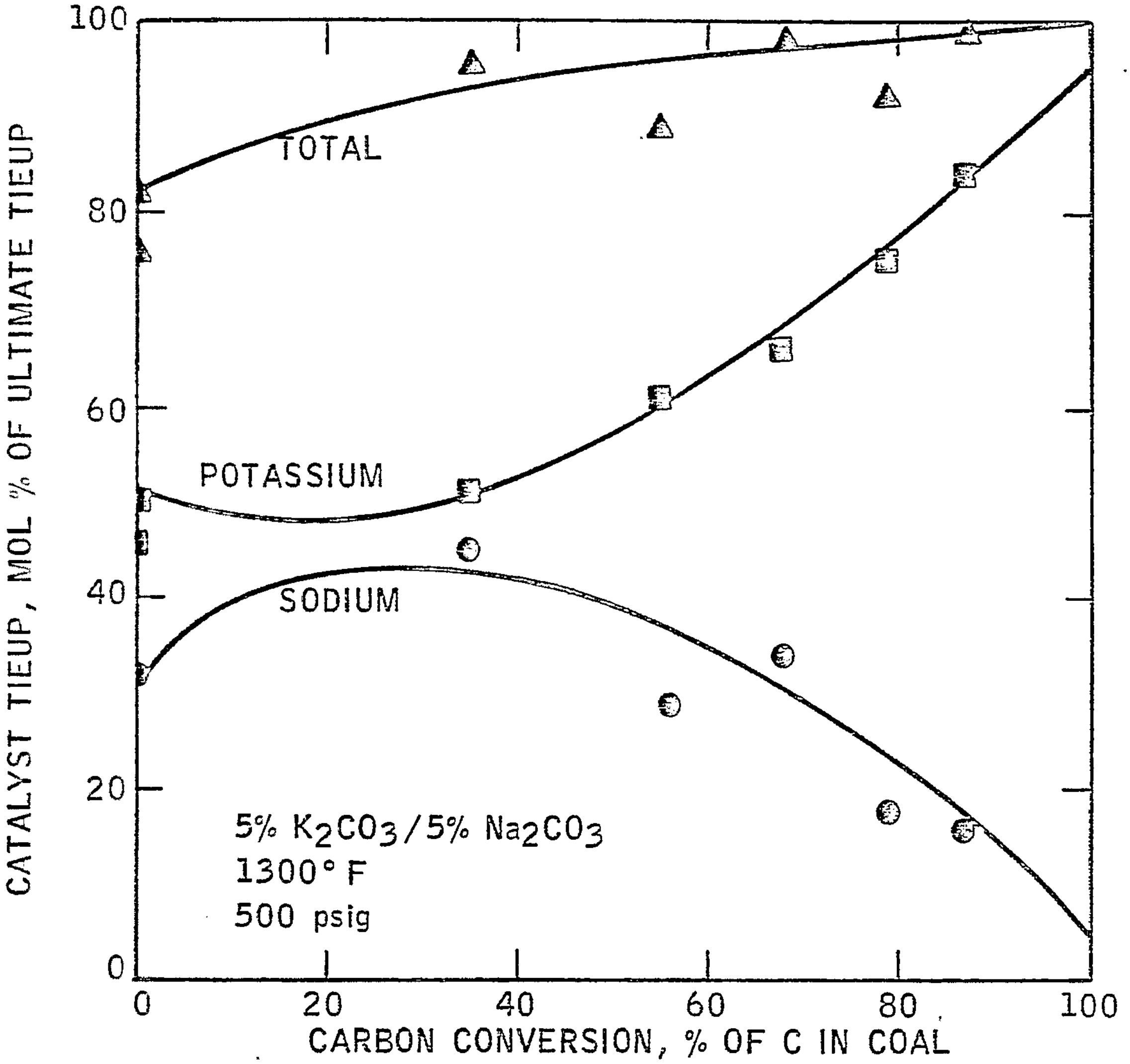
Figure 2.2-5

CATALYST RECOVERY IN MIXED CATALYST SYSTEM



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2.3 RECOVERY OF WATER-SOLUBLE CATALYST

Bench scale studies of water soluble catalyst recovery focused on three major objectives: to identify the chemical forms of potassium present in the recovered catalyst solution; to determine how recovery of water soluble potassium in the CRU could be improved; and to learn more about the physical and chemical effects occurring in catalyst leaching.

Initial investigations revealed that water soluble potassium is present in solution as K_2CO_3, KOH, and potassium-sulfur compounds. Although the proportions of K_2CO_3 and KOH vary with pH, these two compounds together constitute 75-80% of the water soluble potassium in solution. The interconversion of these two compounds is insignificant, as both are active gasification catalysts.

The remaining 15-25% of the water soluble potassium is present in solution as sulfur compounds. Current evidence indicates that K_2S is the predominant potassium-sulfur compound on fresh gasifier char, but this compound is readily oxidized in air to $K_2S_2O_3$ and K_2SO_4. This oxidation was demonstrated in an experiment in which char samples were withdrawn from the FBG under a nitrogen blanket and then leached with water, again under an inert atmosphere. The results were then compared with samples withdrawn under partial blanketing. The table below summarizes the leaching results. The hydroxide analyses were obtained by difference.

Percent of K^+ Tied Up with Various Sulfur

Species in Leaching Solution

	Partial Blanketing						Complete Blanketing	
	1	2	3	4	5	6	7	8
Sulfate Sulfur	4.7	3.3	3.8	4.0	2.8	5.7	1.0	0.2
Sulfide Sulfur	2.9	7.9	7.1	6.7	5.6	8.8	12.0	15.7
Thiosulfate Sulfur	15.5	3.5	9.9	9.1	9.5	11.5	3.0	0.9
Carbonate	47.6	45.8	53.1	53.8	60.4	31.7	65.0	39.3
Hydroxide	29.3	39.5	26.1	26.4	21.7	42.3	19.0	43.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

In order to qualitatively assess the rate at which the oxidation occurs, another brief study was performed. Samples of residue which had been withdrawn from the gasifier in an inert atmosphere were exposed to air for varying periods of time by spreading the samples on a flat pan. The samples were then washed with a large excess of water (20 fold) and the levels of sulfur compounds in solution were determined. These data are shown below.

Time of Air Exposure Before Leaching	Sulfide Sulfur (ppm)	Thiosulfate Sulfur (ppm)	Sulfate Sulfur (ppm)
None	1050	125	15
10 Min.	230	680	375
3 hrs.	50	1240	500

It is evident that relative to a sample which had not been exposed to air, even a ten minute exposure resulted in a substantial reduction in the level of sulfide sulfur with an accompanying increase in the concentrations of thiosulfate and sulfate. After three hours of exposure 95% of the sulfide sulfur was converted to oxidized sulfur forms. However, fresh char withdrawn without contacting air produced little sulfate and thiosulfate, and most of the sulfur in solution is in the form of sulfide. Thus K_2S would be the predominant sulfur form in a commercial unit where ash-char residue would be withdrawn from the gasifier and leached without exposure to air. Although K_2S is believed to be an active gasification catalyst, confirming data are needed. Also, depending on the type of coal drier employed, the sulfide could be converted to K_2SO_4 in the coal drying step, and K_2SO_4 is known to be significantly less active than K_2S

One alternative to the recycle of K_2S is the stripping of the recovered catalyst solution with CO_2 to convert the sulfide to the carbonate:

$$K_2S + CO_2 + H_2O \rightarrow K_2CO_3 + H_2S\uparrow$$

The effect of CO_2 acidification on the water washing of ash/char residue was examined for a residue obtained from a Fluid Bed Gasifier run with 15 wt.% K_2CO_3 on Illinois coal. Care was taken to prevent air exposure and oxidation of the residue. Ten grams of the residue were added to 250 ml of H_2O and the slurries were exposed to either a CO_2 or N_2 atmosphere at 100°C for three hours. Analysis of the solution and residual char are shown below.

Atmosphere	N_2	CO_2
	---Millimoles---	
Solution		
Sulfide	5.0	<0.1
Total Sulfur	5.9	1.2
K	54	51
Si	6	0.7
Char		
Residual Potassium	23	25
Total Sulfur	10	11

Acidification with CO_2 removed essentially all of the sulfide sulfur and reduced the total sulfur in solution by at least a factor of five. The CO_2 treatment also reduced the silica in solution by a factor of ten. The treatment had no effect on the potassium or sulfur remaining on the char. Thus, it would appear that CO_2 stripping will be effective in converting recovered K_2S to K_2CO_3.

Additional catalyst recovery studies were initiated to investigate lower-than-expected recoveries of water soluble catalyst obtained in the CRU during catalyst recycle operations. In order to determine how recovery could be improved, several runs were conducted in which FBG char was serially washed with portions of distilled water. Fresh distilled water was used for each wash (i.e., a cross-current extraction), and the water/char ratio was 3/1 on a weight basis.

Figure 2.3-1 shows the recoveries of water-soluble potassium achieved for 80% and 90% converted chars. It is seen that it is apparently more difficult to remove the "water soluble" potassium from the more highly converted char.

It was postulated that this behavior is due to exposure of the char to air. Highly converted chars are very reactive due to the high effective catalyst loading on the remaining carbon residue. When exposed to air, these chars react with oxygen and/or water vapor in the air, becoming quite hot, and occasionally will spontaneously ignite. Although some precautions are taken to prevent exposure of the char to air, it is possible that sufficient air may leak into the char storage containers over a period of months to react with the char and significantly alter the behavior of the char during water washing.

In order to test this theory a sample of highly converted (90%) char was withdrawn from the FBG taking particular care to cool the char and keep it under inert conditions. The char was then water washed three times with low water/char ratios, the entire procedure being carried out in a nitrogen atmosphere. Then, in order to determine the effect of air exposure on recovery, the procedure was repeated with samples of the same char that had been exposed to air for specific lengths of time.

The results are shown in Figure 2.3-2 and compared to the results obtained for an older, unblanketed char with a catalyst loading and conversion similar to the fresh char. The unexposed char showed more than twice the potassium recovery of the older char after three washes, indicating that preventing air exposure may indeed be the critical factor in allowing high recoveries of water-soluble catalyst.

The fresh char which was exposed to air for 30 minutes also showed a lower potassium recovery than the unexposed char. In addition, even after 30 minutes exposure, the char was still quite warm, indicating that a reaction was still occurring. Thus, it seems likely that longer exposure to air might result in even lower recoveries of water soluble potassium.

Future experiments will test the effect of longer exposure times on recoverability of the catalyst. It is clear that the oxidation of

