EXXON CATALYTIC COAL GASIFICATION PROCESS DEVELOPMENT PROGRAM. ANNUAL TECHNICAL PROGRESS REPORT, JULY 1, 1978-JUNE 30, 1979

EXXON RESEARCH AND ENGINEERING CO.
BAYTOWN, TX

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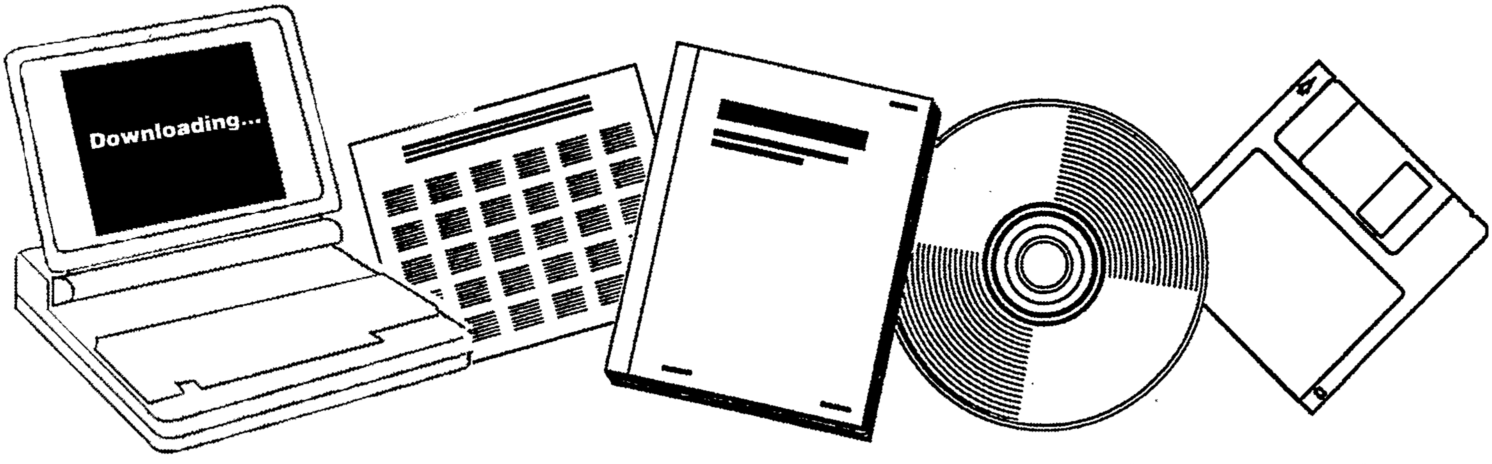

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EXXON CATALYTIC COAL GASIFICATION PROCESS DEVELOPMENT PROGRAM

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

C. A. Euker, Jr. - Program Manager

Exxon Research and Engineering Company
Baytown, Texas 77520

October, 1979

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY UNDER
Contract No. ET-78-C-01-2777

