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# EXXON CATALYTIC COAL GASIFICATION PROCESS DEVELOPMENT PROGRAM

Annual Technical Progress Report
July 1, 1978 - June 30, 1979

C. A. Euker, Jr. - Program Manager

Exxon Research and Engineering Company
Baytown, Texas 77520

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# ABSTRACT

The Exxon Catalytic Coal Gasification (CCG) Development Program began in July, 1978 and is planned to be completed in June of 1981. The program is a coordinated effort involving bench scale R&D, operation of a one-ton-per-day Process Development Unit (PDU), and engineering support. This work is aimed at advancing the catalytic coal gasification technology through the development stage to make it ready for further scale-up in a large pilot plant. One of the major objectives of the program is to demonstrate the feasibility of the integrated process which includes gasification, gas separation, and catalyst recovery. This integrated system will be operated at commercial design conditions feeding bituminous Illinois No. 6 coal catalyzed with potassium hydroxide. This operation will demonstrate the feasibility of the catalytic coal gasification process in integrated operation and will ready the technology for scale-up to the larger pilot plant stage. The conceptual commercial CCG process will be defined. This work will include a flow diagram for the process, heat and material balances, and a definition of key process features unique to catalytic coal gasification, including the catalyst addition, gasification, and catalyst recovery sections.

This report covers the activities for the Exxon Catalytic Coal Gasification Development Program during the year from July 1, 1978 - June 30, 1979. This work is being performed by the Exxon Research and Engineering Company (ER&E) and is supported by the Gas Research Institute and by the United States Department of Energy under Contract No. ET-78-C-01-2777.

The highlights of this report are summarized below:

- Bench Scale Research and Development

Bench studies have shown that many fine particles of 10 μ and less diameter are formed in the catalyst recovery digestion process. The fines are made up of broken down char particles as well as fine lime and calcium carbonate. These fine particles can be separated from the recovered catalyst solution by filtration.

Preliminary results indicate that additional potassium can be recovered from char by soaking char in hot KOH solution without addition of lime. This treatment seems to partially solubilize $KFeS_2$ in the char. Work is continuing to find out how much potassium can be recovered at different soaking conditions without the need for added lime or other chemicals.

Bench apparatus was constructed to measure the extent of gas phase reactions that occur in a mixture of recycle gas and steam containing $H_2$, CO, $CH_4$, and $H_2O$ when preheated to 1575°F for injection into the gasification reactor. Initial results show that carbon deposition is a problem in spite of the large amount of steam mixed with the recycle gas. Work is continuing to find methods to inhibit the carbon deposition including treatment of the metal tubes with $SO_2$ and $H_2S$.

- Process Development Unit (PDU) Operations

A start-up and checkout plan was developed for the one ton per day Process Development Unit (PDU). The construction and start-up of the gasification section, gas separation section, and catalyst recovery section will be carried out sequentially with completion of the whole PDU start-up planned for February, 1980.

Construction of the gasification section was completed in the second quarter of 1979 and the gasification reactor was successfully proof tested for operation at 600 psig and 1400°F. Initial operations with coal and steam at gasification conditions will begin in July, 1979.

Construction of the gas separation section began. This section will use physical absorption to scrub $H_2S$ and $CO_2$ from the product gas and cryogenic fractionation to separate the $CH_4$ product from $H_2$ and CO recycle gas. Construction of the acid gas removal system was completed.

Bench research and pilot unit studies have shown that the proposed leaching system for catalyst recovery is difficult to operate because of a large carryover of fine char and lime particles. Bench research and engineering studies have shown that a filter system will be the most reliable method to separate spent char solids from catalyst solution on the PDU. Preliminary tests on vendor filters have demonstrated the feasibility of this system for PDU operation.

A flow plan for the PDU catalyst recovery system was developed. The system will use filters as the solid-liquid separation device and will be capable of running in a water wash or $Ca(OH)_2$ digestion mode for recovering catalyst from gasified PDU char.

- Data Acquisition and Correlations

The design of the on-line data acquisition system for the PDU was completed. The system is designed to monitor unit temperatures, flow rates, pressures, gas analyses, and weights and is capable of monitoring 600 process variables. A computer program has been written to use this data to calculate an on-line material balance and identify possible operating problems such as faulty instrument readings or process leaks.

An off-line data reconciliation program for the PDU has also been developed, debugged, and tested using a set of simulated data. This program provides a tool for obtaining consistent and reliable data from PDU operations.

A cold model of the PDU gasification reactor was built to help troubleshoot solids flow problems in PDU operation. This cold model has essentially the same dimensions as the PDU gasifier except that it is about one-sixth of the height. A series of experiments were carried out to evaluate the performance of the solids feed and the fines return systems of the PDU and recommendations were made regarding purge locations and gas rates through them. Modifications have been made to the cyclone and the intersection block of the PDU as a result of these studies.

- Advanced Study of the Exxon Catalytic Coal Gasification Process

The start-up and validation of two bench scale gasification reactors is in progress. One unit is a mini-fluidized bed reactor that operates at atmospheric pressure and the second unit is a fixed bed reactor that operates at 500 psia. Both reactors will be used to study gasification kinetics over a broad range of conditions to screen process conditions for further PDU study as well as expand the data base for the kinetic model.

Bench studies showed that the current catalyst addition techniques did not adequately impregnate coal particles larger than 20 mesh. This inadequate catalyst loading leads to caking and agglomeration problems when the coal is fed to the gasification reactor. As a result of this discovery, only coal less than 20 mesh will be fed to the PDU reactor for initial operations and work is planned to learn how to add catalyst to particles larger than 20 mesh.

- Engineering Research and Development

Work was completed on a revised offsites facilities definition and cost estimate to update the CCG Commercial Plant Study Design prepared during the predevelopment program. This update included a more detailed study of water treatment and reuse options and a flue gas desulfurization (FGDS) study design for a lime scrubbing system. For a pioneer commercial plant feeding Illinois No. 6 coal and producing 257 billion Btu/SD SNG, the updated investment estimate is 1,530 M$ and the updated gas cost is 6.18 $/MBtu. These economics are on a January, 1978 cost basis, and reflect 100% equity financing and a 15% current dollar DCF return. The investment is down 7% and the gas cost is down 4% from the Predevelopment Program Study Design. Revised cost estimating tools for materials handling equipment and the use of lime scrubbing for FGDS were the main factors leading to cost reductions.

A study has been initiated to determine the types and performance of coal crushing equipment appropriate for commercial CCG plants.

A laboratory guidance study has been made to estimate the economic impact of evaporating dilute catalyst solutions from catalyst recovery to concentrations suitable for direct addition to the gasifier feed coal. The incremental gas cost for concentrating a 10% (wt) KOH solution is about 0.12-0.19 $/MBtu, or 2-3% of the CCG Study Design gas cost. The use of dilute catalyst solutions will reduce the number of stages required for catalyst recovery. Studies will be conducted later in the program to find the optimum balance between evaporation costs and catalyst recovery investment.

Catalyst recovery system screening studies were started to evaluate the economic impacts of alternative processing approaches and solid-liquid separation techniques. The process basis has been set for a first case which combines calcium hydroxide digestion with counter-current water washing using filters.

A brief incentive study of an alternative two-stage gasification concept was completed. Preliminary economics indicate an incentive for staged gasification, but additional laboratory data are required to develop a better estimate of the incentive.

A study has been completed in which the composition and physical properties of CCG char from prior FBG runs were summarized. The information collected will be used as initial input for solids balance modeling of the CCG process.

The process basis has been set for an evaluation of Integral Steam Reforming for heat input for CCG. A reformer coil outlet temperature of 1500°F, steam conversion of 48%, and use of a portion of the product from the first stage of acid gas removal as fuel were identified as the preferred process conditions. The possibility of carbon laydown was identified as the main process uncertainty for this heat input option. Alternatives for dealing with carbon laydown will be identified as part of the study.

An engineering screening study to evaluate the economic incentive for cryogenic distillation for acid gas removal has resulted in a gas cost 3.2% less than the Study Design gas cost. However, recent studies by Air Products and Chemicals, Inc., under contract to DOE, have concluded that the selective heavy glycol solvent absorption process specified in the CCG Study Design can be optimized to save about 1-2% in gas cost. This reduces the incentive for cryogenic acid gas removal to only 1-2%. This incentive is small relative to the probable problems in handling $CO_2$ freeze-out. Optimization of the cryogenic acid gas removal system would likely reduce its cost but would make it more difficult to deal with $CO_2$ freeze-out. Thus, there is little incentive for research on the cryogenic acid gas removal system as defined by this study.

Systems modeling work is underway with the objective of developing material and energy balance tools which will reduce the effort required to do engineering studies under the present contract. A material balance model for the catalyst recovery system was completed. Work is continuing on the development of a material and energy balance model for the CCG reactor system.

A coordinated set of engineering technology programs was initiated to develop fundamental process and equipment technology to support the overall laboratory and engineering process development effort. The activities to date have included:

- Development of a five-part materials evaluation program for the PDU to assemble a data base for materials in CCG process environments. The program consists of corrosion racks, corrosion probes, nondestructive testing, component examination, and stream sampling. The eight corrosion racks for the PDU were assembled and are ready for installation.

- Formulation of an experimental program to obtain data needed for modeling vapor-liquid equilibrium in sour water/catalyst systems containing ammonia, hydrogen sulfide, carbon dioxide, and potassium hydroxide. A subcontract covering this experimental program is expected to be executed shortly.

- Initiation of a program to collect physical and thermodynamic property information for catalyst recovery solutions. A literature search has been completed for properties of aqueous solutions of potassium hydroxide or potassium carbonate. A satisfactory method has been found for predicting mixture densities of the water/potassium hydroxide/potassium carbonate system.

- Development of an environmental control program to obtain and characterize liquid and solid waste samples from the PDU in order to identify any potential effluent quality problems in a commercial CCG plant.

- Initiation of a second environmental control program to identify potential atmospheric emissions in a commercial CCG plant and, where possible, to quantify these emissions through testing in the PDU. Potential sources of commercial emissions were inventoried, and representative PDU streams were selected for sampling.

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# LABORATORY PROCESS RESEARCH AND DEVELOPMENT

## 1. Bench Scale Research and Development (Reporting Category C01)

### 1.1 Catalyst Recovery Studies

#### Background

Under the predevelopment program (Contract No. E(49-18)-2369), potassium carbonate and potassium hydroxide were used as coal gasification catalysts. Fluid Bed Gasifier (FBG) pilot plant operations with catalyst recycle demonstrated that water washing of the char would remove approximately 70% of total potassium. Solid-liquid separation was accomplished by using a series of mixing tanks with hydroclones between each tank. Operation of the hydroclones in these pilot plant tests was troublesome. Relatively high levels of fines in the liquid overflow were observed and required intermittent filtering of the liquid during the pilot plant operation. In addition, no definitive measurement of the catalyst forms in the solution from catalyst recovery was made. This work identified three areas for improvement in catalyst recovery:

- Increased level of potassium recovery
- Improved solid-liquid separation in catalyst recovery operations
- Identification of catalyst forms in solution from catalyst recovery

#### Increased Level of Potassium Recovery

Bench scale work under the predevelopment contract identified a way of increasing the level of potassium recovery. This research showed that part of the potassium impregnated on the coal reacts with the coal mineral matter under gasification reactor conditions. The following are the major mineral-potassium reactions:

$$K_2CO_3 + 2SiO_2 \cdot Al_2O_3 \cdot 2H_2O \rightarrow 2KAlSiO_4 + 2H_2O + CO_2$$

$$K_2CO_3 + 2FeS_2 + H_2 \rightarrow 2KFeS_2 + H_2O + CO_2$$

Both $KAlSiO_4$ and $KFeS_2$ are water insoluble and catalytically inactive forms of potassium. However, a hydrothermal reaction of char with $Ca(OH)_2$ at high pH and temperatures at or above 300°F causes the following chemical reactions to proceed:

$$2KAlSiO_4 + 4Ca(OH)_2 + 2H_2O \rightarrow Ca_3Al_2SiO_4(OH)_8 + 2KOH + CaSiO_3 \cdot H_2O$$

$$2KFeS_2 + 6KOH \rightarrow Fe_2O_3 + 4K_2S + 3H_2O$$

Consequently, these potassium forms can be converted to soluble and catalytically active forms of potassium (KOH and $K_2S$, respectively).

This hydrothermal chemistry was studied in a 100-gallon digester (Figure 1.1-1). Approximately 50 lbs of char, 25 lbs of lime, and 300 lbs of KOH solution were charged to the digester. Steam and resistance heaters were used to heat the slurry to process conditions between 300-400°F. After digestion, water was fed to the coil which cooled the slurry down to approximately 120°F. The solids were then filtered from the liquid and washed. Results shown in Figure 1.1-2 demonstrate that potassium recoveries of above 90% could be achieved with this apparatus.

A one-gallon char-lime digester (Figure 1.1-3) was then constructed during the present contract to evaluate hydrothermal catalyst recovery. This unit can heat its slurry contents from 150°F (below digestion reaction temperature) to 300°F in three minutes and to 400°F in approximately twenty minutes. The reactor can be cooled from 400°F to 150°F in 15 minutes. Reactor temperature and residence time can therefore be controlled more accurately than was possible in the 100-gallon digester used in the predevelopment work. The one-gallon digester is also designed to investigate effects of agitation and lime particle size on potassium recovery from char.

Figure 1.1-2 also shows results from two matching runs to compare results from the one-gallon digester and the 100-gallon digester. As the figure shows, the two data points from the small unit fall very close to the curve drawn through the data from the 100-gallon digester.

Table 1.1-1 presents initial process variable results from this unit.

Table 1.1-1

Initial Process Variable Results

| Run | Ca/K | Reactor Temperature, °F | Reactor Residence Time, min. | Agitation | Lime Mesh Size | Overall $K^+$ Recovery % (wt.) |
|---|---|---|---|---|---|---|
| A | 1.06 | 325° | 15 | 225 RPM* | 20 x 50 | 92 |
| B | 1.06 | 325° | 30 | 225 RPM* | 20 x 50 | 94 |
| C | 1.03 | 400° | 30 | No Agitation | -325 | 95 |
| D | 1.05 | 400° | 60 | No Agitation | 20 x 50 | 96 |

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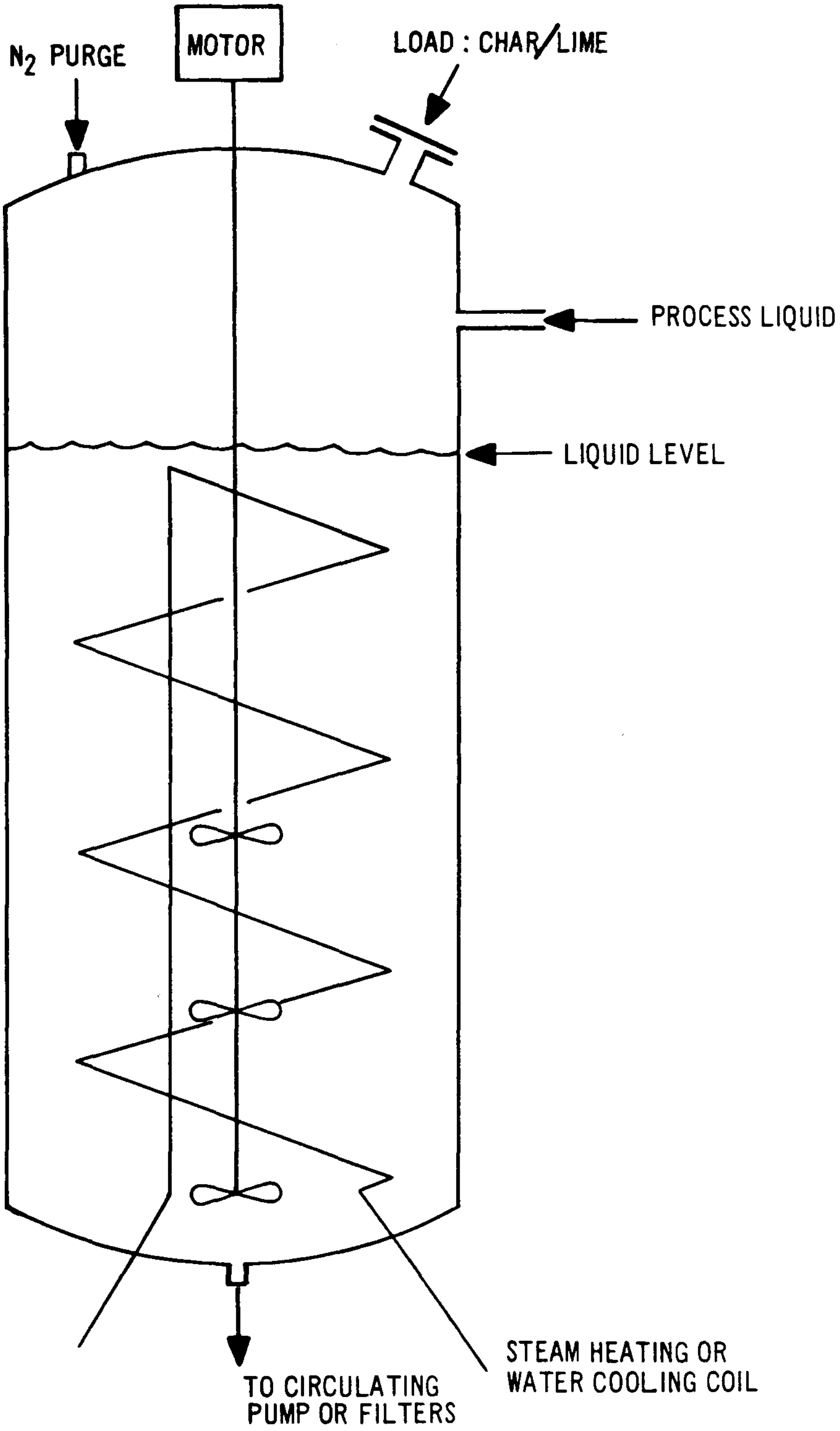
* During time of reaction

# FIGURE 1.1-1

## 100 GALLON DIGESTER



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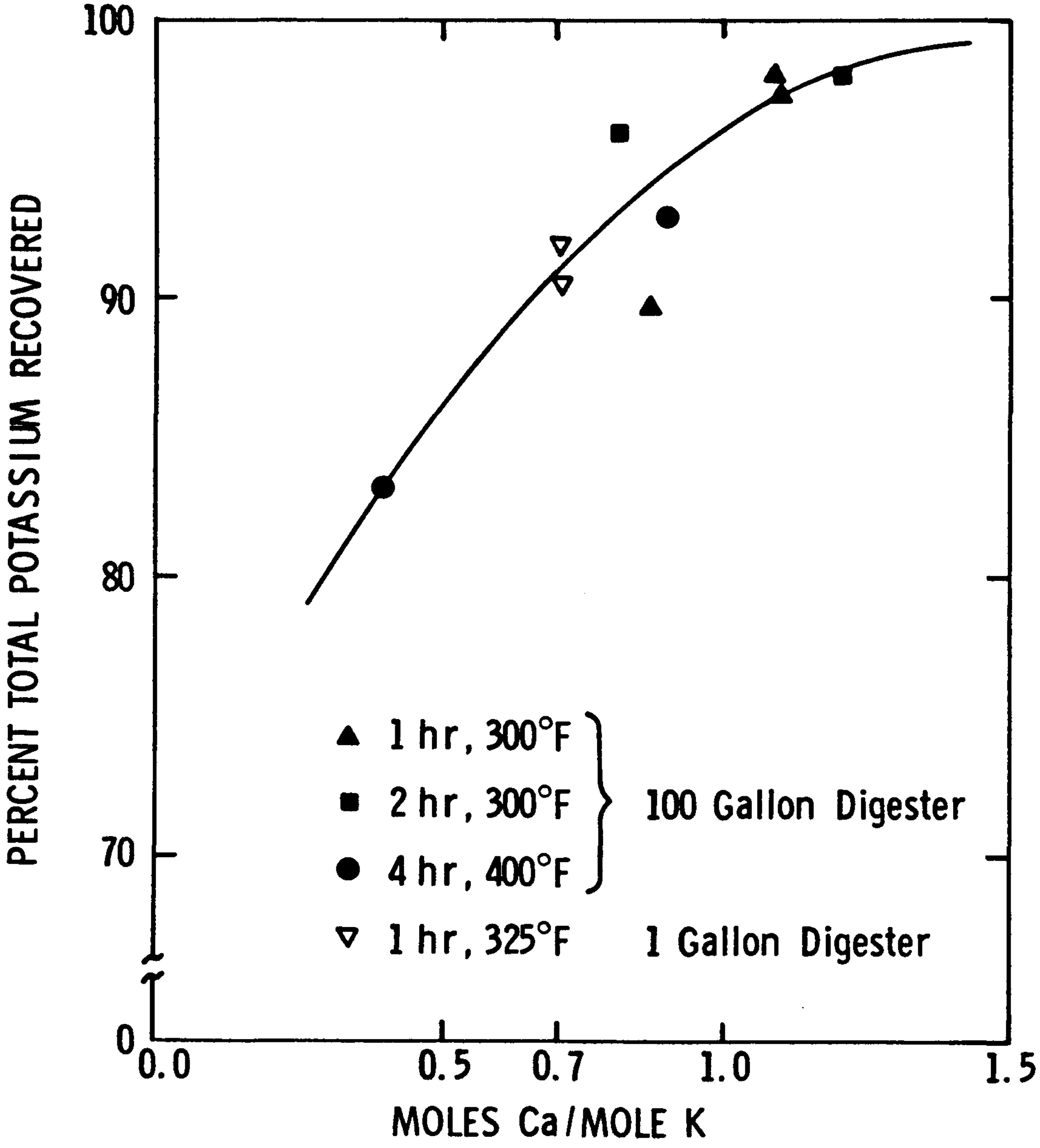
# FIGURE 1.1-2

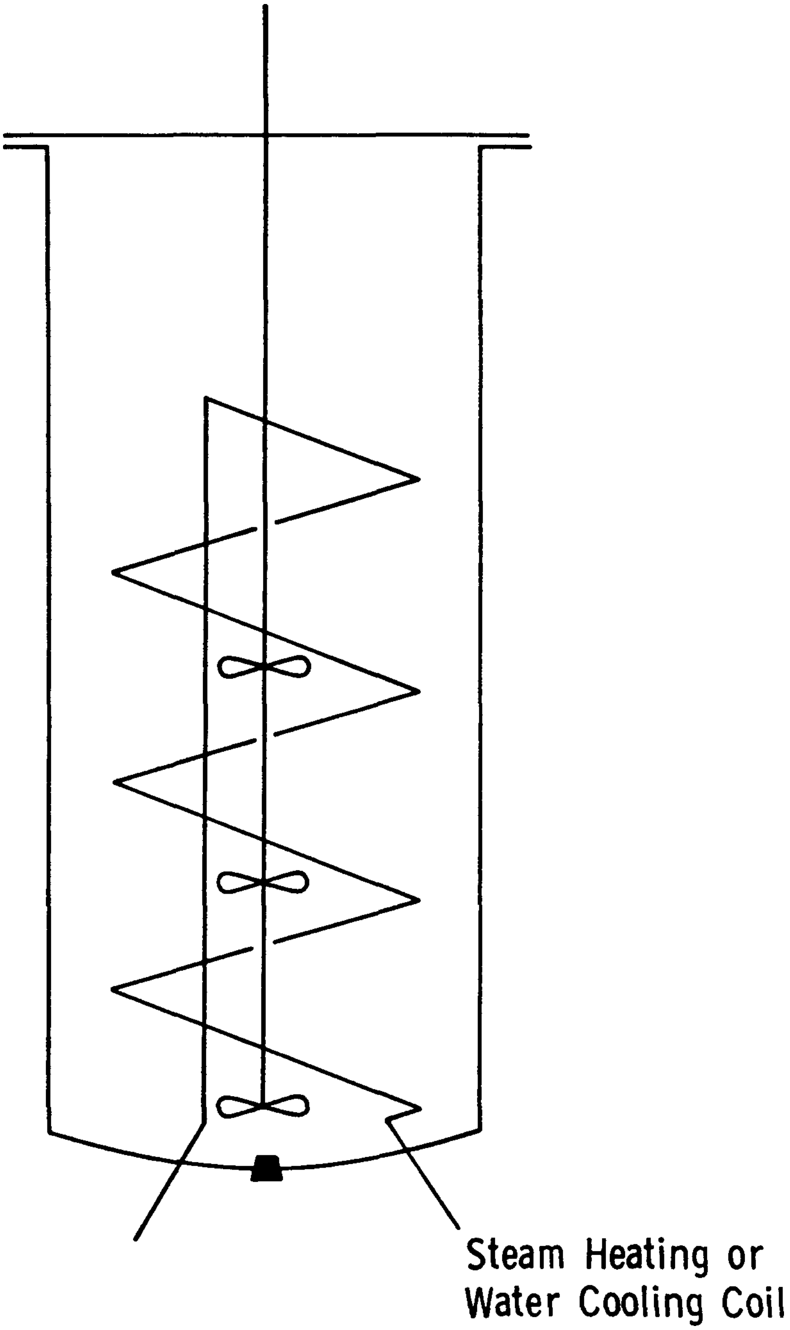
## CALCIUM HYDROXIDE DIGESTION RECOVERS POTASSIUM

## ILLINOIS NO. 6 CHAR



## FIGURE 1.1-3

## ONE GALLON RAPID HEATUP-COOLOFF DIGESTER



The following preliminary observations may be made based on these data:

- A potassium recovery of 92% is possible at a digestion temperature of 325°F, 15 minutes residence time, and Ca/K molar ratio of 1.06 with continuous agitation (Run A).
- Digestion at 400°F with no agitation yields total potassium recoveries of 95% and 96% (Runs C and D). Therefore, agitation may not be necessary for potassium solubilization although it will probably be necessary for process operability.

Figure 1.1-4 is a particle size distribution of the char/lime solids before and after digestion. The plots show that the weight of particles smaller than 10 μ increases from 25% to 43% during digestion. Analysis of these fine particles shows that 45% (wt.) of the particles smaller than 10 μ are $CaCO_3$. Therefore, $CaCO_3$ is produced as fine particles under typical digestion conditions.

In the digestion process $KFeS_2$ on char may react with KOH as shown in the reaction below:

$$2KFeS_2 + 6KOH \rightarrow Fe_2O_3 + 4K_2S + 3H_2O$$

This hypothesis was tested in the one-gallon digester by measuring the sulfur species solubilized during digestion. Char was slurried with 1 M KOH solution and heated to 450°F for one hour. Table 1.1-2 is a summary of the results.

Table 1.1-2

Reaction of Illinois No. 6 Char with 1M KOH Solution

Reaction Conditions: 15% (wt.) char slurry digested at 450°F, 410 psig, 1 hr. residence time

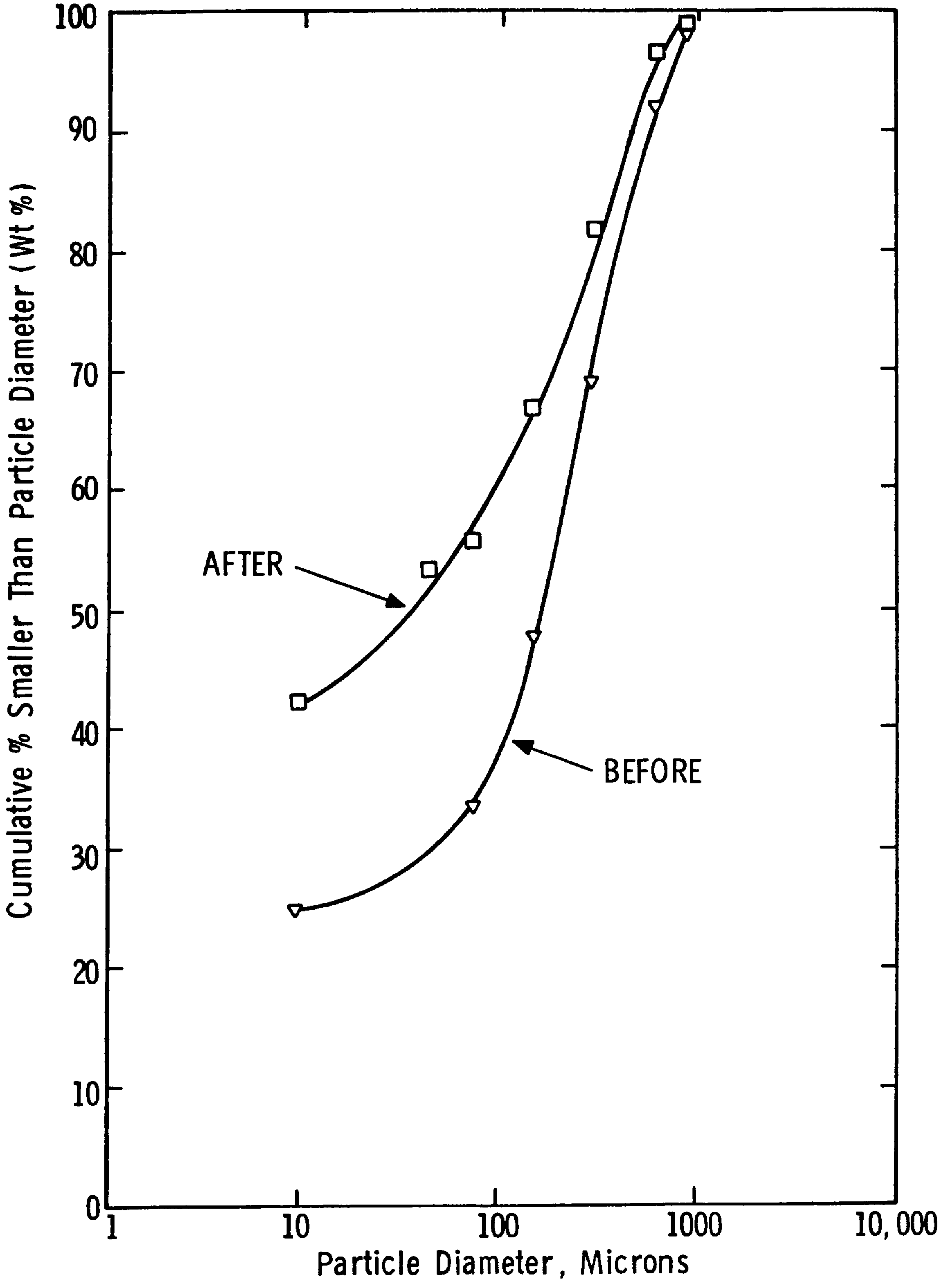
Results:

- 75% potassium recovery
- 90% sulfur in digested liquid
- Analysis of sulfur forms in liquid after digestion:

| Sulfur Species | Sulfur in that form (ppm) |
|---|---|
| $SO_4^=$ | 1525 |
| $SO_3^=$ | 62 |
| $S_2O_3^=$ | 2967 |
| $S^=$ | 2208 |
| $S_x^=$ | 124 |

## FIGURE 1.1-4

## PARTICLE SIZE DISTRIBUTION BEFORE AND AFTER DIGESTION



These results indicate that approximately 90% of the sulfur originally on the char is in the digested slurry liquid. As the table shows, there is a significant amount of sulfide in the digested slurry liquid, supporting the hypothesis that $KFeS_2$ is broken down to produce $K_2S$ during digestion. The oxidized sulfur forms may be a result of slow oxidation of the old char samples used in this study. Future work on fresh PDU char is planned.

## Bench Scale Leaching Tanks

After the char has been digested, the solubilized potassium compounds may be washed from the char. One possible washing technique is countercurrent leaching. To test the feasibility of this approach, a small leaching unit shown in Figure 1.1-5 was built to leach potassium from Illinois No. 6 char-lime solids. This unit permits small scale study of the solid-liquid separation process.

A char slurry is loaded into the leaching unit and then water or KOH solution is fed into the bottom of the leacher. During a leaching run, the fines content of the liquid overflow from the tanks is determined and used as a measure of the solid-liquid separation efficiency.

These single tank leaching runs were made to generate fundamental information to be used in estimating leaching performance on chars from catalytic coal gasification. Figures 1.1-6 through 1.1-8 present the results of runs made in this unit.

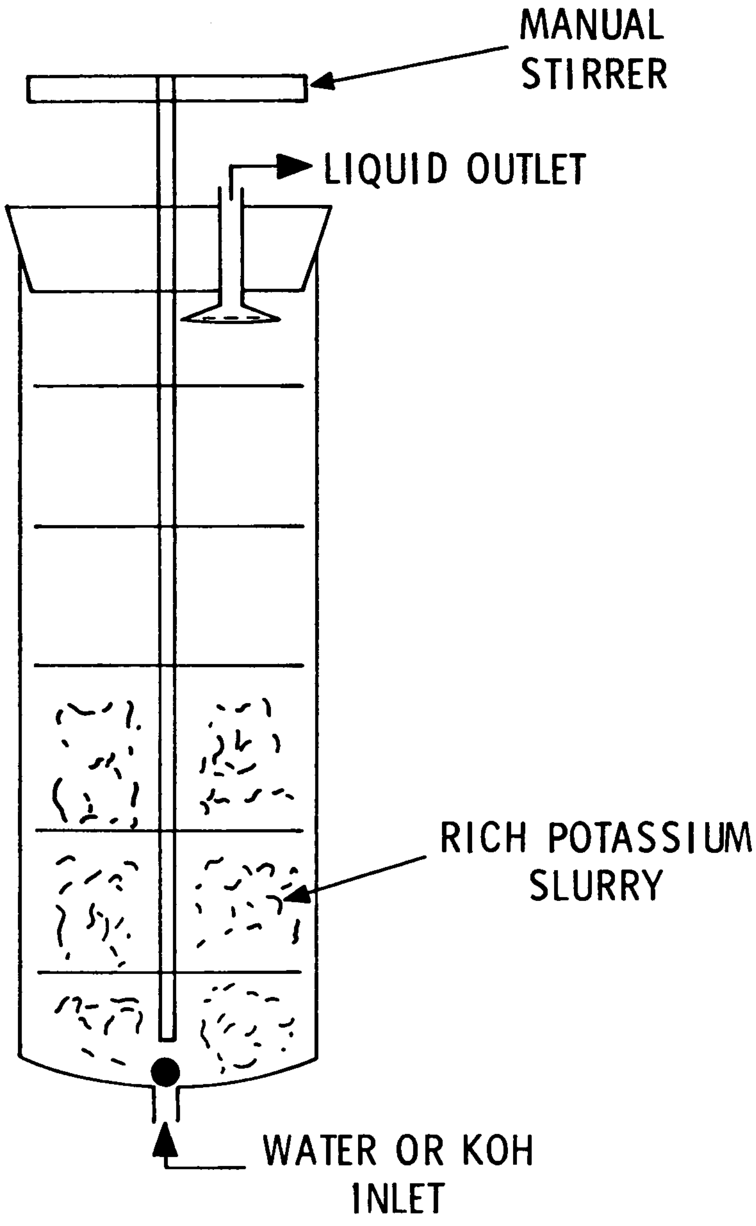
The material used to generate Figures 1.1-6 and 1.1-8 was char-lime solids from digestion runs. These figures show the solids carryover increased with increased potassium concentration in the leaching liquid. Increasing solids concentration in the slurry from 8 to 15% (wt.) solids appears to have a minor effect on solids carryover. Figure 1.1-7, a run with undigested char, shows a reduction in the char carryover at comparable superficial velocities. This could be because digestion produces smaller particle size material which overflows to a greater extent than the larger undigested char particles.

## Potassium Forms on Char

Potassium salts washed off char into solution are of great importance. Most forms are catalytically active; however, $K_2SO_4$, which can be present in the char solution, is not active. Table 1.1-3 is a summary of the mole percent of potassium tied up with various anions.

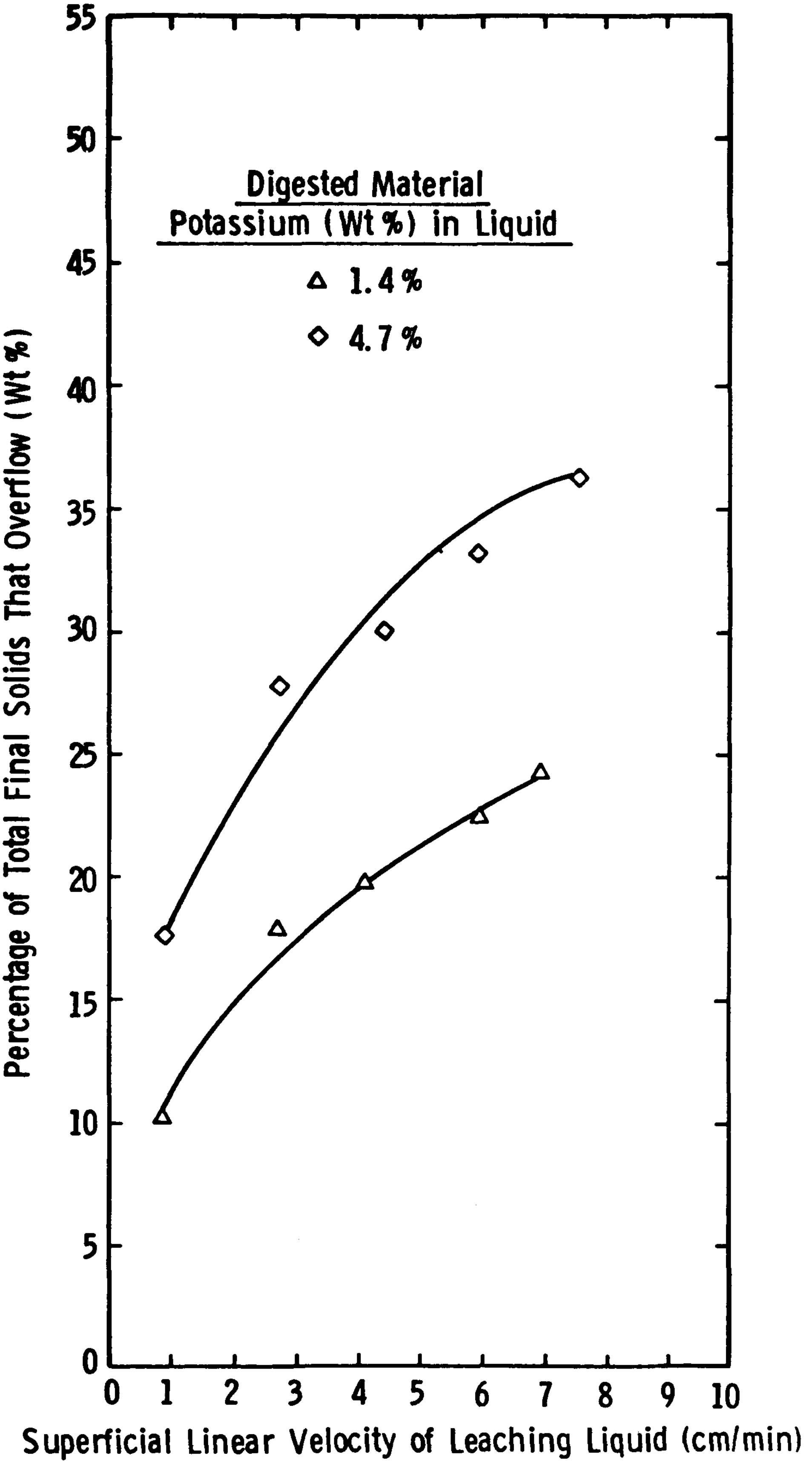
## FIGURE 1.1-5

## SINGLE TANK LEACHING UNIT



## FIGURE 1.1-6

## LEACHING TANK CARRYOVER AT 8% SOLIDS LOADING



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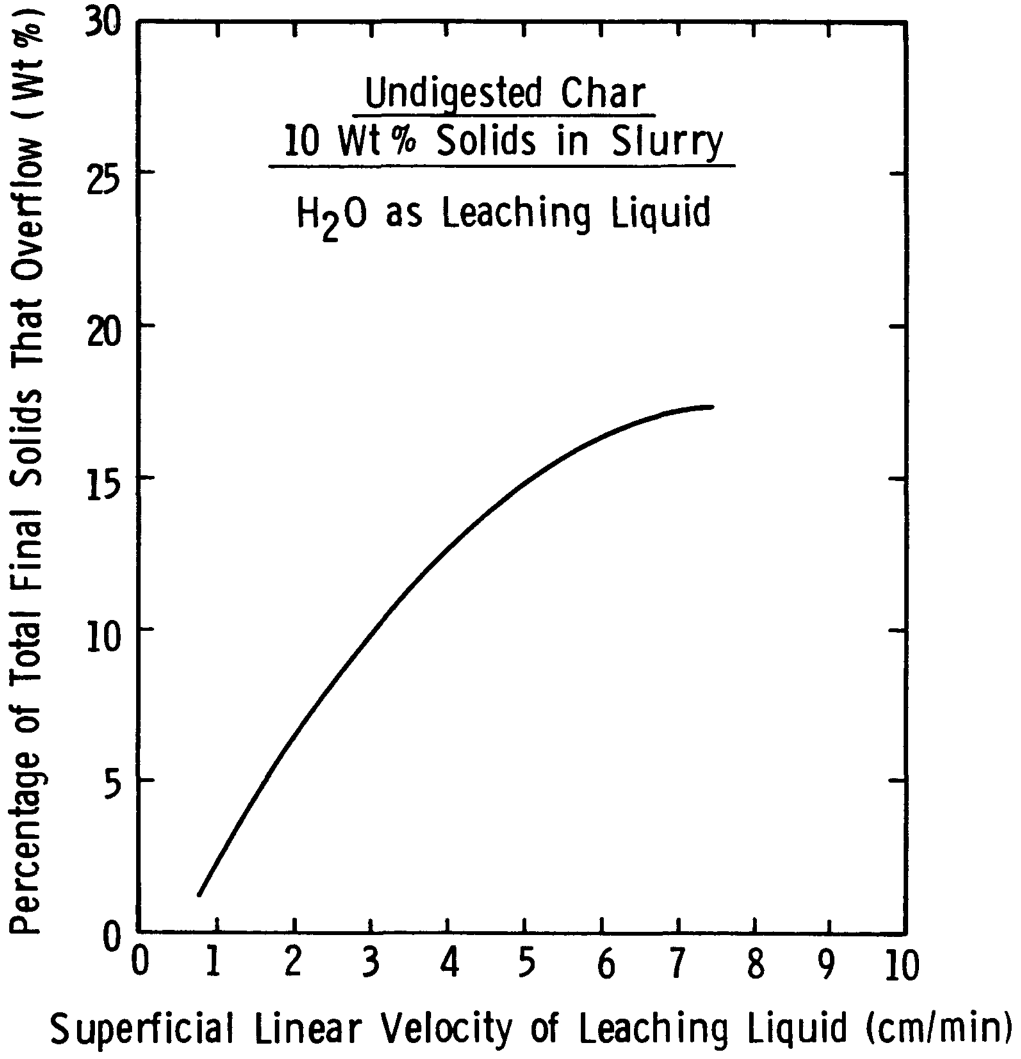
## FIGURE 1.1-7

## LEACHING TANK CARRYOVER AT 10 % SOLIDS LOADING



## FIGURE 1.1-8

## LEACHING TANK CARRYOVER AT 15% SOLIDS LOADING

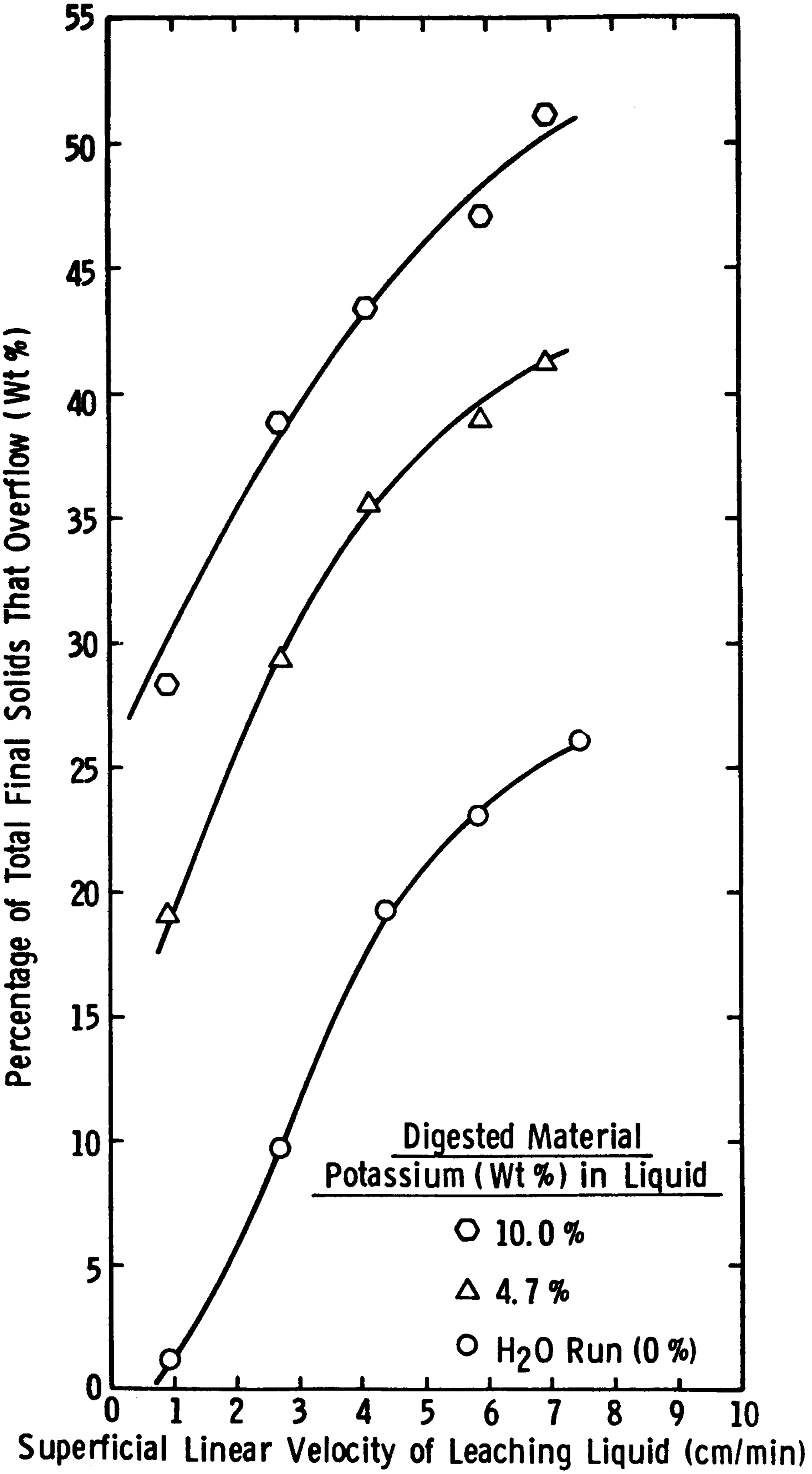


Table 1.1-3

Potassium Forms From Illinois No. 6 Water Washed Char

| Potassium forms | Potassium forms in solution from water washing of char (mole %) | | | | |
|---|---|---|---|---|---|
| | Run A | Run B | Run C | Run D | Run E |
| $K_2CO_3$ | 68.2 | 69.2 | 68.6 | 60.0 | 62.0 |
| $K_2SO_4$ | 15.1 | 19.8 | 20.9 | 22.7 | 19.4 |
| $K_2S_2O_3$ | 13.2 | 7.5 | 5.3 | 12.7 | 11.4 |
| "$K_2SiO_3$" | 3.5 | 3.5 | 5.2 | 4.6 | 7.2 |
| $K_2S$ | - | - | - | - | - |
| $K_2SO_3$ | - | - | - | - | - |
| pH | 10.0 | 10.4 | 10.4 | 10.3 | 10.1 |

The presence of $K_2SO_4$ and $K_2S_2O_3$ is probably due to the exposure of the char to air.