FIGURE 2.3-1

POTASSIUM RECOVERY BY CROSS-CURRENT WATER WASHING AT LOW WATER/CHAR RATIOS

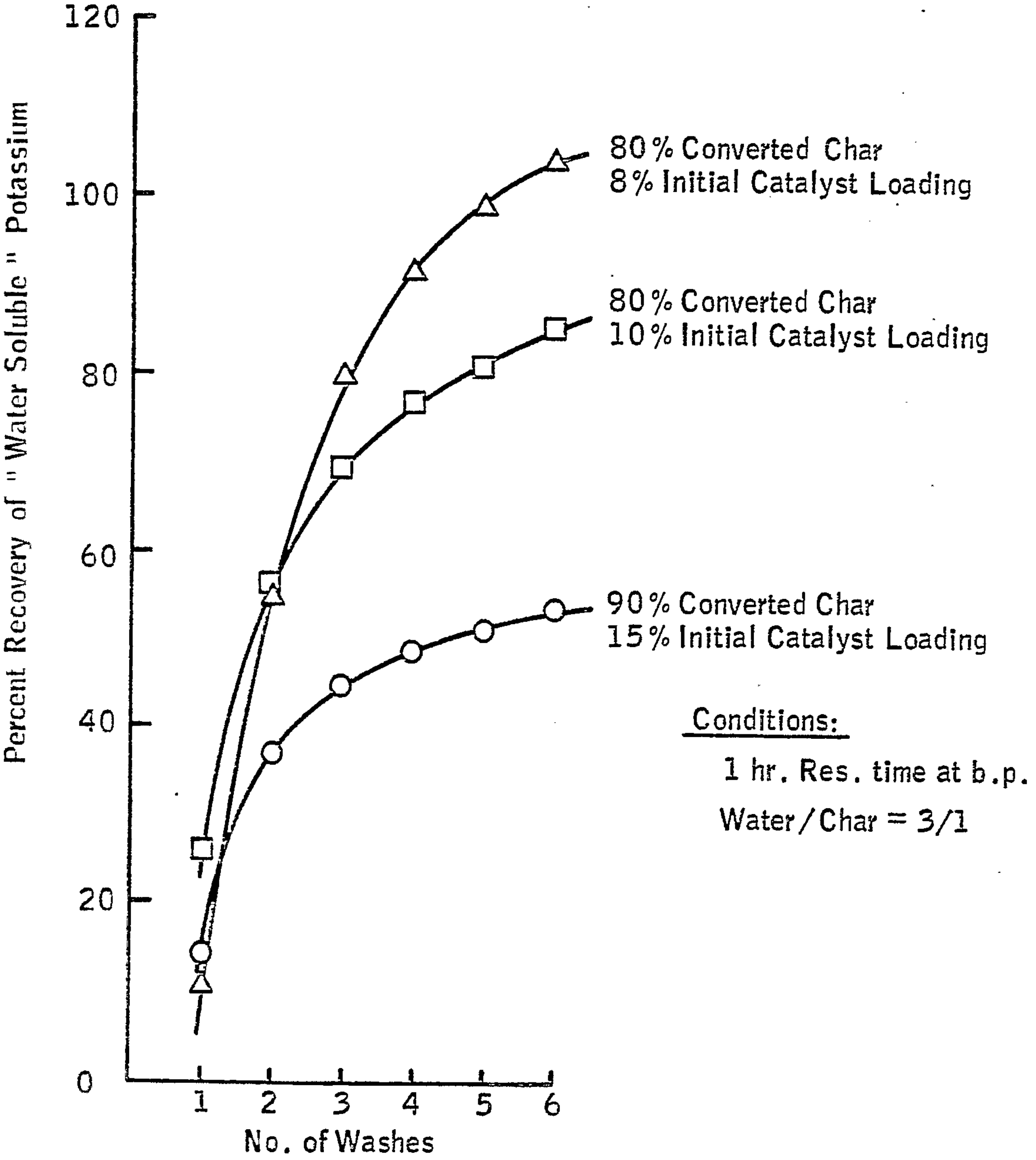

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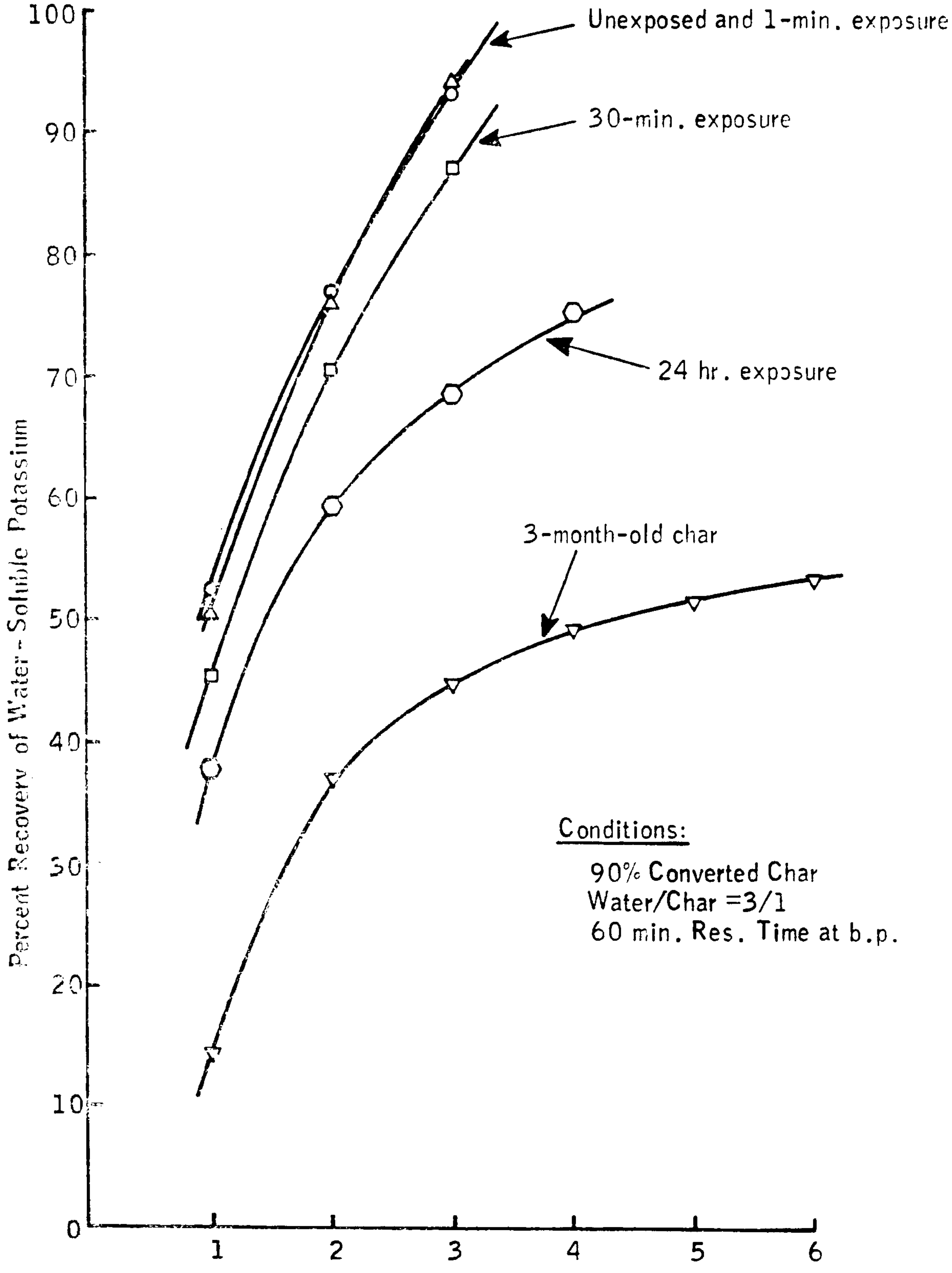
Figure 2.3-2

EFFECT OF AIR EXPOSURE ON POTASSIUM RECOVERY BY WATER WASHING



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sulfide can not explain the reduced recoveries obtained after air exposure, as both potassium thiosulfate and potassium sulfate are soluble in hot water. Also, since sulfur compounds constitute only 15-25% of the water soluble potassium, it would be impossible to attribute a 50% reduction in catalyst recovery to sulfur conversion. Therefore, investigations are now underway to find another mechanism by which air exposure affects recovery.

Investigations have also begun into the "fundamentals" of water washing. Several runs were conducted in which FBG char was serially washed at a water/char ratio of 50/1. Although this ratio is not commercially viable, the results obtained are very interesting. The results of one series of washes are shown in Figure 2.3-3. Notice that the first wash removes slightly more potassium than the amount analyzed as "water-soluble". This is expected since "water-soluble" potassium is determined by a separate analysis in which one gram of char is washed with 250 grams of distilled water, and the extracted potassium measured. The "water-soluble" analysis and the amount of potassium removed in our laboratory test agree within 10 percent.

The surprising fact about the data shown in Figure 2.3-3, however, is that amounts of potassium far exceeding the "water-soluble" limits can indeed be removed by water washing. Unfortunately, such recovery of "water-soluble" potassium is only possible with large amounts of water and long contact times between the water and char. One possible explanation for this behavior is that the "insoluble" potassium remaining on the char which has so far been found to be principally in the form of aluminosilicates has a finite, albeit small, solubility, and thus could be removed by water washing. Another explanation suggests that some of the residual potassium is held on active char sites by ion-exchange and that displacement by hydrogen ions in the water wash is difficult, especially in the basic potassium solution.

As a test of this ion-exchange hypothesis, one series of cross-current washes was carried out using a saturated calcium hydroxide solution instead of distilled water. The results of this test are shown in Figure 2.3-4 and compared to the results obtained using distilled water.

A significant improvement in potassium recovery was observed when using limewater. Of course it is uncertain whether this is due to ion-exchange or to another (possibly chemical) effect. Investigations of this behavior will continue.

2.4 RECOVERY OF WATER-INSOLUBLE CATALYST

The chemistry involved in the recovery of water insoluble potassium was briefly summarized in the January-March, 1977 Quarterly Report. Recent work has resulted in a better understanding of the chemistry involved, as summarized below.

The major constituent of the water-insoluble potassium in the gasifier char is synthetic kaliophilite ($KAlSiO_4$). This compound is produced

FIGURE 2.3-3

POTASSIUM RECOVERY BY CROSS-CURRENT WATER WASHING AT HIGH WATER/CHAR RATIO

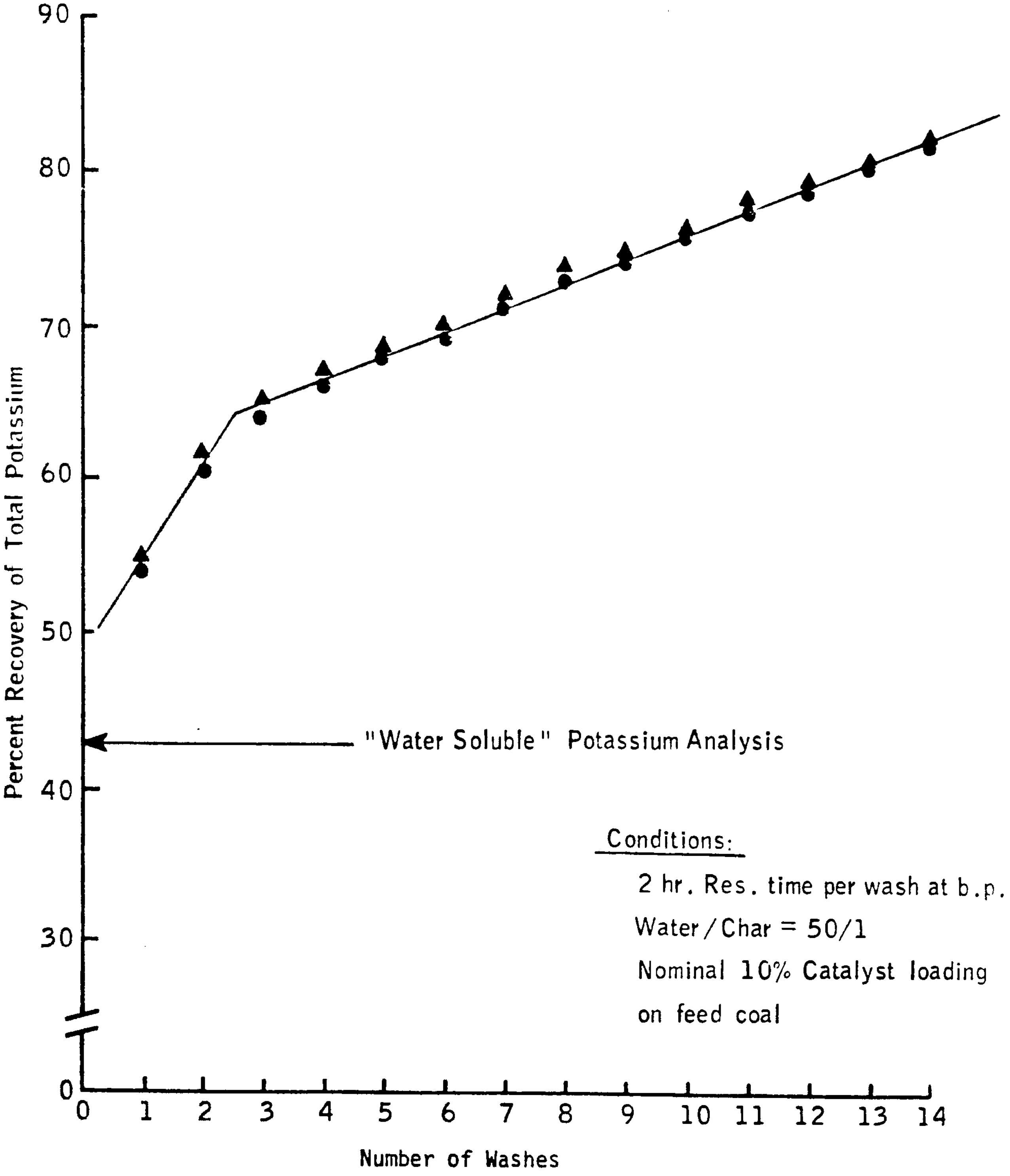
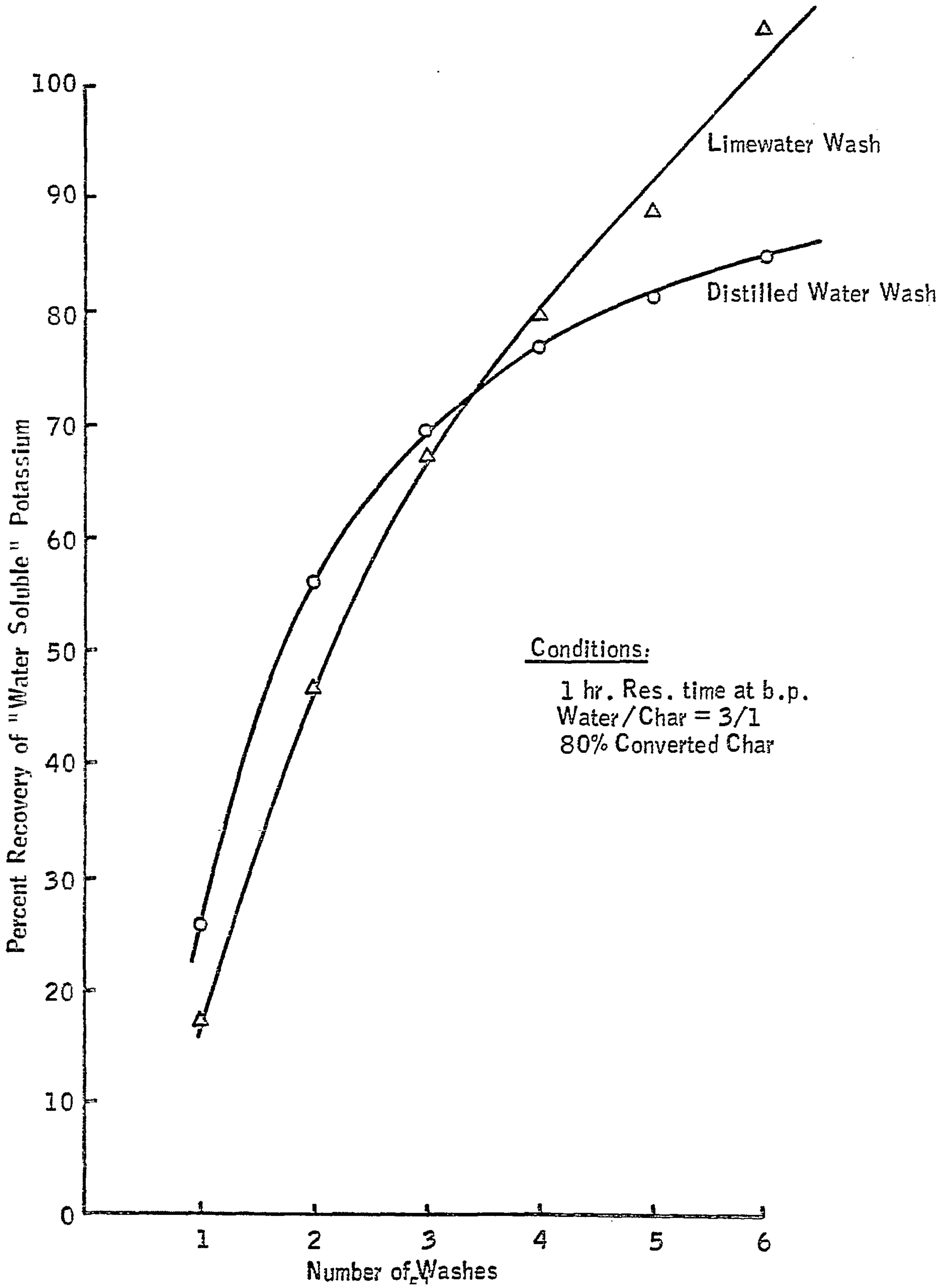


Figure 2.3-4

EFFECT OF LIMEWATER WASHING ON POTASSIUM RECOVERY



in the gasifier by the reaction of clay minerals (e.g., kaolinite) originally in the coal with the added K_2CO_3 catalyst:

$$\underset{\underline{\text{kaolinite}}}{Al_2Si_2O_5(OH)_4} + K_2CO_3 \xrightarrow[\text{in Gasifier}]{1400°F} \underset{\underline{\text{kaliophilite}}}{2KAlSiO_4} + CO + 2H_2O \qquad (A)$$

The hydrothermal reaction of the gasifier char residue with $Ca(OH)_2$ at 300°-400°F results in a variety of solid products. Two major components have been identified and studied by X-ray diffraction techniques. The two compounds are hydrogarnet, a calcium aluminum silicate hydrate, and tobermorite, a hydrated calcium silicate. The hydrogarnet formation is represented by the following reaction:

$$3Ca(OH)_2 + 2KAlSiO_4 \xrightarrow[\text{2 hours}]{300°F} \underset{\underline{\text{hydrogarnet}}}{Ca_3Al_2SiO_4(OH)_8} + SiO_2 + 2KOH \qquad (B)$$

The hydrogarnet species formed has a 3:1 Ca/Si ratio as determined by the X-ray diffraction results. The excess silica produced in reaction (B) along with "free" silica already present in the char reacts directly with $Ca(OH)_2$ to form a poorly-crystallized tobermorite:

$$6SiO_2 + 5Ca(OH)_2 \xrightarrow[\text{2 hours}]{300°F} \underset{\underline{\text{tobermorite}}}{(CaO)_5(SiO_2)_6(H_2O)_5} \qquad (C)$$

In Illinois coal, the Si/Al molar ratio is approximately 2:1. Assuming that virtually all of the aluminum is in the form of kaliophilite (which has 1:1 Si/Al ratio), then there is about a 50/50 distribution of silica as kaliophilite and as "free" silica. Taking into account this silica stoichiometry, an overall reaction can be presented by appropriately combining reactions (B) and (C) as follows:

$$4KAlSiO_4 + 11Ca(OH)_2 + 4SiO_2 + 4H_2O \xrightarrow[0.1\ \underline{M}\ KOH]{300°F}$$

$$4KOH + 2\underset{\underline{\text{hydrogarnet}}}{Ca_3Al_2(SiO_4)(OH)_8} + \underset{\underline{\text{tobermorite}}}{(CaO)_5(SiO_2)_6(H_2O)_5} \qquad (D)$$

In the January-March 1977 Quarterly Report, it was suggested that significant amounts of $KAlO_2$ would be present in the reaction solution. However, only $7 \times 10^{-3}\underline{M}$ was actually found in the solution of a typical hydrothermal run. This observation is readily explained by the formation of the calcium aluminum silicate hydrate (hydrogarnet).