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

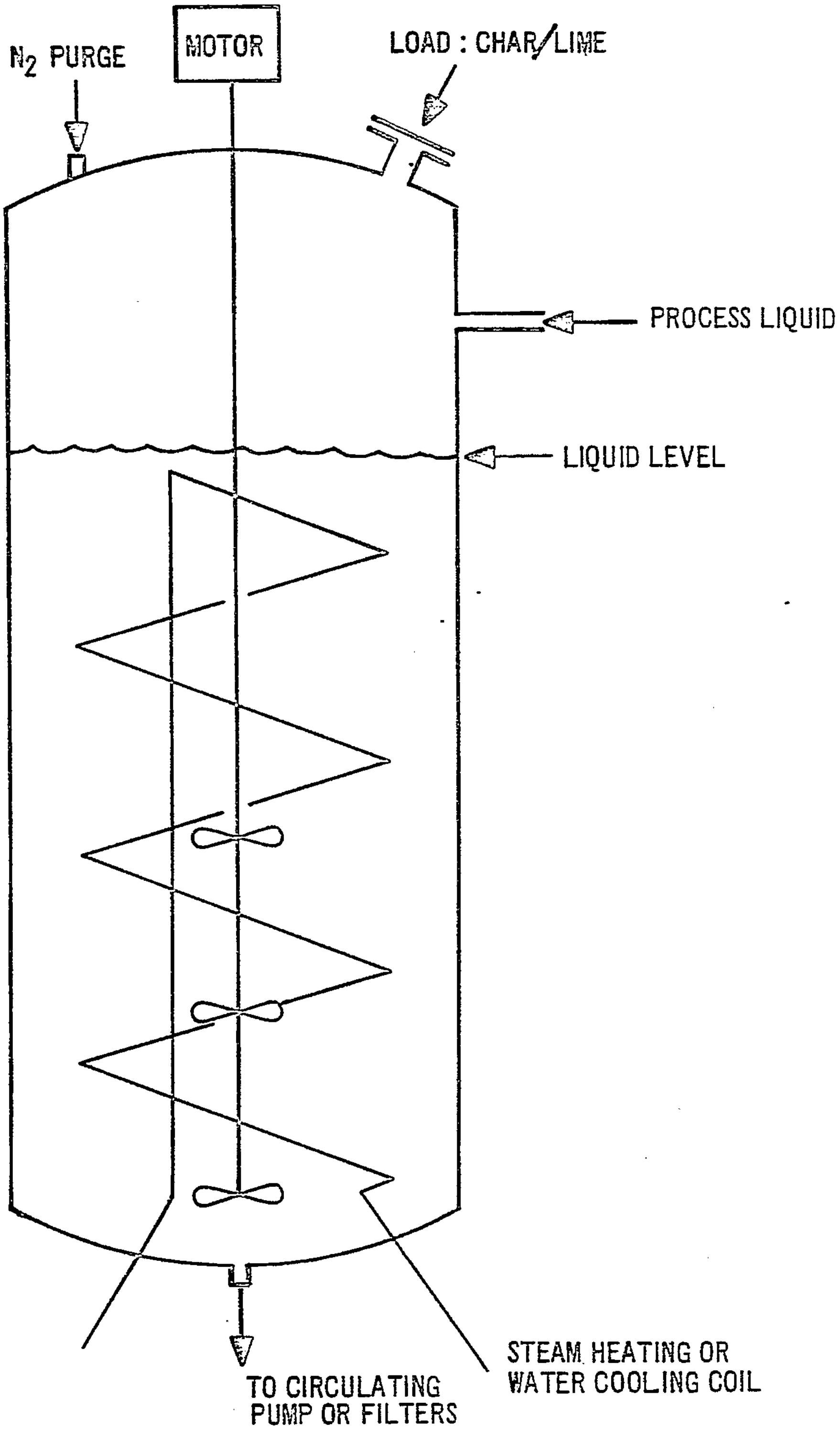

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FIGURE 1.1-2

CALCIUM HYDROXIDE DIGESTION RECOVERS POTASSIUM

ILLINOIS NO. 6 CHAR

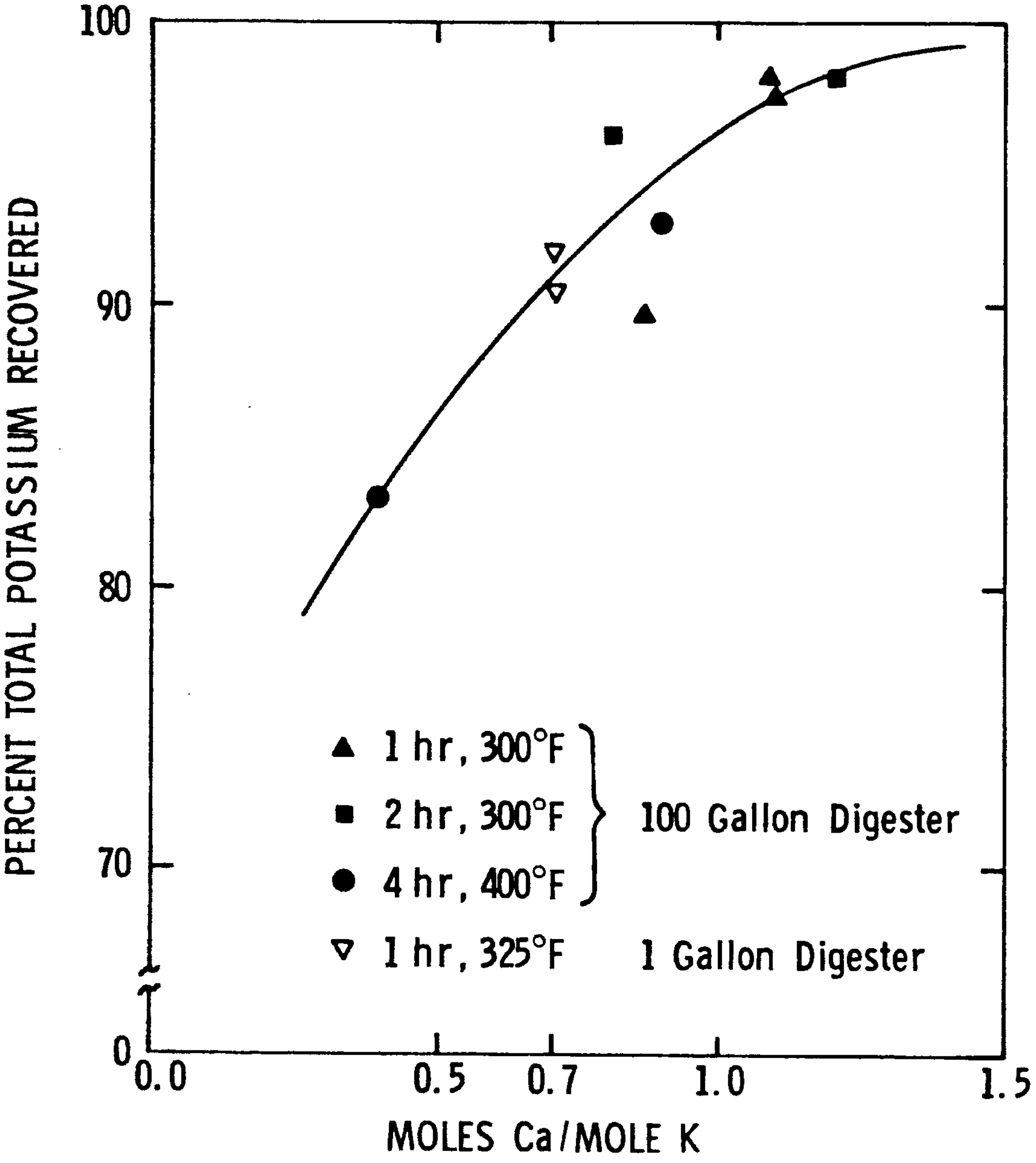

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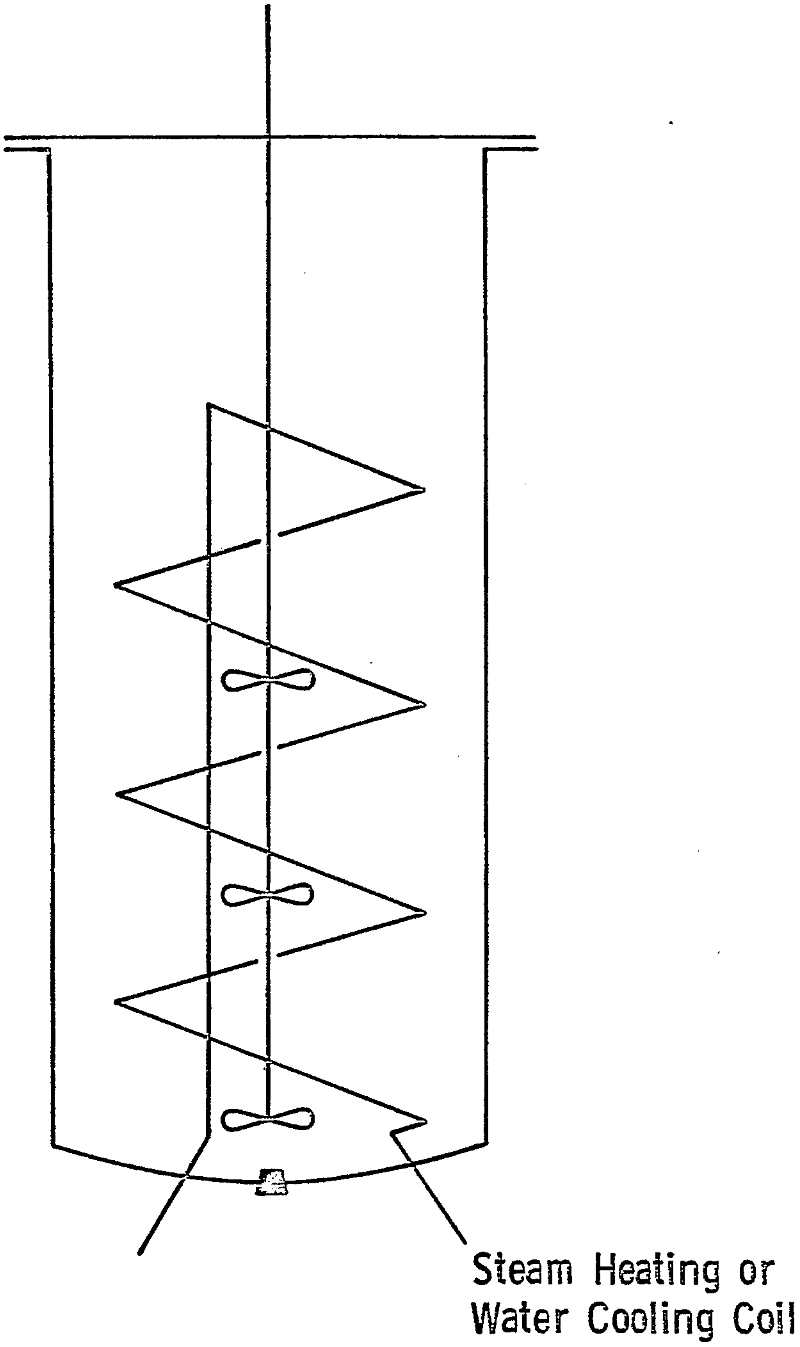
FIGURE 1.1-3

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

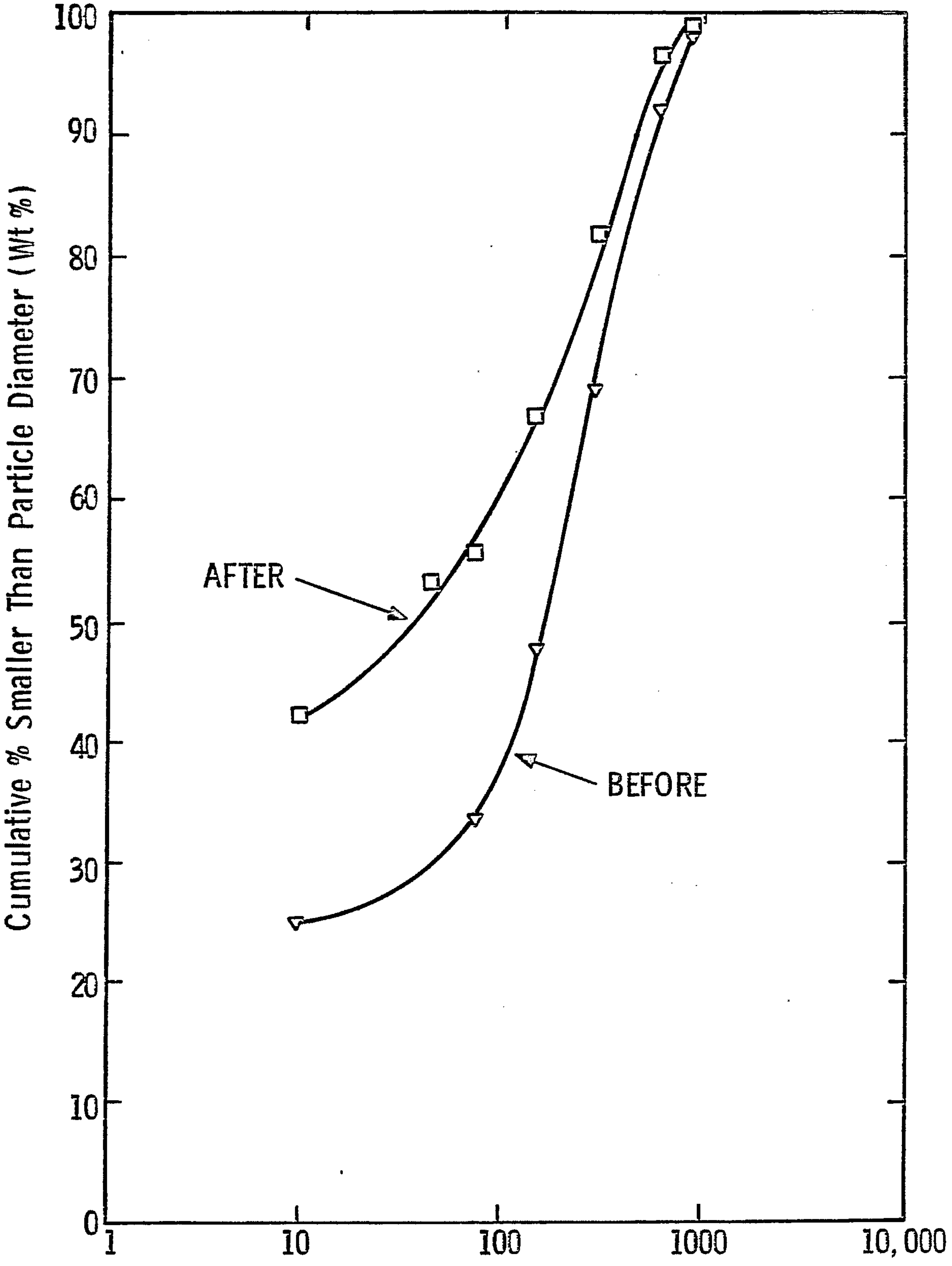
Results:

- 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

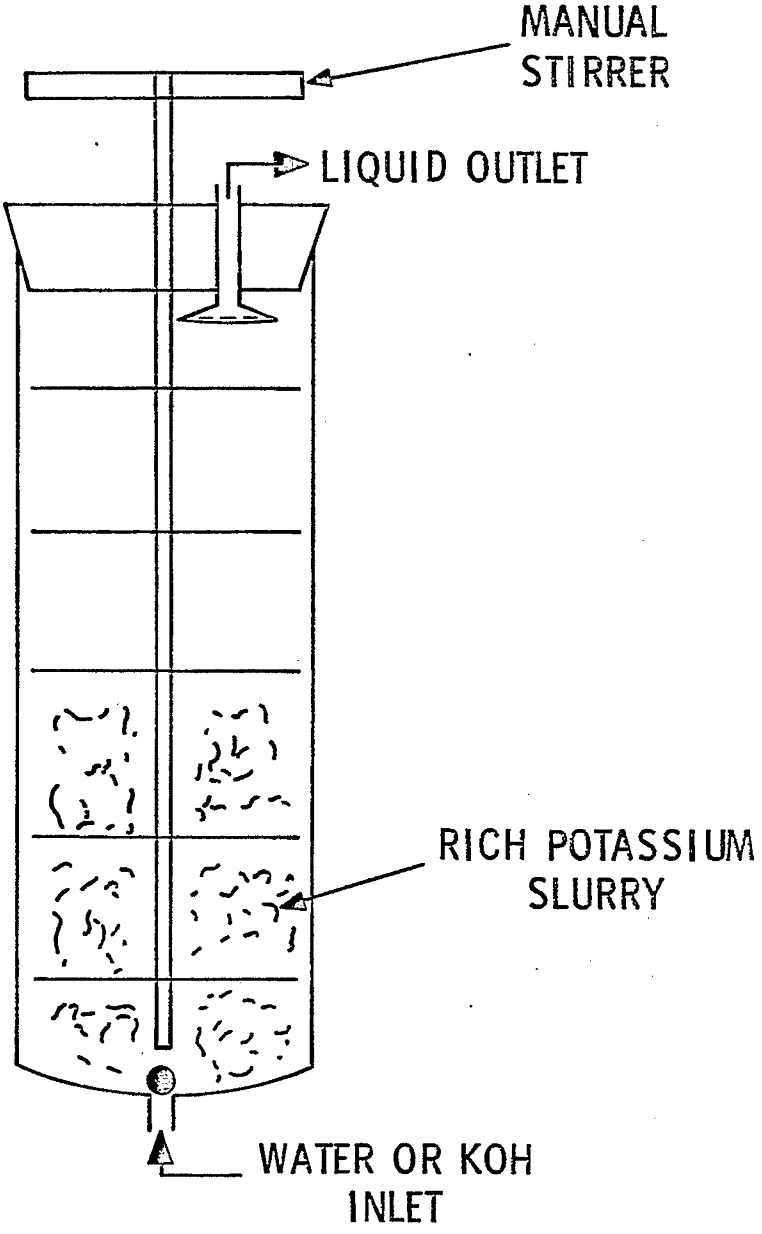


FIGURE 1.1-6

LEACHING TANK CARRYOVER AT 8% SOLIDS LOADING

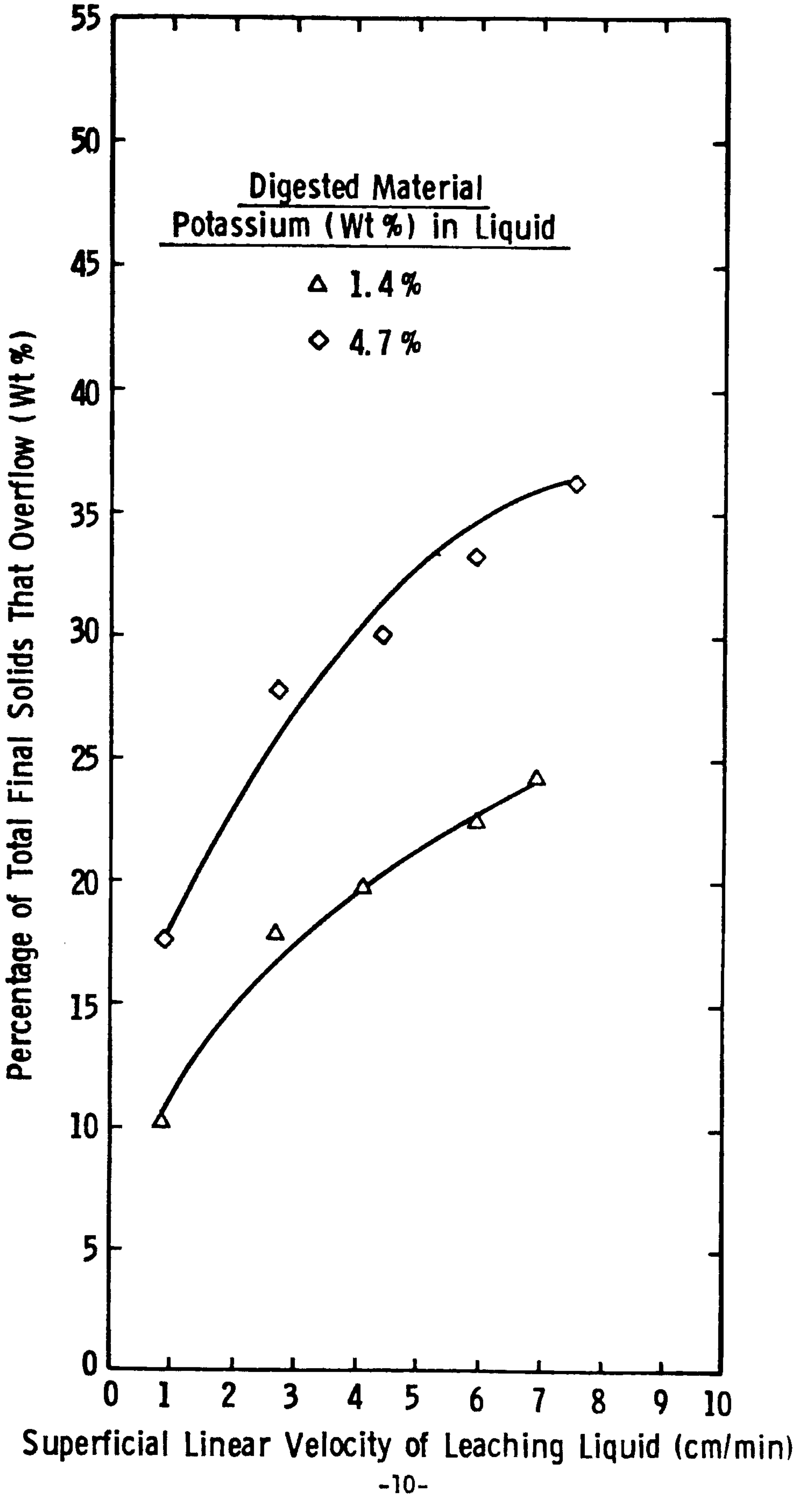


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FIGURE 1.1-7

LEACHING TANK CARRYOVER AT 10 % SOLIDS LOADING

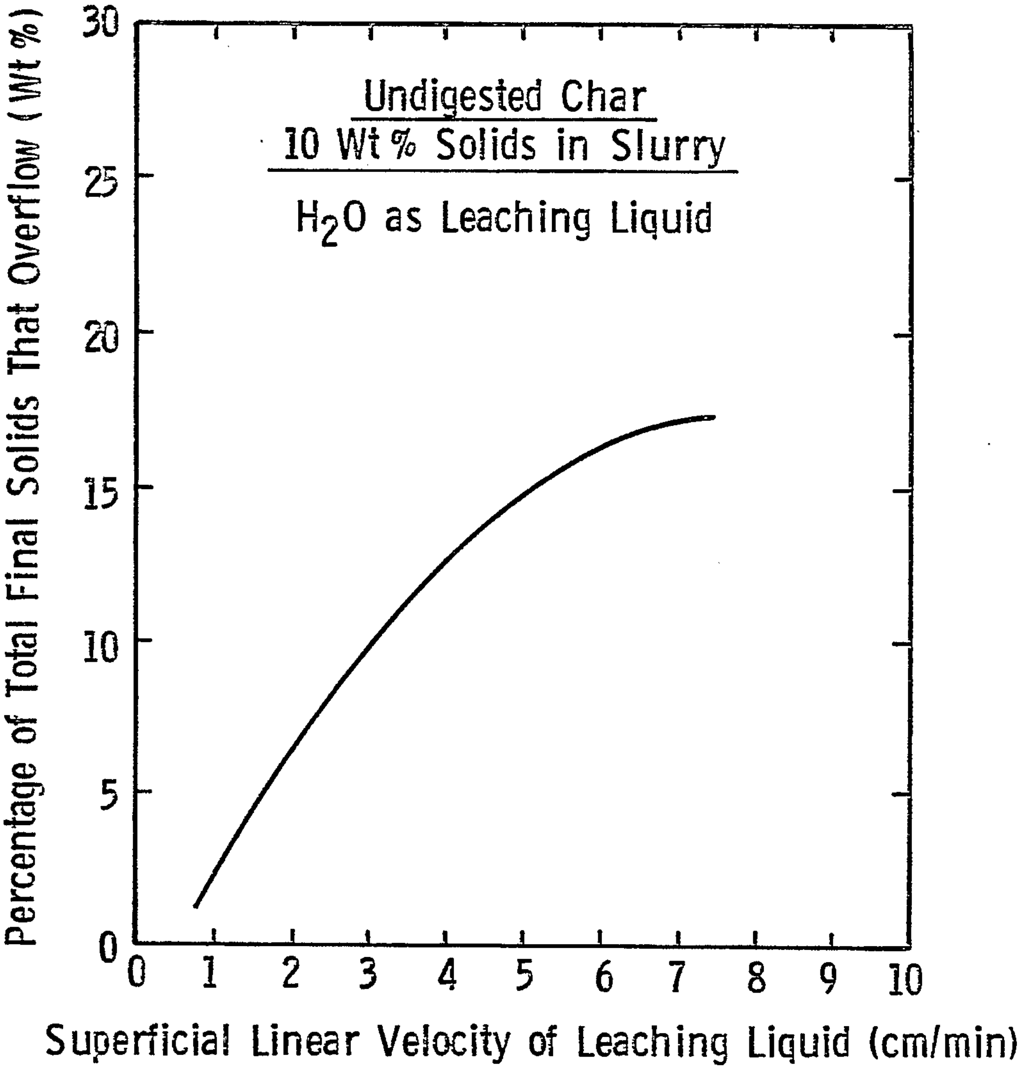

FIGURE 1.1-8

LEACHING TANK CARRYOVER AT 15% SOLIDS LOADING

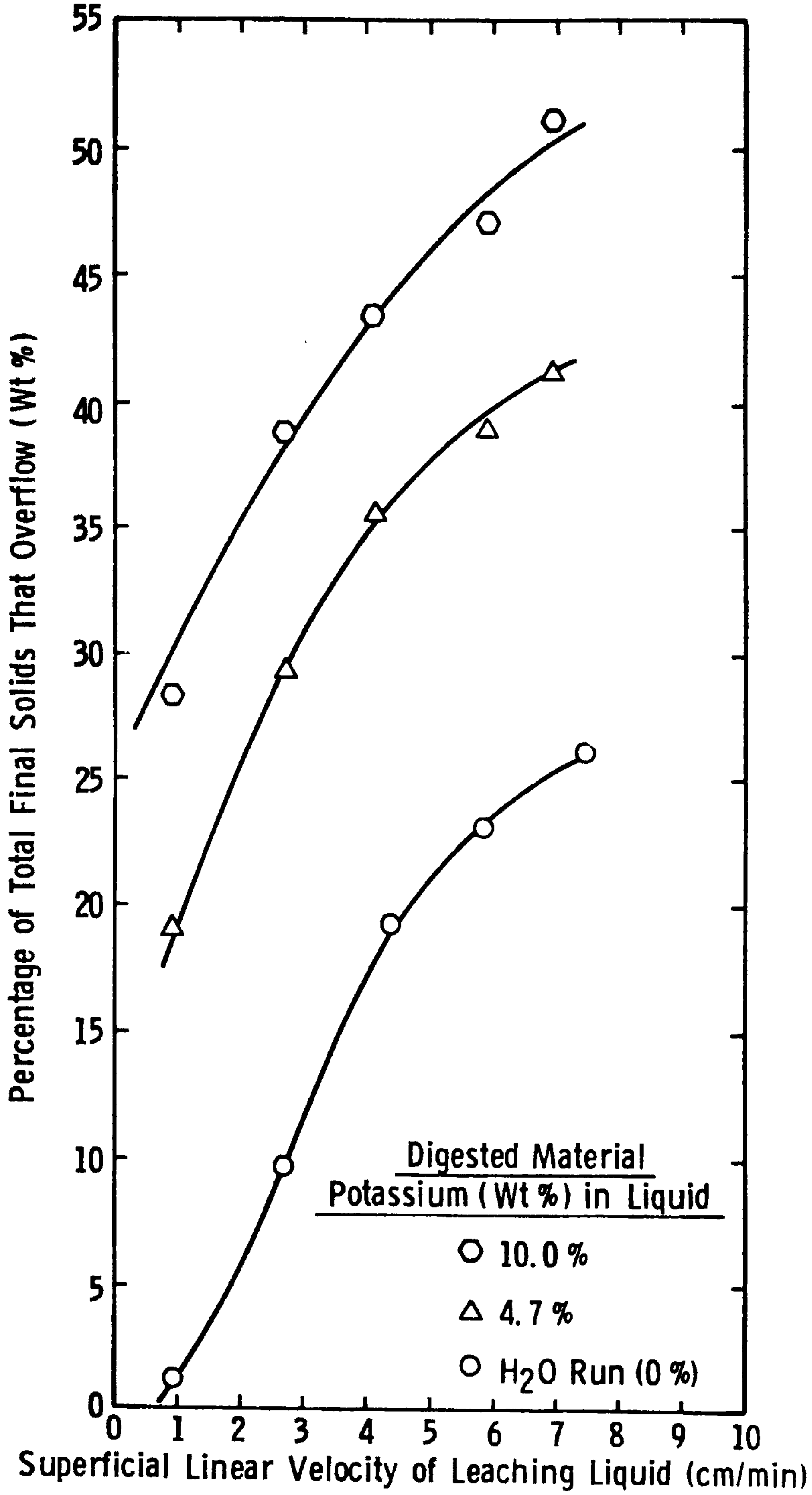

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Table 1.1-3

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

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

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

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