Future work to determine sulfur forms on char will be done using fresh PDU char which has not been exposed to air. A large nitrogen-blanketed box will be built to perform these washes.

## 1.2 Gas Phase Reactions Study

### Background

In the Exxon Catalytic Coal Gasification Process study design, a gas recycle stream of $H_2$, CO and some $CH_4$ is preheated with steam to approximately 1575°F to provide heat input to the gasification reactor. This heat input comes from two sources: sensible temperature difference and chemically stored energy. At the reactor temperature of 1300°F, the recycle mixture is not at equilibrium with respect to the mildly exothermic water-gas shift reaction

$$H_2O + CO \rightleftarrows H_2 + CO_2 \qquad \Delta H \approx -8 \text{ kcal/gmole}$$

so when the gases are equilibrated in the gasifier, the shift reaction provides an additional heat input. If, however, the shift reaction occurs in the recycle preheat furnace, that heat of reaction is not released in the gasifier and must be replaced by a larger sensible heat contribution. This in turn requires a higher coil outlet temperature from the furnace which will result in increased furnace costs.

Engineering evaluations have shown that a reformer may be cost competitive with a furnace if a coil outlet temperature higher than 1575°F is required from the furnace. A reformer uses the endothermic reforming reaction

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO \qquad \Delta H \approx 50 \text{ kcal/gmole}$$

to add energy to the recycle stream at lower temperatures, in the opposite manner from which the exothermic shift reaction necessitates a higher coil outlet temperature. Investigation of the extent of the shift and reforming reactions in the recycle stream at commercial conditions is therefore necessary to choose and design the best recycle stream heat input option.

## Experimental

The apparatus for this study is shown in Figure 1.2-1. A bottled mix of $H_2$, CO and $CH_4$ in the proportions of the recycle gas (70%, 19%, and 11%, respectively) is combined with steam generated by pumping a metered amount of water at pressure through a steam preheater. This mixture then passes through the reactor at conditions representative of a commercial recycle gas furnace. A condenser removes unreacted steam from the reactor effluent and a gas chromatograph analyzes the product gas mixture for any change in composition.

The variables to be studied are temperature and the possible catalytic effect of different metals in contact with the hot gas stream. Catalysis of the shift and reforming reactions by the furnace tube walls will be studied by adding various alloy wire meshes to the reactor using a range of stainless steels and nickel alloys.

The reactor and its internals are shown in Figure 1.2-2. The pipe is 36" long, with the middle 18" encased in the furnace. The remainder is exposed to allow for radiative cooling of the flanges, which are limited to 1175°F at 525 psig. A mullite (ceramic) liner prevents contact of the gas with the reactor walls.

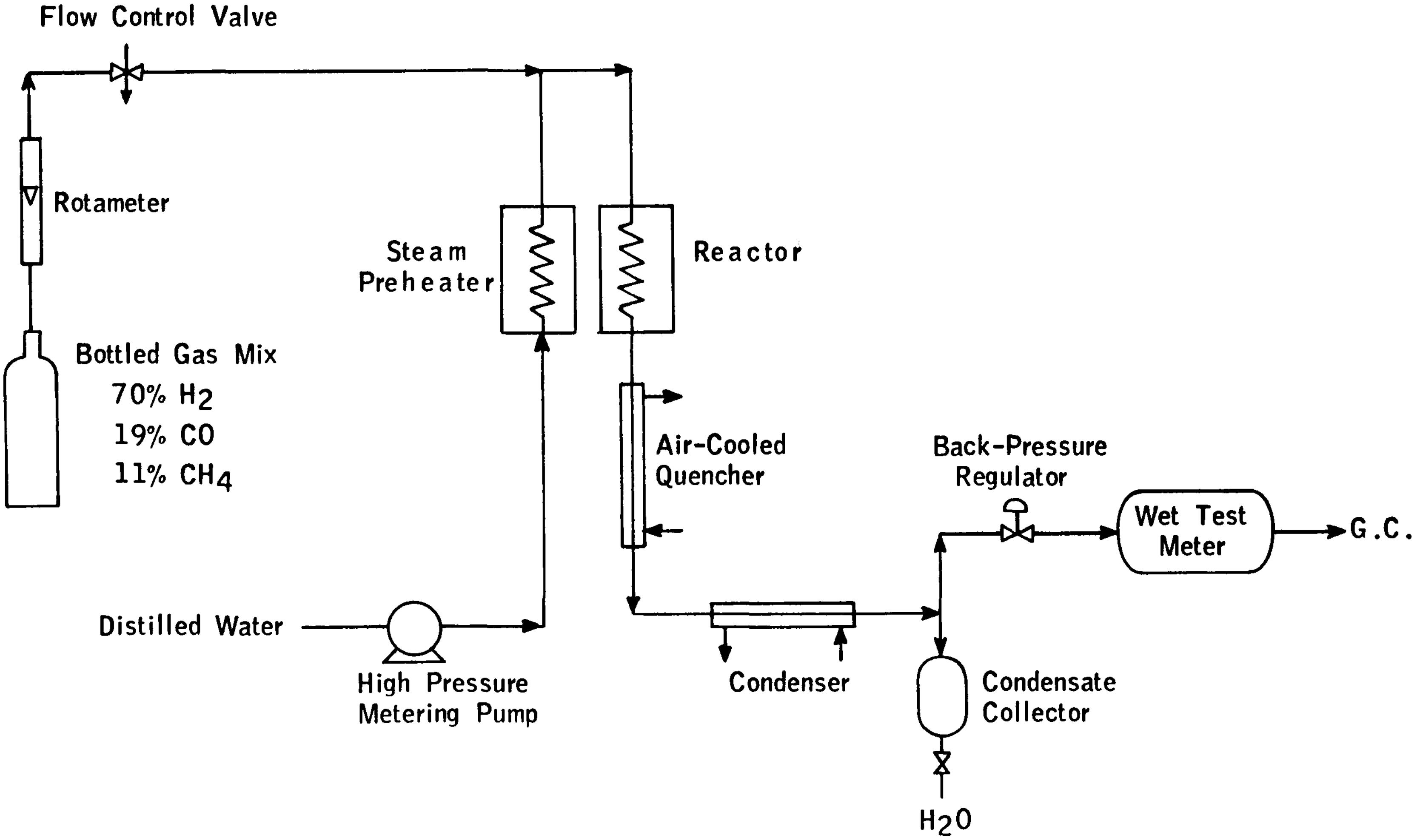
The bottled $H_2/CO/CH_4$ gas mixture is mixed with steam and enters the reactor through a 1/4" tube about four inches inside the lower flange. This allows space for the gas and steam to mix before entering the reaction zone. The reaction zone is a four-inch section in the center of the furnace where temperature control is most accurate. This zone will be filled with mullite beads or with alloy wire mesh to test the catalytic effects of different alloys. Immediately above the reaction zone is an endplate to minimize mixing in the dead space above the reaction zone and to position the 1/4" product gas line which leads to the quencher.

## Results

Initial blank runs without wire mesh were terminated due to carbon deposition in the feed and product gas lines. Carbon deposition in the feed line was corrected by modifying the feed system to that shown in Figure 1.2-2 from previous configurations which used separate gas and steam lines entering the reactor. Plugging of the product gas line was corrected by treating the reactor internals with a dilute concentration of sulfur dioxide ($SO_2$). According to the literature, this has the effect of preventing or retarding carbon deposition by forming an iron sulfide film on the metal surface. Cumulative blank runs of over twenty hours after the $SO_2$ pretreatment have been attained without plugging of the product gas line. However, the catalytic activity toward $CO_2$ formation of the sulfided metal is not negligible.

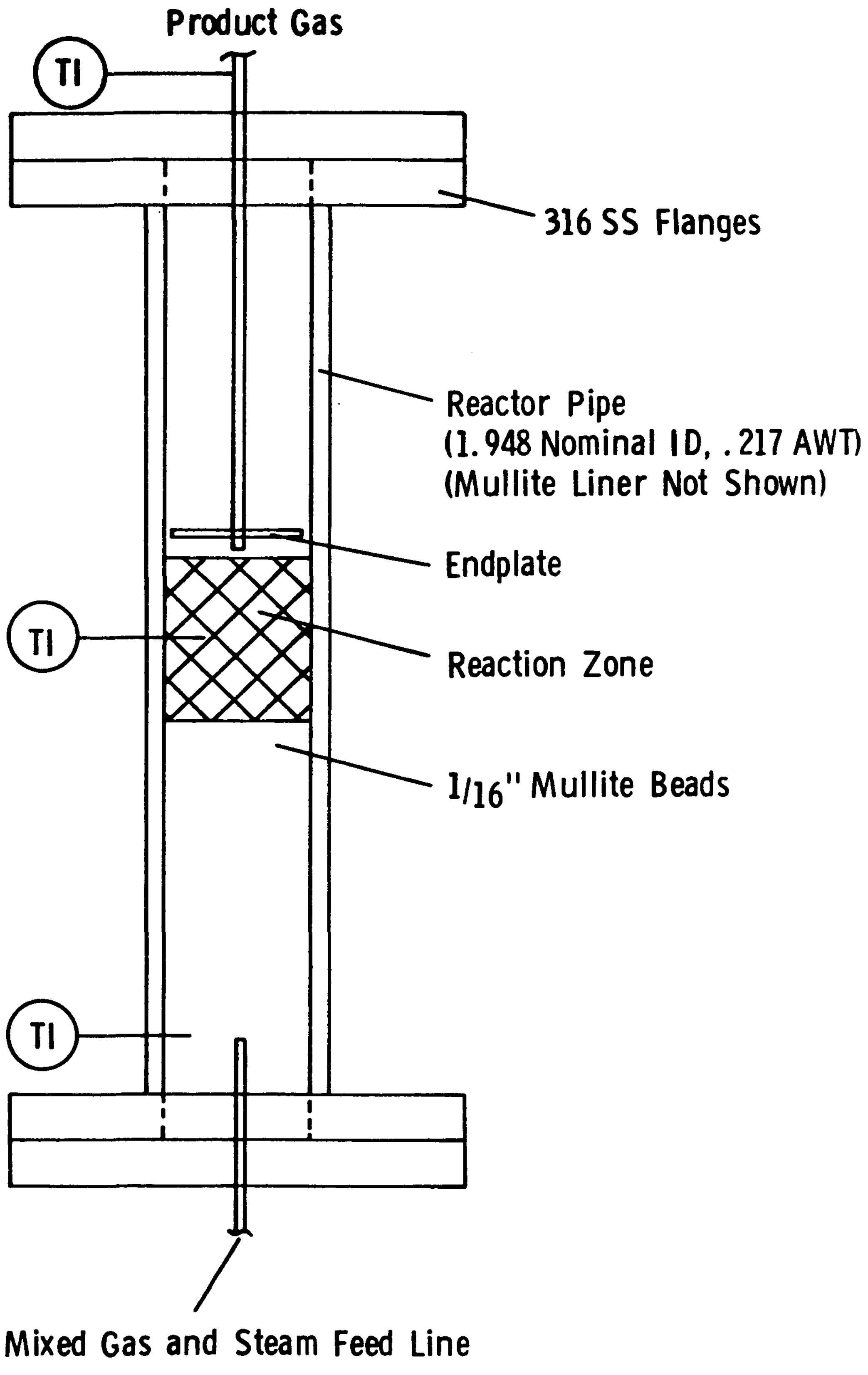
## FIGURE 1.2-1

## REVISED GAS PHASE REACTIONS UNIT



## FIGURE 1.2-2

## RECYCLE FURNACE EXPERIMENTAL REACTOR



Future work will address the inerting or minimizing of the internal metal surface of the reactor in order that the catalytic effect of the various metal alloys may be clearly distinguished.

# 2. Process Development Unit Operations
## (Reporting Category C02)

### 2.1 PDU Startup and Initial Operations

#### Startup and Initial Operation Schedule

The entire PDU system will be started up in stepwise procedure. The construction of the gasification section has been completed. It will be started up in a once through operation before construction of the gas separation section is completed. This will result in smooth operation of the gasifier before the acid gas removal, molecular sieve cleanup, and cryogenic systems are started up. Recycle gas to the gasifier will be simulated by blending hydrogen and carbon monoxide from trailers during this period.

The catalyst recovery system will be constructed while the gas separation system is coming on line.

By use of this stepwise startup procedure of the entire PDU system, the most efficient use may be made of the technical, operating, and construction personnel. It has the added benefit of debugging and establishing operation of one system at a time so that reliable operations may be built up sequentially during the startup period.

#### Checkout Test Plan

Unit checkout of the PDU gasification section has been completed. The general Checkout Test Plan is presented in Table 2.1-1. Step 1, hydrostatic testing, has been completed for all vessels.

In addition to the steps listed in Table 2.1-1, further testing and inspection of the gasifier was conducted during May in order to answer questions raised by DOE's contractor, Pullman Kellogg, about the selection of HK-40 alloy as the material of construction of the gasifier. The proof testing procedure for the gasification vessel consisted of raising the temperatures of all heaters together in small degree increments. When the gasifier reached 1400°F, this temperature was held for 48 hours. Several tests were conducted which consisted of cutting power to an individual heater and observing the dynamic response. The gasifier was then cooled slowly to ambient temperature and standard dye penetration tests were performed on all welds. To complete the proof testing procedure, the gasifier was hydrostatically tested at approximately 3400 psia and for a second time dye tests were performed on all welds. No failures or cracks were detected. Hardness tests were also conducted on the vessel which confirmed that the reactor had been hardened as expected during the proof testing procedure.

#### Initial Startup Plan

Initial startup operations began with full shift coverage after a three day operator training school in February.

## Table 2.1-1

## Checkout Test Plan for the PDU Gasification Section

| Summary of Steps | Criteria for Satisfactory Performance |
|---|---|
| 1. Hydrostatic Testing - All systems liquid filled with water. Hydrostatic Test Pressure = $(1\text{-}1/2) \times (\text{Design Pressure at Design Temperature}) \times \frac{(\text{Allowable Stress for Material at Ambient Temperature})}{(\text{Allowable Stress for Material at Design Temperature})}$ | No ruptures, cracks, or leaks. |
| 2. Gas Pressure Testing - Similar to above. All pipe and tubing joints to be tested with liquid leak detector. Flanges to be wrapped with tape and a pinhole tested with leak detector. | No leaks. |
| 3. Commissioning and Checkout of Equipment | Inspection by qualified technical person to determine proper functioning of all systems. |
| a. Programmable Controller<br>"Burn-in" of electronics to eliminate initial failures. Check each circuit internally on CRT for proper programming action by forcing inputs to simulate signals from the field, and observe action of output on CRT. Check each system for proper integrated function resulting from individual circuits. | |
| b. Checkout of Block Valves<br>All block valves must be checked visually in the field for proper open/close operation, forced from the programmable controller. In sequenced double block valves, verify tandem operation of both valves to be sure of proper wiring of actuation signal through limit switches of the other valve. | Verification of operation in field as forced from programmable controller. |
| c. Checkout of Alarm Systems<br>Verify from alarm sensors in the field or other source, through all associated circuits, to the alarm in the control room. Verify analog alarms from analog controllers, through current to contact closure devices to alarm. Check alarms in both the alarm annunciators and graphic display, including redundancy in graphic display lights when specified. | Verification of complete circuit function for each individual alarm. |
| d. Graphic Display<br>Verify approximately 100 status lights (in addition to the alarm lights) indicating open block valves, motors and pumps, pressure switches and other miscellaneous status lights. | Verification from source to each light. |
| e. Analog Controllers<br>Check all wiring on loop diagrams against installed wiring to be sure the sensor, current to contact closure device, and 3-pen recorder are properly looped on the input signal, and the output signal operates the final control device. Set initial tuning constants as specified by instrument engineer. | Visual wiring check. Observe operation of final control device by manually adjusting the output at the controller. |
| f. Temperature Controllers<br>Check for proper range and type. Verify output wiring of temperature controllers (TIC) and temperature limit switches (TL) through power relays, heater breakers, power controllers and field wiring to heaters by individual voltage checks at heaters. Check analog action of TIC's and on/off action of TL's. | Individual voltage checks in field. Later, as heaters are turned on, check controller thermocouples and other skin couples on analog multiplexer as heaters warm up. |

The steps and procedures for the PDU initial startup are outlined in Table 2.1-2. These steps have been integrated with the Checkout Test Plan wherever possible in order to expedite the startup of the gasification section.

Item 1, gas flow testing, was carried out concurrently with gas pressure testing. The system was pressured with nitrogen and gas was fed to the unit using the compressors at full reactor pressure of 500 psia and ambient temperature. This work included further checkout of the instrumentation and controls in the gas feeding and pressure control systems.

When smooth operation of the gas control system was achieved, testing of cold solids circulation with nitrogen was initiated (Step 2). Coal was transported by automatic control from the Coal Preparation Unit (CPU) approximately 600 feet to the storage hopper on the PDU, LH-3. The rotary feeder, the Catalyst Addition Unit (CAU), and the transporter that lifts the catalyzed coal from the ground level to the surge hopper on the 12th floor, LH-1, were all operated successfully.

Coal feeding was carried out at a range of reactor pressures and feed rates. The automatic sequencing of the lock hoppers and feed lock pots was checked and the effect of changing the locations and rates of driver gas in the coal feed lines was also observed.

Fluidization tests were performed on the coal that was in the gasifier. These tests were helpful in determining bed fluidization characteristics, setting pressure tap purge rates, and realistically testing downstream portions of the unit such as the automatic fines filter system and the gasifier char withdrawal valves.

Following the cold solids circulation experiments, the reactor was heated for proof testing and inspection of the gasifier vessel. Electrical power was turned on at a very low level to the radiant heaters surrounding the gasifier in order to allow moisture to bake out of each ceramic heater element. This was followed by full heat-up of the reactor to 1400°F. Temperature control instrumentation for the gasifier heaters was checked out during this time.

During June several systems were taken through initial startup. Operations began on the catalyst addition system using -16 +100 mesh Illinois No. 6 coal and potassium hydroxide catalyst solution. Continuous operation was achieved after solving some minor problems, which involved the plugging of vertical chutes in the system by wet catalyzed coal. The addition of vibrators and adjustment of catalyst solution concentration solved most of these difficulties. The catalyst addition equipment operated continuously for most of June to prepare catalyzed coal for future gasifier operations.

The steam generator was also started up during June. Work was concentrated on tuning the control instrumentation of the system and repairing leaks particularly around the sight glasses, in the new equipment. A steam

## Table 2.1-2

## PDU Initial Startup

1. Pressurize the Gasification System with Nitrogen

Check all flow, pressure and ΔP controllers with flowing nitrogen. Start up and check operation of compressors. Pressure and flow control must be smooth and controllers must be tuned for stable operation at design conditions of the unit.

2. Cold Solids Circulation with Nitrogen

Demonstrate ability to handle solids through dense-phase solids transporters, lockhoppers, feed lines, fluidized bed reactor, char withdrawal systems, and fines filters. This is to be done with char solids, using nitrogen only, at pressures up to 3500 kPa at ambient temperature. Includes automatic operation of lockhopper (LH) swing and fill systems, feed lockpots, char withdrawal, and fines filters automatic swing and emptying systems.

3. Heatup of Reactor System

Initial conditioning of heaters at low temperatures (below 80°C) may proceed during Step 2 above. When completed, the reactor should be depressured for safety while the heaters are brought up to design temperatures. The TL's and TIC's should be stepped up in 50°C increments during this period to avoid sudden overheating of the radiant ceramic heaters. Final tuning of the controllers should be done at design temperatures. Each heater must respond to process upsets and changes in set point without cycling. Tuning should be optimized to provide stable, slow response, rather than borderline on cycling.

4. Solids Circulation with Nitrogen at Design Temperature

This is the final checkout of the unit prior to introducing gasification streams. All control, alarm, and sensing equipment should be functioning reliably at this point. Operators should be familiar and confident with the operation of the unit and able to handle upsets in a safe manner. All automatic sequencing equipment should be functioning with override capability easily available where specified. All problems of instrument or mechanical nature should be solved during this relatively safe period of unit operation.

5. Startup of Steam Generation System

During Steps 2, 3, and 4 above, the steam generation system may be started and debugged. This is done off-line without feeding steam to the gasifier. The vaporizer may be operated at design temperature and pressure while the steam is going to the condenser. This permits tuning the vaporizer controls off-line. Smooth, reliable operation must be achieved with no detectable cycling of liquid level or pressure.

6. Feed Coal, Steam, and Syngas to the Gasifier

This completes the initial startup of the gasification section. Syngas is used once-through which allows the gasification section to be checked out without the necessity of running the MEA absorbers, molecular sieves, or cryogenic distillation equipment. This begins the shakedown operation and variables study period with simulated syngas recycle. Preliminary material balance data should be available, and data logging by the computer should be debugged by this time.

drum was installed downstream of the steam generator to ensure that no liquid water could be bumped or entrained from the steam generator through the superheater and into the gasifier. The need for this knock-out drum was determined during safety reviews which were held to investigate the safety aspects of the HK-40 alloy used in the gasification vessel construction. Smooth operation of the steam generator was achieved at 600 psia and design steam rates.

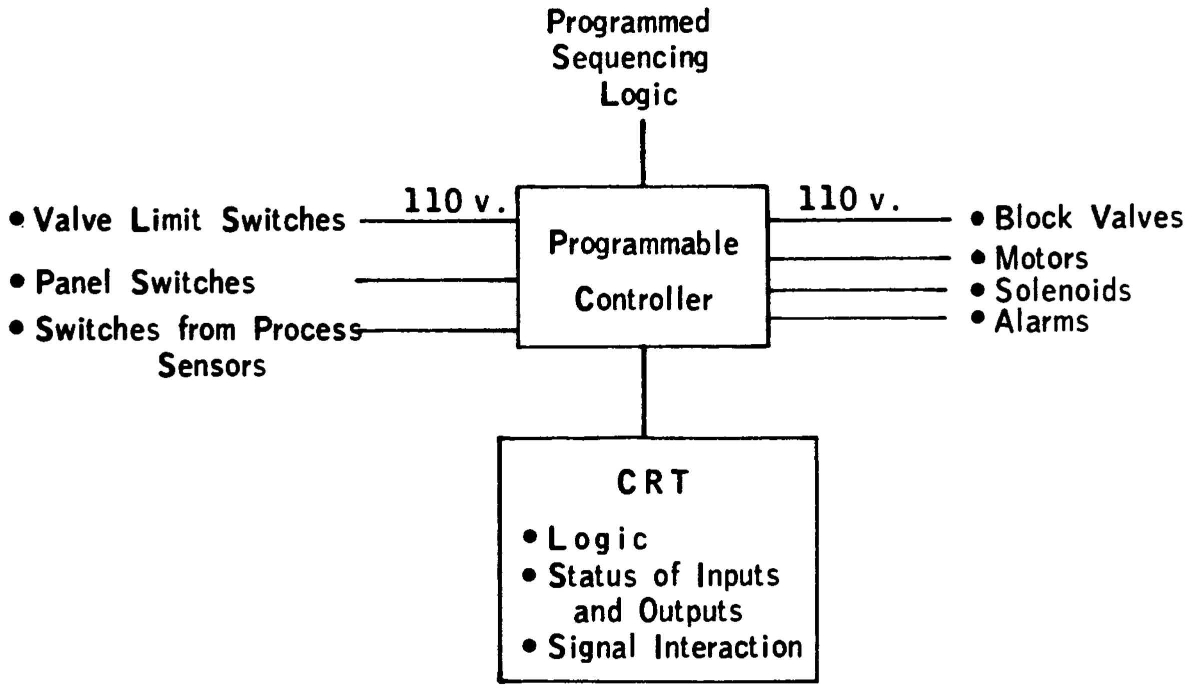
### Programmable Controller

The general functions of the programmable controller (Figure 2.1-1) on the PDU are:

- Sequencing double block valves
- Switching parallel trains on and off line; regenerating the off-line train
- Emergency shutdowns of individual systems
- Automating iterative batch processes (lockpots)

FIGURE 2.1-1

PROGRAMMABLE CONTROLLER



Input and output signals were assigned for existing systems. Programmed logic was checked during cold operations for the coal feed, gas feed, and filter systems. Logic for the char withdrawal system has been programmed but has not been checked.

Several component failures during initial testing and use of the programmable controller indicated the necessity for a backup. This system, consisting of a duplicate CPU (Central Processing Unit) with appropriate interfaces and input/output drivers, monitors input/output states and automatically comes on line in the event of a main CPU failure. This backup system should be available in the near future.

## Materials Testing Program

Initial measurements were taken and the final shipment of equipment was received for the materials testing program. Baseline ultrasonic thickness measurements were completed during the month of April. Measurements at various test sites were repeated by different operators to verify the reproducibility of the data.

Corrosion racks have been received and are ready to be installed in the gasifier.

## 2.2 Pilot Plant Catalyst Recovery Studies

### Background

After the coal has been reacted in the gasifier, the char consisting of unreacted carbon, mineral matter, and catalyst is removed from the gasifier and processed in the catalyst recovery section. Bench scale experiments during the predevelopment program demonstrated that part of the catalyst could be recovered from the char by leaching with water. Catalyst recoveries of approximately 70% of the total potassium present were obtained. The remaining 30% of the catalyst was present in a water insoluble complex of potassium with mineral matter that could not be recovered by water washing alone. Hydrothermal digestion of the char with lime can recover most of the water-insoluble potassium (see Section 1.1).

Although the overall catalyst recovery can be substantially increased using hydrothermal digestion prior to the water washing step, the process involves some economic tradeoffs. The savings resulting from increased potassium recoveries and thereby lower catalyst makeup costs have to be weighed against the added cost of the lime and the increased investment resulting from an additional processing step. Economic screening studies conducted during the Predevelopment research phase indicated that for a commercial plant, the two processing schemes would essentially break even in terms of final gas cost. It was decided that work on both processes would continue through the development program since more data is needed before the most economically attractive recovery process could be selected.

### PDU Catalyst Recovery System

### Requirements

There are two overall requirements for the PDU catalyst recovery system. The first is that the system recycle 90% of the total catalyst fed to the gasifiers when the unit is run in the $Ca(OH)_2$ digestion mode. This large recycle rate should allow any potential buildup problems to be identified as soon as possible on the PDU. The second requirement is that the recycled catalyst solution be at least 20% (wt.) $K^+$, which is the concentration needed in the catalyst addition unit. Any lower concentration would result in excessive drying requirements in the downstream coal feed dryers. However, this concentration need not be reached in the countercurrent water wash since the number of stages required would not be practical or convenient in a plant of this size. Instead the recovered catalyst solution will be concentrated to the 20% (wt.) $K^+$ level in an evaporation step prior to recycle to the CAU.

### Solid-Liquid Separation

The PDU catalyst recovery system will be capable of operating in both a water wash alone and a digestion followed by water wash mode. The water wash sequence will be the same for both operating modes.

This water wash will be carried out in a countercurrent mode. In each stage of the countercurrent system, the char from the previous stage will be contacted with wash liquor from the following stage, resulting in progressively richer catalyst solutions and solids which are progressively leaner in potassium. Any catalyst that is not recovered by the system will leave with the discarded solids stream from the final stage. Each stage of the countercurrent system consists of a contacting step where the liquid and solids streams are mixed and a solid-liquid separation step. The choice of the solid-liquid separator is an important consideration for the catalyst recovery system.

All solid-liquid separation devices may be classified into two groups:

- Those in which liquid is constrained and the particles are free to move. Some examples are sedimentation or centrifugation. These devices rely upon a density difference between liquid and solid to accomplish separation.

- Those in which solids are constrained and the liquid is free to move. Examples are filtration or screening. In these devices a density difference between solid and liquid is not important.

In order to determine which type of separator would be best suited for the PDU catalyst recovery system, additional information concerning the properties of the char slurries was collected from both bench and pilot scale units. A 100-gallon prototype digester was constructed and operated to determine the properties of digested char slurries. Both water washed and digested slurries were examined in terms of possible separation techniques. In general, the results indicated that the solid-liquid separations in the catalyst recycle loop would not be easy to accomplish.

One of the major difficulties facing solid-liquid separation is the relatively low density difference between the solid char particles and the surrounding catalyst solution. Gasified Illinois char at 90% carbon conversion is nearly two-thirds pore space. When this is filled with catalyst solution, the resulting particle density is only slightly greater than the density of the surrounding fluid. This results in low driving forces for separation in devices that rely upon a density difference to capture solid particles. In the catalyst recovery slurries examined, the average density difference between particle and solution was about 0.3 g/cc.

A second difficulty facing solid-liquid separation is the small particle diameter of most of these solids. Small particles cause both low settling velocities and blind filters. In the prototype equipment, the slurries generated consisted of as much as 70% (wt.) particles which were smaller than 10 μm in diameter. In general, the digested slurries were finer than undigested slurries. Attempts to reduce the amount of particle degradation occurring in the digester have met with some success, but it appears to be impossible to completely eliminate the problem.

With these difficulties in mind, it was necessary to examine the different solid-liquid separation devices in order to determine which device was best suited for the PDU catalyst recovery system. The method used to evaluate the different separation devices consisted of three steps. First, bench scale tests were conducted to determine what the performance of a particlar separation device was likely to be. This performance or efficiency will vary greatly with the type of separator being examined and is an important part of any material balance around the system. Once this efficiency had been determined, a process flow scheme was developed which tried to use the particle separator to its greatest advantage. Finally, a material balance was performed to ensure that the proposed flow scheme met the overall requirements of the catalyst recovery system. These requirements as well as the data on slurry properties and digester performance make up the material balance basis.

## PDU Catalyst Recovery Material Balance Basis

Table 2.2-1 lists the requirements or basis items used in the PDU catalyst recovery material balance. Many of the items, such as the solids loading to the digester and the expected particle size distribution, are based on the performance of the FBG during the predevelopment contract. The performance of the digester is based on data gathered in the prototype and bench scale units. This basis was used only to obtain approximate overall potassium recoveries and stream rates. Actual equipment design will be based on maximum or minimum basis values to allow flexibility in unit operation.

From an operability standpoint, the most important basis is the particle size distribution expected in the slurry feed to the water wash section. This will determine the ease with which solid-liquid separations can be accomplished. For these material balances it was assumed that no particle degradation occurred anywhere outside of the gasifier; that is, no degradation of char and overhead fines was assumed to occur in the char slurry pots, the slurry let down valves, or in the digester itself. Any lime added to the digester in excess of that needed to free insoluble potassium in the hydrothermal reactions was assumed to go to fine precipitates of $CaCO_3$ or $Ca(OH)_2$. These assumptions on particle degradation are deliberately optimistic. Any configuration which is unsuccessful in recovering the desired amount of potassium from this relatively coarse particle size distribution would not be acceptable as the actual PDU system.

## Solid-Liquid Separation Techniques

The first solid-liquid separation technique to be examined for the PDU catalyst recovery system was gravity settling. It was chosen because it appeared to be the least costly method of separation and would minimize any particle attrition that might occur. It was incorporated into the processing scheme as a series of leaching tanks. Figure 2.2-1 shows the proposed flow plan for this processing scheme.

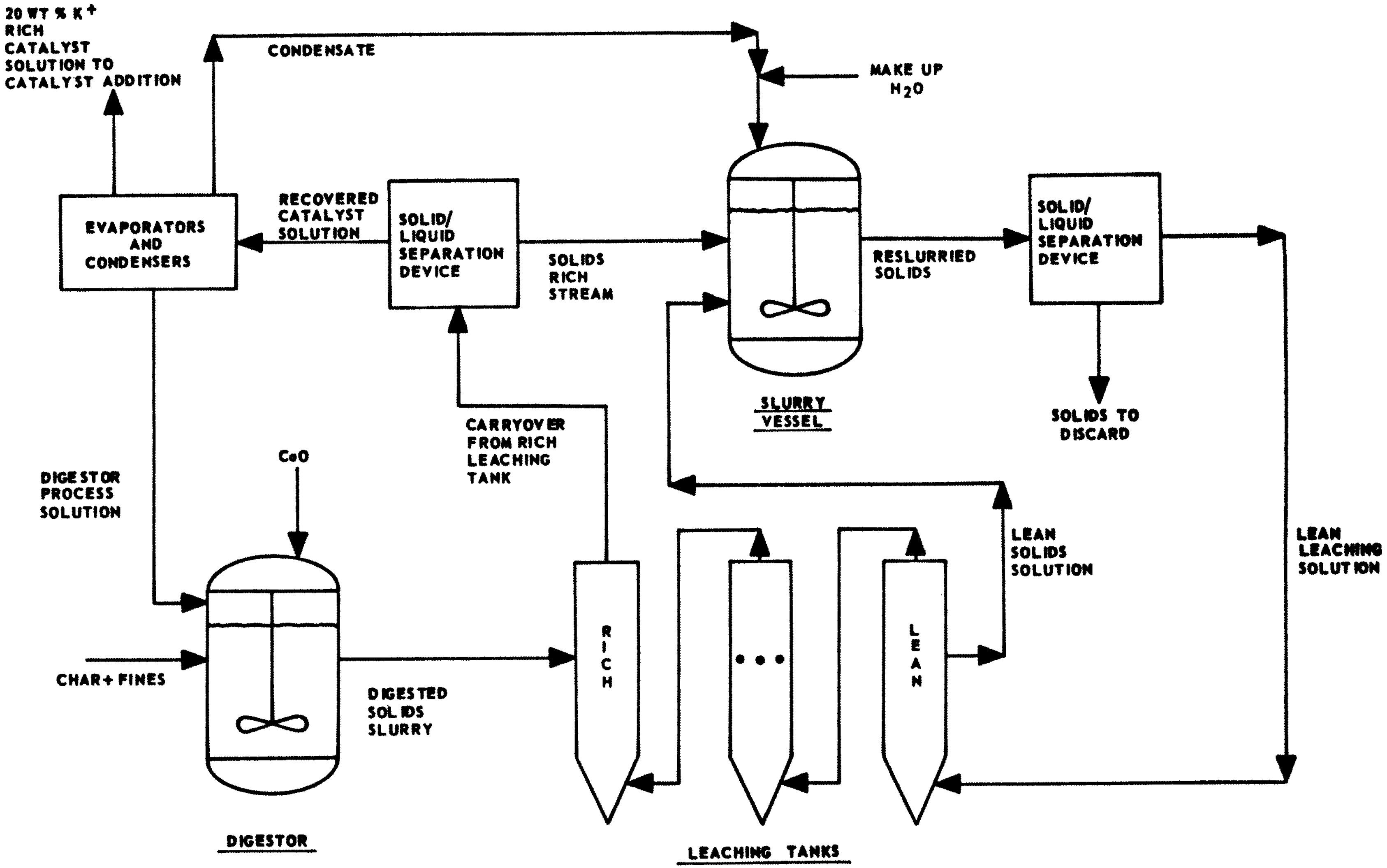
## Table 2.2-1

## Catalyst Recovery Material Balance Basis

| Basis Item | | Technical Backup/Comments |
|---|---|---|
| • Solids loading to digester | | Based on performance of FBG solids removal system. |
| - 25 lbs/hr bottoms char | | |
| - 10 lbs/hr overhead fines (all <75 μ) | | |
| - 12 lbs/hr CaO | | In digestion case only. Results in a Ca/K ratio of 1.0. |
| • Catalyst forms in feed to digester | | |
| - Catalyst loading of 24% (wt.) on char and fines fed to digester | | Based on analysis of FBG char and fines. |
| - Water soluble forms | % Total $K^+$ | |
| $K_2CO_3$ | 59.55 | |
| KOH | 6.77 | |
| Sulfur forms | 3.68 | |
| Total water soluble | 70.00 | |
| - Water Insoluble forms | % Total $K^+$ | |
| $KAlSiO_4$ | 25.50 | |
| $KFeS_2$ | 4.50 | |
| Total water insoluble | 30.00 | |
| • Digester Performance | | |
| - 98% of total $K^+$ assumed soluble after digestion for one hour at 300°F | | Based on bench and prototype work. |
| - No particle breakdown assumed in digester | | This assumption is optimistic and will be modified before the final design of the catalyst recovery system is completed. Past digestion runs have shown severe particle degradation. However, attempts to modify the digester to reduce this degradation are being made. |
| • Leaching tank performance | | |
| - Solids carryover | | |
| + Assume all particles less than 75 μ are carried out in rich leaching tank carryover | | Based on performance of bench and prototype scale leaching tanks. |
| + 15% of bottoms char is less than 75 μ | | Consistent with particle sizes obtained in FBG. |
| + Assume all CaO not needed to react with mineral matter is carried out of rich leaching tank | | Consistent with theory that unused lime forms fine $CaCO_3$ and $Ca(OH)_2$ precipitates. |
| + Assume all gasifier overhead fines caught in secondary cyclone are carried out of rich leaching tank | | Based on particle size distributions on overhead fines obtained in FBG. |
| • Performance of solid/liquid separation devices | | |
| + Assume solids rich stream contains 30% (wt.) solids | | Based on optimistic guess at best performance of filters or centrifuges. |
| + Assume solids lean stream contains no solids | | |

FIGURE 2.2-1

LEACHING TANKS IN SERIES



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The leaching tanks act as upflow fixed bed leachers which wash the char with progressively weaker solutions of KOH. Leaching solution is pumped into the bottom of each tank and flows upwards through the bed of suspended char particles. The upward velocity of the liquid keeps the solids suspended, while the settling velocity of the particles prevents them from being carried out of the tank. Any solids that do not have a sufficient settling velocity to remain in the leaching system will be carried out in the overflow from the rich leaching tank. These solids are captured by a positive solid/liquid separation device such as a filter or centrifuge, then reslurried with water in a final washing step. The rich liquor from the separation device is the recovered catalyst solution which will be concentrated to 20% (wt.) $K^+$ in an evaporator before being sent to catalyst addition. Spent solids leave the system as a dry cake.

The leaching tank system was the preferred PDU catalyst recovery system at the beginning of the development contract. To examine the operablity of this concept, a full PDU scale leaching tank was constructed and operated in conjuction with the prototype digester. This prototype equipment yielded important material balance and particle size distribution information as well as providing the necessary performance data to design a leaching tank system. It was found that the leaching tanks worked well on particles that were larger than 75 µ in diameter. Particles smaller than 75 µ, however, were likely to be carried out of the leaching vessel in the overflow solution. Unfortunately, 15% of the PDU bottoms char and all of the cyclone fines are expected to be smaller than 75 µ. In addition, most of the lime that does not react in the digester should be present as a fine precipitate. The result is that approximately 50% of the solids fed to the leaching tanks would be carried out the top of the first stage. Half of the solids in the system will see only one stage of water wash. Therefore, potassium recoveries of 90% are possible only at extremely dilute recovered catalyst solution concentrations. In addition, any further particle degradation in the digester or char slurry valves would make this problem even worse. Because of these problems with fines, it was decided not to use leaching tanks as the catalyst recovery system for the PDU. Instead, a search was begun for a simple system that would be capable of handling fine particles.

Two such systems were proposed:

- Digestion followed by one stage water wash.
- Digestion followed by countercurrent water wash using mixing tanks and separators.

Both systems rely upon an effective solid/liquid separation device to separate the washed char from the leaching solution. The basis chosen for this device was 100% recovery of solids as a 30% (wt.) solids cake.

Figure 2.2-2 shows the flow plan for digestion followed by one stage water wash. The digested slurry is diluted in a large slurry tank to such a low catalyst concentration that the solids discard stream from the subsequent separation device has only a small fraction of the total potassium. The recovered catalyst solution is then concentrated in an evaporator and sent to catalyst addition.

This system is probably the simplest that could be devised. Only one solid-liquid separation is required. However, recovered catalyst solution concentrations are of necessity very low. To achieve 90% recovery of the total potassium, the concentration would have to be approximately 0.5% (wt) $K^+$. This results in an excessive evaporation duty in order to achieve the 20% (wt.) $K^+$ solution needed in catalyst addition.

Figure 2.2-3 gives the flow plan for digestion followed by countercurrent water wash using mixing tanks and separators. This is the system that will be used to recover catalyst in the PDU. Each stage of the countercurrent wash consists of a mixing tank followed by a solid-liquid separation device. Thus the digester serves as the mixing tank for the first stage. The solids slurry leaving the digester is fed to a solid-liquid separation device. The solution from this device is the recovered catalyst solution which is sent to an evaporation step to be concentrated to a 20% (wt.) $K^+$ solution. The solids from the separator are sent to the second mixing tank where it is slurried with the catalyst solution from the separator associated with stage 3. This countercurrent processing continues until the final stage where the water condensed in the evaporator is added to the nth mixing tank along with any makeup water required.

