EXXON CATALYTIC COAL-GASIFICATION PROCESS DEVELOPMENT PROGRAM. QUARTERLY TECHNICAL PROGRESS REPORT, OCTOBER-DECEMBER 1979

EXXON RESEARCH AND ENGINEERING CO.
BAYTOWN, TX

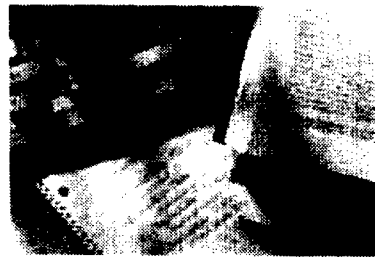MAR 1980

EXXON CATALYTIC COAL-GASIFICATION PROCESS DEVELOPMENT PROGRAM

MASTER

QUARTERLY TECHNICAL PROGRESS REPORT

FOR THE PERIOD

October - December, 1979

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March, 1980

ABSTRACT

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

The highlights of this report are summarized below:

● Bench Scale Research and Development

Bench tests of flocculant treated water washed chars show that the
flocculant increases sedimentation rate by a factor of two or more and remains
effective for multiple settling cycles. Flocculant pretreatment was also
found to increase both sedimentation and filtration rates for digested char
slurries; however, the potential is not as great for digested material as for
previously tested water washed materials.

Deposition of carbon in the bench recycle gas furnace apparatus was
traced to the ceramic mullite beads used as filling in the tube. Carbon
deposition was eliminated by removing the ceramic beads. Some water gas shift
reaction was observed at temperatures above 1100°F, but the reaction rate is
low and the CO_2 concentration in the recycle gas from the commercial furnace
should be less than 1 mole percent.

● Process Development Unit Operations

Syn gas (H_2 and CO) was introduced into the gasifier for the first time
during October. The unit ran for seven days with steam and syn gas as feed to
the bottom of the reactor. During November the Process Development Unit (PDU)
completed two sustained periods of operation of 144 hours and 110 hours with
syn gas (75% H_2 and CO) in the reactor. During December a 145 hour run
was made with carbon conversions of 80 to 90%. The dry nitrogen-free product
gas contained 20 to 30% methane.

Final equipment specifications and detailed flow diagrams were completed
early this quarter for the PDU catalyst recovery unit. Construction began in
October. Currently, all major equipment items are in place and process piping
is nearing completion. Filtration experiments have proceeded using rented
filters.

● Advanced Study of the Exxon Catalytic Coal Gasification Process

Mini-fluid bed runs have shown that impregnating steady-state gasifier
char with additional catalyst increases gasification rate; however, increases
in the potassium-to-carbon ratio via further gasification of a steady-state
gasifier char in the mini-fluid bed did not increase gasification rate.

Bench scale studies have shown that changing the devolatilization pressure from 100 psia to 500 psia significantly alters the char properties. Operation at 100 psia produced chars similar to chars from earlier atmospheric test units; however, 500 psia operation produced both finer particles and lower density chars.

● Engineering Research and Development

Work continued on the catalyst recovery screening studies to evaluate the economic impacts of alternative processing approaches and solid-liquid separation techniques. Equipment specifications have been completed for two cases with countercurrent water washing using rotary-drum filters for the solid-liquid separations. Case 1 includes an initial lime digestion step, while Case 2 uses water washing without digestion. Equipment sizing is in progress for Case 3, employing water washing and gravity settlers.

Material and energy balances have been completed for an alternative methane recovery process configuration using low pressure stripping. The alternative system requires 26% less horsepower than the Study Design system.

A study has been initiated to identify trace components which might be present in the CCG gas loop and to assess their potential impacts on the CCG process. This information will be used to assist in planning an appropriate series of analyses for the PDU gasifier effluent.

A study has been initiated to evaluate the use of a small conventional steam reformer operating in parallel with a preheat furnace for heat input to the catalytic gasifier. This alternative, called supplemental steam reforming, avoids the potential problem of carbon laydown.

Preliminary replies from ten manufacturers are being evaluated as part of a study to determine the types and performance of coal crushing equipment appropriate for commercial CCG plants.

A material and energy balance computer model for the CCG reactor system has been completed. This model consists of four major blocks and a process simulation network which links them together. The new model will provide accurate, consistent and cost-efficient material and energy balances for the extensive laboratory guidance and process definition studies planned under the current program.

Activities continued in the engineering technology programs:

- The materials evaluation program using corrosion racks and probes in the PDU is being implemented as planned.

- Laboratory batch filtration results were revised and reassessed using data now available on potassium ion concentrations in the filtrates. The major conclusions reported previously were not changed by these revisions. In parallel work, the batch filtration unit is being modified to produce thinner cakes more representative of commercial operation.

- Work is underway to develop preliminary estimates of atmospheric emissions from a commercial CCG plant. The plans for sampling potential emissions sources were reviewed with PDU operating personnel.

- A simplified catalytic gasifier solids balance model, which assumes there is only a single solids species, predicted solids losses much lower than those estimated for the Study Design.

- The overall framework of the dynamic simulation of the CCG reactor system has been completed and work on the gasifier module is in progress.

TABLE OF CONTENTS

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

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

1.1 Flocculant Pretreatment of Catalyst Recovery Slurry

A bench scale program has been underway to study the potential benefits of flocculant pretreatment of char-catalyst slurries for solid-liquid separations. Initial screening tests were made on water washed char-catalyst slurries. The results of these tests were presented in the July - September, 1979 Quarterly Report. During this quarter the experimental program was completed for the water-washed slurries and screening studies were initiated on $Ca(OH)_2$ digested slurries.

Sedimentation of Water-Washed Slurries

Bench scale tests were carried out to determine settling rates of water-washed slurries in a 1000 ml hot water jacketed graduated cylinder (6 cm in diameter, 35 cm height). The objectives of these tests were:

a) to obtain settling data that can be used for the screening study of a commercial scale settler or thickener, and

b) to evaluate the integrity of floccules.

The water-washed slurries for lean-end settling tests were prepared by mixing one part (by weight) of Fluid Bed Gasifier (FBG) fines, two parts of FBG char and eight parts of water in a beaker. The slurries were then heated to 200°F, while stirring, for one hour. The slurries contained 8.2 wt.% solids and 2 wt.% KOH. The rich-end slurries were prepared by adding an extra amount of KOH into the char, fines and water such that the slurry liquids contained 10 wt.% KOH. The solid content of the rich-end slurries was 9.0 wt.%.

The sedimentation rate measurements for both blank and flocculant pretreatment cases were carried out repeatedly by remixing the slurries up to six cycles. The desired amount of D-25A flocculant (i.e., 25 ppm for lean-end slurries and 50 ppm for rich-end slurries) was added into the slurries at the first cycle; no additional flocculant was added in subsequent cycles. The final height of the solid-liquid interface of the first cycle was measured after the slurry sat overnight. The final solid-liquid interface height for subsequent cycles was measured after a similarly long period of time.

Figure 1.1-1 shows sedimentation results for the lean-end slurries in the 1000 ml graduated cylinder. Data points for blank runs at various cycles fall on a single curve, indicating that sedimentation rates, within experimental error, stayed about the same from one settling cycle to another.

FIGURE 1.1-1

SEDIMENTATION RATES OF LEAN-END WATER WASHED SLURRIES IN A 1000 ml HOT WATER JACKETED GRADUATED CYLINDER AND IN A 1000 ml BEAKER
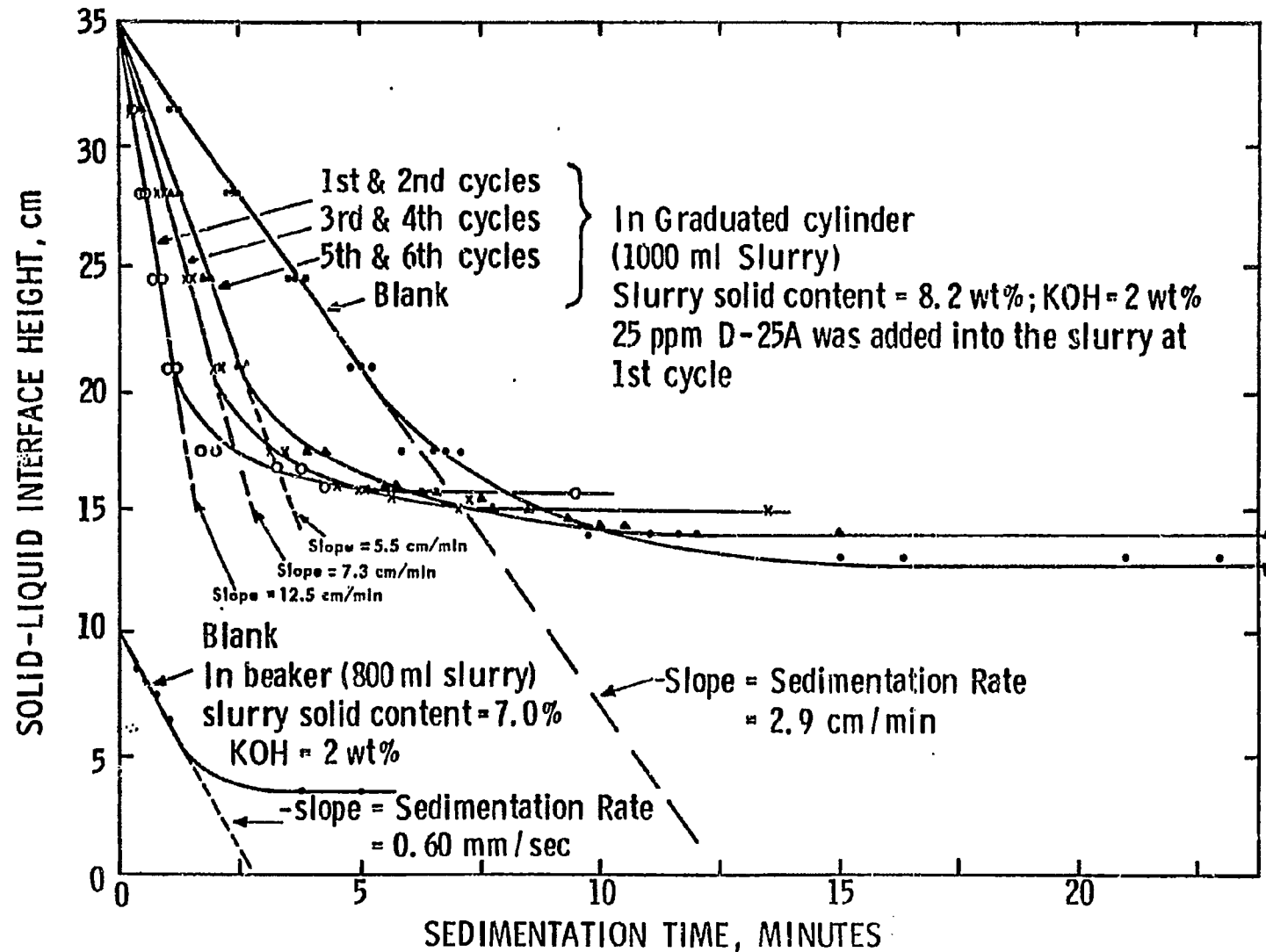
The initial sedimentation rate of blank runs was 2.9 cm/min. The total settling distance of the slurry particles in the graduated cylinder was 22 cm for blank runs, namely the initial and final heights of the solid-liquid interface are at 35 and 13 cm levels, respectively. After reaching the final settling level, the slurry solid content was concentrated from the original 8.2 wt.% to about 22 wt.%.

The data points of 25 ppm D-25A pretreatment runs can be grouped, within experimental error, into three curves; namely, one for the first and second cycles, another for the third and fourth cycles, and a third for the fifth and sixth cycles. The initial sedimentation rates of the three grouped curves are 12.5, 7.3, and 5.5 cm/min. The data show an improvement in the sedimentation rate by a factor of 2 to 4 depending on the cycle.

Figure 1.1-2 shows settling data of the rich-end water-washed slurries in the 1000 ml graduated cylinder. The sedimentation rates of rich-end slurries were, as expected, lower than that of lean-end ones; e.g., 1.8 versus 2.9 cm/min initial settling rate for blank runs. This was due to an increase in viscosity and density of the slurry liquids of the rich-end slurries. However, the characteristics of the settling curves for both lean- and -rich-end slurries were essentially the same. The total settling distance of the slurry particles was 21 cm and the slurry solid content was concentrated from an original 9.0 wt.% to about 22.5 wt.%.

Results of 50 ppm D-25A pretreatment runs can be grouped into two curves; one for the first and second cycles, the other for the third through sixth cycles. The initial settling rates of the two grouped cycles are 5.0 and 3.9 cm/min. The data show an improvement in the sedimentation rate by a factor of 2 to 3 depending on the cycle.

Note that the final solid-liquid interface height swelled about 4 to 8%, when the slurries were pretreated with 25 to 50 ppm of D-25A flocculant. After several settling cycles, it was necessary to add additional flocculant to bring the sedimentation rate back to the first cycle level.

This work concluded the experimental program of flocculant pretreatment on the water-washed slurries. The principal results are summarized below. Results from earlier screening studies (July - September, 1979 Quarterly Report) show that:

1. Anionic flocculants give better improvement in solid-liquid separation for the water-washed catalyst recovery slurries than do other types of flocculants. Furthermore, the D-25A flocculant is the best among the anionic flocculants that have been tested.

2. The optimal dosage of the D-25A flocculant is about 25 ppm.

3. When 2 wt.% K^+ water-washed slurries are pretreated with 25 ppm of the D-25A flocculant at 200°F, the filtration and sedimentation rates will increase by about a factor of 4.

FIGURE 1.1-2

SETTLING RATES OF RICH-END WATER WASHED SLURRIES IN A 1000 ml HOT WATER JACKETED GRADUATED CYLINDER

Blank

3rd & 6th cycles

1st & 2nd cycles

-Slope = 3.9 cm/min

-Slope = 1.8 cm/min

-Slope = Sedimentation Rate = 5.0 cm/min

Slurry solid content = 9.0 wt%
KOH in solution = 10.0 wt%
50 ppm D-25A was added into the slurry at first cycle

SOLID-LIQUID INTERFACE HEIGHT, cm

SEDIMENTATION TIME, MINUTES
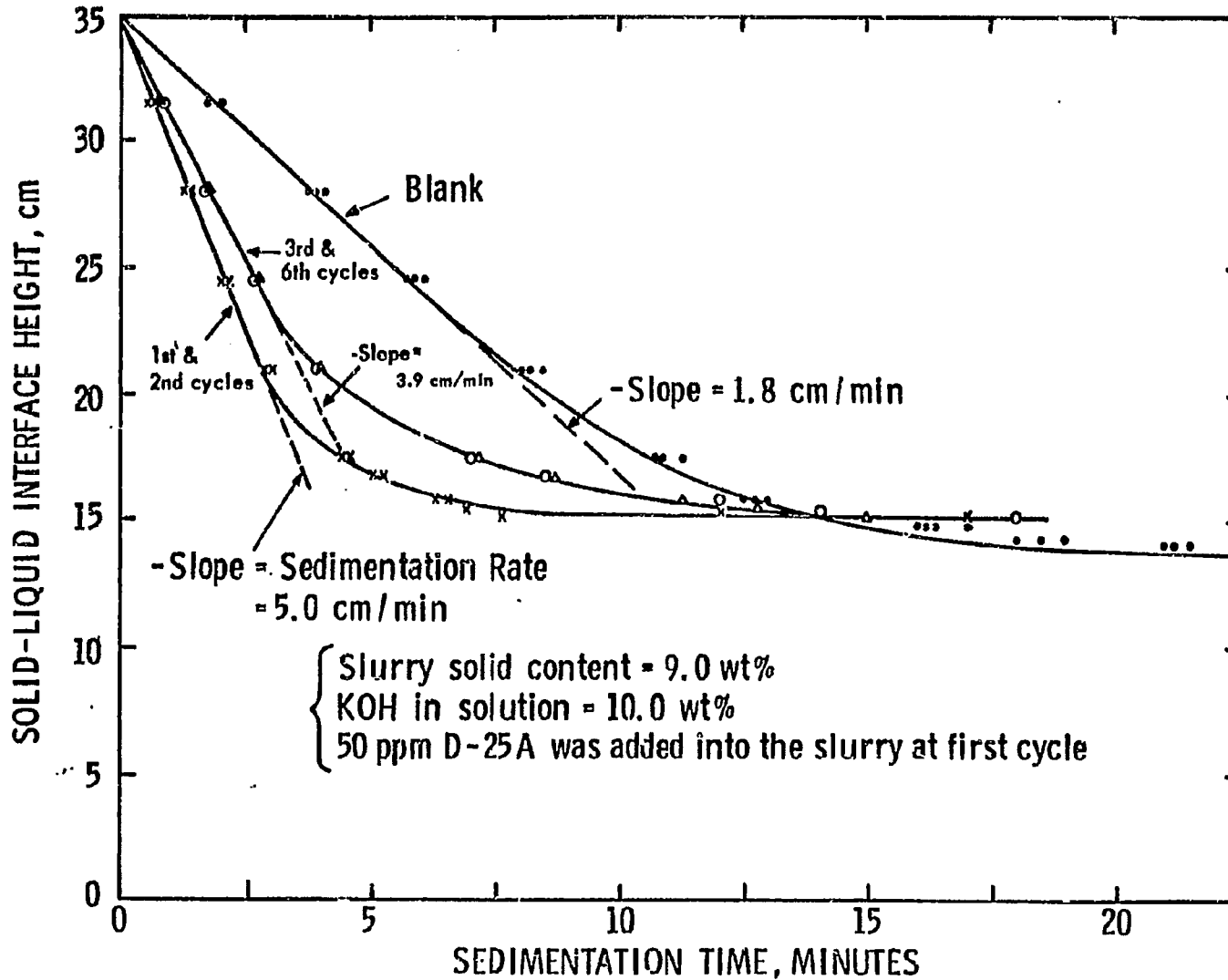
4. The improvement in filtration and sedimentation rates decrease as potassium concentration in the slurry liquids increases because of increases in the slurry liquid viscosity and density. However, flocculant pretreatment of the slurries improves both filtration and sedimentation rates even at a potassium concentration as high as 16 wt.%.

The work this quarter shows that the flocculant remains effective for multiple reslurrying cycles in sedimentation or filtration operation. This indicates that addition of flocculant to each stage is not necessary in a multi-stage solid-liquid separation unit.

Screening Study on Digested Chars

Experimental tests were initiated to study the effect of flocculants on the solid-liquid separation properties of $Ca(OH)_2$ digested slurries. The lime digested slurries were prepared in a prototype digester by mixing 1 part (by weight) of FBG fines, 1.7 parts of lime and 28 parts of 2.8 wt.% KOH solution. The mixture was stirred and heated to 300°F for one hour and allowed to cool to ambient temperature. Figure 1.1-3 gives the particle size analysis of a typical slurry sample. Three hundred (300) ml samples were placed in 400 ml beakers and heated to 200°F, while stirring, before a measured amount of flocculant was added. The solid content of the slurry samples varied from 11.0 to 13.5 wt.%.

Three types of flocculant samples (anionic, nonionic, and cationic) were tested on the basis of filtration and sedimentation rates. Table 1.1-1 gives a list of flocculants that have been tested. Table 1.1-2 shows the results of the screening tests. The principal results are as follows:

1. Among the flocculants that have been tested, D-25A, T-352A, and R-10A appeared to be best for improvement in solid-liquid separation of the digested char-catalyst slurries.

2. Filtration and settling rates were increased by a factor of 1.7 and 1.5 of the base case (blank run), respectively, when the digested slurries were pretreated with 25 ppm of D-25A flocculant. Higher dosages of flocculant increased the rates.

3. The extent of potential improvement in either filtration or settling rate with the flocculant pretreatment was less for the lime digested slurries than that for the water washed ones tested previously (July - September, 1979 Quarterly Report). Flocculant pretreatment was found to increase sedimentation and filtration rates by a factor of 2 to 5 for water washed chars, but only 1.5-1.7 for digested material. This finding may be because the digested slurries have a finer particle size distribution than the water washed ones.

Experiments will be continued on determination of optimum dosage of flocculant and integrity of floccules of the digested slurries.