Work completed early in 1977 indicated that 3-5 wt.% potassium carbonate catalyst on Illinois coal was deactivated by reaction (A). Work began on the recovery of potassium present in the ash/char residue by digestion with $Ca(OH)_2$ in March.

A bench scale "tubing bomb" reactor, shown schematically in Figure 2.4-1, is used for the experimental program. The standard procedure is to load the tubing bomb with char, $Ca(OH)_2$, water or a solution of KOH, and several inert steel balls to provide mixing. The bomb is pressure tested with an inert gas for 500 psig, and then rotated in a furnace. After the run, the bomb is cooled before opening. The contents are separated by filtration, and approximately 300 ml distilled water is used to rinse out the tubing bomb. Several runs were made to determine if additional rinsing of the filter cake would result in further recovery. This additional rinsing was found to have very little effect on recovery, but has been continued to assure that the char pores are flushed with distilled water as completely as possible.

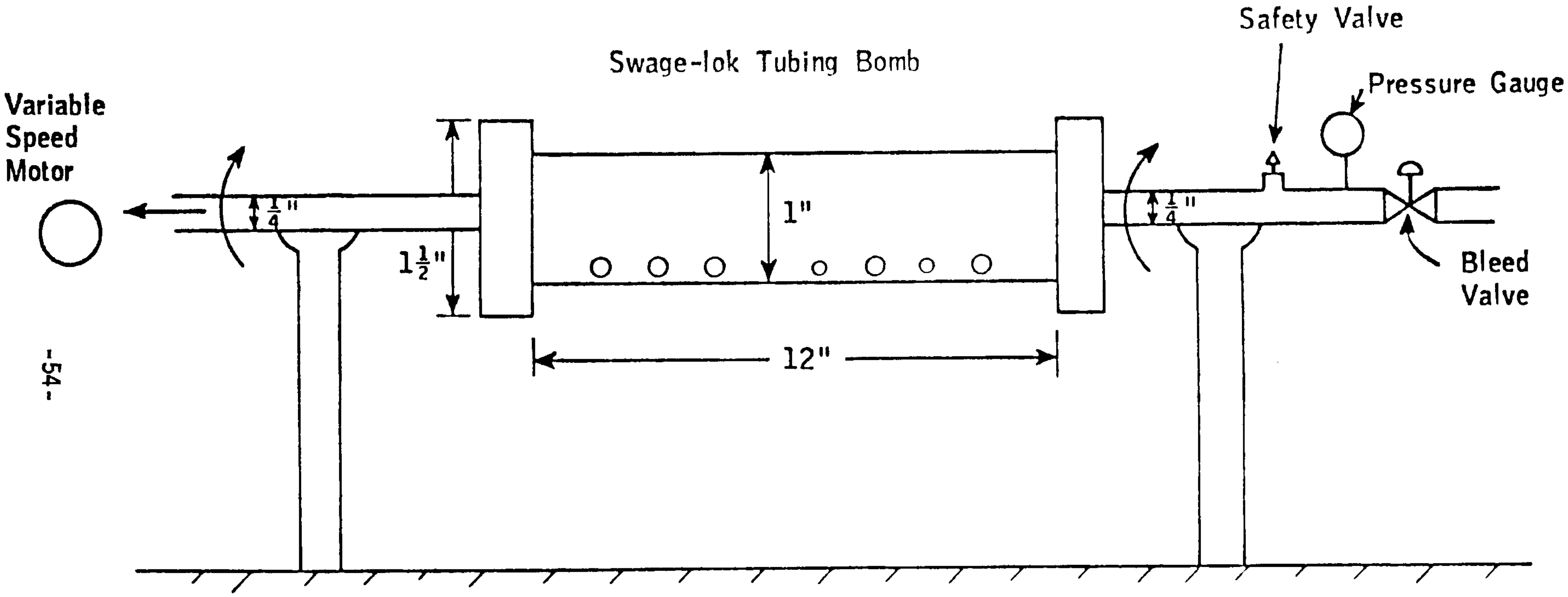
The char is analyzed before and after treatment to determine acid soluble and water soluble potassium. For both tests, small portions of char are combined with 50 ml of liquid and refluxed for 2 hours. Distilled water is used to determine water soluble potassium, and 2M HCl is used to determine acid soluble potassium. The resulting supernatants are analyzed by atomic absorption to determine the weight percent acid or water soluble potassium present on the original char. The difference between these two values is defined as the "water-insoluble" potassium.

Initially, experiments were carried out on char which had been washed to remove the water soluble potassium. However, the recoveries for these runs were low, and a second series of experiments were conducted with char which had not been water washed. In all cases, 10 grams of char and 100 ml of water were added to the reactor. The tests were performed at a temperature of 400°F and a residence time of 4 hours. The recoveries of water-insoluble potassium greatly increased when unwashed char was used. The difference in recoveries is shown by the data summarized below:

Char	Ca/K Insoluble	% Insoluble K Recovered
Washed	1.5	46
Washed	2.9	34
Washed	3.7	40
Unwashed	1.9	83
Unwashed	2.5	73
Unwashed	3.7	86

Figure 2.4-1

BENCH SCALE APPARATUS



CHARGE: 20 GMS CHAR, 80 ML 15% KOH, $Ca(OH)_2$

CONDITIONS: 400°F, 250 PSIA

The calcium to potassium mole ratio (Ca/K) given in the above table is based on the insoluble potassium originally present on the char and the calcium loaded as $Ca(OH)_2$. Apparently, the pH was elevated by the presence of water soluble potassium compounds on the char, which promoted the breakup of the $KAlSiO_4$.

Several runs were made to investigate the effect of elevated pH on the recovery of water-insoluble potassium from the ash/char residue. Both water washed and unwashed char were separately treated with distilled water and with 0.25N NaOH. The runs were made at a temperature of 400°F and a residence time of 4 hours. The data from these runs are summarized below:

Char	Liquid	Ca/K Insoluble	% Insoluble K Recovered
Washed	0.25N NaOH	3.3	61%
Washed	H_2O	3.2	37%
Unwashed	0.25N NaOH	3.7	89%
Unwashed	H_2O	3.7	75%

The significant difference between the recoveries for the washed char confirms that increasing the pH favors the recovery of water insoluble potassium.

The results of these experiments led to several runs with different potassium solutions. In a commercial countercurrent catalyst recovery system, the ash/char residue would be combined with K_2CO_3/KOH solution from the downstream water washing steps. Thus runs were made with water, 15% KOH and 20% K_2CO_3, to assess the impact of these solutions on the recovery of water-insoluble potassium. As in previous runs, the temperature was set at 400°F for a residence time of 4 hours. The data for these runs are summarized below:

Liquid	Ca/K Insoluble	% Insoluble K Recovered
Water	2.3	72%
15% KOH	2.5	73%
15% KOH	2.5	88%
20% K_2CO_3	2.9	41%
20% K_2CO_3	2.4	28%

As might have been expected from previous runs with NaOH solution, the runs made with KOH gave good recoveries, however, very poor recoveries were achieved with K_2CO_3 solution.

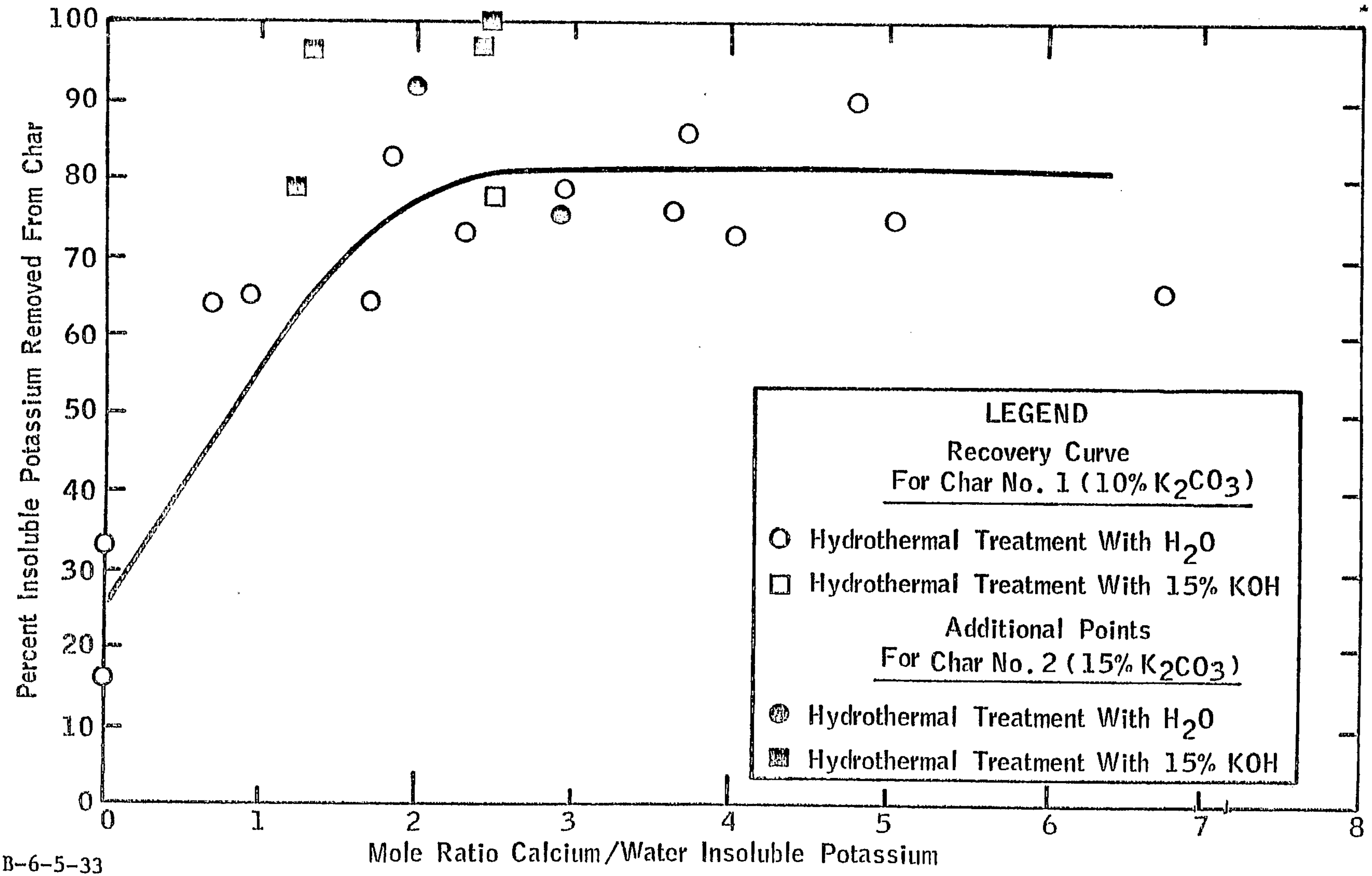
The ash/char residue used in all work up to this point was produced from a feed coal containing 10 wt.% K_2CO_3 catalyst. A second char produced from coal which contained 15 wt.% K_2CO_3 catalyst was used for several recent runs. Both distilled water and KOH solution were used for the runs, which were made at 400°F for 4 hours. These data are shown below and in Figure 2.4-2.

Liquid	Ca/K Insoluble	% Insoluble K Recovered
H_2O	2.9	76%
H_2O	2.0	92%
15% KOH	2.4	97%
15% KOH	1.2	79%
15% KOH	1.3	97%

The recoveries of water insoluble potassium from this second char are generally higher than those reported for the first char. Since the absolute amount of water-insoluble potassium is not a function of the initial catalyst level on the coal, this improvement of water-insoluble potassium recovery was unexpected. Oxidation of the two chars may be a factor in the difference in recoveries shown.

Figure 2.4-2

RECOVERY OF WATER INSOLUBLE POTASSIUM FROM UNWASHED CHAR BY HYDROTHERMAL TREATMENT AT 400°F



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3. ENGINEERING RESEARCH AND DEVELOPMENT (REPORTING CATEGORY 3)

Engineering research and development studies are being carried out under the Catalytic Coal Gasification Predevelopment Program to provide economic evaluations of process alternatives and to develop an estimate of overall process economics at the end of the contract period. This work is organized into the following three sub-tasks: Catalyst Recovery Studies; Gasification Reactor System Studies; and the Catalytic Coal Gasification Study Design.

Work began on the first two subtasks in October, 1976 and studies completed or in progress as of June, 1977 are reported in Sections 3.1 and 3.2. The Catalytic Coal Gasification Study Design began in June, 1977 and is discussed briefly in Section 3.3. All work under Task 3 of this program was carried out at Exxon Research and Engineering Company's Engineering Center located at Florham Park, New Jersey.

3.1 CATALYST RECOVERY STUDIES

Catalyst recovery studies were initiated in October, 1976 to define alternative approaches to catalyst recovery and makeup which minimize overall costs, considering the cost of catalyst makeup in the large quantities required for a commercial gasification plant.

3.1.1 Commercial Sources of Potassium and Sodium Catalyst

Work was initiated to assess the potential sources and costs of potassium (K) and mixed potassium/sodium (K/Na) catalysts when produced in the quantities required for a commercial catalytic gasification industry. Estimates of catalyst costs will help to establish incentives for reducing catalyst makeup requirements, such as by adding facilities for the recovery of water-insoluble catalyst to the multistage countercurrent water wash system included in the current Base Case.

An extensive literature investigation was carried out to determine the domestic consumption patterns of alkali metal carbonates, potential catalyst source minerals and compositions, and commercial and developing technology used to produce potassium hydroxide and carbonates. The results of this investigation are summarized in Tables 3.1-I and 3.1-II.

As shown in Table 3.1-I, there are substantial deposits of sodium carbonates in the United States. Na_2CO_3 exists in conjunction with other Na salts in brine from Searles Lake and Owens Lake in California. Larger sources of naturally occurring Na_2CO_3 are found in Wyoming in the form of trona ($Na_2CO_3.NaHCO_3.2H_2O$). A currently untapped source of $NaHCO_3$ which is found in nature is nahcolite. Nahcolite deposits are found in Colorado, Utah, and Wyoming, usually in association with oil shale deposits. Large quantities of technical grade Na_2CO_3 manufactured from trona or via the Solvay process are marketed domestically. Thus, availability of Na_2CO_3 would not be a problem if it were an active catalyst.

Table 3.1-I

PRINCIPAL SOURCES OF POTASSIUM & SODIUM SALTS

Chemical	Current Sources	Potential Alternate Sources	1975 Domestic Consumption (k ST/Yr)	Identified Domestic Mineral Reserves (MST)
Sodium Compounds:				
● Na_2CO_3	Trona deposits in Wyoming and brines in California; also manufactured from NaCl via Solvay process	-	7,500(1)	50,000
● $NaHCO_3$	Carbonation of N_2CO_3 solution; also as a Solvay process intermediate	Nahcolite deposits in Utah, Wyoming and Colorado	200	Very large
Potassium Compounds:				
● K_2CO_3	Carbonation of KOH	Various chemical processes using KCl or K_2SO_4 feed	65	Nil
● $KHCO_3$	Carbonation of K_2CO_3 solution	Engel-Precht process using KCl feed	Small	Nil
● KOH	Electrolysis of KCl (Hg cells)	Electrolysis of KCl (diaphragm and membrane cells)	200	Nil
● KCl	Deposits in New Mexico, Utah, California and Saskatchewan	Deposits in Arizona, Montana, Nebraska, N. Dakota, New Brunswick, U.S.S.R. and Israel	7,900	300(2)
● K_2SO_4	Deposits in New Mexico, Utah, California & Texas	Various chemical processes using KCl	400	Large

Notes: (1) 4,500 kST/yr from trona and 3,000 kST/yr from Solvay process.