Table 2.2-2 presents the results of the material balances performed on this system. Recovered catalyst solution concentrations of 1, 4, and 10% (wt.) $K^+$ were examined. For a concentration of 1% (wt.) $K^+$, the desired recovery of 90% can be obtained in only two stages.

For a concentration of 4% (wt.) $K^+$, five stages are required. However, the evaporation costs are greatly reduced over those for the 1% (wt.) cases. To obtain a recovered catalyst solution concentration of 10% (wt.) $K^+$, sixteen stages would be required.

While it is important to obtain high potassium concentration in the recovered catalyst solution for the commerical plant to save on evaporation costs, it is not essential to do so in the PDU. The goal for the PDU is to demonstrate catalyst chemistry at a recovery level typical of that projected for commerical operation.

As stated earlier, this goal can be achieved by recovering dilute solutions. The PDU catalyst recovery system will therefore consist of two stages, recovering 90% of the total catalyst in a 1% (wt.) $K^+$ solution. Additional data on the impact of higher concentrations of performance of the solid-liquid separation device will be obtained off-line.

## FIGURE 2.2-2

## ONE STAGE RECOVERY

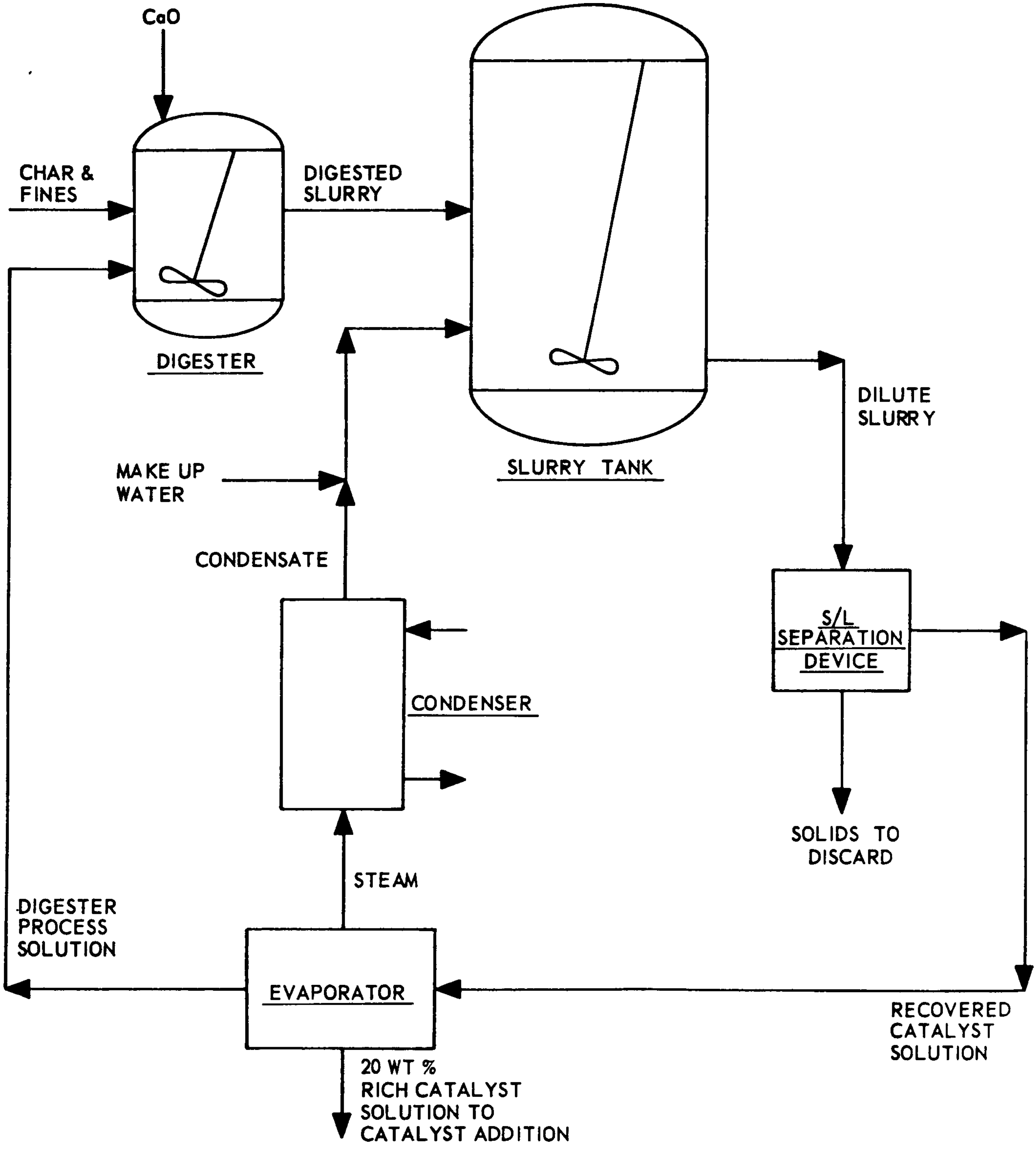
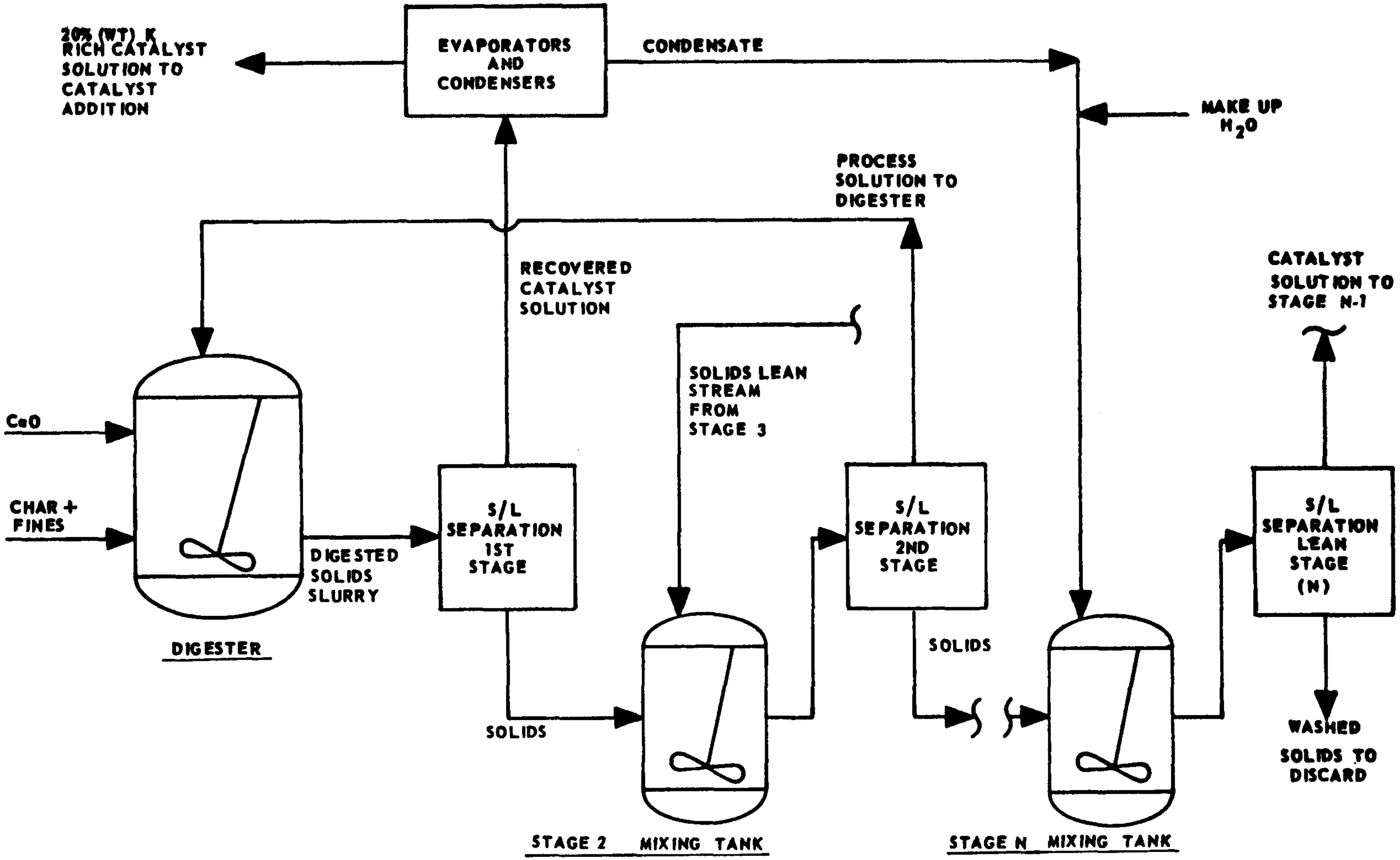


FIGURE 2.2-3

SEPARATORS AND MIXING TANKS IN SERIES



## Table 2.2-2

## SUMMARY OF MATERIAL BALANCE RESULTS FOR SEPARATORS AND MIXING TANKS IN SERIES*

| Case | Recovered Catalyst Solution Concentration, % (wt.) $K^+$ | Number of Stages | Recovery, % of Total $K^+$ | Required Water Evaporation Rate to Obtain 20% (wt.) $K^+$ Concentration, lb/hr | Makeup Water, lb/hr |
|---|---|---|---|---|---|
| 1 | 1 | 2 | 93.41 | 767 | 122 |
| 2 | 1 | 3 | 95.15 | 781 | 122 |
| 3 | 1 | 4 | 95.40 | 783 | 123 |
| 4 | 1 | 5 | 95.43 | 783 | 123 |
| 5 | 4 | 5 | 91.18 | 162 | 122 |
| 6 | 10 | 16 | 90.23 | 41 | 122 |

---

*All cases assume 30% (wt.) solids in solids rich streams.

The critical factor in this proposed catalyst recovery system is the device chosen to perform the solid-liquid separations. In order to maintain potassium recoveries in excess of 90% total $K^+$, a solids concentration of at least 20% (wt.) is required in the solids rich stream from the device. In addition, the clear liquor should contain as few fines as possible to avoid problems in the evaporation and catalyst addition steps. Finally the device must be capable of handling a slurry in which the majority of the particles are smaller than 10 $\mu$ in diameter. This fine particle size distribution could result if particle degradation occurred in the char withdrawal system or in the digester. Devices examined for this service included hydroclones, centrifuges, and filters. Due to the possibility of treating large amounts of fine particles, filters were chosen as the most promising device for this application.

## Filter Testing

To test the feasibility of using filters for this type of separation, batch filtration tests were conducted by a vendor on three PDU catalyst recovery slurries. These slurries cover the spectrum of possible filter duties expected in the PDU.

Table 2.2-3 lists the results of these tests. The digested solids slurry is considered the worst case that can be expected in the PDU. These solids were broken down in a recirculation pump until approximately 70% (wt.) were smaller than 10 $\mu$ in diameter. The slurry was tested using a metal screen, a nylon cloth, and a metal screen coated with diatomaceous earth as the filter medium. When only the metal screen was used, the filtrate contained many fine particles and the average rate was low (9 gph/ft$^2$). The nylon cloth gave a clear filtrate but reduced the filtration rate. However, when the metal screen was coated with diatomaceous earth prior to filtration, the rate increased to 20 gph/ft$^2$.

Test D represents filter performance using a slurry that would be expected in a water wash only processing scheme. Both this test and Test E (which represents the filter performance using the solids carryover from a rich leaching tank) filtered very easily using the metal screen and clear filtrates were obtained. This was expected since these samples had a much coarser particle size distribution than the material used in Tests A, B, and C. This relative ease of separation may be an important consideration in future comparisons between digestion followed by water wash and water wash only catalyst recovery schemes.

The results of these batch tests indicate that filtration is a viable option for solid-liquid separation on the PDU. The ability to operate with a precoat will be desirable although it may not be required in the water wash only case. Filter cakes consisting of 40 to 50% (wt.) solids can be obtained.

## Table 2.2-3

## Summary of Batch Filtration Tests on PDU Catalyst Recovery Slurries

| Test | Sample Description | Medium | Effluent | Initial Rate, gph/ft$^2$ | Final Rate, gph/ft$^2$ | Average Rate, gph/ft$^2$ |
|---|---|---|---|---|---|---|
| A | Digested FBG bottoms char and lime. Severe particle attrition (~70% <10 μ) | Metal screen ~140 μ aperture | Filtrate cleared after 10% of solution but spot bled periodically. | 32 | 10 | 19 |
| B | Same as above. | Nylon cloth ~20 μ aperture | Cleared after 10%, no spot bleeding. | 8 | 2 | 4 |
| C | Same as above. | 24 x 110 screen filter medium was coated with diatomaceous earth before filtration. | Cleared immediately. | 17 | 7 | 20 |
| D | Sample of FBG bottoms char and fines combined to simulated slurry expected in "water wash" only case. | Metal screen ~140 μ aperture | Cleared at 5%. | 32 | 13 | 20 |
| E | Sample of carryover from rich leaching tank handling "water wash" slurry (Sample D). | Metal screen ~140 μ aperture | Cleared immediately. | 40 | 22 | 30 |
| F | Same as A. | Nylon cloth ~20 μ aperture | Cleared almost immediately. | -- | -- | 4 |

---

Notes:
- Tests were conducted at a constant pressure of 50 psi in a nitrogen atmosphere at 200-220°F.
- Tests A through E were carried out on a 0.01 ft$^2$ filter; Test F was carried out on a 1.1 ft$^2$ filter.

## Selection of PDU Filters

The next step in the design was to choose the actual filter equipment for the PDU system. Several types of filtration equipment were examined to determine which would best fulfill the PDU requirements. The types of filters evaluated included rotary vacuum filters, horizontal belt filters, filter presses, and several types of pressure filters. After obtaining and evaluating information concerning the operation of each of these filtration devices, it was decided that two horizontal tank vertical leaf pressure filters would best meet the requirements of the PDU catalyst recovery system.

This type of filter has several advantages that make it well suited to PDU operation:

- It is capable of high pressure (50 psig) operation which results in a higher filtration rate than could be obtained with vacuum or gravity filters.
- The filter is capable of operating in an inert atmosphere so that any air exposure of the char can be avoided.
- It is capable of either dry cake or slurry discharge and can be operated with either a precoat or body feed filter aid.
- The leaves of the filter are easily accessible for replacement or repair if damaged or blinded during operation.

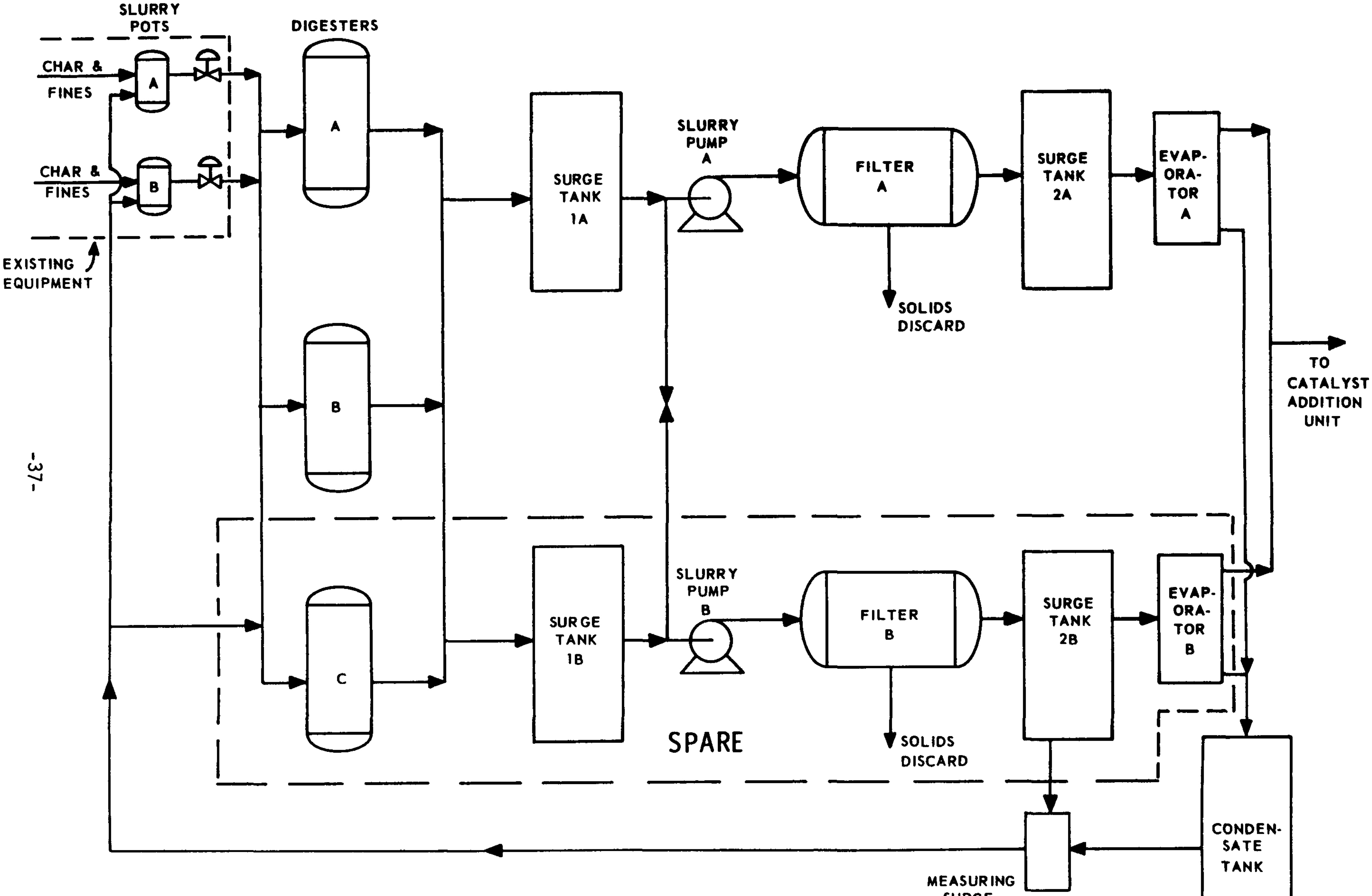
In addition to these advantages, the filters purchased for the PDU are relatively simple in concept and less expensive than many of the other filters examined.

## Detailed Design of PDU Catalyst Recovery System

Once the filters had been chosen for the PDU catalyst recovery system, the detailed design work could begin. Figure 2.2-4 is a simplified schematic flow plan for the entire PDU catalyst recovery system. This drawing shows all the major process vessels as well as the pumps and process lines. Startup of this system will occur in two steps. Initially the system will run with digesters A and B and Filter A and will be capable of recovering 90% of the catalyst under base case conditions. After this equipment is operating smoothly, the equipment marked "spare" on the drawing will be started up. This equipment can be used either in conjuction with the first train to allow greater system flexibility or by itself for off-line testing.

Due both to the uncertainty concerning the particle size of the PDU char and to the many different conditions at which the PDU will run, the catalyst recovery system was designed to be very flexible. When the PDU is running in its base case mode, the catalyst recovery system will be processing 25 lbs/hr of gasifier bottoms char and 10 lbs/hr of overhead fines. At normal dilution the system would recover 90% of the catalyst from this char in a 1% (wt.) $K^+$ solution. However, the system is designed to operate at twice normal

## FIGURE 2.2-4
## PDU CATALYST RECOVERY FLOW PLAN



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dilution or a recovered catalyst solution concentration of 0.5% (wt.) $K^+$. At this concentration overall recovery would be close to 95%. It is also capable of handling twice the base case solids feed rate at the normal 90% recovery level.

As shown in the catalyst recovery flow plan (Figure 2.2-4), char enters the catalyst recovery system through the char slurry pots. These units are currently in place on each of the gasifier solids withdrawal legs. Each pot cycles between accepting char from the gasifier and emptying that char into one of the three digesters. The cycle length will depend upon the rate of solids withdrawal but it should average around 20-30 minutes.

The slurry pots are first filled with lean catalyst solution from surge tank 3. This solution is approximately 0.5% (wt.) $K^+$ and is added to the pots so that when they are filled with char the solids concentration will be around 20% (wt.). One slurry pot working continuously could handle the base case solids loading from the gasifier. However, two pots are provided in case one pot becomes inoperable and to allow for greater solids withdrawal rates should they be desired.

The slurry pots will always be maintained at approximately the same pressure as the gasifier. This configuration requires a slurry depressurization downstream of the slurry pots since catalyst recovery will operate close to atmospheric pressure.

There are two ways of performing this depressurization. For the base case, the slurry leaving the char slurry pots would be depressured across a valve from 500 psia down to atmospheric pressure. The digesters would therefore be at atmospheric pressure when filling. However, there is concern that this rapid depressurization across a valve would cause excessive particle attrition which would further complicate downstream solid/liquid separations. For this reason the digesters were designed to fill at pressures up to 500 psia. In this mode of operation there would be just enough pressure differential between the slurry pots and the digesters to allow for the slurry transfer. Once the digesters had been filled with slurry the pressure could be vented slowly over the gas space. Each digester is designed to handle four hours production of gasifier solids. For the base case this amounts to 140 lbs of char and fines. Filter fines can be added either to the char slurry pots or directly into the digesters if desired. To these solids is added another 48 lbs of lime from the lime slurry tank. This results in a Ca/K ratio of 1.0, which will be the initial lime loading for the digester. Finally, enough lean catalyst solution is added from surge tank 3 to bring the solids concentration down to 12% (wt.). This has proven to be a reasonable concentration for operation of the digesters in the prototype equipment.

Once the digester is filled with solution it is ready to begin a digestion cycle. The cycle consists of one hour to heat the contents to reaction temperature (300-400°F), one hour reaction residence time, and one hour to cool the contents to 200°F. The remaining hour is divided into 30 minutes for emptying the contents and 30 minutes for cleaning and preparing for the next filling cycle. At least two digesters are required to operate the catalyst recovery system in this mode of operation. One must be accepting char from the gasifier while the other is digesting. However, a third digester has been provided to allow greater system flexibility such as longer residence times or as a spare in the event that one of the other digesters malfunctions.

After the digested slurry has been cooled to 200°F, it is transferred into surge tank 1A. Here it is diluted to the target recovered catalyst solution concentration of 1% (wt.) $K^+$ by adding lean catalyst solution from surge tank 3. At this point the system is ready to begin a filtration cycle.

The filters in the PDU catalyst recovery system will also run on a four hour cycle. During this period, both stages of the countercurrent water wash will be completed. Each filter contains 75 square feet of filter area and holds 375 gallons of slurry. One filter operating alone could handle the filtration requirements for the base case. However, two filters are provided to allow greater system flexibility.

The filter cycle consists of a precoating step, a filtration step, a reslurry step, and a final filtration. This is the cycle which is now planned to be used for the initial startup of the PDU catalyst recovery system. However, there are many different ways in which the system can be operated. The cycle that will be described was chosen for initial startup because it gives two stages of countercurrent wash in one filter. This facilitates the construction and operation of the system.

The precoat to be used in this system is a special alpha-cellulose material which is designed to be inert at conditions of high temperature and high pH. It is applied to the filter medium by circulating a low concentration solution of the precoat across the filter leaves. Approximately 6-10 lbs of the material will be needed for each filter cycle. The precoating step should require 20-30 minutes to complete.

After the filter leaves are precoated, the slurry from surge tank 1A is filtered and the clear filtrate sent to the evaporators. This is the recovered catalyst solution which will be concentrated to 20% (wt.) for recycle to the catalyst addition unit. The solids caught by the filter build up on the outside of the filter leaves in the form of a cake. Filtration continues until either the pressure drop across the cake or the cake thickness itself becomes excessive. Once this occurs, filtration is stopped and the rich slurry remaining in the filter vessel is blown back into surge tank 1A. At this point in the cycle there is a dry cake on the filter leaves consisting of digested char solids and a solid free recovered catalyst solution of 1% (wt.) $K^+$. This is the end of the first stage of the countercurrent water wash.

To begin the second stage of the water wash, the dry cake must be reslurried with water. Rather than removing the cake from the filter at this point and reslurrying it in a separate tank, it was decided to perform the reslurrying step inside the filter itself. To do this the filter is filled with enough water to bring the catalyst concentration to 0.5% (wt.). The rest of the filter volume is made up with lean catalyst solution from surge tank 2A. When the filter is completely filled with solution, the leaves are vibrated by a pneumatic device on the outside of the filter shell. This vibration causes the solids to drop off the leaves and become redispersed in the solution. Thus the reslurrying step is completed in the same vessel that was used for filtration.

The final step in the filtration cycle is to redeposit the newly suspended char particles back on the filter leaves. This amounts to the final separation step in the countercurrent water wash. To perform this step the contents of the filter are circulated across the filter leaves until all the solids have been recaptured. This should require a turnover of approximately three filter volumes and will take approximately 30-45 minutes.

Once the solids have been redeposited on the leaves, the clear lean catalyst solution is pressured into surge tank 2A. This solution will be used in future digestion and filter cycles. The spent solids are removed from the filter by drawing the leaves out of the filter housing and vibrating them until the solids fall off into a collection hopper. From this hopper the solids are dropped into 55-gallon drums and are weighed before going to sample storage. The filter is then cleared if necessary and closed up to be ready for the next filtration cycle.

# 3. Data Acquisition and Correlations (Reporting Category C03)

## 3.1 On-line Data Acquisition

The main purpose of the on-line data acquisition and reduction system is to monitor the PDU pilot plant operation and to provide means for the evaluation of the operating data. The design of the system is shown schematically in Figure 3.1-1. The analog signals from sensors on the unit, such as pressure transmitters, weigh cells, and thermocouples are converted to digital form in the analog/digital converter. This data is then transferred to the memory core in the central process unit (CPU) of a mini-computer. The memory core contains software programs necessary for the alarming, logging, and operator interface functions for the Process Development Unit (PDU). Data reduction is accomplished through application of software programs. The reduced data are stored on the disc for future displays on cathode ray tubes (CRT) or printers, and for storage on magnetic tapes.

The system provides several interrelated functions discussed briefly as follows:

### Routine Data Processing and Acquistion

The routine data processing includes scanning of all digital and process data variables at intervals ranging from once every 20 seconds to once every hour and the converting of digital and analog data to engineering units. The types and approximate number of process variables are tabulated below.

| Type of Measurement | Number of Measurement Points |
|---|---|
| Temperatures | 400 |
| Flows | 30 |
| Pressures | 60 |
| Gas Analyses | 100 |
| Weights | 10 |
| TOTAL | 600 |

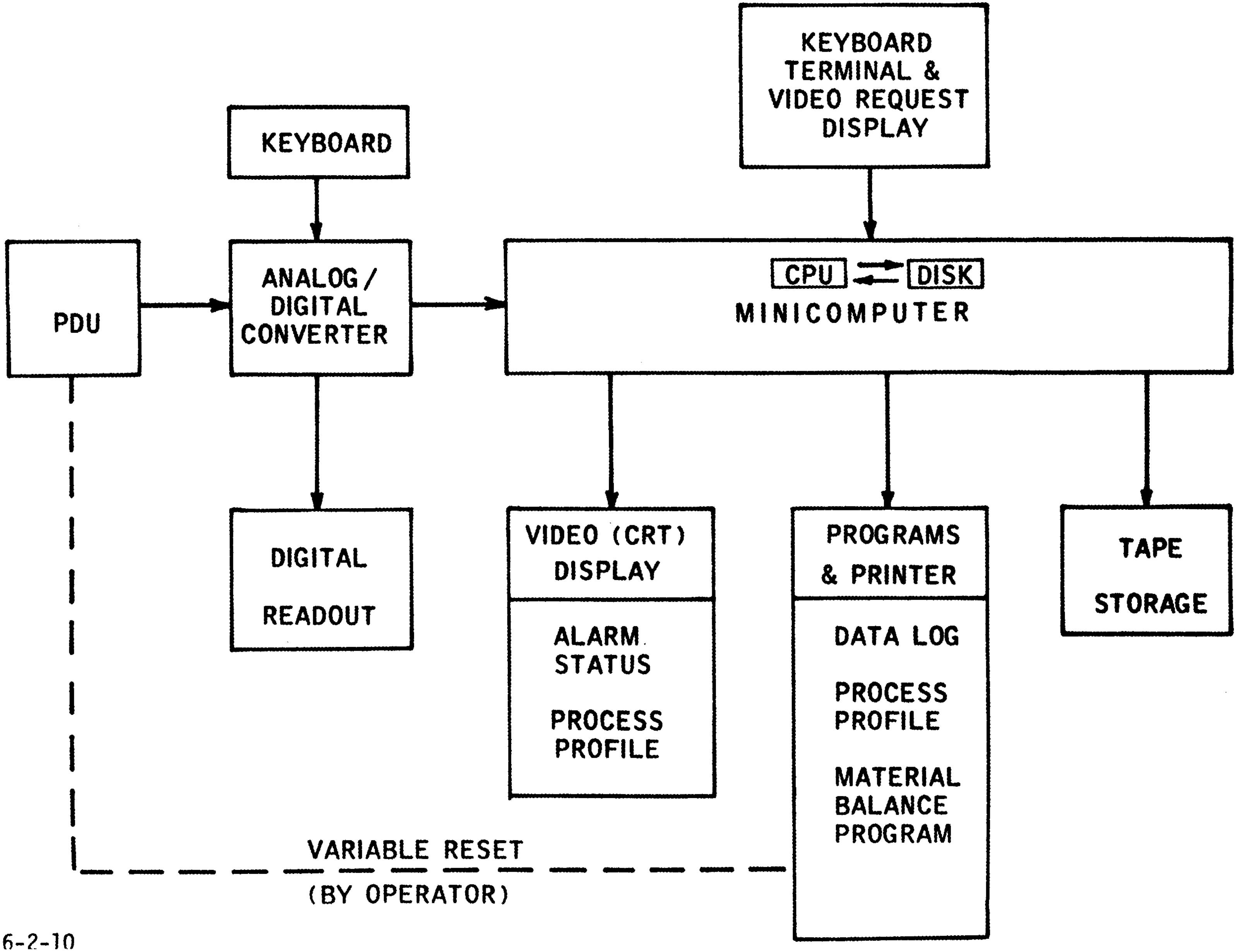
During unit operations, the values of all process variables will be instantly available to the operators in the form of a digital readout accessed by a keyboard in the control room. The computer has also been programmed to provide process operation profiles displayed on the operator request CRT screens.

### Alarm Processing and Checking

The system is capable of determining if the process variables go above or below their maximum or minimum allowed values. Variable alarms result in a

## FIGURE 3.1-1

## PDU ON-LINE DATA ACQUISITION SYSTEM



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printed message displayed on alarm CRT's and printers. For most variable alarms, the system also updates the variable's status. The displays on alarm CRT's are updated once a minute with current alarm information.

### Data Logging

Three different log formats are available. An hourly log consists of all the values for a shift through the last hour for each variable. A period log consists of averages for a specified period for each variable. A demand log consists of the current value and previous hour average, maximum, and minimum for each variable. Both the demand and period average logs can be requested as desired.

### On-line Data Evaluation

On-line data evaluation is accomplished through applications of a material balance program stored in the memory core of the computer. This program input consists of 44 automatic computer measurements such as temperatures, pressures, flows, etc. Four material balances (overall, hydrogen, oxygen, and syngas balances) as well as average unit conditions are computed and printed in hard copy. This program not only provides guidance on conditions required to achieve a desired conversion but also aids in locating operating problems. An example of the output is shown in Table 3.1-1 using simulated data as input.

The required software programs have been tested and implemented as part of PDU operations.

## 3.2 Off-line Data Reduction and Reconciliation

The primary purpose of the off-line data reduction and reconciliation is to provide consistent and reliable data for use in correlations, commercial plant study design, and kinetics model development. For the integrated catalytic gasification PDU pilot plant, more than 500 process measurements including gas and solids analyses will be collected. Much of the data describing plant operations have some inaccuracies due to random instrumentation errors. Furthermore, some data points may be in error as a result of faulty or incorrectly calibrated meters. As a result, raw operations data may not exactly satisfy material balance constraints. Use of these inconsistent and erroneous data for feasibility studies and decision making may lead to incorrect conclusions. To resolve the inconsistencies in the pilot plant data, a data reconciliation technique is used. Data reconciliation consists of adjusting the measured operations data based on the estimated tolerances assigned to each variable. That is, the most reliable data will be changed least and the least reliable data the most in order to satisfy the material balance constraints. In this way, the random instrumentation errors will be corrected, unmeasured quantities will be determined, and faulty measurements will be isolated and flagged for correction.

## Table 3.1-1

### PDU On-Line Gasifier Material Balance
### English Unit System (simulated data)

**Gasifier Material Balance**

| Input: | (lbs/hr) | Output: | (lbs/hr) | |
|---|---|---|---|---|
| Coal + Catalyst | 123.46 | Product Gas | 191.34 | |
| Steam | 179.01 | Product Water | 114.75 | Pres(A-I) |
| Syn Gas | 47.47 | Char Entrained | 6.00 | hr PSI |
| | | Char Withdrawn | 29.98 | Last 6.1 |
| TOTAL | 349.94 | TOTAL | 342.07 | /1st 6.1 |
| Closure: (output + Accum/input) = 97. | | Accumulation | 0.0 | |

**Syn Gas Balance**

| Input: | (SCFH) | Output: | (SCFH) |
|---|---|---|---|
| Gasifier syn gas | 2115.0 | $H_2$ + CO in product gas | 1995.0 |

Closure: Output/input = 94.3

**Hydrogen Balance (SCFH $H_2$)**

| Input: | | Output: | |
|---|---|---|---|
| Coal + Cat | 1106.3 | Product Gas | 388.5 |
| Steam | 3769.0 | Pg Water | 2416.0 |
| Syn Gas | 1586.2 | Char Entrnd | 7.9 |
| | | Char Wthdrn | 4.4 |
| TOTAL | 6461.5 | TOTAL | 68.8 |

Closure: (Out/in) = 97.6%

**Oxygen Balance (SCFH $O_2$)**

| Input: | | Output | |
|---|---|---|---|
| Coal + Cat | 176.6 | Product Gas | 1064.4 |
| Steam | 1884.5 | Pg Water | 9360.2 |
| Syn Gas | 264.4 | Char Entrnd | 0.0 |
| | | Char Wthdrn | 0.0 |
| TOTAL | 2325.4 | TOTAL | 2424.6 |

Closure: (out/in) = 104.

| Unit Conditions | | Actual Unit Conditions | Target Conditions |
|---|---|---|---|
| Gasifier Temperature | (DEG F) | 12.8 | -- |
| Gasifier Pressure | (PSIA) | 515.1 | -- |
| Carbon Conversion (GC Analysis) | % | 81.1 | -- |
| Steam Conversion ($H_2O$ balance) | % | 37.4 | 43.1 |
| Steam Conversion($H_2$ balance) | % | 33.5 | " |
| Steam Conversion ($O_2$ balance) | % | 34.7 | " |
| TOTAL $CH_4$ made (SCF $CH_4$/lb C in feed) | | 15.5 | 10.9 |
| $CH_4$ in Dry $N_2$ Free Product Gas (mol%) | | 28.9 | 30.3 |

| Unit Control Variables | | | | | NFW set point | | |
|---|---|---|---|---|---|---|---|
| Steam Feed Rate | (lbs/hr) | | 179.0 | | 152.7 | | 165.8 |
| Syn Gas Feed Rate | (SCFH) | mol% | 2115.0 | mol% | 1642.7 | mol% | 1878.8 |
| $H_2$ Feed Rate | (SCFH) | 75.00 | 1586.2 | 77.71 | 12.6 | 76.18% | 1431.4 |
| CO Feed Rate | (SCFH) | 25.00 | 528.7 | 22.29 | 366.2 | 23.82 | 447.5 |

| Equilibrium Constant | | Equili. Constant | Target Conditions | Actual Conditions | Equili. Temperature |
|---|---|---|---|---|---|
| Graphite + $H_2O$: | $C + H_2O=CO + H_2$ | 1.8474 | 1.5778 | 1.4979 | 1281.0 |
| Shift: | $CO + H_2O=CO2 + H_2$ | 1.5157 | 1.5157 | 1.2991 | 1368.9 |
| Methanation: | $CO + 3H_2=H20 + CH_4$ | 0.0665 | 0.0665 | 0.0578 | 1311.7 |
| Overall: | $2C + 2H_2O=CO2 + CH_4$ | .3440 | 0.2509 | 0.1686 | |

The mathematical formulation of the data reconciliation problem consists of:

$$\text{minimize:} \quad f(R) = \sum_i \frac{(Mi - Ri)^2}{\sigma_i^2} \qquad \begin{array}{l} i = 1, \ldots, NVAR \\ j = 1, \ldots, NC0N \end{array}$$

$$\text{subject to: } E_j(R) = 0$$

where: $Mi$ = Measured value of variable i
$Ri$ = Reconciled value of i
$\sigma_i$ = Standard deviation of the ith measurement
$E_j$ = Set of nonlinear equations representing the physical relationship among the variables
NVAR = Number of variables
NC0N = Number of constraints

Standard deviation is defined in terms of reliability for each measured variable as follows:

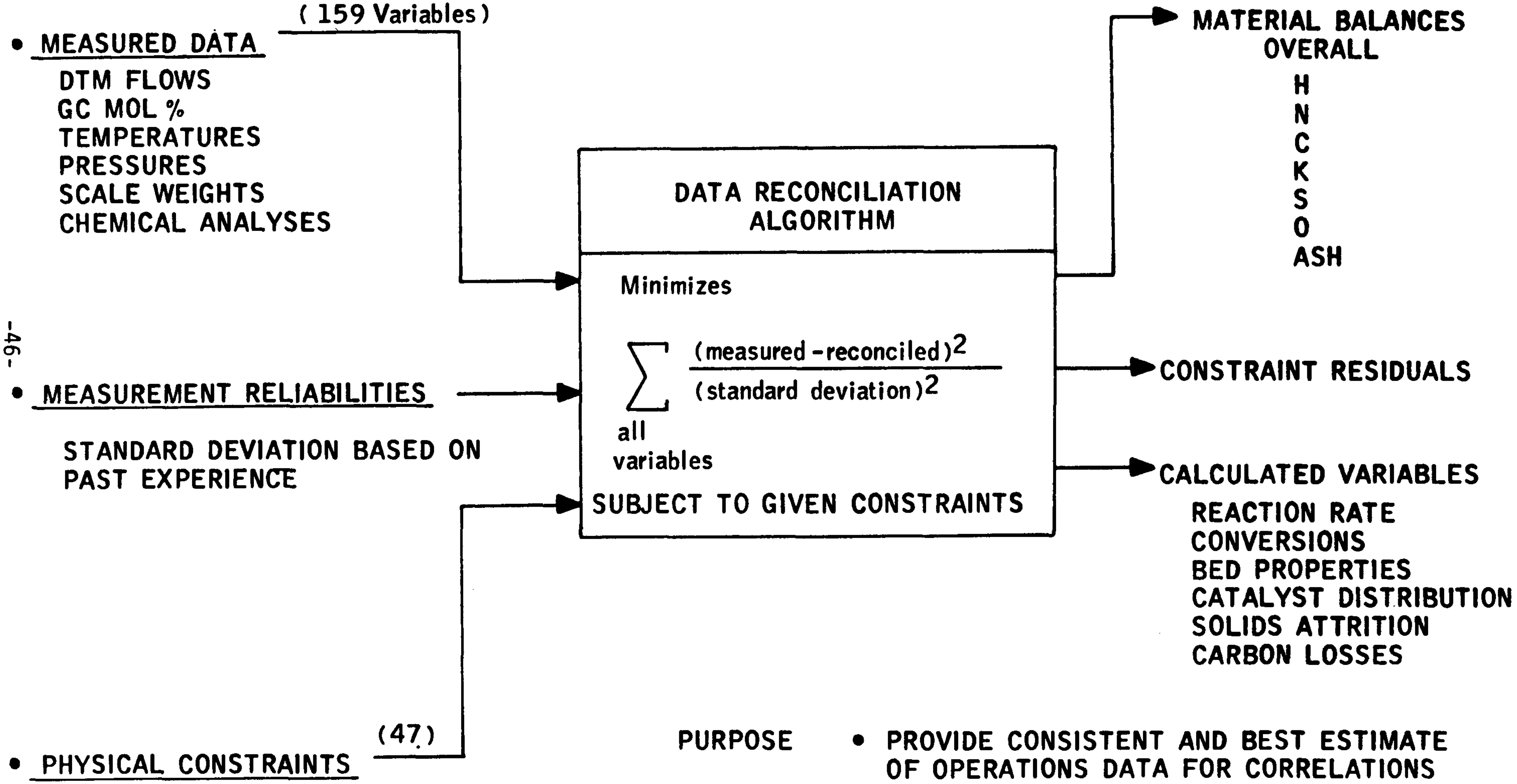
$$\sigma_i = M_i \cdot rel_i/200$$

Reliability ($rel_i$) is an estimate of the quality of the individual data points based upon the user's experience. For example, a reliability of 10% implies that if a measuring device is functioning properly, it will measure to within ±10% of the true value 95% of the time (i.e., two standard deviations). Thus, a small numerical value for reliability indicates the measured value is of high quality.

The objective function (f) represents the sum of the deviations of the reconciled variables from the measurement values. These deviations are weighted by the user's estimate of the reliability of the measurements. During the iterative minimization of the objective function, the algorithm attempts to keep the reconciled values for the reliable measurements close to the measured values. The constraints which describe the physical relationships of the process variables (such as material balances) must be satisfied during the minimization of the objective function. The algorithm is shown in Figure 3.2-1.

For integrated PDU operations, 159 variables are defined which are involved in the material balances. Among these are the input and output volumetric flows, gas streams compositions and the gasifier solids analyses. Table 3.2-1 lists these variables and their reliabilities. The constraints are elemental and material balances of each section of the PDU (gasification, acid gas removal, and cryogenic distillation). The constraints for the catalyst recovery section have not been defined at this time. Forty-six constraints will be used and are listed in Table 3.2-2. The basic structure and the flow chart of the computer program have been worked out. Program development is underway and will be finished prior to the initial startup of the PDU.