FIGURE 1.1-3

PARTICLE SIZE DISTRIBUTION OF THE LIME DIGESTED SLURRY

Analysis of The Lime Digested Slurry

KOH in Liquid, Wt%	3.42
Solid Content, Wt%	13.5
pH of Liquid	13.7

CUMULATIVE % SMALLER THAN PARTICLE DIAMETER

PARTICLE DIAMETER, MICRONS
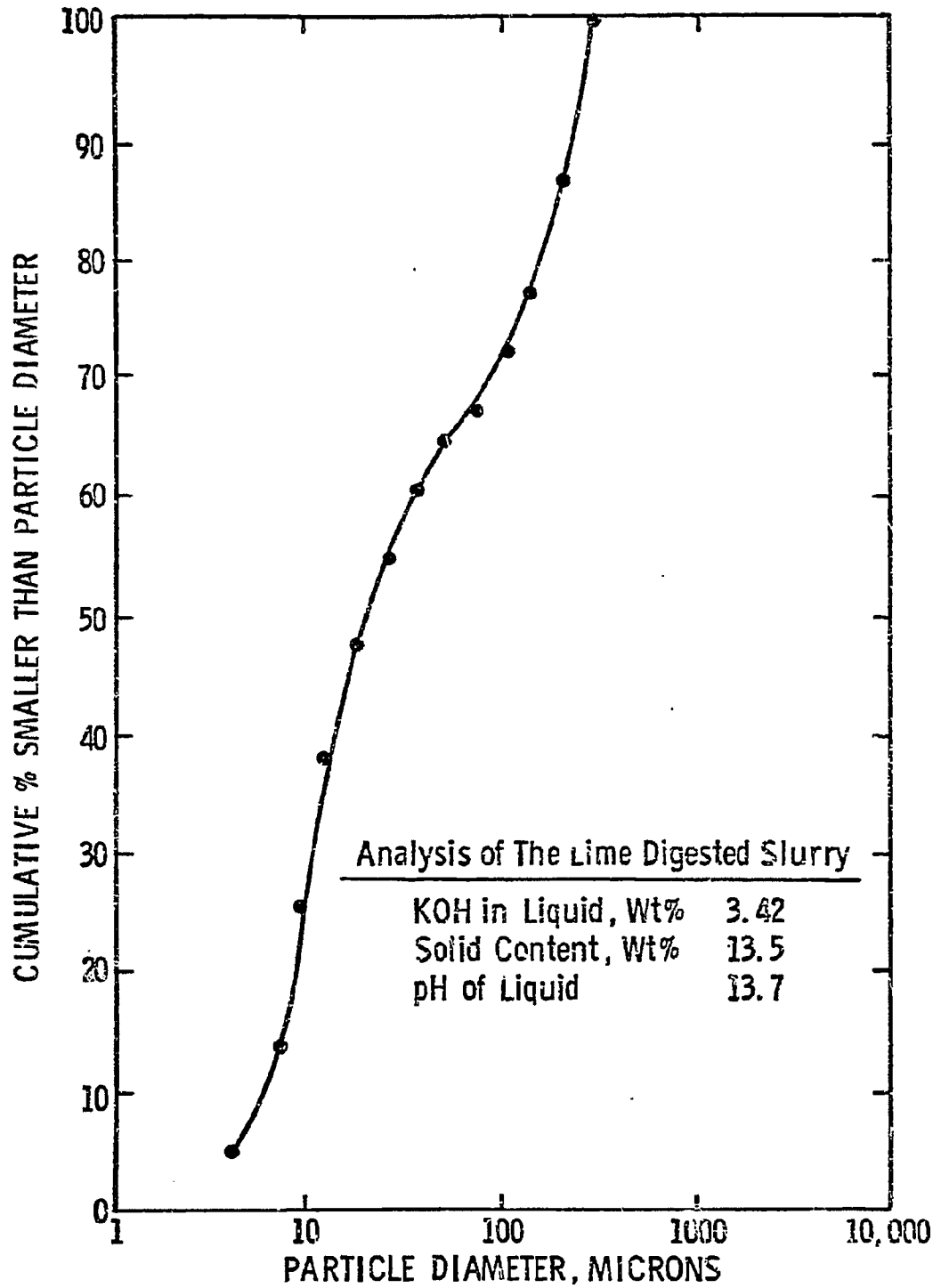
Table 1.1-1

Flocculants

Flocculant	Type
D-43C	Cationic
D-25A	Anionic
A-515C	Cationic
A-572C	Cationic
A-585C	Cationic
A-1839A	Anionic
A-1906N	Nonionic
T-5A	Anionic
T-2C	Cationic
T-352A	Anionic
T-381N	Nonionic
R-3C	Cationic
R-1129A	Anionic
R-1141A	Anionic
R-1142A	Anionic
R-10A	Anionic

Table 1.1-2

Flocculant Screening for Lime Digested Slurry

Flocculant	Dosage ppm	Relative Filtration Rate,% of Base	Relative Sedimentation Rate,% of Base	Slurry Solid Content, wt.%
None	0.0	Base (15 ml/min)	Base (3.2 cm/min)	12.2
D-43C	25	115	111	11.9
D-25A	25	170	150	12.8
D-25A	50	260	165	11.6
A-515C	25	98	110	11.8
A-572C	25	94	103	12.1
A-585C	25	110	120	11.1
A-1839A	25	150	111	11.7
A-1906N	25	123	95	11.4
T-365A	25	133	110	12.1
T-362C	25	140	116	12.2
T-352A	25	167	130	11.9
T-381N	25	125	90	12.1
R-3C	25	112	108	11.8
R-1129A	25	157	75	11.8
R-1141A	25	130	97	12.0
R-1142A	25	145	97	13.1
R-10A	25	175	140	13.5

Note: 1. Tests were done at 200°F.
2. Gravity filtration.
3. Slurry samples were 300 ml.
4. pH of the slurry liquids were 13.7.

1.2 Recycle Gas Furnace Studies

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. A bench scale program has been underway to investigate the extent of the shift and reforming reactions in this recycle gas stream at commercial conditions. The variables to be studied are temperature and the possible catalytic effect of different metals in contact with the hot gas stream. The bench scale apparatus is described in the July, 1978 - June, 1979 Annual Report. A comparison between the design parameters of the Study Design Recycle Gas Furnace and the bench apparatus is shown in Table 1.2-1.

Table 1.2-1

Design Parameters for Recycle Gas Furnace

	Study Design	Bench Unit
Gas Rate (lb. mole/hr)	131,000	0.04
Tube Passes	128	1
Flow Per Tube (lb. mole/hr)	1023	0.04
Metal Surface (ft^2 per tube)	413	0.02 → 1
Space Time (ft^2-hr/lb. mole)	0.4	0.5 → 25
Residence Time (sec.)	2.97	~3

Initial runs in this unit were terminated due to plugs formed by carbon deposition in the reactor. Operations early in this quarter were aimed at eliminating carbon deposition. Hydrogen sulfide (H_2S) was added to the reactor during runs. The addition was accomplished by bubbling a 10% H_2S in hydrogen gas mixture through the water reservoir before each run. The H_2S saturated water was used to raise steam for the reactor. Concentrations of H_2S as high as 150 ppm were attained in the total feed mixture by this method. Total CO_2 formation declined; however, carbon specks still appeared in the product line condenser indicating carbon laydown somewhere inside the reactor.

Photomicroscopic inspection of the mullite beads used as filling in the gas mixing section of the reactor tube revealed that carbon deposition was occurring on the surface of these ceramic beads. During November, the ceramic beads were removed from the reactor and crushed quartz was used as the fill material. Subsequent runs showed no evidence of carbon deposition anywhere in the gas line.

After solving the carbon laydown problem, interest shifted back to the extent of gas phase reactions in the simulated recycle stream. Table 1.2-2 shows the product gas compositions from a series of runs made with Alloy 617 in contact with the hot gas stream. For this series of runs, the residence time of the gas in the heated tube was held at study design conditions (2.97 sec.). The ratio of metal surface area to gas flow rate was slightly greater than the study design conditions (0.40 ft^2-hr/lb mole study design versus 0.51 ft^2-hr/lb mole experimental). Below about 1200°F, only negligible amounts of CO_2 were detected in the exit gas.

Table 1.2-2

Product Gas for Alloy 617 Runs

T, °F	CO	H_2	CH_4	CO_2	H_2O
			Mole %		
752	5.71	27.5	3.60	0.04	63.2
951	5.69	27.5	3.61	0.07	63.2
1151.	5.67	27.6	3.60	0.07	63.1
1350	5.48	27.7	3.61	0.20	63.0
1557	4.92	28.3	3.59	0.80	62.4

In order to test the sensitivity of this result to metal surface area, Alloy 20 wire mesh was placed in the heated reaction zone. For these experiments, the ratio of metal surface area to gas flow rate was 25.5 ft^2-hr/lb mole, over 60 times the commercial metal loading. Table 1.2-3 shows the product gas compositions for this series of runs. The CO_2 concentrations were greater for this series of runs. Furthermore, some of the CH_4 reformed to CO and H_2 in the 1560°F run, but this is probably due to using a fresh (unsulfided) metal surface for this run.

Table 1.2-3

Product Gas for Alloy 20 Runs

T, °F	CO	H_2	CH_4	CO_2	H_2O
			Mole %		
751	5.69	27.5	3.60	0.06	63.2
952	5.60	27.6	3.60	0.09	63.1
1154	5.16	28.0	3.59	0.54	62.7
1354	4.18	29.1	3.51	1.53	61.7
1560	4.98	32.1	2.41	1.80	58.7

In Figure 1.2-1, the CO_2 concentrations observed in the product gas for both series of runs are compared to CO_2 concentration levels calculated by assuming the feed gas mixture (5.7% CO, 27.5% H_2, 3.6% CH_4, and 63.2% H_2O) was allowed to come to shift equilibrium. The deviation from shift equilibrium decreases as temperature increases for both sets of runs. For the first series of runs, the observed CO_2 concentration was 18% of the equilibrium value at 1557°F. For the Alloy 20 runs, the CO_2 concentration was 42% of shift equilibrium at 1560°F.

The results from these runs indicate that the shift reaction is not rapid at study design conditions for the recycle gas furnace and the CO_2 concentration in the gas from the furnace should be less than 18% of equilibrium.

FIGURE 1.2-1

SHIFT REACTION IN RECYCLE FURNACE SIMULATOR

RESIDENCE TIME : 3 SECONDS

Calculated for
shift equilibrium

○ 1.2 times commercial loading
of Alloy 600

△ 60 times commercial loading
of Alloy 20

(Y-axis: % CO_2 IN RECYCLE GAS STREAM)

(X-axis: TEMPERATURE, °F)
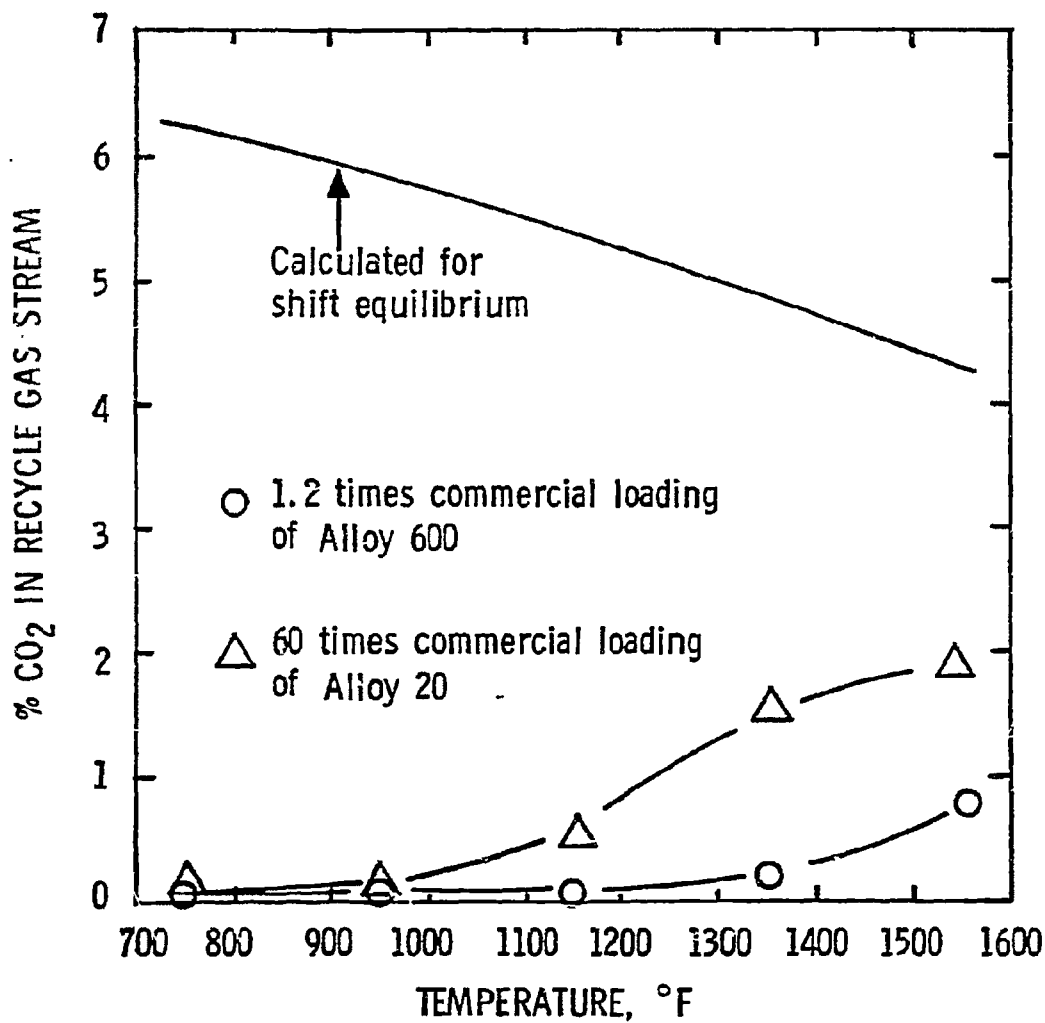
2. Process Development Unit Operations
(Reporting Category CO2)

2.1 PDU Startup and Initial Operations

PDU operations for the month of October consisted of flow tests, fluidization tests, and the introduction of hydrogen and carbon monoxide (syn gas) to the feed of the gasifier. A turnaround of the unit for syn gas startup was completed in the first part of the month. This was followed by a series of flow and fluidization tests aimed at increasing the precision of measurement of several process variables. Near the end of the month, the unit was started up and ran for seven days with steam and syn gas as feed to the bottom of the reactor.

Flow Tests

During the turnaround, changes were made to increase the accuracy of reactor pressure drop measurements. In the old system, reactor pressure drop was determined by measuring the pressure difference between a controlled intermediate reference pressure and the reactor pressure. In its place, a system connecting each tap through a differential pressure transmitter to the tap at the top of the gasifier was installed. The new system has eliminated many of the inaccuracies of the reference pressure system.

After the turnaround, operations of the PDU began with several flow tests. These tests were conducted in an effort to increase the accuracy of the information used in the PDU material balance program. Several of the studies dealt with pressure drop measurements across the fluidized bed and the sensitivity of the new instrumentation used. Pressure taps are purged with gas that flows into the reactor to keep solids from clogging the line to the transmitter.

Fluidization tests with FBG char saved for PDU startup were conducted in order to check out the pressure tap system under dynamic conditions. A fluidized bed density of about 15 lb/ft^3 was measured which is comparable to FBG fluidized bed densities measured with the same char.

Synthesis Gas Introduced to Gasifier

Leak testing of the PDU syn gas systems was delayed for several days by failures in the programmable controller and the C-2 compressor. Once the problem with the programmable controller was found, several days were spent reworking and changing out all of the system input/output housings. Shortly thereafter, a connecting rod in the C-2 compressor came loose.

Compressor C-1 was also inspected and found to be heavily worn. The compressors were rebuilt after consulting with the factory representative. Three possible causes of the compressor failures were discussed: poor quality control in the construction of the compressor; a hydraulic relief valve that was set at too high a pressure; and the use of a non-recommended oil in the compressor.

Testing of the syn gas systems was completed with a successful cold leak test of the unit using hydrogen gas. When hydrogen was first introduced, the safety relief valves on the gasifier, the hydrogen manifold, and the carbon monoxide manifold released below their set points. This caused some concern for the frequency of inspections of safety valves in severe service. These valves were identified and the routine inspection frequency was increased to four times per year. After the safety relief valves were reset, the hydrogen leak testing was completed.

Syn gas was introduced to the bottom of the reactor in a series of short intervals. This procedure was used in order to minimize the chances of a serious fire resulting from any leaks on the unit. The intervals began with a 60-second burst and increased through five minutes, thirty minutes and one hour before syn gas was put in continuously. No detectable leaks occurred during the introduction of syn gas.

After continuous addition of syn gas was achieved, steam and coal were put in the unit. The unit ran well for about two hours, then trouble developed in the char withdrawal system. Chunks of char appeared in the char slurry system and reduced the char withdrawal rate. The coal and steam feed had to be reduced accordingly and even had to be stopped altogether several times, for periods up to five hours, in order to compensate for the slow char withdrawal rate. After about five days of rough operations, the chunks disappeared and unit operations smoothed out.

The unit ran smoothly for the next two days, feeding at a nominal 100 lbs/hr coal feed rate. Operating conditions were 1250°F and 500 psia, with rates of 150 lbs/hr steam, 2000 SCFH fluidization syn gas and 1500 SCFH nitrogen purge. Typical dry and nitrogen free product gas analyses during this period were 64% hydrogen, 18% carbon dioxide, 9% carbon monoxide, 8% methane and 1% hydrogen sulfide. The unit was brought down when a pressure let-down valve on the filter/scrubber bypass system eroded through.

A new type of stainless steel filter element was installed in October to remove fines carried over in the product gas stream. The previous system used a glass weave construction that would tear when subjected to high pressure drops resulting in contamination and plugging of the water scrubber. The new filter element consists of 316 stainless steel wires drawn in a random matrix, compressed and sintered. This provides a rugged media which can be cleaned by backflushing. The new filter element was found to be a definite improvement. The new filter system started leaking fines into the scrubber after several weeks of operation. It was found that the unsupported filters fail when subjected to large pressure drops during unit upsets. Steps are being taken to eliminate this problem.

November Operation with Simulated Recycle

The highlights of November operations were two sustained runs of the gasifier section with syn gas (75% H_2 and 25% CO) in the bottom of the gasifier. The service factor of the gasifier for the entire month increased to 30%. During the two runs the unit was operating at conditions of 1250-1300°F and 500 psia with feed rates of 100 lbs/hr steam, 2500-3500 SCFH syn gas and 40 to 100 lbs/hr coal. The catalyst loading was 12.5 wt.% KOH on coal. Superficial velocity at the bottom of the reactor was 0.2 to 0.25 ft/sec.

In the first run, the material balances were in the 85-90% range with 50% carbon conversion and 20% steam conversion. The overall run time was 144 hours; however, several interruptions of feeding and withdrawing for four to six hours occurred. The run was terminated by a leak on the filter bypass line downstream of the gasifier.

The second run lasted for 110 hours. The operation was smooth and well controlled except for a four-hour interruption to change a filter blow-down valve. Nitrogen was replaced with syn gas in all injection points except the coal feed line. Nitrogen content in the dry product gas dropped from 45% to 30%. Typical dry and nitrogen free product gas contained 55% hydrogen, 6% carbon monoxide, 23% methane, 15% carbon dioxide and 1% H_2S. This analysis represents a significant increase in methane over previous operations. Carbon conversions were between 55% and 70% and steam conversion reached 30%. The estimated gasification rate (devolatilization included) was about 65%/hr.

The unsteady coal feed rate was due to occasional feed line plugs and slow char withdrawal operation. Pressure tap readings showed the presence of small bridges at or above the feed point on a few occasions. The bridges were probably formed when the coal was fed above the bed in the reactor. The char withdrawal legs were plugged by chunks a few times. There were two types of chunks--a porous, shiny type with high carbon content (62%) and harder chunks with low carbon (3%) and high ash (88%) contents. The chunks with high carbon content may be caused by collapsed bridges. Those with high ash content probably result from stagnant zones at the gasifier bottom. In the latter part of this month's operation, the bed level was always kept above the feed point and bed slumping was avoided. Preliminary indications are that chunk formation was reduced.

December Operations

PDU operations for the first half of December consisted of a short turnaround during which the char withdrawal valves were repacked. This turnaround was followed by a six-day gasification run.