(2) An additional 100,000 MST reserve of KCl is in Canada.

(3) $k = 10^3$ $M = 10^6$

Table 3.1-II

ALTERNATIVE PROCESSES FOR PRODUCTION OF POTASSIUM CARBONATE

Process	Developmental Status	Reactions
Electrolysis of KCl	Presently commercial in U.S. (Hg cells). Final development work required to apply diaphragm or membrane cells.	$2\ KCl + 2\ H_2O \longrightarrow 2\ KOH + Cl_2 + H_2$ $2\ KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$
Engel-Precht Process	Commercial in Germany prior to 1938 as a batch operation; during past several years, University of Saskatchewan has done bench-scale work to modify batch operation to continuous.	$MgO + H_2O \longrightarrow Mg(OH)_2$ $Mg(OH)_2 + CO_2 + 2H_2O \longrightarrow MgCO_3 \cdot 3H_2O\downarrow$ $3(MgCO_3 \cdot 3H_2O) + CO_2 + 2KCl \longrightarrow 2(KHCO_3 \cdot MgCO_3 \cdot 4H_2O)\downarrow + MgCl_2$ $KHCO_3 \cdot MgCO_3 \cdot 4H_2O \longrightarrow KHCO_3 + MgCO_3 \cdot 3H_2O\downarrow + H_2O$
Formate Process	Commercial in pre-WW II Germany, ca 1938.	$K_2SO_4 + Ca(OH)_2 + 2CO \longrightarrow 2KHCO_2 + CaSO_4\downarrow$ $2KHCO_2 + O_2 \longrightarrow K_2CO_3 + CO_2 + H_2O$
Reduction of K_2SO_4	Bench-scale studies.	$K_2SO_4 + 3H_2 + CO \longrightarrow K_2S + 3H_2O + CO_2$ $K_2S + CO_2 + H_2O \longrightarrow K_2CO_3 + H_2S$
Electrolysis of K_2SO_4	Bench-scale studies on analagous Na_2SO_4.	$2K_2SO_4 + 2H_2O + 4Hg \longrightarrow 4K(Hg) + O_2 + 2H_2SO_4$ $2K(Hg) + 2H_2O \longrightarrow 2KOH + H_2 + 2Hg$ $2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$

Presently, only limited quantities of potassium are marketed as K_2CO_3 in the United States, and no significant deposits of K_2CO_3 are found in nature. However, the United States and Canada do have large deposits of other K salts from which substantial quantities of KCl and K_2SO_4 are extracted for sale as fertilizer. Such K salts are commonly known as "potash". Potassium carbonate--and other catalytically active K salts such as KOH, $KHCO_3$, and perhaps $KHCO_2$-- must be manufactured from these available KCl or K_2SO_4 source minerals. The K_2CO_3 which is sold today is manufactured by carbonation of KOH produced by electrolysis of KCl.

In addition to electrolysis of KCl, four other processes have been identified for conversion of K salts to K_2CO_3. The development status and major reaction steps for these five K_2CO_3 processes are shown in Table 3.1-II. The final step in some of the processes involves conversion of KOH, $KHCO_3$ or $KHCO_2$ to K_2CO_3. This step may be unnecessary, since these salts are likely to be active gasification catalysts based on earlier bench-scale screening tests. Literature sources indicate adequate reagent availability for the Engel-Precht reaction and the formate reaction. Large quantities of both MgO and $Ca(OH)_2$ are available from normal market sources.

Potassium salt manufacturers have been contacted to supply non-proprietary information on commercial and developing routes to make KOH and K_2CO_3. At present, almost all domestic KOH is made via mercury cell electrolysis of KCl. The small remainder is made via diaphragm cell electrolysis of KCl. K_2CO_3 is made subsequently by carbonating KOH. By the 1985-1990 time frame, the presently developing membrane cell technology will be commercially available for KCl electrolysis. Also recently identified is an Amine Process (or "Modified Solvay" Process) now commercial in France to produce $KHCO_3$. Additional information on these processes will be obtained during the latter half of 1977, including cost information for electrolysis alternatives as discussed below.

3.1.2 "Cash Flow" Analysis of Alternative Catalyst Manufacturing Processes

Scoping studies were carried out to define and compare the "cash flows" for the alternative processes for potassium catalyst manufacture listed in Table 3.1-II. The objective of these studies was to screen the manufacturing alternatives to select candidates for further, more detailed evaluation.

The initial step in defining the "cash flows" was to develop costs and values for the various raw materials and byproducts involved in these processes. Representative prices (f.o.b. source) were developed for all chemicals of interest based on Chemical Marketing Reporter cost trends and vendor contacts. Typical rail shipping costs to the Illinois area were added to the f.o.b. prices of the raw materials.

The results of the catalyst manufacture "cash flows" studies are summarized in Table 3.1-III. For each process, the "minimum catalyst cost" shown in the table consists of the estimated catalyst manufacture plant raw materials costs, the estimated investment charges and operating costs for utilities, and any additional costs due to changes required in the SNG plant.

Table 3.1-III

CATALYST MANUFACTURE CASH FLOW STUDIES

ECONOMIC SUMMARY

Catalyst Source	Catalyst Form	Relative Minimum Catalyst Cost (1) (% of Purchased KOH Cost on K-Equivalent Basis)	Estimated Added Investment Level
• Purchased Chemicals at Market Price:			
+ Purchased KOH	45% KOH Solution	100 (Base)	Base
+ Purchased K_2CO_3	Calcined K_2CO_3	121	Nil
• Catalyst Manufacture via Electrolysis:			
+ KCl Electrolysis	30-45% KOH Solution	26-33	High
+ K_2SO_4 Electrolysis	45% KOH Solution	71	High
• Catalyst Manufacture via "Chemical" Processes:			
+ Engel-Precht Process (KCl Feed)	25% $KHCO_3$ Solution	74	Medium
+ Formate Process (K_2SO_4 Feed)	87% $KHCO_2$ Solution	96	Low/Medium
+ K_2SO_4 Reduction	Calcined K_2CO_3	105	Medium

Note:

(1) Minimum Catalyst Cost consists of the raw materials costs, investment charges and operating costs for utilities, and any additional costs (investment and operating) due to changes in the SNG plant. It excludes the cost of investment for the catalyst manufacturing facilities and associated product tankage.

It excludes the investment charges (maintenance and return) for the catalyst manufacturing facilities and associated product tankage.

The "minimum catalyst costs" are shown as percentages of the cost of KOH solution purchased on the open market at the price listed in the Chemical Marketing Reporter. This price was confirmed by contacts with KOH manufacturers. As indicated previously, all domestic KOH is produced by electrolysis of KCl. As indicated in Table 3.1-III, purchased K_2CO_3 is more expensive than KOH at market prices. This is a reflection of the fact that K_2CO_3 is presently manufactured from KOH using additional carbonation and drying steps. Since KOH has been shown to be at least as effective a gasification catalyst as K_2CO_3 in fixed bed gasification tests, it appears that KOH is the preferred form of makeup catalyst for catalytic gasification, if electrolysis is the method of catalyst manufacture.

"Cash flows" for two major categories of manufacturing processes have been developed for comparison with purchased KOH: electrolysis processes and chemical processes. On an economic basis consistent with the basis used for gasification screening studies, the "minimum cost" for KOH manufacture via KCl electrolysis ranges from 26-33% of the KOH market price. As indicated above, this "cash flow" is based on estimated feedstock and utilities requirements, and does not include capital charges on electrolysis investment. Since the investment for electrolysis is expected to be fairly large, the "gap" between the "minimum cost" and the market price could be eliminated when investment charges are included. On the other hand, projected costs for catalyst makeup, even for KOH from KCl electrolysis, could differ from current market prices because of differences in factors such as plant size and location, electrolysis technology, KCl feedstock grade and cost, unit costs of utilities, acceptable return on investment, and the contractual basis for supply. As an example of the latter, KOH might be supplied by a chemical company under long-term contract at a price below that prevailing in the open market. In order to help in understanding the potential impact of such factors on the economics of KOH manufacture, more detailed studies of KCl electrolysis are underway. Vendor contacts are being made to obtain estimates of electrolysis investments and operating cost factors for use in these studies. The total and relative costs of KCl electrolysis alternatives in the context of a future commercial catalytic gasification industry should be better defined at the completion of these studies in the latter half of 1977.

"Cash flows" were also estimated for presently non-commercial manufacturing alternatives: electrolysis of K_2SO_4 and three "chemical" processes (the Engel-Precht process, the formate process, and direct reduction of K_2SO_4). The chemistry and development status of each of these alternatives was discussed in Section 3.1.1. Although different makeup catalyst forms are involved, all have similar catalytic activity per potassium equivalent. The relative "minimum catalyst costs" have been expressed on a potassium-equivalent basis to eliminate the effect of the differences in form. To put these minimum cash flows in better perspective, the last column of Table 3.1-III indicates what the relative magnitudes of added investment for the catalyst manufacturing alternatives are likely to be based on current information and judgement.

Based on these scoping studies, the most attractive chemical process appears to be the KCl-based Engel-Precht process. The K_2SO_4-based processes (K_2SO_4 electrolysis, formate, and K_2SO_4 reduction) all suffer from the fact that potassium from K_2SO_4 is estimated to cost approximately twice as much as potassium from KCl. With investment charges included, it is likely that these processes would exceed the cost of purchased KOH.

Although the Engel-Precht process is more costly on this "cash flow" basis than KCl electrolysis, the latter is expected to require the larger investment. Thus, it is not apparent, from these studies alone, how the total cost of KOH from a grass-roots KCl electrolysis plant would compare with purchased KOH or the equivalent $KHCO_3$ from a grass-roots Engel-Precht plant. To help in this comparison, a more definitive screening evaluation of the Engel-Precht process was carried out, including an estimate of the investment required. The results of this study are presented in the following section.

3.1.3 Screening Evaluation of the Engel-Precht Process

A screening-quality evaluation of the Engel-Precht process for manufacturing potassium catalyst for the catalytic gasification process has been completed. Based on the "cash flow" scoping studies reported above, the Engel-Precht process appeared to be the most economically attractive of the alternative chemical processes which were considered.

Historically, the Engel-Precht process was used in Germany to manufacture potassium carbonate and bicarbonate commercially as a batch operation from about 1900 to 1938. In about 1938, the formate process (K_2SO_4 to $KHCO_2$) superceded the Engel-Precht process. In the last 20 years, Israel and Saskatchewan have had renewed interest in the Engel-Precht process to convert their KCl deposits to K_2CO_3 or $KHCO_2$ in a continuous operations. All the process basis information used in developing this study was taken from the open literature. Significant uncertainties exist as to the quality and consistency of the available data. Based on the literature, no commercial Engel-Precht plants, continuous or batch, are presently in operation.

The Engel-Precht process involves four reaction steps, as follows:

$$(1)\quad MgCl_2 + CaO.MgO + 2H_2O \rightarrow 2Mg(OH)_2 \downarrow + CaCl_2$$

$$(2)\quad Mg(OH)_2 + CO_2 + 2H_2O \rightarrow MgCO_3.3H_2O \downarrow$$

$$(3)\quad 3(MgCO_3\cdot 3H_2O) + CO_2 + 2KCl \rightarrow 2(KHCO_3\cdot MgCO_3\cdot 4H_2O) \downarrow + MgCl_2$$

$$(4)\quad KHCO_3\cdot MgCO_3\cdot 4H_2O \rightarrow KHCO_3 + MgCO_3\cdot 3H_3O \downarrow + H_2O$$

Because reaction (4) requires careful control of reaction conditions to produce reusable $MgCO_3 \cdot 3H_2O$, only a dilute $KHCO_3$ solution can be made directly (about 9 wt.% maximum). Steam-heated evaporators have been included in the screening case to concentrate the product solutions to 25 wt.% for feed to the catalyst addition facilities.

Investment costs for this Engel-Precht screening evaluation fall into three main categories: costs of materials handling and processing equipment to carry out the Engel-Precht reactions, costs of facilities required to supply needed utilities (principally the steam for the evaporators) and net costs of modifying the catalytic gasification plant to receive catalyst makeup as 25% $KHCO_3$ solution. The Engel-Precht process facilities were cost-estimated based on individual equipment specification, and the remaining facilities were prorated from the catalytic gasification "Base Case".

The breakdown of the product $KHCO_3$ cost for the Engel-Precht process screening evaluation is shown in Table 3.1-IV. Costs are shown as percentages of the cost of KOH solution purchased on the open market (on a potassium-equivalent basis). This is consistent with the basis used in presenting the results of the "cash flow" analyses in Table 3.1-III. As shown in Table 3.1-IV, this screening study indicates that the total estimated cost of $KHCO_3$ catalyst from an Engel-Precht plant is about 94% of the cost of purchased KOH. This 6% advantage appears to be insufficient to justify further development work on the Engel-Precht process as a catalyst source for catalytic gasification. However, a final comparison must await completion of ongoing studies to better define the cost of KCl electrolysis to produce KOH.

3.1.4 "Cash Flow" Analysis of Alternative Catalyst Recovery Processes

Scoping studies to evaluate the "cash flows" for several alternatives to recovering water-insoluble catalyst from spent gasifier char and fines have been completed. The alternatives studied include two cases involving the "hydrothermal digestion" of gasifier solids with $Ca(OH)_2$ and three processes which combine recovery of water-insoluble catalyst using acid wash with catalyst manufacture via electrolysis of potassium salts or the formate process. These screening economics provide an initial estimate of the incentives for the recovery of insoluble catalyst to help guide ongoing laboratory studies.

To provide economic basis information for these "cash flow" studies the current sources and costs of lime (CaO) and hydrated lime ($Ca(OH)_2$) were investigated, including inquiries to vendors of these materials in the Illinois area. Also, estimates of typical transportation costs for the shipment of calcium compounds to a commercial gasification plant were developed. Raw materials costs favor the use of lime rather than hydrated lime as the source calcium chemical. In turn, lime is normally produced by calcination of limestone ($CaCO_3$) at plants located near natural limestone deposits.

Table 3.1-IV

ENGEL-PRECHT PROCESS SCREENING EVALUATION BREAKDOWN OF RELATIVE PRODUCT CATALYST COST

Basis: Cost of Purchased KOH = 100 (Note 1)

● Raw Materials:	
- KCl (Agricultural Grade)	32
- CaO·MgO (Calcined Dolomite)	6
● Utilities:	
- Coal Fuel	4
- Raw Water	Nil
- Cooling Water	Nil
- Electric Power	5
- Low Pressure Steam (Note 2)	(3)
● Byproduct Sulfuric Acid	(1)
● Labor and Related Costs	5
● Investment-Related Costs	7
● Capital Charges (Note 3)	39
Total Product Catalyst Cost	94

Notes:

(1) On a potassium-equivalent basis.

(2) Operating cost credit for low pressure steam based on using non-condensing steam turbine drivers to back out purchased power.

(3) Capital charges based on 100% equity financing with 10% DCF return.

The results of the catalyst recovery "cash flows" are summarized in Table 3.1-V. As in Table 3.1-III, the minimum catalyst cost, estimates for the alternatives are compared to the cost of purchased KOH. In each case, this cost consists of chemicals costs, utilities operating cost, and additional costs due to changes required in the existing SNG plant. However, the "minimum catalyst cost" excludes investment charges associated with the additional catalyst recovery system investments required for recovery of the water-insoluble catalyst. The last column of Table 3.1-V indicates the relative magnitudes of these investments based on current information and judgment. For the hydrothermal digestion cases, the "minimum catalyst cost" refers to the incremental catalyst which is recovered in hydrothermal processing over and above catalyst recovered in water washing only. For the acid wash cases which incorporate catalyst manufacture, this cost refers to the total catalyst supplied by the combined system.