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

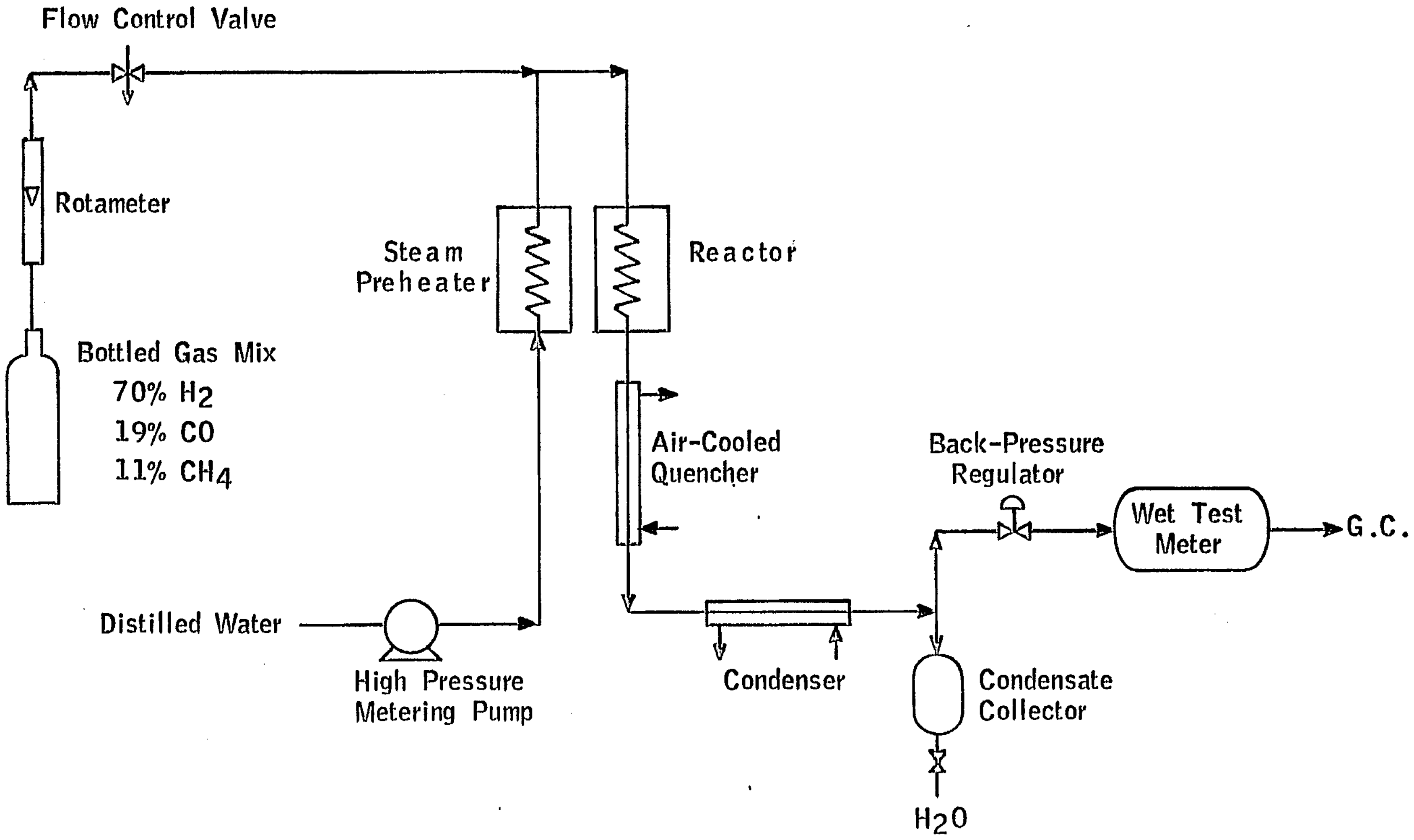
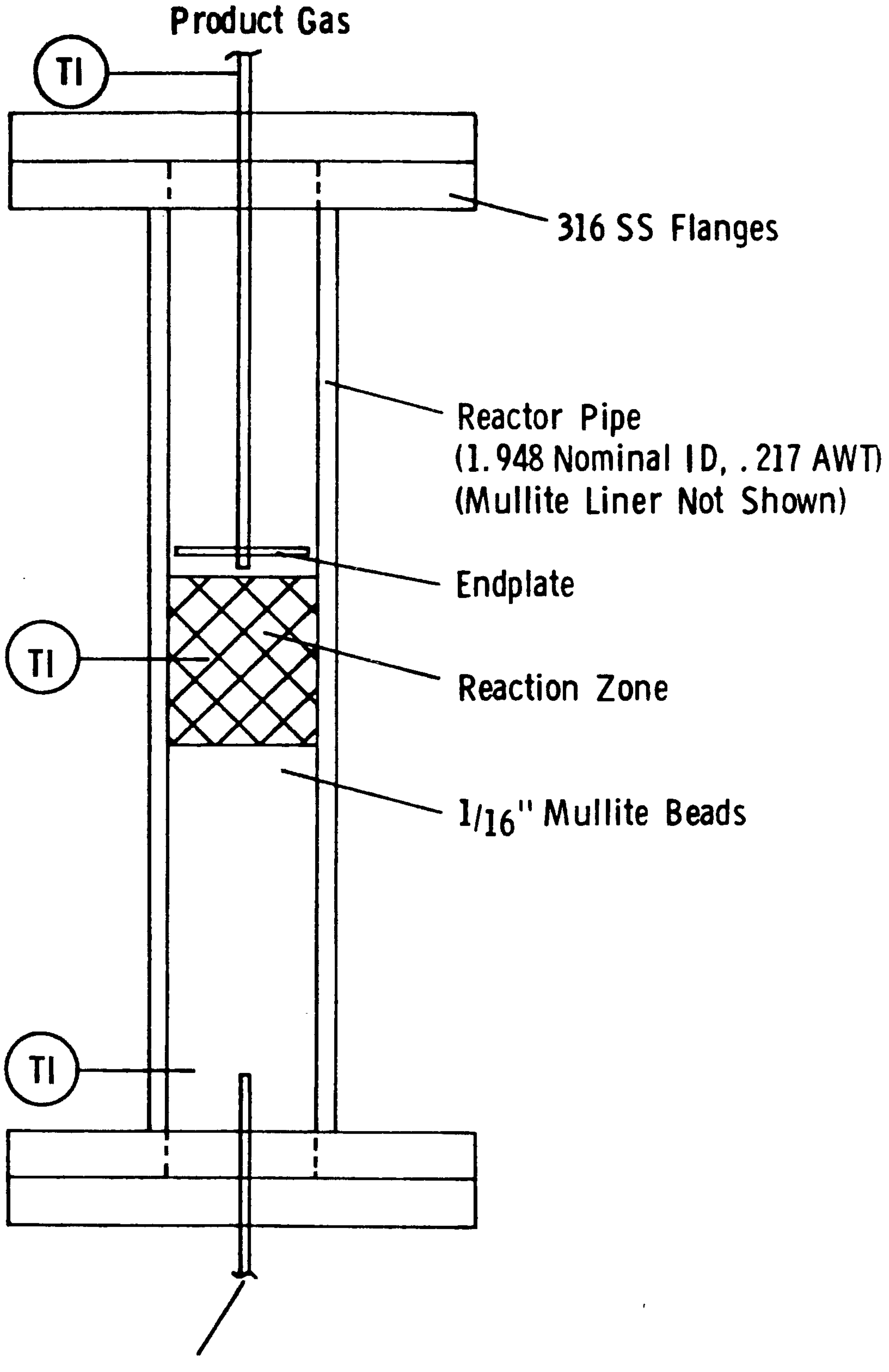


FIGURE 1.2-2

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 a. Programmable Controller "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.	Inspection by qualified technical person to determine proper functioning of all systems.
b. Checkout of Block Valves 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 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 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 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 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.

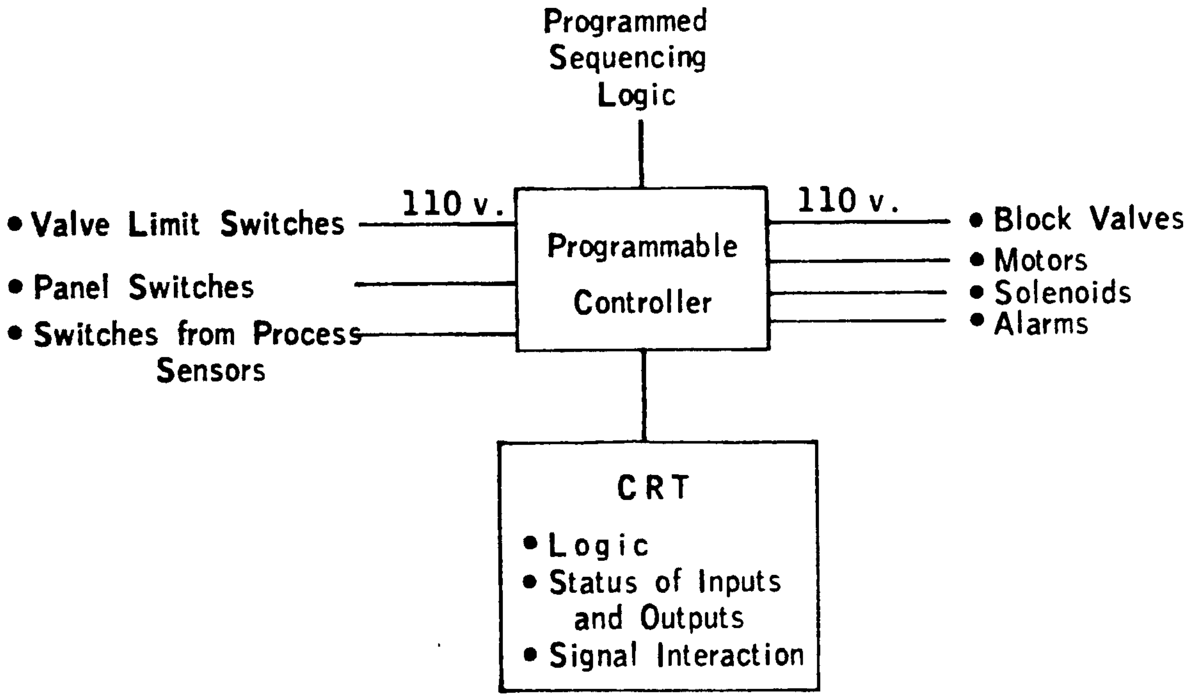
Programmable Controller

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.