During startup a gas leak was discovered coming from the middle char withdrawal valve going to char slurry pot D-6. The packing material used on these valves was an asbestos weave impregnated with graphite. In service this packing was found to harden causing the valve stem to stick and to

promote leaks. Consultation with the valve manufacturer revealed that this leakage is a common problem with this type of material. Packing on all char withdrawal valves was changed to an all graphite compressed ribbon on the four inner packing rings and an all graphite weave packing on the ends. The new packing has given excellent service with no leakage and has not required replacement to date.

In preparation for the gasification run, a fluid coke was loaded as an initial startup material for the unit. This material has advantages for startup over regular gasifier char. It is a relatively dense, inert material with a narrow size distribution. It is easy to transport, load, fluidize and withdraw from the unit. During startup fluid coke behaves well and does not tend to elutriate or form chunks.

The gasification run for December consisted of 146 hours of operation of the gasifier section with syn gas (75% H_2 and 25% CO) and steam. Nitrogen continued to be used in the coal feed line. The unit operated at 1280°F and 500 psia with feed rates of 100 lbs/hr steam, 3500 SCFH syn gas, and 50 lbs/hr catalyzed coal. The catalyst loading was 12.5 wt.% KOH on raw coal. Material balances were in the 90-100% range with carbon conversions of 80 to 90%. Steam conversion was about 25%. Nitrogen content of the dry product gas was 34% and the dry nitrogen-free product gas contained 24% methane. Table 2.1-1 compares the December run with study design conditions and with an earlier run made during August, 1979 before syn gas had been introduced to the gasifier. This data shows that the PDU gasifier chemistry is approaching study design conditions.

Table 2.1-1

Gasification Chemistry Approaches Study Design

	August 1979	December 1979	Study Design
Pressure, PSIA	500	500	500
Temperature, °F	1200-1250	1280	1275
Recycle Gas	N_2	H_2, CO, N_2	H_2, CO, CH_4
Run Duration, hrs.	165	146	
Carbon Conversion, %	80-90	80-90	90
Methane in Product Gas (N_2 Free)%	5-10	20-30	34

During the run difficulty was encountered feeding coal and on several occasions the feed line plugged and had to be blown clear. Char withdrawal was also difficult because of the presence of chunks. On one occasion, efforts to clear the char withdrawal leg resulted in a plugged product gas line. This plug was cleared and the run resumed. Operations were terminated when it became apparent that deposits were forming in the gasifier. These deposits were washed out during the turnaround after the unit had been cooled. The deposits were water soluble. These deposits are believed to be initially formed in the coal feed line. In subsequent operations higher gas flow rates in the feed line will be used to disperse the coal going into the gasifier more effectively.

2.2 PDU Catalyst Recovery Design and Construction

During this quarter, detailed flow diagrams were completed for the PDU Catalyst Recovery System. Once the flow diagrams were complete, process and instrumentation equipment was ordered, and unit construction was begun. In addition, tests were run this quarter on rental filters to develop the operation scheme for the PDU system.

Unit Construction

The first step of construction was setting the foundation for the unit. When the foundation was complete, the platform was erected. This platform is twelve feet high and supports the filter and evaporators. Supporting the filters above ground level allows the filter cake to fall into drums on the ground level where it can be easily weighed. In addition, the platform allows easy access for service and repair of the agitators on the surge tanks.

Next the vessel weigh platforms were installed and the surge tanks were placed in the structure on the weigh platforms as they were received. A char slurry transfer line was installed between the PDU char withdrawal system and the digesters. Finally, utilities such as industrial water, plant air, and plant nitrogen were installed in the unit.

Process construction was also started during this quarter. Figure 2.2-1 is a schematic of the Catalyst Recovery Unit as outlined in the July, 1978 - June, 1979 Annual Report. In order to begin startup of the unit as soon as possible, it was decided to concentrate upon building the main train of the system for use in the water/wash mode. This train consists of one digester, two surge tanks, one filter, one slurry pump, one evaporator, and the condensate tank. In order to speed up initiation of catalyst recovery operations, the digester will be used as a surge tank and not for lime digestion. With completion of this single train, catalyst recovery operations without lime digestion will be possible while construction of the spare train proceeds.

FIGURE 2.2-1
PDU CATALYST RECOVERY FLOW PLAN

-18-
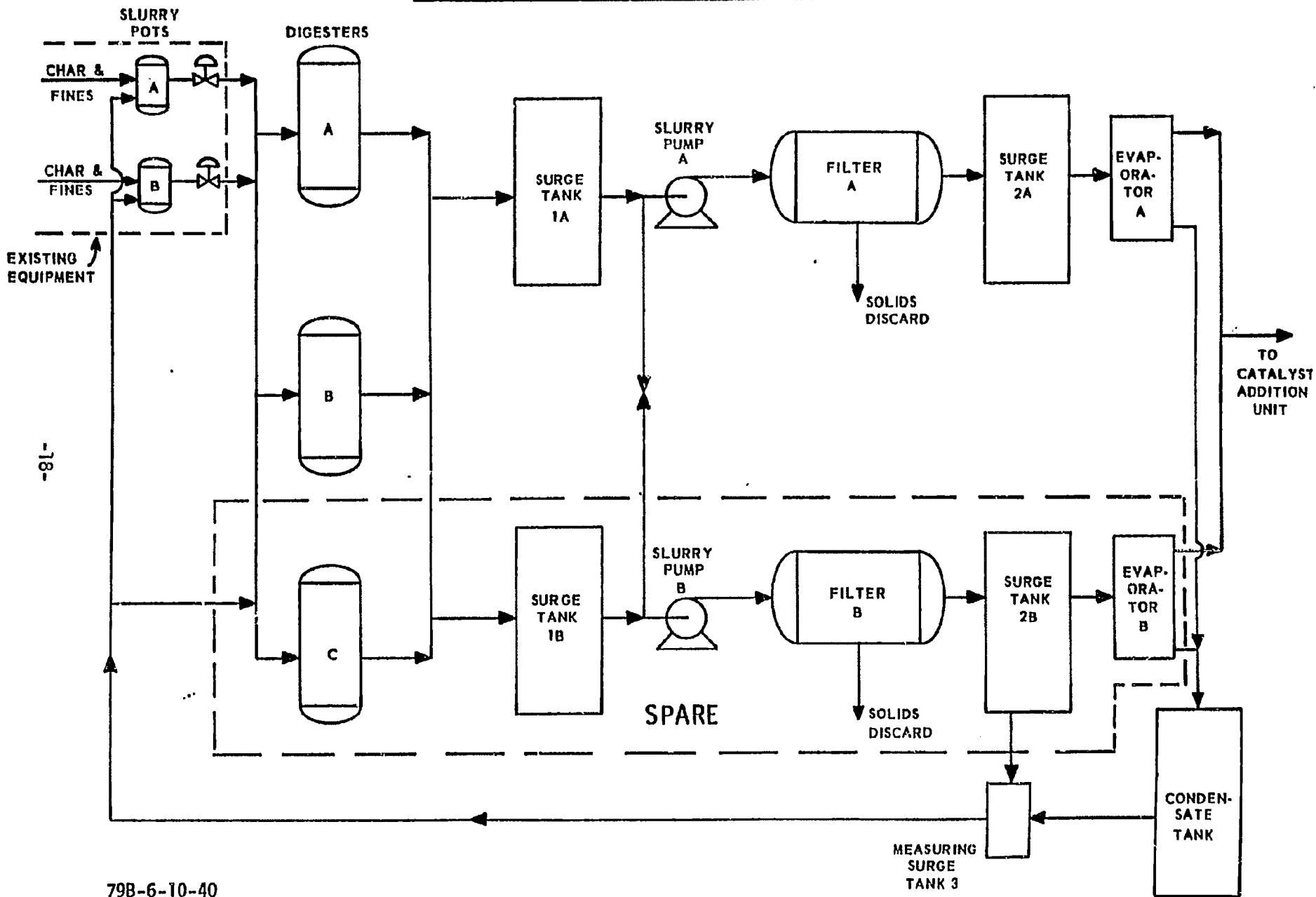
As another step to further facilitate unit startup, process piping for the major equipment items of the single train is being completed sequentially. This means that all the necessary piping for the digester will be completed first followed by that for surge tank 1A, then the filter, and so on until the entire train is complete. This allows test operation with the major equipment items to discover and correct problems before the train as a whole is ready for operations.

Currently, all major equipment items are in place and process piping is nearing completion for the surge tank 1 digester. It is anticipated that test operations will begin in January, 1980.

Filtration Experiments

During this quarter, filtration experiments were initiated using PDU char in rented filters. These tests were made to develop the operating procedure for the Catalyst Recovery Unit (CRU) of the PDU. The PDU chars used in these tests were obtained from initial gasifier operations.

A minimum feed rate to the filter of 70 gpm of 5 wt.% char slurry was necessary to avoid solids settling in the filter vessel. The filter feed rate was maintained at 70 gpm by recycling char slurry from the filter body. As the filter cake thickness approached 2 inches, the filtration rate decreased to 15 gpm when the pressure drop across the cake was limited to 50 psi. Draining the filter vessel, with minimal solids carryout, was accomplished by gently pressurizing the vessel with N_2 and carefully opening the filter drain line. The entire vessel was emptied in five to seven minutes. Deep cracking across the filter cake was evident upon inspection; however, it was impossible to tell whether this cracking had occurred as a result of the blowdown process or because of movement as the filter was opened. The filter cake could easily be removed by shaking the filter leaves. Reslurrying the filter cake was impossible without the aid of a nitrogen gas sparger across the bottom of the vessel to agitate the char slurry. The agitation provided by the N_2 sparger has also proven useful for reslurrying and then recaking the char slurry. This technique allows multiple char rinses in a single filter.

3. Data Acquisition and Correlations
(Reporting Category C03)

3.1 Process Modeling

The reactor model for Catalytic Coal Gasification (CCG) has been revised on numerous occasions since the time that the CCG predevelopment base case study design was completed. A comprehensive review of the current CCG gasifier models was made during this quarter, and an interim model was proposed as a working tool until additional data are available. The interim model differs from the current ones with respect to some fluidization characteristics. Table 3.1-1 contains a summary of these differences, and compares the interim model to both the original study design model and the more recent version which was presented at the 72nd Annual Meeting of the A.I.Ch.E. in November, 1979.

Although the interim model is based on the best available data on catalytic coal gasification, several inadequacies in our knowledge point to areas for further research. These areas can be lumped into the following categories: fluidization behavior, devolatilization yield, and kinetics of gasification and methanation. The bubble size is an important fluidization variable in scale-up of fluid bed processes. We intend to collect data on the PDU which will enable us to estimate the actual bubble size in this unit; however, the data for design of a commercial scale reactor will be obtained when a large diameter pilot unit gasifier is operated. At present, there is insufficient data on devolatilization yields of K-catalyzed coals under the conditions of temperature, pressure, gas atmosphere, and heat-up rate found in a gasifier. Additional data will be developed by PDU operations. Prediction of many operating conditions of interest is hindered by lack of some fundamental kinetic data. At present, experiments are being conducted to examine the effects of high potassium/carbon ratio. (Both high potassium loadings and high carbon conversions are being examined.) Data is still needed to better define the temperature dependence of gasification rates.

The fluidized bed gasifier model uses a Languir-Henshelwood type of kinetic expression for the gasification reaction rate. Bench scale fixed bed data were used in a regression analysis to determine the reaction and adsorption constants. Many expressions can be generated to fit the fixed bed data. The four different expressions shown below gave good fits to the fixed bed data. These models were substituted into the fluid bed model to predict the performance of the FBG runs. As shown in Figure 3.1-1, all four expressions appear to predict the FBG data equally well, even though the expressions contain different inhibition terms. Additional experimental work is planned to better define the rate expression for the kinetic model.

COMPARISON OF STUDY DESIGN AND A.I.Ch.E. MODELS

Points	Study Design Model	A.I.Ch.E. Model	Suggested Interim Model	Comments
Jet penetration distance	0. Bubble formation at distributor plate assumed.	1-2 ft. from Mori-Wen Correlation ("Fluidization Tech" McGraw-Hill, 1976).	Follow Study Design Model.	Bubble formation at distributor plate suggested in a recent study by Rowe, et al [Trans. Inst. Ch. E. 57, 194, 1979].
Bubble growth with bed height	Geldart's correlation (Powder Tech. 6, 201, 1972).	Same as Study Design Model.	Rowe's correlation (Chem. Eng. Sc. 31, 285, 1976).	Rowe's correlation is based on X-ray pictures of bubbles. The correlation agrees very well with Darton et al's theoretical development (Trans. Inst. Ch. E. 55, 274, 1977).
Maximum bubble size	Proprietary bubble size correlation.	Same as Study Design Model.	Use existing correlation.	Bubble size is important in sizing reactor volume. Need large diameter pilot plant for scale-up data base.
Transition between bubbling and slugging	No transition region defined.	Transition zone defined with use of Churchill's interpolation.	Follow A.I.Ch.E. Model.	Treatment of bubble mass transfer (Kunii & L. Levenspiel "Fluidization Eng'g", Wiley, 1969) and slug mass transfer (Hormand & Davidson "Fluidization", Academic Press, 1971) need to be reexamined for consistency.
Devolatilization yield	Devolatilization yield depends on coal composition only.	Proprietary correlation for uncatalyzed coal. Devolatilization yield depends on hydrogen partial pressure.	Follow A.I.Ch.F. Model.	There is at present insufficient data on devolatilization yields of K-catalyzed coal. Some data will be generated by PDU. Proprietary model is directionally in agreement with literature on the effects of hydrogen pressure (Anthony & Howard A.I.Ch.E. 22, 625, 1976).
Gasification Kinetics	Based on fixed bed gasification data. (a)	Based on the same data with more comprehensive search of kinet'c forms. (b)	Follow A.I.Ch.E. Model.	Both models show agreement with FBG data. However, FBG data does not support the contention that f_G decreases with increasing K/C. The basis for the f_G correlation needs to be reexamined. The A.I.Ch.E. form reduces to the simple "Longer Range" Model in the limiting cases.
Methanation kinetics	Based on fixed bed data. (c)	Based on FBG data. (d)	Follow A.I.Ch.E. Model.	The A.I.Ch.E Model incorporates the more recent findings from FBG experiments. Methanation kinetics should be reexamined upon getting new data.

(a) $r_G = \dfrac{f_G C_k k_G \left[P_{H_2O} - \dfrac{P_{CO}P_{H_2}}{K_c K_G}\right]}{1 + b_1 P_{CO} + b_2 P_{H_2O}}$; $f_G = 1.0$

(b) $r_G = \dfrac{f_G C_k k_G \left[P_{H_2O} - \dfrac{P_{CO}P_{H_2}}{K_c K_G}\right]}{P_{H_2} + b_1 P_{CO}P_{H_2} + b_2 P_{H_2O}}$; $f_G = 1.- \exp\left[-.22\left(\dfrac{C}{K}\right)\right]$

(c) $r_M = k_m [P_{H_2}{}^3 P_{CO} - P_{H_2O}P_{CH_4}/K_M]$

(d) $r_M = \dfrac{C_k k_m [P_{H_2}{}^3 P_{CO} - P_{CH_4}P_{H_2O}/K_M]}{1 + b_3 P_{H_2}}$

Model 1: $r_G = \dfrac{4.0 \times 10^7\ C_k[\exp\ (-E/RT)](P_{H_2O} - P_{CO}\ P_{H_2}/K_G)}{P_{H_2} + 0.21\ P_{CO}\ P_{H_2} + 0.06\ P_{H_2O}}$

Model 2: $\dot{r}_G = \dfrac{4.6 \times 10^7\ C_k[\exp\ (-E/RT)](P_{H_2O} - P_{CO}\ P_{H_2}/K_G)}{P_{H_2}}$
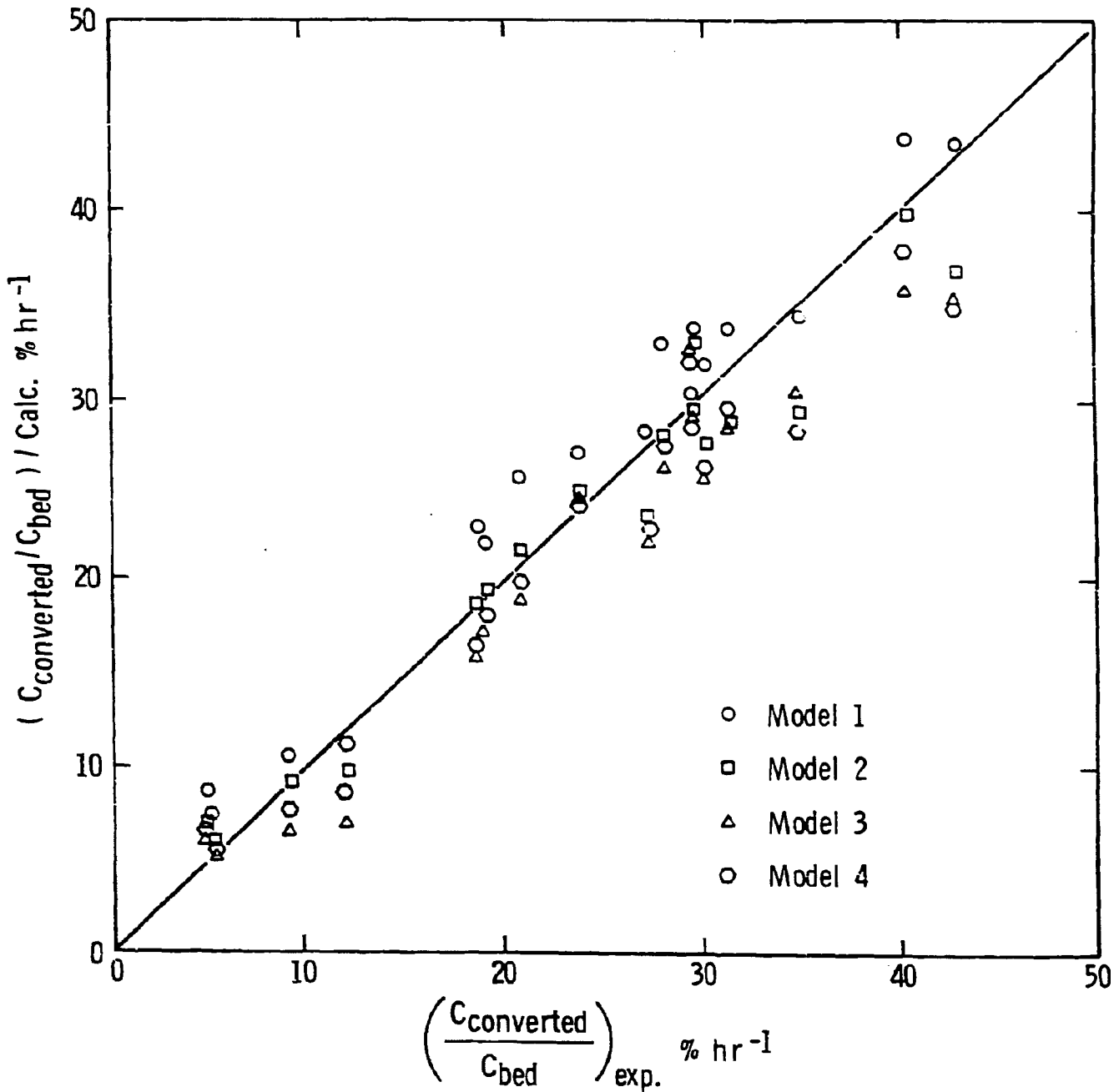
Model 3: $r_G = \dfrac{2.6 \times 10^8\ C_k[\exp\ (-E/RT)](P_{H_2O} - P_{CO}\ P_{H_2}/K_G)}{1 + 46.4\ P_{CO}}$

Model 4: $r_G = \dfrac{2.8 \times 10^8\ C_k[\exp\ (-E/RT)](P_{H_2O} - P_{CO}\ P_{H_2}/K_G)}{1 + 13.8\ P_{H_2}}$

FIGURE 3.1-1

COMPARISON OF MODELS WITH FBG DATA

Total Carbon Conversion Rates

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

4.1 Kinetics of Gasification and Devolatilization

The investigation of the gasification behavior of steady-state Illinois
No. 6 chars continued during this quarter. The chars used for this study were
produced earlier this year by the Fluid Bed Gasifier (FBG). Experiments are
being conducted in an atmospheric mini-fluid bed reactor to determine the
effect of carbon conversion and catalyst loading on the gasification rate.
Details of the experimental unit can be found in the January - March, 1979
Quarterly Report.