Based on these scoping studies, catalyst recovery via hydrothermal digestion with $Ca(OH)_2$ offers the potential for substantial savings relative to purchased KOH at the market price. The "minimum cost" of the incremental potassium recovered via this route was estimated to be 36-54% of the cost of purchased KOH, depending on $Ca(OH)_2$ requirement. This evaluation was based on bench-scale experiments showing 80% recovery of water-insoluble potassium with a calcium-to-potassium mole ratio ranging from 0.53-0.8 ($Ca(OH)_2$ added per total potassium originally present). Although investment charges for hydrothermal digestion are not included in the "minimum cost", the added investment required for these facilities is expected to be relatively small.

Catalyst recovery via acid wash integrated with catalyst manufacture appears less attractive. Three process concepts of this type were screened. The first two combine recovery of water-insoluble catalyst using acid wash with electrolysis of potassium salts (i.e., KCl and K_2SO_4). These salts are produced by acidifying the water-washed gasifier solids (char and fines) with HCl or H_2SO_4, and then neutralizing with KOH to precipitate and separate catalytically inactive cations such as aluminum, silicon, and iron. Makeup potassium as KCl or K_2SO_4 is also fed to electrolysis. The KOH produced is sent to the neutralization step and to the catalyst addition step upstream of the gasifier. The third process concept also begins by acidifying the gasifier solids with H_2SO_4. Then, the solids are neutralized with $Ca(OH)_2$, precipitates are removed, and carbon monoxide is added along with additional $Ca(OH)_2$ to carry out the "formate" process reaction producing catalytically active $KHCO_2$ and solid $CaSO_4$. Since all three of these cases are expected to require large investments, it is apparent from the "minimum catalyst costs" in Table 3.1-V that the total costs for these alternatives will probably exceed the cost of purchased KOH.

Based on the results of these "cash flow" studies, a screening study will be carried out for catalyst recovery via $Ca(OH)_2$ digestion in the latter half of 1977. Investments and operating costs for this case will be compared with costs for water washing only to select the preferred catalyst recovery approach for inclusion in the study design described in Section 3.7.

Table 3.1-V

CATALYST RECOVERY CASH FLOW STUDIES

ECONOMIC SUMMARY

Catalyst Source	Catalyst Form	Relative Minimum Catalyst Cost(1) (% of Purchased KOH Cost on K-Equivalent Basis)	Estimated Added Investment Level
o Purchased KOH at Market Price:	45% KOH Solution	100 (Base)	Base
o Catalyst Recovery via "Hydrothermal Digestion":			
+ Gasifier Solids + $Ca(OH)_2$ (Ca/K=0.53)	35% Mixed K-Salt Solution	36(2)	Low
+ Gasifier Solids + $Ca(OH)_2$ (Ca/K=0.80)	35% Mixed K-Salt Solution	54(2)	Low
o Catalyst Recovery via Acid Wash Integrated with Catalyst Manufacture:			
+ Gasifier Solids + HCl + KCl Electrolysis	30% KOH Solution	83	Very High
+ Gasififer Solids + H_2SO_4 + K_2SO_4 Electrolysis	30% KOH Solution	92	Very High
+ Gasifier Solids + H_2SO_4 + Formate Process	30% $KHCO_2$ Solution	100	High

Note:

(1) Minimum Catalyst Cost consists of chemicals costs, operating costs for utilities, and any additional costs (investment and operating) due to changes in the existing SNG plant facilities. It excludes the cost of investment for catalyst recovery and, where present, catalyst manufacturing and associated product tankage.

(2) Minimum Catalyst Cost for the hydrothermal treating alternatives reflects the cash flow per unit of incremental catalyst recovered above that recoverable by water wash.

3.2 GASIFICATION REACTOR SYSTEM STUDIES

Studies were undertaken to identify preferred reactor system configurations for catalytic gasification and estimate the impacts of reactor operating conditions on reactor volume and other process variables.

3.2.1 Evaluation of the Incentive for Secondary Gasification

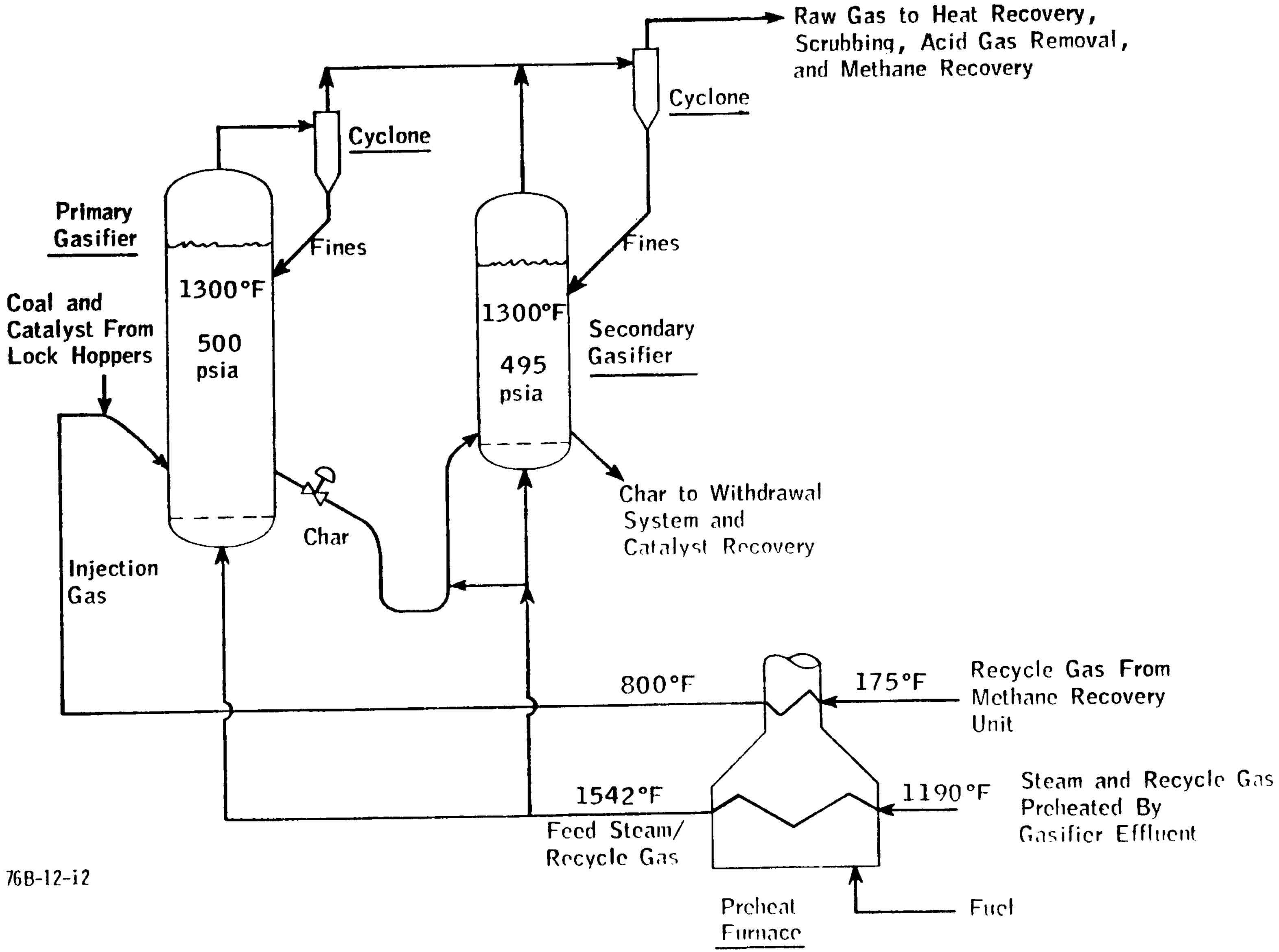
During the fourth quarter of 1976, an engineering screening study was carried out to determine whether there is an economic incentive for adding a secondary gasification step to the Exxon Catalytic Coal Gasification Process. The objective of secondary gasification is to raise overall process efficiency by increasing carbon conversion above that attainable in a single fluidized bed. The gas cost with secondary gasification was estimated to be only 0.8 percent less than the "Base Case" gas cost. This small economic credit does not appear to offset the development risks due to greater system complexity and the potential for added technical problems. However, this conclusion could change if it were not practical to obtain high carbon conversions in a single reaction step or if coal or catalyst costs increase significantly. The basic assumptions, results, and economic sensitivities for the secondary gasification case are discussed below.

A schematic reactor system flow plan with secondary gasification is shown in Figure 3.2-1. The primary stage of the gasifier gasifies 90 percent of the feed carbon as in the current Catalytic Gasification "Base Case", and the secondary stage gasifies enough additional carbon so that the overall carbon conversion is 95 percent. The secondary gasifier operates at a slightly lower pressure than the primary gasifier and receives as feed all of the entrained solids which can be captured from the primary effluent gas by an overhead cyclone and all of the char withdrawn from the primary gasifier. The secondary gasifier is fed a portion of the preheated steam/recycle mixture and operates at a relatively low gas velocity to minimize fines entrainment. The coal injection gas supplies a second source of recycle gas for the primary gasifier. Since the steam and recycle mixture is split on the basis of the steam required for each gasifier, the two gasifiers are not individually in recycle gas balance. (Recycle gas balance is achieved when CO + H_2 in equals CO + H_2 out.) Recycle gas balance could have been achieved by heating the steam and recycle streams separately and blending the appropriate mixture for each gasifier. Since this would have increased the complexity and cost of the preheat furnace, it was judged that the simpler scheme would be better.

The process basis and some results of the material and energy balances are presented in Table 3.2-I. The key process basis items are unchanged from the Base Case except where indicated in the table. The material balance was calculated assuming shift, methanation, and steam-graphite equilibrium in each gasifier. The assumption of steam-graphite equilibrium results in feed steam conversions of 43 percent in the primary and 54 percent in the secondary which appear reasonable based upon the kinetic data obtained to date. The temperature in the primary gasifier was fixed at 1300°F and the secondary gasifier temperature was determined by a trial-and-error material and energy balance. The secondary gasifier temperature was

Figure 3.2-1

EXXON CATALYTIC GASIFICATION PROCESS WITH SECONDARY GASIFICATION



76B-12-12

Table 3.2-I

INCENTIVE FOR SECONDARY GASIFICATION SUMMARY OF PROCESS BASIS AND HEAT AND MATERIAL BALANCE(1)

	Base Case	Secondary Gasification Incentive Case
Reactor System	"Primary" Gasifier Only	Primary and Secondary Gasifiers (Figure 1)
Feed Carbon Conversion:		
Primary Gasifier	90%	90%
Overall	90%	95%
Conditions:		
Primary Gasifier	1300°F/500 psia	1300°F/500 psia
Secondary Gasifier	--	1300°F/495 psia
Secondary Gasifier Sizing Basis:		
Superficial Outlet Velocity	--	22.5% of Primary
Volumetric Gasification Rate	--	50% of Primary
Preheat Furnace Coil Outlet Temperature	1540°F	1542°F
Key Stream Rates:(2)		
Coal Feed to Gasifiers	14,490 ST/SD	13,835 ST/SD
Coal to Boiler Fuel	1,860 ST/SD	1,925 ST/SD
Coal to Dryer Fuel	650 ST/SD	620 ST/SD
Total Coal	17,000 ST/SD	16,380 ST/SD
Total Gasifier Steam Rate	84,164 moles/hr	85,633 moles/hr
Total Recycle Rate	51,292 moles/hr	51,605 moles/hr
Split of Preheated Steam/Recycle	All to Primary	94.0/6.0% to Primary/Secondary
By-Product Rates:		
Ammonia	239 ST/SD	234 ST/SD
Sulfur	400 LT/SD	403 LT/SD
Sulfuric Acid	177 ST/SD	179 ST/SD
Utilities Requirements:		
Electric Power	159 MW	157 MW
Raw Water	5,500 GPM	5,500 GPM
Overall Thermal Efficiency(3)	67.1%	69.5%

Notes:

(1) For plant sized to produce 257 GBtu/SD SNG.

(2) All coal rates are for Illinois coal as received from coal cleaning. Higher heating value is 10,620 Btu/lb.

(3) Thermal efficiency includes purchased electric power (evaluated at a power plant heat rate of 8,950 Btu/KWH) and by-products.

found to be essentially the same as that for the primary gasifier, 1300°F. Also, the steam/recycle preheat furnace coil outlet temperature was calculated to be almost identical to the Base Case value of 1540°F.

Stream rates are presented in Table 3.2-I for the Base Case and the Secondary Gasification Incentive Case for plants producing 257 GBtu/SD net SNG product. Steam and recycle rates are up slightly, but the gasifier coal rate is down about 5 percent because of the higher overall carbon conversion. This increase in gas production per unit of coal increased the overall process thermal efficiency from 67.1 percent to 69.5 percent. These thermal efficiencies take into account all energy losses including those in the power plant supplying the purchased electrical power. In sizing the secondary gasifier, the outlet gas velocity was assumed to be 22.5 percent of the Base Case primary velocity and the volumetric carbon gasification rate was assumed to be 50 percent of the rate in the primary.

A breakdown of the relative investment for the Secondary Gasification Incentive Case as compared to the Base Case is presented in Table 3.2-II. The total plant investment with secondary gasification has increased by 1.0 percent over the Base Case investment. The addition of the secondary gasifier increased the investment for gasifier vessels by about 20 percent. Reductions in the investment for other areas of the plant offset about half the added investment in the gasifier area. The reduced coal rate decreased the investment for the coal feed and catalyst handling areas. The lower coal rate and higher overall carbon conversion reduced the spent solids rate to the catalyst recovery area to 84 percent of the Base Case rate. This resulted in investment savings in the char withdrawal, catalyst recovery, and waste treating areas.

A breakdown of the relative gas cost for the Secondary Gasification Incentive Case as compared to the Base Case is shown in Table 3.2-III. The total gas cost with secondary gasification is 0.8 percent less than the Base Case gas cost. Savings in coal and catalyst are partially offset by increased capital charges associated with the net added investment. Thus, based on these results, there appears to be only a marginal incentive for adding a secondary gasification step at this stage in the development.

This conclusion is dependent on the validity of the basis assumptions, which will become clearer as the development proceeds. If conversion of 90 percent of the feed carbon in a single reactor is not practically obtainable--such as with a relatively friable coal feed which would produce excessive fines--or if coal cost or catalyst cost increases significantly, then there would be increased incentive to develop secondary gasification. The incentive would also be larger if the disposal of char containing nearly 50 carbon becomes an economic or environmental problem. For example, if a significant charge per ton is added for solid waste disposal, the savings shown for secondary gasification could increase from the present 0.8 percent to about 1.5-2.5 percent, depending on the assumptions made. Another area of uncertainty is gasification rate. If the volumetric carbon gasification rate in the secondary gasifier is equal to the rate in the primary, rather than 50 percent of that rate, then the Secondary Gasification Case would save an additional 0.5 percent relative to the Base Case.