FIGURE 3.2-1
DATA RECONCILIATION



PURPOSE

- PROVIDE CONSISTENT AND BEST ESTIMATE OF OPERATIONS DATA FOR CORRELATIONS AND MODELING EFFORT
- IDENTIFY PDU OPERATIONS PROBLEMS

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## Table 3.2-1

| Reconciliable Variable | Unit | Reliability, % |
|---|---|---|
| Coal + Catalyst Feed | lb/hr | 5.0 |
| Gasifier Steam Rate | lb/hr | 5.0 |
| Product Gas Knockout water rate | lb/hr | 5.0 |
| Char withdrawn | lb/hr | 5.0 |
| Char entrained | lb/hr | 5.0 |
| Gasifier syn gas (or R.G.) flow rate | CFH | 5.0 |
| Gasifier Product gas flow rate | CFH | 10.0 |
| S in PRD gas knockout water | % (wt.) | 15.0 |
| $NH_3$ in PGKO water | % (wt.) | 5.0 |
| H in gasifier starting GMC | % (wt.) | 15.0 |
| H in gasifier ending GMC | % (wt.) | 15.0 |
| H in char withdrawn | % (wt.) | 5.0 |
| H in coal + catalyst feed | % (wt.) | 5.0 |
| H in entrained char | % (wt.) | 5.0 |
| Carbon in gasifier starting GMC | % (wt.) | 15.0 |
| Carbon in gasifier ending GMC | % (wt.) | 15.0 |
| Carbon in char withdrawn | % (wt.) | 5.0 |
| Carbon in feed coal + catalyst | % (wt.) | 5.0 |
| Carbon in entrained char | % (wt.) | 5.0 |
| S in gasifier starting GMC | % (wt.) | 20.0 |
| S in gasifier ending GMC | % (wt.) | 20.0 |
| S in char withdrawn | % (wt.) | 15.0 |
| S in coal + catalyst feed | % (wt.) | 15.0 |
| S in entrained char | % (wt.) | 15.0 |
| O in starting C | % (wt.) | 20.0 |
| O in ending GMC | % (wt.) | 20.0 |
| O in char withdrawn | % (wt.) | 15.0 |
| O in coal + catalyst feed | % (wt.) | 15.0 |
| O in entrained char | % (wt.) | 15.0 |
| N in starting GMC | % (wt.) | 15.0 |
| N in ending GMC | % (wt.) | 15.0 |
| N in char withdrawn | % (wt.) | 10.0 |
| N in coal + cat feed | % (wt.) | 10.0 |
| N in entrained char | % (wt.) | 10.0 |
| Cl in starting GMC | % (wt.) | 40.0 |
| Cl in ending GMC | % (wt.) | 40.0 |
| Cl in char withdrawn | % (wt.) | 35.0 |
| Cl in coal + catalyst feed | % (wt.) | 35.0 |
| Cl in entrained char | % (wt.) | 35.0 |
| $SO_3$-free ash in starting GMC | % (wt.) | 15.0 |
| $SO_3$-free ash in ending GMC | % (wt.) | 15.0 |
| $SO_3$-free ash in char withdrawn | % (wt.) | 10.0 |
| $SO_3$-free ash in feed coal + catalyst | % (wt.) | 10.0 |
| $SO_3$-free ash in entrained char | % (wt.) | 10.0 |

| | | |
|---|---|---|
| A.S. $K_2O$ in gasifier starting GMC | % (wt.) | 15.0 |
| A.S. $K_2O$ in gasifier ending GMC | % (wt.) | 15.0 |
| A.S. $K_2O$ in char withdrawn | % (wt.) | 5.0 |
| A.S. $K_2O$ in coal + catalyst | % (wt.) | 5.0 |
| A.S. $K_2O$ in entrained char | % (wt.) | 5.0 |
| A.S. $Na_2O$ in gasifier starting GMC | % (wt.) | 25.0 |
| A.S. $Na_2O$ in gasifier ending GMC | % (wt.) | 25.0 |
| A.S. $Na_2O$ in char withdrawn EED | % (wt.) | 20.0 |
| A.S. $Na_2O$ in coal + catalyst feed | % (wt.) | 20.0 |
| A.S. $Na_2O$ in entrained char EED | % (wt.) | 20.0 |
| ASTM ash in gasifier starting GMC | % (wt.) | 15.0 |
| ASTM ash in gasifier ending GMC | % (wt.) | 15.0 |
| ASTM ash in char withdrawn | % (wt.) | 10.0 |
| ASTM ash in feed coal + catalyst | % (wt.) | 10.0 |
| ASTM ash in entrained char | % (wt.) | 10.0 |
| C/H residue in gasifier starting GMC | % (wt.) | 15.0 |
| C/H residue in gasifier ending GMC | % (wt.) | 15.0 |
| C/H residue in char withdraw GMC | % (wt.) | 10.0 |
| C/H residue in feed coal + catalyst | % (wt.) | 10.0 |
| C/H residue in entrained catalyst | % (wt.) | 10.0 |
| $SO_3$-free C/H res in starting GMC | % (wt.) | 15.0 |
| $SO_3$-free C/H res in ending GMC | % (wt.) | 15.0 |
| $SO_3$-free C/H res in char withdrawn | % (wt.) | 10.0 |
| $SO_3$-free C/H res in feed coal + cat | % (wt.) | 10.0 |
| $SO_3$-free C/H res in entrained char | % (wt.) | 10.0 |
| $SiO_2$ in $SO_3$-free ash in starting GMC | % (wt.) | 20.0 |
| $SiO_2$ in $SO_3$-free ash in ending GMC | % (wt.) | 20.0 |
| $SiO_2$ in $SO_3$-free ash in char withdrawn | % (wt.) | 15.0 |
| $SiO_2$ in $SO_3$-free ash in coal + cat feed | % (wt.) | 15.0 |
| $SiO_2$ in $SO_3$-free ash in entrained char | % (wt.) | 15.0 |
| $Fe_2O_3$ in $SO_3$-free ash in starting GMC | % (wt.) | 20.0 |
| $Fe_2O_3$ in $SO_3$-free ash in ending GMC | % (wt.) | 20.0 |
| $Fe_2O_3$ in $SO_3$-free ash in char withdrawn | % (wt.) | 15.0 |
| $Fe_2O_3$ in $SO_3$-free ash coal + cat | % (wt.) | 15.0 |
| $Fe_2O_3$ in $SO_3$-free ash in entrained char | % (wt.) | 15.0 |
| $Al_2O_3$ in $SO_3$-free ash in starting GMC | % (wt.) | 20.0 |
| $Al_2O_3$ in $SO_3$-free ash in ending GMC | % (wt.) | 20.0 |
| $Al_2O_3$ in $SO_3$-free ash in char withdrawn | % (wt.) | 15.0 |
| $Al_2O_3$ in $SO_3$-free ash in coal + cat feed | % (wt.) | 15.0 |
| $Al_2O_3$ in $SO_3$-free ash in entrained char | % (wt.) | 15.0 |
| Ca in $SO_3$-free ash in starting GMC | % (wt.) | 25.0 |
| Ca in $SO_3$-free ash in ending GMC | % (wt.) | 25.0 |
| Ca in $SO_3$-free ash in char withdrawn | % (wt.) | 20.0 |
| $CaO$ in $SO_3$-free ash in coal + cat feed | % (wt.) | 20.0 |
| $CaO$ in $SO_3$-free ash in entrained char | % (wt.) | 20.0 |
| $MgO$ in $SO_3$-free ash in starting GMC | % (wt.) | 25.0 |
| $MgO$ in $SO_3$-free ash in ending GMC | % (wt.) | 25.0 |
| $MgO$ in $SO_3$-free ash in char withdrawn | % (wt.) | 20.0 |
| $MgO$ in $SO_3$-free ash in coal + cat feed | % (wt.) | 20.0 |
| $MgO$ in $SO_3$-free ash in entrained char | % (wt.) | 20.0 |

| | | |
|---|---|---|
| $TiO_2$ in $SO_3$-free ash in starting GMC | % (wt.) | 30.0 |
| $TiO_2$ in $SO_3$-free ash in ending GMC | % (wt.) | 30.0 |
| $TiO_2$ in $SO_3$-free ash in char withdrawn | % (wt.) | 25.0 |
| $TiO_2$ in $SO_3$-free ash in coal + cat feed | % (wt.) | 25.0 |
| $TiO_2$ in $SO_3$-free ash in entrained char | % (wt.) | 25.0 |
| $P_2O_5$ in $SO_3$-free ash in starting GMC | % (wt.) | 40.0 |
| $P_2O_5$ in $SO_3$-free ash in ending GMC | % (wt.) | 40.0 |
| $P_2O_5$ in $SO_3$-free ash in char withdrawn | % (wt.) | 35.0 |
| $P_2O_5$ in $SO_3$-free ash in coal + cat feed | % (wt.) | 35.0 |
| $P_2O_5$ in $SO_3$-free ash in entrained char | % (wt.) | 35.0 |
| $H_2$ in gasifier product gas | % (mol.) | 5.0 |
| CO in gasifier product gas | % (mol.) | 20.0 |
| $CH_4$ in gasifier product gas | % (mol.) | 1.0 |
| $CO_2$ in gasifier product gas | % (mol.) | 5.0 |
| $H_2S$ in gasifier product gas | % (mol.) | 20.0 |
| $N_2$ in gasifier product gas | % (mol.) | 1.0 |
| $H_2$ in gasifier syn gas | % (mol.) | 10.0 |
| CO in gasifier syn gas | % (mol.) | 10.0 |
| Starting differential pressure (B-A) | psi | 5.0 |
| Starting differential pressure (C-B) | psi | 5.0 |
| Starting differential pressure (D-C) | psi | 5.0 |
| Starting differential pressure (E-D) | psi | 5.0 |
| Starting differential pressure (F-E) | psi | 5.0 |
| Starting differential pressure (G-F) | psi | 5.0 |
| Starting differential pressure (G-H) | psi | 5.0 |
| Starting differential pressure (H-I) | psi | 5.0 |
| Starting differential pressure (A-I) | psi | 5.0 |
| Ending differential pressure (B-A) | psi | 5.0 |
| Ending differential pressure (C-B) | psi | 5.0 |
| Ending differential pressure (D-C) | psi | 5.0 |
| Ending differential pressure (E-D) | psi | 5.0 |
| Ending differential pressure (F-E) | psi | 5.0 |
| Ending differential pressure (G-F) | psi | 5.0 |
| Ending differential pressure (G-H) | psi | 5.0 |
| Ending differential pressure (H-I) | psi | 5.0 |
| Ending differential pressure (A-I) | psi | 5.0 |
| Make-up $H_2$ gas rate | CFH | 5.0 |
| Make-up CO gas rate | CFH | 5.0 |
| Acid gas flow rate | CFH | 10.0 |
| Gas from mol sieves flow rate | CFH | 10.0 |
| SNG product gas flow rate | CFH | 10.0 |
| Cryo gas output flow rate | CFH | 10.0 |
| $H_2$ in gas from mol sieves | % (mol.) | 5.0 |
| $H_2$ in cryo gas output | % (mol.) | 20.0 |
| CO in gas from mol sieves | % (mol.) | 20.0 |
| CO in SNG product | % (mol.) | 20.0 |
| CO in cryo gas output | % (mol.) | 20.0 |
| $CH_4$ in gas from mol sieves | % (mol.) | 1.0 |
| $CH_4$ in SNG product | % (mol.) | 1.0 |
| $CH_4$ in cryo gas output | % (mol.) | 1.0 |

|  |  |  |
|---|---|---|
| $CO_2$ in acid gas | % (mol.) | 5.0 |
| $H_2S$ in acid gas | % (mol.) | 10.0 |
| $N_2$ in gas from mol sieves | % (mol.) | 1.0 |
| $N_2$ in cryo gas output | % (mol.) | 1.0 |
| $CH_4$ in gasifier syn gas | % (mol.) | 1.0 |
| $CO_2$ in gasifier syn gas | % (mol.) | 10.0 |
| $H_2S$ in gasifier syn gas | % (mol.) | 10.0 |
| $N_2$ in gasifier syn gas | % (mol.) | 1.0 |
| Purge gas rate | CMH | 10.0 |
| Injection gas (other than RG or SG) rate | CMH | 10.0 |
| $H_2$ in injection syn gas | % (mol.) | 10.0 |
| CO in injection syn gas | % (mol.) | 10.0 |
| $CH_4$ in injection syn gas | % (mol.) | 10.0 |
| $CO_2$ in injection syn gas | % (mol.) | 10.0 |
| $N_2$ in injection syn gas | % (mol.) | 10.0 |

## TABLE 3.2-2

## CONSTRAINTS USED IN RECONCILING PDU OPERATIONS DATA

| Constraint No. | Constraint |
|---|---|
| 1 | Gasifier Hydrogen Balance |
| 2 | Gasifier Carbon Balance |
| 3 | Gasifier Oxygen Balance |
| 4 | Gasifier Sulfur Balance |
| 5 | Gasifier Nitrogen Balance |
| 6 | Gasifier Acid Soluble Potassium Balance |
| 7 | Gasifier $SO_3$-Free Ash Balance |
| 8 | Gasifier Ash Balance |
| 9 | Gasifier C/H Residue Balance |
| 10 | Gasifier $SiO_2$ Balance |
| 11 | Gasifier $Fe_2O_3$ Balance |
| 12 | Gasifier $Al_2O_3$ Balance |
| 13 | Gasifier CaO Balance |
| 14 | Gasifier MgO Balance |
| 15 | Gasifier $TiO_2$ Balance |
| 16 | Gasifier $P_2O_5$ Balance |
| 17 | Gasifier Acid Soluble Sodium Balance |
| 18 | Gasifier Chlorine Balance |
| 19 | Sum of All Product Gas Components |
| 20 | Sum of All Makeup (or Recycle) Syngas Components |
| 21 | Sum of Entrained Char Components |
| 22 | Sum of Coal + Catalyst Feed Components |
| 23 | Sum of Withdrawn Char Components |
| 24 | Sum of Starting Mid Char Components |
| 25 | Sum of Ending Mid Char Components |
| 26 | Sum of Ash Components in Entrained Char |
| 27 | Sum of Ash Components in Coal + Catalyst Feed |
| 28 | Sum of Ash Components in Withdrawn Char |
| 29 | Sum of Ash Components in Starting Mid Char |
| 30 | Sum of Ash Components in Ending Mid Char |
| 31 | Sum of Starting Gasifier Differential Pressures |
| 32 | Sum of Ending Gasifier Differential Pressures |
| 33 | MEA Absorber $H_2$ Balance |
| 34 | MEA Absorber CO Balance |
| 35 | MEA Absorber $CH_4$ Balance |
| 36 | MEA Absorber $CO_2$ Balance |
| 37 | MEA Absorber $H_2S$ Balance |
| 38 | MEA Absorber $N_2$ Balance |
| 39 | Sum of Gas Components from Acid Gas Regeneration |
| 40 | Sum of Gas Components from Molecular Sieves |
| 41 | Cryogenic Fractionator $H_2$ Balance |
| 42 | Cryogenic Fractionator CO Balance |
| 43 | Cryogenic Fractionator $CH_4$ Balance |
| 44 | Cryogenic Fractionator $N_2$ Balance |
| 45 | Sum of Gas Components in SNG Product |
| 46 | Sum of Gas Components in Cryo. Gas Output |

The off-line data reconciliation program for the PDU has been developed, debugged, and tested using a set of simulated data. This program provides a tool for obtaining consistent and reliable data from PDU operations. To perform this analysis, the program accepts raw operations data from different sections of the PDU, processes the data, and then generates detailed stream reports for use in correlations, commercial plant study design, and simulation studies. The program was written so that calculation of different models of PDU operations such as once-through or recycle can be carried out with the same program. The program can also be used to reconcile operations data from other catalytic gasification pilot plants. The operation of the data reconciliation program is summarized as follows.

## Input Data

Two types of input data, reconcilable and nonreconciliable, must be submitted to execute this program. Reconcilable data are gas and solid flow rates and compositions which will be adjusted to satisfy the material balance constraints. Nonreconciliable data are the stream and unit temperatures and pressures.

The program accepts input data in either metric or English units. It is necessary that all data be entered on the same basis. The following metric and English units should be used:

| Variable | English Units | Metric Units |
|---|---|---|
| Solid flows | lb/hr | KG/Hr |
| Gas flows | CFH | CMH |
| Temperatures | Deg. F | Deg. C |
| Pressures | PSI | KPa |

## Reconciliation Algorithm

The reconciliation algorithm is an iterative procedure which makes minimal adjustments to the process data to satisfy the constraints. In each iteration, a new set of reconciled data is determined through the use of redundant data and the knowledge of the reliabilities of instrumentation. The iteration procedure is continued until a set of self-consistent values is obtained.

## Reporting Data

A complete listing of the measured and reconciled values of all reconcilable variables will be reported. The report also lists the reliabilities associated with the measured values and the percent changes between the measured and reconciled values. This report aids the users in detecting erroneous measured data.

The reconciled data will be used in the following calculations:

- Gasification and methanation reaction rates
- Approach to reaction equilibrium
- Gasifier fluid bed properties
- Solids entrainment
- Carbon and steam conversions

The results will be put in a detailed report together with the following information:

- Unit conditions and performance
- Unit material balances
- Gas and solid stream compositions
- Solids particle size distributions
- Catalyst distribution

## 3.3 Cold Model Studies

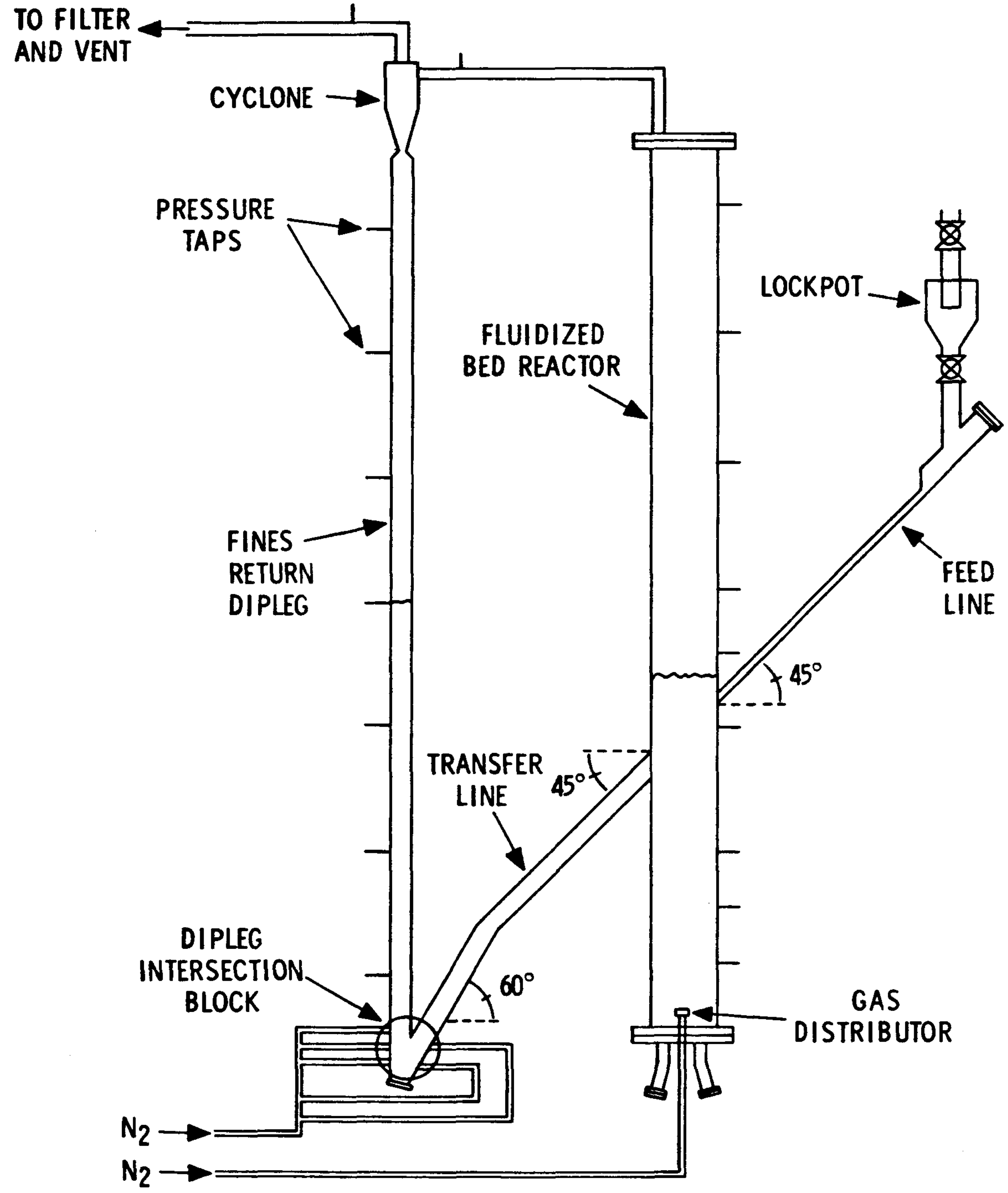
A cold model of the PDU was constructed to assist in troubleshooting solids flow problems as they arise in PDU operations. Throughout the startup and initial operation of the PDU, the transparent cold model has proved valuable in providing visual understanding of many of the solids flow problem areas. A diagram of the cold model is shown in Figure 3.3-1. The unit consists of a fluidized bed reactor, a cyclone, a fines return system, and solids feeding equipment.

Most dimensions of the cold model are the same as the PDU except that the model gasifier is 14 feet in height versus the 83 feet of the PDU. This height difference should not affect the solids transfer studies. The inside diameter of the model reactor is 9-1/2 inches compared to 9-7/8 inches for the unit reactor. The inside diameter of the model dipleg is 2-5/8 inches which is identical to that of the PDU.

Polypropylene powder is the particulate solid used in the model. The particle density of the polypropylene is 44 $lb/ft^3$ (0.70 g/cc) and the surface volume mean particle diameter is about 230 microns. These properties, as well as the shape factor for polypropylene, are similar to those of the gasified char produced in the small fluid bed gasifier (FBG). In addition, the negligible attrition of the polypropylene makes it a particularly good solid substitute for char.

## FIGURE 3.3-1

## COLD MODEL OF GASIFICATION REACTOR SECTION OF PDU



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The areas requiring detailed experimentation were identified during preliminary operations. These included:

- Performance evaluation of solids feeding system
- Fines return system studies

## Solids Feeding System Studies

In the PDU, coal is fed to the reactor in a cyclic manner from a lockpot with a volume of 0.1 $ft^3$. First the lockpot is filled from above. The contents of the lockpot then flow through a vertical line into a 45° feed line and finally into the reactor. The coal feed rate is controlled by the frequency of the feed cycle. Figure 3.3-2 is a diagram of the feed system of the cold model. Dimensions of the model feed system are similar to those of the PDU except that the length of the 3/4 inch feed line is much longer in the PDU.

Successful solids feeding depends on proper value sequencing, gas purge rate to the system, and purge location. Performance of the equipment was evaluated with respect to these operating variables and to reactor conditions including bed height and superficial gas velocity.

## Feed Line Operation

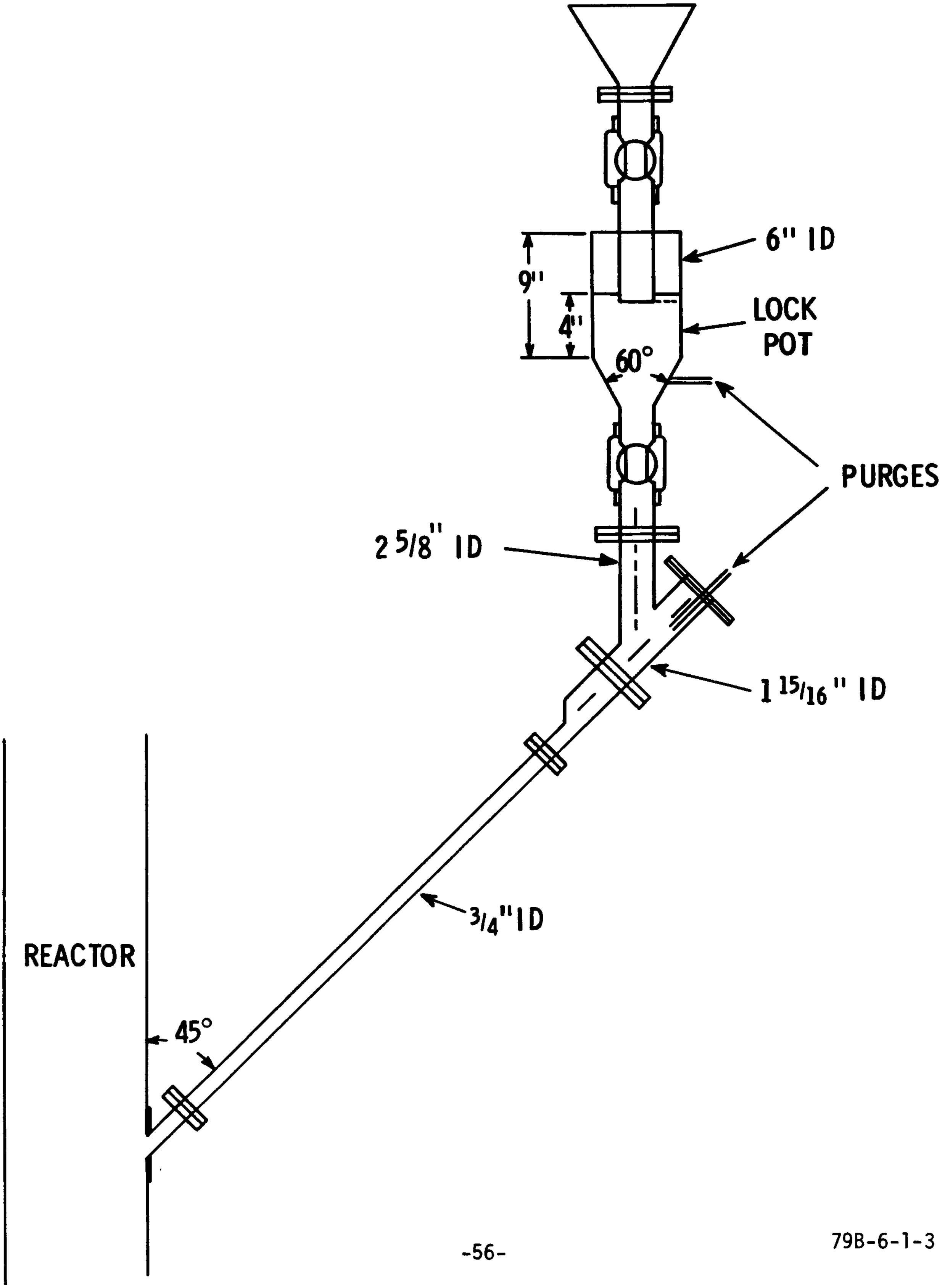
The first experiments conducted were to determine whether solids from the reactor could be kept from backing up into the feed line. The effects of bed height above the feed point, superficial gas velocity in the reactor and gas purge rate to the feed line were examined.

The distance that the solids backed up from the reactor into the feed line was measured for reactor bed heights of 2, 3-1/2, 5, 6-1/2, and 8 feet above the feed point. The superficial gas velocity in the reactor was 0.45 ft/sec for each case. Higher bed heights forced solids farther up the feed line when there was no gas purge; however, a low flow of gas purged to the feed line from a tap located at the upper end of 45° section of the line effectively eliminated the problem for all the bed height studies. Figure 3.3-3 shows the distance the solids backed up from the reactor as a function of bed height above the feed point and purge rate to the feed line.

A second set of experiments was carried out with a decrease in the reactor superficial velocity from 0.45 ft/sec to 0.11 ft/sec. The decreased superficial velocity reduced the solids backup in the feed line. The problem could be controlled in these cases by maintaining a low gas purge rate to the feed line as before. Figure 3.3-4 shows the results of experiments for two reactor superficial gas velocities with a bed height above the feed point of 8 feet.

## FIGURE 3.3-2

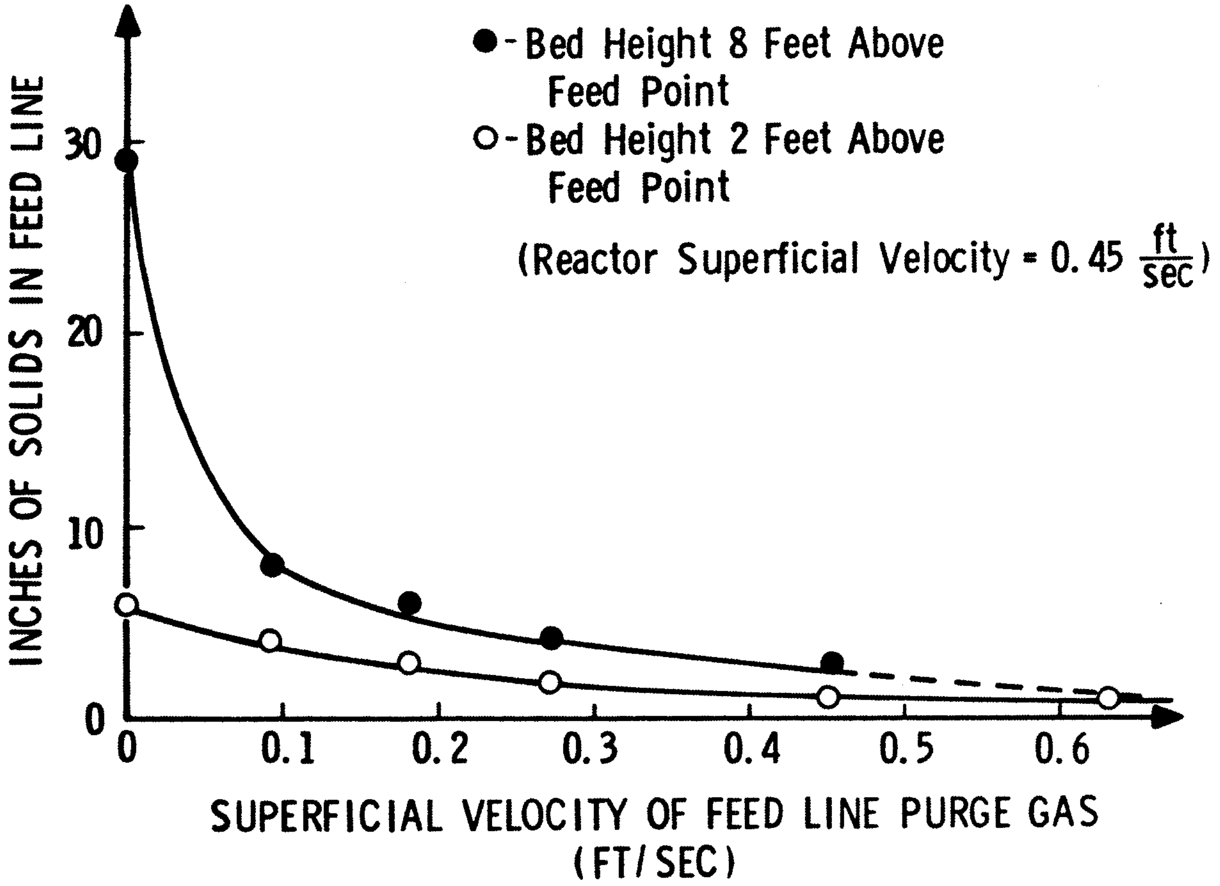
## SOLIDS FEED SYSTEM FOR COLD MODEL



# FIGURE 3.3-3

## PURGE GAS REQUIREMENTS TO PREVENT SOLIDS FROM BACKING UP INTO FEED LINE

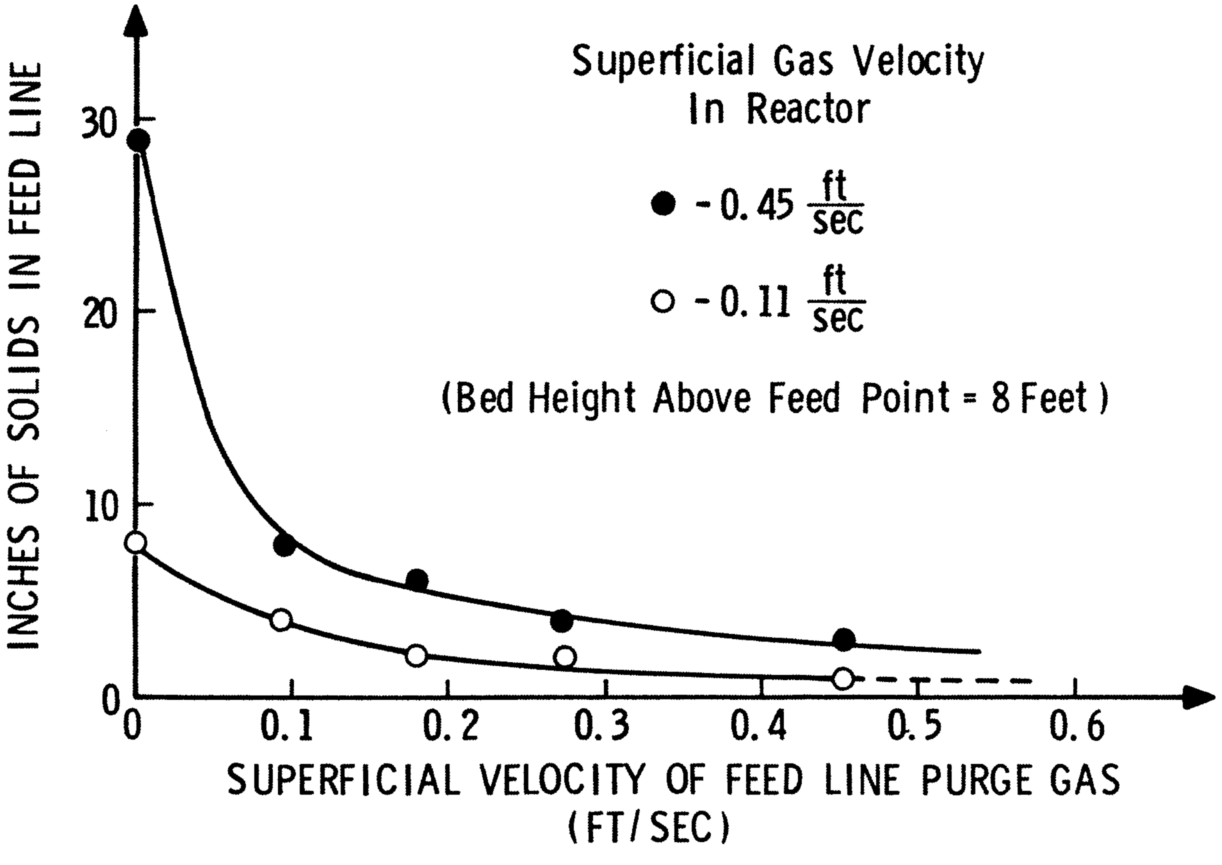
### EFFECT OF BED HEIGHT



# FIGURE 3.3-4

## PURGE GAS REQUIREMENTS TO PREVENT SOLIDS FROM BACKING UP INTO FEED LINE

## EFFECT OF SUPERFICIAL VELOCITY IN THE REACTOR



The results of these experiments indicate that the problem of solids moving from the reactor into the feed line can be controlled by maintaining a gas purge so that the superficial gas velocity through the 3/4 inch line is at least 0.2-0.3 ft/sec.

## Lockpot Operation

As mentioned earlier, solids feed rate is controlled by the frequency of the feed cycle. A catalyzed coal feed rate of 115 lbs/hr (the PDU design basis) would require one complete feed cycle every 140 seconds if the lockpot filled and emptied completely during the cycle. Experiments were carried out to determine how to operate the feed system in order to achieve the necessary cycle time. Initial experiments were designed to determine the length of time to empty the lockpot under different operating conditions.

The lockpot would not empty when the bottom valve was opened unless there was a gas purge directly to the lockpot of about 8 ACFH. At this low purge rate the lockpot drained erratically and occasionally would not empty completely. When the purge rate to the lockpot was increased above 8 ACFH, not only did the time required to empty the lockpot decrease but also the reproducibility of duplicate runs improved because the lockpot drained more smoothly. Purge location was very important in these experiments. A gas purge to the feed line below the lockpot was not as effective as a direct purge to the lockpot. Figure 3.3-5 shows how an increase in gas purge results in a decrease in the time required to empty the lockpot.

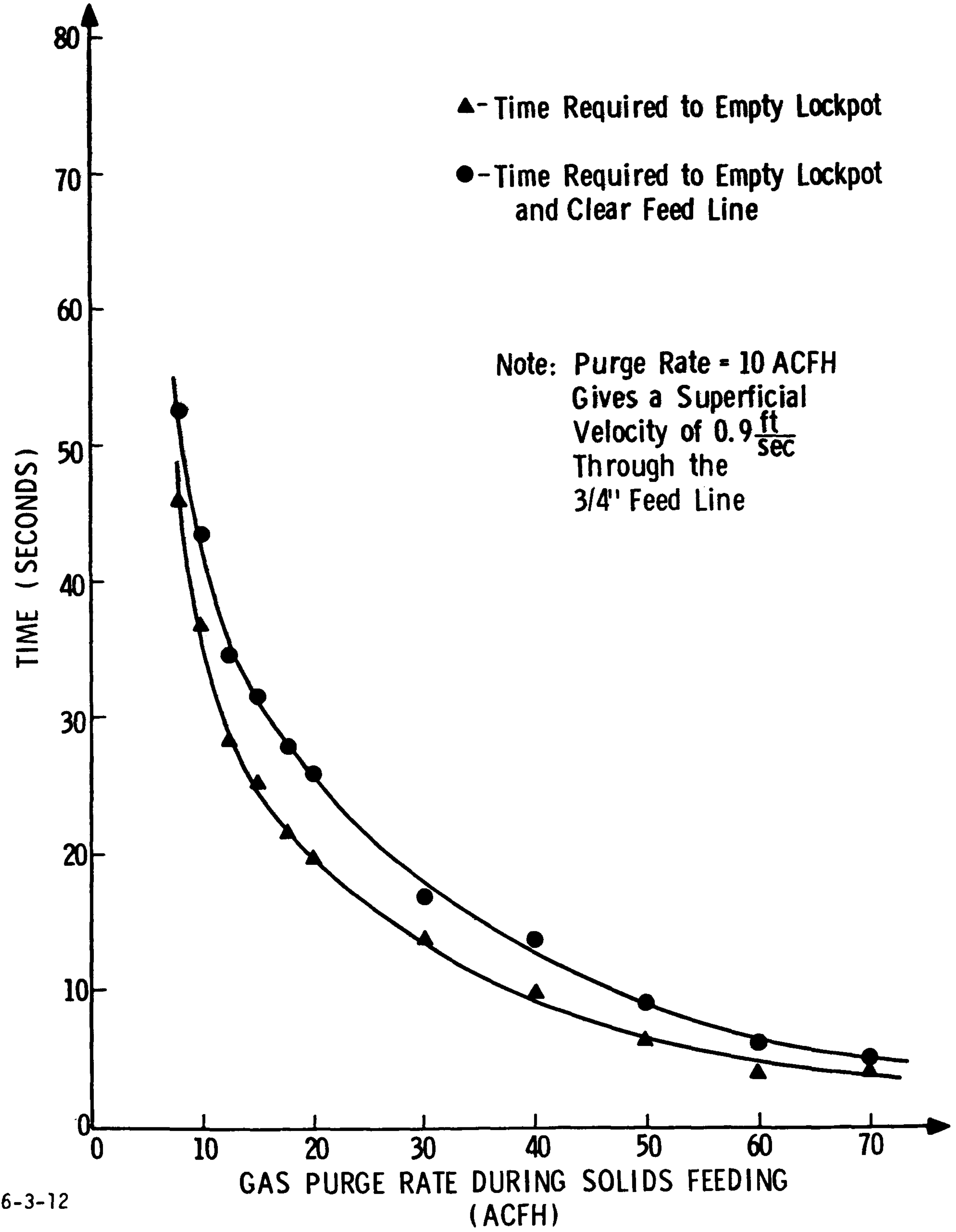
As shown in Figure 3.3-2, after the solids leave the lockpot, they travel through the feed line and into the reactor. The first part of the line is vertical with an inside diameter of 2-5/8 inches. It then goes through a 45° bend and into an eccentric reducer where the line is reduced to 3/4 inches inside diameter.

Experiments were conducted in the cold model to determine how fast the solids woud move through the feed line and into an actively fluidized bed. The feed line on the cold model is six feet long, which is considerably shorter than that of the PDU. The longer feed line in the PDU should not have a significantly higher resistance to solids flow than the feed line in the model because most of the resistance to solids flow results from bends and constrictions in the line and the resistance of solids flow into the fluidized bed. These effects are present in both the cold model and the PDU.

It has already been shown that solids will back up from the fluidized bed into the feed line unless a small gas purge is maintained. When feeding solids into the reactor, a higher purge rate of at least 12 ACFH was needed. This is more than the minimum purge required to empty the lockpot. If the purge rate was below 12 ACFH, the solids did not move into the reactor from the 3/4 inch section of the feed line as fast as they drained from the lockpot and so the level of solids in the feed line rose. Frequently this resulted in compacting and bridging of solids which caused the feed line to plug.

## FIGURE 3.3-5

## PURGE GAS REQUIREMENTS FOR FEEDING SOLIDS INTO THE COLD MODEL



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At purge rates in the range of 12 to 18 ACFH, the solids moved through the feed line and into the reactor in spurts. Above 18 ACFH there was enough gas moving with the solids to keep the material from compacting and maintain smooth solids flow. Figure 3.3-5 shows the time required to empty the lockpot and to clear the feed line for a range of gas purge rates from 10 to 70 ACFH. Higher purge rates gave greater solids mass flow rates into the reactor.

## Recommendations for PDU Operation

The results from the cold model have indicated that it should be possible to achieve smooth operations and the required coal feed rates to the PDU by supplying gas purges to the feed system. When the lockpot is being filled or the bottom lockpot valve is closed, purge gas must enter directly into the feed line below the lockpot at a rate of at least 2.5 ACFH (0.25 ft/sec) to keep solids from moving from the reactor up into the feed line. When the bottom lockpot valve is opened to feed solids, a gas purge directly into the lockpot in the range of 20-60 ACFH is needed to drain solids from the pot. Once the solids are out of the lockpot, a gas purge is required to feed the solids into the fluidized bed. This gas can be supplied through the lockpot purge if the bottom lockpot valve remains open.

## Fines Return System Studies

As demonstrated by past operations of fluid bed catalytic coal gasification pilot plants, solid particles are entrained in the gas stream leaving the reactor. These particles are generally less than 50 microns in diameter and have a higher carbon content than char in the fluidized bed. The difference in the carbon content of the two types of char can be attributed to relatively low residence times for the smaller particles which leave the reactor more quickly than larger particles. The fine char carried overhead in the gas stream comes from two sources. Part of it is char from fine feed coal particles, while the rest is the product of attrition of larger particles in the fluidized bed. This fine, high carbon char should be returned to the reactor for further gasification to achieve a higher overall carbon conversion and higher process efficiency.

On the PDU, the system to return the fine char to the reactor consists of a cyclone, dipleg, intersection block and a transfer line as shown in Figure 3.3-1. The cyclone and dipleg are not inside the reactor due to its relatively small diameter. The fact that the cyclone and dipleg are external to the reactor results in a special design for the dipleg return which is characteristic of smaller fluidized bed units. At the bottom of the dipleg is an intersection block from which a transfer line leads back to the reactor. The transfer line begins at an angle 60° from the horizontal, goes through a 15° bend and enters the reactor at 45° from the horizontal.

The design of the fines return system is such that the rate of fines return to the bed should be controlled by pressure balance. If the solids in the dipleg, intersection block, transfer line, and reactor are properly fluidized, the system should behave like a manometer. As fine char falls into the dipleg from the cyclone, the level of solids rises in the dipleg, causing an increase in static pressure at the bottom of the dipleg. If this pressure is greater than that at the point at which the transfer line enters the reactor, then the fines should move from the dipleg into the reactor.

The cold model is equipped with a fines return system like the one previously described. Internal dimensions of the model are nearly identical to those of the PDU except that the length of the dipleg is approximately 14 feet compared to the 70 foot dipleg on the PDU. Initial experiments on the model were designed to investigate solids flow behavior in the dipleg and transfer line.

## Dipleg Operation

The fines in the dipleg should be fluidized slightly above minimum fluidization if they are to flow smoothly through the intersection block and into the transfer line. Too little purge gas in the cold model resulted in solids slumping, compacting, and bridging in the dipleg, causing solids flow to stop. Once this occurred, it was difficult to reestablish a fluidized state in the dipleg. Sudden increases in gas flow caused plugs of solids to move up the dipleg like a piston. This behavior was accompanied by an increase in pressure drop which was characteristic of flow through a packed bed. The most successful procedure for refluidizing compacted solids was to slowly increase and decrease the gas flow to the dipleg. This resulted in a smooth transition from a packed to a fluidized bed. Excess gas flowing up the dipleg led to slugging in the bed of fines.