For any given char sample, the potassium-to-carbon mole ratio (K/C)
can be increased in either of two ways: (1) the carbon content of the char
can be reduced by gasification of the char, or (2) additional potassium
catalyst can be added to the char. Studies during this quarter have dealt
with the effect of increased K/C ratio via each method on the observed overall
gasification rate.

First a series of runs was made in the mini-fluid bed gasifier at various
steam flow rates using a char whose K/C ratio at the start of run was 0.122.
The results from these runs are presented in Figure 4.1-1. The data are
plotted as percent of carbon in the bed gasified per hour versus the corre-
sponding K/C ratio at the instant the rate was measured. The molar ratio of
steam fed-to-carbon content of the char is used as a correlating parameter.
The gasification rates plotted at K/C ratios of approximately 0.150 were
determined at the 20% carbon conversion point of a run. Rates at higher K/C
ratios correspond to higher carbon conversion levels. The data show that the
carbon gasification rates of steady-state chars increase with the ratio of
steam fed-to-carbon content of the char. This result is the same as that
found earlier for chars produced in bench-scale muffle furnaces.

The data in Figure 4.1-1 also indicate that the carbon gasification
rate does not increase when the K/C ratio is increased by gasification of the
char in the mini-fluid bed gasifier. This result is different from that
indicated by data presented in the July - September, 1979 Quarterly Report.
As discussed in that report, two steady-state chars produced in the FBG were
gasified in the mini-fluid bed gasifier and their initial carbon gasification
rates were measured. The K/C ratios of these two chars differed by a factor
of approximately 2.0. Since the chars were produced from coal with identical
initial catalyst loadings, the difference in K/C mole ratios of these chars
resulted from gasification of the coal in the FBG. The observed gasification
rates of these FBG chars at identical steam fed-to-carbon ratios, however, were
found to be substantially different from one another.

A series of runs was made in the mini-fluid bed gasifier using samples
of FBG steady-state char to which additional K_2CO_3 catalyst was added.
The base char sample for these runs had a potassium-to-carbon mole ratio of
0.122. The results from these runs are presented in Figure 4.1-2. The open

-24-

FIGURE 4.1-1

EFFECT OF CARBON CONVERSION ON GASIFICATION
RATE IN MINI-FLUID BED REACTOR

Reactor Charge: FBG Steady-State Char, K/C = 0.122
K/C Varied by Decreasing Carbon Content

T = 1300°F
P = 0 PSIG

$\frac{H_2O}{C}$ = 6.0 $\frac{moles/hr}{mole}$

= 3.5

= 0.85

% CARBON IN BED GASIFIED PER HOUR

CATALYST LOADING, K/C MOLE RATIO

80B-6-2-7
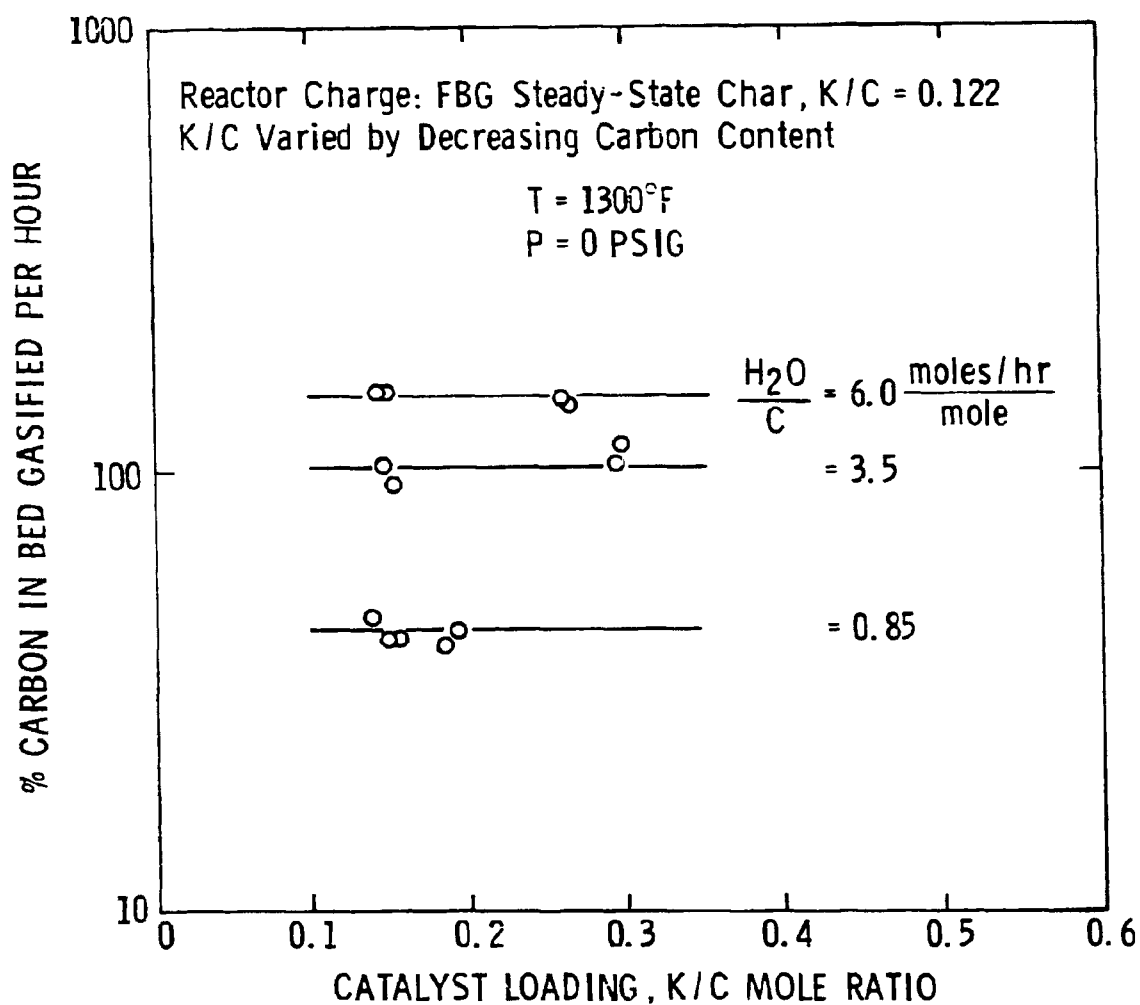
FIGURE 4.1-2

EFFECT OF CATALYST LOADING ON GASIFICATION RATE IN MINI - FLUID BED REACTOR

Legend within figure:

◇○△□ – FBG STEADY - STATE CHARS; FLUIDIZED BED OPERATION
● – FBG STEADY - STATE CHAR (○) PLUS K_2CO_3; FLUIDIZED BED OPERATION
●– – FBG STEADY - STATE CHAR (○) PLUS K_2CO_3; FIXED BED OPERATION

$$\frac{H_2O}{C} = 6.0 \frac{moles/HR.}{mole}$$

T = 1300°F

P = 0 psig

Y-axis: % CARBON IN BED GASIFIED PER HOUR

X-axis: CATALYST LOADING, K/C MOLE RATIO

80B-6-3-33
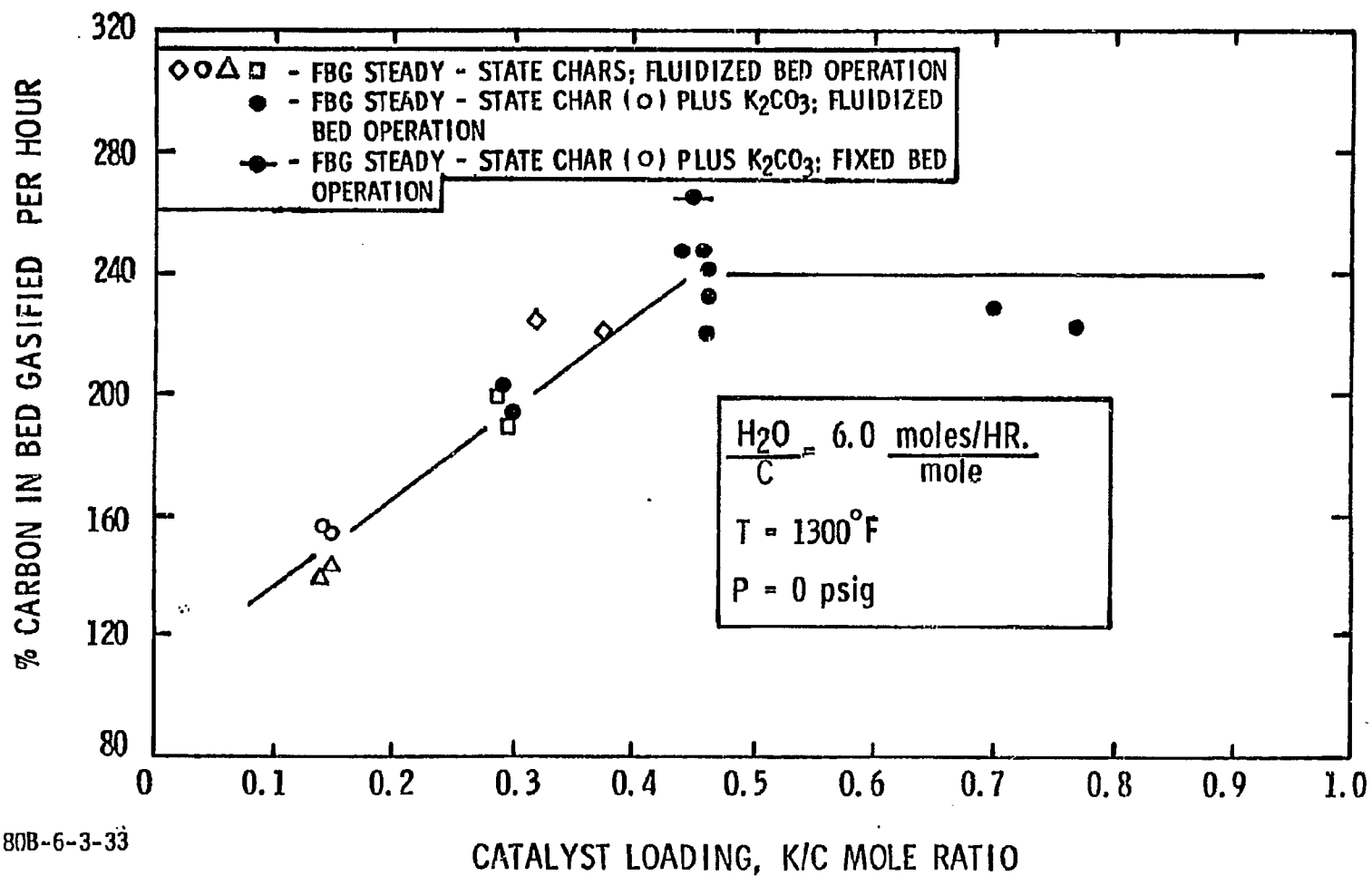
circles represent the base char samples while the dark circles represent those samples to which additional potassium was added. The data are plotted as percent of carbon gasified per hour at the 20% carbon conversion point of a run versus the corresponding potassium-to-carbon mole ratio at the instant the rate was measured. The ratio of steam flow rate to carbon in bed at this same instant was 6.0 (moles/hr)/mole. These data clearly show that increasing the K/C mole ratio by adding additional potassium to a char sample increases the overall carbon gasification rate.

Figure 4.1-2 also includes data taken with two other FBG steady-state chars. All chars corresponding to the open points were produced in the FBG from coal with identical initial catalyst loadings. The difference in K/C mole ratios of these chars is a result of the gasification of the coal. The data in the vicinity of K/C equal to 0.3 is of particular interest. Note that the same increase in gasification rate can be obtained by adding additional catalyst to a char sample, as well as by reducing the carbon content of the char via gasification in the FBG. As the above results indicate, however, the gasification rate does not increase when the carbon content of the char is reduced via gasification in the mini-fluid bed unit. This may be due to the low pressure or short residence time in the mini-gasifier.

Furthermore, Figure 4.1-2 shows that as K/C mole ratio is increased beyond about 0.5 mole/mole, the gasification rate shows no further increase. Initially, it was believed that this result might be due to inadequate fluidization and gas bypassing of the char sample at the high catalyst loadings. Therefore, the configuration of the mini-reactor was changed to allow for operation as a down flow fixed bed. Figure 4.1-2 shows that similar results are obtained when the mini-reactor is operated in the fixed bed mode as when the char bed is fluidized.

4.2 Catalyst Reactions with Coal and Ash

The goal of these studies is to determine the effects of variations in coal pretreatment, catalyst addition method, and catalyst composition on the density of the devolatilized char. A high density char is desirable in order to maximize the amount of material handled by any given size gasifier.

Earlier data (July - September, 1979 Quarterly Report) have shown that exposure of catalyzed coal to air increases the density of the devolatilized char produced. Chars from both K_2CO_3 catalyzed and KOH catalyzed coals showed increased densities after exposure to air at room temperature.

Current work is aimed at the study of air exposure at conditions more closely simulating those likely to be present in a catalyst addition unit. These include:

- Elevated temperatures

- Air exposure of wet coal during the drying process

- Long-term air exposure of catalyzed coal at ambient temperature

Atmospheric Pressure Devolatilizer Studies

A small fluidized bed reactor is being used for this study. As described in earlier reports (July, 1978 - June, 1979 Annual Report), this unit simulates coal addition to a hot fluidized bed gasifier in all respects except pressure conditions and produces chars which closely resemble chars produced in the 100 psia Fluid Bed Gasifier (FBG).

Figure 4.2-1 presents recent data obtained from air exposures at 350°F. Previous data obtained at ambient temperature is included for comparison.

Effective air exposure is seen to be obtained in a shorter time at the higher temperature. After only six hours of exposure at 350°F in the laboratory unit, the coal produced a char with a density comparable to that seen only after much longer exposure times at ambient temperature.

Further work then centered on air exposure of coal which had been catalyzed with KOH solution, but had not been dried. This is a better method of simulating the operation of the PDU catalyst addition unit where catalyzed coal is exposed to air during the drying process. Since wet coal is known to be less susceptible to oxidation, this difference should have an effect on the length of air exposure required at a given temperature.

Data was obtained for a number of samples at 350°F and 400°F. All samples produced chars with low bulk densities (0.22 g/cc) even after as much as 24 hours of exposure time. This may be due to ineffective contact of the air stream with the dried coal. Formation of aggregates during drying may be causing severe channeling of the air in the drying tube. In prior work, coal which had been predried in a vacuum oven was rehomogenized with a mortar and pestel before air exposure.

These difficulties have led to modifications in the procedures for both air exposure and devolatilization. During air exposure, effective contact of the gas stream with the coal is important. Previously, air flowed up through a packed bed. In order to avoid any channeling effects, the system was modified such that air flows down through the packed bed. Secondly, in order to minimize fluctuations in coal addition rate to the devolatilization unit, a simple feed system which regulated the coal flow was assembled. An earlier system which attempted to feed a nitrogen entrained coal sample into the middle of the bed had failed due to plugging of the feed line (July - September, 1979 Quarterly Report). The current system merely regulates the flow of coal into the top of the reactor by passing the feed coal through a throttling valve. The valve is adjusted to feed the 10 gram sample into the reactor in about 1 minute. These modifications are currently being tested.
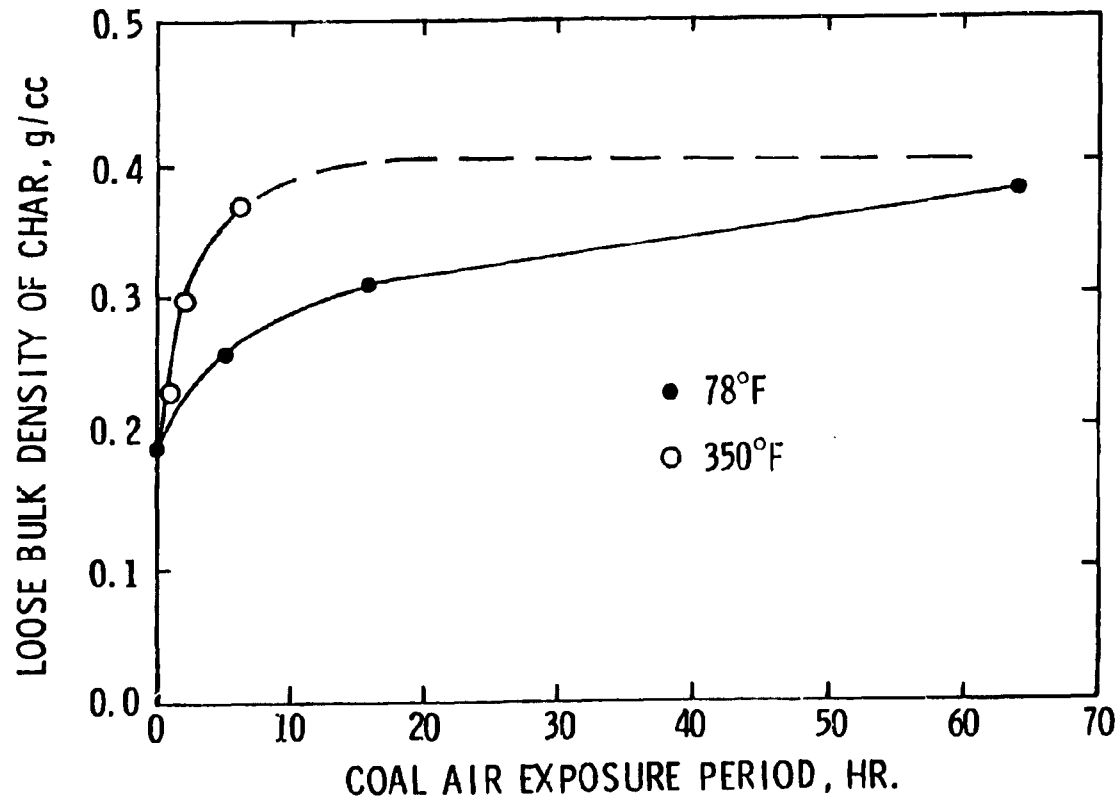
Pressurized Free Fall Unit Studies

The fluidized bed devolatilization unit, described above, can operate only at atmospheric pressure. A pressurized free fall unit (FFU) is being used to study the effect of pressure on char properties.

FIGURE 4.2-1

AIR EXPOSED COAL PRODUCES HIGH DENSITY CHAR

- ILLINOIS COAL
- 12% KOH CATALYZED
- 0.6 SCF/HR AIR FLOW

The FFU is shown in Figure 4.2-2. A 10 gram sample of -80 +100 mesh coal is loaded into the feeder and the reactor is brought to the desired pressure and temperature. The coal is allowed to trickle into the reactor, which is a .3/4 inch O.D. x 8 foot tube. The coal is heated rapidly, producing a char sample which is collected in a cold receiver beneath the reactor and liquids which are condensed in a cell immersed in liquid nitrogen. The solids produced are retained for analysis.

The experiments performed are summarized in Table 4.2-1. Illinois #6 coal catalyzed with K_2CO_3 with a minimum of air exposure during handling produced high density chars when devolatilized at atmospheric pressure or 100 psia (the pressure at which the FBG was operated). Changing the gaseous atmosphere to 80% N_2, 20% H_2 at 100 psia total pressure did not affect the density. However, all attempts to feed unoxidized or mildly oxidized Illinois coal catalyzed with K_2CO_3 failed due to plug formation in the reactor. The plugs formed are similar to feed line plugs experienced in recent PDU operations. Plug formation is an indication of swelling and agglomeration during the pyrolysis. This data suggests that swelling and agglomeration problems increase with increasing pressure.

Unoxidized Illinois coal plugged the reactor at 500 psia regardless of catalyst form (KOH or K_2CO_3); however, Wyodak coal catalyzed with K_2CO_3 did not plug the reactor and formed a high density char (0.44 g/cc). Therefore, two oxidized Illinois coal samples were tried. Both samples were air exposed for 16 hours at 100°C. The first sample was first catalyzed and then air exposed; however, the second sample was air exposed before catalyst impregnation. The first sample did not plug the reactor, but it produced a low density char of only 0.25 g/cc. The second sample plugged the reactor.

The char samples obtained from operations which did not plug the reactor were analyzed for particle size distribution. The results are plotted in Figure 4.2-3. These data show that higher pressure devolatilization tends to produce a greater number of fine particles.