Table 3.2-II

INCENTIVE FOR SECONDARY GASIFICATION INVESTMENT BREAKDOWN

Basis: Base Case Total Investment = 100

	Base Case	Secondary Gasification Incentive Case
Coal Prep. and Materials Handling		
Coal Handling	5.3	5.2
Char/Ash Handling	1.1	1.1
Catalyst Handling	1.2	1.2
Coal Drying/Catalyst Addition	3.7	3.6
Subtotal	11.3	11.1
Onsites		
Reactor System	17.4	19.1
Preheat Furnace	5.6	5.6
Product Gas Cooling/Scrubbing	9.7	9.7
NH_3/H_2S Recovery	2.7	2.6
Acid Gas Removal/Sulfur Recovery	14.2	14.2
Methane Recovery/Refrigeration	8.6	8.6
Catalyst Recovery	1.9	1.5
Common Facilities	4.4	4.4
Subtotal	64.5	65.7
Offsites		
Waste Treating	2.9	2.8
By-product Handling	0.7	0.7
Miscellaneous Offsites	4.7	4.7
Subtotal	8.3	8.2
Utilities		
Raw Water/CW/BFW Treating	2.0	2.0
Steam Generation	7.2	7.3
Flue Gas Desulfurization	3.4	3.4
Electric Power Distribution	2.9	2.9
Miscellaneous Utilities	0.4	0.4
Subtotal	15.9	16.0
TOTAL	100.0	101.0

Table 3.2-III

INCENTIVE FOR SECONDARY GASIFICATION
SUMMARY OF RELATIVE GAS COSTS

Basis: Base Case Total Gas Cost = 100

	Base Case	Secondary Gasification Incentive Case
● Coal	26.1	25.2
● Gasification Catalyst	6.3	5.9
● By-products		
- Ammonia	(3.2)	(3.2)
- Sulfur	(1.9)	(1.9)
- Sulfuric Acid	(0.6)	(0.6)
Subtotal	(5.7)	(5.7)
● Operating Costs		
- Electric Power	7.9	7.8
- Raw Water	0.1	0.1
- Labor and Related Costs	5.6	5.6
- Investment-Related Costs	9.3	9.4
- Other Catalysts and Chemicals	0.6	0.6
Subtotal	23.5	23.5
● Capital Charges(1)	49.8	50.3
TOTAL GAS COST	100.0	99.2

Note: Capital charges based on 100% equity financing with 10% DCF return.

There may be benefits in catalyst recovery performance due to the reduced carbon content of the residual solids from secondary gasification The present study takes credit only for the reduced weight of char/ash solids to be washed. If catalyst recovery can be operated with more concentrated slurries of char/ash solids after those solids are processed in a secondary gasifier, the gas cost savings for secondary gasification might increase from 0.8 percent to about 2 percent. If two or more of these revised assumptions prove to be applicable, the potential gas cost savings for secondary gasification could increase to 3 percent or more. Thus, the secondary gasification alternative should be held in reserve pending further definition of the catalytic gasification process performance in the base configuration.

3.2.2 Impacts of Catalytic Gasifier Operating Conditions

Engineering screening studies were carried out to evaluate the commercial impacts of alternative catalytic gasifier operating conditions, such as catalyst composition and loading, temperature, and steam rate. Four commercial-scale cases have been evaluated for economic impacts as sensitivities to the current "Base Case". They are as follows: a case with the base temperature (1300°F) and 15 wt.% K_2CO_3 catalyst loading on feed coal (rather than the Base 7.5% K_2CO_3/7.5% Na_2CO_3); a case with lower catalyst loading (10% K_2CO_3); a case with lower temperature (1200°F) and 15% K_2CO_3 catalyst; and a case with a higher steam rate at 1300°F with 15% K_2CO_3 catalyst. In addition, the Base Case itself has been revised to reflect the recent laboratory data showing in low activity for sodium and a selective tie-up of potassium as inactive aluminosilicates in the mixed K_2CO_3/Na_2CO_3 system.

A summary of the cases evaluated is presented in Table 3.2-IV. In each of these cases, the steam and recycle gas rates were set based on assumptions made about the extent of three reactions in the gasifier effluent gases:

Shift $CO + H_2O = CO_2 + H_2$

Methanation $CO + 3H_2 = CH_4 + H_2O$

Steam-Carbon $C_{(s)} + H_2O = CO + H_2$

The gases were assumed to be in shift equilibrium in all cases. The gasifier model described below was used to predict the effective methanation equilibrium temperature for each case. Methanation was estimated to be essentially at equilibrium for all of the 1300°F cases. However, the methanation equilibrium temperature for the 1200°F case was estimated to be 1210°F, that is, a 10°F approach. In all cases except the "Higher Steam Rate" case, the approach to steam-carbon equilibrium was held constant so that the volumes calculated by the gasifier model would reflect differences due only to reaction kinetics and not to equilibrium. The technique used to do this was to set steam rate so that the gasifier effluent gas was "at equilibrium" for the steam-carbon reaction over graphite. (Since the carbon in coal de-

Table 3.2-IV

IMPACTS OF CATALYTIC GASIFIER OPERATING CONDITIONS
SUMMARY OF CASES AND ECONOMICS (1)

	"Current" Base Case 15% Mixed Catalyst Previous Evaluation	 15% Mixed Catalyst Present Evaluation	Sensitivity Cases 15% K_2CO_3 Catalyst	 10% K_2CO_3 Catalyst	 Lower Temperature	 Higher Steam Rate
• Gasifier Operating Conditions						
+ Pressure, psia	500	500	500	500	500	500
+ Temperature, °F	1300	1300	1300	1300	1200	1300
+ Catalyst Loading, Wt% on Dry Coal						
- K_2CO_3	7.5	7.5	15	10	15	15
- Na_2CO_3	7.5	7.5	-	-	-	-
• Extent of Gasifier Reactions						
+ Steam Conversion, % Feed Steam	43.0	43.0	43.0	43.0	40.3	38.9
+ Carbon Conversion, % Feed C	90.0	90.0	90.0	90.0	90.0	90.0
+ Approach to Methanation Equili.	0	0	0	0	10	0
• Results of Heat and Material Balance						
+ Coal Rates, ST/SD (2)						
- Coal to Process, ST/SD	14,490	14,520	14,505	14,480	14,360	14,[illegible]
- Coal to Boilers, ST/SD	1,860	1,865	1,865	1,860	2,150	2,3[illegible]
- Coal to Dryers, ST/SD	650	640	635	470	625	6[illegible]
- Total Coal, ST/SD	17,000	17,025	17,005	16,810	17,135	17,[illegible]
+ Gasifier Feed Steam, Moles/hr	84,164	84,291	84,225	84,062	88,927	101,4[illegible]
+ Total Recycle Rate, moles/hr	51,292	51,353	51,353	51,253	34,314	61,[illegible]
+ Normal Steam/Recycle Preheat, °F	1540	1554	1548	1534	1397	15[illegible]
• Relative Gasifier Volume (3)	100	201	88	119	135	71
• Relative Plant Investment (4)	100.0	113.3	100.0	101.4	98.0	102.4
• Relative Gas Cost (4)	100.0	111.0	105.4	104.9	103.6	107.5

Notes:

(1) For plants sized to produce 257 G Btu/SD SNG.
(2) Coal rate is for Illinois coal as received from coal cleaning. Higher heating value is 10,620 Btu/lb
(3) Relative fluid bed volumes are shown as percentages of the volume previously estimated for the "Base Case."
(4) Relative investments and gas costs are shown as percentages of the totals for the previous evaluation of the "Base Case."

mixed chars has a thermodynamic activity greater than graphite, the steam-carbon gasification reaction still proceeds at a significant rate when the gases are at steam-graphite "equilibrium.")

The gasifier volumes for the sensitivity cases and the present evaluation of the Base Case were predicted using a fluidized bed kinetics/contacting model of the catalytic gasifier developed with Exxon funds prior to the start of the Predevelopment Program. (This model will be updated later in the current program.) The model predictions were based on preliminary estimates of the gasifier char properties, based largely on data obtained in Fluid Bed Gasifier operations conducted prior to the present program. These inputs to the model will be updated in the latter part of 1977 when more information is available from the current operations of the Fluid Bed Gasifier. Sensitivity studies using the gasifier model have identified the weight fraction catalyst in the gasifier char as the most important char property. Char bulk and particle densities also have a moderate impact on predicted gasifier volumes.

The predicted gasifier volumes are shown in Table 3.2-IV as percentages of the volume estimated for the previous evaluation of the Base Case with 7.5% K_2CO_3/7.5% Na_2CO_3 mixed catalyst. In using the gasifier model, the activity of this same mixed catalyst in the current "Base Case" was assumed to be 50 percent of the activity of 10% K_2CO_3 catalyst. This may be somewhat optimistic based on recent laboratory data from fixed-bed gasification runs, which showed only about one-third the relative activity for mixed catalyst. As shown, the fluid bed volume now predicted for the 15% mixed catalyst "Base Case" is roughly twice the previous estimate. However, with 15% K_2CO_3, the volume is 12 percent less than the previous case. And, with 10% K_2CO_3, the volume is only 19 percent greater than the previous estimate. All cases are sized to produce 257 GBtu/SD SNG. Four gasifier trains are provided in all cases except the present evaluation of the Base Case, which has six trains because of the large volume required.

Total plant investments and gas costs are shown in Table 3.2-IV as percentages of the corresponding values for the previous evaluation of the Base Case. The "current" Base Case has increased in cost by 11.0%, reflecting increased gasifier volume and increased catalyst makeup cost due to the preferential tie-up of potassium as inactive aluminosilicates.

The sensitivity cases using K_2CO_3 catalyst, all provide investment and gas cost savings relative to mixed catalyst in the <u>present</u> evaluations. However, the gas costs are increased by 3-5% relative to the previous evaluation of the Base Case due to the higher cost of K_2CO_3 relative to Na_2CO_3. With K_2CO_3 catalyst, the incentive increases to reduce catalyst makeup cost by recovering water-insoluble catalyst tied up with the ash. As described previously, laboratory and engineering studies are underway to evaluate catalyst recovery alternatives.

To identify the impacts of gasifier conditions, it is best to compare the 15% K_2CO_3 catalyst case with each of the other three sensitivity cases in turn. Based on these comparisons, lowering the gasifier temperature from 1300°F to 1200°F saves about 2%, reducing K_2CO_3 catalyst loading from

15% to 10% saves about 0.5%, and increasing the gasifier feed steam rate by 20% costs an extra 2%.

It is premature to draw firm conclusions regarding preferred gasifier operating conditions from these screening studies, because the bases do not necessarily reflect the extensive data being obtained in bench and FBG runs. In particular, the gasifier model has not yet been updated to reflect the recent FBG operations. Also, the economic impacts are not necessarily linear or additive, because of the complexity of the various gasification plant balances. However, it is clear that data on FBG and fixed bed operations at temperatures lower than 1300°F or at K_2CO_3 catalyst loadings lower than 15% should be closely reviewed to determine whether the gasifier volumes used in these sensitivity studies are representative and, hence, whether the savings shown are attainable.

Heat and material balances and gasifier model volume predictions were developed for several cases in addition to the cases presented in Table 3.2-IV. Table 3.2-V presents the key results for all cases studied. The cases in the table are sensitivities to the 15% K_2CO_3 case. This catalyst and loading was maintained as a common basis in all but the catalyst composition and loading sensitivities. However, the process stream rates are shown relative to the previous evaluation of the 15% mixed catalyst Base Case. Gasifier volumes are shown relative both to that case and to the 15% K_2CO_3 common basis case. All cases have been sized to produce 257 GBtu/SD SNG.

3.3 CATALYTIC COAL GASIFICATION STUDY DESIGN

Work began in June, 1977 on the development of the process basis for a new Catalytic Coal Gasification Study Design. The Study Design will reflect the current conception of a commercial catalytic gasification plant producing approximately 250 MSCF/SD of SNG from Illinois coal. Estimates will be made of both investment and operating costs. Preparation of this Study Design will involve the major share of the engineering effort on the Predevelopment Program during the second half of 1977.

During June, an initial plan for the Study Design was prepared. The first major step is to develop the process basis for the gasifier, recycle loop, and catalyst loop. Information from several sources will be gathered and reviewed as part of the basis-setting effort. Laboratory data generated during the current program will be reviewed to determine their impact on the Study Design. Technical experts in Exxon Engineering's Technology Department will contribute special studies and recommendations on critical plant areas. Work done under the separate contract on "Scale-Up Requirements of the Exxon Catalytic Coal Gasification Process" (ERDA Contract No. Ex-76-C-01-2480) will also be reviewed to incorporate applicable technical findings.

Other key steps in the Study Design effort include developing the onsites process flowsheets, detailed heat and material balances, and equipment specifications lists. Overall plant balances will be prepared for steam, electric power, and other utilities, and equipment lists will be compiled for all required utilities and general offsites facilities. The

Table 3.2-V

IMPACT OF CATALYTIC GASIFIER OPERATING CONDITIONS ON GASIFIER VOLUME REQUIREMENT

Cases are Defined in Terms of Changes Made from the Following Common Gasifier Basis:

500 psia, 1300°F, 15% K_2CO_3 Catalyst Loading, 90% Carbon Conversion (1)

	Percentage Change --------in Flow Rates-----			Normal	Relative Gasifier Volume	
Cases	Coal	Steam	Recycle	Preheat Temperature	vs. Previous Base Case (2)	vs. Common Basis Case
Impact of Catalyst Composition						
• Previous Evaluation of Base Case: 7.5% K_2CO_3/7.5% Na_2CO_3 Catalyst	Base	Base	Base	1540°F	100	114
• Present Evaluation of Base Case: 7.5% K_2CO_3/7.5% Na_2CO_3 Catalyst	0%	0%	0%	1554°F	201	229
Impact of Catalyst Loading						
• Common Basis Case: See Above (15% K_2CO_3 Catalyst)	0%	0%	0%	1548°F	88	100
• 10% K_2CO_3 Catalyst	0%	0%	0%	1534°F	119	136
Impact of Gasifier Temperature						
• 1200°F	-1%	+6%	-32%	1397°F	135	154
• 1350°F	+1%	+1%	+29%	1603°F	77	88
Impact of Gasifier Steam Rate						
• Base Steam + 20%	0%	+20%	+20%	1502°F	71	81
• Base Steam - 20%	0%	-20%	-17%	1616°F	142	162
Impact of Two Simultaneous Changes						
• 1200°F and Base Steam + 32%	-1%	+32%	-12%	1353°F	115	131
• 10% K_2CO_3 Catalyst and Base Steam + 20%	0%	+20%	+19%	1491°F	97	111
Impact of Gasifier Pressure						
• 350 psia	0%	+1%	+27%	1491°F	129	147
• 700 psia	+1%	0%	-19%	1630°F	66	75
Impact of Carbon Conversion						
• 80% Carbon Conversion	+10%	-4%	-2%	1601°F	100	114

Notes:

(1) For plant sized to produce 257 G Btu/SD SNG.

(2) In this column, fluid bed volumes are shown as percentages of the volume previous estimated for the Base Case.

total capital investment for the plant will be estimated. Operating costs and overall product cost will also be estimated. The Study Design will be completed at the end of the contract period, December 31, 1977.