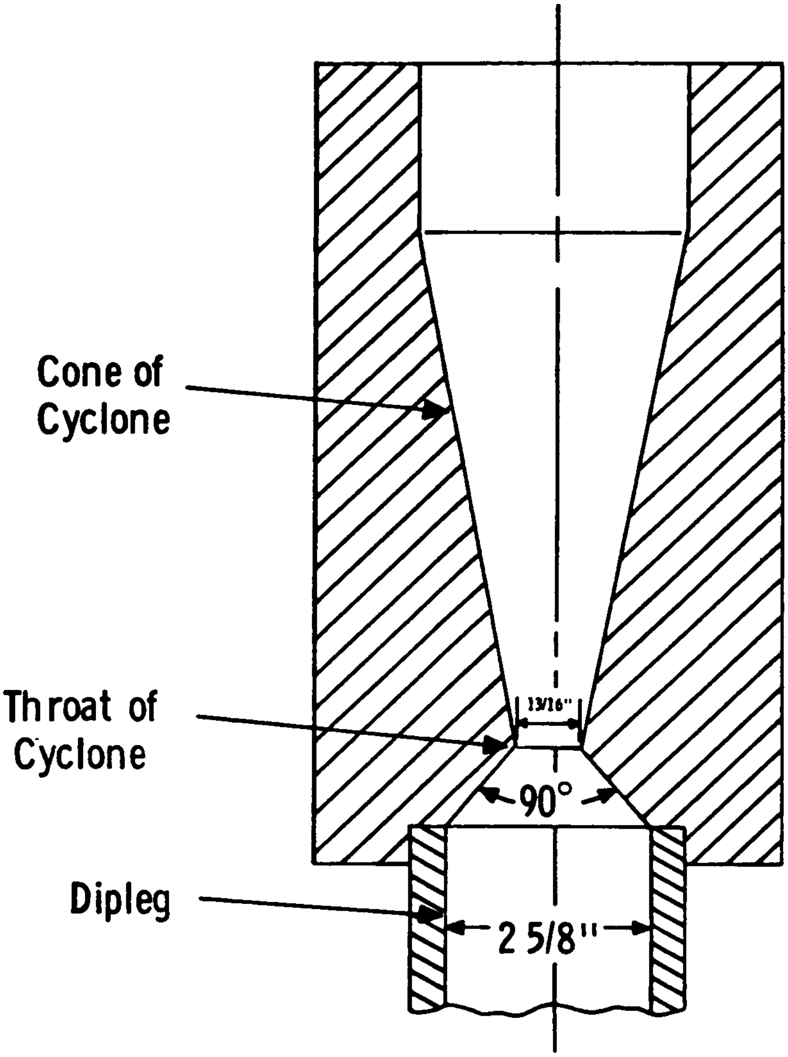
The gas flowing through the dipleg must pass through the base of the cyclone and out the top with the gas from the reactor. The original cyclone design called for a throat diameter of 13/16 inch, as shown in Figure 3.3-6. This would mean that the superficial gas velocity of the dipleg purge gas would be ten times greater through the cyclone throat than through the 2-5/8 inch ID dipleg. Experiments were carried out to determine whether cyclone performance was affected by the dipleg purge gas passing through the cyclone.

Dipleg purge rates above 3 ACFH resulted in cyclone plugging. Beginning at the throat of the cyclone, the polypropylene powder clung to the walls of the cyclone cone and accumulated there until it plugged completely. The cyclone did not plug when the dipleg purge rate was below about 3 ACFH. These results indicate that gas flowing up through the cyclone does affect cyclone performance. The total purge gas rate to the dipleg should be kept to a minimum during operation of the PDU to avoid high superficial gas velocities at the cyclone throat which would interfere with cyclone performance.

A change was made in the cyclone design for the PDU based on these experiments. The throat diameter was increased from 13/16 inches to 1-1/8 inches, reducing the gas superficial velocity by nearly one-half in the throat of the cyclone. This should reduce the frequency of cyclone plugging.

# FIGURE 3.3-6

## ORIGINAL CYCLONE DESIGN - BOTTOM OF CYCLONE



## Transfer Line Operation

Solids must travel up the inclined transfer line to return to the reactor from the dipleg. Gas must be fed into the transfer line to keep the particles moving in order that they will flow back into the reactor. Gas was supplied to the transfer line at various rates and the behavior of the solids in the inclined tube was observed.

Gas superficial velocities below about 0.20 ft/sec in the transfer line resulted in stagnant solids along the entire length of the line. As the superficial gas velocity was increased, solids activity increased along the top of the transfer line while solids in the bottom of the line remained stationary. Solids in the top half of the 60° section of the line began to slug at a superficial gas velocity of about 0.3 ft/sec. Slugs broke up at the angle between the 60° and 45° sections and solids in the 45° section were motionless. Gas velocities of about 1-2 ft/sec. were required to eliminate zones of stagnant solids along the bottom of the transfer line. At these gas velocities, the solids slugged up the line and then flowed back down the bottom of the line. Generally, the solids activity in the 60° part of the transfer line was greater than that in the 45° part of the line.

## Intersection Block Studies

Subsequent experiments on the cold model were designed to determine how to control dipleg and transfer line fluidization simultaneously by varying purge gas rates and locations. The purge gas can enter the system at any of five locations in the intersection block. A diagram of the intersection block with the purge locations numbered 1 through 5 is shown in Figure 3.3-7. Based on the experiments described above, most of the gas entering the fines return system at the intersection block should travel up the transfer line. High gas flow rates are required in the sloping line to eliminate zones of stagnant solids. Purge gas flow traveling up the vertical dipleg should be kept to a low value to avoid interference with cyclone performance but should be enough to keep the solids in the dipleg fluidized.

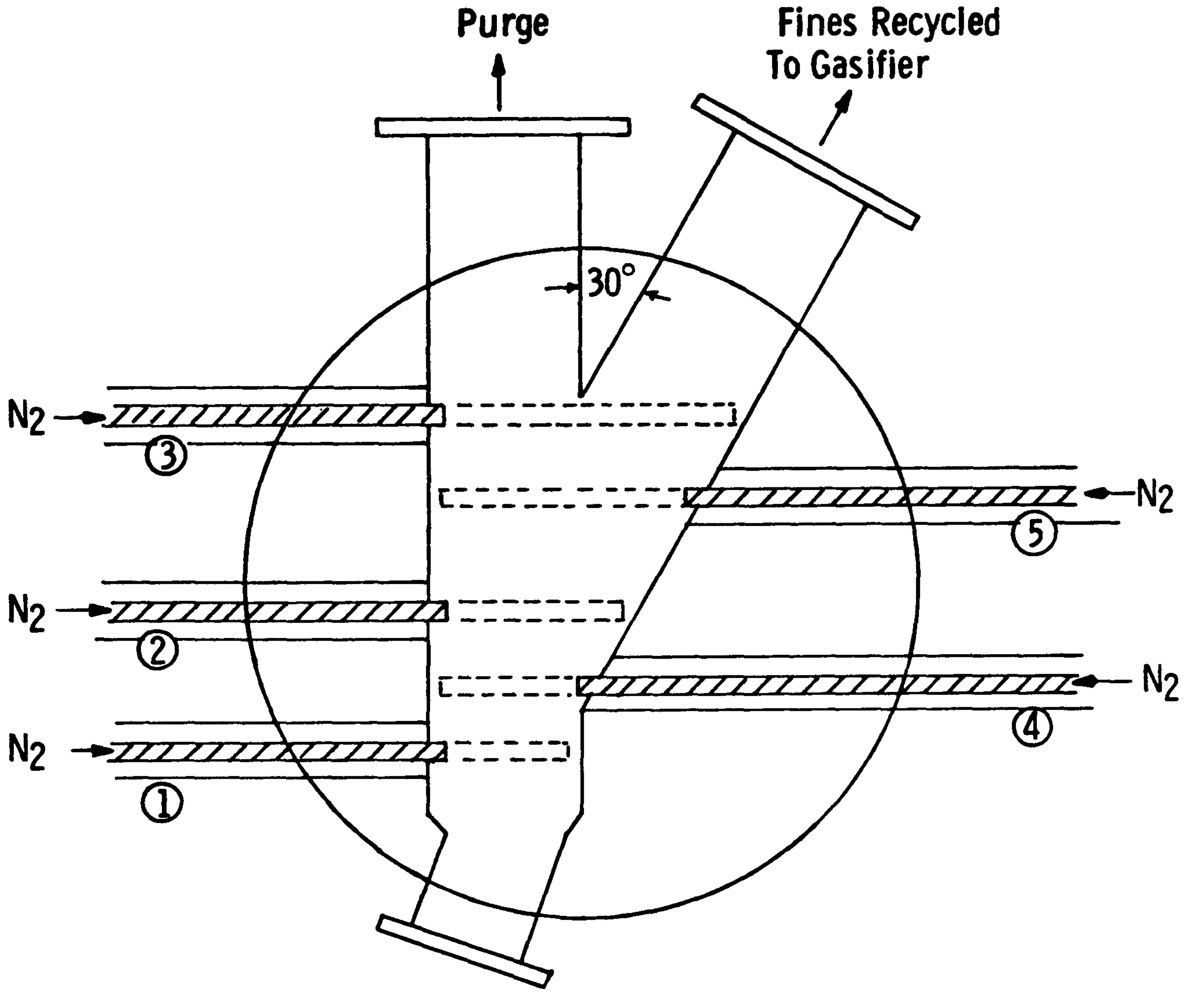
Each of the intersection block purges is equipped with a sliding tube that can be moved into the intersection block as indicated in Figure 3.3-7. Sliding the tube into the intersection block to different positions results in different gas flow patterns.

Purge location #3 gave the best control of flow up either the dipleg or the transfer line but not to both simultaneously. When the tube was extended beyond the entrance to the dipleg, most of the gas went into the tranfer line and there was little solids motion in the dipleg. When the tube was retracted to the wall (as shown in Figure 3.3-7), most of the purge gas flowed up the dipleg. Purge location #2 produced gas flow patterns similar to location #3 but control was not as good. Most of the purge gas flowed up the transfer line in the most extended tube position, but there was intermittent slugging in the dipleg which did not occur when purge location #3 was used. Purges #1 and #4 supplied purge gas only to the vertical dipleg at all tube extensions.

# FIGURE 3.3-7

## DIPLEG INTERSECTION BLOCK

## Cold Model Version



Purge #5 gave little control of flow up the transfer line. Most of the purge gas flowed up the dipleg when the tube was extended to greater than 1/3 of the maximum extension into the intersection block.

These results indicate that purge location is important in controlling fluidization of the fines return system. A purge directly into the base of the transfer line is required to supply high gas flow rates to the transfer line while allowing negligible amounts of gas into the dipleg. Required flow to the dipleg can be supplied from other purge locations in the intersection block.

On the basis of the above work, the PDU intersection block has been modified to provide purge locations which should control flow of purge gas to the dipleg and intersection block.

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

## 4.1 Kinetics of Gasification and Devolatilization

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

The kinetics of char gasification have previously been investigated during the predevelopment phase of catalytic gasification research. The majority of the kinetic data was obtained using a fixed bed reactor at 1300°F and catalyst loadings of 10 and 20% (wt.) potassium carbonate on dry Illinois coal. The coal was devolatilized under an inert atmosphere before loading in the fixed bed reactor. Some data was also obtained at 1200°F.

Engineering sensitivity studies using the limited temperature data have indicated an economic incentive for lowering the gasifier temperature below 1300°F. Additional kinetic data at various temperatures on steady state char is necessary before a confident optimization of the gasifier conditions can be made.

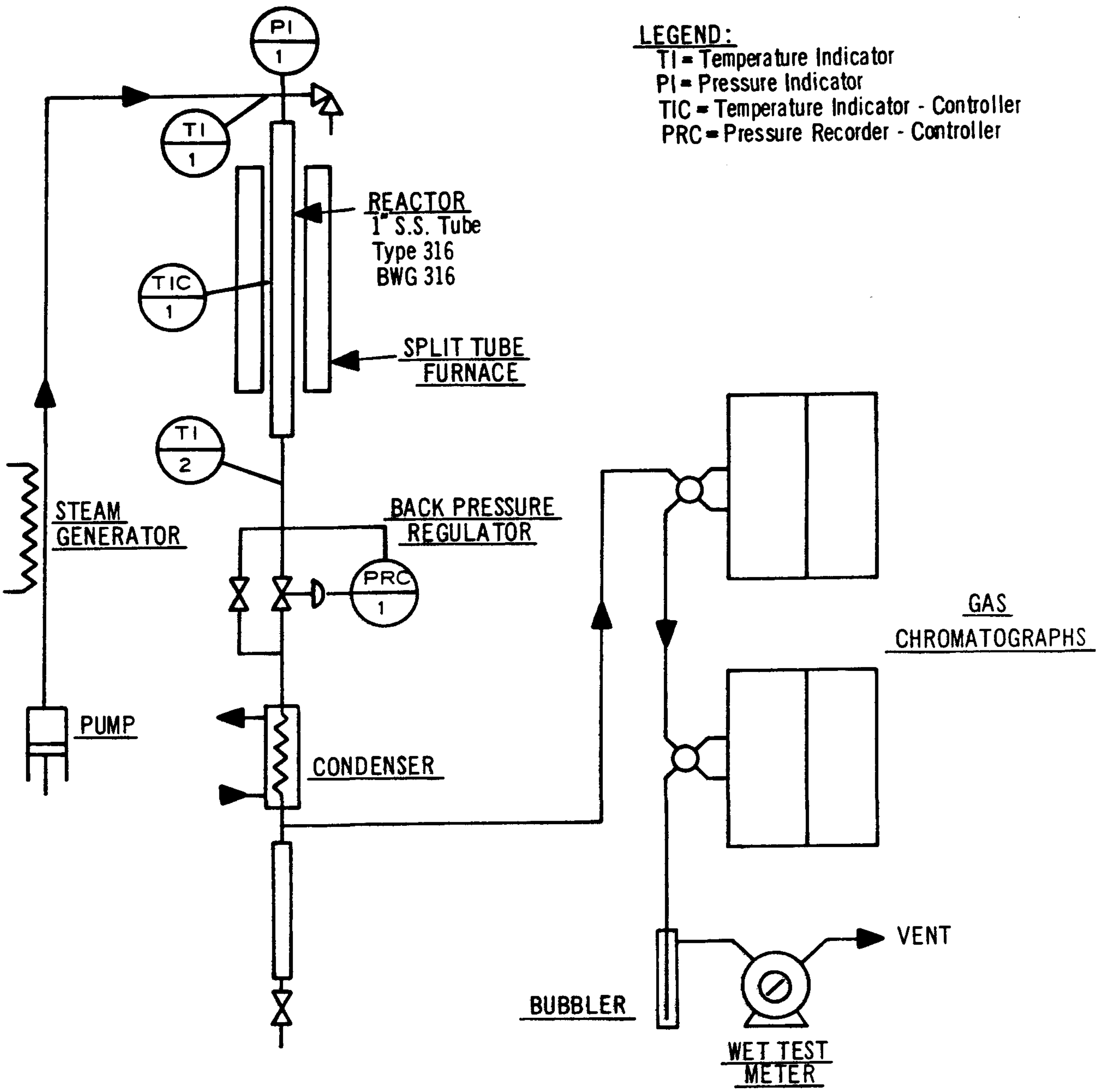
In view of this need, a laboratory program was designed to expand the kinetic data base for steam gasification of Illinois char. Feed for these studies is Illinois char produced at various levels of carbon conversion by the Fluid Bed Gasification Unit (FBG) under steady state conditions rather than the devolatilized coal used previously. The process variable studies will include:

- Effects of variations in potassium/carbon ratio in the steady state char.
- Variations in temperature and pressure around the base conditions of 1300°F and 500 psig, respectively.

A fixed bed unit was recommissioned for use in this program. A simplified flow diagram of this unit is shown in Figure 4.1-1. The unit consists of a high pressure water pump, steam generator, fixed bed reactor, unreacted steam condenser, gas chromatographs, and dry gas flow measurement system.

## FIGURE 4.1-1

## SIMPLIFIED FLOW DIAGRAM OF BENCH SCALE GASIFICATION UNIT



Numerous instrumentation problems were identified and corrected. These problems included a leaking gas chromatograph sampling valve system as well as several faulty temperature and pressure indicators.

A series of shakedown runs was then made at 1300°F and 500 psig using Illinois No. 6 char with a catalyst loading of 20% (wt.) potassium carbonate on dry coal. The purpose of these runs was to check the operability of the unit before initiating the temperature study. During the data workup for these runs, a problem with the gas analyses was discovered. The sum of the unnormalized compositions of the individual product gases was significantly less than 100%.

Two possible causes of this low total were:

(1) incorrect calibration gas analysis, and

(2) nonlinear response of the gas chromatograph with respect to gas composition.

Samples of product gas were collected during subsequent runs and analyzed on a mass spectrometer as well as on several other gas chromatographs on site. A comparison of the results from the on-line gas chromatograph with those from the other systems indicated a nonlinearity in the on-line analysis with respect to hydrogen concentration. This nonlinearity was confirmed through the analysis of gas samples of known hydrogen composition on the on-line unit.

Although the incorporation of a nonlinear hydrogen response factor into the data workup procedure resulted in unnormalized product gas analyses totaling essentially 100%, the final results indicated a much lower gasification rate than that obtained during the predevelopment phase of catalytic gasification research. As a result of these observations, the entire gas chromatograph system was again checked for gas leaks. Several leaks were found throughout the gas chromatograph sampling system as well as a malfunctioning thermal conductivity detector. The entire gas chromatograph sampling and detection system was then rebuilt. A new thermal conductivity detector as well as new automatic switching valves were installed in the unit. New chromatographic columns were also installed in accordance with the gas chromatograph manufacturer's specifications. The stability of the gas chromatograph's response, unfortunately, was not significantly increased following the replacement of the items mentioned above. In addition, various efforts to service the unit by the manufacturer were not successful.

In view of the recurring problems with the on-line gas chromatograph as well as the lack of success by the manufacturer in servicing the instrument, a new gas chromatograph system was purchased for the fixed bed unit. The experimental program using the high pressure fixed bed unit was postponed until the delivery and installation of the new chromatograph.

An atmospheric pressure mini-fluid bed gasification unit was subsequently recommissioned for use in the gasification kinetic program. A schematic of this unit is shown in Figure 4.1-2. The reactor portion of the unit consists of a 1/4" I.D. quartz U-tube inside a hot steel block. Water is fed to the U-tube using a small syringe pump and is vaporized in the reactor. Ceramic beads are placed in the inlet leg of the U-tube to enhance the vaporization process and help disperse the flow. The exit gases from the reactor flow into an oxidizer where all carbon species are converted to carbon dioxide. After condensing any unreacted steam, the gas stream is bubbled through a sodium hydroxide solution where the amount of total carbon converted is automatically monitored using the change in conductivity of the solution. Initial studies will be made using Illinois No. 6 char produced by the FBG earlier this year.

Feed to the mini-fluid bed unit consists of steam and/or hydrogen. Hydrogen is used to simulate the presence of synthesis gas (75% hydrogen) in the feed to a commercial gasifier. Feed flow compositions to the unit are being chosen to match either (a) the conditions under which the FBG was operated during the predevelopment program of gasification research, or (b) the conditions specified in the predevelopment commercial study design. These conditions are shown below.

Gasification Reactor Conditions

| | FBG Conditions | Study Design Conditions |
|---|---|---|
| $\frac{\text{Moles Steam Fed/hr}}{\text{Moles Carbon in reactor}}$ | 0.53 | 1.34 |
| $\frac{\text{Moles Syn Gas Fed/hr}}{\text{Moles Steam Fed/hr}}$ | 1.54 | 0.49 |

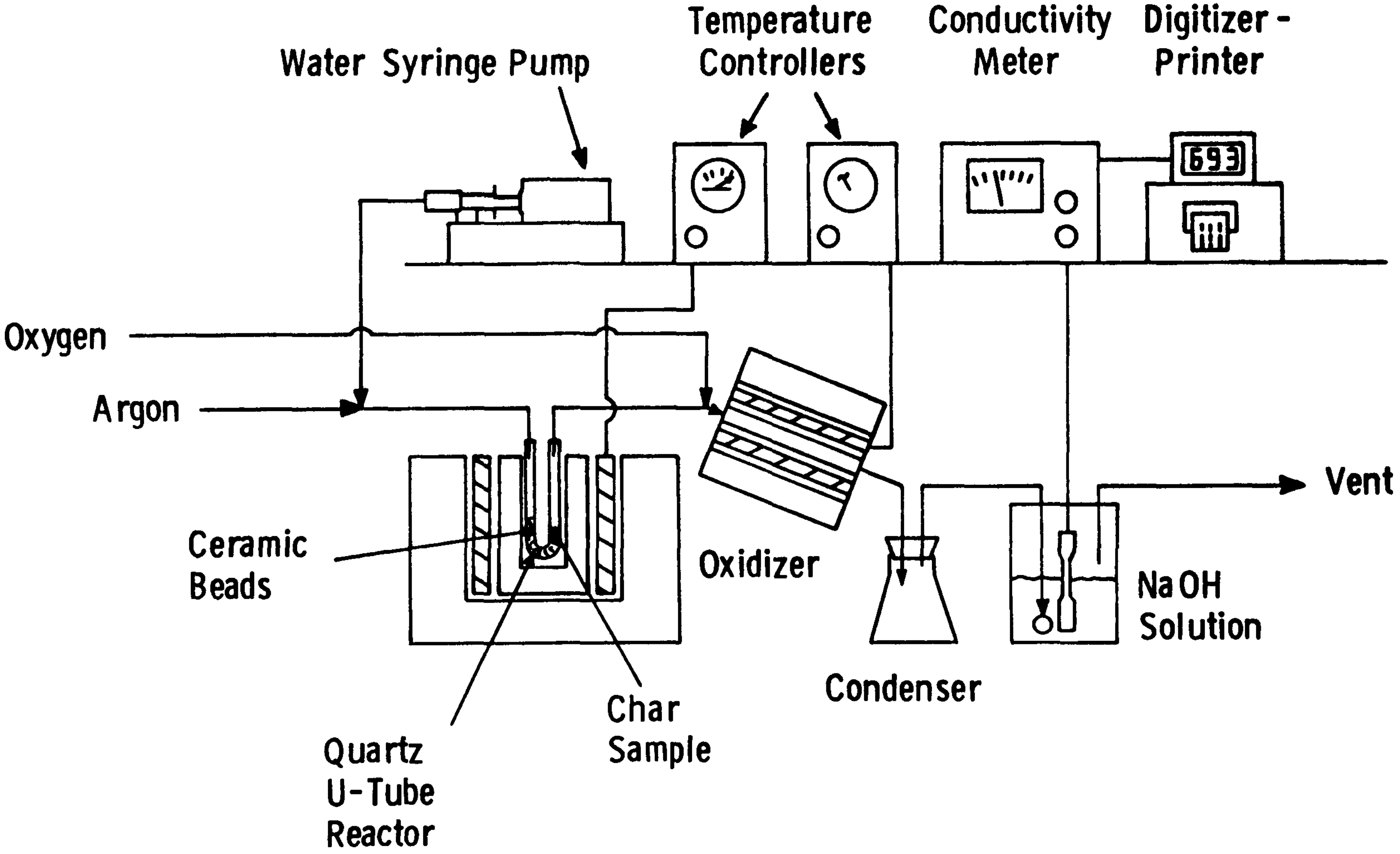
For comparison, runs will also be made using steam only as feed.

Initial kinetic studies are being made using steady-state Illinois No. 6 chars at different levels of carbon conversion produced earlier this year by the FBG. The available chars are listed below along with their degree of carbon conversion and catalyst loading.

| Sample No. | Percent Carbon Conversion | Catalyst Loading, K/C Molar Ratio |
|---|---|---|
| A | 83 | 0.169 |
| B | 76 | 0.118 |
| C | 74 | 0.122 |
| D | 76 | 0.148 |
| E | 84 | 0.233 |

## FIGURE 4.1-2

## SCHEMATIC OF MINI-FLUID BED REACTOR UNIT



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The kinetic behavior of these chars is being investigated as a function of their potassium to carbon molar ratio.

Numerous runs have been made in the mini-fluid bed gasifier at both FBG and Study Design conditions. During the course of the experimental program, a gas leak was discovered in the hydrogen feed line to the unit. This leak caused the $H_2/H_2O$ feed ratio to be lower than the target conditions. The affected runs were repeated once the leak was eliminated. Subsequent data workup of the runs revealed much scatter in the observed gasification rate for duplicate runs. These results were believed to be caused by a lack of fluidization of the reactor bed. The reactor was then inspected at typical operating conditions and indeed, the reactor bed was not fluidized. In addition, gas channeling was observed in the bed. To alleviate this problem, the reactor feed system was modified. Argon, an inert gas, was added to the feed stream in sufficient amount to produce a fluidized bed. This modification should lead to better reproducibility in the data. The experimental investigation of the FBG chars is continuing using the new reactor configuration.

## 4.2 Catalyst/Char Equilibrium Studies

Bench scale studies are in progress to determine the effects of variable pH and potassium ion concentration on the amount of catalyst remaining on the char. This information is needed for the design of a multiple stage char washing process to recover potassium from the char. The equilibrium concentration of potassium on digested char, undigested char, and fines will be determined as a function of potassium concentration in solutions of constant pH and as a function of the pH of solutions of constant potassium concentration. Data will be obtained at room temperature and at the solution boiling temperature. This fundamental information will be used in both the PDU and the commercial CCG catalyst recovery system process definition.

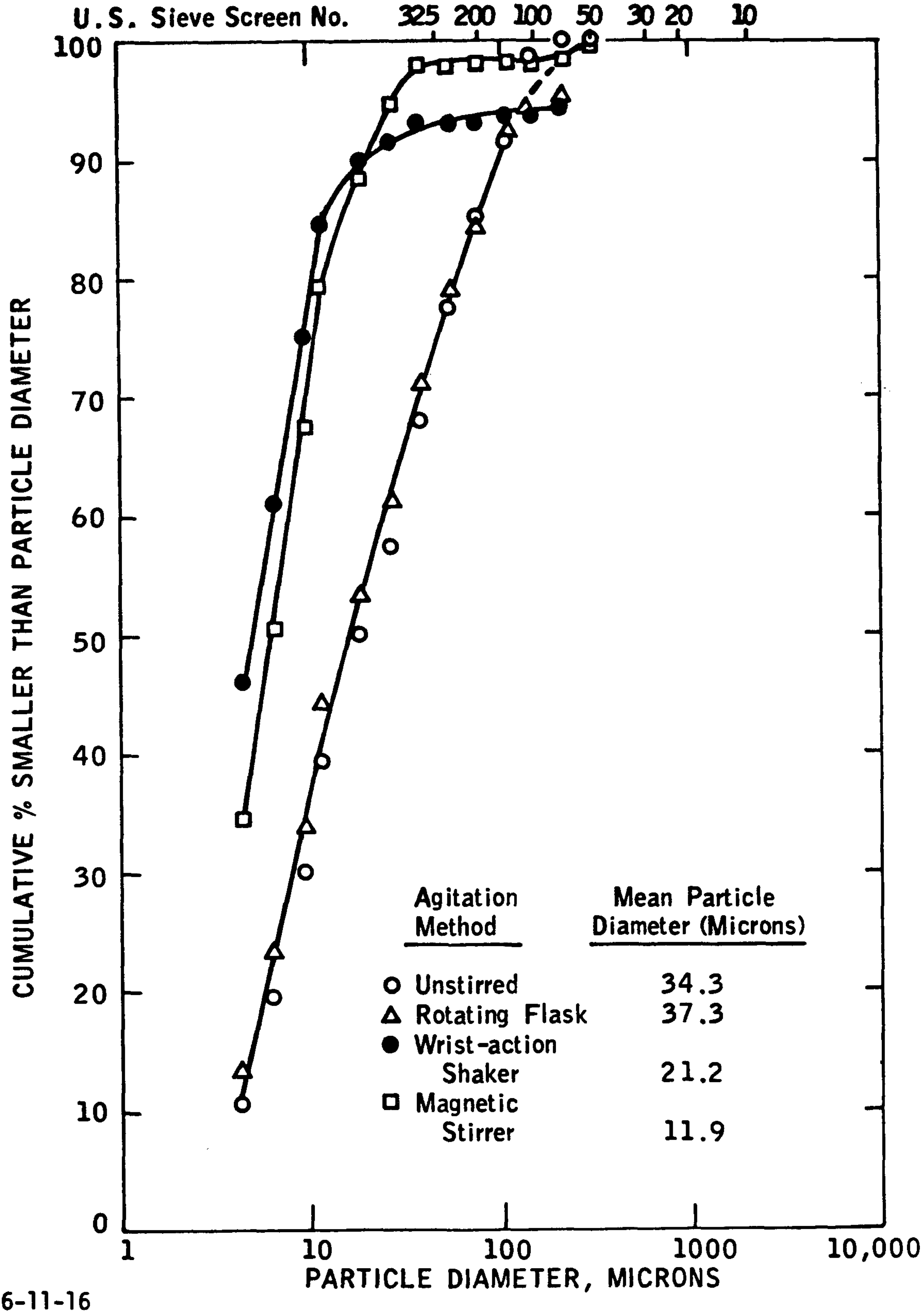
Preliminary experiments on the effect of agitation on equilibration and on particle breakdown have been completed. Methods of agitation considered were 1) magnetic stirrer, 2) rotating flask, 3) wrist-action shaker, and 4) no agitation.

Figure 4.2-1 shows the effects of the four methods on the particle size distribution of digested FBG bottom char. Both the magnetic stirrer and the wrist-action shaker cause particle breakdown. The rotating flask method did not decrease the particle sizes.

Table 4.2-1 shows the effect of agitation on the potassium absorbed on digested char in contact with solutions containing the same potassium concentration at the same pH. The data indicates that agitation is necessary and that the rotating flask method does not provide sufficient agitation.

FIGURE 4.2-1

DIGESTED CHAR BREAKS DOWN UNDER EFFICIENT AGITATION



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### Table 4.2-1

### Effect of Agitation on Potassium Absorption

- Digested FBG Bottom Char
- Ambient Temperature
- $[K^+] = 1.0M$ (pH = 13.0)

| Agitation Method | % (wt.) $K^+$ Absorbed on Char |
|---|---|
| None | 0.09 |
| Rotating Flask | 0.10 |
| Wrist-action Shaker | 2.08 |

As a result, all ambient temperature equilibrations are being performed using the wrist-action shaker since $K^+$ absorbtion rather than particle breakdown is considered to be of primary importance in these experiments. This method was chosen over the magnetic stirrer because the shaker can handle a larger number of samples simultaneously. Since gasifier fines are also to be studied, the extent of particle breakdown for this material using the wrist-action shaker was then determined. Figure 4.2-2 shows that the particle size distribution of this material is not changed with agitation by this method.

## 4.3 Effect of Catalyst Impregnation on Char Properties

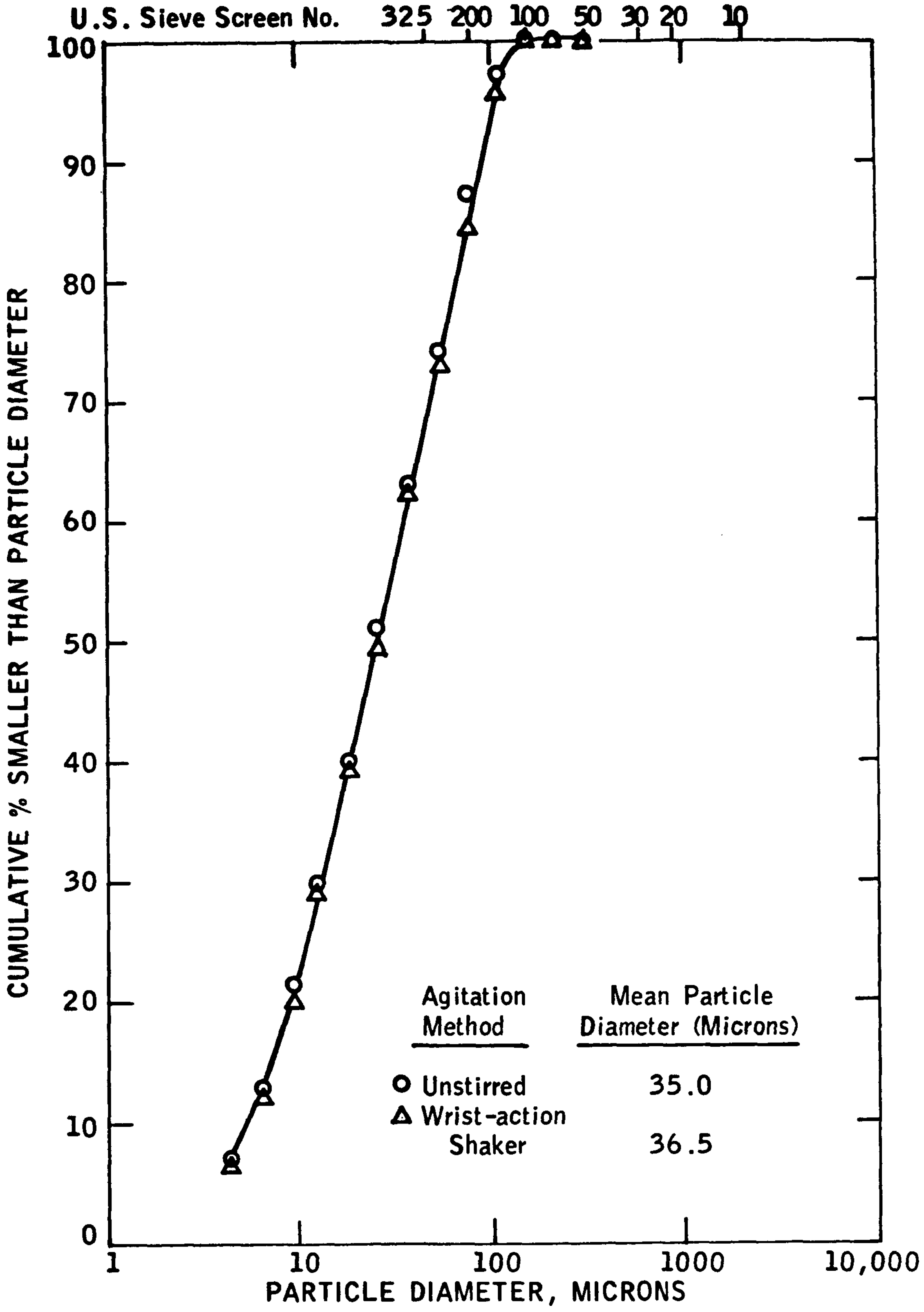
The FBG had been operated successfully during the predevelopment contract on a feedstock of potassium carbonate ($K_2CO_3$) catalyzed Illinois No. 6 coal. During the last quarter of 1978, operation with a new carload of Illinois No. 6 coal and with potassium hydroxide (KOH) as the catalyst was accompanied by some initial operability problems. Operations were improved by removing the large (+16 mesh) particles from the feed coal.

Bench scale studies were initiated to address the effect of variables in catalyst impregnation on both agglomeration and the bulk density of devolatilized coal (char).

The particle size distributions of the coals used in the predevelopment work and in recent work (1978) are shown in Tables 4.3-1 and 4.3-2. $K_2CO_3$ catalyzed coal used in predevelopment operations did not contain as many large particles (+20 mesh) as that currently used. The +20 mesh particles account for 4.7% of the weight of the predevelopment feed coal and 28.1% of the recent feed coal. For both coals the catalyst loading of these large particles is low versus the smaller size fractions as shown by the potassium analyses in Tables 4.3-1 and 4.3.2. Since the catalyst inhibits swelling and agglomeration during devolatilization, the low catalyst loading on the large +20 mesh particles was thought to account for the poor operability of the FBG when feeding a coal with a relatively large fraction of such particles.

## FIGURE 4.2-2

## GASIFIER FINES DO NOT BREAK DOWN WITH SHAKING



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## Effect of Coal Particle Size

Samples of both the 1977 and 1978 feed coals and the large particles (+20 mesh) only from the 1978 feed were charred in the laboratory at 1300°F and atmospheric pressure in nitrogen. The results are pictured in Figure 4.3-1. The 1977 feed did not agglomerate. The 1978 feed did form some agglomerate with the agglomerates containing most of the large particles initially present. The sample containing only +20 mesh particles agglomerated severely.

### Table 4.3-1

### Sieve Analysis of Predevelopment (1977) FBG Feed Coal

- Illinois No. 6 coal
- 15% $K_2CO_3$ treated
- Sampled 6/12/77

| Mesh Size | % (wt.) of Sample | % $K_2O$ $H_2O$ Soluble | % $K_2O$ Acid Soluble |
|---|---|---|---|
| +20 | 4.7 | 3.90 | 7.36 |
| -20 + 60 | 59.3 | 5.41 | 7.96 |
| -60 + 100 | 21.1 | 6.51 | 9.13 |
| -100 + 200 | 11.4 | 7.08 | 9.86 |
| -200 + 325 | 2.0 | 11.24 | 13.08 |
| -325 + 400 | 0.5 | 11.83 | 15.48 |
| -400 | 1.0 | 14.65 | 18.47 |

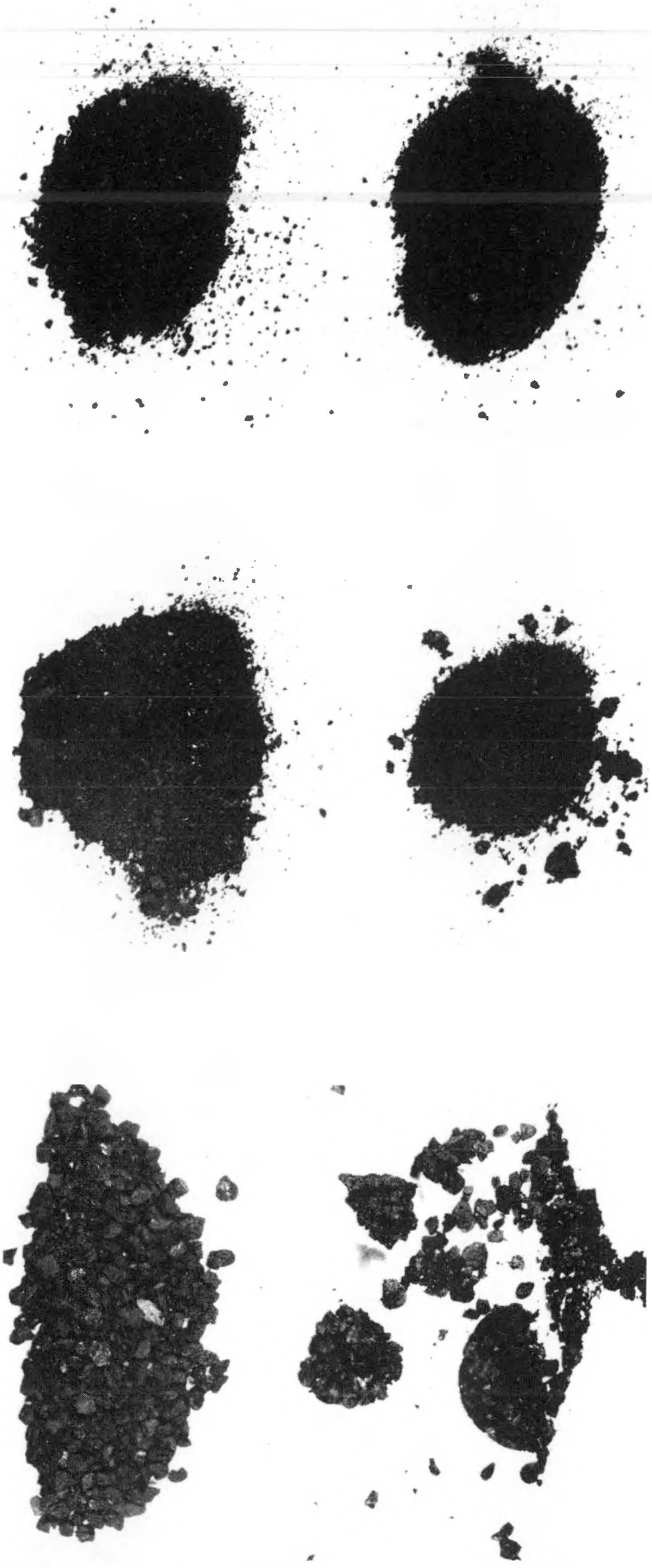
### Table 4.3-2

### Sieve Analysis of 1978 FBG Feed Coal

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

| Mesh Size | % (wt.) of Sample | % $K_2O$ $H_2O$ Soluble | % $K_2O$ Acid Soluble |
|---|---|---|---|
| +20 | 28.1 | 5.58 | 9.98 |
| -20 + 60 | 52.6 | 8.25 | 11.49 |
| -60 + 100 | 14.8 | 8.83 | 12.91 |
| -100 + 200 | 2.7 | 5.8 | 11.41 |
| -200 + 325 | 1.3 | 10.40 | 13.75 |
| -325 + 400 | 0.4 | 14.85 | 17.40 |
| -400 | 0.1 | -- | -- |

FIGURE 4.3-1
AGGLOMERATION TESTS



PREDEVELOPMENT FBG FEED COAL

RECENT FBG FEED COAL

+20 MESH FROM RECENT FBG FEED COAL

The data in Tables 4.3-1 and 4.3-2 show that the large (+20 mesh) particles in the 1978 FBG feed coal had a lower catalyst loading than the remainder of the feed. Laboratory chars prepared from these larger particles showed a high degree of agglomeration (Figure 4.3-1). The study described below was performed to address the question of whether or not the low catalyst loading was the cause of agglomeration of the large particles during devolatilization.

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

The mixture was then dried under nitrogen and the treated coal samples were charred in a laboratory muffle furnace. The chars were examined for agglomeration and their loose bulk densities measured. The results are shown in Tables 4.3-3 and 4.3-4 below.

Table 4.3-3

KOH Catalyzed FBG Feedstock

- Illinois No. 6 Coal
- 12% KOH treated

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

Table 4.2-4

$K_2CO_3$ Catalyzed FBG Feedstock

- Illinois coal
- 15% $K_2CO_3$ catalyzed

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

The lack of agglomeration, particularly for the +20 mesh particles, suggests that uniform catalyst impregnation would allow this sieve size to be included in the reactor feed. In addition, the observed loose bulk densities have virtually the same value for chars from coal of all particle sizes and for equivalent loadings of both KOH and $K_2CO_3$ catalysts.

It would be desirable to be able to use larger size particles in the gasifier feed than the -16 + 100 mesh range that is currently used. The analytical data reported above (Tables 4.3-1 and 4.3-2) shows that the large (+20 mesh) particles in the FBG feed coals had a lower catalyst loading than the remainder of the feed. Laboratory chars prepared from these particles showed a high degree of agglomeration. Further bench scale studies (Tables 4.3-3 and 4.3-4) then showed that when particles of this size contained the desired catalyst loading, agglomeration was no longer observed. This was done by impregnating individual sieve cuts of raw coal separately. Therefore, it should be possible to include larger size particles in the gasifier feed if a method of uniform catalyst impregnation is obtained.

## Char Bulk Density

The observed value of the bulk density of the devolatilized coal (0.51-0.58 g/cc) is higher than densities of char from the fluidized bed pilot plant reactor (0.2-0.4 g/cc) which suggests that muffle furnace char may not be directly comparable to reactor char.

Scanning electron microscope analysis showed that all of these chars consisted of particles which remained angular and irregular in shape, indicating that they did not go through a plastic state during devolatilization. FBG bottom chars consist of rounded, enlarged particles that have melted and resolidified.