4.3 Catalyst/Char Equilibrium Studies

The proposed PDU catalyst recovery procedure uses a batch countercurrent solid-liquid separation system. In this system, the spent gasifier char is subjected to contacting with aqueous solutions of varying catalyst (potassium ion) concentrations ranging from rich catalyst solution to makeup water.

Previous work (July - September, 1979 Quarterly Report) looked at solutions of constant potassium concentration but variable pH. The pH was varied using mixtures of KCl with KOH. Ambient temperature data was presented.

FIGURE 4.2-2

FREE FALL PYROLYSIS UNIT
(FFU)

Enclosed Screw
Feeder

Regulated
High-Pressure
H_2

Free Fall
Reactor
1000°F
Up to 2000 psi
$\frac{3}{4}$" O.D. x 7'

Pressure Letdown,
Metering, Vent

Gas
Trap
(13X
Molecular
Sieves)

-100°F

300°F

35°F

-100°F

Char
Receiver
700°F

Liquid Collection
Traps (Shell &
Tube Condensers)
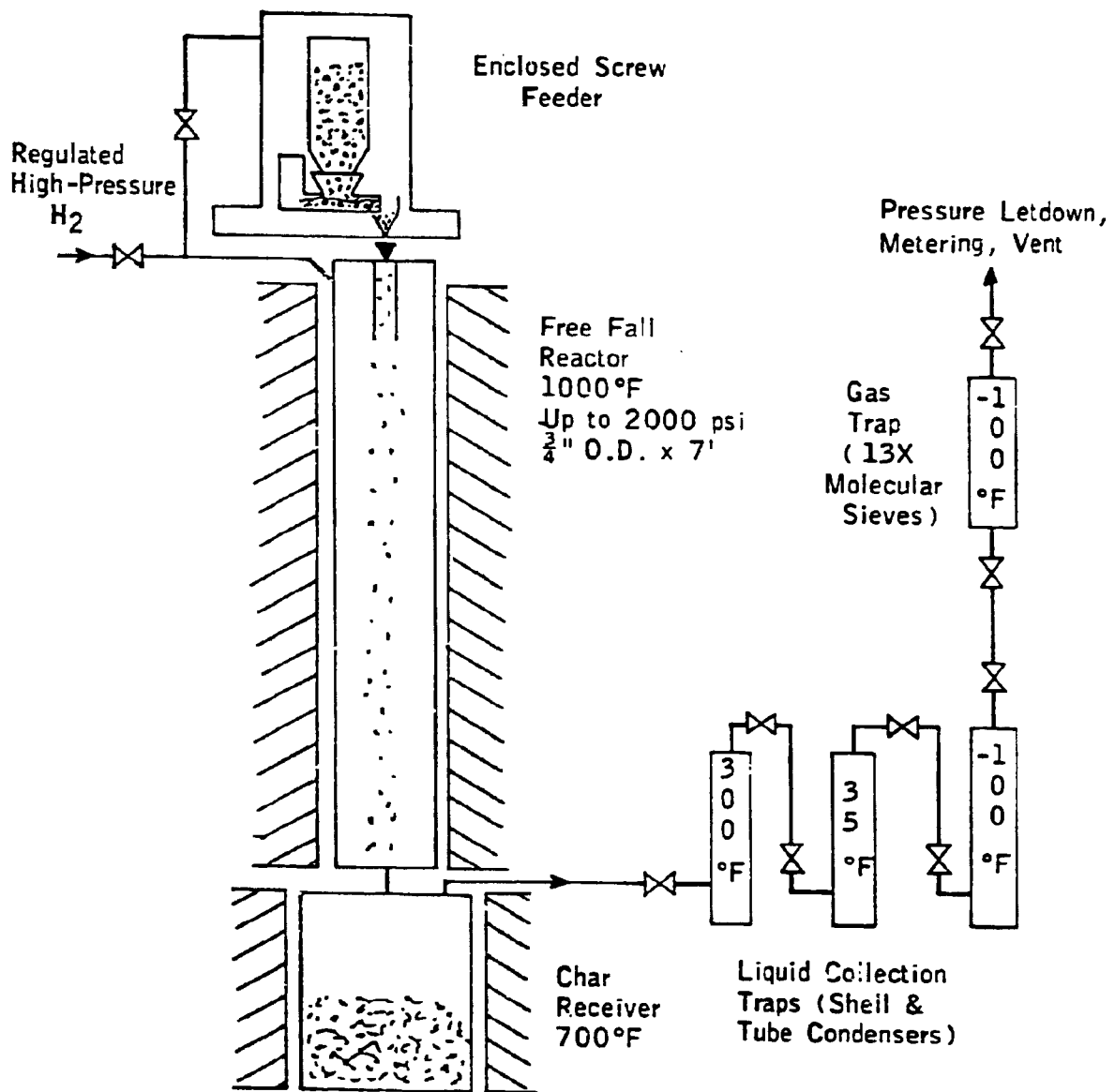
Table 4.2-1

Free Fall Unit Char Densities

Sample	Atmosphere	Loose Bulk Density, g/cc
15% K_2CO_3 on Illinois #6	1 atm N_2	0.39
15% K_2CO_3 on Illinois #6	100 psia N_2	0.46
15% K_2CO_3 on Illinois #6	80 psia N_2* 20 psia H_2	0.44
15% K_2CO_3 on Illinois #6	500 psia N_2*	Reactor plugged
15% K_2CO_3 on Illinois #6	400 psia N_2 100 psia H_2	Reactor plugged
12% KOH on Illinois #6	400 psia N_2 100 psia H_2	Reactor plugged
15% K_2CO_3 on Wyodak	400 psia N_2 100 psia H_2	0.44
15% K_2CO_3 on Illinois, catalyzed and then dried in air for 16 hr. @ 100°C	400 psia N_2 100 psia H_2	0.25
15% K_2CO_3 on Illinois, dried in air for 16 hr. @ 100°C, then catalyzed	400 psia N_2 100 psia H_2	Reactor plugged

*Duplicate runs performed on each of these samples

FIGURE 4.2-3

INCREASED DEVOLATILIZATION PRESSURE PRODUCES
SMALLER CHAR PARTICLES

- FREE FALL PYROLYSIS UNIT
- ILLINOIS #6 COAL
- 15% K_2CO_3 CATALYZED
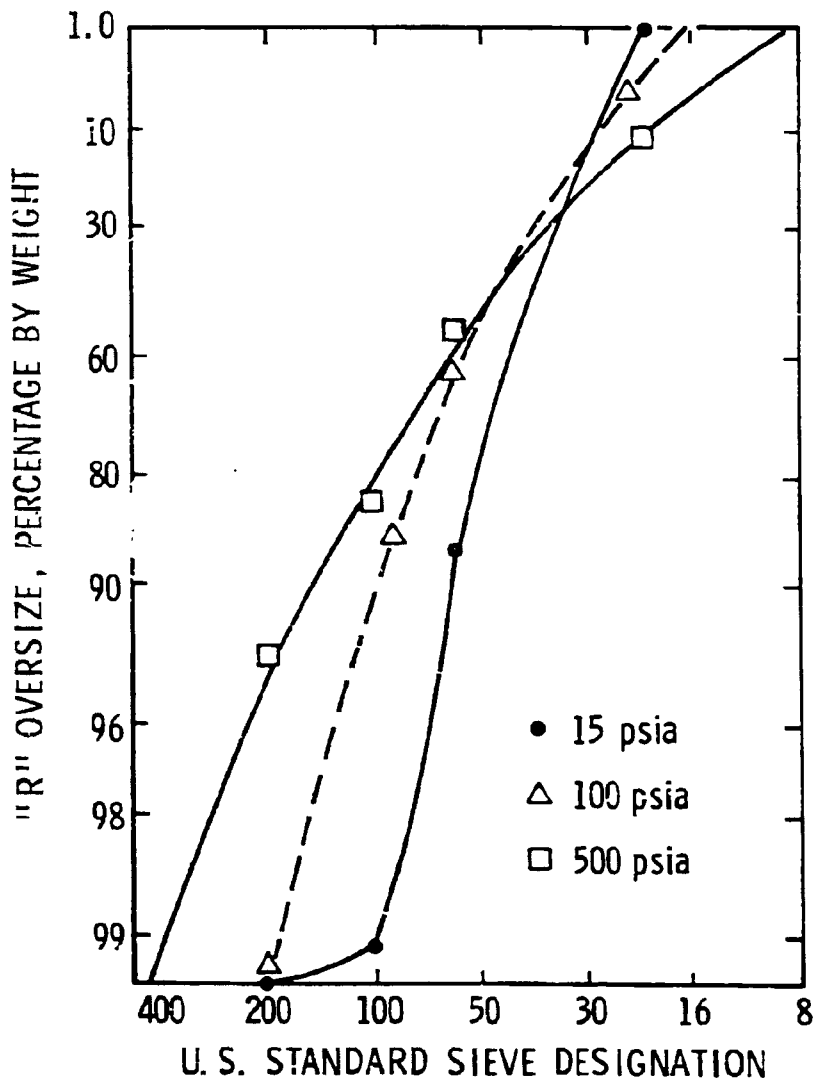
This quarter, equilibrium studies at an elevated temperature were begun. Digested char was stirred in a round bottomed flask in contact with a refluxing potassium solution. The same concentrations were used as for the room temperature work, and the pH was again adjusted by varying the relative amounts of KCl and KOH. After refluxing overnight, a small aliquot of solution was removed by a syringe equipped with a filter. The mixture was then cooled, and all materials analyzed. It was hoped that the difference in concentration of the cold solution and the aliquot removed while at temperature would enable calculation of the equilibrium potassium distribution. However, the concentration differences were at or below the order of magnitude of the error in solution analysis. Therefore, no results are available and another method of performing the high temperature equilibrium studies is being sought.

5. Engineering Research and Development
(Reporting Category C20)

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

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

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

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

5.1 Cost Reduction and Laboratory Guidance Studies

Catalyst Recovery Screening Studies

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

The work on these catalyst recovery screening studies is following a standard sequence. First, a process basis is established based on available information and data. A material and energy balance is then made for lime digestion (if included) and water wash to determine the number of washing stages required to recover 95% of the soluble catalyst at a desired concentration. The Catalyst Recovery Material Balance Model described in the July, 1978 - June, 1979 Annual Report is used to facilitate this balance. Equipment sizes and specification lists are developed based on the material

balance, and the investment and operating costs are estimated. These costs will be compared to those predicted for alternative processing approaches and solid-liquid separation devices to select the most attractive alternatives for further study.

Three catalyst recovery screening studies are currently underway. Case 1 is an evaluation of countercurrent water wash combined with lime digestion, using filters for the solid-liquid separations. The process basis, material and energy balance, and process flow scheme for this study were completed in September and reported in the July - September, 1979 Quarterly Report. Equipment specifications for this case have now been completed. The pressure rotary-drum filters used in the washing sequence were sized based on a cake resistance estimated from bench-scale filtration tests on digested gasifier solids.

The other two cases now underway are evaluations of countercurrent water wash without an initial lime digestion step. In Case 2, the solid-liquid separation device is again filters. The process basis, material and energy balance, and equipment specifications for this case were also completed in this quarter. For Case 2, the filters were sized based on bench test results on gasifier solids not subjected to lime digestion. More details on the basis, approach, and results of filter sizing calculations for Cases 1 and 2 are provided later in this report.

Case 3 differs from Case 2 in that gravity settlers are used for the solid-liquid separations. The process basis and material and energy balance for Case 3 were completed in November, and equipment sizing is nearing completion. Laboratory settling tests for gasifier solids at two potassium concentrations have been carried out to provide the basis for estimating the size of commercial gravity settlers for this service.

A schematic flowsheet for Case 1, Digestion with Filters, is shown in Figure 5.1-1. Except for the deletion of the lime (calcium hydroxide) digesters and associated facilities, the flowsheets for Cases 2 and 3 are similar to this. The major subsections for Case 1 are lime digestion, countercurrent water wash using pressure rotary-drum filters, rich catalyst solution evaporation, and venturi scrubber fines slurry processing. This flowsheet was discussed in more detail in the July - September, 1979 Quarterly Report. Case 2 has no lime digesters but still uses pressure rotary-drum filters in the water-wash sequence. Case 3 replaces these filters with gravity settlers.

The process bases for all three cases are presented in Table 5.1-1. The process basis for Case 1 was described in the July - September, 1979 Quarterly Report. The basis for Case 2 is essentially the same, except for the deletion of lime digestion and related basis items and a different assumption concerning the heats of mixing and catalyst reactions. The lime digestion step in Case 1 solubilizes 90% of the total potassium in the char and fines fed to the digesters. In Cases 2 and 3, with just water wash, only about 70% of the total potassium is soluble. All three cases have a target recovery in the water-wash section of 95% of the total water-soluble

FIGURE 5.1-1

CATALYST RECOVERY: DIGESTION WITH FILTERS

Semi-Rich Solution To Fines Slurry Drum 282°F

Semi-Rich Solution To Char Slurry Drum 232°F

65 psig Steam

Lime 60°F

65 psig Steam

Rich Catalyst Solution 230°F

Polishing Filter

Fines Slurry From Venturi Scrubber 279°F

30 psia Steam

Air Fin Condenser 4 psia

Makeup Catalyst 60°F

Cooling Water 85°F

Fines Filter

Spent Solids To Disposal 175°F

Double-Effect Evaporator

Air Fin Cooler

Concentrated Catalyst Solution To Catalyst Addition 137°F

230°F

Semi-Rich Catalyst Solution 230°F

Contact Condenser

Slurry 9°F
Slurry 6°F

Ca (OH)₂ Digester 300°F 70 psia

Digester Flash 230°F 20 psia

Makeup Water 60°F

Stage 1 Filter 230°F 55 psia

Stage 2 Filter 230°F 55 psia

Stage 6 Filter 230°F 55 psia

Stage 8 Filter 230°F 55 psia

Stage 9 Filter 230°F 55 psia

Stage 10 Filter 146°F 15 psia

Spent Solids To Disposal 146°F

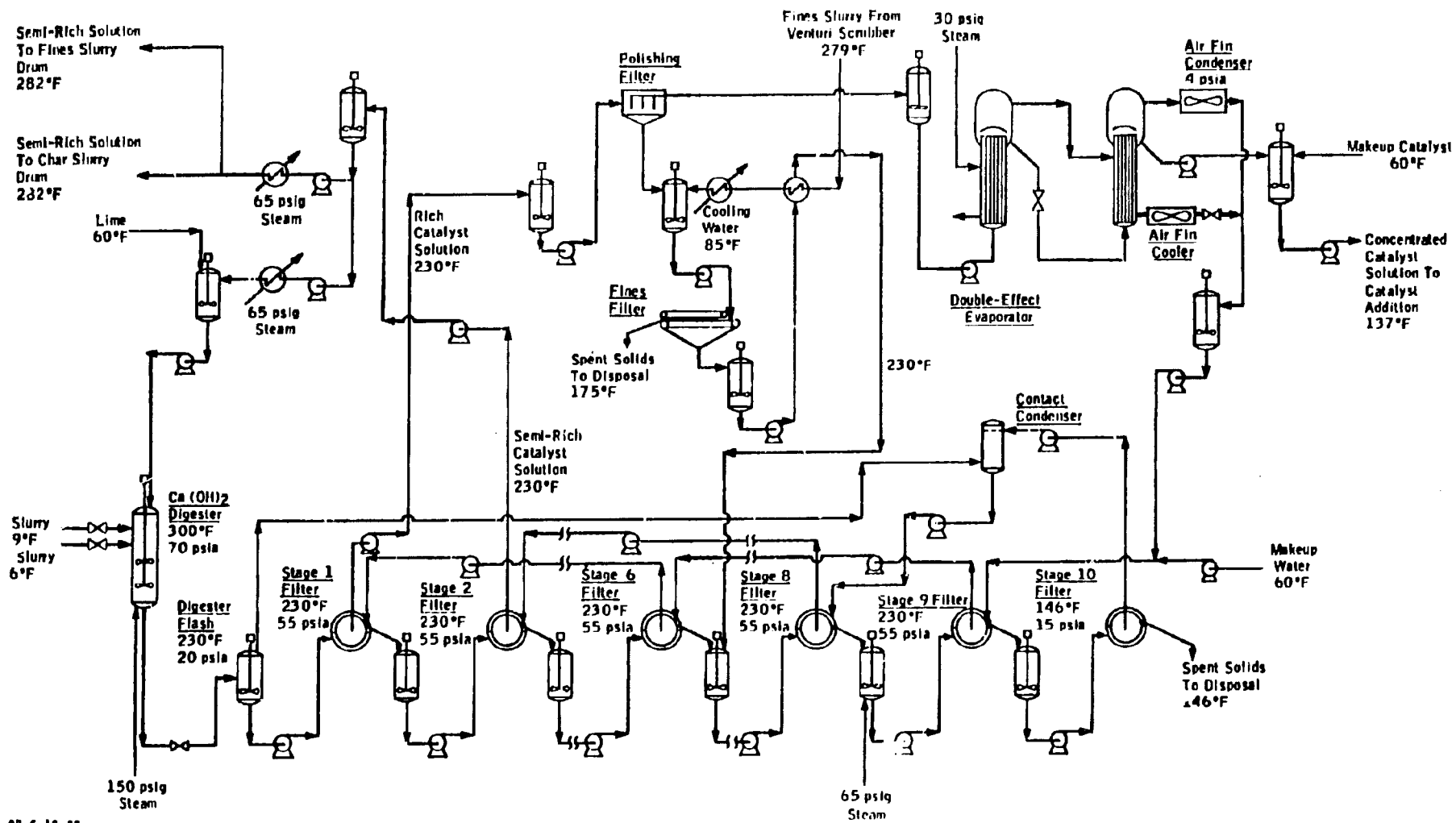150 psig Steam

65 psig Steam

98-6-12-33

Table 5.1-1

CATALYST RECOVERY SCREENING STUDIES

SUMMARY OF PROCESS BASES

- For all three cases, total gasifier coal feed rate, catalyst loading on coal (15 wt% K_2CO_3 equivalent on dry coal), and solids rates leaving the gasifiers are the same as in the "CCG Study Design".

Basis Item	Case 1 Lime Digestion With Filters	Case 2 Water Wash With Filters	Case 3 Water Wash With Gravity Settlers
Concentrations of Key Solutions, wt% K^+:			
● Rich Solution from Catalyst Recovery	11.8	11.7	6.9
● Concentrated Solution from Evaporators	22.8	22.8	22.9
● Makeup Catalyst Solution	20.9[1]	20.9[1]	20.9[1]
Basis for Lime Digestion			
● Digestion Conditions:		Digestion	Digestion
- Temperature, °F	300	Not	Not
- Pressure, psia	70	Included	Included
- Residence Time, hour	1		
- Ca/K, mole/mole	0.7		
Basis for Water Wash/Solid-Liquid Separations			
● Percent of Total K Fed to Water Wash which is Ultimately Water-Soluble	90	69.6	69.6
● Water Wash Conditions:			
- All Stages Except Last Stage:			
+ Temperature, °F	230	230	212
+ Pressure, psia	55	55	15
- Last Stage:			
+ Temperature, °F	146	150	167
+ Pressure, psia	15	15	15
● Separator Performance:			
- Type of Device	Filter	Filter	Gravity Settler
- Solids Content of Underflow, wt%	30	30	15[2]
- Solids Content of Overflow, wt%	0.2-0.5	0.2-0.5	0.8-1.3
- Solids Separation Efficiency, %[3]	99	99	ca. 90[4]
● Overall Target Recovery of Soluble K Fed	95	95	95
Basis for Evaporation			
● First Effect Steam Pressure, psig	30[5]	30[5]	30[5]
● Number of Effects	2	2	4
Basis for Heat Balance			
● Temperatures of Major Feeds, °F:			
- Bottoms Char	600	600	600
- Cyclone Fines	600	600	600
- Lime for Digestion	60	-	-
- Makeup Catalyst Solution	60	60	60
- Makeup Wash Water	60	60	60
● Steam Services and Pressures, psig:			
- Direct Injection to Digesters	150	-	-
- Direct Injection to Water Wash Stages	65	65	30
- Indirect Heating of Semi-Rich Solution	65	-	-
- Evaporators	30	30	30
● Key Heat Effects:			
- Sensible Heat Changes	Included	Included	Included
- Net Heats of Mixing and Catalyst Reactions	0	(6)	(6)
- Heat Losses from System	0	0	0

Notes:

(1) Makeup catalyst is received as a 30 wt% KOH solution (20.9 wt% K^+).
(2) The solids content in the underflow from all stages of thickeners is 15 wt%. However, the final stage includes filtration of the thickener underflow and the resulting solids concentration in the underflow (filter cake) leaving this stage is 30 wt%.
(3) Defined as weight percent of feed solids recovered in underflow.
(4) Separation efficiency for Case 3 varied from 89.4 to 91.6% for all stages except the first. The efficiency for the first stage was 97.4%.
(5) The 30 psig steam used in the evaporators is raised in gasifier effluent waste heat boilers.
(6) In water wash cases, net heats of mixing and catalyst reactions were taken as -8 kcal/g mole of K^+ dissolved.

catalyst fed. In Cases 1 and 2, the water wash takes place at 230°F, a temperature chosen to avoid flashing on the downstream side of the filter medium at 20 psia, while maintaining a relatively high temperature to improve filtration by reducing solution viscosity. In Case 3, this temperature is lowered to 212°F to avoid the cost of pressurizing the gravity settlers above atmospheric. By maintaining a temperature above ambient, a higher settling rate is obtained because of lower solution viscosity and density. The settlers still must be enclosed to prevent exposure to air which would oxidize sulfur-containing potassium salts to forms with low catalytic activity. For all three cases, the temperature in the final stage is reduced to facilitate solids removal in a final vacuum filtration step. This step provides a firm filter cake for disposal in the spent solids landfill.