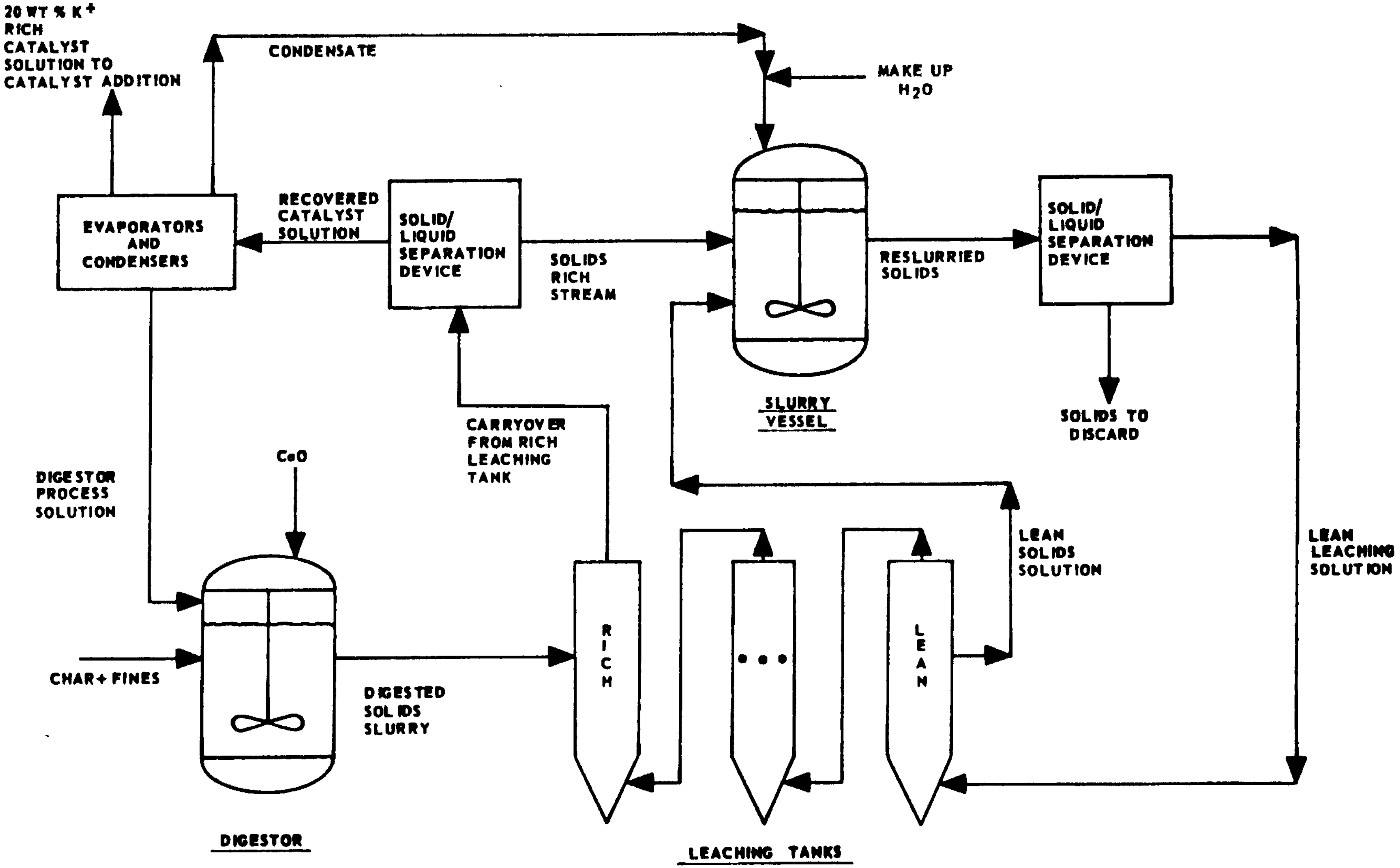
Table 2.2-1

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

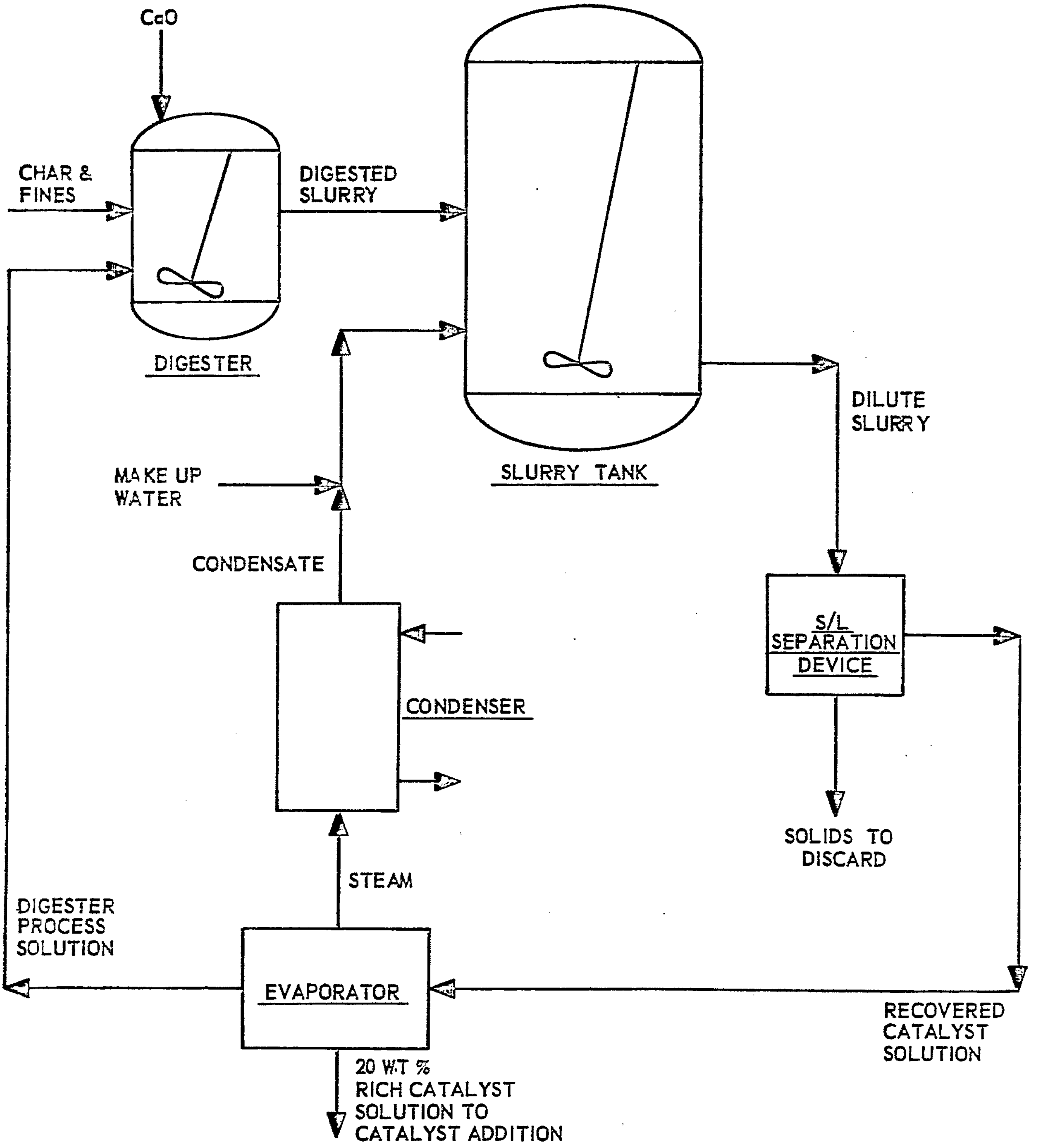


FIGURE 2.2-3

SEPARATORS AND MIXING TANKS IN SERIES

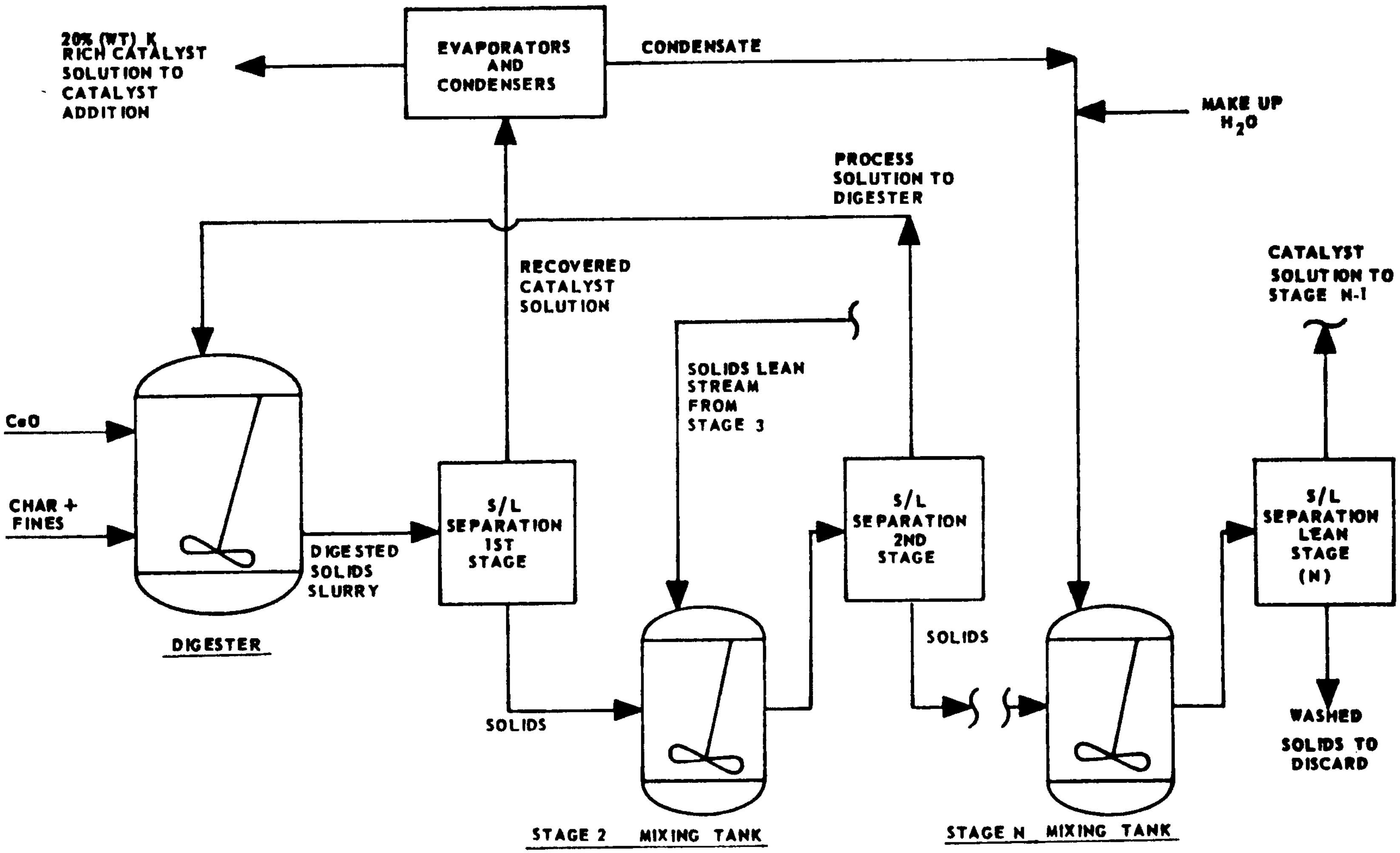


Table 2.2-2

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 µ 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 µ 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.