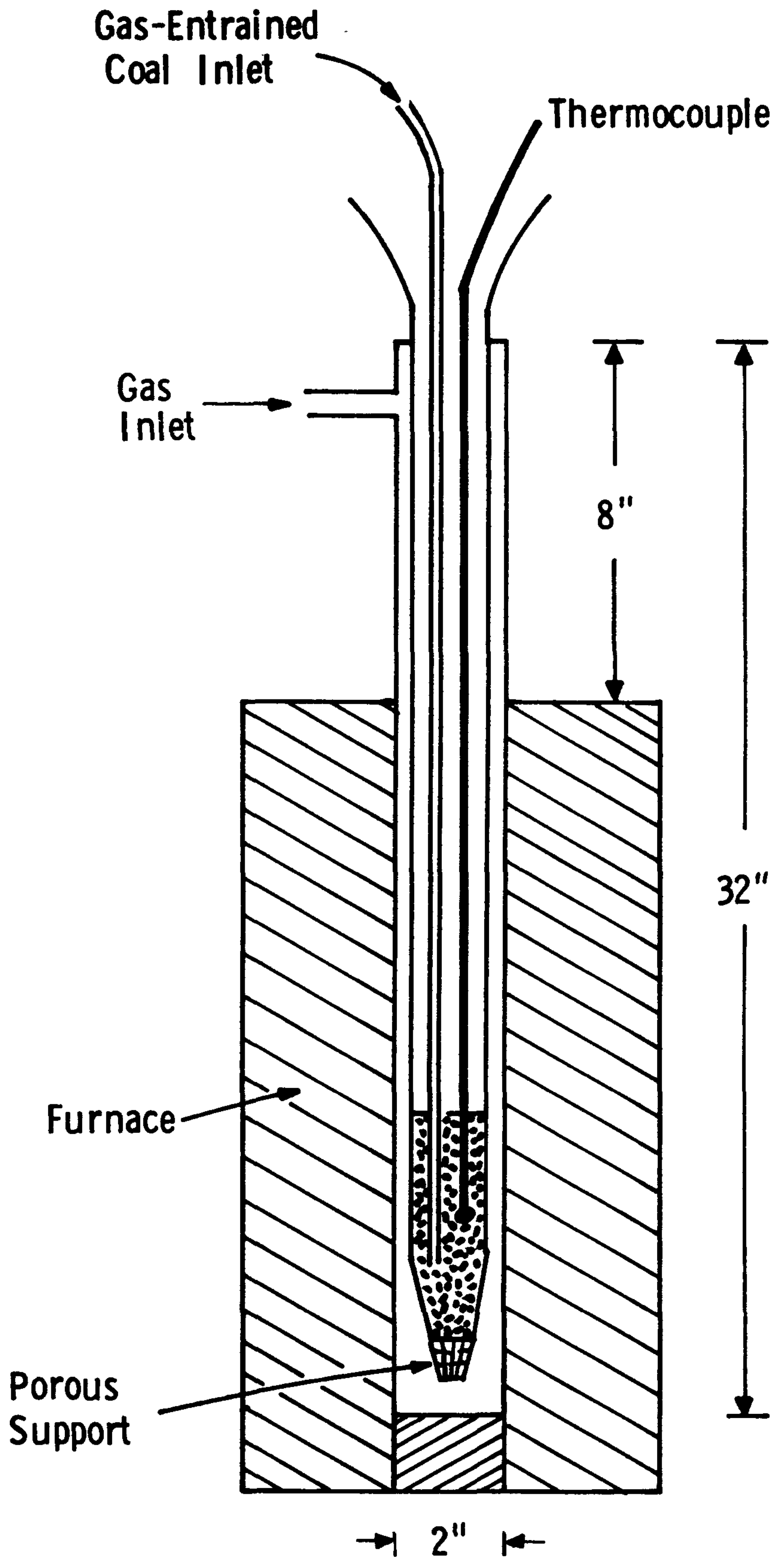
Therefore, work is in progress to obtain a devolatilization process which is a reproducible test of the characteristics of the coal sample devolatilized. A procedure which closely simulates pilot unit devolatilization is considered desirable.

An existing small fluidized bed reactor is being modified for this purpose. The unit is designed to simulate coal addition to a hot, fluidized bed gasifier in all respects except pressure conditions. Figure 4.3-2 illustrates the unit. The reactor system is constructed of quartz while the coal addition system is stainless steel. The bed is supported by a porous screen and is fluidized by gas which is preheated in the outer section of the vessel. The coal addition tube is adjustable to allow entrance of the coal sample at variable positions within or above the bed. A movable thermocouple is used to measure bed temperature at any desired position.

Preliminary experiments have shown that fine (100 - 200 or - 200 mesh) char cannot be used as a bed material because it would not properly fluidize. Therefore, 100 - 200 mesh sand has been chosen for the bed material for the reactor due to its fluidizing properties. A fine cut of bed material is required in order to separate the bed from the product char. Future work will study the effect of catalyst impregnation variables or char bulk density with the goal of learning how to make high density char.

# FIGURE 4.3-2

## BENCH SCALE FLUIDIZED BED UNIT



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## 5. Engineering Research and Development (Reporting Category C20)

Engineering research and development studies are being carried out under the Catalytic Coal Gasification (CCG) Process Development Contract in conjunction with the laboratory bench-scale research and process development unit (PDU) operations. This work includes both engineering and cost studies to evaluate process improvements and to guide the continuing laboratory programs, and engineering technology programs to develop fundamental process and equipment technology to support the laboratory and engineering efforts. The overall objective of the engineering work is to define the conceptual commercial CCG process at the end of the contract period.

The engineering research and development work under the CCG Process Development Contract is divided into four major subtasks:

Cost Reduction and Laboratory Guidance Studies
Systems Modeling
Process Definition
Engineering Technology Studies

During the period covered by this report, the engineering efforts focused on the first, second, and fourth sub-tasks. Work on the Process Definition is not scheduled until July, 1980.

### 5.1 Cost Reduction and Laboratory Guidance Studies

### 5.1.1 CCG Commercial Plant Study Design - Offsites Revision

A Catalytic Coal Gasification Commercial Plant Study Design was prepared during the latter part of the CCG Process Predevelopment Program which was completed in January, 1978 under Contract No. E(49-18)-2369. The results of the "CCG Study Design" are documented in the Final Project Report for that contract (FE-2369-24). This was a detailed study involving substantial engineering efforts on material and energy balances, equipment specifications, and investment cost estimating.

Offsites facilities (including materials handling, utilities, and general offsites) constituted 40% of the total plant direct and indirect investment cost for the CCG Study Design. Although considerable effort was involved in specifying the offsites facilities for the Study Design, for the most part these areas were studied in less engineering depth and specified in less detail than the onsites process sections. Because the onsites and offsites design work proceeded at the same time, some inconsistencies developed between the final onsites utilities demands and the estimated demands used in specifying the utilities sections. Also, the process wastewater rate used in sizing the wastewater treating facilities was underestimated. A preliminary plant layout was used in specifying common onsite facilities and offsite piping for utilities distribution and for industrial sewers. A final look at the plant layout indicated that these requirements were probably overestimated.

In view of these factors, a revised offsites facilities definition and cost estimate was prepared to firm up the CCG Study Design in this important area. The revised Study Design will serve as the "base case" for screening studies to evaluate new data, process improvements, and optimum process conditions under the present Process Development Contract. As a result of the offsites revision, the accuracy of such screening studies will be improved.

### Changes in Offsite Facilities

Most of the changes in this offsites revision were simply adjustments to equipment sizes to correct for inconsistencies between the initial and final utilities demands and plant layout requirements. However, more extensive changes were made in two sections. First, in the wastewater treating section, more detailed consideration was given to water quality and reuse options to better define treating needs and further reduce plant makeup and effluent water rates. Second, the flue gas desulfurization (FGDS) process was changed from a regenerative system using sodium carbonate to a once-through system using lime scrubbing. This change allowed integration of lime scrubbing offsites with other CCG plant offsites. For example, lime receipt for FGDS was integrated with lime receipt for onsite catalyst recovery, which uses lime as feed to $Ca(OH)_2$ digestion. Common absorbers were utilized to handle flue gas from the offsite boilers, the feed coal dryers, and the catalyst addition dryers, all of which are coal fired. In addition to these integration advantages, the technology and costs for lime (and limestone) scrubbing are better defined today than for regenerative FGDS.

In general, the revised Study Design was prepared using the same approaches as the earlier Predevelopment Program Study Design. Except for the change in the FGDS process described above, the project basis is the same. The onsites process bases and material and energy balances are also unchanged. Utilities balances were updated to reflect the final onsites demands and the demands of the revised offsites facilities. Equipment lists for the revised offsites were developed by engineers specializing in offsites design. Direct equipment costs were estimated using the same techniques and cost bases used for Exxon's commercial projects. Indirect costs were estimated based on recent experience with large projects. Contingencies were included in the total investment estimate, also based on Exxon practices for actual projects.

### Revised Investment

The revised investment for the CCG Study Design is presented in Table 5.1-1. (This updates Table 4.8-1 of the Predevelopment Report FE-2369-24.) The total investment is 1,530 M$ for the pioneer commercial plant feeding Illinois No. 6 coal and producing 257 billion Btu per stream day of SNG

## TABLE 5.1-1

## CATALYTIC COAL GASIFICATION
## COMMERCIAL PLANT STUDY DESIGN

## INVESTMENT FOR PIONEER PLANT

Basis:
- January, 1978 Instant Plant
- Eastern Illinois Location
- 257 Billion Btu/Stream Day SNG (HHV Basis)

| Plant Section | Investment Breakdown | |
|---|---|---|
| | Million $ | % (1) |
| **ONSITES** | | |
| Coal Drying | 27 | 2 |
| Catalyst Addition | 18 | 2 |
| Reactor System | 197 | 18 |
| Product Gas Cooling and Scrubbing | 86 | 8 |
| Sour Water Stripping and Ammonia Recovery | 20 | 2 |
| Acid Gas Removal and Sulfur Recovery | 161 | 15 |
| Methane Recovery System | 44 | 4 |
| Refrigeration | 31 | 3 |
| Catalyst Recovery | 39 | 3 |
| Common Onsite Facilities | 55 | 5 |
| ONSITES SUBTOTAL | 678 | 62 |
| **MATERIALS HANDLING** | | |
| Coal Handling and Storage | 19 | |
| Coke/Char Handling | 5 | |
| Chemicals Handling and Storage | 20 | |
| By-Products Storage and Shipping | 3 | |
| Waste Solids Handling and Disposal | 27 | |
| MATERIALS HANDLING SUBTOTAL | 74 | 7 |
| **UTILITIES** | | |
| Raw Water/BFW Treating | 29 | |
| Steam Generation and Distribution | 120 | |
| Cooling Water | 9 | |
| Electric Power Distribution | 23 | |
| Miscellaneous Utilities | 5 | |
| Flue Gas Desulfurization (2) | 51 | |
| UTILITIES SUBTOTAL | 237 | 22 |
| **GENERAL OFFSITES** | | |
| Wastewater Treating | 48 | |
| Safety and Fire Protection | 13 | |
| Site Preparation | 6 | |
| Miscellaneous Offsites | 34 | |
| GENERAL OFFSITES SUBTOTAL | 101 | 9 |
| TOTAL DIRECT AND INDIRECT COSTS | 1,090 | 100 |
| PROCESS DEVELOPMENT ALLOWANCE (25% of Onsites Direct & Indirect Costs) | 169 | |
| PROJECT CONTINGENCY (25% of Total Direct & Indirect Costs) | 271 | |
| TOTAL ERECTED COST | 1,530 | |

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**Notes:**

(1) Percentage breakdown of investment is based on total direct and indirect costs excluding process development allowance and project contingency.

(2) Includes desulfurization for flue gases from steam generation (coal-fired boilers) and from coal drying and catalyst addition.

(substitute natural gas). This is for a January, 1978 cost level at an Eastern Illinois location.

The revised Study Design investment is 110 M$ less than the investment estimated during the Predevelopment Program, a reduction of about 7%. The investment changes are broken down by plant section in Table 5.1-2, starting with the Predevelopment Program Study Design investment of 1,640 M$. The key factors which have contributed to the overall investment change are:

- Costs are substantially lower in materials handling sections (including coal drying and catalyst addition, which are grouped with the onsites). The lower investments stem in part from modest reductions in facilities requirements made as part of the offsites revisions. For example, the electrostatic precipitators used to remove fines from flue gases produced in the coal dryers and the catalyst addition dryers were deleted. Fines removal from these flue gases is now accomplished by venturi scrubbers located in the flue gas desulfurization section upstream of the lime absorbers. Also, surge coal storage silos were reduced in size. However, the major factor which lowered the estimated investment in these sections is improvements in the methods and cost bases used in cost estimating materials handling equipment, such as silos, conveyors, and associated structures and foundations. Exxon's commercial experience with materials handling equipment was quite limited when the Predevelopment Program investment estimate was prepared in late 1977, and cost estimating tools were not well developed. Experience since that date, including the Exxon Coal Liquefaction Pilot Plant now under construction, has led to improved estimating approaches. Applying these new tools shows that the cost estimates for silos and conveyors were too high in the earlier Study Design.

- Costs for common onsite facilities (piperacks, utility headers, roads, sewers, lighting, etc.) are reduced based on the final plant layout.

- Steam generation and distribution has slightly increased in cost. This is due primarily to an upward revision of coal-fired boiler cost bases, also resulting from learning experience since the previous estimate was completed over a year ago. Boiler capacity is actually down 8%, due mainly to lower steam demands for lime FGDS.

- The flue gas desulfurization facilities costs are down as a result of the change from regenerative FGDS to lime scrubbing. The investment shown for FGDS is especially low because lime receipt and handling is shared with the onsites catalyst recovery system. The investment for the shared lime facilities is included under chemicals handling and storage. Even so, the cost for the latter section is lower because of the new cost estimating approaches for silos and conveyors.

## TABLE 5.1-2

## CCG STUDY DESIGN
## SUMMARY OF INVESTMENT CHANGES

| | | Investment<br>Million $ |
|---|---|---|
| • TOTAL ERECTED COST FOR PREDEVELOPMENT PROGRAM STUDY DESIGN | | 1,640 |
| • CHANGES IN TOTAL ERECTED COST | | |
| ONSITES | | |
| Coal Drying | (11) | |
| Catalyst Addition | ( 6) | |
| Common Onsite Facilities | ( 8) | |
| Other Sections | 2 | |
| MATERIALS HANDLING | | |
| Coal Handling and Storage | (33) | |
| Chemicals Handling and Storage | ( 7) | |
| Other Sections | ( 3) | |
| UTILITIES | | |
| Steam Generation and Distribution | 3 | |
| Flue Gas Desulfurization | (16) | |
| Other Sections | (10) | |
| GENERAL OFFSITES | | |
| Wastewater Treating | 7 | |
| Other Sections | - | |
| TOTAL DIRECT AND INDIRECT COSTS | | (82) |
| PROCESS DEVELOPMENT ALLOWANCE | | ( 6) |
| PROJECT CONTINGENCY | | (22) |
| • TOTAL ERECTED COST FOR REVISED STUDY DESIGN | | 1,530 |

- The investment for wastewater treating is up because of the increase in process wastewater rate and in facilities for reuse. As a result of more detailed study of water reuse options, the estimated average raw water makeup rate for the CCG Study Design has been reduced from 7,300 gpm to 5,600 gpm.
- The percentage add-ons for process development allowance and project contingency are down in proportion to the reductions in onsites and total plant direct and indirect costs.

Thus, overall, the estimated investment for the CCG Study Design is reduced from 1,640 M$ to 1,530 M$.

Revised SNG Cost

Consistent with this revised investment, the cost of SNG produced from Illinois coal in a pioneer CCG plant is now estimated to be about 6.18 $/MBtu on a 1978 basis, as shown in Table 5.1-3. (This updates Table 4.9-2 of the Predevelopment Report.) This gas cost is a required initial selling price based on 100% equity financing with a 15% current dollar DCF return. It was assumed that SNG product revenues will escalate at 6% per year and that operating costs and by-product revenues will escalate at 5% per year. On a financing basis of 70% debt/30% equity with 9% interest on debt, the initial gas cost is 4.65 $/MBtu. This cost is also based on the same DCF return on the equity and the same escalation assumptions. The complete economic basis for these gas costs is documented in the Predevelopment Report.

The revised SNG cost in the 100% equity case is 0.24 $/MBtu less than the gas cost calculated during the Predevelopment Program. The changes in the SNG cost can be summarized as follows:

| | SNG Cost, $/MBtu | | |
|---|---|---|---|
| SNG Cost Component | Predevelopment Study Design | Revised Study Design | Net Change |
| Coal | 1.40 | 1.41 | 0.01 |
| Major Chemicals | 0.37 | 0.41 | 0.04 |
| Other Operating Costs | | | |
| - Utilities | 0.35 | 0.35 | - |
| - Labor and Related | 0.40 | 0.39 | (0.01) |
| - Materials and Overheads | 0.64 | 0.60 | (0.04) |
| - Other | 0.10 | 0.09 | (0.01) |
| By-Product Revenues | (0.19) | (0.18) | 0.01 |
| Capital Charges | 3.35 | 3.11 | (0.24) |
| Total | 6.42 | 6.18 | (0.24) |

## TABLE 5.1-3

## CATALYTIC COAL GASIFICATION
## COMMERCIAL PLANT STUDY DESIGN

## COST OF SNG FROM PIONEER PLANT WITH 100% EQUITY FINANCING

**Basis:**
- January, 1978 Instant Plant, Eastern Illinois Location
- 257 Billion Btu/Stream Day SNG (HHV Basis)
- 90% Capacity Factor
- 100% Equity Financing
- 15% Current Dollar DCF Return
- Escalation Rates:
  - Operating Costs and By-Product Revenues at 5%/Year
  - SNG Revenues at 6%/Year
- Total Erected Cost of 1,530 M$ (From Table 5.1-1)

| SNG Cost Components | Requirements (At Full Capacity) | Unit Costs (1978) | SNG Cost Breakdown $/Million Btu (1978) |
|---|---|---|---|
| ● Illinois No. 6 Coal (Cleaned) | | | |
| - To Gasifiers | 14,490 ST/SD (2) | 20 $/ST | 1.128 |
| - To Coal Dryer Fuel | 710 ST/SD | 20 $/ST | 0.055 |
| - To Offsite Boiler Fuel | 2,960 ST/SD | 20 $/ST | 0.230 |
| Subtotal | 18,160 ST/SD | | 1.413 |
| ● Major Chemicals | | | |
| - KOH Solution (30 wt%) | 189 ST/SD (Contained) | 300 $/ST | 0.221 |
| - Lime (97% CaO) to Catalyst Recovery | 1,005 ST/SD | 39 $/ST | 0.153 |
| - Lime (97% CaO) to FGDS | 272 ST/SD | 39 $/ST | 0.041 |
| Subtotal | | | 0.415 |
| ● Other Operating Costs | | | |
| - Purchased Electric Power | 147 MW | 2.5 ¢/kWh | 0.343 |
| - Raw Water | 5,600 gpm | 15 ¢/k gal | 0.005 |
| - Other Catalysts and Chemicals | Many Items | 4.7 M$/yr | 0.056 |
| - Wages and Benefits | 980 Men | 21 k$/man/yr | 0.244 |
| - Salaries and Benefits | 260 Men | 25 k$/man/yr | 0.077 |
| - Labor Overheads and Supplies | 20% of Wages, Salaries, and Benefits | | 0.064 |
| - Materials and Overheads | 3.3% of Total Erected Cost/Year | | 0.598 |
| - Ash Disposal | 8,400 ST/SD (Wet) | 1 $/ST | 0.033 |
| Subtotal | | | 1.420 |
| ● By-Product Revenues | | | |
| - Ammonia (20 wt%) | 231 ST/SD (Contained) | 160 $/ST | (0.144) |
| - Sulfur | 324 LT/SD (2) | 25 $/LT | (0.031) |
| Subtotal | | | (0.175) |
| ● Capital Charges | Per Above Basis | | 3.104 |
| TOTAL SUBSTITUTE NATURAL GAS COST (RISP) (3) | | | 6.177 |
| CALL | | | 6.18 |

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Notes:

(1) k = $10^3$, M = $10^6$, G = $10^9$.

(2) ST/SD = short tons/stream day (i.e., one day's operation at full plant capacity). LT = long tons.

(3) Required initial selling price in first year of plant operation (1978).

A lower capital charge associated with the drop in investment is the main factor contributing to the reduction in gas cost. This is partially offset by the added cost of purchasing lime (included under "major chemicals") for the lime scrubbing process now used for flue gas desulfurization.

Despite the 8% reduction in offsite boiler capacity mentioned earlier, the coal to boiler fuel is up about 3% in the revised Study Design. This is the reason for the small increase in coal cost shown above. The increase in boiler fuel is a reflection of a change in the approach used to estimate average requirements for all plant utilities. As described in the Predevelopment Report, the total design capacities for CCG Study Design utilities systems included: (1) normal requirements calculated from the onsite and offsite equipment lists; (2) intermittent requirements also calculated from the equipment lists; (3) allowances for estimated increases in utilities loads as facilities definition improves during project development; and (4) an additional allowance for reserve capacity in source facilities for startup and emergency needs. (Source facilities include offsite boilers, BFW treating, cooling tower, etc.) This approach is consistent with Exxon practices for commercial projects; the allowances for items (3) and (4) are based on Exxon's experience for a broad range of commercial process plants. For the Predevelopment Program Study Design, average plant utilities requirements for operating costs were based on the calculated normal requirements plus the average intermittent requirements. For the revised CCG Study Design, the allowances for estimated increases in utilities loads during project development (item (3)) were also included in the average utilities requirements for operating costs. This is consistent with the experience showing that such increases do occur, on average, in actual projects. Adding these allowances in the revised Study Design has increased operating costs only for coal fuel purchased to generate steam in the offsite boilers. Utilities savings resulting from the use of lime FGDS, more complete utilization of available steam in non-condensing steam turbine drivers, and increased reuse of wastewaters have offset these additional allowances for the other utilities. Thus there has been no net change in the electric power requirements (147 MW) and a substantial reduction in the raw water makeup rate (as noted earlier).

As discussed in the Predevelopment Report cited earlier, estimates of coal gasification costs can vary widely depending on the philosophy used to set the process and offsites bases, the detail of the equipment design, and the approach to the investment estimate. In addition, the method of financing, plant size, coal type, and the maturity of the technology can have significant impacts on SNG costs. The time frame for which costs are presented is also an important factor. Thus, caution must be used when comparing these economics with published estimates for other coal gasification processes. A consistent comparison of CCG with state-of-the-art gasification technology has been made by Exxon Research and Engineering Company, and it has been concluded that significant incentive exists for development of the Catalytic Coal Gasification Process.

### 5.1.2 Coal Crushing Machinery for CCG

A study is underway to determine the type(s) and performance of coal crushing equipment appropriate for commercial catalytic coal gasification plants. Initially, effort has been directed toward determining design pressure requirements.

To arrive at appropriate design requirements, the safety requirements in regard to pressure containment in the event of a coal dust explosion are being investigated for coal crushing equipment and its associated ductwork, fans, cyclones, etc. In this effort, applicable National Fire Protection Association (NFPA) standards have been reviewed. This review and associated discussions with NFPA contacts and an outside coal handling safety consultant have provided the following information:

- No NFPA standards have been written especially for coal gasification facilities.
- Those individual equipment components which are covered by NFPA standards should be designed for NFPA standards.
- Unless a reliable inerting system is available for coal crushers and associated ductwork, fans, cyclones, etc. in the system, a 50 psig design pressure should be assumed initially. (A reliable system would have to provide inerting at start-up and shutdown as well as during normal operations).

Work on this study will continue with vendor and consultant contacts with the intent of selecting the appropriate type(s) of machinery for coal crushing at a CCG facility. At the same time, the issue of design pressure requirements will be reviewed with these contacts for their additional input.

### 5.1.3 Evaporation of Catalyst Solutions

A laboratory guidance study has been made to estimate the economic impact of evaporating dilute catalyst solutions from catalyst recovery to concentrations which are suitable for direct addition to the gasifier feed coal. These estimates of evaporation costs will be used to help assess technical and economic tradeoffs in the catalyst recovery section. As recovered solution concentration is reduced below the level in the CCG Study Design, fewer washing stages are required to achieve the same overall recovery. Also, the solid-liquid separations are easier in dilute solutions, due to lower viscosities, and in the case of separations based on gravitational forces (e.g., settlers, centrifuges), due to larger particle-solution density differences. The potential cost savings for dilute solutions must be weighed against the added costs to concentrate the recovered solution to the same level used in the Study Design.

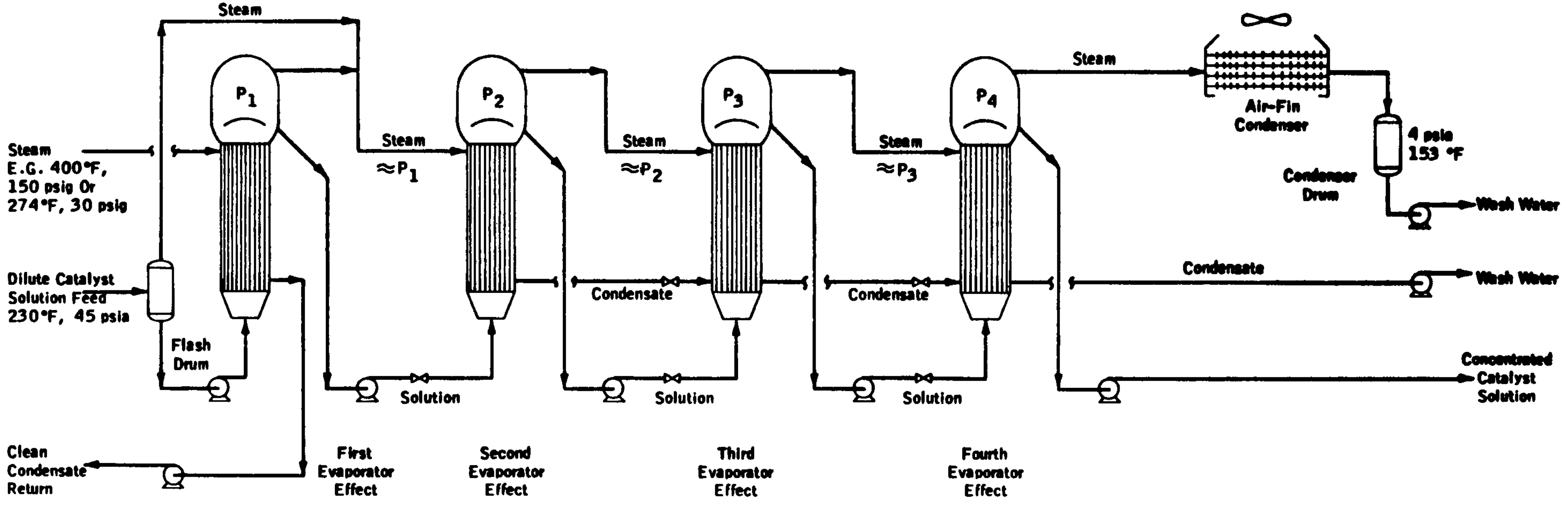
In order to estimate the costs for evaporation, a series of screening studies were carried out. Figure 5.1-1 shows the general process flowsheet for these screening studies. It includes a conventional, multiple-effect evaporator for concentrating the catalyst solution and an air-fin condenser for recovering the evaporated water for recycle to catalyst recovery. The multiple-effect evaporator uses process steam in the first effect to concentrate the catalyst solution. Vapor raised in the first effect is condensed in the second effect to further concentrate the remaining solution. The vapor from the second effect is then condensed in the third effect, and so on. The vapor from the last effect is condensed in the air-fin condenser. To operate the evaporator in this manner, the solution pressure in each effect is maintained lower than the pressure in the preceding effect. The pressure in the last effect was set at 4.5 psia. This pressure is typical of multiple-effect evaporators and was selected because it gave the lowest combined evaporator-condenser area for representative cases.

The process basis for the current studies was set based on the CCG Study Design. The catalyst feed rate to the evaporator is the same as the catalyst rate from catalyst recovery in the Study Design (equivalent to 122.8 klb/hr of KOH). Two catalyst solution concentrations, 5 and 10% (wt.) were considered as feeds to the evaporator system. The concentrated product from the evaporator is a 32.2% (wt.) KOH catalyst solution, which is the same concentration as the recovered catalyst solution fed directly to the catalyst addition/entrained drying system in the Study Design. Steam to concentrate the solution in the evaporator is potentially available from two sources. Low pressure steam (e.g., 10-30 psig) can be produced from onsite waste heat, and higher pressure steam (e.g., 150 psig) can be produced by letting down high pressure steam from offsite boilers across non-condensing steam turbine drivers.

To estimate the economic impact of concentrating the dilute catalyst solutions, heat and material balances were made for each catalyst solution feed (5 and 10% (wt.) KOH) with each steam source and with a variable number of effects in the evaporator. Based on these balances, both onsite and offsite equipment was sized and utility demands were determined. The number of parallel evaporation trains was set to maintain individual evaporator area below 32,000 $ft^2$ (the approximate maximum commercial size today). The incremental investment and operating costs were estimated based on comparable equipment and operatring costs for the CCG Study Design. The incremental impact on the gas cost was then estimated using the CCG Study Design economic basis (100% equity financing, 15% DCF return on investment, January 1978 cost level, East Illinois location). By minimizing these incremental gas costs, the approximate optimum number of effects for each feed concentration at each steam pressure were selected. Table 5.1-4 summarizes these optimum cases. The range of incremental gas costs shown in the table reflects the sensitivity of the gas cost to uncertainties in the evaporator costs and the inclusion of a 25% process development allowance.

Figure 5.1 - 1

FORWARD FEEDING MULTIPLE-EFFECT EVAPORATOR



Note: (1) Pressures Are Cascaded So That $P_1 > P_2 > P_3 > P_4$ = 4.5 psia

## TABLE 5.1 - 4

## INCREMENTAL GAS COST FOR CONCENTRATING DILUTE CATALYST SOLUTIONS BY EVAPORATION

### Process Basis

| | |
|---|---|
| • Catalyst Feed: | 122.8 k lb/hr KOH (dry basis) |
| • Feed Concentration: | 5 wt% KOH or 10 wt% KOH |
| • Product Concentration: | 32.2 wt% KOH |
| • Available Steam: | Offsite boiler steam at 150 psig and/or onsite waste heat steam at 10-30 psig |

### Economic Basis

- CCG Study Design producing 257 GBtu/SD SNG
- 100% equity financing/15% DCF return

| | 5% KOH Feed | | 10% KOH Feed | |
|---|---|---|---|---|
| Evaporator Steam Basis | Evaporator Effects @ Steam Pressure, Psig | Incremental Gas Cost, $/MBtu SNG | Evaporator Effects @ Steam Pressure, Psig | Incremental Gas Cost, $/MBtu SNG |
| • All Offsite Boiler Steam | 5 @ 150 | 0.37-0.47 | 5 @ 150 | 0.17-0.22 |
| • "Unlimited" Waste Heat Steam | 2 @ 30 | 0.25-0.33 | 2 @ 30 | 0.11-0.14 |
| • "Limited" Waste Heat Steam (Limit set by 1977 CCG Study Design) | 4 @ 30<br>3 @ 10<br>5 @ 150 | 0.32-0.46 | 4 @ 30 | 0.12-0.19 |

A comparision of the results for the high-pressure (offsite boiler) steam and unlimited low-pressure steam cases shows that for both feed concentrations, the impact on gas cost is minimized by utilizing the onsite waste heat to raise the required low-pressure steam. However, evaluation of the Study Design heat balance indicates that there is not sufficient waste heat available to raise the low-pressure steam required to operate the evaporator at the optimum conditions. With this constraint, either more effects must be added to the evaporator to make it more thermally efficient or high-pressure steam must be used to fill the deficit. If more effects are added to the evaporator, less steam is required, but the incremental gas cost will increase due to high investment charges. If only a few effects are added, the incremental gas cost increases above the optimum, but is still less than that for all high-pressure steam. The last line in Table 5.1-4 summarizes the rough optimum cases using the low-pressure steam estimated to be available based on the CCG Study Design heat balance.

In the case of 5% KOH feed with limited steam, all available 30 psig steam is used in a four-effect evaporator to concentrate about 40% of the total feed. Additionally, the low-level waste heat which remains after raising the 30 psig steam is used to raise 10 psig steam. The 10 psig steam is used in a three-effect evaporator to concentrate about 30% of the feed. The remaining feed (30%) is concentrated in a five-effect evaporator with high-pressure steam. (The incremental gas cost of using all 10 psig steam is greater than the incremental gas cost of using a combination of 10 psig and 30 psig steam.) In the case of 10% (wt.) KOH feed, the solution can be evaporated to 32.2% (wt.) entirely with 30 psig steam in a four-effect evaporator.

The impacts of evaporating dilute catalyst solutions on the overall CCG process efficiency and gas cost are much less if the solution from catalyst recovery is 10% (wt.) KOH rather than 5% (wt.). For 10% (wt.) KOH solution, no supplemental offsite steam is required, and thus the impact on process efficiency is slight. The 10% (wt.) KOH case also shows a clear economic incentive over the 5% (wt.) case. The incremental gas cost for concentrating the 10% (wt.) solution to 32.2% (wt.) is 0.12-0.19 $/MBtu, only 2-3% of the CCG Study Design gas cost of 6.18 $/MBtu. However, evaporating more dilute solutions could have a significantly greater cost impact. The incremental gas cost for concentrating the 5% (wt.) solution is 0.32-0.46 $/MBtu. As discussed above, the use of dilute catalyst solutions will reduce the number of stages required for catalyst recovery. Studies will be conducted later in the program to find the optimum balance between evaporation costs and catalyst recovery costs.

### 5.1.4 Catalyst Recovery System Screening Studies

A series of engineering screening studies have begun to evaluate the economic impacts of alternative processing approaches and solid-liquid separation devices for catalyst recovery. The results of these studies will be used in selecting the most attractive alternatives for more detailed laboratory and engineering study later in the current program. These screening studies will assess the process and economic impacts of countercurrent water-washing of the char to recover the catalyst both with and without an initial calcium hydroxide digestion step. Filters, settlers, centrifuges, and hydroclones will be considered to carry out the solid-liquid separations between washing stages.

Work thus far has centered on establishing a representative process basis for the studies. Particular attention has been given to the catalyst reactions and material balance around the catalyst recycle loop and to the anticipated particle size distributions for the solids. The catalyst reactions are important in comparing the cases without digestion with those utilizing digestion. The particle size distributions are important in comparing cases utilizing different solid-liquid separation techniques.

The first case to be considered is countercurrent water-wash with digestion, using filters for the solid-liquid separations to produce a moderately concentrated catalyst solution (about 17% (wt.)). The feed rates of spent gasifier char and potassium catalyst to catalyst recovery are the same as in the CCG Study Design. The char feed consists of 68% coarse char withdrawn from the bottom of the gasifier and 32% fines collected in external cyclones.

In this first screening study, the char feed is slurried with semi-rich catalyst solution from the first water-wash stage and is digested at 300°F and 70 psia with a residence time of one hour. Here, lime is added to give a calcium/potassium ratio of 0.7 mole/mole. About 90% of the total potassium fed is solublized during digestion. The slurry from digestion is filtered to remove all of the solids. This clarified solution contains about 17% (wt.) potassium salts. The solids in the filter cake are sent to the countercurrent water-wash to recover the remaining solubilized catalyst.

In the countercurrent water-wash, the digested solids are repeatedly washed in slurry mixing vessels and filtered to recover 95% of the solubilized catalyst. Each countercurrent water-wash stage operates at atmospheric pressure and near the boiling point of the catalyst solution. The filters used between each washing stage remove 99% of the solids from the catalyst solution. The filter cake from each stage contains 70% moisture and 30% solids.

Future work on this first catalyst recovery screening study includes making a material balance for digestion and water-wash to determine the number of washing stages required to recover 95% of the soluble catalyst at the desired concentration. The Catalyst Recovery Material Balance Model described later in this report will be used to facilitate making the material balance. Equipment sizes and specification lists will be prepared based on the material balance, and the investment and operating costs for catalyst recovery with this basis will be estimated. These costs will be compared to those predicted for alternative processing approaches and other solid-liquid separation devices to select the most attractive alternatives for further study later in the program.

### 5.1.5 Two Stage Gasifier Incentive Study

In the Catalytic Coal Gasification Study Design, a simple fluidized bed gasifier with one gasification stage was used to achieve a target carbon conversion of 90%. A previous study done during the Predevelopment Phase of research investigated the use of a second gasification stage to increase overall carbon conversion to 95%. In this study, fines and char withdrawn from the first gasification stage were fed to the second gasification stage. The primary gasifier was operated the same as the gasifier in the study design and the secondary gasifier was operated in parallel at the same temperature. Steam and recycle gas from the preheat furnace were fed in parallel to each gasification stage. This process configuration showed only a small gas cost savings of about 0.6% relative to the single stage base case.

A brief incentive study of an alternative two-stage gasification concept has been completed. The two-stage gasifier process configuration selected for this study is illustrated in Figure 5.1-2. In this scheme, coal is fed to the first stage gasifier which operates at low temperature (1225°F). The coal is fluidized and gasified by product gas from the second stage gasifier. A carbon conversion of 80% is achieved in this first stage. The char and fines from the first stage are withdrawn and fed to the second-stage gasifier. This operates at a higher temperature (1325°F) to achieve high carbon conversions. Steam and recycle gas from the preheat furnace are fed to the secondary gasifier to achieve an overall carbon conversion of 95% for the two gasifier stages.

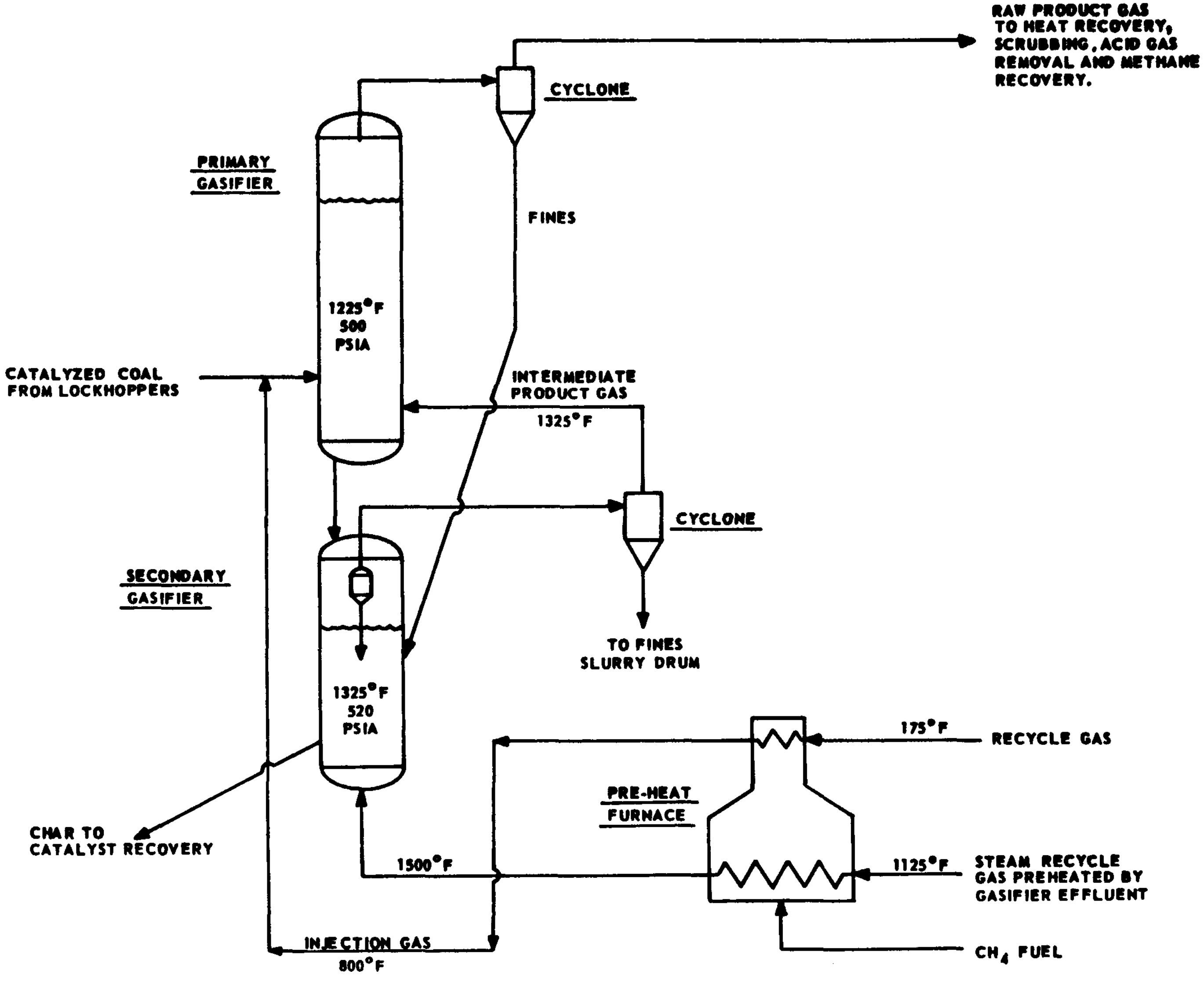
This concept differs from that evaluated in the predevelopment research phase in that the two gasification stages are operated in series with respect to steam and recycle gas flow. This permits operating the gasifiers at different temperatures. Reduced recycle gas rates are achieved by operating the upper stage at a lower temperature (1225°F) and high carbon conversions are obtained by operating the bottom stage at a higher temperature (1325°F).

A summary of the process basis and heat and material balance is provided in Table 5.1-5. The two-stage gasifier case was evaluated on the basis of the same coal feed rate to gasification as the CCG Study Design. Total gasifier steam required increased by 10% while the recycle gas rate decreased by 12%. Due to the lower temperature in the first-stage reactor, the preheat furnace coil outlet temperature decreased from 1543 to 1500°F. The net SNG product rate increased to 271 GBtu/SD (up 5.6%) while the overall plant efficiency increased by 3%.

Rough screening economics were developed for this two-stage gasification scheme. As shown in Table 5.1-6, total investments are up by 5% over the base case. This is a slightly smaller percentage increase than the increase in plant SNG output (5.6% increase). The most significant investment increase is associated with a larger first stage gasifier volume required for the lower reactor temperature (1225°F) than the base case and for the addition of the separate second stage gasifier. Also, steam generation investments are increased due to the increased steam requirements for this case.

FIGURE 5.1-2

## SIMPLIFIED FLOW PLAN FOR TWO STAGE GASIFICATION



79B-6-7-20

## Table 5.1-5

## INCENTIVE STUDY FOR TWO-STAGE GASIFICATION

| Reactor System | Base Case(1)<br>"Primary" Gasifier Only | Two-Stage Gasification<br>Primary and Secondary Gasifiers |
|---|---|---|
| Free Carbon Conversion | | |
| Primary Gasifier | 90% | 80% |
| Overall | 90% | 95% |
| Conditions: | | |
| Primary Gasifiers | 1275°F/500 psia | 1225°F/500 psia |
| Secondary Gasifier | - | 1325°F/520 psia |
| Key Stream Rates: | | |
| Coal Feed to Gasifier, ST/SD (2) | 14,490 | 14,490 |
| Coal to Boilers, ST/SD | 2,840 | 3,030 |
| Coal to Dryer Fuel, ST/SD | 710 | 710 |
| Total Coal, ST/SD | 18,040 | 18,230 |
| Total Gasifier Steam, MPH | 86,000 | 95,000 |
| Total Recycle Rate, MPH | 57,520 | 50,700 |
| Preheat Furnace Coil Outlet Temperature, °F | 1,543 | 1,500 |
| Net SNG Product Rate, GBtu/SD | 257.0 | 271.3 |
| Utilities Requirements: | | |
| Electric Power, MW | 147 | 151 |
| Raw Water, GPM | 7,300 | 7,300 |
| Overall Thermal Efficiency (3) | 62.6 | 65.7 |

---

Notes:

(1) Base case refers to CCG Study Design completed in the Predevelopment Program and documented in the Final Report FE-2369-24.

(2) Two-stage gasification evaluated on the basis of constant coal feed rate to gasification.