As previously discussed, Cases 1 and 2 use rotary-drum filters for the interstage solid-liquid separations. These filters recover 99% of the solids fed to them in the form of a cake which is approximately 30 wt% solids. The catalyst is recovered in a rich solution which is about 12 wt% K^+ (or about 17 wt% KOH). This solution is then concentrated in double-effect evaporators to 22.8 wt% K^+. The gravity settlers used in Case 3 are not as efficient as the filters and recover only about 90% of the solids fed to them in an underflow stream which contains 15 wt% solids. They are also not as effective at higher catalyst concentrations where the density difference between the particles and the solution is small. For these reasons, Case 3 recovers the catalyst in only a 6.9 wt% K^+ (or 10 wt% KOH) solution. This solution will then be concentrated to 22.9 wt% K^+ in quadruple-effect evaporators before recycle to catalyst addition.

For the water wash cases (Cases 2 and 3), laboratory data on the heat of mixing catalyzed char with water provided the basis for estimating a total heat effect of -8 kcal/g mole of K^+ dissolved. For the digestion case--where no data were available--it was judged that this exothermic heat of mixing would be directionally offset by the heat required to drive the digestion reactions. Thus a net heat of zero was assumed.

The results of the detailed material and energy balances for these three cases are summarized in Table 5.1-2. Some general comparisons between Cases 1 and 2 can be drawn from this table. In both cases, the countercurrent water wash recovers about 95% of the water-soluble potassium fed to the system in ten washing stages. However, with lime digestion the percentage of the total potassium recovered is significantly higher due to the solubilization of previously water-insoluble salts during the digestion process. Thus for Case 1 employing lime digestion, the overall potassium recovery is 84% and the makeup potassium hydroxide requirement is 19.4 klbs/hr. In Case 2 without digestion, the overall potassium recovery is only 66% and the makeup KOH requirement increases to 41.3 klbs/hr.

The larger KOH makeup requirement for Case 2 will mean a larger operating cost for its purchase. The current screening studies will allow this economic debit for Case 2 to be weighed against the increased capital and operating costs associated with the lime digestion step in Case 1. Not only will there be increased costs due to lime storage and handling and

Table 5.1-2

CATALYST RECOVERY SCREENING STUDIES
SUMMARY OF MATERIAL BALANCE RESULTS

Material Balance Result	Case 1 Lime Digestion With Filters	Case 2 Water Wash With Filters	Case 3 Water Wash With Gravity Settlers
• Number of Stages in Countercurrent Water Wash	10	10	8 (+ 1 spare)
• Recovery in Water Wash, % of Soluble K^+ Fed	94.3	94.9	93.1
• Rich Solution Concentration, wt% K^+	11.8	11.7	6.9
• Catalyst Makeup Requirement			
- Percent of Catalyst on Feed Coal	16.0	33.9	35.2
- Rate, ST/SD KOH (Dry)	233	495	513
- Rate, klbs/hr KOH (Dry)	19.4	41.3	42.7
• Lime Requirement, ST/SD (97% CaO)	1005	-	-
• Wash Water Rate, klbs/hr	1054	712	1017
• Water Evapcration Requirement, klbs/hr	288	235	558
• Spent Solids to Disposal, klbs/hr (Dry)			
- From Polishing Filters	15	14	18
- From Final Stage of Water Wash	291	200	196
• Total Slurry Feed to Solid-Liquid Separators, klbs/hr			
- To Stage 1	1750	1280	2450
- To Stage 2	2570	1810	3820
- To Stage 5	2400	1680	3650
- To Final Stage	2040	1390	2460

the lime digestion equipment, but also, as Table 5.1-2 shows, the entire water wash section is approximately 50% larger for Case 1 than for Case 2. This increase is due to the additional lime and lime-derived solids which must be handled in the digestion case. Furthermore, bench data have shown that the digestion process significantly reduces the particle sizes in the char slurry, making the subsequent solid-liquid separations more difficult. This impact on separations performance has been reflected in these studies, based on available particle size, filtration, and settling data. (The number of filters required for Cases 1 and 2 is discussed below.)

Table 5.1-2 also helps in understanding the basic tradeoffs between Cases 2 and 3. Although the makeup KOH requirement is very similar for the two cases, the flow rates in water wash are about twice as large in Case 3. This results from the lower rich solution concentration in Case 3 and the less efficient separations in the gravity settlers. The evaporation requirement is also up for the same reason. However, 93% recovery of water-soluble potassium is obtained in only eight stages of washing. A ninth spare stage in series is also provided. (In Cases 1 and 2, spare filters are provided in parallel for each stage.) The economic comparison between Case 2 and Case 3 will provide an initial indication as to whether filters or gravity settlers appear more attractive for the catalyst recovery solid-liquid separations.

The continuous rotary-drum filters in Cases 1 and 2 were designed starting with specific cake resistances calculated from bench-scale pressure filtration tests. If the resistance of the filtration medium is neglected, the specific cake resistance (α) is defined at any time during the buildup of a filter cake by the equation:

$$q = \frac{\Delta P_c g_c}{\mu \alpha \rho_c t_c}$$

where, q = volumetric filtration rate per unit area, $ft^3/sec \cdot ft^2$
ΔP_c = pressure drop across the cake, lb_f/ft^2
g_c = gravitational constant, 32.17 $lb_m \cdot ft/sec^2 \cdot lb_f$
μ = liquid viscosity, $lb_m/sec \cdot ft$
α = specific cake resistance, ft/lb_m
ρ_c = density of solids in cake, lb_m/ft^3
t_c = thickness of cake, ft

This fundamental equation can be integrated to provide an equation for calculating α from bench-scale filtration tests in which cumulative filtrate volume is measured as a function of time. The same equation can also be integrated to provide a design equation for sizing continuous rotary-drum filters. Using the latter equation with α's calculated from the former, the early batch filter test results have been scaled up to calculate the required total filtration area and number of filters for these commercial screening studies.

-41-

The filtration experiments carried out to date have used digested and undigested (water wash only) solids obtained from the Fluidized Bed Gasifier (FBG) unit operating at 100 psig. Most of these tests were conducted as part of the engineering technology program on slurry rheology and solid-liquid separations. (A revised summary of these laboratory batch filter results is tabulated in Section 5.3 of this report.) Some results were also available from bench filtration tests done in a vendor shop. The available results on cake resistance are summarized below along with the "base case" assumptions made for designing the filters in Cases 1 and 2.

Basis for Filter Cake Resistances

	Cake Resistance, ft/lb x 10^{-11}			
	Calculated from Bench Data			
	Tests in	Technology Program Tests		Basis Assumed
	Vendor	All	Representative	for Initial
Solids Type	Shop	Feeds	Feeds	Screening Cases
Digested	5-13	1.2-36	15-36	10
Digested with Flocculant	No Runs	0.6-22	22?	5 (Case 1)
Water Washed	3-6	0.17-1.0	0.9-1.0	1.0
Water Washed with Flocculant	No Runs	------- No Runs -------		0.5 (Case 2)

As is evident from the ranges shown above, there has been much variation in the calculated cake resistances for solids samples of the same general type. (This variability is also discussed in Section 5.3 of this report.) For the technology program tests, the results for the feed samples judged to be more representative are shown separately. For digested and water washed solids without flocculants, base cake resistances were assumed which are in the lower part of the overall range of values obtained in the vendor and representative technology program tests. Flocculants were assumed to cut these cake resistances in half, based on technology program results with digested solids plus flocculants and on laboratory flocculant screening studies. These latter values were used for sizing the filters in Case 1 (digested solids with flocculant) and Case 2 (water-washed solids with flocculant). Test results on water-washed solids with flocculants are expected shortly from the engineering technology program.

In addition to cake resistance, several other process and mechanical specifications were set in order to size the pressure rotary-drum filters. These design basis items are listed in Table 5.1-3. Important items for filter sizing are the pressure drop (35 psi), the initial cake thickness (0.25 in.) and the maximum filter drum size (12 ft diameter by 36 ft long,

Table 5.1-3

CATALYST RECOVERY SCREENING STUDIES

DESIGN BASIS AND CONSIDERATIONS
FOR PRESSURE ROTARY DRUM FILTERS IN CASES 1 AND 2

Process Specifications

● Temperature	230°F
● Slurry Feed Pressure	55 psia
● ΔP Cake	35 psi
● Initial Cake Thickness	0.25 in.
● Final Cake Thickness (Minimum)	0.75 in.
● Cake Solids Content	30 wt%
● Specific Cake Resistance[1]	
- Digested Solids	5×10^{11} ft/lb
- Water-Washed Solids	0.5×10^{11} ft/lb

Mechanical Specifications

● Maximum Drum Size	12 ft $\emptyset$ x 36 ft[2]
● Submergence	40%
● Maximum Rotational Speed	1 rpm
● Filter Drum Drive	15 hp
● Discharge	Knife Scraper with Sluice
● Knife Approach to Drum	0.25 in.
● Medium	Cloth
● Materials	Stress-Relieved Carbon Steel

Considerations

● Filter Availability	85%
● Minimum Sparing	1 Spare Filter per Stage
● Operators	1 per 5 Operating Filters
● Scale-up Allowance	25% of Theoretical Area

Notes:

(1) With addition of flocculant.

(2) These drum dimensions result in a maximum area of 1,360 ft^2 per filter.

or 1,360 ft^2). The total area required for each filtration stage is constrained either by the minimum final cake thickness (0.75 in.) if the solids filter slowly as in Case 1, or by the maximum rotational speed (1 rpm) if the solids filter rapidly as in Case 2. Although not shown in Table 5.1-3, the design basis for the vacuum rotary-drum filters serving the tenth and final washing stage is generally analogous. The feed conditions are 15 psia and about 150°F, and the cake pressure drop is reduced to 10 psi. In all cases, a 25% scale-up allowance on filter area is included.

The number and average size of the filters required for Cases 1 and 2 are summarized below.

Summary of Rotary-Drum Filter Designs

Case	Pressure Filters		Vacuum Filters	
	Number[1]	Average Area	Number[1]	Average Area
Case 1 (Digested Solids)	70N/15S	1,240 ft^2 ea.	34N/6S	1,320 ft^2 ea.
Case 2 (Water-Washed Solids)	18N/ 9S	750 ft^2 ea.	4N/1S	870 ft^2 ea.

(1) N = normally operating; S = spare

Case 1 with digested solids requires both more filters and larger average area per filter. The debit for these extra facilities will be compared to the credit for reduced makeup KOH when economics are developed for Cases 1 and 2.

As indicated previously, these initial catalyst recovery screening studies are intended only to identify data needs and to select the more promising process and solid-liquid separation alternatives for further study. There is clearly much uncertainty in the current cake resistance measurements and the resulting filter sizes for digested and water-washed solids. The conclusions drawn from the current studies will have to reflect this uncertainty. More bench filtration data are obviously needed, and such data will be obtained when representative char and fines solids are available from the lined-out PDU.

Work will continue on these first three catalyst recovery screening studies in the first quarter of 1980. Initial economics for these cases are expected to be developed by the end of the quarter. Additional cases to evaluate centrifuges and hydroclones will also be initiated during the coming quarter.

Gas Separation Screening Studies

Work continued on engineering screening studies to develop an optimized process basis for the acid gas removal and methane recovery sections of the CCG process. This effort is based primarily on the work being done by Air Products and Chemicals, Inc. of Allentown, Pennsylvania under DOE contract ET-78-C-01-3044. One of the objectives of the Air Products contract is to recommend the most attractive combination of acid gas removal and cryogenic methane separation for the CCG process. The information developed by Air Products will be assessed and assimilated into the mainstream of the CCG process development.

Initial efforts have focused on optimization of the methane recovery system. In the Study Design methane recovery system, methane was separated from CO and H_2 in a cryogenic distillation tower operating at about 410 psia with an external cascade refrigeration system. In the alternative scheme developed by Air Products, methane is separated from CO and H_2 by cooling the feed to about $-250°F$ at 410 psia followed by stripping of the resulting liquid at 40 psia. The external cascade used in the Study Design is replaced by autorefrigeration via the pressure reduction. The potential advantages of this new scheme include greater relative volatilities at the lower pressure, bypassing of the cooled vapor around the low pressure stripper, and elimination of the cascade refrigeration system.

A preliminary horsepower estimate has been developed for this alternative methane recovery scheme and is compared below to the horsepower estimate for the Study Design system.

Gas Separation Screening Studies
Material and Energy Balance Comparison

	Base CCG Study Design	Alternative CH_4 Recovery System
Tower Pressure, psia	410	40
Percent CO and H_2 Bypassing Tower	-	85
Number of Trays	30	10
Tower Diameter (one of two trains), ft	10	10
Reboiler Duty, MBtu/hr	66	34
Total Refrigeration Compression, HP	65,000	-
Recycle Gas Compression, HP	17,000	36,000
Product Gas Compression, HP	56,000	66,000
Total Compression, HP	138,000	102,000

The horsepower requirement for the alternative methane recovery system is 26% lower than that for the Study Design system. The CCG Study Design includes some allowance for heat leak into the system. The horsepower for the alternative methane recovery system shown here does not include an

allowance for heat leak. This will be included later when the equipment sizes in the alternative system have been better defined. It is expected that heat leak will not significantly increase system horsepower requirements.

In addition to the substantial horsepower savings, it appears that the low pressure stripping system will have a lower investment than the Study Design system as indicated by the reduced number of trays and design pressure for the tower and elimination of the entire cascade refrigeration system. This will be confirmed by developing investments and economics for the low pressure stripping system. However, to avoid duplication of effort, this work will be deferred until issue of Air Products' final report for their DOE contract.

Assessment of Trace Components in CCG Gas Loop

A study has been initiated to identify and quantify trace components which might be present in the CCG gas loop and to assess their potential impacts on the CCG process. The broad classes of impurities which will be considered include light hydrocarbons, nitrogen compounds, sulfur compounds, light and heavy oils, tars, halogen compounds, and components which could combine with these in the gas phase. Potential concerns to be evaluated associated with these impurities include effects on corrosion, fouling, plugging, purge stream balances, cryogenic freezeout, waste water treating and plant emissions.

The levels of trace components assumed for the Study Design and the bases for those levels are presented in Table 5.1-4. In the initial phase of this study, potential trace components have been identified, and the most probable concentration range in the gasifier effluent will be defined. This will provide guidance for efforts to identify and quantify key impurities in the PDU gasifier effluent. Data from PDU base case operations will then be used to set the bases for studies that will assess the impacts of trace components on the CCG process.

Supplemental Steam Reformer Heat Input Study

A study which considered the use of an integral steam reformer as a method of heat input to the catalytic gasifier was recently completed. In this concept, the preheat furnace in the CCG Study Design is replaced with a reforming furnace. Methane present in the recycle gas is reformed to make CO and H_2 which then methanate in the gasifier providing additional heat input. This permits greater heat input flexibility because additional heat input to the gasifier can be supplied by increasing the methane fed to the reformer. In the case of the preheat furnace, additional heat could be supplied only by increasing the furnace outlet temperature which significantly increases furnace investment. The Integral Reformer Study showed a 3% reduction in gas cost relative to the CCG Study Design, as described in the July - September, 1979 Quarterly Report.

Table 5.1-4

ASSESSMENT OF TRACE COMPONENTS IN CCG GAS LOOP

Gasifier Effluent Components	Level in Study Design Gasifier Effluent lb/ST maf Coal	Basis for Study Design	Impacts and Concerns
• Light Hydrocarbons			
Ethane	0.34	Ethane content set by equilibrium; levels of other light hydrocarbons judged to be negligible.	Light hydrocarbons dissolved in solvent used in acid gas removal are vented to the atmosphere. CO_2 vent stream must meet hydrocarbon emission standards.
Propane	-		
Ethylene	-		
Propylene	-		
Acetylene	-		
• Nitrogen Compounds			
Total Nitrogen	200.	Nitrogen is introduced to the gas loop by N_2 generated from coal and N_2 introduced from lock hoppers. It is assumed that 5% of the coal nitrogen goes to N_2 and an equal amount of N_2 enters the gasifier from the lock hopper feed system giving a total of 4.1 lb N_2/ST maf coal to be purged. As a result, nitrogen is built up in the recycle gas. The extent of N_2 buildup is limited by a purge of 7% of the recycle gas to the lock hopper system. This buildup results in 200 lb N_2/ST maf coal recycled to the gasifier.	Buildup of nitrogen in the system sets purge rates and affects plant fuel balance.
Once-Through Nitrogen	4.1		
Ammonia	44.	90% of coal nitrogen goes to NH_3.	Sets the basis for design of the NH_3 recovery facilities and the NH_3 by-product rate.
Hydrogen Cyanide	0.013	Estimated based on FBG sour water analyses.	May impact wastewater treating.
Thiocyanates	0.026		
Ring-substitutes	-		
• Sulfur Compounds			
H_2S	73.	90% of organic coal sulfur goes to H_2S.	Impacts on design basis for acid gas removal, sulfur recovery, and sour water facilities, and sets sulfur by-product rate.
COS	1.9	COS content set by equilibrium.	The heavy glycol solvent of the acid gas removal section is stripped with air to remove CO_2. COS that is present could be oxidized to form S which could cause plugging. Also, COS, if vented, is subject to emission limitations. Upstream of the acid gas removal section 85% of the COS was converted to H_2S.
CS_2	-	Assumed that levels of these components would be small and have negligible impact on plant facilities.	If higher levels, could have impact on sour water treatment, acid gas removal, and molecular sieve systems.
Organic Sulfides	-		
Mercaptans	-		
Thiophenes	-		
Ring-Substitutes	-		
• Organic Liquids			
Benzene	2.8	Nominal value assumed for design of molecular sieve/activated carbon cleanup systems.	Impacts acid gas removal and molecular sieve systems.
Phenols	0.086	Estimated based on FBG sour water analyses.	Impacts sour water treating. May foul high level heat recovery equipment. Could contaminate acid gas removal solvent.
Heavy Oils	0.026		
Tars	-		
• Halogen Compounds			
HCL	-	Assumed not to be present.	May cause corrosion problems. Could react with NH_3 to precipitate NH_4Cl and plug equipment.
• Other Components			
Aluminum	-	Assumed not to be present.	May be present as various compounds such as oxides, chlorides, hydrides, sulfides, sulfates, etc. Probably not a limiting factor in any equipment specification.
Potassium	-		
Sodium	-		
Phosphorous	-		

The potential for carbon laydown (by the reaction $2CO \rightarrow CO_2 + C$) was identified as the major process uncertainty for the integral reformer concept. For purposes of the study, it was assumed that carbon laydown would not occur. However, bench-scale research on gas phase reactions has shown that carbon laydown can occur in a gas stream with compositions similar to those envisioned commercially for integral reformer feed.

Two methods of preventing carbon formation have been identified. The first consists of adding CO_2 via a shift reactor or CO_2 injection to increase the CO_2/CO ratio to prevent carbon laydown. The second method consists of operating a small conventional steam reformer in parallel with the preheat furnace. This process concept is called supplemental steam reforming and it is shown and compared to integral steam reforming in Figure 5.1-2. The feed to the supplemental steam reformer consists of SNG and steam and thus carbon laydown cannot occur by the CO reversion reaction. The preheat furnace coil outlet temperature can be lowered to reduce its investment and carbon laydown can be prevented by the injection of a small amount of sulfur compound as in the CCG Study Design. The injection of H_2S cannot be used for the integral reformer because it would poison the reforming catalyst.