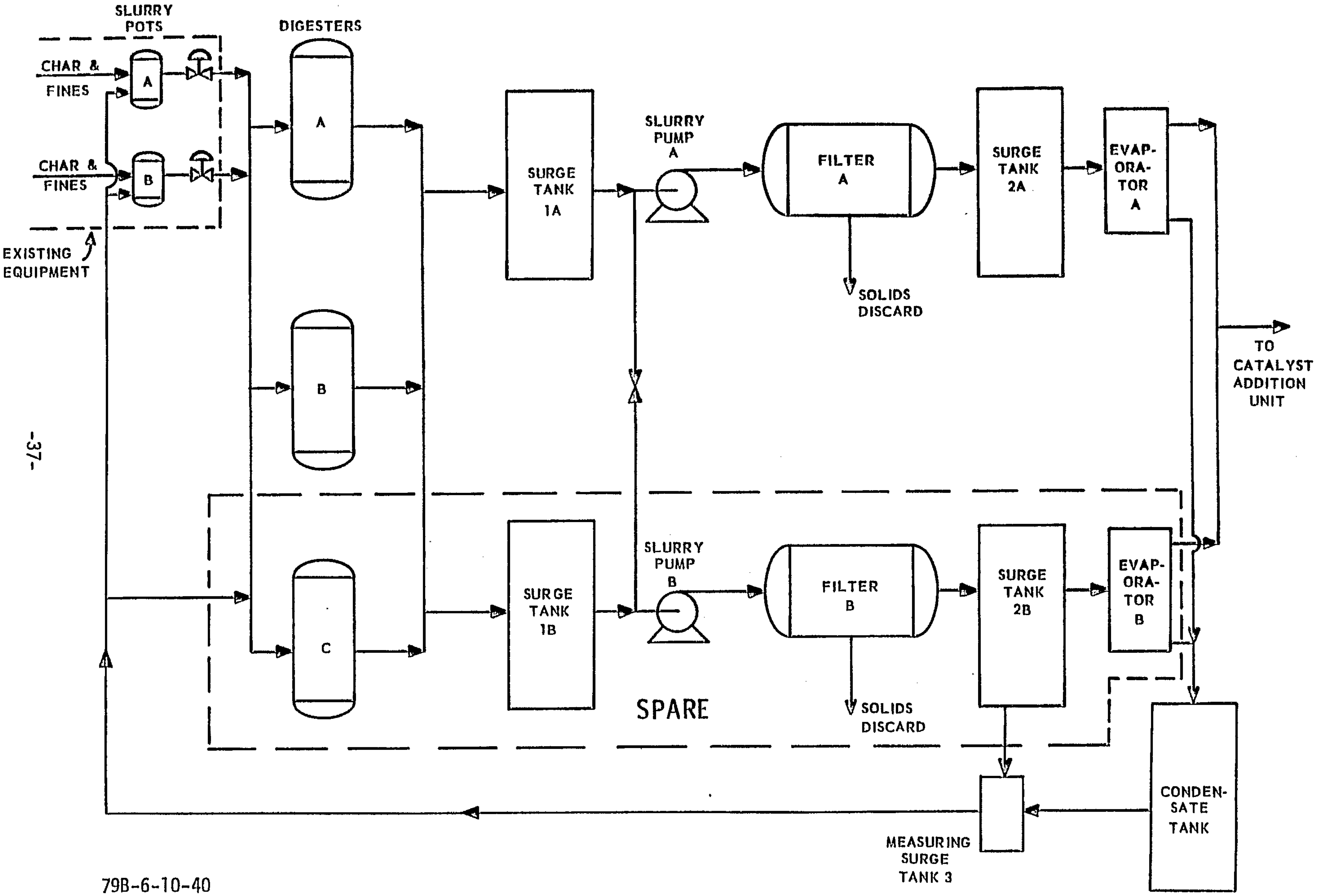
Detailed Design of PDU Catalyst Recovery System

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



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

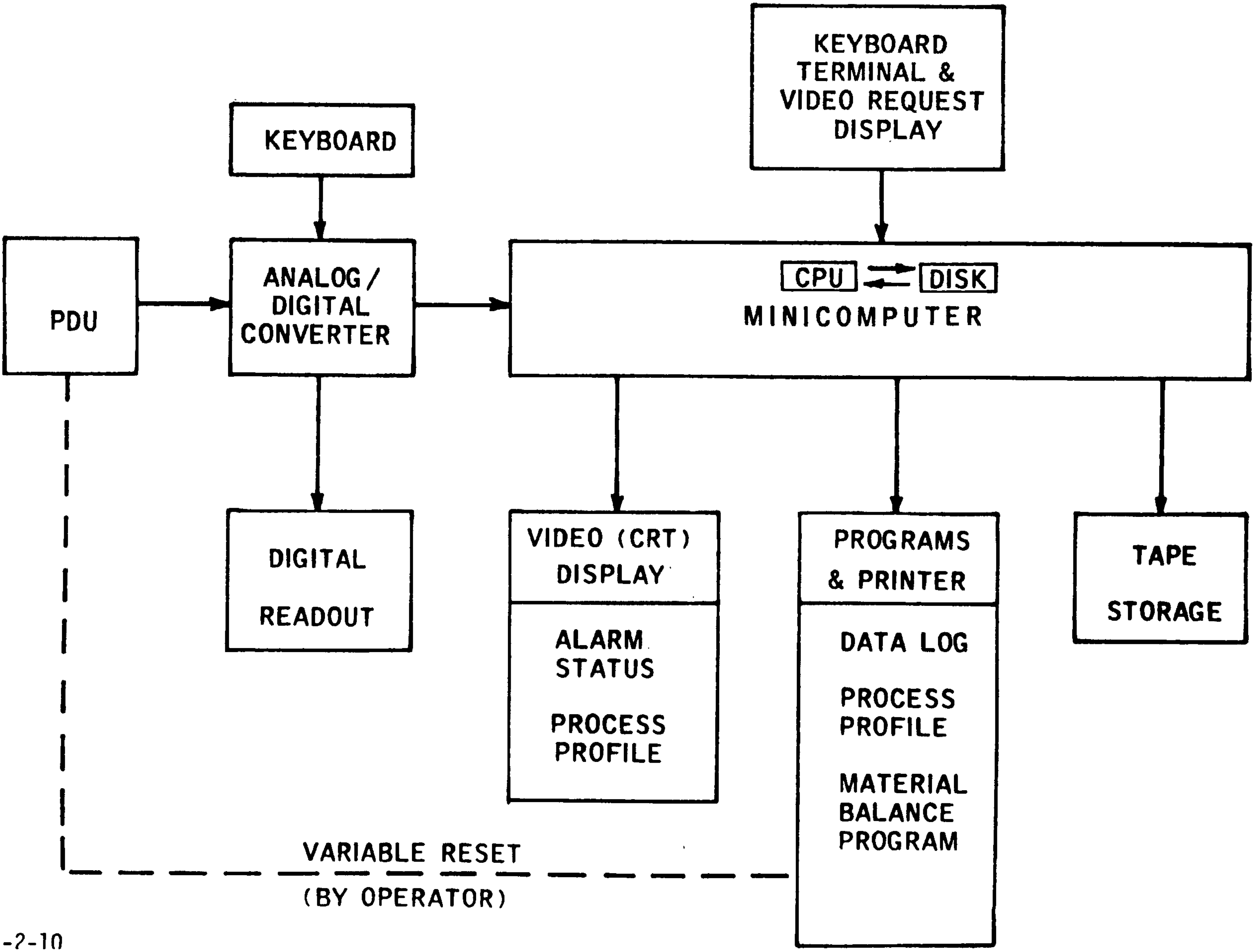
During unit operations, the values of all process variables will be instantly available to the operators in the form of a digital readout accessed by a keyboard in the control room. The computer has also been programmed to provide process operation profiles displayed on the operator request CRT screens.

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:	$CO + 3H_2=H2O + CH_4$	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

σ_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:

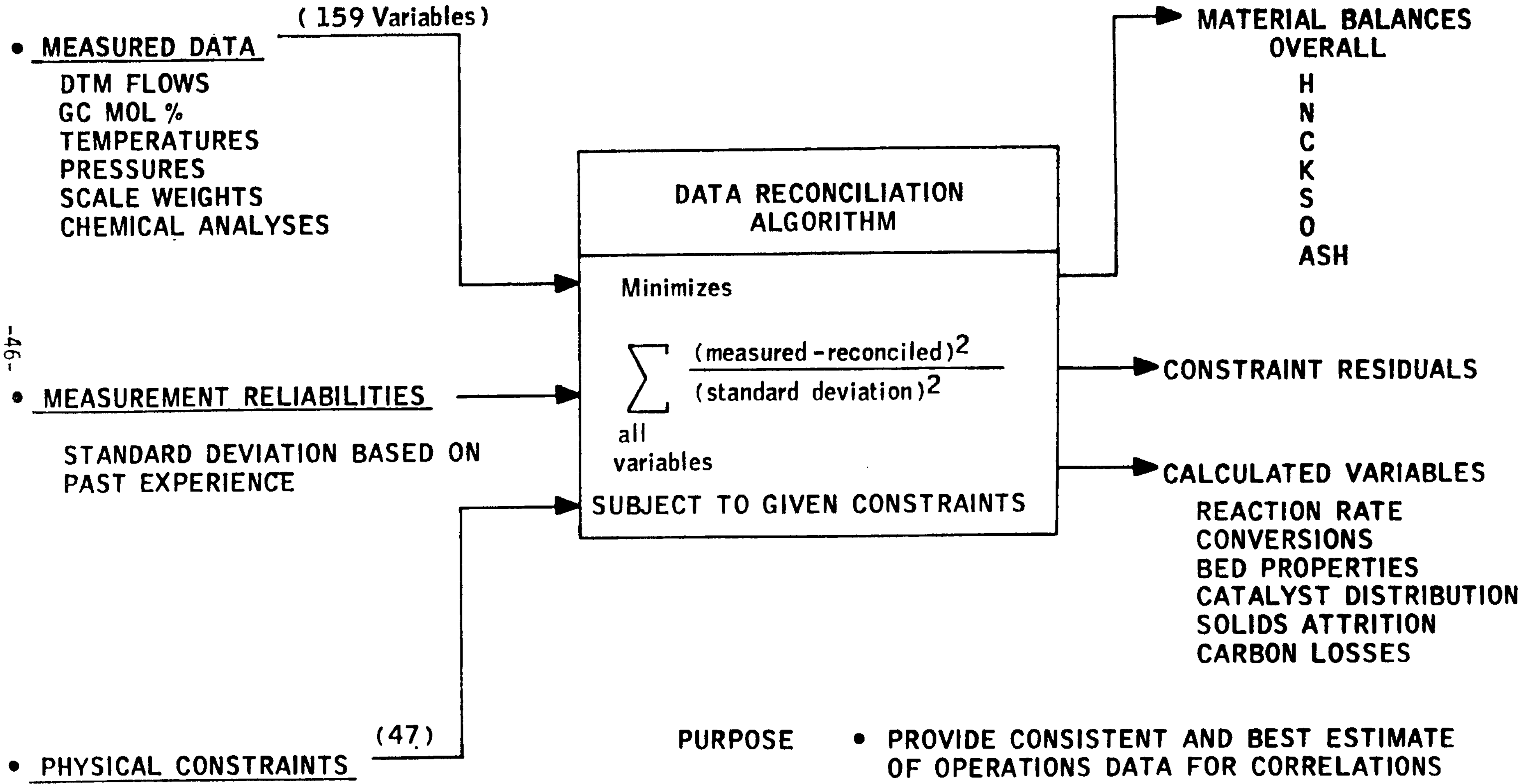
$$\sigma_i = M_i \cdot rel_i/200$$

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

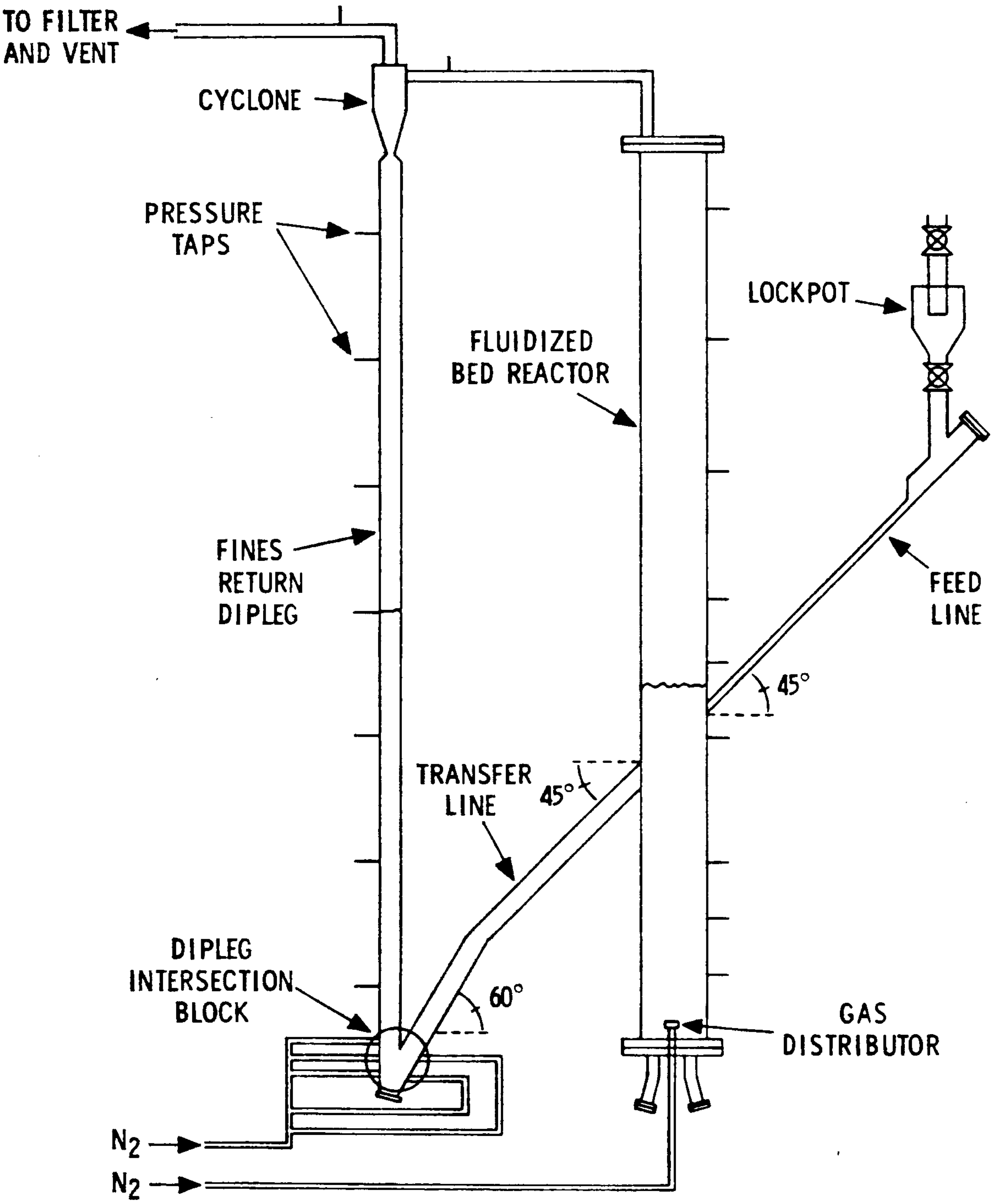
A cold model of the PDU was constructed to assist in troubleshooting solids flow problems as they arise in PDU operations. Throughout the startup and initial operation of the PDU, the transparent cold model has proved valuable in providing visual understanding of many of the solids flow problem areas. 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