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

## Table 5.1-6

## TWO-STAGE GASIFICATION INCENTIVE STUDY RELATIVE INVESTMENT BREAKDOWN

Basis: Base Case Total Investment = 100

| | Base Case | Two-Stage Gasification |
|---|---|---|
| **Onsites** | | |
| Coal Drying/Catalyst Addition | 4.7 | 4.7 |
| Reactor System | 15.2 | 19.0 |
| Product Gas Cooling/Scrubbing | 6.5 | 6.2 |
| Sour $H_2O$ Stripping/$NH_3$ Recovery | 1.5 | 1.6 |
| Acid Gas Removal/Sulfur Recovery | 12.0 | 12.0 |
| Methane Recovery | 3.3 | 3.3 |
| Refrigeration | 2.3 | 2.4 |
| Catalyst Recovery | 3.0 | 2.9 |
| Common Facilities | 4.8 | 4.9 |
| Subtotal | 53.3 | 57.0 |
| **Offsites** | | |
| Utilities | 19.8 | 20.5 |
| Materials Handling | 8.9 | 9.0 |
| General Offsites | 7.2 | 7.2 |
| Offsites Subtotal | 35.9 | 36.7 |
| Process Development Allowance (25% of Onsite Direct & Indirect Cost) | 10.8 | 11.4 |
| Total Plant TEC | 100.0 | 105.1 |

Process economics are presented in Table 5.1-7. The total gas cost with two-stage gasification is 2.3% less than the Study Design gas cost. Savings are achieved in coal, catalyst, and operating costs. Thus, based on these results, there appears to be a small incentive for staged gasification. However, additional research and supporting engineering studies would be required to develop a better estimate of the incentive for two-stage gasification. Additional data are required to firm up reaction kinetics at the lower gasifier temperature of 1225°F and at carbon conversions over 90%. The current data base at these conditions is limited since the Fluid Bed Gasifier (FBG) runs made during the predevelopment research phase were generally at temperatures of 1300°F and carbon conversions of 80-90%. Additional data are also required to allow better prediction of the rate of fines entrained from the primary gasifier and the ability of the two-stage system to retain and gasify the fines. Data on lower gasification temperatures, higher carbon conversions and fines generation will be obtained as part of the current Process Development Program. This data can then be used for a more definitive estimate of the incentive for a two-stage gasification system.

### 5.1.6 CCG Char Properties

Data on solids properties for the catalytic gasifier are needed as input information for Activity A of Subtask 4.4, Catalytic Gasifier Solids Balance Model. Such data is also needed as input information for the CCG Gasifier Reactor Model. A brief study to summarize solids properties data from Fluid Bed Gasifier (FBG) operations during the predevelopment research phase has been completed. This data will be used to start work on the Gasifier Solids Balance Model since solids properties data from the PDU are not yet available.

Composition and physical property data has been summarized for the feed coal, overhead fines, mid char and bottoms withdrawal char. Estimates have been made of solids composition, and physical properties such as particle size distribution and density. This information will enable scoping studies and development of calculational procedures leading to the development of a Catalytic Gasifier Solids Balance Model. However, when data is available from the 1 T/D Process Development Unit, this will be used for definitive development of the Solids Balance Model and for input to the gasifier kinetics-contacting model.

### 5.1.7 Integral Steam Reformer Heat Input Study

A key feature of the Exxon Catalytic Coal Gasification process is the recycle of CO and $H_2$ to the gasifier. This forces the net products of gasification to be only $CH_4$ and $CO_2$ along with smaller amounts of $H_2S$ and $NH_3$. Using this approach, the overall chemistry can be represented as follows:

$$\text{Coal} + H_2O \rightarrow CH_4 + CO_2 \qquad \Delta H \simeq 0$$

## Table 5.1-7

## Two-Stage Gasification Incentive Study
## Summary of Relative Gas Cost

Basis: Base Case Total Gas Cost = 100

| Gas Cost Components | Base Case | Two Stage Gasification |
|---|---|---|
| Coal to Gasifiers | 17.6 | 16.6 |
| Coal to Dryer Fuel | 0.9 | 0.8 |
| Coal to Offsite Boilers | 3.4 | 3.5 |
| Subtotal | 21.9 | 20.9 |
| Major Chemicals | | |
| KOH Solution (30 wt %) | 3.4 | 3.2 |
| Lime (97% CaO) | 2.4 | 2.2 |
| Subtotal | 5.8 | 5.4 |
| Other Operating Costs | | |
| Purchased Electric Power | 5.3 | 5.2 |
| Raw Water | 0.1 | 0.1 |
| Other Catalysts & Chemicals | 1.1 | 1.0 |
| Wages and Benefits | 4.0 | 3.9 |
| Salaries and Benefits | 1.3 | 1.2 |
| Labor Related Operating Costs | 1.0 | 1.0 |
| Investment Related Op. Costs | 10.0 | 9.8 |
| Ash Disposal | 0.4 | 0.4 |
| Subtotal | 23.2 | 22.6 |
| By-Products Credits | (2.9) | (2.9) |
| Capital Charges (1) | 52.0 | 51.7 |
| Relative Gas Cost, %/MBtu | 100.0 | 97.7 |
| Gas Cost Savings, % | | 2.3 |

---

**Note:**

(1) Capital charges based on 100% equity financing with 15% DCF return.

Thus, coal is converted to methane in a single reaction step which is approximately thermally neutral. A small amount of heat input is required to preheat the feed coal, recycle gas, and steam to reaction temperature, to account for catalyst reactions, and to provide for gasifier heat losses.

In the 1977 CCG Study Design, this heat input was supplied by heating the steam and recycle gas in a furnace to 1540°F. This preheat is sufficient to provide for the heat input requirements listed above. The preheat furnace design temperature was set at 1575°F to allow for operating flexibility and control. A schematic flow plan for this system is shown in Figure 5.1-3.

During previous work, the concept of using a steam reformer for heat input was identified. In this concept, a small amount of methane is reformed to make additional CO and $H_2$ for feed to the gasifier. This CO and $H_2$ forms methane in the gasifier, thus providing both chemical and sensible heat input. The use of a reformer provides greater flexibility than the base case heat input scheme which uses only sensible heat for heat input. The reformer could be either a small reformer operating in parallel with the preheat furnace, or the reformer could replace the preheat furnace by reforming methane already present in the recycle gas. This last alternative, called an Integral Steam Reformer, was shown by previous rough screening studies to be lower in cost than a parallel reformer but was an economic standoff with the base case utilizing a preheat furnace.

A study was initiated during February to consider the Integral Steam Reformer in greater depth. A schematic flow plan for this system is also shown in Figure 5.1-3. Several alternative processing conditions have been evaluated including a range of steam reformer coil outlet temperatures and steam conversions. The CCG reactor system material and energy balance model was modified to incorporate the steam reforming process option. Initial study results for reformer coil outlet temperature and steam conversion are summarized below.

- Reformer Coil Outlet Temperature - Steam reformer coil outlet temperatures (COT) from 1400°F to 1500°F have been evaluated. A comparison of the cases is shown below:

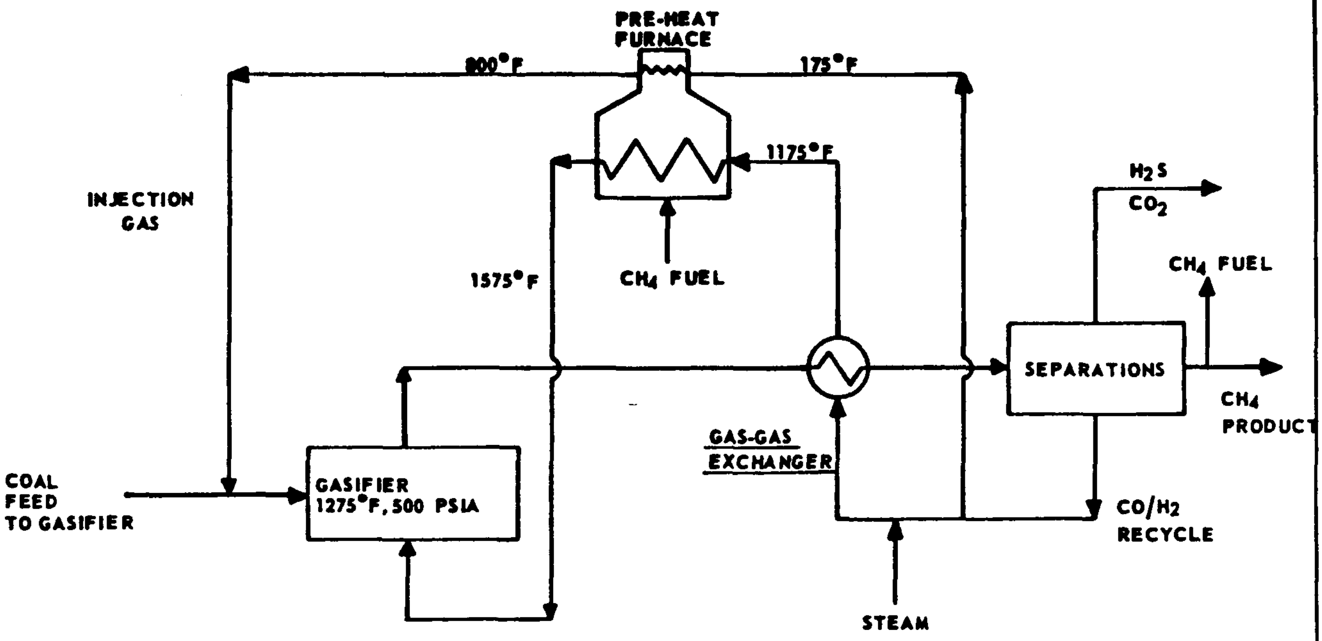
Basis: 14,490 ST/SD Coal feed to gasifier
Gasifier operating conditions of 1275°F, 500 psia.

| Coil Outlet Temperature | 1400°F | 1500°F |
|---|---|---|
| Recycle Gas Rate, lb moles/hr | 66,300 | 53,100 |
| Raw Gasifier Product Rate, lb moles/hr | 181,600 | 152,800 |
| Acid Gas Removal Feed, lb moles/hr | 127,000 | 105,800 |
| Overall Steam Conversion, % | 39 | 42 |
| Offsite Steam Required, lb moles/hr | 64,400 | 55,700 |
| Relative Gasifier Volume | 100 | 95.4 |
| Reformer Furnace Fuel Fired, MBtu/hr | 680 | 630 |
| Net Methane Product, GBtu/SD | 252.1 | 254.8 |

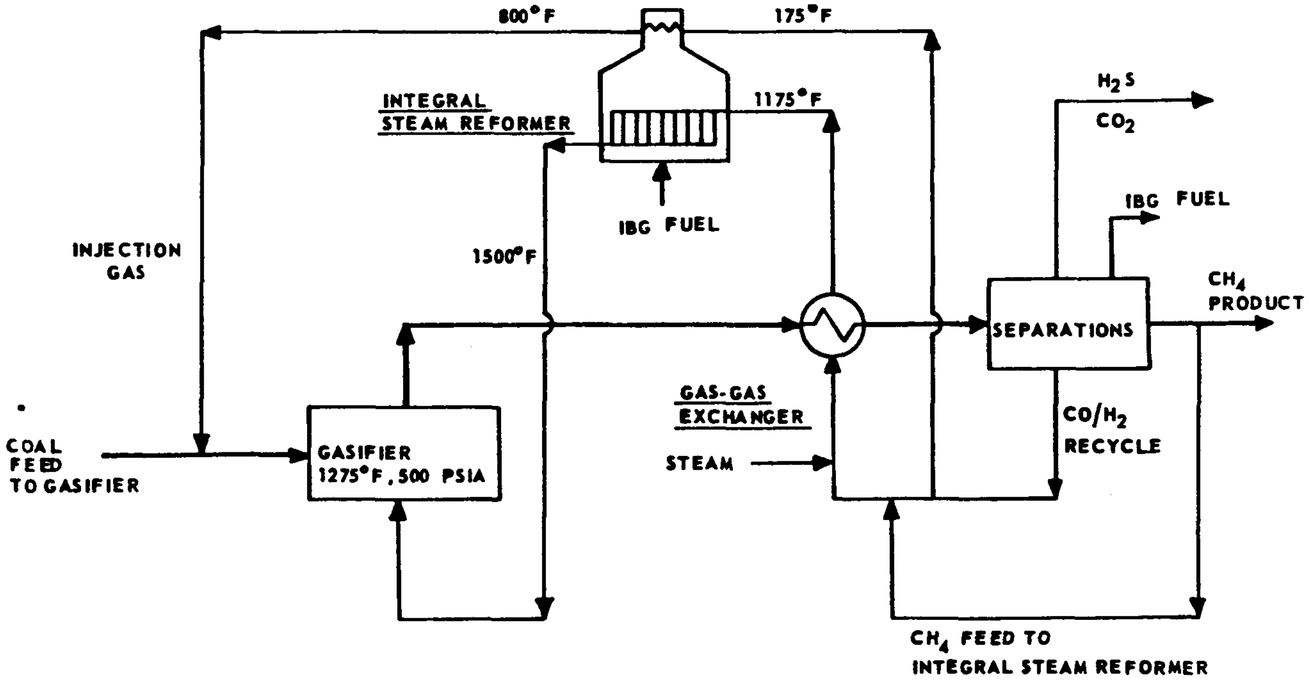
# FIGURE 5.1-3

## INTEGRAL STEAM REFORMING HEAT INPUT STUDIES - SIMPLIFIED SCHEMATIC FLOW PLAN

CCG STUDY DESIGN



INTEGRAL STEAM REFORMING CASE



The credits for higher temperature include reduced gas flow rates, reduced steam requirements, reduced furnace duty, etc. The debit for the higher temperature will be a higher furnace investment. It is believed that the credits of higher reformer outlet temperature offset the debits.

- Steam Conversion - A range of overall steam conversions from 41 to 50% was evaluated. These results are shown below:

Basis: 14,490 ST/SD Coal feed to gasifier,
Gasifier operating conditions of 1275°F, 500 psia, and
steam reformer coil outlet temperature of 1450°F.

| Overall Steam Conversion, % | 41 | 47 | 50 |
|---|---|---|---|
| Recycle Gas Rate, lb moles/hr | 59,200 | 53,700 | 51,300 |
| Gasifier Product Rate, lb moles/hr | 163,200 | 148,000 | 141,400 |
| Acid Gas Removal Feed, lb moles/hr | 113,500 | 109,600 | 108,100 |
| Offsite Steam Required, lb moles/hr | 58,600 | 48,400 | 44,000 |
| Reformer Furnace Fuel Fired, MBtu/hr | 650 | 630 | 620 |
| Relative Gasifier Volume | 100 | 130 | 160 |
| Net Methane Product, GBtu/SD | 253.7 | 254.0 | 254.1 |

The credits for higher steam conversion include reduced gas flow rates, reduced steam requirements, reduced furnace duty, etc. The debit for the higher steam conversion will be higher gasifier investment. It is believed that the 47% steam conversion case represents the optimum balance.

The high steam reformer coil outlet temperature (1500°F) and high steam conversion (47%) process conditions were selected as the basis for evaluating additional process options. Two additional cases were evaluated. First, a lower heating value fuel was evaluated in place of methane product as the fuel for steam reforming. The stream selected was the gasifier product stream downstream of $H_2S$ removal. This stream contained a mixture of CO, $H_2$, $CH_4$, and $CO_2$ and had a heating value (HHV) of about 500 Btu/SCF. The objective of using this lower heating value stream is to achieve investment and operating cost savings by reducing the feed rate to the $CO_2$ removal and cryogenic methane separation sections of the CCG process and by increasing the nitrogen purge from the recycle gas loop.

The second option was to use this same stream (gasifier product downstream of $H_2S$ removal) as direct feed to steam reforming. This would be used to control gasifier heat input in place of the methane product used in the base steam reformer case. This also offers potential cost reductions in the $CO_2$ removal and cryogenic methane separation sections. The results of these process options studies are summarized below. All cases were run at a reformer coil outlet temperature of 1500°F and 48% steam conversion.

|  | Case 1<br>Base | Case 2<br>Lower Heating Value Fuel | Case 3<br>Syn Gas As Reformer Feed |
|---|---|---|---|
| Fuel | $CH_4$ | $CO/CH_4/H_2/CO_2$ | $CO/CH_4/H_2/CO_2$ |
| Reformer Heat Input Control | $CH_4$ | $CH_4$ | $CO/CH_4/H_2/CO_2$ |
| Recycle Gas Rate, lb moles/hr | 50,900 | 46,200 | 44,700 |
| Raw Gasifier Product Rate, lb moles/hr | 140,400 | 138,000 | 139,400 |
| Acid Gas Removal Feed, lb moles/hr | 103,800 | 101,400 | 102,300 |
| Methane Recovery Feed, lb moles/hr | 80,700 | 75,000 | 72,300 |
| Reformer Furnace Duty, MBtu/Hr | 620 | 660 | 660 |
| Relative Gasifier Volume | 100.0 | 97.0 | 98.6 |
| Net Methane Product, GBtu/SD | 254.7 | 254.6 | 254.7 |

As shown above, there is little difference in the material balances among the cases. Screening economics develped for these alternatives showed a small economic advantage (4 ¢/MBtu) for Cases 2 and 3 over Case 1. Case 2 was selected as the process basis for the Integral Steam Reformer Study. Economic advantage is gained by using product from $H_2S$ removal as fuel. However, the use of this stream for supplemental reformer feed would result in the risk of $H_2S$ poisoning of the reformer catalyst during process upsets. Thus product methane will be used for gasifier heat input control.

During the process variable studies described above, the potential for carbon formation and laydown on the steam reforming catalyst or upstream equipment has been identified as a key data need for the integral steam reformer system. Carbon laydown could result in reformer catalyst deactivation or in a severe corrosion phenomenon known as "metal dusting". This is not a serious problem for the preheat furnace used in the CCG Study Design because the injection of small amounts of a sulfur compound into the gas stream can prevent carbon laydown. This cannot be done if an integral reformer is used because the sulfur would poison the reformer catalyst.

Carbon can be formed from one of the following reactions:

$$2CO \rightarrow CO_2 + C$$

$$CO + H_2 \rightarrow H_2O + C$$

$$CH_4 \rightarrow 2H_2 + C$$

Figure 5.1-4 shows the equilibrium curves which define the carbon formation region for C-H-O atomic compositions at 1000°F and 1500°F at 520 psia. The composition of the reformer feed stream on this basis is: carbon 4 mole %, hydrogen 69 mole %, and oxygen 27 mole %. This point is shown on Figure 5.1-4 and is clearly out of the carbon formation region. Thus, with the high steam to carbon ratios for the integral reformer process conditions, equilibrium conditions are <u>not</u> favorable for carbon formation. However, the feed to the integral reformer is not in chemical equilibrium. Thus, it is possible that a nonequilibrium situation may exist in which carbon is laid down, for instance by the reaction $2CO \rightarrow CO_2 + C$, at a rate faster than it can be gasified away by the steam-carbon reaction, $C + H_2O \rightarrow CO_2 + H_2$. Thus, though solid carbon cannot be present at equilibrium, it is possible that it could exist during the time the species are reacting to reach equilibrium. Thus, kinetics of the competing reactions could be important.

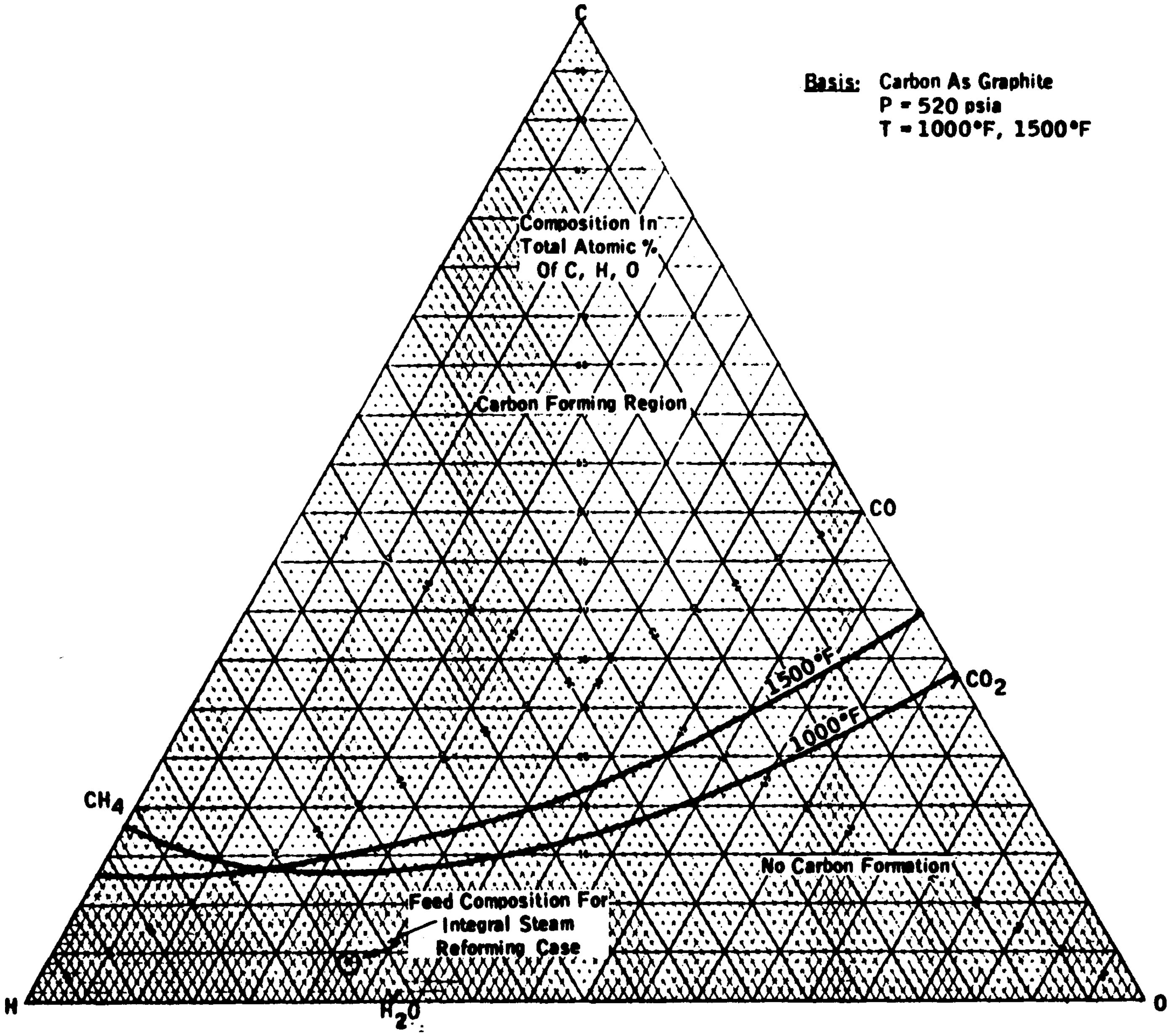
Recent data from bench-scale research on Gas Phase Reactions (see Section 1.3 of this report) have shown that carbon laydown can occur in a gas stream with compositions similar to those envisioned commercially for integral reformer feed. However, this research was directed at studies of the shift reaction, and conditions were not commercially representative for carbon laydown in terms of residence times, wall effects, etc. These factors can affect the kinetics of the competing reactions. More representative experiments directed at the issue of carbon laydown are planned as part of the Engineering Technology Study under Activity I, Preheat Furnace Tube Selection. These experiments will address the issue of carbon formation and, if necessary, explore ways to avoid it. One potential way which has been identified to avoid carbon laydown is to alter the gas composition by increasing the $CO_2/CO$ ratio.

The process basis for the Integral Steam Reformer Heat Input Study is now complete. The design of the steam reformer furnace has been initiated. The furnace will then be cost estimated and utilities and operating costs will be developed. Investments for other plant sections will be prorated from the CCG Study Design and overall economics for Integral Steam Reforming will be developed. This study is expected to be completed during the third quarter of 1979.

### 5.1.8 Cryogenic Acid Gas Removal Incentive Study

An engineering screening study has been completed which evaluated the economic incentives for using a cryogenic fractionation scheme for acid gas removal in the Exxon Catalytic Coal Gasification Process. This study included the definition of the process flow scheme, detailed material and energy balances, design of the required equipment, and development of investment, operating costs and economics for this process concept.

## FIGURE 5.1-4
## CARBON FORMATION EQUILIBRIUM ISOTHERMS



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Previous work done under the CCG Predevelopment Contract led to the conclusion that carbon dioxide ($CO_2$) freeze-out would occur in some part of the acid gas fractionation system over the entire range of possible tower operating conditions. For the current study, it was assumed that the freeze-out problem could be handled in a simple manner within the system. Further work to determine the actual effect of $CO_2$ freeze-out would be necessary to determine the actual technical feasibility of the proposed scheme.

A simplified block flow diagram of the Cryogenic Acid Gas Removal (AGR) Scheme is presented in Figure 5.1-5. The scheme incorporates two new distillation towers. In the first tower, the Acid Gas Fractionator (AGF), $CO_2$ and $H_2S$ are separated from an overhead $H_2$, CO, and $CH_4$ stream. The overhead stream is then fed to cryogenic Methane Recovery. The bottoms $CO_2$ and $H_2S$ stream from the Acid Gas Fractionator is fed to the second tower, the Acid Gas Splitter (AGS), where the overhead is essentially pure $CO_2$ and the bottoms is an 80/20 mixture of $CO_2/H_2S$. This bottoms stream is then sent to sulfur recovery. A flow plan showing process operating conditions and major equipment is presented in Figure 5.1-6.

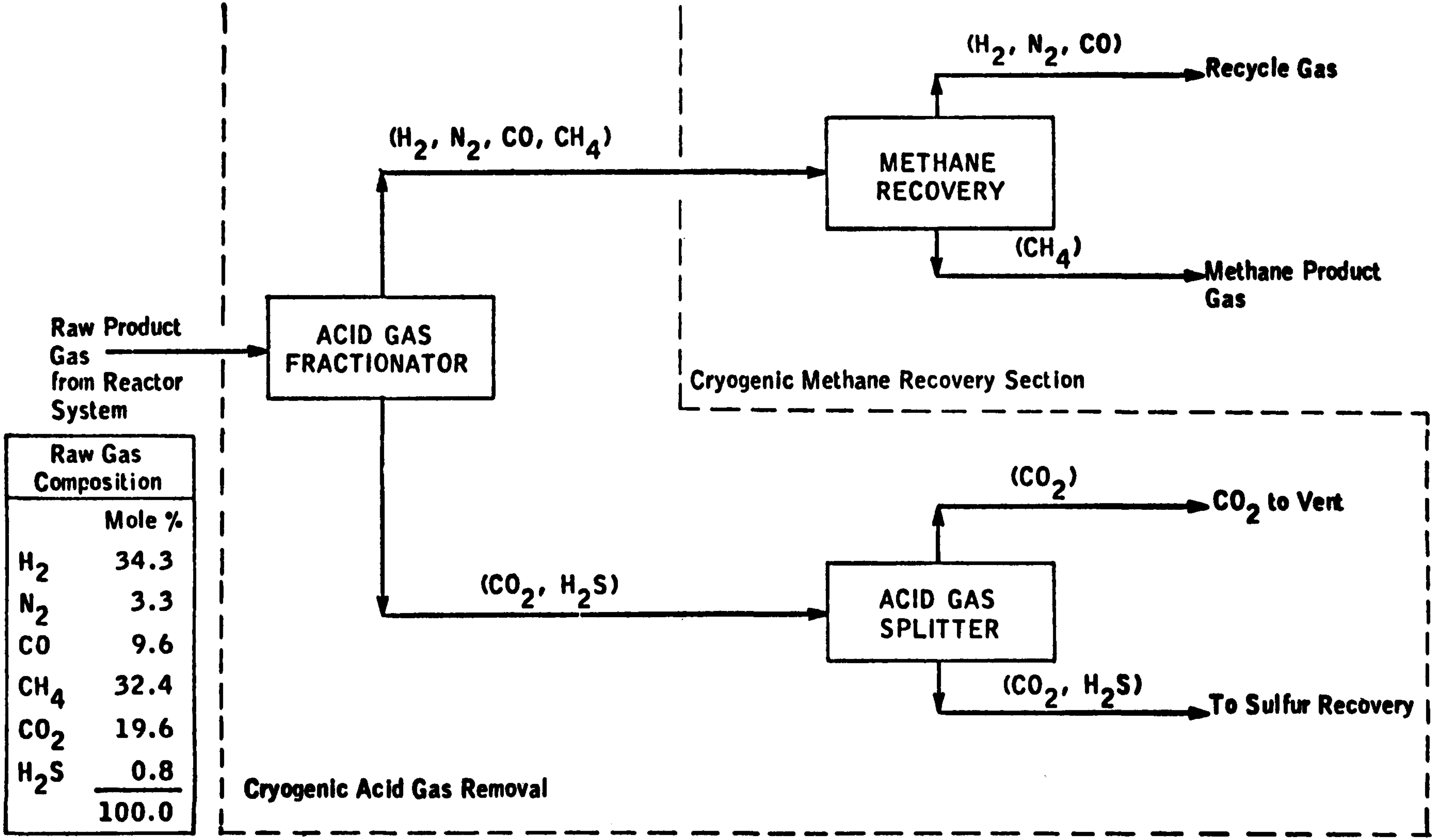
During the study, various process conditions, flow schemes, and heat integration/refrigeration options were investigated. The alternatives were compared on the basis of minimizing total system horsepower requirements. This is believed to be the major investment and operating cost parameter in cryogenic systems. The design bases for the three towers involved in the study are described below.

In the Acid Gas Fractionator, an overhead $CO_2$ concentration of 150 vppm was specified to eliminate the need for molecular sieve adsorption for $CO_2$ removal upstream of methane recovery. The AGF bottoms specification was set to limit methane losses to 0.1% of the methane fed to the tower. This low level of methane losses is relatively easily achieved and compares to methane losses of about 1% for the heavy glycol solvent absorption system used in the CCG Study Design. The reduced methane losses result in a higher product SNG rate for the cryogenic acid gas removal case compared to the Study Design. Alternative AGF operating pressures were evaluated. High pressure is desirable to increase tower operating temperatures which might minimize the impact of $CO_2$ freeze-out. Pressures of 1000 psia and 850 psia were evaluated and the lower pressure level provided about a 7% savings in feed/product compression and refrigeration power requirements. AGF feed temperatures between -60°F and -140°F were evaluated and the minimum power requirements were obtained at a feed temperature of about -115°F. This produced a 17% savings versus a feed temperature of -60°F.

The Acid Gas Splitter (AGS) separates a $CO_2$ overhead product from an 80% $CO_2$/20% $H_2S$ bottoms product. After energy and refrigeration recovery, the $CO_2$ stream is vented to the atmosphere. An overhead $H_2S$ concentration of 10 vppm in the $CO_2$ vent stream was specified, consistent with the Study Design. The $H_2S$ containing bottoms product is fed to a Claus Plant for sulfur recovery. The AGS operating conditions selected enable use of a heat pump loop with propylene refrigerant for both the condenser and reboiler duties. The specification of a lower $CO_2$ level

FIGURE 5.1-5

CRYOGENIC ACID GAS REMOVAL FLOW SCHEME



Raw Gas Composition

| | Mole % |
|---|---|
| $H_2$ | 34.3 |
| $N_2$ | 3.3 |
| CO | 9.6 |
| $CH_4$ | 32.4 |
| $CO_2$ | 19.6 |
| $H_2S$ | 0.8 |
| | 100.0 |

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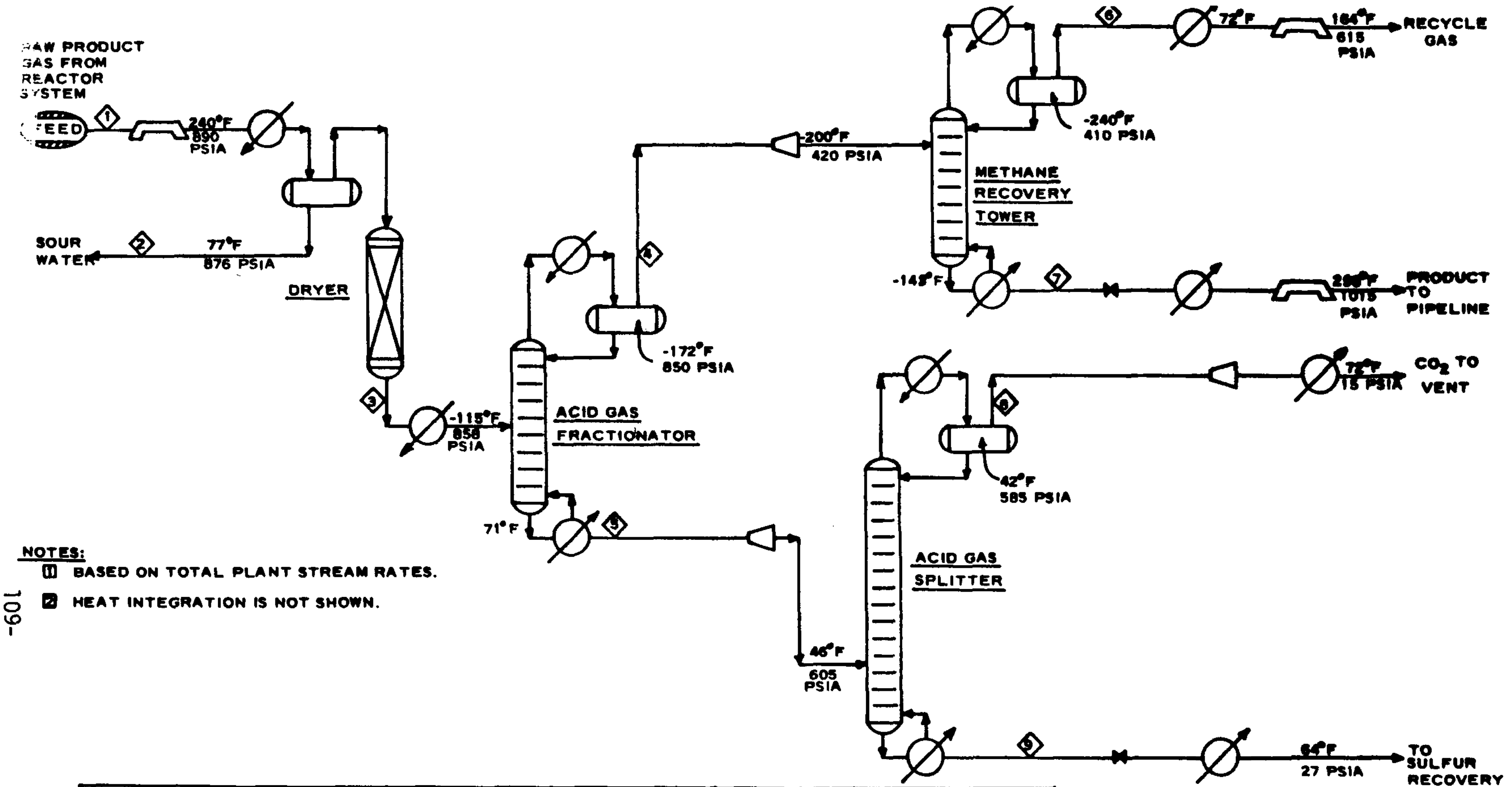

NOTES:

1. BASED ON TOTAL PLANT STREAM RATES.
2. HEAT INTEGRATION IS NOT SHOWN.

| STREAM NUMBER | ① | ② | ③ | ④ | ⑤ | ⑥ | ⑦ | ⑧ | ⑨ |
|---|---|---|---|---|---|---|---|---|---|
| PRESSURE (PSIA) | 450 | 876 | 866 | 850 | 865 | 410 | 420 | 585 | 606 |
| TEMPERATURE (°F) | 100 | 77 | 77 | -172 | 72 | -240 | -143 | 43 | 53 |
| FLOWRATES, MPH(1) | | | | | | | | | |
| CO | 10510 | | 10510 | 10510 | | 10480 | 30 | | |
| $CO_2$ | 21633 | | 21633 | 13 | 21620 | | 13 | 18106 | 3514 |
| $H_2$ | 37671 | | 37671 | 37671 | | 37671 | | | |
| $H_2O$ | 233 | 175 | | | | | | | |
| $CH_4$ | 35657 | | 35657 | 35635 | 22 | 5750 | 29885 | 22 | |
| $C_2H_6$ | 5 | | 5 | | 5 | | | 4 | 1 |
| $H_2S$ | 878 | | 878 | | 878 | | | | 878 |
| COS | 14 | | 14 | | 14 | | | | 14 |
| $N_2$ | 3585 | | 3585 | 3585 | | 3585 | | | |
| TOTAL | 110,186 | 175 | 109,953 | 87414 | 22539 | 57486 | 29928 | 18132 | 4407 |

Figure 5.1-6
SIMPLIFIED FLOW PLAN (2)
CRYOGENIC ACID GAS REMOVAL
AND METHANE RECOVERY

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in the AGS bottoms would require additional stages and/or reboiler duty and would raise the bottoms temperature. This would significantly increase power requirements in the propylene heat pump loop. Cost savings in the Claus plant would be unlikely to offset these debits.

In the Methane Recovery Tower (MRT), a $CO/H_2$ overhead stream is separated from the $CH_4$ bottoms product. The tower specifications are consistent with the Study Design (0.1% CO in product methane, 10% $CH_4$ in the recycle gas). The MRT feed from the AGF overhead is cooled and flashed to 420 psia (the same as in the Study Design). Tower feed temperatures from -198°F to -240°F were evaluated, and -200°F was chosen as the basis. At this condition, expanding the bottoms product provides the entire MRT condenser and feed cooling duty. This stream is also used to help cool the AGF feed.

An effort was made during the study to optimize the heat integration/ refrigeration scheme for the process. The final scheme, as shown in Figure 5.1-7, consists of the following:

- An external three-level cascade refrigeration system utilizing methane, ethylene and propylene refrigerants provides both the Acid Gas Fractionator condenser duty (-172°F process temperature) and a portion of the feed cooling duty.
- A single heat pump loop of propylene refrigerant accomplishes both the condenser and reboiler duty for the Acid Gas Splitter.
- The overhead stream from the Methane Recovery Tower (MRT) is used to subcool the methane bottoms product. This bottoms stream is then adiabatically expanded to provide the refrigeration requirements for the condenser (-240°F process temperature) and feed cooling of the MRT.
- The remainder of the Acid Gas Fractionator feed cooling is accomplished by feed/effluent heat exchange with the methane product, recycle gas, and $CO_2$ vent gas.

The utility requirements developed for this system are presented below:

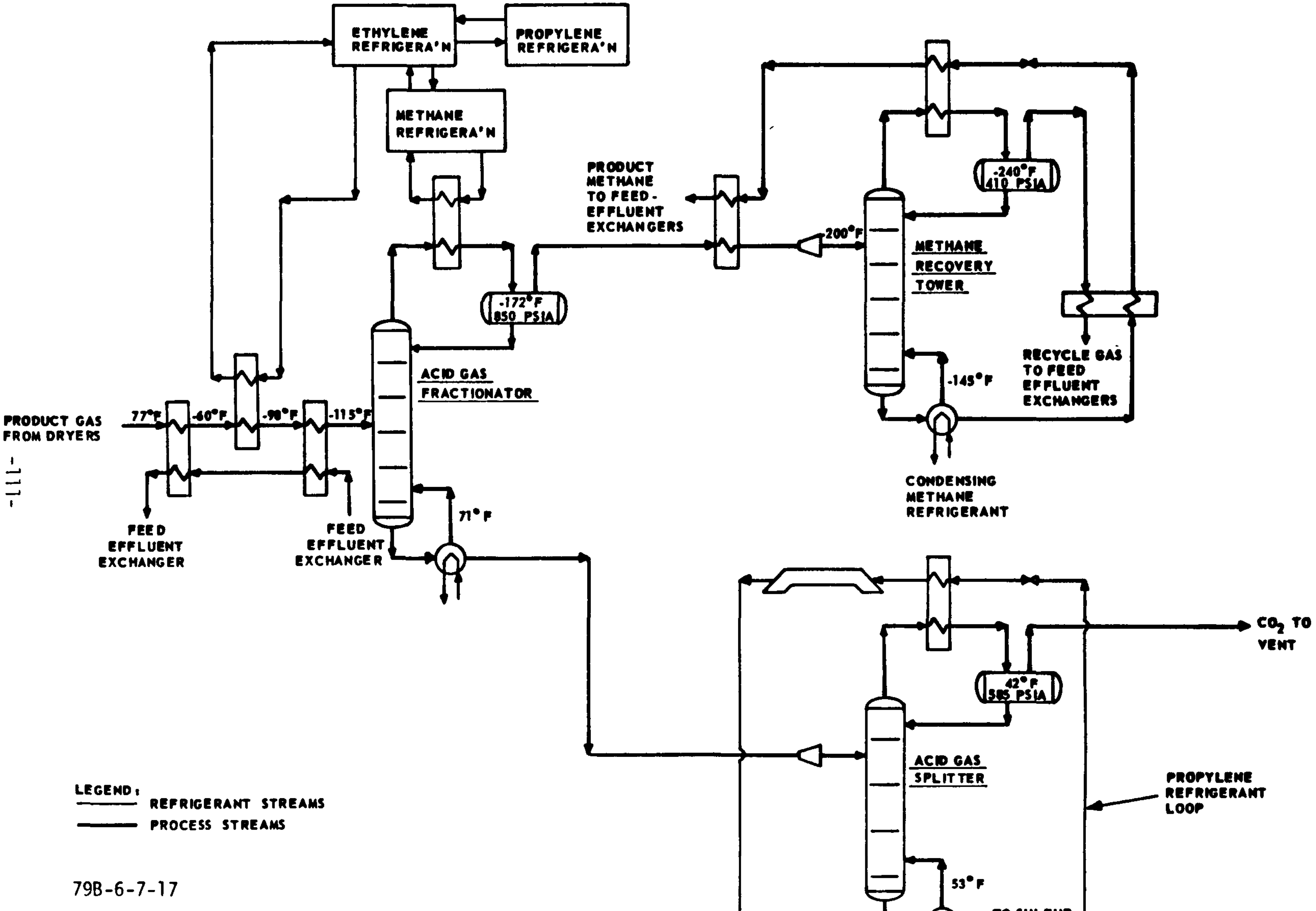
Utility Requirements

| | CCG Study Design | Cryogenic Acid Gas Case |
|---|---|---|
| Brake Horsepower | 194,000 | 267,000(1) |
| AGR Steam (65 psig), klb/hr | 415 | - |
| Total Cooling Water, kgpm | 79 | 59 |

Note: (1) Includes 21,000 HP credit for expanders.

## FIGURE 5.1-7

## CRYOGENIC ACID GAS REMOVAL REFRIGERATION AND HEAT INTEGRATION FLOW SCHEME



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The total brake horsepower requirement for the new system is 38% greater than for the CCG Study Design. Steam requirements for the Acid Gas Removal Section have been completely eliminated in the new scheme, and total plant cooling water requirements have been reduced 25%.

A breakdown of the investment for the Cryogenic Acid Gas Removal Case compared to the Study Design is presented in Table 5.1-8. The investment for the cryogenic acid gas removal section is 59 M$ lower than the Study Design investment for heavy glycol acid gas removal. Investment savings in sulfur recovery, methane recovery and other onsites are balanced by increased investment for refrigeration. The offsite investment in water and steam systems is reduced by 10 M$ because of reduced steam requirements. This is somewhat offset by a 5 M$ investment increase for electric power distribution because of the larger power requirement. Overall, the investment for the cryogenic acid gas removal case is reduced by 100 M$ compared to the Study Design.