Appendix A

SUMMARY OF DATA FROM SELECTED FDG YIELD PERIODS

Material Balance Period	11	12	13	16	18	19
Yield Period	YP-202	YP-203	YP-204	YP-207	YP-209	YP-210
Date & Time	11:30 2-11-77 11:30 2-12-77	11:30 1-19-77 6:30 2-20-77	15:30 3-9-77 7:30 3-10-77	8:30 3-13-77 8:30 3-14-77	21:30 3-24-77 21:30 3-25-77	21:30 3-25-77 21:30 3-26-77
% of Time Onstream						
Coal feed	99.0	99.0	100.0	100.0	100.0	100.0
Steam	99.0	100.0	100.0	100.0	100.0	100.0
Syngas	99.0	100.0	100.0	100.0	100.0	100.0
Unit Temperatures						
Feed line temp (°F)	674	717	662	645	735	745
Bed btm temp (°F)	1140	1073	1217	1225	1178	1161
Average bed temp (°F)	1270	1260	1296	1293	1291	1284
Active bed temp (°F)	1295	1292	1311	1305	1311	1295
Gasifier exit temp (°F)	1203	1185	1111	1187	1121	1123
Conversions						
Steam (Converted/fed) (1)						
Gasification (%)	11.9	10.1	38.5	29.7	14.2	17.9
Water-gas shift (%)	29.7	29.7	35.8	26.8	29.4	28.8
Methane reforming (%)	-9.9	-9.8	-11.0	-12.1	0.9	-1.5
Overall (%)	31.8	28.7	63.3	44.4	44.6	45.1
Carbon (Converted/fed)						
Devolatilization (%)	21.5	23.9	23.5	22.6	34.8	27.1
Gasification (%)	18.7	27.0	66.5	61.1	28.9	36.1
Overall (%)	40.2	50.9	90.0	83.7	63.7	63.2
Carbon Conversion Rate (Converted/C in Bed)						
Devolatilization (%/hr)	2.3	2.2	8.8	11.0	6.7	4.5
Gasification (%/hr)	1.9	2.4	25.1	29.6	5.5	6.1
Overall (%/hr)	4.2	4.6	33.9	40.6	12.2	10.6
Carbon Gasified/Stm fed (mol/mol)	0.11	0.16	0.43	0.38	0.17	0.11
Solids Data						
Solids Composition						
Feed compositions (wt. %)						
K_2CO_3	10.1	10.9	10.8	13.4	6.8	6.8
Na_2CO_3	0	0	0	0	5.5	5.5
Carbon	64.4	63.4	67.5	61.6	62.7	64.4
Ash	11.1	11.0	12.2	12.0	12.9	12.7
Bed composition (wt.%)						
K_2CO_3	20.9	21.7	49.4	48.9	16.7	15.9
Na_2CO_3	0	0	0	0	13.5	13.2
Carbon	54.0	54.1	21.6	21.6	50.1	51.8
Ash	20.0	19.3	22.6	21.0	16.3	14.8
Carryover Composition (wt. %)						
K_2CO_3	19.1	18.7	47.8	40.6	17.5	17.3
Na_2CO_3	0	0	0	0	15.7	15.8
Carbon	65.2	65.4	26.1	35.8	52.1	52.2
Ash	12.1	11.9	21.6	17.9	8.9	10.1

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(1) Sign convention for steam conversion is as follows: Water used in RXN is (+), water formed in RXN is (-), Based on Oxygen Balance
(2) Volume/surface mesh particle diameter calculated as 1.0/ (weight fraction solids on sieve/mean sieve size opening)
(3) As -325 mesh portion increases, this value rapidly loses accuracy since size below 11 are extrapolated.

APPENDIX B

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                         NONRECONCILED DATA

                         MATERIAL BALANCE PERIOD  13.

* * * * * YIELD PERIOD 204. UNIT OPERATIONS * PAGE 1 * * * * * *


   *                                 TIME        DATE

                         FROM        15:30     03-09-77

                         TO          07:30     03-10-77

                         DURATION         16.00 HRS


   * PERCENT OF TIME ON STREAM

                         COAL FEED                      100.0%

                         PRIMARY STEAM                  100.0%

                         PRIMARY SYNGAS                 100.0%


   * GASIFIER PROCESS TEMPERATURES

                          GASIFIER       PRIMARY      GASIFIER
                         BED HEIGHT
                                         PROCESS       TEMP
                            (FT)        VARIABLES     (DEG F)

                           43.2           T211         1111.

                           38.4           T210         1069.

                           32.1           T209         1276.

                           26.6           T208         1323.

                           21.2           T207         1313.

                           16.0           T206         1320.

                           10.9           T205         1307.

                            6.4           T204         1294.

                            0.4           T203         1217.
```

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* * * * * * YIELD PERIOD 204. UNIT PROCESS VARIABLES * PAGE 2 * * * *

   * UNIT TEMPERATURES              PROCESS          SKIN
                                    (DEG F)         (DEG F)
      LOCK HOPPER 1 TOP              282.            306.
      LOCK HOPPER 1 BTM              249.            205.

      LOCK HOPPER 2 TOP              236.            303.
      LOCK HOPPER 2 BTM              219.            321.

      PRI GASIFIER FEED  LINE        662.            917.
      PRI GASIFIER STEAM LINE       1079.           1140.

     PRIMARY GASIFIER
      TOP OF BED                    1323.           1361.
      BTM OF BED                    1217.           1233.
      TOTAL BED AVERAGE             1296.           1316.

     ROUGH CUT CYCLONE
      CYCLONE TOP                    948.            992.
      CYCLONE BTM                    688.           1021.
      STANDPIPE TOP                  824.           1000.
      STANDPIPE MID                  818.           1014.
      STANDPIPE BTM                  789.           1041.
      STANDPIPE SLOPE TOP                           1051.
      STANDPIPE SLOPE BTM           1178.            999.


     PRIMARY GASIFIER BACKEND
      GS1  INLET                                     548.
      GF   INLET                                     510.

      SCRUBBER INLET                 431.            415.
      SCRUBBER OUTLET                 68.

      PRODUCT GAS DTM                 86.


   * UNIT PRESSURES                 (PSIA)

      LOCK HOPPER 2                 117.5
      PRI GASIFIER FEED LINE        116.7
      PRI BYPASS  N2   (DTM)        172.8
      PRI SYN GAS IN   (DTM)        163.0

     PRIMARY GASIFIER
      PRI GASIFIER TOP              113.7
      PRI GASIFIER BTM              116.7

      ROUGH CUT CYCLONE OUTLET      113.1
      GF OUTLET                     113.6
      SCRUBBER OUTLET               113.6

      PRODUCT GAS OUT  (DTM)        114.7
```

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* * * * * * YIELD PERIOD 204. FLUID-SOLIDS DATA * PAGE 3 * * * * * *

     * GASIFIER BED PROPERTIES                                PRIMARY
                                                              GASIFIER
     BED BOTTOM DENSITY          (LBS/CF)                       19.3
     BED TOP DENSITY             (LBS/CF)                       10.1
     BED AVERAGE DENSITY         (LBS/CF)                       14.7
     BED HEIGHT                  (FT)                           29.7
     BED HOLDUP                  (LBS)                          77.9
     BED VOLUME                  (CF)                            5.3
     ACTIVE BED TEMPERATURE      (DEG F)                      1311.4
     ACTIVE BED VOLUME           (CF)                            4.7
     SPACE VELOCITY (ACT BED)    (ACF/CF/HR)                    92.9
     BTM SUPERFICIAL VELOCITY    (FT/SEC)                       0.63
     TOP SUPERFICIAL VELOCITY    (FT/SEC)                       0.68

     * CYCLONE PERFORMANCE                                 GS1  CYCLONE

     TEMPERATURE                 (DEG F)                       548.0
     PRESSURE                    (PSIA)                        113.7
     INLET GAS RATE              (SCFH)                        986.6
       "    "    "               (ACFH)                        247.4
     INLET GAS VELOCITY          (FT/SEC)                       19.4
     SOLIDS ENTERING             (LBS/HR)                        0.1
     DUST LOADING                (LBS/ACF)                    0.0003
     SOLIDS CAPTURED             (LBS/HR)                        0.1
     SOLIDS ESCAPING             (LBS/HR)                        0.0
     OVERALL EFFICIENCY     (CAPTURED/ENTERING,WT%)             90.0

     * SOLIDS CARRYOVER LOSS                         TOTAL          -325 MESH

     COAL+CATALYST FEED          (LBS/HR)            10.54            0.04
     TOTAL CARRYOVER             (LBS/HR)             0.08            0.08
      GS1 CYCLONE                (LBS/HR)             0.07            0.07
      GF  FILTER                 (LBS/HR)             0.01            0.01
     CARRYOVER/FEED              (WT%)                0.8%            0.7%

     CARRYOVER/FEED
      (FEED FINES BACKED OUT)    (WT%)                                0.4%

     * SOLIDS CARBON LOSS

     CARBON IN FEED              (LBS/HR)             6.33            0.02
     CARBON IN CARRYOVER         (LBS/HR)             0.02            0.02
     CARRYOVER/FEED              (WT%)                0.3%            0.3%

     CARRYOVER/FEED
      (FEED FINES BACKED OUT)    (WT%)                                0.0%

     * SALTATION IN FEED LINE

     COAL PARTICLE SALTATION VELOCITY      (FT/SEC)              21.3
     FEED LINE GAS VELOCITY                (FT/SEC)              41.4
     MAXIMUM ALLOWABLE SOLIDS FEED RATE    (LBS/HR)              22.9
```

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* * * * * * YIELD PERIOD 204. UNIT CONVERSIONS * PAGE 4 * * * * * *



    * CARBON CONSUMPTION                                   PRIMARY
                                                           GASIFIER

            CARBON IN COAL+CATALYST      (LBS/HR)            6.59

            CARBON FROM DEVOLATIZATION (LBS/HR)              1.75

            CARBON GASIFIED
             BASED ON GC ANALYSES        (LBS/HR)            3.53
             BASED ON RECOVERED SOLIDS (LBS/HR)              4.20

            TOTAL CARBON CONVERTED
             BASED ON GC ANALYSES        (LBS/HR)            5.27
             BASED ON RECOVERED SOLIDS (LBS/HR)              5.95



    *CARBON CONVERSION (C CONVERTED/C IN FEED)

            GASIFICATION ONLY
             BASED ON GC ANALYSIS            ( % )           53.5
             BASED ON RECOVERED SOLIDS       ( % )           63.7

            INCLUDING DEVOLATIZATION
             BASED ON GC ANALYSIS            ( % )           80.0
             BASED ON RECOVERED SOLIDS       ( % )           90.3



    * SPECIFIC REACTION RATES  (C CONVERTED/C IN BED)

             GASIFICATION ONLY
              BASED ON GC ANALYSES           ( %/HR )   21.0
              BASED ON RECOVERED SOLIDS      ( %/HR )   25.0

             INCLUDING DEVOLATILIZATION
              BASED ON GC ANALYSES           ( %/HR )   31.4
              BASED ON RECOVERED SOLIDS      ( %/HR )   35.4
```

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* * * * * * YIELD PERIOD 204. UNIT CONVERSIONS * PAGE 5 * * * * * *
      * STEAM CONSUMPTION                                 PRIMARY
                                                          GASIFIER
              STEAM INTO UNIT                  (LBS/HR)   14.78

              STEAM REACTED WITH CARBON        (LBS/HR)    5.29

              STEAM REACTED IN SHIFT           (LBS/HR)    5.29

              STEAM FROM METHANATION
               BASED ON RECOVERED H2O          (LBS/HR)   -1.99
               BASED ON H2 BALANCE             (LBS/HR)   -3.83
               BASED ON O2 BALANCE             (LBS/HR)   -2.35

              TOTAL STEAM CONSUMED
               BASED ON RECOVERED H2O          (LBS/HR)    8.59
               BASED ON H2 BALANCE             (LBS/HR)    6.75
               BASED ON O2 BALANCE             (LBS/HR)    8.23

      * STEAM CONVERSION   (STEAM CONSUMED/STEAM INTO BED)

              GASIFICATION                       ( % )     35.8

              WATER-GAS SHIFT                    ( % )     35.8

              METHANATION
               BASED ON RECOVERED H2O            ( % )    -13.5
               BASED ON H2 BALANCE               ( % )    -25.9
               BASED ON O2 BALANCE               ( % )    -15.9

              TOTAL STEAM CONVERTED
               BASED ON RECOVERED H2O            ( % )     58.1
               BASED ON H2 BALANCE               ( % )     45.6
               BASED ON O2 BALANCE               ( % )     55.7
                                     *
      * REACTION RATE PARAMETERS

              CARBON CONVERTED/STEAM FED
               GASIFICATION ONLY              (LBS/LBS)   0.284
               GASIFICATION ONLY              (MOL/MOL)   0.426

               INCLUDE DEVOLATILIZATION       (LBS/LBS)   0.402
               INCLUDE DEVOLATILIZATION       (MOL/MOL)   0.604

              CARBON CONVERTED/BED VOLUME
               GASIFICATION ONLY           (LBS/HR)/CFT   0.796
               GASIFICATION ONLY           (MOL/HR)/CFT   0.066

               INCLUDE DEVOLATILIZATION(LBS/HR)/CFT   1.126
               INCLUDE DEVOLATILIZATION(MOL/HR)/CFT   0.094

              CARBON IN BED/STEAM FED  LBS/(LBS/HR)   1.137
              CARBON IN BED/STEAM FED  MOL/(MOL/HR)   1.706

      * CARBON CONVERTED BASED ON RECOVERED SOLIDS
```

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* * * * * * YIELD PERIOD 204. UNIT COMPOSITIONS * PAGE 6 * * * * * *



                                *
* CATALYST DISTRIBUTION
                                                          PRI
                         FEED    GTC     GMC     GB       C/O
                        (WT%)   (WT%)   (WT%)   (WT%)   (WT%)
        K AS K20          7.4     0.0    33.7    33.3    32.5
        K AS K2CO3       10.8     0.0    49.4    48.9    47.8
        K AS K            6.1     0.0    27.9    27.6    27.0
        K WATER/ACID
        SOLUBLE RATIO   0.800   0.0     0.714   0.727   0.746
        K2O  H2O INSOL    1.5     0.0     9.6     9.1     8.3
        K2CO3 "  INSOL    2.2     0.0    14.2    13.4    12.1
        K     "  INSOL    1.2     0.0     8.0     7.6     6.9

        NA AS NA2O        0.1     0.0     0.5     0.5     0.5
        NA AS NA2CO3      0.1     0.0     0.8     0.8     0.9
        NA AS NA          0.1     0.0     0.3     0.3     0.4
        NA WATER/ACID
        SOLUBLE RATIO   3.000   0.0     1.043   1.022   1.020
        NA2O H2O INSOL   -0.2     0.0    -0.0    -0.0    -0.0
        NA2CO3 " INSOL   -0.3     0.0    -0.0    -0.0    -0.0
        NA     " INSOL   -0.1     0.0    -0.0    -0.0    -0.0

        TOTAL AS M2O      7.4     0.0    34.1    33.7    33.0
        TOTAL AS M2CO3   10.9     0.0    50.2    49.6    48.6
        TOTAL AS M        6.2     0.0    28.3    28.0    27.4

        CARBON           62.5    32.0    21.6    19.3    26.1
        K    ON CARBON    9.8     0.0   129.5   143.3   103.6
        NA   ON CARBON    0.1     0.0     1.6     1.7     1.4
        TOTAL " CARBON    9.9     0.0   131.1   145.0   105.0

        ASTM ASH         23.1    63.1    72.8    74.7    70.2
        K      ON ASH    26.4     0.0    38.4    37.0    38.5
        NA     ON ASH     0.3     0.0     0.5     0.4     0.5
        TOTAL  ON ASH    26.6     0.0    38.9    37.4    39.0

        M2CO3-FREE ASH   12.2    63.1    22.6    25.1    21.6
        K  ON " FREE "   50.0     0.0   123.8   110.1   124.9
        NA ON " FREE "    0.5     0.0     1.5     1.3     1.7
        TOTAL " FREE "   50.5     0.0   125.3   111.4   126.6

* BASED ON ACID SOLUBLE DETERMINATION
```

* * * * * * [illegible] PERIOD 204. SOLIDS DATA * PAGE 7 * * * * * *

* PARTICLE SIZE DISTRIBUTION

		CUMULATIVE WT% LESS THAN MESH SIZE					
	325 MESH	200 MESH	100 MESH	50 MESH	30 MESH	20 MESH	10 MESH
FEED COAL+CATALYST(FC)	0.4	1.3	11.2	40.2	78.0	93.8	100.0
GASIF TOP CHAR (GTC)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
GASIF MID CHAR (GMC)	0.7	2.5	12.3	33.5	68.3	85.8	99.[illegible]
GASIF BTM CHAR (GB)	0.4	0.8	6.3	26.9	54.4	89.3	99.[illegible]
GASIF CYCLONE 1 (GS1)	95.4	97.6	98.7	99.4	99.4	99.7	100.0
GASIF FILTER (GF)	97.2	97.9	98.6	99.3	99.7	99.9	100.0