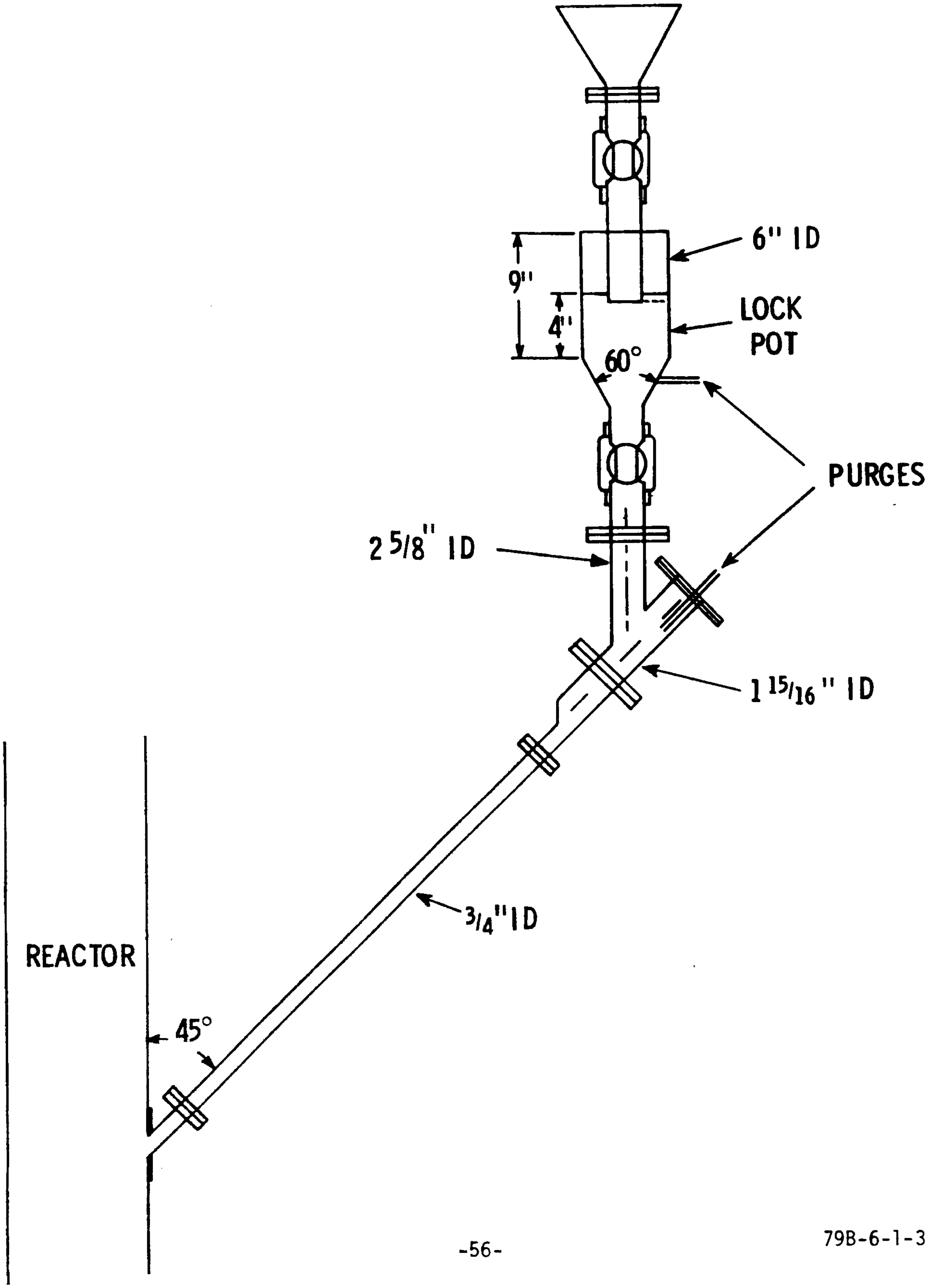


FIGURE 3.3-3

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

EFFECT OF BED HEIGHT

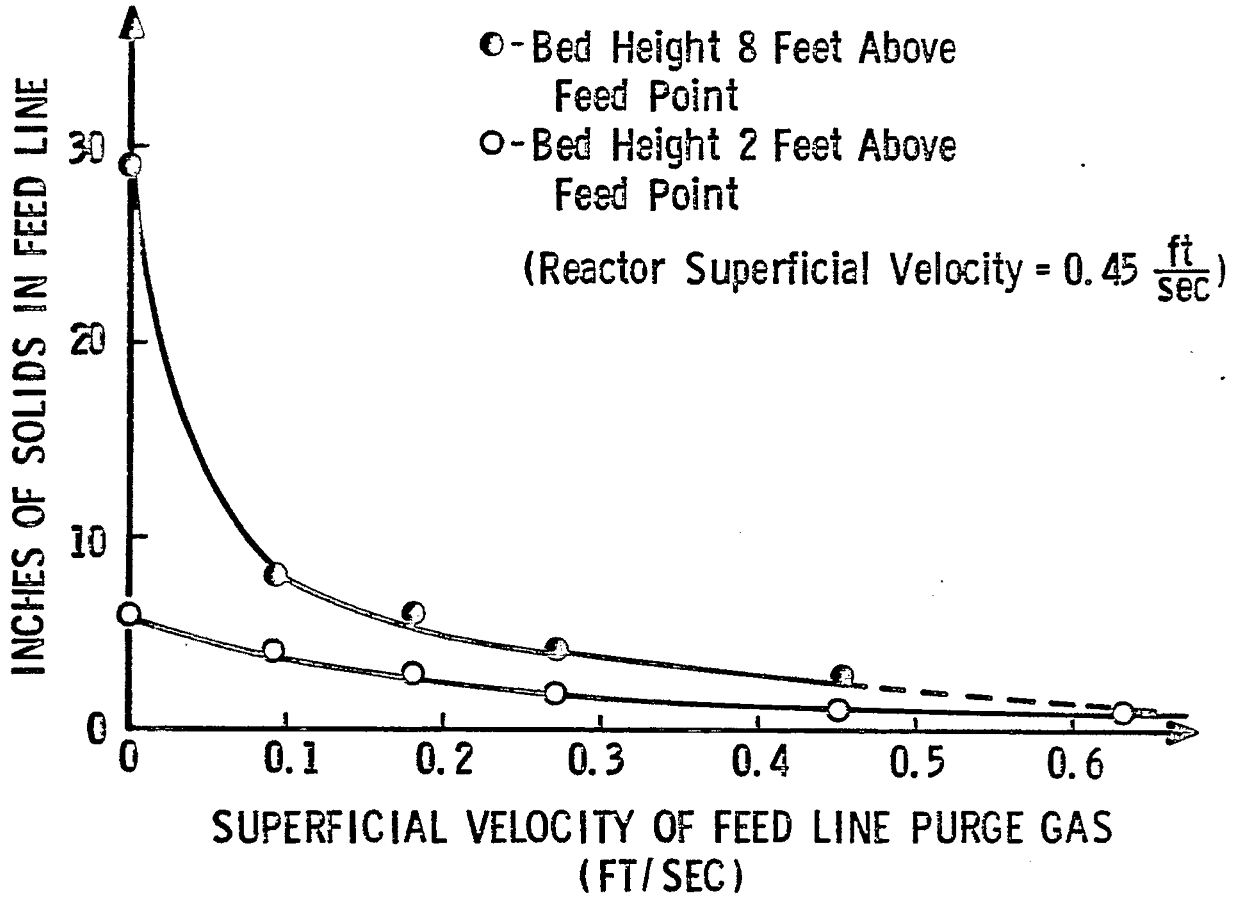
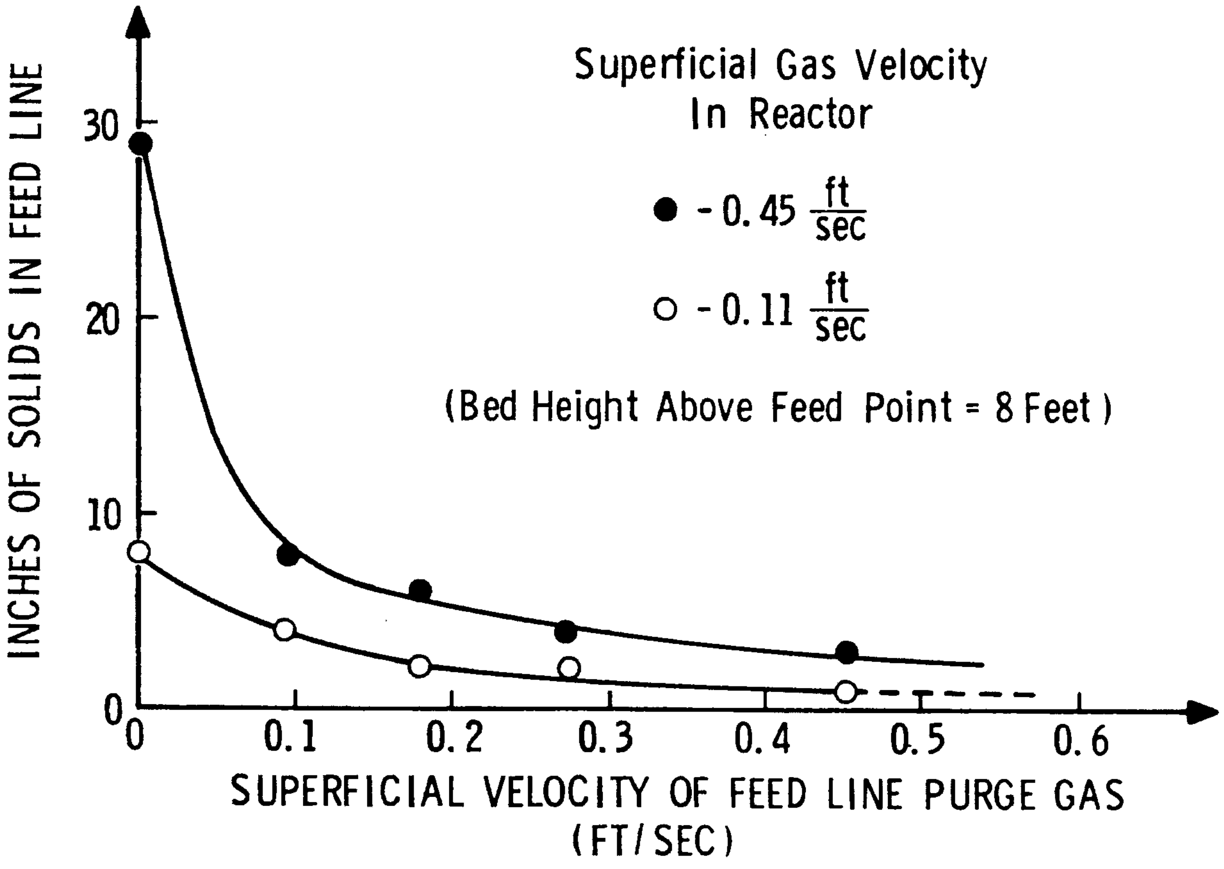


FIGURE 3.3-4

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.

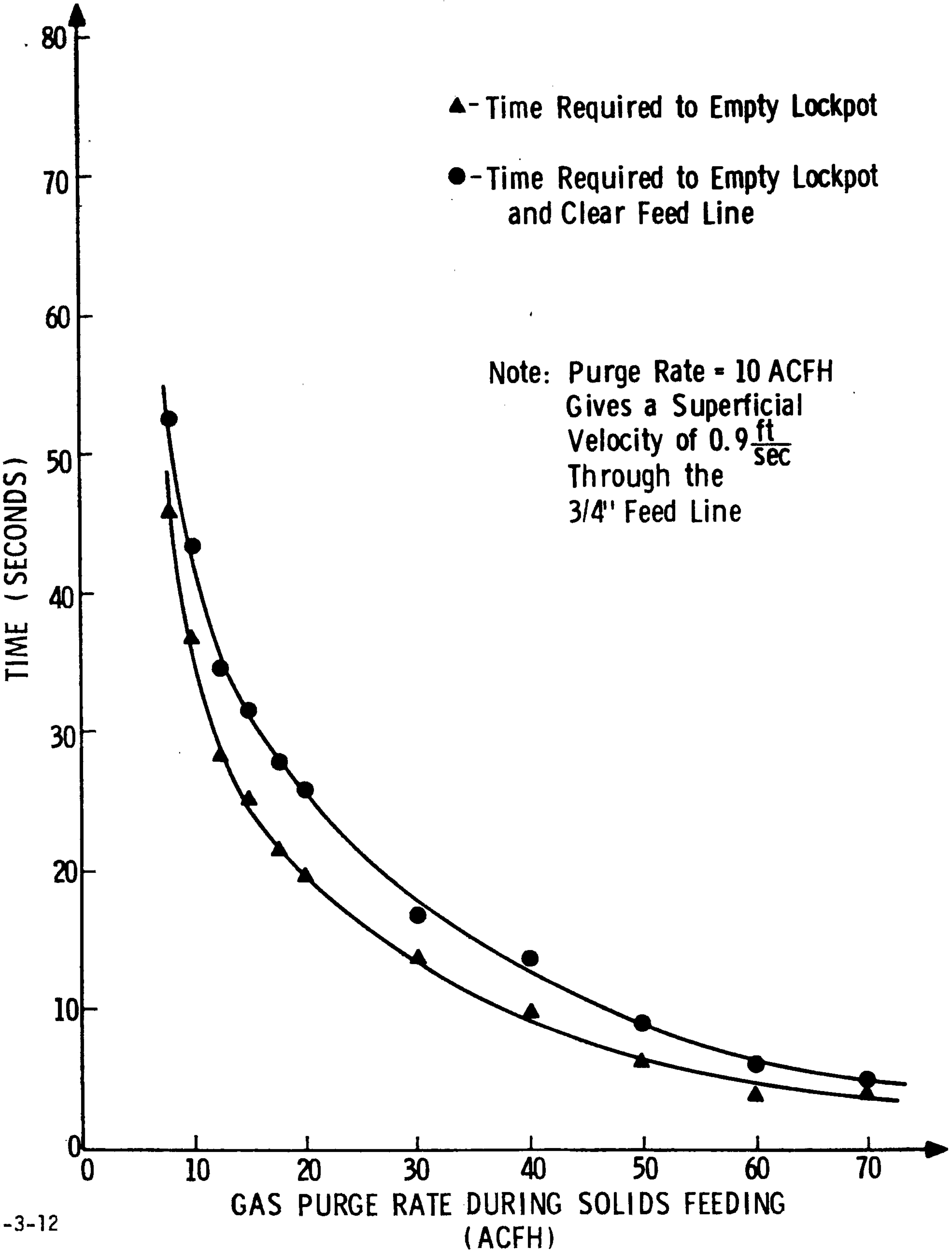
As shown in Figure 3.3-2, after the solids leave the lockpot, they travel through the feed line and into the reactor. The first part of the line is vertical with an inside diameter of 2-5/8 inches. It then goes through a 45° bend and into an eccentric reducer where the line is reduced to 3/4 inches inside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



Note: Purge Rate = 10 ACFH Gives a Superficial Velocity of 0.9 $\frac{ft}{sec}$ Through the 3/4" Feed Line

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