A breakdown of the gas cost for the Cryogenic Acid Gas Removal Case is presented in Table 5.1-9. A summary of the gas cost for the new case as compared to the Study Design is shown below:

Gas Cost Summary

| | CCG Study Design | Cryo. Acid Gas |
|---|---|---|
| Coal Feed to Gasifier | 14,490 ST/SD | 14,490 ST/SD |
| Net SNG Product | 257 GBtu/SD | 261 GBtu/SD |
| Plant Investment | 1,530 M$ | 1,430 M$ |
| SNG Cost Components | ---------Gas Cost, | $/MBtu--------- |
| Illinois No. 6 Coal | 1.41 | 1.37 |
| Major Chemicals | 0.41 | 0.40 |
| Utilities | 0.35 | 0.51 |
| Other Operating Costs | 1.08 | 1.01 |
| By-Product Revenues | (0.18) | (0.17) |
| Capital Charges (15% DCF Return) | 3.11 | 2.86 |
| Total SNG Gas Cost (RISP) | 6.18 | 5.98 |
| Savings | | 3.2% |

The total gas cost with cryogenic acid gas removal is 3.2% less than the Study Design gas cost. The debit caused by increased power requirements is more than offset by savings from increased net SNG product and lower capital charges associated with the net reduced investment. However, recent studies by Air Products and Chemicals, Inc., under contract to DOE, have concluded that the selective (two-stage) heavy glycol solvent absorption process specified for the CCG Study Design can be optimized for use with the CCG process. Their results indicate that the gas cost for the optimized system can be reduced by about 1-2% versus the configuration used in the CCG

## TABLE 5.1-8

## CATALYTIC COAL GASIFICATION
## CRYOGENIC ACID GAS REMOVAL STUDY

## INVESTMENTS

**Basis:** ● **Same Coal Feed to Gasifier (14,490 ST/SD) as CCG Study Design**

| Plant Section | Study Design Base Case (M$) | Cryo. Acid Gas Case (M$) | Change (M$) |
|---|---|---|---|
| Onsites | | | |
| Acid Gas Removal | 140 | 81 | (59) |
| Sulfur Recovery | 22 | 19 | ( 3) |
| Methane Recovery | 44 | 41 | ( 3) |
| Refrigeration | 31 | 38 | 7 |
| Other Onsites | 442 | 439 | ( 3) |
| Onsites Subtotal | 679 | 618 | (61) |
| Offsites | | | |
| Water Systems | 38 | 35 | ( 3) |
| Steam Systems | 171 | 164 | ( 7) |
| Electric Power Distribution | 23 | 28 | 5 |
| Other Offsites | 179 | 179 | - |
| Offsites Subtotal | 411 | 406 | ( 5) |
| Total Direct and Indirect Costs | 1,090 | 1,024 | (66) |
| Process Development Allowance | 169 | 153 | (16) |
| Project Contingency | 271 | 253 | (18) |
| TOTAL ERECTED COST | 1,530 | 1,430 | (100) |

## TABLE 5.1 - 9

## GAS COST SUMMARY
## CRYOGENIC ACID GAS REMOVAL INCENTIVE STUDY

Basis:
- January, 1978 Instant Plant, Eastern Illinois Location
- 261 Billion Btu/Stream Day SNG (HHV Basis)
- 90% Capacity Factor
- 100% Equity Financing
- 15% Current Dollar DCF Return
- Escalation Rates:
  - Operating Costs and By-Product Revenues at 5%/Year
- Total Erected Cost of 1430 M$

| SNG Cost Components | Requirements (At Full Capacity) | Unit Costs (1978) | SNG Cost Breakdown $/Million Btu (1978) |
|---|---|---|---|
| • Illinois No. 6 Coal (Cleaned) | | | |
| - To Gasifiers | 14,490 ST/SD(2) | 20$/ST | 1.111 |
| - To Coal Dryer Fuel | 705 ST/SD | 20$/ST | 0.054 |
| - To Offsites Boiler Fuel | 2,660 ST/SD | 20$/ST | 0.205 |
| Subtotal | 17,855 ST/SD | | 1.370 |
| • Major Chemicals | | | |
| - KOH Solution (30 wt%) | 189 ST/SD (Contained) | 300$/ST | 0.217 |
| - Lime (97% CaO) | | | |
| + To Catalyst Recovery | 1,005 ST/SD | 39$/ST | 0.151 |
| + To Flue Gas Desulfurization | 249 ST/SD | 39$/ST | 0.037 |
| Subtotal | | | 0.405 |
| • Other Operating Costs | | | |
| - Purchased Electric Power | 219 MW | 2.5 ¢/kWh | 0.504 |
| - Raw Water | 5,400 gpm | 15¢/kGal | 0.004 |
| - Other Catalysts and Chemicals | Many Items | 5.4 M$/yr | 0.065 |
| - Wages and Benefits | 935 Men | 21 k$/man/yr | 0.228 |
| - Salaries and Benefits | 250 Men | 25 k$/man/yr | 0.072 |
| - Labor Overheads and Supplies | 20% of Wages, Salaries and Benefits | | 0.060 |
| - Materials and Overheads | 3.3% of Total Erected Cost/Year | | 0.551 |
| - Waste Solids Disposal | 8,391 ST/SD | 1$/ST | 0.032 |
| Subtotal | | | 1.516 |
| • By-Product Revenues | | | |
| - Ammonia (20 wt%) | 231 ST/SD (Contained) | 160 $/ST | (0.142) |
| - Sulfur | 324 LT/SD (2) | 25 $/LT | (0.030) |
| Subtotal | | | (0.172) |
| • Capital Charges | | | 2.858 |
| TOTAL SUBSTITUTE NATURAL GAS COST (RISP) (3) | | | 5.977 |
| CALL | | | 5.98 |

---

Notes:

(1) k = $10^3$, M = $10^6$, G = $10^9$.

(2) ST/SD = short tons/stream day (i.e. one day's operation at full plant capacity). LT = long tons.

(3) Required initial selling price in first year of plant operation.

Study Design. Thus the actual incentive for cryogenic acid gas removal as defined in this study is a gas cost savings of only 1-2%. This incentive is small relative to the likely problems in handling $CO_2$ freeze-out. Optimization of the cryogenic acid gas removal system could reduce its cost but would make it more difficult to deal with $CO_2$ freeze-out. Thus, there is little incentive for research on the cryogenic acid gas removal system as defined by this study.

### 5.1.9 Incentive Study for Removing Methane from Recycle Gas

A brief screening study was carried out to determine whether there is an incentive for reducing the methane content of the gas stream recycled to the catalytic gasifier. In the CCG Study Design the recycle gas contained 10 mole % methane. This was thought to be the lowest methane content in the recycle gas that could be practically achieved with a cascade refrigeration system consisting of propylene, ethylene, and methane loops. Lower methane content would require lower temperatures and the addition of a nitrogen refrigerant loop to the cascade.

The effect of removing methane from the recycle gas was simulated using a material and energy balance program for catalytic coal gasification. The process basis and conditions were identical to the CCG Study Design except for the removal of all the methane from the recycle gas stream. The design changes required in the cryogenic methane recovery system were not evaluated at this time. The key differences between the "no methane in recycle gas" case and the CCG Study Design are listed in Table 5.1-10 and summarized below:

- Total recycle gas rate reduced by 17%.
- Raw gasifier effluent gas rate reduced by 8%.
- Feed to methane recovery tower reduced by 11%.
- Preheat furnace fuel fired down by 6%.
- Overall net methane product increased by 0.2%.
- Offsite steam requirement reduced by 6.8%.
- Feed to acid gas removal reduced by 9%.
- Gasifier volume reduced by 4%.

Although the preheat furnace duty requirement to heat balance the gasifier was lower in the "no methane in recycle gas" case, the furnace coil outlet temperature was calculated to be 32°F higher. This is due to the steam/recycle gas rate being about 10% lower than in the Study Design.

## TABLE 5.1-10

## SUMMARY OF SCREENING STUDY FOR REMOVAL OF $CH_4$ IN CCG RECYCLE GAS

Study Design Base Case - 10% $CH_4$ in Recycle Gas

Incentive Study - 0% $CH_4$ in Recycle Gas

|  | Base Case(1) | No $CH_4$ in Recycle Gas | % Change |
|---|---|---|---|
| Gasifier Temperature, °F | 1,275 | 1,275 | - |
| Coal Feed to Gasifier, ST/SD | 14,490 | 14,490 | - |
| **Plant Rates and Operating Conditions** |  |  |  |
| Net $CH_4$ Product, lb moles/hr | 27,973 | 28,015 | + 0.2 |
| Total Recycle Gas, lb moles/hr | 57,200 | 47,500 | -17 |
| Gasifier Steam/Recycle Gas, lb moles/hr | 131,000 | 117,200 | -11 |
| Raw Gasifier Product, lb moles/hr | 164,800 | 151,000 | - 8 |
| Acid Gas Removal Feed, lb moles/hr | 110,400 | 100,400 | - 9 |
| Methane Recovery Feed, lb moles/hr | 87,100 | 77,200 | -11 |
| Normal Preheat Furnace COT, °F | 1,543 | 1,575 | +32°F |
| Preheat Furnace Fuel Fired, MBtu/hr | 530 | 500 | - 6 |
| Steam Consumption, lb moles/hr(2) | 38,900 | 37,500 | - 4 |
| Steam Conversion, % | 41 | 42 | + 2 |
| Overall Net $CH_4$ Product, GBtu/SD | 257.0 | 257.4 | + 0.2 |
| Steam Generated Offsite, lb moles/hr | 59,300 | 55,300 | - 7 |
| Relative Gasifier Volume | 100 | 96 | - 4 |

---

(1) Base Case refers to CCG Study Design completed in the Predevelopment Program and documented in the Final Report FE-2369-24.

(2) Steam consumption = steam in preheat furnace inlet + water with coal + cooling steam - steam in reactor effluent.

In the methane recovery section of the plant, more refrigeration would be required to reduce the methane content of the recycle gas stream. This would require greater investment and operating cost in that section.

Overall, it was concluded that there are incentives for reducing the methane content of the recycle gas stream. More detailed studies, including the impact of higher methane recovery section refrigeration requirements, will be made at a later time.

## 5.2 Systems Modeling

Systems modeling work is being carried out as part of the CCG Process Development Program to develop material and energy balance tools which will reduce the engineering effort required to do screening studies and process definition studies. A material balance model for the catalyst recovery system was completed in March, 1979. Work is continuing on the development of a material and energy balance model for the CCG reactor system.

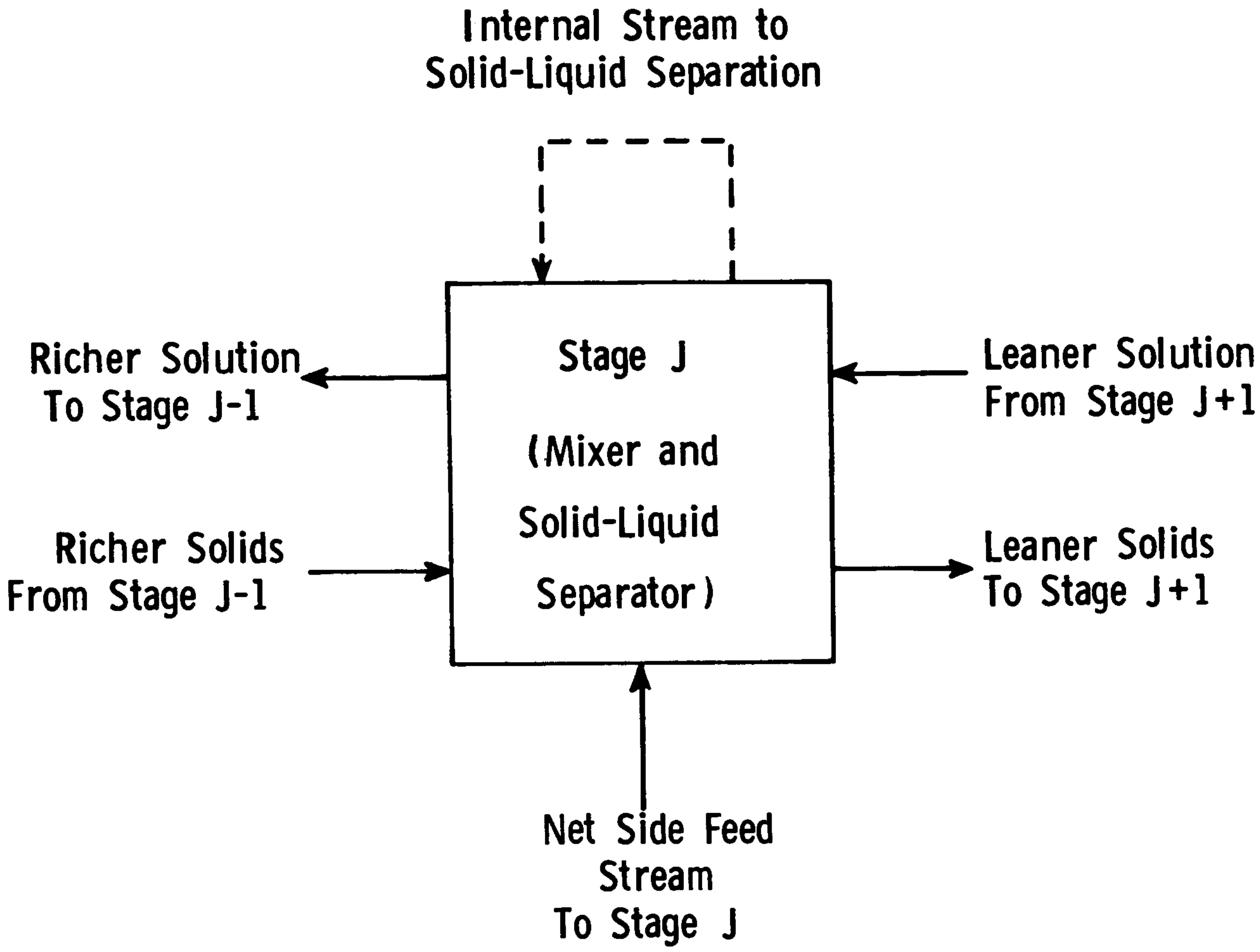
### 5.2.1 Catalyst Recovery Material Balance Model

Catalyst recovery as incorporated in the CCG Commercial Plant Study Design involves "digestion" of gasifier char and fines with $Ca(OH)_2$ to solubilize most of the catalytic potassium salts, followed by multi-stage countercurrent leaching with water to remove the soluble catalyst from the gasifier and calcium solids. Material balances for this system have required extensive stage-by-stage hand calculations, as well as some simplifying assumptions. The new catalyst recovery material balance model has been developed to perform rigorous stage-by-stage calculations taking into account the solid-liquid separation efficiencies for individual stages. This computer model will be used shortly in catalyst recovery system screening studies to evaluate alternative processing approaches and solid-liquid separation techniques.

Figure 5.2-1 represents one stage in the countercurrent leaching sequence. Each stage involves mixing of solids from a richer (more concentrated) stage with solution from a leaner (less concentrated) stage, followed by solid-liquid separation to produce a richer solution stream and a leaner solids stream. The catalyst recovery model is capable of handling these four streams as well as an internal stream representing the feed to the solid/liquid separation device and a net side feed stream. The latter stream would be used to represent any special feeds or products that may be involved. One example is $Ca(OH)_2$ digestion, where calcium solids are added and water is consumed in chemical reactions. Provision is also made within the model to reflect adsorption of soluble potassium salts on the solids.

## Figure 5.2-1

## CATALYST RECOVERY MATERIAL BALANCE MODEL: STAGE CONFIGURATION AND STREAMS



The model is capable of calculating any one of the following three parameters, with the remaining two specified by the user:

- Overall catalyst recovery
- Recovered "rich" solution concentration
- Number of washing (leaching) stages.

Varying rich solution concentration is equivalent to varying wash water rate. Other required inputs are the rich solids feed to the first (richest) stage as well as the solid-liquid separation performances and side feed streams for all stages.

The material balance routines in the model were validated by duplicating the catalyst recovery material balance for the CCG Study Design. The material balances for soluble catalyst salts, water, and insoluble solids all closed to within ± 0.01%. Numerous test cases were run to validate various material balance convergence and output options. After minor modifications to improve the convergence methods, all cases converged satisfactorily. Computer costs per run were very low. The model is now available for use in engineering and laboratory studies of the catalyst recovery system.

### 5.2.2 CCG Reactor System Material and Energy Balance Model

A second systems modeling effort began in December, 1978, to develop updated material and energy balance tools for the CCG reactor system. The catalytic gasification reactors and the associated recycle gas loop and preheat furnaces are key parts of the commercial process flowsheet. Five of the eight process blocks in the CCG Commercial Plant Study Design are involved in the reactor system modeling effort. These include the Reactor, the Product Gas Cooling and Scrubbing, the Acid Gas Removal, the Methane Recovery, and the Refrigeration sections. These sections carry out the gasification step and the cleanup and separation of the raw gasifier product gases.

A "first pass" reactor system material and energy balance model was used in preparing the CCG Commercial Plant Study Design. Although this model is accurate and proved satisfactory for use in the Study Design effort, the gasifier material balance routine is not specifically intended for coal gasification and the energy balance calculations are complex and cumbersome. In applying this first-pass model, extensive hand calculations are necessary to set up the material balance and to develop solids enthalpy terms for the overall energy balance. Improved reactor system material and energy balance techniques and computational tools are desirable to allow the laboratory guidance and process definition studies planned under the current program to be carried out efficiently and consistently.

The updated CCG reactor system model will be incorporated within the framework provided by Exxon's proprietary process network simulation program, known as "COPE". Three main blocks and a fourth optional block are being programmed to model the gasifier itself:

- The first block models the CCG gasifier solids material and energy balance. This block feeds coal and catalyst and produces "reacting coal" (the portion of the solids feed which is gasified) and spent solids (residual char, ash, and catalyst). Solids stream enthalpies, including the effects of catalyst-coal reactions, are also calculated.

- The second block feeds the "reacting coal" and the various gaseous feed streams and produces an effluent gas at specified shift and methanation equilibria.

- The third block carries out the overall gasifier energy balance. The model has the flexibility to energy-balance other related reactor systems, such as steam reformers.

- The fourth block incorporates the gasifier kinetics/contacting model as updated during the CCG Predevelopment Program. This optional feature allows calculation of the gasifier bed size along with the material and energy balance.

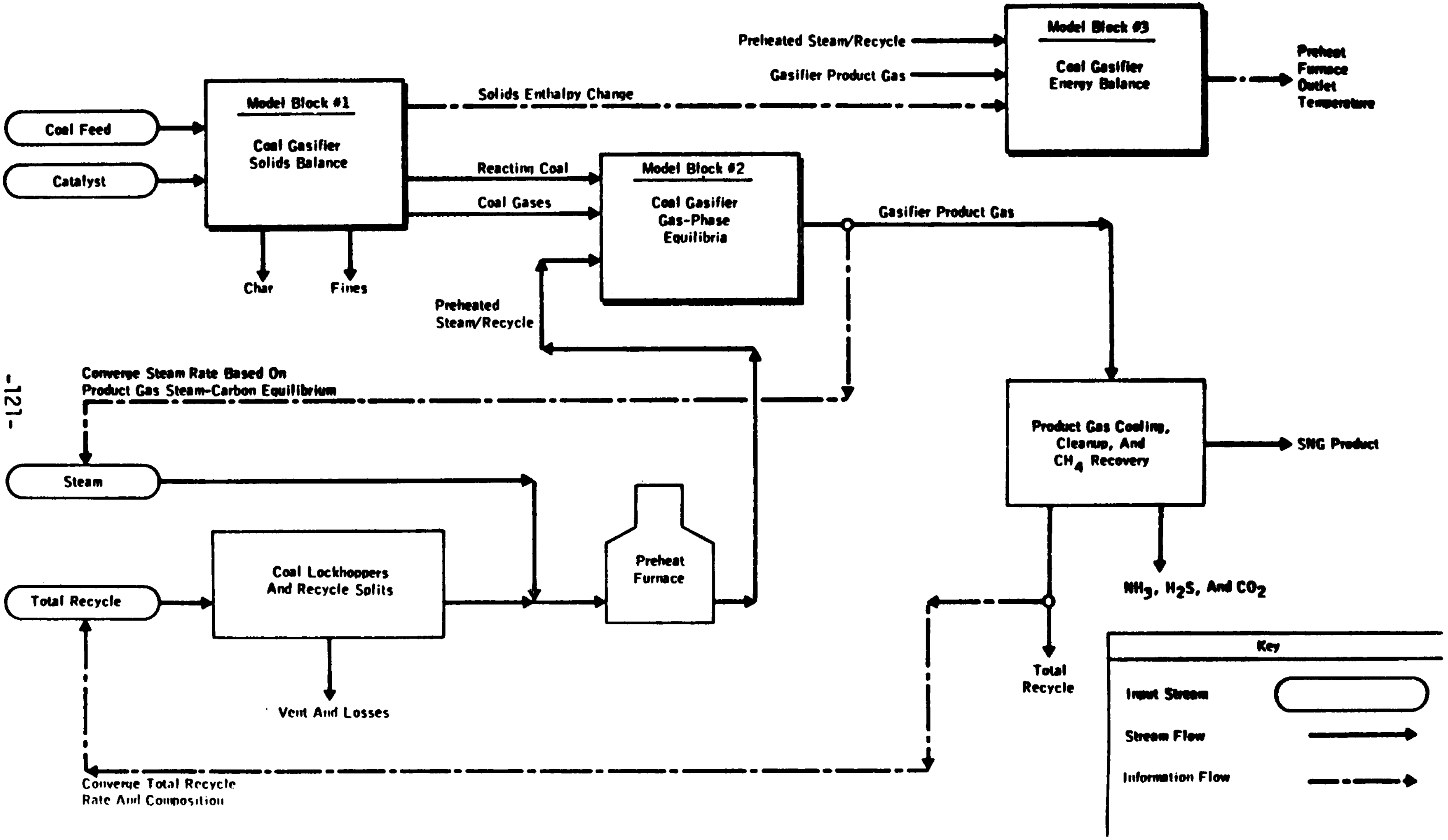
The gasifier model was broken down into these four independent functional blocks to facilitate modeling of flowsheets or gasifier configurations different from the base case in future lab guidance and process improvement studies.

In order to simulate the material and energy balance for a CCG reactor system, the model blocks are incorporated in a COPE process network. The network used to model the reactor system for the CCG Commercial Plant Study Design is illustrated in simplified form in Figure 5.2-2. The network joins together the three required blocks, models the material balances for the product gas cleanup and separations steps downstream of the gasifier, and converges the overall material balance and gasifier/preheat furnace energy balance.

The calculations are relatively complex. Two nested loops are used to converge upon the overall material balance. The inner loop determines the steam rate to the gasifier based on product gas steam-carbon equilibrium (or gasifier steam conversion). Within this inner loop, the gasifier material balance is calculated by model blocks one and two. The principal feeds are coal, catalyst and preheated steam/recycle, and the principal products are char, fines and gasifier product gas. The outer loop converges the recycle (synthesis gas) stream rate and composition, using a series of COPE operations. After the material balance is converged, the gasifier energy balance is closed by model block three. The gas-phase feed and product streams are fed to model block three directly. The impacts of solids on the gasifier energy balance are accounted for by using a solids enthalpy change transferred from model block one. Model block three calculates the steam/recycle preheat furnace outlet temperature required to maintain the desired gasifier operating temperature. An option to reflect shift reaction in the preheated steam/recycle stream has been included in this block. Under this option, the

FIGURE 5.2-2

FLOW DIAGRAM FOR COMPUTER SIMULATION
OF CCG COMMERCIAL PLANT STUDY DESIGN



computer routine will converge upon the required preheat temperature assuming a specified percentage (0-100%) of the shift reaction which would occur if the stream were in full equilibrium.

The overall modeling effort was about two-thirds complete at the end of the reporting period. The equilibria and energy balance blocks--blocks two and three--were completed, and were validated using the commercial base case (the Predevelopment Program CCG Study Design) and other selected cases. The gasifier solids balance block has also been completed and validated, with the exception of subroutines to model catalyst-coal reactions. The material and energy balance bases for catalyst-coal reactions are being developed, and programming of these reactions will begin shortly. Other work still remaining includes the programming of the fourth block containing the gasifier model, and the final validation and documentation of the overall model.

Initial validation runs for the overall model have shown considerable savings in computer charges. For example, a run using the new tools to model a commercial gasifier with an integral steam reformer for heat input cost 50% less than the same case modeled using the old methods. In addition, the energy balance model block saves considerable engineering effort by eliminating development of a complex network of computer operations to perform heat balance calculations for each different CCG case.

## 5.3 Engineering Technology Studies

As part of the CCG Process Development Program, a coordinated set of engineering technology programs is being conducted to develop fundamental process and equipment technology to support the overall laboratory and engineering process development effort. As of June, 1979, work was underway on five of these programs, as described below. Additional programs will be initiated later in 1979.

### 5.3.1 Evaluation of Construction Materials for Catalytic Gasification

The overall objective of this engineering technology program is to assembly a data base on materials performance for those plant sections which have materials considerations unique to catalytic gasification. A five-part in-situ materials testing/ corrosion monitoring program has been devised for the PDU to identify problem areas and to assemble a data base for selecting materials for CCG process equipment. The program consists of corrosion racks, corrosion probes, nondestructive testing inspection, component examination, and stream sampling. In a separate effort, materials screening tests in alkali-containing gasifier environments have been instituted cooperatively with the Bureau of Mines. These separately-funded bench-scale tests are to be conducted at the Bureau of Mines Tuscaloosa Metallurgy Research Center.

Construction materials for the CCG Commercial Plant Study Design were specified conservatively, based heavily on limited materials data from earlier work on thermal gasification processes. Accordingly, materials test and development work are required for conditions specific to the CCG process. These include equipment items in the gasification, raw gas heat exchange, wet scrubbing, sour water, char handling, and catalyst recovery systems. Potential materials problems identified in these areas are high temperature sulfidation, chloride and caustic stress corrosion cracking, sour water corrosion, and erosion in solids/gas and liquid/slurry services.

## Materials Evaluation Program for the PDU

The major objective of the PDU materials evaluation program is to assemble a data base for designing full-scale commercial equipment, with emphasis on hostile process environments. Specific objectives are listed below:

(1) Determine corrosion/erosion behavior of selected metals in the PDU via corrosion racks, corrosion probes, and non-destructive testing (NDT) inspection. Also evaluate chemical and erosion resistance of refractory specimens in gasifier.

(2) Evaluate chloride and/or caustic induced stress corrosion cracking by means of U-bend specimens in char digester.

(3) Relate process conditions to corrosion phenomena by chemical analyses of stream samples.

(4) Determine corrosion/failure mechanisms from analysis of failed equipment components. In addition, perform systematic metallurgical examination of critical working components to assess in-service deterioration.

During the reporting period, efforts have focused on defining and initiating a program to meet these objectives. An extensive program for materials evaluation in the PDU has been developed. This program consists of five interrelated elements:

- Corrosion racks
- Corrosion probes
- NDT inspection
- Component examination
- Stream sampling

These five program elements are discussed in more detail in the following paragraphs.

Corrosion racks are devices on which small metal specimens (coupons) are assembled and secured for in-situ exposure inside operating equipment. Their purpose is to yield time-averaged corrosion rates based on weight loss measurements. Also, coupons are useful for predicting severity of pitting, and identifying corrosion mechanism. Table 5.3-1 itemizes the location and test materials for the eight corrosion racks provided for the PDU. Note that one of the three racks installed in the gasifier is fitted with specimens consisting of castable refractory. The racks were designed, fabricated and assembled by the ER&E Corrosion Laboratory at Florham Park, New Jersey, which is responsible for pre- and post-exposure evaluations of specimens. All of the racks are mounted on blind flanges (nozzles) or pipe plugs (couplings). They are at site and will be installed after the PDU shakedown period. A second set of corrosion racks will be fabricated during the second half of 1979.

Electric resistance corrosion probes, the type to be employed at the PDU, measure corrosion rate as a function of increasing electrical resistance of a corroding wire element. Through their quick response characteristics, they can flag large fluctuations in corrosion rate which would remain undetected from time-averaged weight loss measurements obtained from coupons. The two probes to be installed in the PDU are described in Table 5.3-1. They are of the non-retractable type, which is considered appropriate for pilot plant applications where fairly frequent shutdowns provide ample opportunity for probe removal. The probes have been purchased and will be installed after the unit is lined out.

Nondestructive testing (NDT), also called nondestructive examination (NDE), is a useful inspection technique for measuring wall thickness of equipment. Ultrasonic thickness testing (UT), the technique being employed at the PDU, may be performed during operation, within the temperature limitations of the transducer. The NDT program set up for the PDU is outlined in Table 5.3-2. All baseline UT measurements have been completed except for the gasifier shell and for the char digester. The latter has not yet been fabricated.

The fourth element of the PDU materials evaluation program is component examination. Failure analysis of equipment components is an important adjunct to coupon, probe, and NDT generated data for assessing materials performance in catalytic gasification applications. In addition, it is highly instructive to examine destructively critical equipment components which are still in working order after extended service exposure. Accordingly, a two-part program has been set up for the PDU, which provides for selected components to be examined in the ER&E Metallurgical Laboratory at Florham Park. The first part involves routine failure analysis of components to determine the cause and mode of failure. In the second part, similar types of examinations will be performed on intact working components from the following potential problem areas:

- Lock hopper valves
- Char slurry drum letdown valves

## TABLE 5.3-1

## CATALYTIC COAL GASIFICATION PDU CORROSION RACKS AND PROBES

| Test Site | Equipment Location | Location | Type of Device | Specimen Type | Test Materials(1) |
|---|---|---|---|---|---|
| 1 | Gasifier | Dense phase | Rack | Refractory cylinders | Kaiser Lo-Erode(2) |
| 2 | Gasifier | Dense phase | Rack | Metal cylinders | HK-40, 304 SS, 309 SS |
| 3 | Gasifier | Dilute phase | Rack | Metal discs | HK-40, 310 SS, 304 SS, 309 SS, 304 SS Alonized |
| 4 | Sour water accumulator | Liquid | Rack | Metal cylinders | CS, 304 SS, 316 SS, Carpenter 20Cb3, Ti, Monel |
| 5 | Sour water accumulator | Liquid | Probe(3) | Wire element | CS |
| 6 | Sour water stripper | Packing | Rack | Metal cylinders | 304 SS, 316 SS, CS |
| 7 | Sour water stripper | Packing | Rack | Metal cylinders | Carpenter 20Cb3, Monel, Ti |
| 8 | Char slurry drum | Liquid | Rack | Metal cylinders | CS, 316 SS, Inconel 625 |
| 9 | Char digester | Liquid | Rack | Metal U-bends | CS, 316 SS, Monel, Inconel 600, Allegheny Ludlum 29-4 |
| 10 | Char digester | Liquid | Probe(3) | Wire element | CS |

Notes: (1) Abbreviations:
CS - carbon steel
304 SS - Type 304 stainless steel (18 Cr-8 Ni)
309 SS - Type 309 stainless steel (25 Cr-12 Ni)
310 SS - Type 310 stainless steel (25 Cr-20 Ni)
316 SS - Type 316 stainless steel (18 Cr-8 Ni-2 Mo)
HK-40 - Cast 25 Cr-20 Ni-0.4 C alloy

(2) Kaiser Lo-Erode specimens, with and without 304 SS fiber reinforcement

(3) Non-retractable electric resistance probe

## Table 5.3-2

## Catalytic Coal Gasification PDU NDT Inspection Program

| Equipment Item | Inspection Points | Frequency |
|---|---|---|
| Gasifier | Opposite cyclone inlet, plus 4-6 selected spots | 3 mo interval |
| Gasifier O/H line to cyclone | Every 3 feet and at elbows | 3 mo interval |
| Cyclone | 4-6 selected spots, including inlet area | Each turnaround |
| Cyclone dipleg | Every 2 feet of last 6 feet at gasifier inlet | Each turnaround |
| Cyclone line to filter | Every 20 feet | Each turnaround |
| Scrubber | Bottom 1 foot | 3 mo interval |
| Gasifier line to char pot | Every 4 feet | Each turnaround |
| Char pot | Bottom head and lower shell, plus 4-6 selected spots | 3 mo interval |
| Char digester | Body head and shell | Each turnaround |

- Gasifier overhead line
- Recycle gas preheater coil

Initial component examinations are expected to be carried out during the second half of 1979.

Interpretation of corrosion data and inspection results necessitates information on the aggressive stream constituents present in the environment. Accordingly, stream sampling has also been incorporated into the materials evaluation program. The requested analyses are tabulated in Table 5.3-3.

CGU Failure Analyses

Two failure analyses have already been performed on cracked 316SS and 310SS piping removed from ER&E's small Continuous Gasification Unit (CGU). Lessons learned from these analyses are pertinent to CCG equipment design and operation, and were factored into the PDU materials testing program. For this reason, these results are reported here.

The failed 316SS tubing section was part of the CGU char withdrawal system, used for transferring char from the reactor to a char pot. Normal operating temperature is about 800°F; however, overheating in excess of 1000°F had been reported. The sectioned tubing revealed four cracks in the form of mixed mode stress corrosion cracking (i.e., a combination of intergranular and transgranular crack paths). Chlorides were detected in trace amounts in one crack, whereas sizeable quantities of potassium were found in all four cracks. Based both on the presence of potassium and the crack morphology, the failure is attributed to hydroxyl ion induced stress corrosion cracking. More familiarly known as caustic embrittlement, it can produce either pure intergranular or mixed mode cracking.

Chloride stress corrosion cracking, originally suspected as the cause of failure, was held unlikely because it characteristically propagates in a highly branched transgranular fashion. Also ruled out was polythionic acid stress corrosion cracking which cracks stainless steels in a purely intergranular mode. It was recommended that the tubing be replaced in Incoloy 825. This material has improved resistance to all forms of stress corrosion cracking, and moreover possesses good high temperature strength and sulfidation resistance.

The failed 310SS (25 Cr-20 Ni) tubing section was located between the CGU reactant mix point and a blowdown pot used intermittently to clear plugs in the feed line. The normal process environment is a mixture of catalyzed coal, synthesis gas and steam at 500 psig and 1300°F. Two ball valves suspended directly from the tubing may have imposed considerable bending stresses. The failure was in the form of transgranular cracking suggestive of chloride stress corrosion, but no evidence of chloride was detected. Significantly, as with the above described char piping failure,

## TABLE 5.3-3

## CATALYTIC COAL GASIFICATION PDU STREAM SAMPLING AND ANALYSES

| Location/Service | Type of Sample | Required Analyses | Sampling Frequency |
|---|---|---|---|
| Gasifier overhead | Gas(1) | Chemical composition | Monthly |
| Sour water accumulator | Liquid | pH, $Cl^-$, $CN^-$, $NH_3$, $H_2S$, phenol | Monthly |
| Filter pot | Solid | Chemical analysis | Quarterly |
| DEA regenerator overhead | Gas | $CO_2$, $H_2S$, $NH_3$ | Monthly |
| Char pot | Slurry | Liquid - pH, $Cl^-$, $CN^-$, $NH_3$, $H_2S$<br>Solid - chemical analysis | Monthly |
| Char digester | Slurry | Chemical analysis | Quarterly |
| Char for disposal | Solid(2) | Chemical analysis | Quarterly |
| Recycle gas | Gas | Chemical composition | Monthly |

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Notes: (1) Gas composition calculated from liquid samples taken at scrubber and sour water accumulator.

(2) Sample taken at catalyst recovery area.

appreciable amounts of potassium were found inside the crack. However, unlike the char piping crack, there was no intergranular propagation. In view of these conflicting pieces of evidence, the cause of failure remains somewhat speculative. All in all, a stronger case can be made for potassium hydroxide as the more likely crack-inducing substance. This conclusion is based on the observation that the cracks were not as extensively branched as classic transgranular chloride stress corrosion cracks. Incoloy 825 was recommended as a replacement material. As with the char piping failure, the basis for this recommendation is the better resistance of Incoloy 825 to all forms of stress corrosion cracking as compared to 300 series stainless steels.

### Materials Screening Tests at Tuscaloosa Metallurgy Research Center

As a result of a joint DOE/BM/ER&E meeting in March, 1979, a materials test program geared to the CCG process will be conducted at the Bureau of Mines Tuscaloosa Metallurgy Research Center in University, Alabama. Funding for this program will be through modification of the active Interagency Agreement EX-76-A-01-2219 between DOE and the Bureau of Mines. These tests are to be conducted in test apparatus already built and used for similar experiments studying materials for thermal gasification processes.

The objective of the test program is to screen candidate metals and refractories in simulated CCG environments. Specifically, the intent is to evaluate the effect of potassium hydroxide (gasification catalyst) in accelerating attack on construction materials, and to elucidate the nature of such attack. Close attention will be given to complex liquid phases composed of alkalis and metal sulfides. Such aggressive slags have not been encountered in CCG laboratory units, but are nevertheless possible from thermodynamic considerations. The detrimental effect of alkali contamination on refractories was demonstrated at Tuscaloosa in a series of 1978 test runs simulating thermal gasification environments at 980°C (1800°F).

The test conditions and parameters proposed in the work statement are summarized in Table 5.3-4. Standard post-exposure evaluation techniques (weight and dimension changes) will be supplemented by selective chemical analyses, X-ray diffraction and electron microscopy, all to be performed by Tuscaloosa. The projected starting date is July, 1979.

## 5.3.2 Vapor-Liquid Equilibria in Sour Water/Catalyst Systems

This program's objective is to develop a vapor-liquid equilibrium (VLE) model applicable to the design of the sour water systems in the CCG Process. The systems for which such a model would be used include the wet scrubbers and condensate drums for the gasifier product gas, as well as the sour water stripping facilities.

## TABLE 5.3-4

## CONDITIONS/PARAMETERS FOR MATERIALS SCREENING TESTS (BUREAU OF MINES, TUSCALOOSA METALLURGY RESEARCH CENTER)

| | |
|---|---|
| Temperature<br>Pressure<br>Flow rate<br>Number of runs<br>Run length | 1350°F (730°C)<br>500 psig<br>2 SCFH<br>2<br>100 hours |
| Gas Composition, mole% | $H_2$ 21.5<br>$H_2O$ 31.9<br>CO 6.0<br>$CO_2$ 14.1<br>$CH_4$ 21.8<br>$N_2$ 2.1<br>$NH_3$ 1.4<br>$H_2S$ 1.2 |
| Alkali contamination of gas atmosphere | Run 1 - Crucibles of molten KOH placed in gasifier<br>Run 2 - Same as Run 1 plus KOH solution pumped to gasifier in amount of 50 ppm KOH (mole basis) per mole of gas |
| Alkali contamination of test specimens | I - None<br>II - Soaked in KOH solution<br>III - Dipped in KOH melt<br>IV - Contacted with KOH impregnated coal (Illinois #6) |
| Metal specimens | 304 SS<br>310 SS<br>446 SS (or E-Brite)<br>Incoloy 800<br>Incoloy 800 Alonized |
| Refractory specimens (dense) | 50% alumina castable<br>95% alumina castable<br>50% alumina brick |

A detailed review of the anticipated sour water streams was conducted to identify the compositions, temperatures, and pressures of interest. Subsequently, a literature search was conducted to identify the available experimental data on the volatility of ammonia, carbon dioxide, and hydrogen sulfide in aqueous solutions, including solutions containing catalytic potassium compounds. Preliminary screening of the quaternary data (ammonia-carbon dioxide-hydrogen sulfide-water) has shown that they are of poor quality above 140°F. Accurate high-temperature quaternary data must therefore be obtained. Additional data on the volatility of ammonia, carbon dioxide, and hydrogen sulfide in aqueous solutions containing potassium compounds are also needed.

An experimental program to obtain these data has been formulated. The program (shown below) consists of twelve runs on aqueous mixtures containing ammonia, carbon dioxide, hydrogen sulfide, and potassium hydroxide.

Experimental Vapor-Liquid Equilibrium Measurements

| | Liquid-Phase Mole Fractions | | | | | |
|---|---|---|---|---|---|---|
| Run Number | NH3 | H2S | CO2 | KOH | Water | Temp., °C |
| 1 | 0.23 | 0.04 | - | - | 0.73 | 120 |
| 2 | 0.056 | 0.006 | - | - | 0.938 | 140 |
| 3 | 0.036 | 0.004 | 0.032 | - | 0.928 | 50 |
| 4 | 0.027 | 0.004 | 0.004 | - | 0.965 | 130 |
| 5 | 0.076 | 0.013 | 0.003 | - | 0.908 | 130 |
| 6 | 0.046 | 0.010 | 0.004 | - | 0.94 | 170 |
| 7 and 8 | - | 0.015 | 0.015 | 0.03 | 0.94 | 130 and 190 |
| 9 and 10 | 0.01 | - | 0.03 | 0.03 | 0.93 | 130 and 190 |
| 11 and 12 | 0.01 | 0.03 | - | 0.03 | 0.93 | 130 and 190 |

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Note: All chemicals should be at least 99% pure.

An acceptable cost quotation was received from a vendor for these measurements. A subcontract to perform this work was prepared and the consent of the DOE contracting officer was obtained. The subcontract should be executed shortly by the vendor and Exxon Research and Engineering Company. Work in the near future will involve monitoring this experimental program.

### 5.3.3 Physical and Thermodynamic Properties of Catalyst Recovery Solutions

The objective of this program is to collect the physical and thermodynamic properties needed to design the processing equipment in the catalyst recovery system. A review of this system has identified the important properties as: viscosity, density, enthalpy, and boiling point for aqueous solutions containing up to about 30 weight percent dissolved potassium compounds. Temperatures of interest range from 60 to 300°F. Potassium hydroxide and potassium carbonate are the potassium compounds of primary interest.

A literature search for properties of aqueous solutions containing potassium hydroxide or potassium carbonate has been completed. Pertinent articles are still being collected and evaluated. Preliminary results indicate that the data base for potassium hydroxide-water mixtures is adequate for all properties of interest. For potassium carbonate-water mixtures, experimental data may not extend much above 200°F. Methods have to be developed to extend the available data to the higher temperatures of interest and to solutions containing several potassium compounds.

A book by H. S. Harned and B. B. Owen ("The Physical Chemistry of Electrolyte Solutions," ACS Monograph Series #137, Third Edition, Reinhold Publishing Corporation, New York, 1958) has been found to provide useful methods for predicting properties of aqueous solutions containing several dissolved electrolytes. Their method for predicting densities of multi-component solutions gave errors of less than 1% when tested against data on the potassium hydroxide-potassium carbonate-water system. Future work will involve testing Harned and Owen's methods for predicting other properties of multi-component solutions.

### 5.3.4 Environmental Control: Water and Solids Effluents

The objective of this program is to generate the data needed for a quantitative assessment of the environmental impact of the CCG Process. The main focus of this program will be to characterize wastewaters, spent solids, and solids slurries produced in the CCG PDU. Once the effluent characteristics are known, potential treatment alternatives will be identified.

This engineering technology program began in January, 1979. The potential solid and liquid waste streams were identified using process flow charts. As a followup, a trip was made to become familiar with the PDU and to insure that all sampling port locations are accessible. It appears that there will be a need for four liquid sampling locations and for two or three solids sampling locations. A list of analyses to be run on the liquid and solid wastes and on the solids leachates has been set up along with a short guide to sampling methods and preservation techniques for gasification wastewaters. Each of the samples will be tested extensively to determine what contaminants will be present and, of those, which might present effluent quality problems in a commercial plant.

Two samples of CCG solids slurries, containing digested and undigested chars from bench-scale catalyst recovery experiments, were obtained for study. The samples had previously been washed with hot water. The samples were leached by the EPA method, and the leachate was submitted for detailed analyses. The following contaminants will be determined: alkalinity, ammonia nitrogen, Kieldahl nitrogen, nitrate nitrogen, $Cl^-$, $F^-$, $CN^-$, free $CN^-$, $SCN^-$, $S^=$, $SO_4^=$, $SO_3^=$, and phenol. Preliminary testing indicates that leachate from the digested sample contained 7-8 times the amount of Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) found in the undigested char leachate.

The full testing program will begin when the PDU is through its initial shakedown phase.

### 5.3.5 Environmental Control: Atmospheric Emissions

This second environmental control program is directed toward identification of potential atmospheric emissions sources and, where possible, the quantification of these emissions through testing in the PDU. An assessment will then be made of the air quality impact of a commercial CCG plant, and control alternatives will be identified for potential problem sources.

An inventory of atmospheric emissions sources in a commercial-scale CCG plant has been initiated. The major potential sources are expected to be the coal handling facilities, waste solids handling, and the $CO_2$ vent stream from acid gas removal. Emission streams from the PDU have been examined to identify those which might be representative of a commercial plant. Three streams have been selected for field sampling during the PDU operation; these include the coal dryer vent, the lock hopper surge bin vent, and the catalyst recovery waste disposal stream. Emission estimates for other potential sources in the commercial plant will be based on emission factors from the literature or on the experience of other operating plants with similar facilities.

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