* MEAN PARTICLE SIZE AND DENSITY *

MEAN PARTICLE DIAMETER (MICRONS)

	NUMBER MEAN	VOLUME/ SURFACE MEAN	WEIGHT MEAN	BULK GM/CC	DENSITY LBS/CU FT
FEED COAL+CATALYST(FC)	54.	276.	445.	0.686	42.8
GASIF TOP CHAR (GTC)	0.	0.	0.	0.0	0.0
GASIF MID CHAR (GMC)	40.	279.	541.	0.340	21.2
GASIF BTM CHAR (GB)	44.	351.	572.	0.449	28.0
GASIF CYCLONE 1 (GS1)	22.	23.	32.		
GASIF FILTER (GF)	22.	23.	29.		

```
* * * * * * YIELD PERIOD 204. SOLIDS COMPOSITION * PAGE 8 * * * * * *

    * ULTIMATE ANALYSIS       (WT% OF TOTAL SOLIDS, DRY)
                             FEED       SOLIDS W/O  CARRYOVER C/O
          COMPONENT          (FC)          (GB)       (GS-1 + GF)
                             (WT%)         (WT%)         (WT%)
              H               4.21          0.58          0.0

              C              62.5          20.3          26.1

              S               3.7           5.5           3.6

              O              12.3           9.5           8.7

              N               0.57          0.17          0.10

              CL              0.04          0.18          0.28

         SO3-FREE ASH        16.6          63.8          61.3
                            ------        ------        ------
           TOTAL            100.0         100.0         100.0

    * ASH  ANALYSIS            (WT%, OF TOTAL SOLIDS)
             ASH             23.1          74.7          70.2

         C/H  RESIDUE        21.5          79.3          79.1

         SO3-C/H RES.        15.0          65.4          70.1

    *ASH ELEMENT ANALYSIS   (WT% OF SO3-FREE ASH)
            SIO2             27.4          27.6          24.0

            FE2O3             8.6           9.8           7.7

            AL2O3             9.8           9.7           8.1

            CAO               1.48          2.01          1.60

            MGO               0.60          0.55          0.50

            TIO2              1.52          0.42          0.59

            P2O5              0.21          0.37          0.15

          CATALYST          (FROM ACID SOLUBLE ANALYSES)
            K2O              44.25         52.16         53.07

            NA2O              0.48          0.71          0.82
                            ------        ------        ------
            TOTAL            94.30        103.37         96.47
```

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* * * * * * YIELD PERIOD 204. PRODUCT GAS DATA * PAGE 9 * * * * * *


      * PRODUCT GAS PARTIAL PRESSURES          PRIMARY GASIFIER

        BALANCE USED                        H2O          O2          H2

        TOTAL PRESSURE        (PSIA)       113.7       113.7       113.7

              H2              (PSIA)        42.7        42.4        41.1
              CO              (PSIA)        16.5        16.3        15.8
              CH4             (PSIA)         9.7         9.6         9.3
              CO2             (PSIA)        12.9        12.8        12.4
              H2S             (PSIA)         0.3         0.3         0.3
              H2O             (PSIA)        15.1        15.9        18.9

              N2              (PSIA)        16.5        16.3        15.8

              H2O/CO                         0.9         1.0         1.2
              H2O/CO2                        1.2         1.2         1.5



      * UNIT GAS DATA                                  PRIMARY
                                                       GASIFIER

        SYN GAS MWT              (LBS/MOL)               11.1

        PRD GAS MWT(DRY)         (LBS/MOL)               17.7

        PRODUCT GAS
         PG AT DTM (DRY)            (SCFH)              848.8
          (DRY N2-FREE)             (SCFH)              706.9
                               *
         PG AT GASIF OUTLET         (SCFH)              986.6
          (INCLUDES N2+H2O)         (ACFH)              385.3
                               *
         PG AT GASIF OUTLET         (SCFH)              844.7
          (EXCLUDES N2)             (ACFH)              329.9

      * BASED ON O BALANCE
```

```
* * * * * * YIELD PERIOD 204. PRODUCT GAS DATA * PAGE 10 * * * * * *

     * UNIT GAS YIELDS
                                                             PRIMARY
        PRODUCT GAS (DRY)                                    GASIFIER
              H2               (MOL %)                         43.3
              CO                  "                            16.7
              CO2                 "                            13.1
              CH4                 "                             9.8
              H2S                 "                             0.3
              N2                  "                            16.7

        PRODUCT GAS (DRY,N2-FREE)
              H2               (MOL %)                         52.0
              CO                  "                            20.1
              CO2                 "                            15.7
              CH4                 "                            11.8
              H2S                 "                             0.4

        PRODUCT GAS
              H2               (MOL %)                         37.3
              CO                  "                            14.4
              CO2                 "                            11.3
              CH4                 "                             8.4
              H2S                 "                             0.3
              H2O*                "                            14.0
              N2                  "                            14.4

        PRODUCT GAS (N2-FREE)
              H2               (MOL %)                         43.5
              CO                  "                            16.8
              CO2                 "                            13.2
              CH4                 "                             9.8
              H2S                 "                             0.3
              H2O*                "                            16.4

        SCFH CH4/LB C ACTIVE BED                                5.0

        SCFH CH4/LB C FEED                                     12.6

     * EQUILIBRIUM CONSTANTS                                   *
                                      REACTION             ACTUAL      CORRESPONDING
                                  EQUILIBRIUM AT       EQUILIBRIUM     EQUILIBRIUM
                                 ACTIVE BED TEMP       EXPRESSION      TEMPERATURE
                                     (1311.4 F)                          (DEG F)

GRAPHITE-H2O: C +H2O=CO +H2       2.0036               2.9562 ----- 1354.2
SHIFT       : CO+H2O=CO2+H2       1.4847               2.0936 ----- 1178.8
METHANATION : CO+3H2=CH4+H2O      0.0581               0.0265 ----- 1363.4

     * BASED ON O BALANCE
```

```
* * * * * * YIELD PERIOD 204. MATERIAL BALANCES * PAGE 11 * * * * * *



   * OVERALL MATERIAL BALANCE

 INPUT:                  (LBS/HR)         OUTPUT:                    (LBS/HR)

  COAL FEED(EX N2)     10.48            PRI PRODUCT GAS(EX N2)   29.09
  PRI GASIF STEAM      14.78            PRI PRODUCT GAS N2       10.46
  PRI GASIF SYN GAS    13.47            PRI PRODUCT WATER         6.19
  LOCK HOPPER N2        0.0             PRI CHAR CARRYOVER        0.08
  PRI BYPASS  N2        0.0             SOLIDS WITHDRAWN          2.03

   TOTAL(EX N2)        38.73             TOTAL(EX N2)            37.40

   ACCUMULATION:     PRIMARY   GASIFIER   =    0.22 LBS/HR

   CLOSURE: (OUTPUT+ACCUM)/INPUT          =   97.1%



   * SYNTHESIS GAS BALANCE

  INPUT:                    (SCFH)         OUTPUT:                      (SCFH)

   PRI GASIF SYN GAS     483.1           H2+CO IN PRI PRD GAS     509.3
      H2 MOL %   61.5                          H2 MOL %   43.3
      CO MOL %   33.3                          CO MOL %   16.7

    PRI CLOSURE:OUTPUT)/(INPUT  105.4%
```

```
* * * * * * YIELD PERIOD 204. MATERIAL BALANCES * PAGE 12 * * * * * *


* MOLECULAR MATERIAL BALANCES

                                   NITROGEN            HYDROGEN
        INPUT:                    (SCFH N2)           (SCFH H2)

         COAL+CATALYST                0.8                 83.4
         PRI GASIF STEAM              0.0                310.9
         PRI GASIF SYN GAS            0.0                297.1
         LOCK HOPPER N2               0.0                  0.0
         PRI PROCESS N2               0.0                  0.0

          PRI TOTAL                   0.8                691.5


        OUTPUT:

         PRI PRODUCT GAS            141.8                536.5
         PRI PRODUCT WATER            0.0                130.3
         PRI CHAR CARRYOVER           0.0                  0.0
         SOLIDS WITHDRAW              0.0                  2.2

          PRI TOTAL                 141.8                668.9

          ACCUMULATION:
          PRIMARY   GASIFIER          0.1                  0.1

          CLOSURE: (OUTPUT+ACCUM)/INPUT
          PRIMARY   GASIFIER                              96.8%
```

```
* * * * * * YIELD PERIOD 204. MATERIAL BALANCES * PAGE 13 * * * * * *

    * ELEMENT BALANCES
                                 CARBON      OXYGEN      SULFUR     CHLORINE
  INPUT:                       (LBS/HR)    (LBS/HR)    (LBS/HR)    (LBS/HR)
                      *
   COAL+CATALYST                  6.59        1.30       0.394       0.004
   PRI GASIF STEAM                0.0        13.13       0.0         0.0
   PRI GASIF SYN GAS              5.10        6.79       0.0         0.0

    TOTAL                        11.69       21.21       0.394       0.004

  OUTPUT:

   PRI PRODUCT GAS               10.65       15.37       0.215       0.0
   PRI PRODUCT WATER              0.0         5.50       0.002       0.0
   PRI CHAR CARRYOVER             0.02        0.01       0.003       0.000
   SOLIDS WITHDRAWN               0.41        0.19       0.112       0.004

    TOTAL                        11.08       21.07       0.333       0.004

    ACCUMULATION:
    PRIMARY   GASIFIER            0.21       -0.17       0.037      -0.001

    CLOSURE
     (OUT+ACCUM)/IN              96.6%       98.5%       93.8%       70.1%

     *EXCLUDES CARBON AND OXYGEN IN CATALYST


     * CATALYST BALANCE
                          ACID SOL  ACID SOL          H2O SOL   H2O SOL
                         POTASSIUM   SODIUM          POTASSIUM   SODIUM
                          (LBS/HR)  (LBS/HR)          (LBS/HR)  (LBS/HR)
  INPUT:

   COAL+CATALYST            0.64      0.01              0.51      0.02

  OUTPUT:

   PRI CHAR CARRYOVER       0.02      0.00              0.02      0.00
   PRI PRODUCT WATER        0.0       0.0               0.0       0.0
   SOLID SAMPLES            0.56      0.01              0.41      0.01

    TOTAL                   0.58      0.01              0.42      0.01

    ACCUMULATION:
       PRI GASIF            0.02     -0.00             -0.13      0.00

    CLOSURE:
     (OUT+ACCUM)/IN        93.2%     98.0%             57.2%     52.3%

     *CARBON BALANCE NOT INCLUDE CATALYST CARBONATE
```

```
* * * * * * YIELD PERIOD 204. MATERIAL BALANCES * PAGE 14 * * * * * *


   * ASH AND FINES BALANCES                               -325
                                C/H   SO3 FREE SO3 FREE   MESH
                    ASTM ASH  RESIDUE ASTM ASH C/H RESD  FINES
INPUT:              (LBS/HR) (LBS/HR) (LBS/HR) (LBS/HR) (LBS/HR)

 COAL+CATALYST        2.44     2.27     1.75     1.58     0.04

OUTPUT:

 PRI CHAR CARRYOVER   0.06     0.06     0.05     0.06     0.08
 SOLIDS WITHDRAWN     1.52     1.61     1.30     1.33     0.01

  TOTAL               1.57     1.67     1.34     1.38     0.08

  ACCUMULATION:
     PRI GASIF       -0.02    -0.13     0.15     0.49    -0.07

  CLOSURE:
  (OUT+ACCUM)/IN     63.9%    68.1%    85.2%   118.7%    35.6%

  -325 MESH FINES PRODUCED IN UNIT (OUTPUT+ACCUM-INPUT)  -0.03

                              PRODUCED/(OUTPUT+ACCUM)  -180.7%


   * ASH ELEMENT BALANCE
                    SIO2  FE2O3 AL2O3  CAO   MGO   SO3  TIO2  P2O5
INPUT:              LB/HR LB/HR LB/HR LB/HR LB/HR LB/HR LB/HR LB/HR

 COAL+CATALYST      0.480 0.150 0.171 0.026 0.011 0.686 0.027 0.004

OUTPUT:

 PRI CHAR CARRYOVER 0.012 0.004 0.004 0.001 0.000 0.007 0.000 0.000
 SOLIDS WITHDRAWN   0.357 0.127 0.126 0.026 0.007 0.283 0.005 0.005

  TOTAL             0.369 0.131 0.130 0.027 0.007 0.291 0.006 0.005

  ACCUMULATION:
     PRI GASIF      0.040 0.012 0.014 0.002 0.001-0.003 0.001 0.000

  CLOSURE
   (OUT+ACCUM)/IN    85.%  95.%  84.% 110.%  78.%  42.%  24.% 136.%
```

```
* * * * * YIELD PERIOD 204. MATERIAL BALANCES * PAGE 15 * * * * * *




       * MOLE BALANCE

GAS   INPUT    (MOLES/HR)                 GAS   OUTPUT     (MOLES/HR)
               ------------------------                    ------------------------
SYNGAS          C       H       O      S  PRODUCT GAS   C       H       O       S
H2( 0.784) 0.0     1.568 0.0     0.0      H2 ( 0.970) 0.0     1.940 0.0     0.0
CO( 0.425) 0.425 0.0     0.425 0.0        CO ( 0.374) 0.374 0.0     0.374 0.0
                                          CO2( 0.293) 0.293 0.0     0.587 0.0
                                          CH4( 0.219) 0.219 0.878 0.0     0.0
                                          H2S( 0.007) 0.0     0.013 0.0     0.007
STEAM
  ( 0.820) 0.0     1.641 0.820 0.0        H2O( 0.344) 0.0     0.687 0.344 0.000
TOTAL----- ----- ----- ----- -----        TOTAL------ ----- ----- ----- -----
  ( 2.029) 0.425 3.209 1.245 0.0             ( 2.207) 0.887 3.518 1.305 0.007

SOLIDS INPUT (MOLES/HR)                   SOLIDS OUTPUT   (MOLES/HR)
----------------------------------------  ----------------------------------------
   K     NA     C      H      O      S       K     NA      C      H      O      S
          COAL+CATALYST FEED                          CHAR FINES CARRYOVER
0.0160.000 0.549 0.440 0.081 0.012  0.001 0.000 0.002 0.0     0.000 0.000
                                                  CHAR SAMPLES WITHDRAWN
                                    0.014 0.000 0.034 0.012 0.012 0.004
                                                  CHAR ACCUMULATION
                                    0.000-0.000 0.018 0.000-0.011 0.001
                              TOTAL ----- ----- ----- ----- ----- -----
                              SOLIDS .015 0.000 0.053 0.012 0.002 0.005

               TOTAL INPUT                         TOTAL OUTPUT+ACCUMULATION
----------------------------------------  ----------------------------------------
   K     NA     C      H      O      S       K     NA      C      H      O      S
0.0160.000 0.973 3.649 1.326 0.012  0.015 0.000 0.940 3.530 1.306 0.012

  MOLE BALANCE CLOSURE   (OUT+ACCUM)/IN   (%)
   K     NA     C      H      O      S    OVERALL
  93.   98.   96.6   96.8   98.5   93.8    97.1


      *CARBON BALANCE NOT INCLUDE CATALYST CARBONATE
```

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