A study has been initiated to evaluate the supplemental steam reforming process option. The CCG reactor system material and energy balance model will be used to develop material and energy balances for supplemental steam reforming. Initial studies are underway to examine the effects of several process variables. These studies will be used to set a final process basis after which investments and economics will be developed for the best supplemental reformer case.

Coal Crushing Machinery for CCG

The study to determine the type(s) and performance of coal crushing equipment appropriate for commercial CCG plants is continuing.

In the quarter, a reply was received to an interpretation request made to the National Fire Protection Association (NFPA) Committee on Dust Explosion Hazards concerning crushing system safety design requirements. The reply answered some of the questions asked of the Committee but requested further information in order to be able to answer the interpretation request more fully. A second letter to the NFPA is being prepared.

Also in this quarter, preliminary replies were received from the last of ten manufacturers contacted concerning the suitability of their mills to commercial CCG plant application. These vendors had been asked to supply information about the size, type, and safety design requirements for mills to be supplied to such a plant in 1985. Evaluation of the positive replies is in progress.

FIGURE 5.1-2

SUPPLEMENTAL STEAM REFORMING HEAT INPUT STUDIES -
SIMPLIFIED SCHEMATIC FLOW PLAN

SUPPLEMENTAL STEAM REFORMING CASE

INTEGRAL STEAM REFORMING CASE
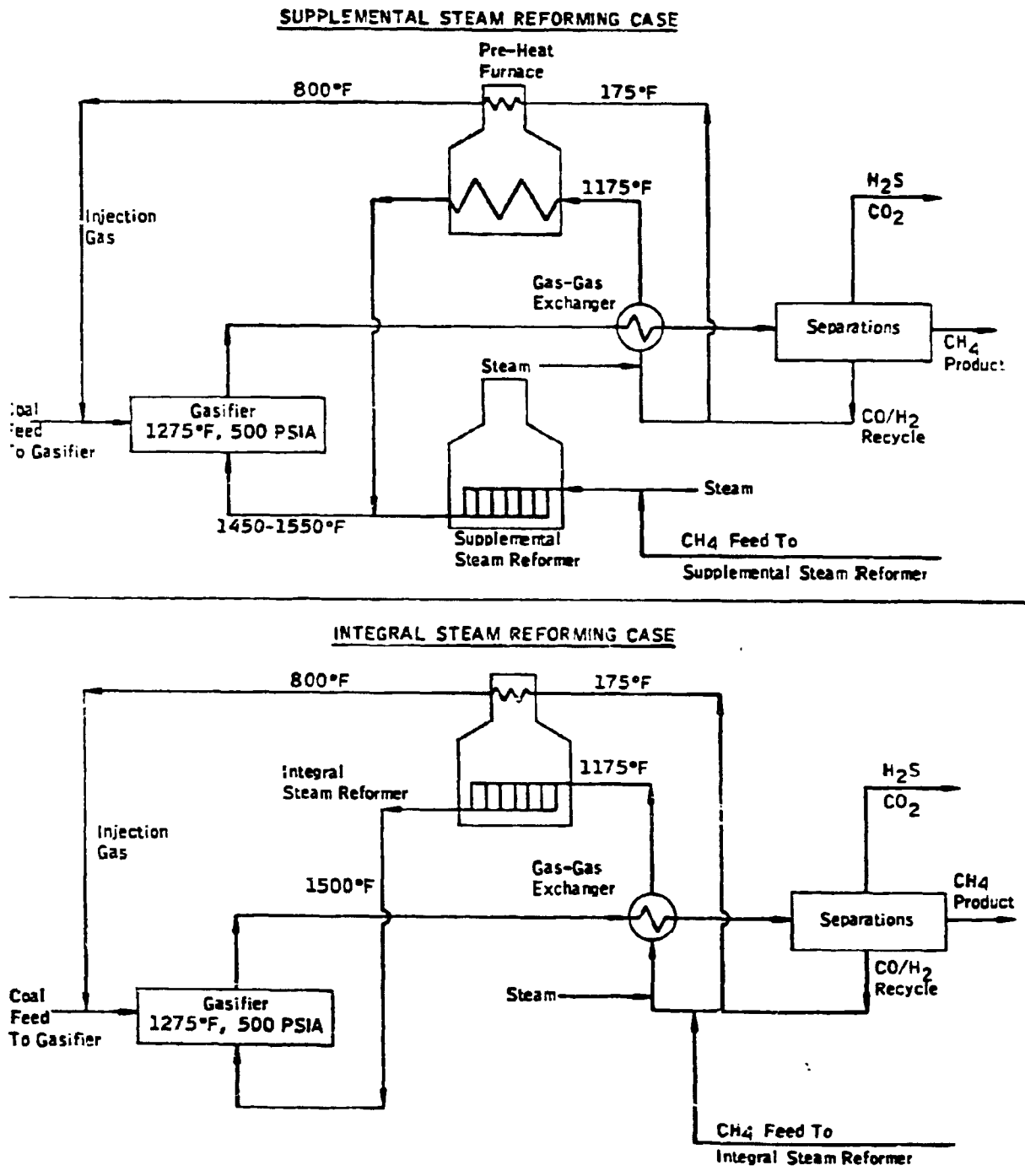
5.2 Systems Modeling

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

CCG Reactor System Material and Energy Balance Model

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

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

The new CCG reactor system computer model calculates the overall material and energy balance for the gasifiers, recycle gas loop, and preheat facilities in a commercial CCG plant. The major independent variables which must be specified by the user are as follows:

- Coal feed rate and composition
- Catalyst feed rate (or loading) and composition
- Gasifier pressure and temperature
- Carbon conversion in the gasifiers
- Approaches to shift and methanation equilibria in the raw gasifier product gas
- Steam-carbon gasification reaction equilibrium constant (or steam conversion or steam rate)
- Gasifier heat losses and heat input control allowance
- Extent of shift reaction (if any) in the preheat furnace

Additional information defining the composition and properties of the solids in the gasifier fluid bed must be provided if the user wants the model to calculate gasifier bed volume using the current gasifier kinetics/contacting model.

The new CCG model is incorporated within the framework provided by Exxon's proprietary process network simulation program, known as "COPE". Four main blocks have been programmed to model the gasifier itself:

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

● The second block feeds the "reacting coal" and the various gaseous feed streams and produces a product gas at specified shift and methanation equilibria.

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

● The fourth block incorporates the current gasifier kinetics/contacting model. This optional feature allows calculation of the gasifier bed volume along with the material and energy balance.

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

In order to simulate the material and energy balance for a CCG reactor system, the model blocks are incorporated in a COPE process network. The network used to model the reactor system for the CCG Commercial Plant Study Design is illustrated in simplified form in Figure 5.2-1. The network joins together the three required blocks, models the material balances for the product gas cleanup and separations steps downstream of the gasifier, and converges the overall material balance and gasifier/preheat furnace energy balance.

The calculations are relatively complex. Two nested loops are used to converge the overall material balance. The inner loop determines the steam rate to the gasifier based on product gas steam-carbon equilibrium (or gasifier steam conversion). Within this inner loop, the gasifier material balance is calculated by model blocks one and two. The principal feeds are coal, catalyst and preheated steam/recycle, and the principal products are char, fines, and gasifier product gas. The outer loop converges the recycle (synthesis gas) stream rate and composition, using a series of COPE operations. After the material balance is converged, the gasifier energy balance is closed by model block three. The gas-phase feed and product streams are fed to model block three directly. The impact of solids on the gasifier energy
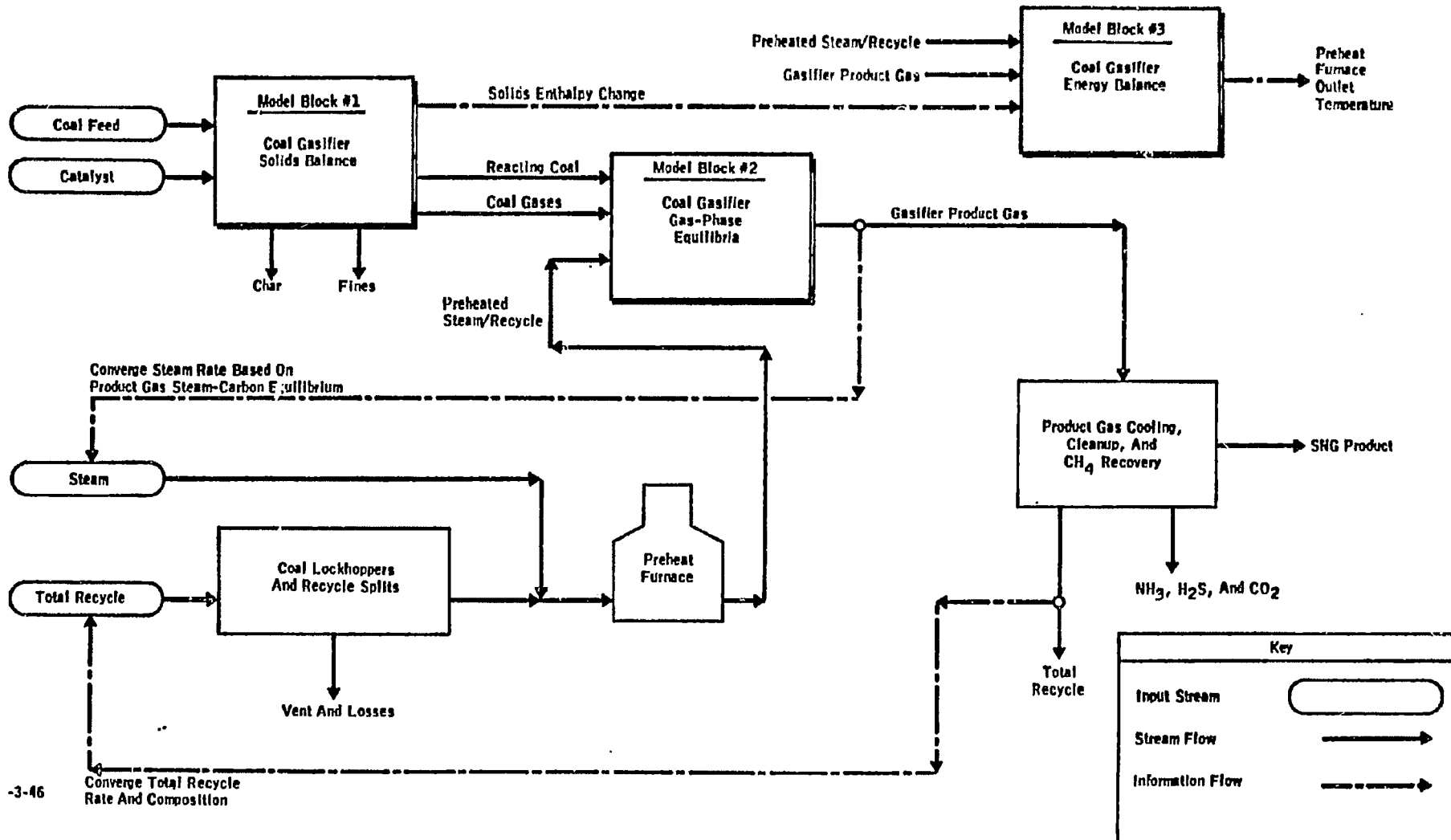
balance is accounted for by using a solids enthalpy change transferred from model block one. Model block three calculates the steam/recycle preheat furnace outlet temperature required to maintain the desired gasifier operating temperature, with or without allowance for potential shift reaction in the furnace.

In developing the converged overall balance, the COPE network is used to simulate the material balance impacts of several process systems. For example, the network models, in simplified fashion, the acid gas removal, molecular sieve, and cryogenic methane recovery steps. The effects on the recycle gas loop of the coal lock hopper pressurization system, the coal injection system, the gasifier char withdrawal system, and gas losses in the various processing steps are also simulated.

The majority of the CCG model development effort centered on programming the four main blocks described above. Additional details on each of these blocks are provided in the following paragraphs.

First, the coal gasifier solids balance block feeds coal and catalyst, produces char and fines streams which include the catalyst leaving the gasifier, and calculates the total enthalpy change of the solids across the gasifier. The routine requires knowledge of the coal pyritic sulfur, sulfatic sulfur, alumina, silica, and "inert" ash (excluding alumina and silica) to calculate the extent of reactions between catalyst and coal mineral matter. This information is inputted by specifying the coal feed stream analysis in the manner shown in the left column of the table below. The components listed in the right column of the table are accepted in the catalyst streams to and from the model block.

Components for CCG Gasifier Solids Balance Block

Coal Stream	Catalyst Streams	
Carbon	KOH	Principal forms
Hydrogen	K_2CO_3	in catalyst fed
Oxygen	K_2S	to gasifier
Nitrogen	$KHCO_3$	
Organic Sulfur	KHS	
Pyritic Sulfur	K_2SO_3	
Sulfatic Sulfur	K_2SO_4	
Ash*	$K_2S_2O_3$	
Alumina (Al_2O_3)	K_2S_2	
Silica (SiO_2)	Inert Forms	
Coal Moisture	K (in K·Char)**	Principal forms
	$KFeS_2$	in catalyst leav-
	$KAlSiO_4$	ing gasifier,
	$K_2O·xSiO_2$	along with K_2CO_3

*Excluding alumina and silica.

**K·Char represents the complex formed between catalytically active potassium salts and coal-derived char under gasification conditions. E.g., the reaction for its formation from K_2CO_3 can be written $K_2CO_3 + 2H·Char \rightarrow 2K·Char + H_2O + CO_2$.

A key objective of the CCG Process Development Program is to better define the catalyst forms and amounts which will be present when the CCG catalyst recycle loop is closed. It is currently expected that the first three catalyst components listed will be the predominant forms in the catalyst fed to the gasifier. The last four catalyst forms, along with K_2CO_3, are expected to be predominant in the catalyst leaving the gasifier. Smaller amounts of the other components may also be present in the closed loop.

The enthalpy change of the solids across the gasifier is calculated in this first model block beginning with the complete material balance for feed and product solids broken down into the components listed above. Heats of formation for the organic portions of the coal, char, and fines streams are calculated using an equation derived from the Mott-Spooner heat of combustion correlation (Mott, R. A, and C. E. Spooner, Fuel, 19 (10), 226-231, 242-251 (1940)). Heats of formation for most of the catalyst components and for alumina and silica compounds in the coal mineral matter were available in the general literature. It was necessary to estimate heats of formation for $KFeS_2$ and $K_2O \cdot xSiO_2$. An approximate heat of formation for K·Char was developed from calorimetry data on the heat of mixing catalyzed char with water. The heat of dehydration for any $K_2CO_3 \cdot 1.5\ H_2O$ in the catalyzed feed coal can be reflected in the energy balance at the user's option. Heat capacity relationships for coal, char, and ash were developed from a paper by Lee (Lee, A. L., "Heat Capacity of Coal," Am. Chem. Soc., Div. of Fuel Chemistry, Preprints, 12 (3), 19-31 (1968)). Heat capacities were not available in the literature for a few of the catalyst compounds. These were set equal to the heat capacity (on a weight basis) of either K_2O or K_2SO_4, as judged appropriate. Because of the approximations and assumptions involved, there is some uncertainty in the CCG gasifier enthalpy balance as currently calculated by the model. Work to reduce this uncertainty is planned later in the current program.

The second block calculates the gasifier product gas rate and composition based on simultaneous shift and methanation equilibria. For specified coal and gas feed streams, shift equilibrium temperature, methanation equilibrium temperature, and gasifier pressure, an equilibrium product gas is calculated. The two reactions considered along with their associated equilibrium expressions are:

● Shift reaction:

$$CO + H_2O = CO_2 + H_2 \qquad K_s(T_s) = \frac{(CO_2)(H_2)}{(CO)(H_2O)}$$

● Methanation reaction:

$$CO + 3H_2 = CH_4 + H_2O \qquad K_m(T_m) = \frac{(CH_4)(H_2O)}{(CO)(H_2)^3} \cdot \frac{G^2}{P^2}$$

where:

$K_s(T_s)$ = shift equilibrium constant at equilibrium temperature T_s
$K_m(T_m)$ = methanation equilibrium constant at equilibrium temperature T_m, atm^{-2}
P = gasifier pressure, atm
G = total product flow rate, lb-moles/hr
(x) = flow rate of component x, lb-moles/hr

Equilibrium constants are calculated by the program but may be overriden by the user. First order non-ideality corrections are made using calculated fugacity coefficients. The model block calculates the apparent steam-carbon equilibrium constant based on the composition of the product gas so that the COPE network can converge on equilibrium for this gas-solid reaction. The steam-carbon reaction and the associated equilibrium expression are:

● Steam-carbon reaction:

$$C + H_2O = CO + H_2 \qquad\qquad K_c(T_c) = \frac{(CO)(H_2)}{A_c(H_2O)} \cdot \frac{P}{G}$$

where:

$K_c(T_c)$ = steam-carbon equilibrium constant at equilibrium temperature T_c, atm

A_c = carbon activity (graphite = 1.0)

P, G, (x) are defined as above

In addition to CCG reactors, the equilibrium block can be used to model the material balance for other related reactor systems, including steam reformers, shift reactors, and methanation reactors.

The third block performs an overall energy balance around the CCG gasifier with a total of up to nine feed and product gas streams. Heats of formation at 100°F for the CCG gas components were taken from the literature. Stream sensible enthalpies at conditions and at the reference state (ideal gases at 100°F) are obtained from the proprietary data base built into the COPE program. In calculating the overall enthalpy change around the gasifier, the model takes into account the solids enthalpy change, gasifier heat losses, and heat input control allowance as well as the gas stream enthalpies. The program operates in one of two modes:

● One routine energy-balances the gasifier by varying the temperature of the steam/recycle gas feed, with or without allowance for water-gas shift reaction in preheat. Under this option, the computer routine will converge upon the required preheat temperature assuming a specified percentage (0-100%) of the shift reaction which would occur if the stream were in full shift equilibrium.

● The alternative routine does not attempt to energy-balance the gasifier, but instead uses the specified stream temperatures to calculate the energy balance "miss", or delta enthalpy. This option allows the COPE network to balance the gasifier outside of this block by, for example, varying the flow rate of a feed stream to the unit. (Most cases using steam reforming for heat input to the gasifier are balanced in this manner.)

This block also performs a consistency check to see if the streams to be energy-balanced are in material balance. The model can also close the energy balance by varying the temperature of a product rather than a feed, which may be appropriate in some modeling situations.

To enable its use in conjunction with the material and energy balance routines, the existing stand-alone reactor kinetics/contacting model was incorporated into its own block. This reactor model block receives as feeds the catalyzed coal, the bottom-fed steam/recycle gas mixture, and the coal injection gas, and produces a gasifier product gas predicted by the kinetic and contacting relationships. In addition to the gas feed streams just mentioned, another gas stream may be fed at a specified height above the bottom of the bed. A final optional feed stream slot is available for the gasifier product gas calculated by the gas-phase equilibrium model block, allowing the product streams predicted by the two different methods to be compared.

The reactor model convergence routine is set up to calculate the value of any one of the following variables, with the others held constant:

- carbon conversion
- bed height
- bed diameter (or superficial velocity)
- coal rate

Thus, this fourth model block can be used to calculate the gasifier bed size (height and/or diameter) in the same computer run with the material and energy balance. Alternatively, the reactor model block will allow calculation of the predicted material and energy balance (carbon conversion or coal rate) for a given reactor size.

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

During the coming year, this improved CCG reactor system material and energy balance model will be used extensively in the laboratory guidance and process definition studies planned under the current program. These include gasifier heat input studies and process variable screening studies. It is expected that the model will need to be updated to some extent during the process definition to reflect data from the PDU operations and the results of other laboratory and engineering studies.

5.3 Engineering Technology Studies

As part of the CCG Process Development Program, a coordinated set of engineering technology programs is being conducted to develop fundamental process and equipment technology to support the overall laboratory and engineering process development effort. The work on these programs during this quarter is described below. Additional programs are underway or will be initiated later in the contract period.

Evaluation of Construction Materials for Catalytic Gasification

The overall objective of this engineering technology program is to assemble a data base on materials performance for those plant sections which have materials considerations unique to catalytic gasification. The main focus of the program is in-situ materials evaluation in the CCG PDU at Baytown, Texas.

The materials evaluation program utilizing corrosion racks and probes is being implemented as planned. Test Sites 1-7, described in Table 5.3-1, are installed in the PDU and have seen intermittent operation since September, 1979. Racks for Test Sites 8-10 are on-site and will be installed in early 1980. Test Site 11, a small helical steam coil, will be fabricated and installed after start-up of the catalyst recovery equipment, probably in the second quarter of 1980. This removable coil will be used in the evaporator vessel to evaluate materials performance under actual heat transfer conditions. Test Site 3, intended for dilute phase exposure in the gasifier, is actually located in the dense phase. Dilute phase corrosion testing will therefore require test site relocation in later runs. Removal of the first set of racks and replacement with the second set is planned after integrated operation of the unit is achieved and the process variable studies are initiated.

An updated summary of the PDU stream sampling and analysis requirements is provided in Table 5.3-2. This modified list has been reviewed with PDU operations personnel responsible for obtaining the samples. As noted, most samples will be taken at least once per yield period; however, some special samples, taken on request only, are also included.

A leaking section of 316 SS tubing (3/4" diameter x 0.065" wall) was removed from the PDU gasifier overhead line for failure analysis. This section of tubing was part of a by-pass off the overhead line; it was uninsulated, and normally saw no flow. Preliminary metallurgical examination revealed extensive transgranular cracking and significant quantities of sulfur and potassium. These findings indicate that the cracking is most likely caustic embrittlement caused by KOH-containing aqueous condensate. Examination and analysis of this failure is continuing and the completed results of the investigation will be presented in the next quarter.

Materials screening tests have been initiated at the Bureau of Mines Tuscaloosa Research Center to study the effect of the CCG environment on metal and refractory specimens. (This work is being done under DOE/BOM Contract EX-76-A-01-2219.) Preliminary results from 100-hour and 250-hour test runs in simulated CCG gas mixtures at 720°C (1330°F) and 500 psig are reported in their Fourth Quarter Progress Report for FY 1979, covering the period July - September, 1979. Major findings and results are as follows:

Table 5.3-1

CATALYTIC COAL GASIFICATION PDU
CORROSION RACKS AND PROBES

Test Site	Equipment Item	Location	Type of Device	Specimen Type	Test Materials[1]
1	Gasifier	Dense phase	Rack	Refractory cylinders	Kaiser Lo-Erode[2]
2	Gasifier	Dense phase	Rack	Metal cylinders	HK-40, 304 SS, 309 SS
3	Gasifier	Dense phase	Rack	Metal discs	HK-40, 310 SS, 304 SS, 309 SS, 304 SS Alonized
4	Sour water accumulator	Liquid	Rack	Metal cylinders	CS, 304 SS, 316 SS, Carpenter 20Cb3, Ti, Monel 400
5	Sour water accumulator	Liquid	Probe[3]	Wire element	CS
6	Sour water stripper	Packing	Rack	Metal cylinders	304 SS, 316 SS, CS
7	Sour water stripper	Packing	Rack	Metal cylinders	Carpenter 20Cb3, Monel 400, Ti
8	Char slurry drum	Liquid	Rack	Metal cylinders	CS, 316 SS, Inconel 625
9	Char digestor	Liquid	Rack	Metal U-bends	CS, 316 SS, Monel 400, Inconel 600, Allegheny Ludlum 29-4
10	Evaporator	Liquid	Rack	Metal U-bends	CS, 316 SS, 410 SS, Monel 400, Inconel 600, E-Brite 26-1
11	Evaporator	Liquid	Steam coil	Metal tubing	CS

Notes: (1) Abbreviations:
          CS - carbon steel
    304 SS - Type 304 stainless steel (18 Cr-8 Ni)
    309 SS - Type 309 stainless steel (25 Cr-12 Ni)
    310 SS - Type 310 stainless steel (25 Cr-20 Ni)
    316 SS - Type 316 stainless steel (18 Cr-8 Ni-2 Mo)
    410 SS - Type 410 stainless steel (13 Cr)
     HK-40 - Cast 25 Cr-20 Ni-0.4 C alloy
(2) Kaiser Lo-Erode specimens, with and without 304 SS fiber reinforcement
(3) Non-retractable electric resistance probe

Table 5.3-2

CATALYTIC COAL GASIFICATION PDU
STREAM SAMPLING AND ANALYSES

Location/Service	Type of Sample	Analyses[1]
Gasifier Overhead[2]	Gas	H_2S, CO_2, NH_3, HCl
Sour Water Accumulator	Liquid	pH, Cl^-, CN^-, NH_3, H_2S, phenol
Filter Pot	Solid	Ash, K, Na, Ca, SO_4, SO_3, Cl
DEA Regenerator Overhead	Gas	CO_2, H_2S, NH_3, HCl
Char Pot[3]	Slurry	Liquid: alkalinity, K^+, Cl^-, CN^-, NH_3, H_2S Solid: ash, K, Na, Ca, S, Cl
Char Digester	Slurry	Same as above
Char for Disposal	Solid	Same as Filter Pot
Recycle Gas	Gas	H_2, CO, CO_2, H_2S
Evaporator (Conc. Solution)[3]	Liquid	Alkalinity, K^+, Cl^-

Notes:

(1) Sampling frequency to be once per yield period minimum unless otherwise specified.

(2) Sample taken after water scrubbing.

(3) Samples taken on special request basis only.

Results of 100-Hour Tests

- In alkali vapor (estimated 50 ppm KOH)

  - Metals specifically corroded
  - Refractories apparently unaffected

- In molten KOH/coal mixture

  - Metals moderately corroded
  - Refractories mildly attacked

- In molten KOH

  - Metals severely corroded
  - Refractories badly deteriorated

Results of 250-Hour Tests
(Alkali-containing coal gas mixture)

- Hot flexural strength of 90% alumina concrete had significantly lower strength following exposure to the alkali-containing gas mixture than after exposure to air (at the same temperature and after the same duration).

- Hot flexural strength of 55% alumina concrete was approximately the same in alkali and air exposures.

- Hot flexural strength of 45/50% alumina concretes had significantly higher strength after exposure to the KOH-containing CCG gas than air-fired specimens.

Laboratory examination of exposed specimens is being conducted at Tuscaloosa and will be reported on in future progress reports. Currently, work is underway to modify the test unit prior to initiation of 1000-hour testing.

Slurry Rheology and Solid-Liquid Separations for Catalyst Recovery

The objectives of this program are to identify and evaluate alternatives for solid-liquid separations in catalyst recovery and to investigate the rheological properties of char plus catalyst solution slurries. Work this quarter was focused in two main areas: (1) a revision and reassessment of results from previous laboratory batch filtration experiments; and (2) initiation of new experiments in a modified laboratory batch filter to determine filtration rates and cake washing performance with water-washed char. The latter work is directed toward determining whether continuous belt filtration combined with in-situ washing is a feasible option for catalyst solution recovery.

A review of the experimental filtration data obtained to date has been completed. Data now available on potassium ion (K^+) concentrations in the filtrates enabled more accurate calculations of cake resistance. A potassium specific-ion electrode was used to measure the concentration of K^+ ion in the filtrate from the previous runs and thereby indirectly determine liquid viscosities and solids concentrations more accurately than previously possible. Liquid viscosity was obtained from literature correlations for KOH solutions. Feed solids concentration was previously obtained from the weight of the filter cake after drying. This procedure introduced error because when the wet cake was dried, dissolved salts were left in the cake and were included in the cake weight. This error has been corrected using the measured potassium concentration in the liquid.

The corrected results for all the laboratory batch filter runs reported in the July, 1978 - June, 1979 Annual Report and the July - September, 1979 Quarterly Report are shown in Table 5.3-3. Corrected values include filtration rate (reported as an average value for filtration of the 320 ml of sample), cake resistance, and weight percent solids in the feed. Also shown are the K^+ concentrations in the liquid. Several minor errors in the original analyses have also been corrected. The initial compositions, particle sizes, and digestion conditions of all the samples are presented in Table 5.3-4.

The major conclusions reported previously are not changed by these revisions. The digested char samples D26, D39, and D44 show a wide variation in filtration rates, but the rates observed are generally lower than the 100 gph/ft^2 level typical of commercial filters. Filtration rates for the undigested char and fines samples D31 and D32 are in the typical commercial range.

As reported in the last Quarterly Report, the variability in filtration rates among the various solids samples tested to date makes it difficult to specify the type and sizes of solid-liquid separation devices required for commercial operation. The reasons for the variability are not clear, but the primary contributing factors appear to be particle loading and size distribution, cake properties (porosity, residual moisture, and compressibility), and digestion conditions.

A review of the data from all the runs suggests that low filtration rates correlate with high K^+ in digestion, high solids loading to the filter, and small particle sizes. The degree of agitation of the slurry during digestion was also found to be important. Severe agitation apparently breaks up the solids, resulting in a finer particle size distribution and lower filtration rates. Better knowledge of slurry attrition characteristics will be essential for commercial design. Char slurry attrition tests are planned in 1980.

Cake washing experiments with water-washed (undigested) char were started to determine the feasibility of catalyst solution recovery via continuous belt filtration with in-situ washing (or "leaching"). The possibility of using continuous belt filtration for catalyst recovery has

TABLE 5.3-3

LABORATORY BATCH FILTER RESULTS

Sample	Differential Pressure (psig)	Average Filtration Rate (4) (gph/ft²)	Cake Resistance (ft/lb x 10⁻¹¹)	Residual Cake Water (wt.%)	Cake Compressibility	Feed Solids (5) (wt.%)	Filtrate K+ (6) (wt.%)	Flocculant or Body Feed Type	Body Feed/ Char Ratio
D31 (1,3,8)	15	140	0.17	-	} 0.77	2.6	3.9	-	0
D31 "	20	197	0.17	:		2.6	3.9	-	0
D31 "	25	234	0.26	-		2.6	3.9	-	0
D32 (1,3,8)	25	103	0.90	70	} 0.02	3.5	0.74	-	0
D32 "	20	66	1.01	72		3.5	0.78	-	0
D32 "	15	63	0.90	69		3.5	0.69	-	0
D26 (1,3,7)	30	3.8	14.6	61	} 0.65	11.4	5.3	-	0
D26 "	50	4.6	25.9	60		11.4	5.7	-	0
D26 "	62	5.1	21.9	53		11.4	6.0	-	0
D26 "	71.5	19.9	2.08	29		25.1	2.3	Celite 503	1.0
D26 "	71.5	8.3	29.0	70		6.9	2.2	-	0
D26 "	71.5	6.9	12.3	60		13.2	5.4	Celite 503	0.15
D26 "	71.5	8.5	30.9	67		7.1	3.6	-	0
D26 "	71.5	14.8	6.3	65		11.2	3.2	Celite 503	0.38
D26 "	50.0	16.0	4.3	71		12.3	3.1	Celite 503	0.38
D26 "	50.8	14.1	4.6	69		11.5	3.0	Supercell	0.38
D26 "	71.5	25.9	3.2	69		11.7	2.0	Supercell	0.38
D26 "	30.5	8.4	5.2	73		11.4	2.8	Supercell	0.38
D39 (2,3,7)	50	42	1.2	68		10.8	2.2	-	0
D39 "	50	71	0.57	60		10.1	2.3	D-25A/25 ppm	0
D39 "	50	57	0.61	68		12.9	2.6	D-25A/50 ppm	0
D39 "	50	38	1.05	67		12.1	2.3	A-1906N/10 ppm	0
D39 "	50	35	1.31	68		12.3	2.3	A-1906N/5 ppm	0
D39 "	50	69	0.62	68		12.4	2.3	D-25A/25 ppm and A-1906N/5 ppm	0
D44 (2,3,7,9)	30	5.8	34.8	64		6.5	5.0	-	0
D44 "	40	5.8	21.7	64		6.7	5.5	-	0
D44 (2,3,7)	40	3.9	36.0	54		16.8	9.9	-	0
D44 (2,3,7,9)	70	7.8	22.0	62		0.6	5.8	D-25A/25 ppm	0

Notes:

(1) Temperature = 180°F
(2) Temperature = 190°F
(3) All tests done using a 5 µm millipore medium
(4) Cell volume constant at 320 ml

(5) Corrected for K+
(6) By specific ion electrode
(7) Digested char and fines plus lime
(8) Undigested char and fines
(9) Water added to dilute the original sample

Table 5.3-4

SUMMARY OF BATCH FILTRATION SAMPLES

Sample	Description	Particle Size Distribution		Wt% K⁺ In Solution
		% <10 μm	% <44 μm	
D26	22 lbs char, no fines, 11 lbs lime, 176 lbs of 3.29 wt% K^+ solution digested for 1 hr at 300°F using old digester and pump	71	79	4.55
D31[1]	30 lbs char, 10 lbs fines, no lime, 305 lbs 2.39 wt% K^+ solution leached with 2.87% K^+ solution, overflow from leaching tank	5	16	Approx. 3.5
D32[1]	5 lbs char, 2 lbs fines, 160 lbs water	6	12	Approx. 1
D39	15 lbs char, 6 lbs fines, 10 lbs lime, 168 lbs 0.58 wt% K^+ solution digested for 1 hr at 300°F, no pump, new digester	12	75	2.72
D44	20 lbs char, 9.2 lbs fines, 5.3 lbs lime, 158 lbs 9.61 wt% K^+ solution digested for 1 hr at 300°F, no pump, new digester	28	57	11.58

Note:

(1) Assume particle size distribution is the weighted average of the particle size distributions for char and fines in sample D44.

been discussed with vendor representatives. Such filters would allow countercurrent multi-stage leaching without the need for reslurrying cake, and may represent significant cost savings over staged filters which require intermediate reslurrying. The amount of recovery in these filters depends on how effectively potassium can be washed from the cake of char solids deposited on the belt.

The initial experiment was done by filtering a sample of water-washed char in the 320 ml batch filter cell, followed by a distilled water wash using the one-liter heated wash reservoir added last quarter. This procedure produced a filter cake approximately 5 inches thick as compared to a typical commercial cake of 1 to 2 inches. Consequently, the 320 ml test cell is being replaced with a 100 ml cell. This change will result in a thinner cake, more representative of commercial operation, and will directionally reduce the possible adverse effect of settling on filtration. Calculations indicate that settling during filtration of water-washed char could reduce the measured filtration rate by prematurely building up a cake. A double-pipe filtrate cooler is also being installed on the cell outlet to permit testing at temperatures up to about 200°F.

Resumption of cake washing experiments is planned for the first quarter of 1980 when the above modifications are complete and fresh char samples are available. Char slurry attrition tests and char slurry viscosity measurements are planned for later in 1980.

Environmental Control: Atmospheric Emissions

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

A compilation of air quality regulations potentially applicable to CCG plants has been brought up to date and is being updated on a continuing basis. The EPA is not currently planning to develop final criteria pollutant regulations for coal gasification plants until the mid-1980's. Regulations for the control of toxic chemical emissions are also not expected until then.

The current plans for sampling potential emissions sources in the PDU were reviewed on a preliminary basis with PDU operating personnel. The review covered the type of tests, the accessibility of sampling points, and the type of sampling. The sampling plan appears adequate to characterize process emissions. Further detailed review is planned to identify any desirable test additions or modifications. When available, test results will be studied to develop better estimates of criteria pollutant emissions and determine the potential for toxic emissions from CCG.

Preliminary estimates of criteria pollutants (particulate matter, hydrocarbons, SO_2, NO_x, and CO) expected from a commercial CCG plant should be completed by mid-1980. Only SO_2 emissions have been investigated to date. Based on a sulfur balance for the CCG Study Design, these SO_2 emissions are estimated to be about 38 ST/SD (12,500 ST/year at 90% capacity factor) for a plant using 18,160 ST/SD coal. The balance is shown in Table 5.3-5. Since this emission rate is much greater than 100 ST/year SO_2, such a plant would be defined by the EPA as a large potential emission source subject to the Federal New Source Performance Standards (NSPS), the National Ambient Air Quality Standards (NAAQS), and the Prevention of Significant Deterioration (PSD) Regulations, as well as state and local air quality regulations. The CCG SO_2 emission rate is estimated to be 0.2 lb SO_2/MBtu (based on the Btu content of the input coal). Although this is well in compliance with the expected mid-1980's federal NSPS of 0.6 lb SO_2/MBtu for coal-fired boilers (presently the only basis for comparison), it is possible that ambient air quality regulations could further limit CCG plant SO_2 emissions.

Since potential metallic and organic toxic emissions from the CCG process could be a health and environmental concern, developments in this relatively new area are being followed. Most current related research in toxics--sponsored by the National Institute for Occupational Safety and Health, the Environmental Protection Agency, or the Department of Energy--concerns characterizing the relative toxicity of many trace metals and organic compounds, and determining which of these could be emitted from coal conversion processes. Comprehensive conclusions and recommendations concerning potential toxic emissions from coal conversion processes have not been drawn.

Dynamic Simulation of the CCG Reactor System

The objective of this program is to study the dynamic response, stability, and control requirements for the gasifier reactor and associated recycle gas system. The overall design of the simulation software has been completed and is based on modules for the gasifier, high level heat recovery section, low level heat recovery section, acid gas removal section, and preheat furnace. The level of modeling detail for each module has been determined, and a mechanism has been developed for linking the various modules. To provide a basis for modeling and advanced controls development, a basic regulatory control scheme has been designed.

The gasifier model includes a set of subroutines to model the steady-state concentration profiles within the bed and a set of subroutines to model the unsteady-state energy and solids balances. The former set is undergoing final debugging and testing, while the latter is currently under development. After completion of the individual subroutines, they will be linked by a gasifier executive routine which will also provide linkage to the remaining process models. The gasifier model will show the dynamic response to disturbances in coal feed rate and composition, recycle rate, temperature, and composition, char withdrawal rate, and steam rate.

Table 5.3-5

SULFUR BALANCE FOR A PROPOSED
CATALYTIC COAL GASIFICATION PLANT

Sulfur In	Sulfur, ST/SD
Sulfur in Coal to Process Gasifiers (4.19% S)	523.8
Sulfur in Coal to Coal Dryers (4.19% S)	29.7
Sulfur in Coal to Offsites Boilers (4.19% S)	124.0
Total Sulfur into Plant	677.5

Sulfur Out

Sulfur By-product from Sulfur Recovery Units	356.4
Ash and Char from Catalyst Recovery Units	163.8
Offsites Boiler FGDS Sludge	136.0
Offsites Boiler Incinerated Ash	2.1
Coal Dryer Ash	0.5
Vent and Fugitive Emissions[2]	0.0
Atmospheric Release from Sulfur Recovery Units	3.6
Offsites Boiler FGDS SO_2 Emissions	15.1
Total Sulfur out of Plant	677.5

Sulfur to Atmosphere

SO_2 from the Two Emissions Sources =

$$(3.6 + 15.1) \frac{64}{32} = 37.4 \quad \text{Call 38 ST/SD}$$

Notes:

(1) Sulfur balance is based on the "CCG Commercial Plant Study Design" prepared during the Predevelopment Program and documented in Final Report Number FE-2369-24.

(2) Vent and fugitive emissions of SO_2 are considered negligible for preliminary estimates.

Catalytic Gasifier Solids Balance Model

The objective of this program is to adapt DYNAMOD, a proprietary solids balance computer model developed and validated for other Exxon fluid-solids processes, to predict the steady-state loss rates and particle size distributions both in the catalytic gasifier and of all streams leaving the vessel. A single species solids balance model was developed for a first pass assessment of the effects of variables such as solids attrition and gasification on equilibrium bed size distributions and fines losses. Predicted losses are largely dependent on the assumed char attrition rate. Estimates of char attritability will be made from PDU material balance data as they become available.

In the present model, the char attrition rate was assumed to be five times that of coke produced from petroleum. Gasification was assumed to proceed according to the shrinking core model and a conventional two-stage cyclone design was considered for the gasifier. Predicted losses from the gasifier were eight times lower than estimated in the Study Design. In order to match the Study Design losses, the equilibrium bed size distribution would have to be much finer than assumed in the Study Design. Predicted losses remained about the same when the more realistic reaction model of homogeneous reaction throughout the char was employed. Work will continue on adapting DYNAMOD to CCG by developing a two species char and ash model which will be used to assess the effects of char/ash density differences in solids balances. Data from the PDU will be used to validate the solids balance model.

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